

Creep-induced microstructural evolution of a eutectic Mo-20Si-52.8Ti at.% alloy by correlative electron microscopy

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Dedicated to my beloved sister, Deepthi

Kurzfassung

Turbinenschaufeln in Flugzeugtriebwerken sind stark beanspruchte Bauteile, da sie den aus der Brennkammer austretenden Hochtemperaturgasen ausgesetzt sind. Einkristalline Nickel (Ni)-basierte Superlegierungen werden aufgrund ihrer hervorragenden thermomechanischen Eigenschaften in Turbinenschaufeln eingesetzt, während polykristalline Ni-basierte Legierungen in Düsen, Verkleidungen und Scheiben Verwendung finden. Ihre Leistungsfähigkeit beruht auf einer zweiphasigen Mikrostruktur aus kohärent in die fcc- γ -Matrix eingebetteten $L1_2$ - γ' -Ausscheidungen. Da die Betriebstemperaturen der derzeitigen Werkstoffe durch die Solvustemperatur von γ' auf etwa 1150 °C begrenzt sind, besteht ein Bedarf an neuartigen Materialien, die Temperaturen oberhalb von 1200 °C ohne Luftkühlung standhalten können.

Das Mo-Si-Ti-System stellt aufgrund seiner geringen Dichte (6–7 g/cm³) und hohen Solidustemperaturen ($\approx$ 1800 °C) eine vielversprechende Alternative dar. Eine eutektische Mo-20Si-52,8Ti (at.%) Legierung zeigt dabei hohe Abriebfestigkeit und günstiges Kriechverhalten und besitzt eine zweiphasige Mikrostruktur aus einer kubisch-raumzentrierten (krz) festen Lösung (Mo,Ti,Si)_{ss} sowie dem hexagonalen Silizid (Ti,Mo)₅Si₃. Druckkriechversuche bei 1200 °C und einer wahren Spannung von 100 MPa ergaben ein charakteristisches Minimum der Kriechrate ($\dot{\epsilon}_{min}$) bei 1,3% wahrer Kriechdehnung. Zur Analyse der mikrostrukturellen Entwicklung wurden Proben bis zu wahren Kriechdehnungen von 0,2%, 1,3%, 10%, 20% und 40% untersucht.

Die Charakterisierung erfolgte mittels Transmissionselektronenmikroskopie (TEM), um Versetzungsprozesse und ihre Wechselwirkung mit Ausscheidungen während des Kriechens aufzuklären. TEM-Proben wurden mithilfe von EBSD zur Identifikation verformungsrelevanter Bereiche und anschließendem FIB-Präparieren hergestellt. Versetzungen wurden

mittels STEM-Hellfeldabbildung dokumentiert und unter ausgewählten Zwei-Strahl-Bedingungen hinsichtlich ihres Beugungskontrasts analysiert. Das Unsichtbarkeitskriterium diente zur Bestimmung des Versetzungscharakters und der aktiven Gleitebenen in beiden Phasen.

Im Gusszustand führt die hohe Abkühlgeschwindigkeit zu einer Si-Übersättigung der festen Lösung und zur Ausscheidung von Siliziden während der Erstarrung; umgekehrt treten im Silizid auch Ausscheidungen aus der festen Lösung aufgrund einer Mo-Übersättigung auf. Während des Kriechens bilden sich in beiden Phasen halbkoherente Ausscheidungen, die sich mit zunehmender Dehnung vergrößern. EBSD-KAM-Analysen zeigen, dass beide Phasen ab einer Kriechdehnung von 1,3% ($\dot{\epsilon}_{min}$) aktiv zur Verformung beitragen, wobei die Kriechdehnung durch die Generierung und Bewegung von Versetzungen akkumuliert wird. Die Kriechkurve wird zunächst durch die Keimbildung und das Wachstum der Ausscheidungen bestimmt, während der anschließende Anstieg der Kriechrate durch deren Vergrößerung verursacht wird, was das Versetzungs gleiten erleichtert. Nachgewiesene Kantenversetzungen in der festen Lösung sowie vereinzelte Beobachtungen von Versetzungsaufstieg im Silizid bestätigen einen durch Aufstieg gesteuerten Kriechmechanismus.

Abstract

In the aeroengines, turbine blades are crucial components because they are exposed to hot gases exiting the combustion chamber. The single-crystal, nickel (Ni)-base superalloys are used in turbine blades and polycrystalline Ni-base superalloys are used in turbine nozzles, shrouds and disc applications. Their unique thermo-mechanical properties rely on a two-phase microstructure, where $L1_2$ γ' precipitates are coherently embedded in fcc γ matrix. The operating temperatures seldom exceed 1150 °C due to the solvus temperature of γ' . However, the thermodynamic efficiency of the turbine increases with higher operating temperatures. The goal is to design novel high-temperature materials that can sustain higher operating temperatures (> 1200 °C) without air cooling of turbine blades.

The Mo-Si-Ti system has been explored as an alternative to the existing high-temperature materials because of their lower density (6-7 g/cc) and higher solidus temperatures (≈ 1800 °C). A eutectic Mo-20Si-52.8Ti (at.%) alloy showed pesting resistance and optimal creep behavior. It has a two-phase microstructure: a body-centered cubic (bcc), solid solution consisting of Mo, Ti and Si, $(\text{Mo,Ti,Si})_{ss}$ and hexagonal silicide $(\text{Ti,Mo})_5\text{Si}_3$. Compressive creep tests performed at 1200 °C and true stress of 100 MPa showed a characteristic minimum ($\dot{\epsilon}_{min}$) at 1.3% true creep strain (ϵ_t). To understand the microstructural evolution, the samples were crept to ϵ_t of 0.2%, 1.3%, 10%, 20%, and 40%.

Transmission electron microscopy (TEM) characterization is performed to decipher dislocation-precipitate interactions and other dislocation processes during creep. TEM specimens of crept samples were prepared using electron backscatter diffraction (EBSD) for strain identification and subsequent focused ion beam (FIB) milling. The dislocations were imaged using scanning transmission electron microscopy (STEM)-bright field (BF)

technique and the diffraction contrast of the selected two-beam conditions was analyzed. The Invisibility criterion was used to determine the character of dislocations in solid solution and acting slip planes in silicide, respectively.

In the as-cast (AC) state, the high cooling rates during arc melting lead to Si supersaturation in solid solution and formation of silicide precipitates during cooling. Similarly, solid solution precipitates are also observed in silicide at localized regions, but not as widespread as silicide precipitates in solid solution. These occur due to Mo supersaturation in silicide. During creep, precipitation occurred in both phases, which could be semi-coherent with their respective matrices. They undergo coarsening as a function of creep strain in both phases.

EBSD-kernel average misorientation (KAM) maps reveal that both phases contribute to creep deformation from $1.3\% \varepsilon_t$ ($\dot{\varepsilon}_{min}$) onwards. Both phases accumulate creep strain by the generation of dislocations. The shape of the creep curve is due to nucleation and growth of precipitates until the creep minimum, and an increase in creep rate is due to coarsening of the precipitates in both phases. This leads to reduced obstacle resistance and easier glide of dislocations. The presence of edge dislocations is confirmed by finding the character of dislocations in the solid solution matrix. A few probable instances of dislocation climb around a solid solution precipitate are found in silicide matrix. This confirms the dislocation climb-controlled creep mechanism.

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Acronyms and symbols

Acronyms

bcc	body centred cubic
fcc	face centred cubic
hcp	hexagonal close packed
SEM	scanning electron microscopy
EBS	electron backscatter diffraction
FIB	focused ion beam
TEM	transmission electron microscopy
STEM	scanning transmission electron microscopy
EPMA	electron probe microanalysis
WBDF	weak beam dark field
EDXS	energy dispersive x-ray spectroscopy
SE	secondary electron
BSE	backscattered electron
KAM	kernel average misorientation
IPF	inverse pole figure
BF	bright field
DF	dark field

ADF	annular dark field
HAADF	high angle annular dark field imaging
SAD	selected area diffraction
CTE	coefficient of thermal expansion
AC	as cast
HT	heat treated at 1600 °C for 150 hours
ht	heat treated at 1200 °C for an hour
PFZ	precipitate free zone

Greek symbols and variables

λ	wavelength
λ_p	interparticle spacing
γ	surface energy
Q_c	activation energy
Ω	atomic volume
Ω_a	solid angle
v	average velocity of dislocation
v_c	climb velocity of dislocation
ν	speed of the electron
ε_t	true creep strain
ν_p	Poisson's ratio
ρ	density of material
ρ_m	dislocation density

$\dot{\epsilon}_{ss}$	true steady state creep rate
$\dot{\epsilon}_{min}$	true minimum creep rate
φ	phase shift
τ	shear stress
σ	normal stress
γ_{APB}	antiphase boundary energy
θ	Bragg angle
μ	chemical potential
ξ	extinction distance
ϕ	beam amplitude of incident beam
ϕ_g	beam amplitude of diffracted beam
η	efficiency
δ	misfit
Z	atomic number
G	shear modulus
R	radius
A	atomic weight
n	stress exponent
p	grain size exponent
T	temperature
D	diffusion constant
b	magnitude of Burgers vector
e	charge of an electron

Operators and math symbols

a lattice parameter

$\vec{b}$ Burgers vector

c lattice parameter

$\vec{g}$ diffraction vector

$\vec{u}$ line direction

1. Introduction & Objectives

In the current decade, the aviation sector accounts for 2.5% of the total global carbon emissions, and this sector accounts for 3.8 to 4% of European Union (EU) greenhouse gas emissions [1]. One of the recommendations of the environmental agencies is to improve the airframe and efficiency of the engines. The aircraft manufacturers plan to reduce emissions by switching to net-zero emissions fuels, offsetting carbon emissions, and improving operational efficiencies. Turbine engines generate the required energy in the power industry and aerospace sectors. In these engines, turbine blades are the critical components, as they experience the hot gases exiting the combustion chamber, where fuel is burned with oxygen.

The operating temperature of the turbine engines directly depends on the temperature capability of the high-temperature structural materials. Currently, the turbine blades are made of single-crystal, nickel (Ni)-base superalloys [2, 3]. These superalloys are model systems for any high-temperature structural materials design, as they exhibit necessary oxidation and good creep resistance at high temperatures, which limit the operating time of the alloys. Their operating temperatures reach approximately 0.80 to 0.85 of the alloy's solidus temperature (T_S). In turbine engines, efficiency (η) is defined as how well fuel energy is converted into useful work, thrust for turbine engines [4]. It is defined as follows in Equation 1.1.

$$\eta = 1 - \frac{T_{out}}{T_{in}} \quad (1.1)$$

Here T_{out} and T_{in} are the outlet and inlet temperatures of turbine engines, respectively.

Figure 1.1 shows the specific core power generated in the turbine engine as a function of inlet temperature in the turbine rotor. The red line denotes the ideal performance of the engine, whereas the black circles correspond to the actual performance. The different

shadings of the plot in Fig. 1.1 indicate various efforts to improve the operating temperature. The pink shading corresponds to gains from using advanced materials and efficient design. The sky blue shading indicates the increased efficiency from advanced cooling schemes. The teal color coding indicates the opportunities for development trend. For instance, a 50% improvement in efficiency occurs when the temperature is increased from 1150 °C to 1300 °C without any additional cooling. In addition, higher operating temperatures have the added advantage of increased thermodynamic efficiency, as shown in Fig. 1.1. This results in the judicious use of fossil fuels and reduces the CO₂ emissions [3, 5].

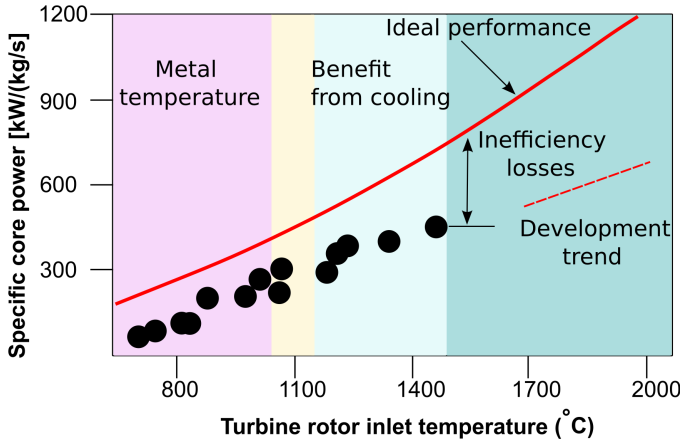


Figure 1.1.: Specific core power as a function of the turbine inlet temperature for commercial turbine engines. Black circles indicate actual core power and red line represents the ideal performance. Figure adapted from Ref. [5]

The microstructure of single-crystal, Ni-base superalloys is composed of two phases: L1₂ γ' precipitates coherently embedded in fcc γ matrix [6]. When the turbine operating temperatures approach the solvus temperature of γ' at 1150 to 1250 °C, the γ' precipitates dissolve into the matrix, and the intended precipitation strengthening is lost. Hence the actual composition of γ' precipitates in γ matrix alloy is not suitable for the envisioned high-temperature application. To improve the turbine efficiency, novel high-temperature structural materials design is needed that can withstand operating temperatures beyond 1200 °C. Moreover, these blades are subjected to centrifugal forces due to continuous rotation in the turbines. Due to harsh environments, novel alloy design approaches aim

to take these into account and interlink properties, such as oxidation resistance, creep behaviour, room temperature ductility, and fracture toughness.

In addition to the restriction imposed by the solvus temperature of the γ' phase, Ni-base superalloys also exhibit relatively high densities (≈ 9 g/cc) [2]. High densities lead to more weight of the component and higher centrifugal forces and, in turn, higher stresses for creep testing. This has prompted researchers to explore alternative material systems, such as those based on refractory metals. Table 1.1 shows the selected mechanical and thermal properties of Ni and molybdenum (Mo). Compared to Ni, Mo has a higher melting point of 2620 °C, slightly higher density of 10.22 g/cm³, higher elastic modulus and shear modulus as well as lower coefficient of linear thermal expansion [7].

Table 1.1.: Selected mechanical and thermal properties of nickel (Ni) and molybdenum (Mo) [7]

Metal	Ni	Mo
Density in $g.cm^{-3}$	8.9	10.22
Coefficient of linear thermal expansion in K^{-1}	13.3×10^{-6}	5.35×10^{-6}
Elastic modulus in GPa	220	330
Shear modulus in GPa	78.5	123.0
Melting point in °C	1455	2620

Mo-Si alloys initially appeared promising due to the ability of silicon to form a protective silica layer at elevated temperatures, enhancing oxidation resistance. However, these alloys suffer from the pesting phenomenon at lower and intermediate temperatures, leading to material degradation [8, 9]. To address this, the Mo-Si-B ternary alloys are developed, typically consisting of a bcc Mo solid solution matrix with dispersed intermetallic phases such as Mo₃Si, and Mo₅SiB₂. The addition of boron enables the formation of a duplex silica–boride layer, further improving oxidation resistance. Nonetheless, these improvements are insufficient to fully mitigate pesting [10, 11]. Furthermore, Mo-9Si-8B alloys have relatively high densities (9.5 g/cc), which is undesirable for structural applications [12].

To compensate for the high density of Mo–Si–B alloys, researchers have introduced Ti as an alloying element with a density of 4.5 g/cc. This approach has led to a favorable

reduction in density, as seen in the Mo-12.5Si-8.5B-27.5Ti alloy, which achieves a density of ≈ 7.8 g/cc [13]. However, this composition exhibits reduced oxidation resistance at intermediate temperatures (820–1200 °C) due to the formation of a complex oxide scale consisting of majorly TiO_2 with amorphous silica and some pores, which is less protective than the silica layer alone. Consequently, efforts have increasingly focused on eliminating the Mo_5SiB_2 and identifying alternative alloy systems within the Mo-Si-Ti ternary system. This system has emerged as a promising candidate for achieving both lower density and improved oxidation as well as pesting resistance. Recent studies have demonstrated that by tailoring the microstructure specifically, through the formation of a pesting-resistant hexagonal silicide, Ti_5Si_3 alongside a ductile Mo-rich solid solution, these alloys can overcome the limitations of higher density and pesting observed in earlier systems [12, 13]. The overarching objective in this work is to evaluate the creep properties of these Mo-Si-Ti alloys for high-temperature structural applications by investigating creep-induced microstructural evolution and deformation mechanisms between the two constituent phases during creep.

The primary goal of this work is to understand the high-temperature mechanical behaviour by micro-structural evolution of a eutectic, two-phase, Mo-20Si-52.8Ti alloy crept at 1200 °C using electron microscopy. The following objectives are addressed in the following thesis:

1. From the Norton plot, which is minimum creep rate plotted as a function of applied creep stress, n value (slope) indicated a transition from dislocation climb-controlled creep ($n=5.3$) to interface-reaction controlled diffusional creep ($n=1.7$) at 100 MPa. From this analysis, the aforementioned creep deformation mechanisms are deduced. However, microstructural understanding is missing. Verifying the dislocation climb-controlled creep mechanism in the alloy system requires either imaging jogs in dislocations or confirming the presence of edge dislocations using TEM. Hence, it is necessary to find the character of dislocations. In the scientific literature, jog formation is observed in both edge and screw dislocations. Therefore, it is necessary to ascertain whether the jogs form in either screw dislocations or edge dislocations.
2. The creep curve of the alloy exhibits a distinct creep minimum. What is the microstructural reason for work hardening before the creep minimum and the

increase in the creep rate after it occurs? How do the two phases deform at different stages of the creep curve? Does the silicide also participate in the initial stages of the creep deformation? This information is critical from the mechanical point of view, as Von-Mises criterion dictates that at least five independent slip systems are required for permanent shape change to occur. Hexagonal silicide has limited slip systems compared to the solid solution.

3. What are the acting slip systems in the solid solution and silicide phases? In bcc metals and alloys, densely packed planes of $\{110\}$, $\{112\}$, and $\{123\}$ are reported in the literature. Whereas in hexagonal materials, some reports found the operation of prismatic and pyramidal planes at high temperatures. This information aids in understanding the partitioning of creep strain in silicide phase at creep temperature of 1200 °C.
4. Do any microstructural changes occur during the creep deformation? In the as-cast (AC) state, precipitation of silicide in solid solution matrix and solid solution in silicide matrix occur. Why does precipitation occur and where does it occur? What type of precipitates form in both phases? The goal is to find out the type of interface between matrix and precipitate and determine the accurate local chemical composition of precipitates in both phases using scanning transmission electron microscopy (STEM)-energy dispersive x-ray spectroscopy (EDXS)?

In this thesis, the contents are arranged in the following manner: Chapter 1 describes the limitations of existing high-temperature materials, requirements of alternate high-temperature materials, the necessity to design them, and the objectives of the current thesis. Chapter 2 summarizes the alloy design efforts carried out in Mo-Si-Ti alloys, microstructural defects that influence high temperature mechanical behavior, creep behavior of high temperature materials, reasons for creep minimum in some Mo-based high temperature materials and electron-beam matter interactions. Chapter 3 describes the experimental methods used for performing metallography, creep testing, electron microscopic investigations, and data analysis. Chapter 4 depicts the obtained results using a combination of scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and TEM characterization techniques. Chapter 5 discusses the results in the current thesis with respect to existing climb theories and other relevant material systems. Chapter 6 concludes the major findings, scope, and relevance of the present thesis.

2. State of the art

Refractory metals such as Mo, Nb, Ta, and W are attractive for high-temperature applications due to their exceptionally high melting points above 2500 °C, which confer inherently high creep strengths [7]. In addition to thermal stability, high-temperature structural materials must exhibit good oxidation resistance [14]. Molybdenum (Mo) is a particularly promising candidate because it has a high melting point (2620 °C), relatively low density (10.22 g/cm³) compared to other refractory elements, and favorable oxidation resistance at elevated temperatures [7]. However, at low to intermediate temperatures, Mo is found to form volatile MoO₃ at grain boundaries, leading to severe mass loss, catastrophic oxidation, and the formation of a porous, structurally compromised component [8, 9]. The ternary Mo-Si-Ti system is designed based on the binary phase diagrams of its constituent systems. It includes the hexagonal silicide (Ti₅Si₃) and tetragonal silicide (Mo₅Si₃) originating from the Ti-Si and Mo-Si systems respectively as well as solid solution from the isomorphous Mo-Ti system [15]. In the following section, the alloy design approach is presented in several steps.

2.1. Alloys of Mo-Si-Ti system and their properties

To achieve dual objectives of pesting resistance and lower density, Mo-Si-Ti system was explored. Two reference eutectic and solid-state transformed alloys were designed and synthesized based on two ordered, intermetallic compounds: (Ti,Mo)₅Si₃ and (Mo,Ti)₅Si₃ [16]. The nominal chemical compositions of a eutectic and solid-state transformed alloys were Mo-20Si-52.8Ti and Mo-21Si-34Ti, respectively. This eutectic alloy comprised of a bcc solid solution (Mo,Ti,Si)_{ss} and a hexagonal silicide, (Ti,Mo)₅Si₃, whereas the solid-state transformed alloy was composed of a bcc solid solution and a tetragonal silicide, (Mo,Ti)₅Si₃. The eutectic alloy did not exhibit any pesting and showed

a small mass gain at 800 °C. In contrast, the solid-state transformed alloy showed drastic mass loss at that temperature [16]. The solid-state transformed alloy showed one order of magnitude lower creep rate than the eutectic alloy. Both alloys had solid solution and intermetallic silicide in 50:50 volume fraction [16]. In addition to $(\text{Mo,Ti})_5\text{Si}_3$, 9 vol.% of $(\text{Ti,Mo})_5\text{Si}_3$ was also observed in solid-state transformed alloy due to the Ti segregation.

This eutectic alloy consists of solid solution and silicide phases. The solid solution phase is a disordered solid solution of Mo, Ti, and Si elements occupying a bcc lattice. The lattice parameter of the solid solution is $a=3.16 \text{ \AA}$ (Strukturbericht A2, W prototype, space group no. 229). The $(\text{Ti,Mo})_5\text{Si}_3$ is an ordered intermetallic compound with a hexagonal crystal structure. The lattice parameters of the hexagonal silicide are $a=7.419 \text{ \AA}$ and $c=5.124 \text{ \AA}$ (Mn_5Si_3 D8₈ space group no. 193), respectively. In this unit cell, Ti occurs in two valencies: Ti^{4+} and Ti^{6+} . Since Mo and Ti form an isomorphous system, Mo also substitutes for Ti lattice positions in the silicide [16]. The chemical composition of both phases of a eutectic Mo-Si-Ti alloy are shown in Table 2.1. From Pandat thermodynamic calculations, the $(\text{Ti,Mo})_5\text{Si}_3$ has a slightly higher Si content of 38 at.% than the stoichiometric amount of 37.5 at.%. The solid solution has 50 at.% of Ti and 47 at.% of Mo with Si as solute with 3 at.%. Hence, Si and Mo are solutes in the solid solution and silicide, respectively. The nominal chemical composition of a eutectic alloy, Mo-20Si-52.8Ti lies on a eutectic trough and solidify by eutectic reaction of $(\text{Mo,Ti,Si})_{\text{ss}}$ and $(\text{Ti,Mo})_5\text{Si}_3$ after reaching eutectic transformation temperature. In addition, the eutectic alloy composition, marked with red square in Fig. 2.1 also falls on liquidus line. During arc melting, the diffusion is limited because of high cooling rates and this leads to supersaturation of solutes in both phases. There is a possibility that precipitation might happen in both phases when any heat treatment exceeds $0.4T_s$, can lead to nucleation and growth of precipitates [17].

Table 2.1.: Calculated chemical composition of two phases from PANDATTM software [16]

at.%	Mo	Si	Ti	Z_{avg}
$(\text{Mo,Ti,Si})_{\text{ss}}$	47	3	50	31
$(\text{Ti,Mo})_5\text{Si}_3$	7	38	55	20

Binary Ti_5Si_3 has an anisotropy of the coefficient of thermal expansion (CTE) value of 2.7 in the c-axis and a-axis [18]. This leads to the formation of cracks in the silicide. The

solid solution phase acted as a crack arrestor, but sometimes the cracks also reached into the solid solution [19]. Raja et al. [20] found out the orientation relationship between two phases of eutectic alloy, manufactured by directional solidification:

$(123)_{(\text{Mo,Ti,Si})_{\text{ss}}} \parallel (0001)_{(\text{Ti,Mo})_5\text{Si}_3}$ and $[111]_{(\text{Mo,Ti,Si})_{\text{ss}}} \parallel [11\bar{2}0]_{(\text{Ti,Mo})_5\text{Si}_3}$. Frommeyer et al. [21] reported an elastic modulus of 156 GPa for polycrystalline Ti_5Si_3 . In contrast, Kishida et al. [22] calculated the elastic modulus of the polycrystalline Ti_5Si_3 to be 234 GPa. The authors suggested that the incorporation of elastically softer phases into Ti_5Si_3 matrix, may have contributed to lower measured elastic modulus in Ref. [21].

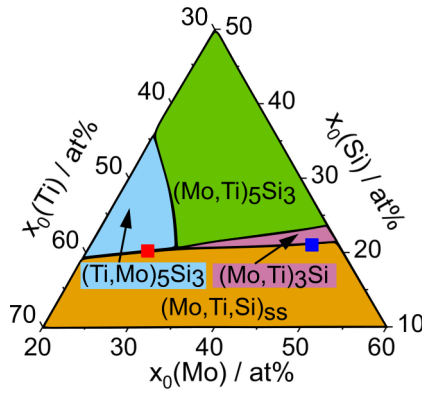


Figure 2.1.: Section of the liquidus projection of the ternary Mo-Si-Ti system, highlighting the primary solidifying phases (colored labels). The investigated eutectic alloy and solid-state transformed are denoted with red and blue squares respectively (coloured symbols). Figure adapted from Ref. [23].

Obert et al. [23, 24, 25, 26] designed and analyzed a series of new Mo-Si-Ti alloys to achieve both pesting resistance and creep properties by tuning the eutectic and solid-state transformed fractions and minimizing the primary solidified solid solution, as listed in Table 2.2. The nominal chemical composition of the investigated alloys and their phase fractions are reported in Table 2.2. Alloys designated in the A and B series have 25% and 40% solid-state transformed regions, respectively. The alloy designated number 1 in these series has $(\text{Mo,Ti})_3\text{Si}$ as the primary solidified phase, whereas alloy designated 2 has a solid solution as the primary solidified phase. The alloys in the C series differ by their Ti content and by variations in their Si content. The alloy C1 has no primary solidified phase, but the C2 alloy has $(\text{Mo,Ti})_3\text{Si}$ as a primary solidified phase. In contrast, D1 and D2 alloys have the $(\text{Mo,Ti})_5\text{Si}_3$ as the primary solidified phase. A summary of the alloy design approach was presented in this thesis, but the complete details can be found in

the doctoral thesis of Obert [27] and associated publications [23, 24, 25, 26]. Obert et al. [27] performed the isothermal oxidation tests and the alloys that showed resistance to peeling were creep tested and compared their creep performance with the solid-state transformed alloy. The initial creep tests of Mo-Si-Ti alloys were accomplished by Schliephake [16] and Obert [27].

Table 2.2.: Lists of alloys investigated in Mo-Si-Ti ternary system [27]

Alloy	Nominal chemical composition	Eutectic percent	Solid state transformed percent	Primary Mo _{ss} percent	Primary (Mo,Ti) ₅ Si ₃ percent
Eutectic	Mo-20Si-52.8Ti	–	–	–	–
solid state transformed	Mo-21Si-34Ti	–	–	–	–
A1	Mo-21.6Si-43.4Ti	49.9 ± 6.0	46.6 ± 6.0	3.5 ± 1.25	–
A2	Mo-20.5Si-43.4Ti	53.9 ± 9.2	33.5 ± 6.0	12.6 ± 4.7	–
B1	Mo-21Si-38.7Ti	45.1 ± 3.3	48.2 ± 2.1	6.7 ± 1.5	–
B2	Mo-20.25Si-38.7Ti	31.3 ± 4.7	56.3 ± 4.9	12.4 ± 1.8	–
AB	Mo-21.5Si-41.5Ti	44.5 ± 6.2	54.1.9 ± 7.7	1.3 ± 2.2	–
C1	Mo-21.6Si-44.2Ti	64.0 ± 4.1	31.3 ± 2.0	–	4.7 ± 0.9
C2	Mo-21Si-47Ti	71.8 ± 7.7	27.56 ± 7.6	–	0.6 ± 0.8
D1	Mo-26Si-40Ti	41.6 ± 6.7	27.8 ± 4.7	–	30.6 ± 4.3
D2	Mo-26Si-44Ti	57.8 ± 7.4	10.7 ± 3.0	–	31.5 ± 4.6

2.2. Microstructural defects which influence high temperature behavior

Taylor [28], Orowan [29] and Polanyi [30] independently proposed the concept of dislocation. They are one-dimensional lattice defects, that control plasticity in materials [31]. The materials accommodate the plastic strain by the movement of dislocations through the crystal lattice under the applied shear stresses. There are three different types of dislocations: edge, screw, and mixed. These dislocations are distinguished based on how the dislocation line is oriented with respect to the Burgers vector ($\vec{b}$). It indicates the magnitude and direction of the slip. The principal characteristics of a dislocation are slip plane (hkl), line direction ($\vec{u}$) and $\vec{b}$ [32, 33, 34, 35].

The edge dislocation is associated with an extra half-plane. The edge dislocation is located at a position where the extra half-plane ends, known as the core of the dislocation. For an edge dislocation, the $\vec{b}$ is perpendicular to the $\vec{u}$. An edge dislocation can only glide in the plane containing the $\vec{b}$ and dislocation line. For instance, the edge dislocation glides along the $\vec{b}$. At high temperatures, an edge dislocation can climb perpendicular to the $\vec{u}$ with either vacancies or interstitial diffusion, in the presence of an acting normal stress [32, 34]. Climb occurs by nucleation and motion of jogs. Jogs are sharp breaks in the dislocation line, moving it out of the slip plane.

For a screw dislocation, the $\vec{b}$ and dislocation line are parallel to each other. The screw dislocation glides perpendicular to the $\vec{b}$. It can cross-slip from one slip plane (primary slip plane) to another slip plane (cross-slip plane) as long as the cross-slip plane contains the same slip direction [34]. However, it requires higher stress. The glide motion of edge dislocations or cross-slip of screw dislocations is conservative motion. Whereas climb of edge dislocation is non-conservative due to the volume change involving the addition or removal of atoms. The strain energy, W of the edge dislocation is higher than the screw dislocation from theory of elasticity [35]

$$\left(\frac{W}{L}\right)_{screw} = \frac{Gb^2}{4\pi} \ln \frac{R}{r_0} \quad (2.1)$$

$$\left(\frac{W}{L}\right)_{edge} = \frac{Gb^2}{4\pi(1-\nu_p)} \ln \frac{R}{r_0} \quad (2.2)$$

Here G is the shear modulus, b is the magnitude of $\vec{b}$, ν_p is Poisson's ratio, L is the length of the dislocation line, R and r_0 are outer and core radius of dislocation line over which elastic field is considered.

With respect to the alloy investigated in this work, dislocations in a bcc and hcp lattice are recapitulated in the following. The bcc metals and alloys are characterized by peculiar dependence of yield stress with temperature and strain rate, twinning-anti-twinning asymmetry and anomalous slip [36]. In these metals and alloys, screw dislocations control the strength by double kink pair nucleation mechanism. Their formation is the rate-controlling step in bcc metals and alloys. The mobility of screw dislocations increases with increasing temperature [37, 38]. The dislocations in the bcc metals have a $\vec{b}$ of $\frac{1}{2}\langle 111 \rangle$ and four $\vec{b}$ are seen in Table A.2. The screw dislocations have a non-planar core [39]. It is spread across the three $\{110\}$ planes along the $[111]$ zone. Two kinds of cores were found to exist: degenerate and non-degenerate. The degenerate cores have two structures: 2-fold diad along the $[10\bar{1}]$ and another one with 180° along the $[10\bar{1}]$ [39]. The cores of edge dislocations are planar. As a result, edge dislocations can glide easily whereas screw dislocations should overcome high Pierels barrier [40]. There are 48 slip systems in bcc metals and alloys. In bcc metals and alloys, there is no close packed plane. $\{110\}$, $\{112\}$ and $\{123\}$ have similar packing fraction and close packed direction is $\langle 111 \rangle$. Typically screw dislocations are very long, ranging up to $20 \mu\text{m}$ were found in single-crystal Mo [41], whereas edge dislocations with short segments were noted in equiatomic MoNbTi [42].

Hexagonal closed packed (HCP) metals and alloys are anisotropic in their mechanical properties, and exhibit limited ductility [43]. Plastic deformation of hcp metals and alloys occurs by activation of $\langle c+a \rangle$ slip [44, 45] or deformation twinning [43, 46]. Taylor [47] proposed that all grains undergo the same deformation as the overall deformation. Five independent slip systems are needed to undergo general shape change by slip [48]. Since hexagonal lattices are anisotropic, 4-index Miller-Bravais system is used to denote the planes and directions in hexagonal lattices [49, 50]. The basal plane is the close-packed plane in the hcp crystal structure. There are three different slip planes in hexagonal materials, namely, basal plane $\{0001\} \frac{1}{3}\langle 11\bar{2}0 \rangle$, prismatic $\{10\bar{1}0\} \frac{1}{3}\langle 11\bar{2}0 \rangle$ ($\langle a \rangle$ slip) and pyramidal $\{10\bar{1}1\}$ and $\{10\bar{1}2\} \frac{1}{3}\langle 11\bar{2}3 \rangle$ planes ($\langle c+a \rangle$ slip) [32]. At low temperatures, only the basal plane undergoes deformation. So, slip systems are limited to 3. With increasing temperature, prismatic and pyramidal slip systems are activated [32]. The $\vec{b}$ of

the hexagonal lattices are shown in Table 4.7. The way how dislocations operate during thermo-mechanical deformation, creep, is described in section 2.3.

Precipitates are three-dimensional defects that nucleate from the matrix in metallic materials [17, 51]. There are three different types of precipitates: coherent, semi-coherent, and incoherent precipitates [17]. Coherent precipitates form when the precipitate has the same crystal structure as the matrix or a small misfit exists between the matrix and precipitate. In exceptional cases, due to energy penalty for the creation of misfit dislocations, the precipitate of the dissimilar crystal structure can also form a coherent precipitate when the size is a few nanometers. Semi-coherent precipitates form when the two crystal structures have interfacial matching and some of the lattice planes match. The mismatch of crystal planes across the semi-coherent interface leads to the formation of misfit dislocations. Incoherent precipitates form when there is no matching between the crystal planes of the matrix and the precipitate. In usual cases, the precipitate often nucleates as coherent and/or semi-coherent type, and with a necessary driving force, they become incoherent during growth or coarsening in Al-Cu alloys [52]. The existence of orientation relationship necessarily does not mean the precipitate is coherent [53]. Even incoherent θ precipitates have an orientation relationship with Al matrix [53].

The precipitation hardening approach involves retaining an excess concentration of solute in the single-phase field by isothermal heat treatment at high temperatures and quenching (or rapid cooling) from holding temperatures to room temperature [54, 55]. The supersaturation solid solution can be further aged at room temperature or artificially aged at a temperature higher than room temperature. Because of the decreasing solubility of solute in the single phase region and the related crossing of the phase boundary at lower temperatures, subsequent heating leads to precipitation. Precipitation hardening is used as a strengthening mechanism in engineering materials such as Al-Cu alloys [52] and Ni-base superalloys [56]. The aging treatment consists of three different stages: nucleation, growth and coarsening [54, 55]. In nucleation stage, the excess solute precipitates out of the solid solution because of a higher concentration than the equilibrium concentration in the matrix. Since nucleation is a statistical process, it leads to the distribution of precipitate sizes [55]. As precipitates grow, the volume fraction of precipitate increases significantly. With increasing time of exposure, the precipitates coarsen to reduce the interfacial energy between the matrix and precipitate interface as the system tries to eliminate excess free energy. The chemical potential (μ) of the precipitate is inversely

proportional to its size, as shown in equation 2.3. During this stage, the precipitate volume fractions stay constant and the number density reduces [51].

$$\mu_{precipitate} = \frac{2\gamma V_m}{r_i} \quad (2.3)$$

where μ is the chemical potential of the precipitate, γ is the surface energy between precipitate and matrix, V_m is the molar volume and r_i is the radius of the precipitate.

Precipitation hardening is an effective way to strengthen materials at high temperatures, compared to solid solution strengthening and dislocation strengthening. High-temperature structural materials are often strengthened by second-phase particles (either dispersoids or precipitates) to retain strength at elevated temperatures [57]. These second-phase particles serve as obstacles to dislocation motion, in addition to lattice obstacles such as forest dislocations, solute atoms, etc. In metallic materials, precipitate-dislocation interactions control the strength. The interaction of dislocations with the defect such as precipitates control strength in metallic materials [53]. The gliding dislocations have to either cut through the precipitate or bend over and bypass the precipitates [57]. When dislocations cut through the coherent particles, the following strengthening mechanisms: chemical strengthening, modulus-mismatch strengthening, coherency strengthening, stacking fault strengthening and atomic order strengthening are operative [57].

2.3. Creep mechanisms of high temperature materials

For any high-temperature structural application, plastic deformation of the components occurs at high temperatures and under acting stresses/loads. Creep is the time-dependent plastic deformation of materials under the combined influence of load/stress and temperature [58, 59]. Creep tests are performed by either applying a constant stress/load or constant strain rate [60] at above 0.7 of homologous temperatures ($T_{hom} = T/T_m$), here T is the test temperature and T_m is the melting temperature of the metal. During a creep experiment, the creep strain as a function of time is recorded, as shown in Fig. 2.2 a. This data is replotted in terms of creep strain rate ($\dot{\epsilon}$) with a unit of $[s^{-1}]$ as a function of creep strain (ϵ) [dimension less] for better interpretation, as shown in 2.2 b. The latter is usually a log-linear plot, which is used to distinguish three stages of creep.

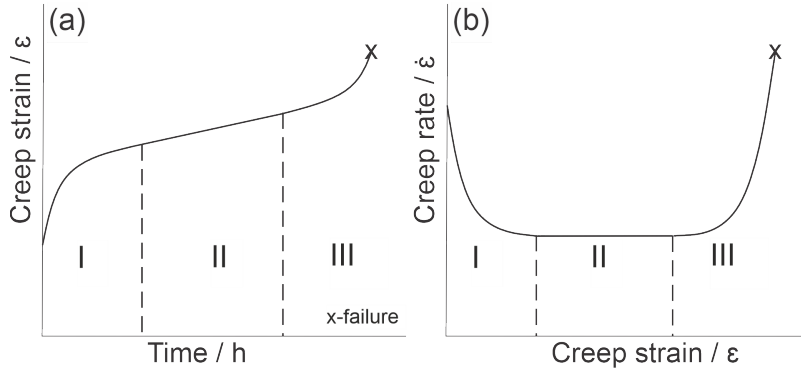


Figure 2.2.: Representation of creep data (a) Creep strain as a function of time, and (b) Creep strain rate as a function of creep strain. The Roman numerals I, II, and III indicate the primary, secondary, and tertiary creep stages, respectively. Adapted from Ref. [58]. Here $\dot{\epsilon}$ denotes $\frac{\partial \epsilon}{\partial t}$.

A typical creep curve shows three stages: primary (I), secondary (II), and tertiary (III) creep, as seen in Fig. 2.2 b. During primary creep, the creep rate decreases drastically due to work hardening of the material associated with a dislocation density increase. During secondary creep, the material develops a steady-state creep rate, where an equilibrium between strain hardening and dynamic recovery, balancing dislocation multiplication and annihilation, establishes. After a long time close to the global creep rate minimum ($\dot{\epsilon}_{min}$) (in the secondary creep regime), an important high temperature material design parameter, the creep rate increases drastically in the tertiary creep regime (III) towards final rupture. This regime is associated with microstructural degradation processes like grain or phase coarsening, dislocation cutting and climbing events, and more. To describe creep, Mukherjee et al. [61, 62] and Norton [63] introduced an empirical equation and plot, correlating the creep minimum ($\dot{\epsilon}_{min}$) obtained from the steady-state creep regime, to the applied stress (σ), as shown in Equation 2.4, known as the Norton's creep power law:

$$\dot{\epsilon}_{min} = A_0 e^{-\left(\frac{Q_c}{kT}\right)} \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad (2.4)$$

Here A_0 is a constant, Q_c is the apparent activation energy of creep in (kJ/mol), k is the Boltzmann's constant [1.38×10^{-23} J/K], T is the temperature in [K], σ is the applied stress [MPa], G is shear modulus [GPa], p is the grain size exponent, d is the grain size in [μm] and n is the apparent stress exponent.

The effect of increasing T and σ on the creep response of a material is shown schematically in Fig. 2.3. These are used to experimentally derive the activation energy (Q_c) and the creep exponent (n) respectively. In general, a Norton power law will always represent

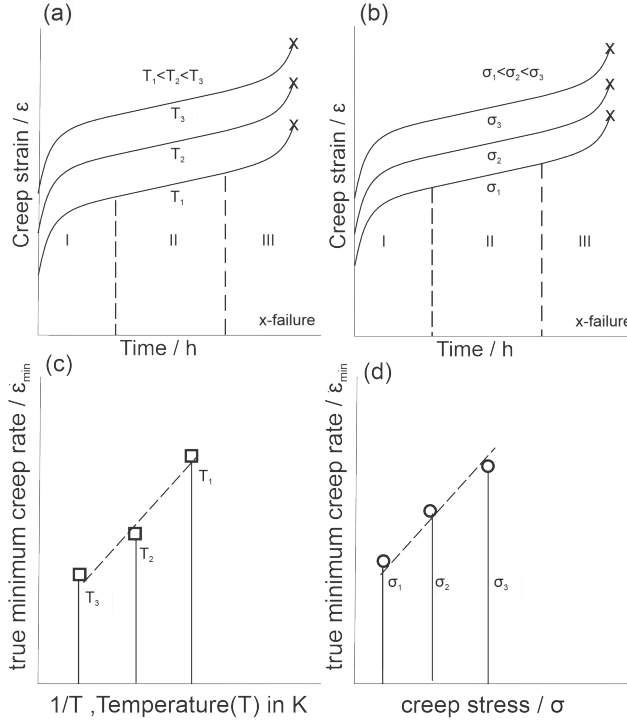


Figure 2.3.: Schematic of creep curves showing the effects of (a) Increasing temperature (b) Increasing stress (c) Activation energy plot and (d) Norton plot. Here σ and T indicate creep stress and temperature, respectively. Schematic adapted from Refs. [32, 64]

an approximation for limited stress ranges as lower stresses favor diffusional (creep) contributions to strain than longer test durations. The n values are, therefore, close to unity. In contrast, high stresses favor dislocation-based mechanisms of creep with n values greater than three. Similar to n value, grain size exponent (p) can be found out by performing creep tests at constant T and constant σ with varying grain size (d). The slope of semi-logarithmic plot, $\dot{\epsilon}_{min}$ plotted as a function of d gives the p value. The Q_c can be obtained by conducting creep tests at different temperatures (e.g., T_1, T_2 and T_3), as shown schematically in Fig. 2.3 a. As expected, increasing T causes the creep curves to shift to higher strains at constant σ . A minimum of three temperatures are

chosen to find out Q_c . The slope of $\dot{\epsilon}_{min}$ as a function of $(1/T)$ multiplied by universal gas constant (R) gives Q_c , as shown in Fig. 2.3 c. Alternatively Q_c can also be determined from two temperatures using Equation 2.5 but this is less accurate and erroneous.

$$Q_c = \frac{R \ln(\frac{\dot{\epsilon}_{min1}}{\dot{\epsilon}_{min2}})}{(\frac{1}{T_2} - \frac{1}{T_1})} \quad (2.5)$$

The alloy's Q_c is used to compare with self-diffusion and grain boundary diffusion activation energies of the pure metals to assess the dominant deformation mechanism. To further distinguish deformation mechanisms, n is taken into account, which is derived from creep tests performed at selected stresses at a constant T schematically shown in Fig. 2.3 b. As expected the creep strain increases with increasing stress. The slope of the $\dot{\epsilon}_{min}$ as a function of σ reveals the n value, as given in Equation 2.6 and shown schematically in Fig. 2.3 d.

$$n = \frac{\Delta \dot{\epsilon}_{min}}{\Delta \sigma} \quad (2.6)$$

It is generally agreed that an n value of 1 indicates deformation dominated by diffusional creep, while an n value between 3 and 8 denotes deformation dominated by dislocation creep. In conclusion, high-temperature materials exhibit distinct responses to changes in T , σ and $\dot{\epsilon}_{min}$ and decades of creep research have culminated in the empirical overview of deformation mechanisms as a function of (σ/G) and (T/T_m) represented in Fig. 2.4. The σ is normalized with shear modulus (G) to provide dimensionless quantity and easily compare creep deformation mechanisms of wide range of materials with taking into account their material parameters.

This deformation mechanism map, displays the relationship between three macroscopic variables: T , σ , and $\dot{\epsilon}_{min}$ [65, 66]. If any of these two variables are chosen, the third can be determined. The map is divided into five regions, each dominated by a specific deformation mechanism: theoretical shear strength, low-temperature plasticity by dislocation glide, low-temperature plasticity by twinning, power-law breakdown by dislocation glide or dislocation creep, and diffusional creep. Low-temperature plasticity is excluded. In the following sections, only the three relevant regions: power-law breakdown by dislocation glide or dislocation creep, and diffusional flow are discussed. The definition of dislocations in selected crystal structures is described in section 2.2.

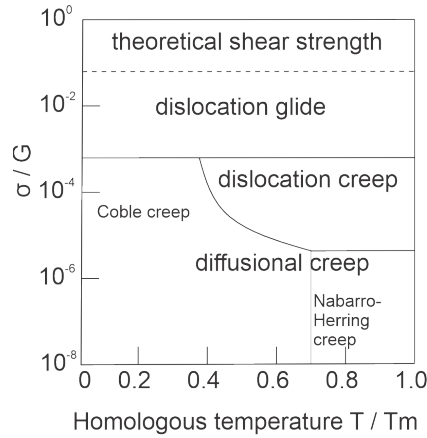


Figure 2.4.: Schematic of creep deformation mechanisms. Schematic adapted from Refs. [65, 66]

Dislocation glide occurs at stress levels that are relatively higher than those normally considered in creep deformation [32]. The creep rate depends on the ease with which dislocations are impeded by obstacles such as precipitates, solute atoms and other dislocations. At elevated temperatures, plastic flow can be considered a thermally activated process. The applied shear stress is opposed by internal stresses from long-range obstacles and short-range obstacles. The long-range obstacles are barriers too high and long to be surmounted by thermal fluctuations. The stress fields of other dislocations, large incoherent particles and massive second phase particles falls into long range obstacles. Short-range obstacles (also called thermal barriers) are less than 10 atom diameters, for which dislocations can surmount these obstacles by thermal fluctuations. The Peierls-Nabarro force, stress fields of coherent precipitates and solute atoms, cross-slip, dislocation climb and intersection of dislocations act as short range obstacles. These are a strong function of T and $\dot{\epsilon}$.

Dislocation creep occurs by dislocation glide aided by vacancy diffusion [32].

Weertman [67, 68, 69, 70] pioneered the early attempts to describe creep in terms of dislocation creep. At high temperatures, if the gliding dislocation is held up by an obstacle, a small amount of climb may permit it to surmount the obstacle, allowing it to glide to the next set of obstacles, where the process is repeated again. The glide step produces almost all of the strain but the climb step controls the velocity. Since dislocation climb requires vacancy or interstitial diffusion, atomic diffusion is the rate-controlling step. From the Norton plot [63], which is steady state creep rate plotted as a function of

creep stress, at low stresses, a linear dependence of steady state creep rate with stress is noted. This is known as Harper-Dorn creep [71]. This could be due to climb-controlled creep under conditions where dislocation density does not change with the stress. At temperatures above $0.5T_m$, for intermediate to high stress levels, the steady-state creep rate is described by a power-law relation given in Equation 2.4. At higher stresses, the measured creep rates are higher than predicted by power-law relation. This is referred to as a “power law breakdown.”

Weertman [67, 68, 69, 70] derived the equation for average dislocation velocity, shown in Equation 2.8.

$$v_c \cong 2\pi \left(\frac{D}{b} \right) \left(\frac{\sigma\Omega}{kT} \right) \ln \left(\frac{R_0}{b} \right) \quad (2.7)$$

where v_c is the rate-controlling velocity of climb, Ω is the atomic volume, D is the diffusion constant, σ is the applied stress and R_0 is the diffusion distance, related to the dislocation spacing.

$$\bar{v} \cong \frac{v_c \bar{x}_g}{\bar{x}_c} \quad (2.8)$$

$\bar{x}_c$ is the climb distance of dislocation, $\bar{x}_g$ is the dislocation glide distance, $\dot{\epsilon}$ is the strain rate and $\bar{v}$ is the average velocity of dislocations.

The Orowan creep equation demonstrates the dependence of creep rate on the average velocity of dislocations, given in Equation 2.9.

$$\dot{\epsilon}_{ss} = \rho_m b \bar{v} \quad (2.9)$$

Here ρ_m is the dislocation density.

In particle-containing systems, where particles are present in a matrix as either precipitates or inclusions, the gliding dislocations can encounter three different scenarios [72]. The first possibility is Friedel’s cutting [73]. Figure 2.5 a shows an edge-on dislocation before cutting and after cutting through a coherent precipitate in the matrix. This is only possible when the precipitate is coherent to the matrix, in the related glide plane. After the cutting event, the precipitate bifurcates, and one half of the precipitate translates with respect to the other, creating a step with a magnitude of the $\vec{b}$. This is generally observed when precipitates are coherent with the matrix. In this mechanism, flow stress is dictated by the ability of dislocations to cut through the precipitates. In the precipitation

hardening engineering systems like Al-Sc-Mg alloys [74] and single-crystal, nickel-base superalloys [75, 76] that have coherent precipitates, the matrix dislocations can cut through the precipitates, Al_3Sc or γ' .

The second possibility is Orowan looping [77]. Figure 2.5 b shows the gliding dislocation interacting with two precipitates in the matrix. Initially, the dislocation bows between the precipitates, and the process continues until the dislocation reaches a critical radius. Then the dislocation leaves behind loops on both sides and encapsulates the precipitate. Finally, the dislocation bypasses the precipitate by Orowan looping around the precipitate. The critical stress required to bow around the precipitate is given by Equation 2.10.

$$\tau_{or} = \frac{Gb}{2\lambda_p} [77] \quad (2.10)$$

Here τ_{or} is the Orowan shear stress and λ_p is the inter-particle spacing.

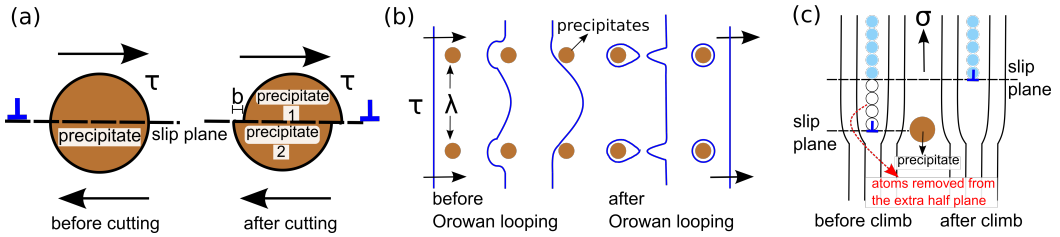


Figure 2.5.: Schematic of three dislocation–precipitate interactions (a) Friedel cutting, (b) Orowan looping, and (c) Dislocation climb around precipitates. Schematic adapted from Refs. [29, 57, 73]

Figure 2.6 illustrates the dominant precipitation hardening mechanisms in particle shearing and Orowan looping with increasing coherent precipitate size. For particle shearing, order strengthening (OS), coherent strengthening (CS), and modulus strengthening (MS) mechanisms are important. These mechanisms are illustrated with black dashed lines and dominant mechanism is marked with blue shading in both Fig. 2.6 a and Fig. 2.6 b. Cui et al. [78] derived the dependence of various precipitation hardening mechanisms of particle shearing based on line tension model and experimental values for bcc and fcc structures, shown in Equations 2.11, 2.12 and 2.13.

$$\Delta\sigma_{OS} \sim R^0 \quad (2.11)$$

$$\Delta\sigma_{CS} \sim \sqrt{R} \quad (2.12)$$

$$\Delta\sigma_{MS} \sim R^{0.275} \quad (2.13)$$

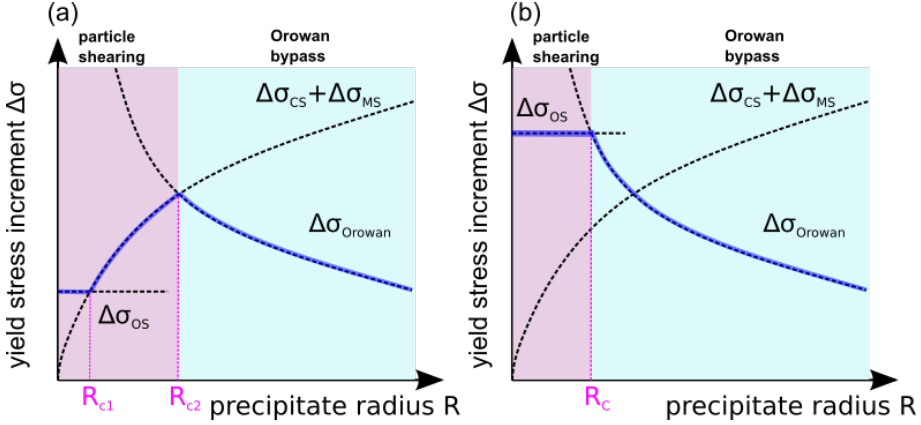


Figure 2.6.: Dominant precipitation strengthening mechanism as a function of coherent precipitate size
a) When the anti-phase boundary boundary energy is small b) When the anti-phase boundary energy is very large. Here, R is the radius of the precipitate, σ is the yield strength, OS is order strengthening, CS is coherent strengthening, and MS is modulus strengthening. Figure adapted from Ref. [78].

Figure 2.6 a depicts the situation where anti-phase boundary energy, γ_{APB} is small. The OS is predominant until critical radius of R_{c1} , as small precipitates have large surface-to-volume ratio, in Fig. 2.6 a. As a result, the OS is a constant value and thus independent of precipitate radius, as shown in Equation 2.11. As particles grow in size, they have higher volume than surface and therefore CS and MS mechanisms predominate. The dependence of CS and MS are shown in Equation 2.12 and 2.13. The CS has a higher contribution than MS because it has square root dependence of particle radius. After attaining the size of R_{c2} , Orowan looping plays a key role rather than shearing of precipitates. Generally at small sizes of precipitates, OS is dominant and later changes to CS and MS and then finally to Orowan looping in Fig. 2.6 a. Fig. 2.6 b visualizes the scenario where γ_{APB} is very large. Initially, OS is very dominant until the critical size of R_C . However, in exceptional circumstances, where γ_{APB} is very high, the strengthening mechanism changes from OS to Orowan looping directly without any intermediate CS and MS mechanism. Figure 2.6 does not take into account the effect of temperature. However, at sufficiently high temperatures, dislocation overcomes precipitates by the climb

mechanism [32, 57] instead of either cutting through precipitates or Orowan looping, which is discussed in the next paragraphs.

The last possibility is to undergo climb around the precipitates. A microscopic view of an edge dislocation lying edge-on, undergoing climb around the precipitate, is shown in Fig. 2.5 c. When this dislocation encounters a precipitate on its slip plane, edge dislocation can overcome the precipitate by climb. Climb is the vertical movement of dislocation to a parallel slip plane, perpendicular to the glide direction, under the action of normal stresses. This requires diffusion of either vacancies or atoms to the edge dislocation so that it can move above or below the current glide plane. If the edge dislocation moves up by diffusion of vacancies, it is called positive climb, and negative climb occurs when atoms are added to the dislocation and it moves down.

There are two theories of the climb in creep of particle-strengthened alloys [57, 79]. In the first theory, climb occurs around the particle by an increase in the length of the dislocation line around the obstacle. The climb stops when the work done by stress is not equal to sustaining the dislocation length increase. Other theory involves the existence of an attractive interaction between dislocations and incoherent particles. There exists a detachment stress to remove the particle from the dislocation particle interface after climb.

In the precipitation-strengthened and dispersion-strengthened metallic materials, the minimum creep rates of the alloy with particles, either precipitates or dispersoids that are usually incoherent, showed much lower creep rates than alloys without any particles [72, 80]. This gave rise to the concept of threshold stresses. If there is any particle in the matrix, additional stress is required to overcome the particle, and this contributes to the strengthening of the alloy. Threshold stresses have been reported in nickel-base superalloys [81], Al-alloys [82], and T91 [83] steels. There are three different cases of climb reported in the scientific literature: local climb [79], general climb [79] and co-operative climb [81]. In local climb, a dislocation segment undergoes climb only around the particle and rest of the dislocation stays in the glide plane. This leads to high curvature of the dislocation segments where the dislocation leaves the particle. Lagneborg [84] supposed that dislocations avoid such large curvatures encountered in local climb by general climb. In this, the line tension causes the dislocation to unravel from the matrix-particle interface. The threshold stresses for general climb are an order of magnitude lower than local climb [72].

Srolovitz et al. [85] conceived the idea of an attractive interaction between a dislocation and the interface of an incoherent particle, if the matrix-particle interface can slip. This attraction causes the dislocation segment near the particle to expand its length. Schröder and Arzt [86] observed that dislocations were pinned at the departure side of the oxide particles in oxide dispersion strengthened (ODS) Ni-base superalloys MA 754 and MA 6000 using weak-beam dark field (WBDF) technique. They identified the same curvature of dislocation segment at the particle and matrix and concluded that climb was complete and the dislocation had surmounted the particle by climb. These results support the existence of an attractive interaction between a dislocation and an incoherent particle. Arzt and Wilkinson [87] estimated the detachment stress of dislocation based on the premise of an attractive interaction between the matrix and the incoherent particle [85]. The physical origin of this interaction is a reduction of dislocation line tension when dislocation lie on the dislocation particle interface rather than in a matrix. When the dislocation is in the matrix-incoherent particle interface, the elastic strain energy of the dislocation is reduced.

Nabarro [88] and Herring [89] proposed that lattice diffusion plays an important role at high temperature ($T \approx T_m$) and very low stresses, shown in Fig. 2.4. In diffusional creep, material can accumulate creep strain by the movement of vacancies. Upon application of tensile stress, vacancies diffuse from the grain boundaries that are oriented perpendicular to tensile stress, to grain boundaries that are parallel to the stress direction. Thus, the grains would elongate without dislocation slip or climb. In Coble creep [90] at temperature ($T \ll T_m$) shown in Fig. 2.4, grain boundary diffusion is prominent than self-diffusion. Diffusion of vacancies through the grain boundaries controls the creep. The steady-state creep rate is inversely proportional to d^3 in coble creep and d^2 in Nabarro-Herring creep as shown in Equation 2.14 and 2.15 respectively.

$$\dot{\epsilon}_{NH} = A_{NH} \left(\frac{D}{kT} \right) \sigma \frac{\Omega}{d^2} \quad (2.14)$$

$$\dot{\epsilon}_C = A_C \left(\frac{D_{GB}\delta}{kT} \right) \sigma \frac{\Omega}{d^3} \quad (2.15)$$

Here δ is the width of the grain boundary. Diffusional creep applies to both materials that show a steady state creep rate and a creep minimum.

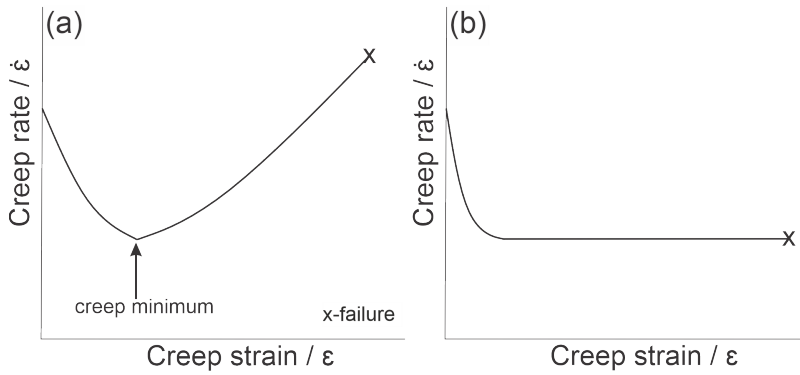


Figure 2.7.: Other types of creep curves exhibited by materials (a) Creep curve with a distinct minimum in the strain rate, and (b) Extended steady-state creep. Schematic curves are drawn from Refs. [58, 72, 80]. Here $\dot{\epsilon}$ denotes $\frac{\partial \epsilon}{\partial t}$.

It is important to note, that realistic technical high temperature materials usually do not follow a steady state behavior in the secondary creep regime, however, always develop a minimum creep rate ($\dot{\epsilon}_{min}$), an important high temperature material design parameter. Creep curves of materials show three different typical shapes, as shown in Fig. 2.2 b and Fig. 2.7 a-b. A distinct three-stage situation, shown in Fig. 2.2 b, is observed in polycrystalline single-phase metallic materials, for example, in polycrystalline Al-alloys [91] and polycrystalline nickel-base superalloys, such as Nimonic PE16 superalloy [56]. A creep curve with a characteristic creep minimum as seen in Fig. 2.7 a, is observed in single-crystal, Ni-base superalloys [92, 93], γ -TiAl [94, 95] and NiAl-Mo directionally solidified composite [96]. Creep curves with only two stages and steady-state creep occurring until fracture, as noted in Fig. 2.7 b, is observed in Al-5Mg [97], Al-4.9Zn [98] and Mo-40Ti [99] alloys.

In the following paragraphs, the influence of plastic strain, particularly the effect of dislocations on the nucleation and subsequent growth of precipitates, is elucidated. Plastic strain has an effect on the precipitation nucleation and growth kinetics as well as the related phases. For example, Deschamps et al. [100] investigated the effect of 10% plastic strain on the precipitation aging in Al-Zn-Mg alloy. The precipitation kinetics were compared with an un-strained sample after isothermal aging treatment at 160 °C. In the undeformed sample, after 1 h of aging, metastable η' precipitated out and at higher durations (50 hours), stable η (in η_1 and η_4 orientations) precipitated out. In comparison, after 1 h of aging in 10% strain and aged samples, metastable η' and stable η precipitates, majorly η_2 and

minor fractions of η_1 , precipitate out. Coarse η_2 precipitates nucleated on dislocations and they were surrounded by small precipitate free zone (PFZ). Around this zone, medium-size η or η' were observed. The influence of dislocations was localized in its surroundings and led to the development of PFZ and precipitates next to PFZ.

Creep strain, a combination of elevated temperature and load affects the nucleation and growth, as well as the coarsening behavior of materials. The effect of creep strain on precipitate nucleation and coarsening has been studied in steels [83, 101, 102, 103] and Al alloy [104] and magnesium alloy [105]. In P92 steels, enhanced coarsening of Cr_{23}C_6 precipitates has been observed during creep tests at 600 and 650 °C, in comparison to isothermally aged samples [103]. The Cr_{23}C_6 coarsening was also rationalized with a solute drag effect, where dislocations carry the substitutional atoms. Eggeler [106] observed the retention of higher dislocation density in subgrain boundaries during creep, in comparison to isothermal annealed samples. As a result, higher pipe diffusion fluxes and faster precipitate coarsening can be anticipated. In contrast, the volume number density of the Laves phase, $(\text{Fe, Cr})_2(\text{Mo, W})$ in the crept sample is two to three times higher than that of the aged sample. They concluded that the occurrence of dislocations and sub-grain movement during creep affects the nucleation of Laves phase precipitates. During coarsening at isothermal aging, the precipitation kinetics are given by Ostwald ripening law [107, 108, 109] given in Equation 2.16.

$$d_1^3 - d_0^3 = Kt \quad (2.16)$$

Here d_1 is the diameter of precipitates after time, t . d_0 is the initial diameter of the precipitates and K is a constant.

Nakajima et al. [104] studied the coarsening behaviour of θ' precipitates in Al-2mass% Cu alloy. The samples were tested by applying a tensile stress of 46 to 49 MPa at 200 °C. The precipitates distributions in the grip and gauge portions of the tensile test specimen were compared. The precipitates have a diameter of 500 ± 3 nm at the gauge whereas they have a diameter of 466 ± 3 nm at the grip. At the grip region, the size exponent of 1 was noted. Whereas the precipitates at the gauge region had larger diameters. Enhanced coarsening of precipitates at the gauge region was observed. This is explained based on the scavenging effect of dislocations. Generally, heat-resistant alloys are alloyed with solutes that have a relatively large size misfit. This contributes to the formation of solute atmospheres around the dislocations. When the moving dislocation interact with the

precipitate, the solutes diffuse to the growing precipitates along the dislocation core. It is much faster than diffusivity along the lattice diffusion in creep regimes. Nakajima et al. [105] also investigated the coarsening behaviour of $\text{Mg}_{17}\text{Al}_{12}$ precipitates in AZ80, a commercial magnesium alloy. Similar to Al-2mass% Cu alloy, enhanced coarsening of $\text{Mg}_{17}\text{Al}_{12}$ precipitates were observed in gauge part, in comparison to grip part. The enhanced coarsening of precipitates is attributed to the scavenging effect of dislocations, wherein moving dislocations collect solute atoms.

2.4. Reasons for creep minimum in some Mo-based and other high-temperature materials

Refractory metals and alloys are interesting as high-temperature structural materials because they have high melting points and good creep resistance. Schliephake et al. [16] explored the ternary Mo-Si-Ti system and developed two reference alloys: one eutectic Mo-20.0Si-52.8Ti and an another solid state transformed Mo-21Si-34Ti. As mentioned in section 2.1, the eutectic alloy showed resistance to pesting and minimal mass loss at 800 °C, whereas a solid state transformed alloy showed a drastic mass loss. Compressive creep tests were also conducted at 1200 °C and 50 MPa stress to evaluate the creep strength of the alloys. The solid-state transformed alloy showed the best creep performance, and the eutectic alloy showed one order of magnitude higher creep than its counterpart. Both alloys showed similar stress exponents of 3.4 and 3.7, respectively. This indicates the operation of dislocation-climb controlled creep mechanism [16].

Obert et al. [23] designed additional alloys with microstructural regions of both eutectic and solid state transformed regions in the same alloy to obtain both pesting and creep resistance. The alloy A was creep deformed at 1200 °C and similar stress of 50 MPa. The alloy A showed creep strength intermediate to both eutectic and solid-state transformed alloy. The authors concluded that it has to be considered that the designed alloys were tested at different homologous temperatures due to different Mo contents in the alloy, and thus the creep strength of the alloys depends on the solidus temperature of the alloy, rather than the inherent creep strength of the alloys.

Srinivasan et al. [19] compared the creep behaviour of the eutectic Mo-Si-Ti alloy during compressive and tensile creep at 1200 °C and 1300 °C. Creep minimum is observed in

both compression and tension. The tensile minimum creep rates are double (1.9 times) of compressive minimum creep rates at 1200 °C. The apparent stress exponents of tensile and compressive creep indicate similar dislocation climb controlled creep with values of 3.2 for tension and 3.7 for compression.

This section discusses the microstructural reasons for the creep minimum in various materials such as single-crystal, Ni-base superalloys [92, 93], polycrystalline nickel-based superalloys [110, 111], directionally solidified NiAl-Mo composites [96], γ -TiAl [112], Fe-61Al [113, 114] and Al-Si-Cu-Mg [115] alloys. These alloys show a creep minimum.

Different viewpoints exist on the reasons for creep minimum in single-crystal, nickel-base superalloys. According to first point of view, the reason for this creep minimum is rafting [92, 93], meaning the directional coarsening of γ' precipitates perpendicular to the stress direction [116, 117]. The γ' precipitates elongate, and the distance between the precipitates increases. In addition to particle coarsening, Henderson and McLean [118] postulated that dislocation density increases at the γ - γ' interface leading to enhanced diffusion controlled climb. The third viewpoint is the climb of dislocations rather than cutting of precipitates for the increase in creep rate [93]. A new jogged screw dislocations model was proposed to explain the creep rates in the ordered γ -TiAl alloy and disordered α -Ti alloy [119]. The deformed microstructure was characterized by the presence of $\frac{1}{2}\langle 111 \rangle$ screw dislocations and jogs pinning the screw segments. This model could predict the creep rate in these alloys accurately.

The creep response of fully lamellar Fe-61Al, consisting of B2 ordered FeAl and triclinic FeAl₂ phases, was evaluated at 600 to 800 °C under a stress of 100 MPa stress. The sample exhibited a distinct creep minimum. The microstructural instability of colony boundaries was believed to be the reason for the creep minimum rather than lamellar coarsening [113]. Detailed TEM investigations were carried out to understand the deformation mode unambiguously [114]. The TEM results revealed that FeAl deformed plastically at the beginning of creep by the accumulation of dislocations before the creep minimum. Both phases showed extensive dynamic recovery by the formation of subgrains at locations where the lamellar microstructure terminated abruptly. The FeAl₂ phase contributed to the plastic deformation from the creep minimum onwards. At strains exceeding the creep minimum, slip and deformation twinning were observed in FeAl₂. At higher strains, the breakdown of the lamellar structure was observed close to colony boundaries.

Dlouhy et al. [112] studied the sequential microstructural evidence for the occurrence of creep minimum in crept γ -TiAl at 1200 °C. The strain hardening during the primary creep was due to the formation of ordinary and super dislocations. The occurrence of creep minimum corresponds to the formation of deformation twins, and their volume fraction increase coincided with creep minimum and increase in creep rate after it is due to relaxation of incompatibility stresses after creep minimum.

Dudová et al. [96] observed the occurrence of a creep minimum in the compressive creep of directionally solidified (DS) NiAl-Mo in-situ composites. They have noticed a creep minimum at about 1% strain. After the production of composites and before creep testing, the Mo fibers are free of dislocations, but dislocations are present in the NiAl matrix due to thermal mismatch strains during the solidification. The free dislocations present in the subgrains of NiAl matrix accumulate at the matrix-fiber interface. After creep testing at high strains, dislocations and nano-precipitates of Ni-Al within Mo fibers are found. From these observations, they postulated that creep minimum corresponds to load bearing capacity of Mo-fibers without dislocations and significant statistical yielding of fibers in the composite. Albeiz et al. [120] proposed a new physical model to explain the shape of the creep minimum in DS NiAl-Mo fibers. The shape was explained as follows: During the primary creep, the fibers behave as linear-elastic and take a part of the load, and at creep minimum, the fibers take up stress and deform plastically. The increasing creep rate in the tertiary stage was due to increase in dislocation density, and thereby softening of fibers.

The Cast Al-6.8%Si-3.05%Cu-0.33%Mg (in wt.%) alloy showed a creep minimum, and the microstructural reason for the increasing creep rate after minimum is the coarsening of Al_2Cu precipitates during creep test [115]. The creep curve of Incoloy 800H also exhibits a creep minimum [111]. The nature of the creep curve was explained in the following manner: creep enhanced the precipitation by providing nucleating sites at the freshly generated dislocations, which are surrounded by a Cottrell cloud. The reason for this particular behavior is the creep-induced precipitation of the fine carbides at the dislocations, which subsequently coarsen rapidly [111].

2.5. Electron beam-matter interactions and electron microscopy

Electrons are negatively charged particles that have strong coulomb forces and low mass [121]. Electrons in the incident electron beam are called primary electrons. When the electron beam interacts with a sample atom, it can pass through the specimen without any interaction, can undergo a scattering or multiple scattering [122]. Scattering is usually defined mathematically in terms of differential cross section ($d\sigma_{atom}/d\Omega$) that describes the angular distribution of scattering from an atom.

$$\frac{d\sigma_{atom}}{d\Omega} = \frac{1}{2\pi \sin \theta} \frac{d\sigma_{atom}}{d\theta} \quad (2.17)$$

Here θ is the scattering angle and Ω is the solid angle. It is expected that σ_{atom} decreases as θ increases. The scattering into all angles greater than θ can be calculated by integrating Equation 2.17

$$\sigma_{atom} = \int_{\theta}^{\pi} d\sigma_{atom} = 2\pi \int_{\theta}^{\pi} \frac{d\sigma_{atom}}{d\Omega} \sin \theta d\theta \quad (2.18)$$

Equation 2.18 gives us a convenient way to measure the scattering of an atom by integrating $(d\sigma/d\Omega) \sin \theta$ from 0 to π angles. If the sample has thickness (t), scattering probability is given by Equation 2.20

$$\sigma_{total} = N\sigma_{atom} = \frac{N_0\sigma_{atom}\rho}{A} \quad (2.19)$$

$$\sigma_{total}t = \frac{N_0\sigma_{atom}(\rho t)}{A} \quad (2.20)$$

Here, t is the thickness, N_0 is the number of atoms, ρ is the density, and A is the atomic number.

In general, two kinds of scattering are possible: elastic and inelastic. Elastic scattering occurs when electron beam loses minimal or insignificant loss of energy, accompanied by change of its trajectory. In contrast, inelastic scattering results in significant loss of energy due to energy transfer. In elastic scattering, two scenarios are possible. On a shell or electron orbital level, the electron interacts with electron cloud, leading to

small angular deviation. If the electron travels through electron cloud and reach closer to nucleus, it will be strongly attracted due to opposite charges and scattered through larger angles. Rutherford [123] derived the high-angle scattering by nucleus and resulting differential cross section as shown in Equation 2.5, taking particle nature of electron into account.

$$\frac{d\sigma_R(\theta)}{d\Omega} = \frac{e^4 Z^2}{4(4\pi\epsilon_0)^2 m^2 \nu^4} \frac{1}{\sin^4\left(\frac{\theta}{2}\right)} \quad (2.21)$$

Here e is the elementary charge, Z is the atomic number of the atom, ϵ_0 is the vacuum permittivity, m is the mass of the electron, ν is the speed of the electron and θ is the scattering angle.

The major shortcomings of Rutherford scattering are twofold. Firstly, it does not account for the screening effect of the surrounding electron cloud, which makes the nucleus appear less positively charged and causes the Rutherford scattering cross section to diverge as the scattering angle approaches zero. So, modified Rutherford cross section equations were derived incorporating screening parameter and relativistic effects into account. For more in-depth understanding, the following references can be referred [121, 122]. In the case of inelastic scattering, the electron beam transfers part of its kinetic energy to the sample atom, and this leads to the excitation of the atom. The predominant interactions are generation of electrons and x-ray as well as plasmons and phonons. The electron energy loss spectroscopy (EELS) uses these electrons that have undergone inelastic scattering to find out the electronic state and chemistry of sample atoms. The characterisitc x-rays are used in energy dispersive X-ray spectroscopy (EDXS) to determine the qualitative and quantitative amount of particular element ($Z>10$) in the sample [121].

In the following paragraphs, a brief operating principles of various electron microscopy methods used in the current thesis are presented lucidly.

Transmission electron microscopy (TEM) is an advanced technique to obtain the microstructural, crystallographic and compositional information from the same region of interest with high spatial resolution [124, 125, 126]. With the advent of probe and spherical aberration corrections, a spatial resolution of 50 pm is possible. In TEM, electrons are used as probing radiation since the wavelength of electrons is on the same order of magnitude as the interplanar spacing. Typical wavelength of the TEM at 200 kV is 2.5 pm, employing relativistic correction. TEM consists of these key components: electron gun, condenser lens, objective lens, sample holder and projection lens system. The electron

gun generates electrons from the filament either by thermionic or field emission. Electromagnetic lenses are used to focus the electrons in TEM. The condenser lens controls the spot size and convergence angle of the electron beam.

The generated electrons are focused by a series of condenser lenses and an objective lens to form a finely focused beam of electrons onto the sample surface. The sample holder can be tilted in two axes: one along the holder axis and the other perpendicular to it. TEM is commonly operated in two modes: image and diffraction. In the image mode, the microstructural images are acquired, whereas the diffraction mode is used to capture the diffraction pattern, which gives crystallographic details of the sample. In diffraction mode, the selected area diffraction (SAD) aperture is used to select the region of image from which the diffraction information is desired. Diffraction pattern forms in the back focal plane of the objective lens. In the image mode, the image plane of the objective lens acts as an object plane for the first projector lens. Whereas for the diffraction mode, the back focal plane of the objective lens acts as the object plane for the first projector lens.

In TEM, electrons are accelerated to high acceleration voltages (typically 100 to 300 kV), giving them very short de Broglie wavelengths on the order of picometers, ≈ 0.0025 nm at 200 kV. As a result, even small interplanar spacings can satisfy Bragg's condition at tiny diffraction angles. The interaction of the electron beam with the atoms of the crystal lattice leads to constructive interference when Bragg's Law is satisfied, resulting in distinct diffraction spots in the back focal plane of the objective lens. Constructive interference occurs when the path difference between electron waves scattered from adjacent crystal planes is an integer multiple of the wavelength.

$$n\lambda = 2d\sin(\theta) \quad (2.22)$$

where n is the diffraction order, λ is the wavelength of the incident electrons, d is the spacing between crystallographic planes, and θ is the Bragg angle. The STEM is a high-resolution mode to characterize the defects [127]. In STEM mode, the convergent beam is scanned over the illuminated sample region rather than parallel illumination in TEM mode, shown in Fig. 2.8. Compared to TEM mode, STEM mode has better resolution but lesser contrast [122]. For more in-depth information, the following textbooks can be referred to Refs. [122, 124, 127].

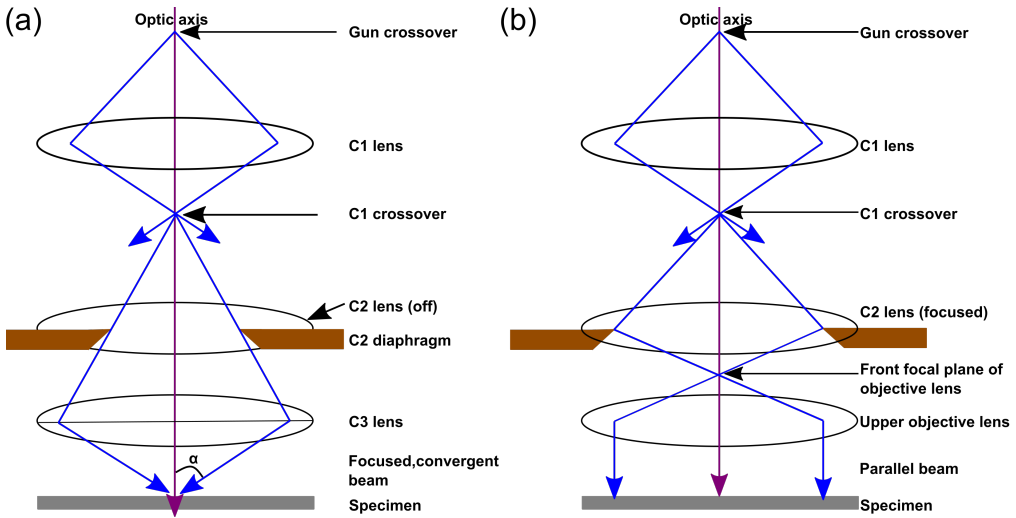


Figure 2.8.: Electron trajectories and condenser lens system (a) Convergent beam in STEM and (b) Parallel illumination in TEM. Figure adapted from Ref. [122].

Scanning electron microscopy (SEM) is a versatile technique used to perform micro structural and chemical characterization of materials at a sub-micron scale [121, 128]. In SEM, the focused electron beam (primary electrons) is incident on the sample surface, rasters across the surface, generating a variety of signals in the interaction volume. Among them, secondary electron (SE), backscattered electron (BSE) and x-rays are most widely used. SE are those electrons that have undergone inelastic scattering, which have kinetic energies less than 50 eV. Since SEs have very low kinetic energy, most SEs are absorbed within the interaction volume. The SEs are generated at a very small depth below the surface, called escape depth. If SEs are travelling towards the surface, they can escape into vacuum. Since the SE signal used in SEM is obtained from SEs that escape into vacuum, the SE image is an inherent property of surface structure and thus the SE image shows topographic contrast. The different components of SE are distinguished based on the location and origin of their emission. The SE_I components are those electrons that are emitted close to the surface. The SE_{II} and SE_{III} components are generated when the BSEs exit the sample surface and when the BSE hit the sample chamber respectively. The SE_{II} carries the same information as BSEs. The SE_I and SE_{II} components are characteristic of a material. The secondary electron yield (δ_{SE}) is defined as number of SE per primary electron. In a sample, δ_{SE} decreases with increasing

acceleration voltage because higher energy primary electrons undergo less inelastic scattering and there will be fewer SEs emanated within the escape depth. The δ_{SE} increases with increasing sample tilt.

BSEs have higher kinetic energies (>50 eV) that are rebound from the sample after having undergone elastic scattering with atomic nucleus of sample atom. Since the cross-section for elastic scattering is proportional to Z^2 seen in Equation 2.5, BSEs can be used to obtain Z-contrast. The back scattering coefficient (η_{BSE}) depends on Z . Comparatively BSEs originate from half the dimensions of interaction volume. The scattered electrons are collected by various detectors: Everhart-Thornley (ET) detector, solid state detector and through-the-lens detector. The ET detector is mounted sideways, collects the SEs by applied positive bias to its Faraday cage (+200-400 V), attracting low-energy SEs. The same detector can also be used to detect the BSEs if a negative bias is applied to repel the SEs but the collection solid angle is limited. The solid state detector mounted below the polepiece collects the BSEs and provides compositional or Z-contrast and channeling or orientation contrast. When the electron beam impinges on grains of polycrystalline material, the BSE yield varies due to channelling effects, where electrons are guided along low-index planes, increasing η_{BSE} from favorably oriented grains. This produces grayscale intensity variations between grains. This is called electron channeling contrast or orientation contrast. The resolution of SEM depends on the interaction volume of the collected signals (SE, BSE and x-rays) and not on beam diameter. Kanaya and Okayama [129] gave an empirical equation to estimate the interaction volume radius, considering both elastic and inelastic scattering shown in Equation 2.23. It encompasses 95% of trajectories from the point of impact of the electron beam.

$$R_{K_0}(nm) = 27.6 \left(\frac{A}{Z^{0.89}\rho} \right) E_0^{1.67} \quad (2.23)$$

Here E_0 is the incident beam energy (keV) and A is atomic weight.

Focused ion beam (FIB) is a sample preparation method to prepare site-specific specimens for TEM and atom probe tomography techniques [130]. Most FIB instruments are manufactured as an additional attachment to SEMs. The FIB instruments use Ga^+ ions as a probing radiation for milling and deposition of the material. It consists of a liquid metal ion source (LMIS) for generating Ga^+ ions and an ion column which houses a series of condenser and objective lenses. The LMIS consists of a W needle connected

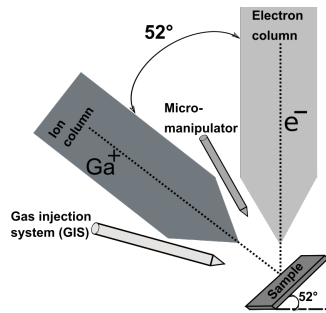


Figure 2.9.: Schematic of a focused ion beam (FIB) system. The ion column is inclined at an angle of 52° with respect to the electron column. Schematic adapted from Refs. [121, 130]

to a metal reservoir. Ga source is used because it has low melting point (28°C), low surface free energy and low volatility. The Ga^+ ion emission occurs after a two-step process. Firstly, the heated Ga flows and wets the W needle. An electric field applied to the end of a wetted tip causes the liquid Ga to form a point source with a diameter of 2 to 5 nm, conical in shape, referred to as a Taylor cone. It forms as a result of force balance between electrostatic and surface tension, due to the applied electric field. Secondly, after the achievement of force balance, the cone tip is so small that the extraction voltage pulls Ga from the W tip and ionizes it efficiently by field evaporation of the metal at the end of the Taylor cone.

Electrostatic lenses are used to focus the ions, as these ions are heavier and higher magnetic fields are required to focus these ions, if electromagnetic lenses are used. The ion column consists of a series of condenser and objective lenses to focus the electron beam. The ion column makes an angle of 52° with the electron beam, as shown in Fig. 2.9. The source and ion column is maintained at high vacuum to avoid any interactions of gas molecules with Ga^+ ions. These ions are accelerated from 5 keV to 30 keV with tunable currents from pA to nA. The penetration of the ion beam into the specimen varies with different materials and grain orientations. Channelling contrast is observed for different grain orientations. The milled regions is protected by depositing a precursor organometallic gas. A controlled amount of gas is introduced into the chamber by a gas injection source (GIS) by opening a valve. The gas molecules are adsorbed only in the vicinity of the gas inlet, and they decompose when the ion beam hits the scanned region. The primary beam current density is chosen in such a way that there is a balance between deposition and sputtering.

3. Materials & Methods

3.1. Alloy system and Manufacturing

A ternary Mo-20Si-52.8Ti eutectic alloy was produced by arc melting high-purity elemental constituents: Mo (99.8%), Ti (99.95%), and Si (99.99%). The thin Mo sheets were purchased from Plansee SE. Ti and Si granules were purchased from Chempur. The alloy was cast using an Edmund Bühler AM/0.5 arc melter equipped with a water-cooled copper mold. Based on the stoichiometric composition, the elements were accurately weighed and melted as shown in Table 3.1 in the presence of a zirconium (Zr) getter, to capture residual oxygen. To ensure an inert environment, the chamber was purged with argon (Ar) gas at least three times prior to melting. To promote chemical homogeneity, the alloy button was flipped and re-melted five times. The button was cut into smaller cuboidal samples for further microstructural and creep tests using electrical discharge machining. The as-cast (AC) sample was subjected to heat treatment at 1600 °C for 150 hours to induce microstructural coarsening (see Fig. 4.5 c). It is performed in a Carbolite Gero GmbH & Co horizontal tube resistance furnace model HTRH 70-600/18. The sample was heated and cooled at constant rates of 100 K/h in a constant flow of Ar gas. This heat-treated sample is referred to as “HT” throughout the thesis.

Table 3.1.: Nominal chemical composition of the investigated Mo-Si-Ti eutectic alloy

Elements	Mo	Si	Ti
at.%	27.2	20.0	52.8
wt.%	45.8	9.9	44.3

3.2. High-temperature mechanical deformation

Creep tests were conducted using a Zwick T100 universal testing machine equipped with a Maytec vacuum furnace. The AC and HT specimens were tested under vacuum at 1200 °C, with applied stresses ranging from 15 MPa to 200 MPa. Before applying the creep stress, initial pre-load of 50 N was applied. Cuboidal specimens with dimensions of 5 x 3 x 3 mm³ were sectioned from the arc-melted samples using electrical discharge machining (EDM) to perform creep tests. Prior to testing, the samples were ground using emery paper up to 2500 grit to achieve a smooth surface finish. Accurate temperature control was ensured by placing thermocouples in the testing zone. The Si₃N₄ punches were used to apply the load, and hexagonal boron nitride (h-BN) was applied to the punch faces to minimize friction at the contact surfaces.

The subsequent microstructural evolution of crept samples was only performed on AC samples crept at 100 MPa. Figure 3.1 shows the true creep rate as a function of time for AC eutectic Mo-20Si-52.8Ti alloys. The AC samples were crept to true creep strains (ϵ_t) of 0.2%, 1.3%, 10%, 20% and 40%. The nomenclature of all the samples investigated in the thesis are tabulated in Table 3.2. For the subsequent microstructural evolution after creep testing, only the AC samples were used. The grain size exponent (p) was calculated from the slope of $\dot{\epsilon}_{min}$ as function of grain size (d). The d was estimated by the P^3 , here P is phase boundary density in [$1/\mu\text{m}$] [99].

$$P = 2 \frac{\overline{N}}{L} \quad (3.1)$$

Here, N is the number of intersections and L is the overall length of the line. In calculating P , boundaries (silicide-silicide grain boundaries and solid-solution grain boundaries) within the individual phases and two-phase interfaces were considered.

3.3. Metallographic preparation

For the 0.2% and 20% samples, the entire cuboidal sample was used for electron microscopic investigations. In contrast, 1.3% and 10% samples were sectioned such that the compression direction (CD) was tracked during sample preparation as shown in the

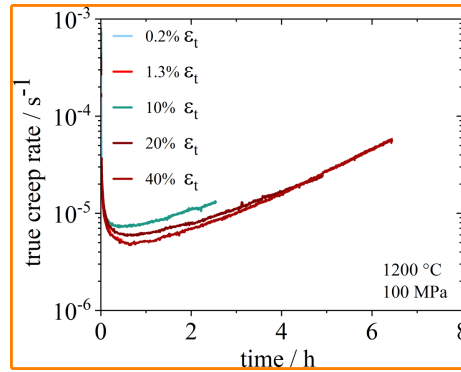


Figure 3.1.: High-temperature mechanical deformation of a eutectic Mo-20Si-52.8Ti alloy, plotted in terms of creep rate as function of time. Each crept sample is indicated by a unique color corresponding to its true creep strain (ε_t): 0.2%—light blue (R:142,G:210,B:249), 1.3%—red (R:255,G:0,B:0), 10%—bluish green (R:27,G:151,B:131), 20%—brown (R:128,G:0,B:0) and 40% — black (R:164,G:4,B:4).

Table 3.2.: Nomenclature of the samples used in this thesis

Abbreviation	Heat treatment procedure
AC	as-cast ingot melted five times
HT	AC sample heat treated at 1600 °C for 150 hours
0.2%	AC sample crept to 0.2% true creep strain (ε_t)
1.3%	AC sample crept to 1.3% ε_t
10%	AC sample crept to 10% ε_t
20%	AC sample crept to 20% ε_t
40%	AC sample crept to 40% ε_t
ht	AC sample heat treated at 1200 °C for one hour without applied stress

Fig. 3.2. Firstly a cylindrical sample is cut from the sample with its longitudinal axis perpendicular to the compression direction (CD). A region of the curved lateral surface was machined flat to serve as a reference for identifying the CD. Smaller samples were cut perpendicular to the CD for microstructural studies. In all the electron microscopy analyses, the CD lies in the viewing plane and is aligned along the y-axis, extending from the top to the bottom of the acquired SEM-BSE or EBSD-KAM maps.

Sample preparation for SEM imaging and/or EBSD was carried out using an Allied High Tech MultiPrep™ System—an 8 inch semi-automatic grinding and polishing unit. Initially, the samples were ground using Buehler CarbiMet® silicon carbide grinding papers with successively finer grit sizes: 600, 1200, 1500, 2000, 2500, and 4000. Polishing was performed sequentially using Buehler MetaDi diamond paste with particle sizes of 3 μm and 1 μm , followed by a final polish using Buehler MasterMet 2 non-crystallizing colloidal silica suspension. To eliminate any residual colloidal silica from the metallographic preparation, the samples were thoroughly cleaned and ultrasonicated in ethanol.



Figure 3.2.: Schematic of the sectioning from the crept sample for subsequent metallographic investigation. Here CD refers to compression direction.

3.4. Electron microscopic investigations

3.4.1. Scanning electron microscopy (SEM)

The SEM characterization was performed on a eutectic AC and crept samples to analyze the phase distributions and precipitation within individual phases. An acceleration voltage of 10 kV, spot size of 4 and working distance of 10 mm were the experimental parameters used for SEM characterization. SEM-BSE images were taken in Thermo Fischer FEI ESEM and Thermo Fischer HELIOS G4TX. The EBSD data was analyzed using the MTEX plugin [131] installed in the MATLAB software. The EBSD data was exported to .ctf format and imported using the wizard, and the specimen reference frame was set. The Euler angles of the MTEX data were also verified by comparing them with the Bruker Esprit software values. With the custom codes, the KAM maps were exported. To extract the KAM distributions, MATLAB code was written.

3.4.2. Electron backscatter diffraction (EBSD)

EBSD is an SEM-based diffraction technique used for phase identification and determining crystal orientations in the materials within an angular resolution of 0.3° [132, 133]. It is performed on a steeply tilted sample that makes an angle of 70° to the horizontal specimen stage and 20° to the electron beam shown in Fig. 3.3. It works on the principle of Kikuchi diffraction. Figure 3.4 shows the two-step scattering process resulting in the formation of Kikuchi pattern in an electron-transparent specimen. In the first step, the electron beam interacts with the specimen and some of the electrons undergo inelastic scattering and diffuse scattering. These electrons undergo Bragg diffraction at a suitably oriented atomic planes.

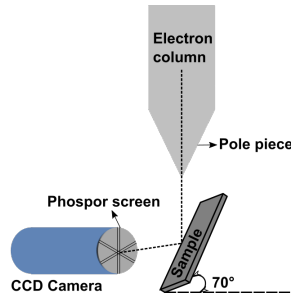


Figure 3.3.: Schematic illustrating sample tilt and detector position for electron backscatter diffraction (EBSD). Schematic adapted from Refs. [132, 133]

Two diffusely scattered beams are shown in Fig. 3.4 a. The beam which is initially close to the optic axis, marked blue in Fig. 3.4 a, undergo Bragg diffraction and diffracts far away from the optic axis, resulting in higher intensity and thus formation of excess line. Whereas the other beam, marked purple in Fig. 3.4 b, forward scattered electrons are dominant and weaker diffraction occurs. As a result, Bragg scattered electrons are added to the excess line and forward scattered electrons form deficient line. Since the incoherently scattered electrons are incident from all directions, the locus of diffracting radiation is surface of a cone that extends perpendicular to the reflecting atomic planes with a half apex angle of $(90 - \theta_B)$. These are called Kossel cones and each plane comprises of set of Kossel cones. When these Kossel cones intersect a flat detector or phosphor screen, they result in the formation of set of parallel lines because θ is very small. These lines are referred to as Kikuchi lines. They have an angular distance of

$2\theta_B$, which is proportional to the interplanar spacing. These patterns are collected by a phosphor screen attached to a charge-coupled device (CCD) camera.

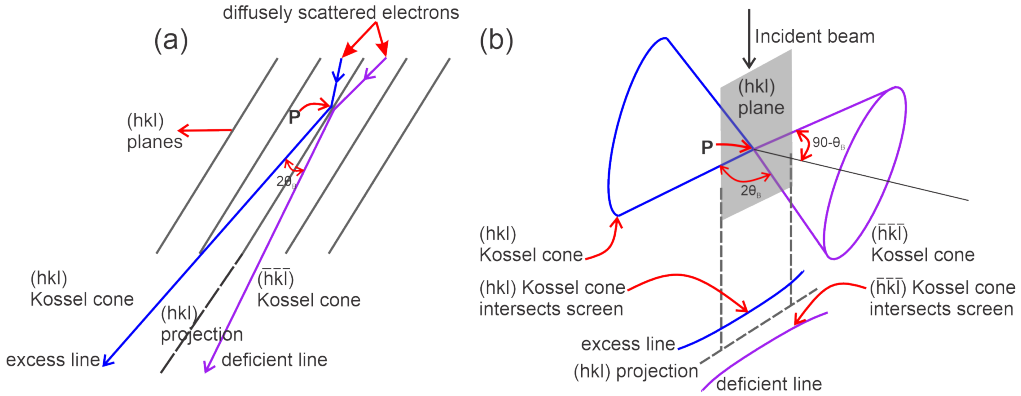


Figure 3.4.: Schematic diagram depicting the formation of Kikuchi patterns in a two-step process (a) Elastic scattering of inelastically scattered electrons forming Kossel cones and (b) Their intersection with the phosphor screen. Schematic adapted from Refs. [122]

The position of the Kikuchi bands and poles are detected using various image processing routines (Hough or Radon transform) and they are indexed by comparing the interplanar angles between detected bands [134, 135]. EBSD was used to identify plastic strain in terms of kernel average misorientation (KAM) maps [136]. These maps are an indirect measure of geometrically necessary dislocations in the microstructure. It is a kernel-based approach for calculating the average misorientation of each pixel with the surrounding pixels, and those pixels that exceed a specific misorientation tolerance can be excluded from the KAM calculation. The data was partitioned into individual phases for better understanding. EBSD scans were ran at 15 kV acceleration voltage, 26 nA electron beam current and 15 mm working distance with a step size of 100 nm. The crystal structures of the two phases were input into the Bruker EBSD mapping software. At least three different scan areas of $80\ \mu\text{m} \times 50\ \mu\text{m}$ were done at the center of the sample to obtain significant statistics.

3.4.3. Focused ion beam (FIB) milling

The region of interest for the TEM specimen was chosen based on EBSD-KAM data, identifying the plastic strain as shown in Fig. 3.5 b. For the TEM specimen preparation, the cross-sectional procedure using FIB procedure was followed [137]. At first, the region

of interest was marked with SEM Pt layer, and the Pt layer was deposited again at 52° using FIB to reduce the beam damage during FIB preparation (Fig. 3.5 d). Then trenches were made on top and bottom of the Pt layer with a regular cross-section. The cleaning cross-section was carried out to a lamella thickness of $1.5\ \mu\text{m}$ of Pt layer. The undercut is performed with lower beam current to detach the lamella from the sample (Fig. 3.5 e). The micromanipulator and gas injection system (GIS) were inserted and lamella was welded to the manipulator needle and the remaining portion connected to the sample is cut off using a rectangle in FIB currents.

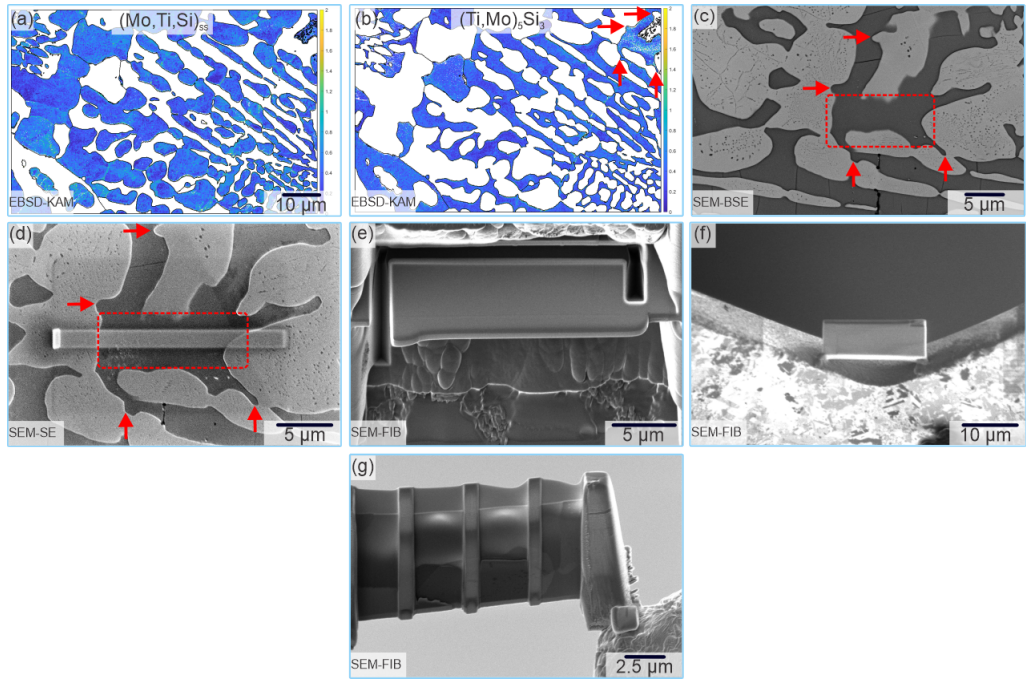


Figure 3.5.: Correlative microscopy approach implemented in the current thesis. (a) EBSD-kernel average misorientation (KAM) maps of solid solution, (b) EBSD-KAM maps of silicide, (c) Scanning electron microscopy (SEM)-backscatter electron (BSE) image of the region previously analyzed by EBSD, (d) SEM-secondary electron (SE) image showing the Pt protection layer over the region of interest (ROI) and (e) SEM-FIB image showing the prepared FIB lamella for transmission electron microscopy (TEM) analysis.

The lamella is lifted out and welded to a chevron notch on both sides for the stability of the lamella and to prevent the curling of the lamella while thinning (Fig. 3.5 f). The lamella is reduced in thickness by cleaning cross section milling on the bottom surface

at 53.5° . To prepare a uniform thick FIB lamella, the lamella is un-tilted back to 0° and using compucentric rotation of 180° . Following this operation, the sample is tilted back to 53.5° to mill the bottom surface. In this manner, uniform thickness reduction of FIB lamella is accomplished from both sides. The milled region was viewed periodically in ISpi mode. To get an estimate of prepared FIB lamella thickness, the sample is untilted back to 0° and thickness measured with line tool.

3.4.4. Transmission electron microscopy (TEM)

The TEM technique is used to image dislocations and find out the crystal structure of the precipitates. The dislocations were imaged by aligning the particular grain to the zone axis by tilting using double-tilt holder to access particular two-beam conditions as shown in Fig. 3.6. The goal is to image the diffraction contrast of specific reflecting planes. The dislocation character is determined by finding out the $\vec{u}$ and $\vec{b}$. The $\vec{u}$ is determined by measuring the angle of projected dislocation line with two $\vec{g}$ where dislocations are visible and using two surface-analysis procedure [138]. The diffraction pattern of the zone axis alignment and two-beam conditions was taken at 700 mm and 950 mm camera length in solid solution and silicide, respectively. Conventional transmission electron microscopy (CTEM) was performed on Philips CM200 TEM equipped with TVIPS 2k x 2k Camera. Initially, the particular phase is aligned to the nearest high-symmetry, low index zone axis, and the diffraction pattern is acquired and indexed using JEMS software. WinKiku software is used to compare the Kikuchi bands seen in TEM with the theoretical Kikuchi band simulations.

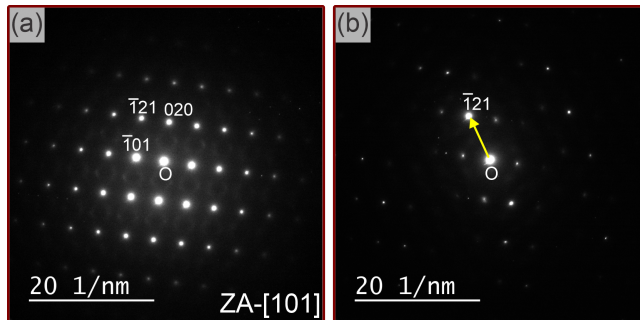


Figure 3.6.: Indexing of the g-vector in the TEM/scanning transmission electron microscopy (STEM)-images. Diffraction pattern of (a) [101] zone-axis alignment and (b) Two-beam condition with $g = (\bar{1}21)$. Here O indicates the direct beam.

The dislocations were imaged at two beam conditions using the bright field (BF) and annular dark field (ADF) images at camera length of 54 mm. The HAADF Z-contrast images were also taken at 54 mm to see the Z-contrast and identify the precipitation within individual phases. STEM-EDXS was processed using the Bruker Esprit software and quantified using Cliff-Lorimer parameters [139]. STEM-HAADF and EDXS measurements were performed in the Thermofischer FEI Tecnai Osiris TEM equipped with high brightness FEG and super-X quad silicon drift detector (SDD). The crystal structure of the precipitate was determined by aligning the matrix grain to zone-axis and using the smallest SAD aperture of 10 μm to acquire the diffraction pattern. The orientation relationships of the precipitate and matrix is determined from at least two zone-axis alignments.

There are several microstructural features visible in the TEM images. Among them, dislocations, precipitates and bending contours are relevant to the current thesis. These features are elaborated further in the following sections:

The contrast of the dislocation was better explained with an edge dislocation shown in the Fig. 3.7 a. An edge dislocation has an elastic strain field around it. Because of this, the lattice planes surrounding it are bent and oriented into the Bragg positions. When the incoming electron beam falls on the lattice planes, the intensity from the position around the dislocation is diffracted away. So, the dislocation appears as a dark line in the bright field (BF) image and vice versa [33]. Generally, dislocations can be in-plane, appearing as lines, or lying edge-on, appearing as points. Sometimes the dislocation appears as alternating bright and dark line contrast. This is because dislocation is inclined to TEM foil [125]. The dislocations are usually imaged in a two-beam condition with a diffraction vector ($\vec{g}$), where $\vec{g}$ is parallel to $\vec{b}$ and hence the dislocation is visible. The $\vec{g}$ is usually annotated on the two-beam condition images. Double line contrast of dislocation occurs when two g-vectors are simultaneously activated in the image [125].

In conventional TEM studies, when the dislocation is imaged, the core is shifted by 30 - 300 Å depending on g-vector used [124]. Figure 3.7 a illustrates dislocation depicted as two continuous lines: p_{+g} and p_{-g} . They indicate the position of dislocation line imaged with -g and +g spots of a particular diffracting plane. The actual core of dislocation is indicated with dashed line in-between +g and -g images. The $\vec{b}$ of a dislocation can be found out by selecting $\vec{g}$ that are perpendicular to $\vec{b}$, and the dislocation is invisible using Invisibility criterion, shown in Equation 3.2. If two such $\vec{g}$ are found, then $\vec{b}$ is

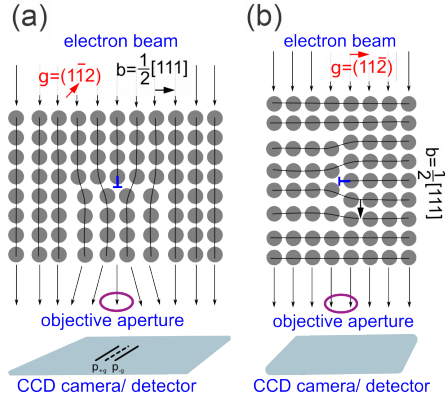


Figure 3.7.: Schematic diagram of dislocation imaging under two-beam conditions (a) Visibility criterion, where $\vec{g} \parallel \vec{b}$ and (b) Invisibility criterion where $\vec{g} \perp \vec{b}$. The p_{+g} and p_{-g} indicate the position of the dislocation line imaged with $+g$ and $-g$ diffraction vectors.

the cross-product of the two $\vec{g}$. Edge dislocations have perpendicular strain fields around them [33, 35], they must satisfy the equation shown in Equation 3.4.

$$\vec{g} \cdot \vec{b} = 0 \quad (3.2)$$

$$\vec{b} = \vec{g}_1 \times \vec{g}_2 \quad (3.3)$$

$$\vec{g} \cdot (\vec{b} \times \vec{u}) = 0 \quad (3.4)$$

The equations for the wave amplitude in the imperfect crystal, which are the basic formulations of dynamical theory are shown in Equation 3.5 and 3.6. These equations predict complementary intensities for bright field and dark field images.

$$\frac{d\phi_0}{dz} = \frac{\pi i}{\xi_0} \phi_0 + \frac{\pi i}{\xi_g} \phi_g e^{+2\pi i(s z + g \cdot R)} \quad (3.5)$$

$$\frac{d\phi_g}{dz} = \frac{\pi i}{\xi_0} \phi_g + \frac{\pi i}{\xi_g} \phi_0 e^{-2\pi i(s z + g \cdot R)} \quad (3.6)$$

Here ϕ_0 is the amplitude of the incident wave, ϕ_g is the amplitude of the diffracted wave, s is the deviation parameter, g is the diffraction vector, R is the displacement vector, z is the position of the defect, ξ_0 is extinction distance of the direct beam and ξ_g is extinction distance of the diffracted beam. In case of an invisibility criterion where $\vec{g}$ is

perpendicular to $\vec{b}$, the $\vec{g} \cdot \vec{R}$ term becomes zero as $\vec{b}$ is analogous to $\vec{R}$, which represents the displacement fields of the crystal defect.

Figure 3.8 shows the three cases of deviation parameter (s) used for setting two-beam conditions for dislocation imaging. Here the Ewald sphere is represented with a finite arc of radius $(1/\lambda)$ and the reciprocal lattice points are indicated as red filled circles with streaks. Streaking is due to the finite thickness of the electron transparent sample and points elongate along the beam direction, perpendicular to thickness. The incident and diffraction vectors are $\vec{k}_0$ and $\vec{k}$. They are set so that a bright line runs through the diffracted spot and a dark line runs through the transmitted spot, where $s=0$ and $\Delta\vec{k} = \vec{g}$. The value of s can be positive or negative based on the position of the reciprocal lattice point within the Ewald sphere. If the reciprocal lattice point lies inside the Ewald sphere, s is positive $\Delta\vec{k} + \vec{s} = \vec{g}$ (Fig. 3.8 c). The origin of s is the intersection of the streak with Ewald sphere to the reciprocal lattice point. The vice versa is true for s being negative (Fig. 3.8 b). For optimal imaging conditions, s is always positive. It should be noted that contrast from the dislocation can be made sharp ($s+\text{ve}$) or hazy and diffuse ($s-\text{ve}$) while setting the two beam conditions [140].

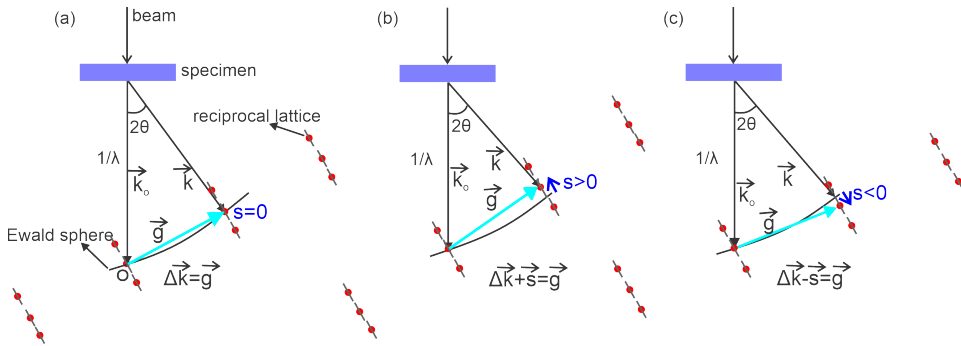


Figure 3.8.: Schematic of optimum imaging conditions for dislocation imaging as a function of the deviation parameter, s (a) s is zero, (b) s is negative and (c) s is positive. Schematic adapted from Ref. [140]

Bending contours are characterized by alternating bright and dark field contrast in the TEM images due to the changing s . They occur due to the localized bending of the samples, resulting in curvature. The lattice planes are bent, around, and oriented to satisfy the Bragg's law at that particular location, leading to diffraction.

The appearance of contrast in the two-beam TEM-BF image can assist in identifying the type of precipitate. Ashby and Brown [141, 142] proposed that the contrast produced by

a misfitting particle depends on its radius ρ , the constrained lattice mismatch ε_c , the exact diffraction conditions, and the particle's position within the thin foil. If the precipitate is coherent with the matrix and has a significant misfit with the matrix, the precipitates exhibit a coffee-bean contrast. It is characterized by two spherical arcs separated by a line of no contrast. It is perpendicular to the g -vector used. Iwamura and Miura [143] studied the coarsening behaviour of Al_3Sc particles in $\text{Al-0.2wt.\%Sc}$ alloy, emphasizing the transition of coherent/semi-coherent interface during aging. They found that when the precipitate transforms from coherent to semi-coherent, the line of no-contrast becomes irregular, as shown in Fig. 3.9.

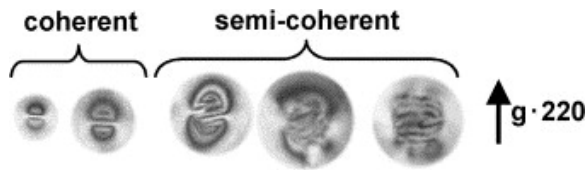


Figure 3.9.: Contrast change from coherent to semi-coherent precipitates. The line of no-contrast becomes indistinct as the precipitate transforms to a semi-coherent precipitate. Figure reproduced with permission from Ref. [143]

If some of the lattice planes of the precipitate match with the matrix, this leads to the formation of the interference pattern, referred to as “Moiré fringe” [122]. There are two types of Moiré fringes: translational Moiré fringe and rotational Moiré fringe. The g -vector is perpendicular to translational Moiré fringes and it is parallel to rotational Moiré fringes [124]. The semi-coherent precipitates show superimposed contrast from strain, orientation and diffraction effects [122, 124]. Incoherent precipitates are often large, having a distinct crystal structure from matrix and show the fringe contrast if they have smooth interface [124]. In case of matrix with precipitates, the diffracted beam of the electron from the matrix can act as incident beam to the precipitate and lead to additional spots around the matrix spots. This is referred to as double diffraction [122].

3.5. Data processing

Precipitate distributions

For the number density calculation, the precipitates were manually counted, and the number of precipitates per unit area was reported. GNU Image Manipulation program GIMP 2.10.36 was used to highlight the precipitates with a paint tool. TIF images were converted to 8-bit size, thresholded, and the area of the precipitate was automatically detected using the particle analysis plugin of ImageJ [144]. Then the precipitate area was fit to an equivalent diameter to calculate the precipitate diameter, area fraction, and size distributions.

Figure 3.10 a shows the SEM-BSE image of silicide precipitates in the solid solution matrix at 10%. For calculating number density, the same accelerating voltage, beam current, and working distance are used. So, the interaction volume and the information depth of the signal remain the same in both 1.3% and 10% samples, respectively. Hence, the number densities of both crept states (1.3% and 10%) can be compared. The precipitates were marked manually to enhance the contrast in the SEM-BSE images as shown in Fig. 3.10 b. The frequency distribution of precipitates and the cumulative frequency distribution (CFD) are shown with blue and red curves respectively in Fig. 3.10 c. Equation 3.7 is used to calculate the particular percentile (d_p) in a grouped frequency distribution [145]

$$d_p = L + \left(\frac{pN - F}{f} \right) \times w \quad (3.7)$$

Here d_p is the desired percentile (e.g., d_{25} , d_{50} , d_{90} , L is lower boundary of the class containing d_p , N is total frequency, p is desired percentile as a decimal (e.g., 0.25 for d_{25}), F is cumulative frequency before the class, f is frequency of the class, w is width of the class interval.

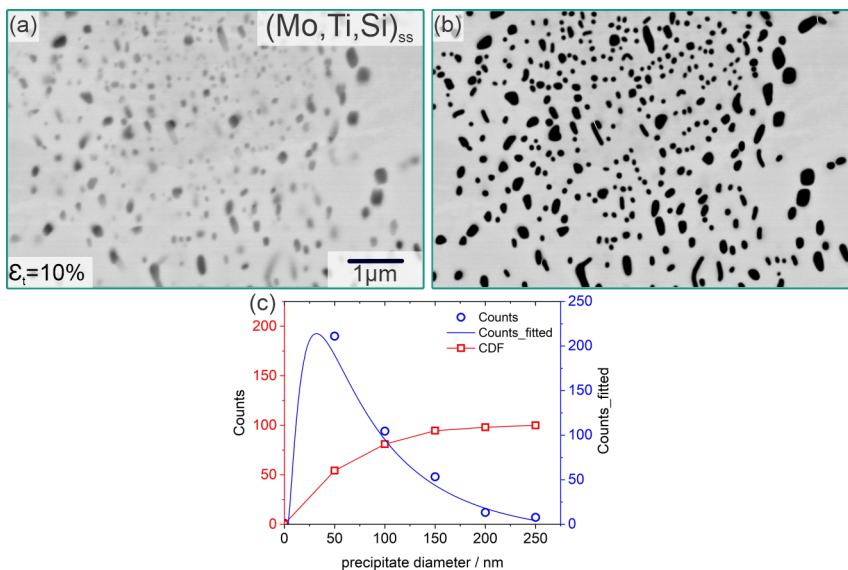


Figure 3.10.: Quantification of silicide precipitates in solid solution matrix from scanning electron microscopy (SEM)-backscattered electron (BSE) images (a) Original BSE image, (b) Original image with precipitates identified, and (c) Precipitate quantification in terms of frequency and cumulative frequency distribution. Silicide precipitates exhibit a dark contrast compared to solid solution matrix.

4. Microstructural evolution of eutectic Mo-20Si-52.8Ti as-cast and crept samples

This chapter presents the results of creep-induced microstructural investigations on a Mo-20Si-52.8Ti eutectic as-cast (AC) sample. The creep microstructure evolves on different length scales. The microstructure is analyzed on the mesoscale by scanning electron microscopy using backscattered electrons (SEM-BSE) as well as by electron backscatter diffraction (EBSD) and, on the microscale, by transmission electron microscopy in bright field mode (TEM-BF) or scanning transmission electron microscopy in bright field mode (STEM-BF) for imaging dislocations in solid solution and silicide phases.

4.1. Selection of samples from creep tests

The high-temperature mechanical strength of a eutectic Mo-20Si-52.8Ti alloy in the AC and HT states were assessed by performing compressive creep tests at 1200 °C; for details, see section 3.2. These studies were done in collaboration with Dr.-Ing. Daniel Schliephake at Institute of Applied Materials-Materials Science (IAM-WK), Karlsruhe Institute of Technology (KIT). This work aims to obtain a microstructural understanding of the creep behavior in a two-phase, eutectic Mo-20Si-52.8Ti alloy, which is reported in the following sections. The major portions of these results have been published in AEM journal [99] and are reused with permission.

To select the most interesting situations of the creep tests for the microstructural analysis, creep test data are considered. Figure 4.1 shows the representative creep curves for a eutectic Mo-20Si-52.8Ti alloy and two bcc solid solution alloys: Mo-40Ti and Mo-3Si-40Ti, obtained at 1200 °C under acting stresses of 100, 150 and 200 MPa. This

eutectic alloy was tested in two microstructural conditions: AC and HT. Since eutectic Mo-20Si-52.8Ti alloy is composed of bcc solid solution and silicide phases, these two single-phase solid solution alloys serve as a reference to compare how the solid solution phase behavior influences the overall creep behavior of two-phase eutectic alloy. The microstructural details of the investigated alloys are mentioned in section 4.2.

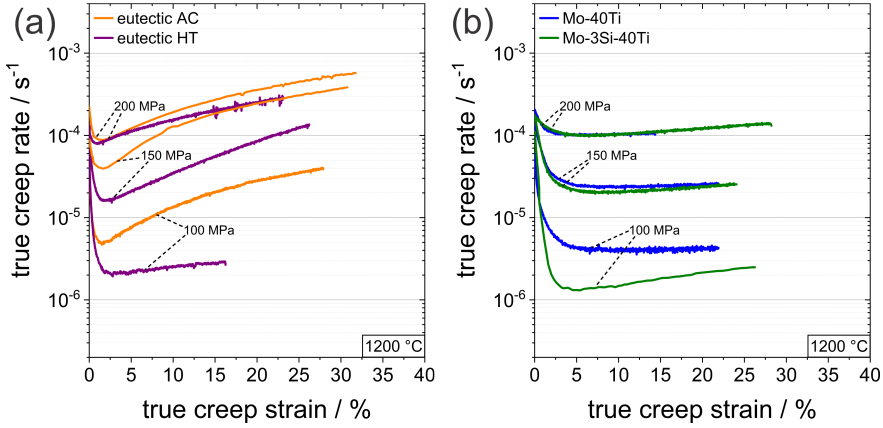


Figure 4.1.: High-temperature mechanical deformation, creep test data represented in terms of true creep rate ($\dot{\epsilon}$) as a function of true creep strain (ϵ_t) of (a) A eutectic Mo-20Si-52.8Ti as-cast (AC) in orange and heat-treated (HT) in purple condition (b) Mo-40Ti in blue and Mo-3Si-40Ti in green respectively. Data provided by D. Schliephake. Figure reproduced with permission from Thota et al. [99]

Following a significant drop in creep rate, by up to two orders of magnitude in the transient creep regime, a distinct $\dot{\epsilon}_{min}$ is observed at varying total strains. Taking into account that elastic strain increases with applied stress (σ), the $\dot{\epsilon}_{min}$ for the eutectic alloy consistently occurs at approximately 1.3%, independent of the HT condition in Fig. 4.1 a. At all investigated stress levels, the $\dot{\epsilon}_{min}$ of the HT eutectic alloy is consistently higher than that of the AC condition. In comparison, both Mo-40Ti and Mo-3Si-40Ti exhibit similar creep resistance and display an extended steady-state creep regime. The steady-state creep rates for these two solid solution alloys are plotted in Fig. 4.1 b alongside the $\dot{\epsilon}_{min}$ of eutectic alloy, as a function of σ at 1200 °C. For simplicity, the steady-state creep rates of Mo-40Ti and Mo-3Si-40Ti are hereafter referred to as minimum creep rates.

To evaluate the influence of the test temperature of 1200 °C on the creep resistance, the T_{hom} was calculated, with T_s being the solidus temperature of the alloy. The T_s was obtained from Pandat calculations [99]. The T_s , T_{hom} and Q_c are summarized in

Table 4.1, including the data for $(\text{Ti},\text{Mo})_5\text{Si}_3$ from a eutectic alloy with the chemical composition Ti–5.6Mo–39.6Si. At 1200 °C, a eutectic alloy exhibits the highest T_{hom} of 0.74 followed by Mo-3Si-40Ti with 0.69. The Ti_5Si_3 and Mo-40Ti are tested at the lowest T_{hom} of 0.62 and 0.61, respectively. This implies that solid solution alloys exhibit lower creep rates than eutectic alloy and this effect is seen in Fig. 4.2. Figure A.4 displays a modified Arrhenius plot of the $\dot{\epsilon}_{min}$ as a function of σ for 200 MPa. This shows that the creep resistances of eutectic alloy and the solid solution alloys are comparable, even though T_s of Mo-40Ti is much higher. The apparent activation energies of creep Q_c from the Arrhenius term, $\dot{\epsilon}_{min} \propto e^{-\frac{Q_c}{RT}}$ are 384, 435, and 652 kJ/mol for a eutectic alloy, Mo-40Ti, and Mo-3Si-40Ti, respectively shown in Table 4.1.

Table 4.1.: Calculated solidus temperature (T_s), homologous temperature (T_{hom}) and activation energy (Q_c) of all investigated alloys and monolithic phases for 1200 °C.

Alloy / Phase	Composition / at. %	T_s / °C	T_{hom}	Q_c in kJ/mol
Eutectic alloy	Mo-20Si-52.8Ti	1723	0.74	384
Mo-40Ti	Mo-40Ti	2158	0.61	435
Mo-3Si-40Ti	Mo-3Si-40Ti	1875	0.69	652
Ti_5Si_3	Ti-37.5Si	2097	0.62	–
$(\text{Ti},\text{Mo})_5\text{Si}_3$	Ti-5.6Mo-39.6Si	2187	0.60	–

Figure 4.2 reveals the Norton plot (described in section 2.3), which depicts the $\dot{\epsilon}_{min}$ plotted as a function of σ for a range of stresses, varying from 30 MPa to 200 MPa at 1200 °C. Orange triangles and purple squares represent the AC and HT conditions; for comparison, creep data of monolithic, Ti_5Si_3 is also shown in Fig. 4.2 with black open hexagons. Additionally, two solid solution alloys: Mo-40Ti and Mo-3Si-40Ti, are also depicted with blue triangles and green circles. At higher stress levels (>100 MPa), the creep rates of eutectic HT, Mo-40Ti, and Mo-3Si-40Ti alloys are comparable. This similarity may be attributed to the lower grain boundary densities present in all three microstructures. HT samples exhibit a lower creep rate compared to the AC sample. This is assigned to the lower boundary density in HT samples (see Fig. 4.5). Additionally, the n value for both Mo-40Ti and Mo-3Si-40Ti are consistent across the entire creep testing range, with an n value of 5.1. This suggests that both solid solution alloys undergo creep deformation through the same mechanism: dislocation climb-controlled creep, according

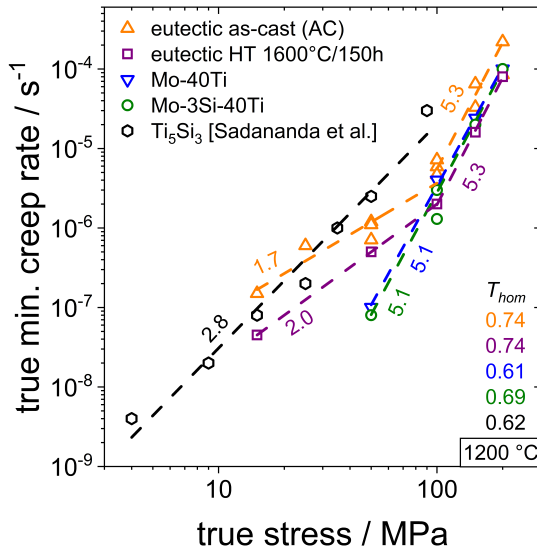


Figure 4.2.: Norton plot of crept eutectic Mo-20Si-52.8Ti alloy at 1200 °C. The true minimum creep rates of AC, HT, and Ti_5Si_3 samples are represented by orange triangles, purple squares, and black hexagons respectively. In addition, two single-phase, bcc, solid solution alloys: Mo-40Ti and Mo-3Si-40Ti, are also depicted with blue triangles and green circles. Data provided by D. Schliephake. Figure adapted with permission from Thota et al. [99] and Sadananda et al. [146]. The T_{hom} of the each sample is also illustrated with same color code.

to Table 4.2. Both AC and HT samples exhibit an n value of 5.3, which indicates dislocation-climb controlled creep mechanism in both microstructural conditions.

At lower stresses (<100 MPa), the n value is 1.7 in the AC state, whereas the n value is 2 in the HT condition. The interpretation of Norton-plot suggests interface-reaction controlled diffusional creep at lower stresses. A similar result is reported for pure 3 mol% yttria-stabilized tetragonal zirconia (3YTZ) with 1.96 at.% Yr based on n value and microstructural observations [147]. According to the Norton plot, the creep mechanism changes when transitioning to higher stresses at 100 MPa, where the AC and HT samples display an n value of 5.3. This indicates dislocation climb-controlled creep. The reference binary silicide, Ti_5Si_3 , shows an n value of 2.8 for the whole true-stress range, indicating dislocation climb controlled creep. From the Norton plot and n values in Fig. 4.2, this eutectic alloy exhibits an interesting transition, hence it is chosen for further microstructural analysis in the thesis. The creep stress at which transition in the creep mechanism

Table 4.2.: Summary of operating creep deformation mechanisms

No	n value	Possible creep deformation mechanism
1	1	diffusional creep, either Nabarro-Herring or Coble creep [88, 90]
2	1.7	interface-reaction controlled diffusional creep [147]
3	2	grain boundary sliding [148, 149]
4	$2.8 \approx 3$	dislocation climb-controlled creep [61, 62]
5	5.1	dislocation climb-controlled creep [61, 62]
6	5.3	dislocation climb-controlled creep [61, 62]

occurs is identified to be 100 MPa. That specific stress was chosen for interrupted creep testing, which is discussed in the following sections.

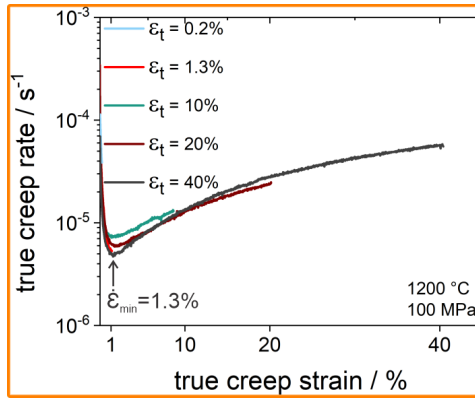


Figure 4.3.: Creep data of eutectic Mo-20Si-52.8Ti alloy at 1200 °C and 100 MPa, represented as $\dot{\epsilon}$ as a function of ϵ_t . The samples are crept to specific true creep strains and each ϵ_t is indicated with a unique color: $\epsilon_t = 0.2\%$ (pre-minimum) - turquoise, $\epsilon_t = 1.3\%$ (creep-minimum)-red, $\epsilon_t = 10\%$ (strain after minimum) - bluish green, $\epsilon_t = 20\%$ - brown, and $\epsilon_t = 40\%$ - black respectively.

Figure 4.3 depicts the $\dot{\epsilon}$ of a eutectic alloy in AC state plotted as a function of ϵ_t at 100 MPa. At the beginning of creep, the creep rate decreases until a characteristic minimum creep rate is reached. For higher true creep strains, the creep rate accelerates, leading to a positive slope of the curve. All the color-coded curves in Fig. 4.3 reflect similar, but interrupted to different ϵ_t such as 0.2% (pre-minimum), 1.3% (creep minimum, $\dot{\epsilon}_{min}$), and post ($\dot{\epsilon}_{min}$) to 10%, 20% and 40%. This interruption is visible in the different lengths

of the individual curves, which in general show a similar behavior. From each interrupted test, samples were extracted to perform microstructural characterization using electron microscopy to study the microstructural evolution during creep.

4.2. Initial microstructure of bcc and eutectic Mo-20Si-52.8Ti alloy samples

Figure 4.4 illustrates the SEM-BSE images of two solid solution alloys, Mo-40Ti in a) and Mo-3Si-40Ti in b), respectively. In Fig. 4.4 a), the microstructure shows the presence of dendrites that form during solidification. Some casting porosity is also observed, characterized by irregular morphology with dark contrast (marked with red arrows in Fig. 4.4 a). The microstructure of Mo-3Si-40Ti shows the Si-rich precipitates that appear dark in the bright matrix (Fig. 4.4 b). In addition, different grains show varying gray scale values indicating orientation contrast. The chemical composition of the Si-rich precipitates are not identified as a part of the present thesis.

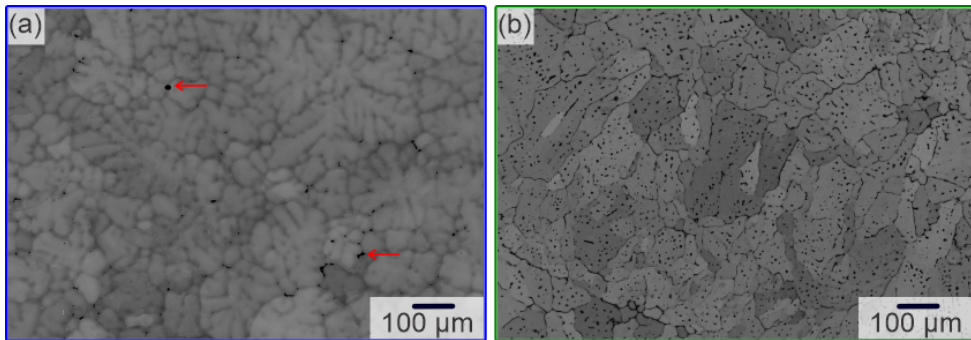


Figure 4.4.: Microstructure of the bcc solid solution alloys depicted by SEM-BSE images (a) Single-phase Mo-40 Ti and (b) Mo-3Si-40Ti with precipitates. Data provided by D. Schliephake

The AC microstructure of a eutectic, Mo-20Si-52.8Ti alloy is shown by the SEM-BSE image in the Fig. 4.5 a and b. Figure 4.5 a shows the microstructure of a $130 \mu m^2$ area, Figure 4.5 b focuses on a detail in the orange-framed region of Fig. 4.5 a. The microstructure consists of two phases: bcc $(Mo,Ti,Si)_{ss}$ solid solution and hexagonal $(Ti,Mo)_5Si_3$ silicide. The average Z values of solid solution and silicide are 31 and 20 respectively, based on their atomic fractions and Z (Table 2.1). Hence the SEM-BSE image shows the Z-contrast with the solid solution appearing bright and the silicide

appearing dark, due to higher Mo content in the solid solution and vice versa in the silicide. The two phases often appear isolated and surrounded by the other phase in the 2-D sections of the acquired BSE images.

The microstructural morphology comprises various components, including lamellar, rod, and equiaxed morphologies of the eutectic phase distribution, as well as the same primary solidified silicide with a hexagonal morphology that appears faceted. One of them is highlighted by the orange arrow (Fig. 4.5 a). Because of the eutectic solidification process, the lateral dimensions of the phases within a colony are found to be finer compared to coarser dimensions at the inter-colony, the phases appear with different lateral extensions. For instance, the solid solution in the lamellar colony (indicated with L in Fig. 4.5 a) has a longest length of $30\ \mu\text{m}$, while the solid solution in the neighboring rod colony (indicated with R in Fig. 4.5 a) has the largest diameter of $1\ \mu\text{m}$. It should also be noted that the appearance of different eutectic morphologies is due to the orientation of colonies, which are being cut at different angles by the metallographic section for SEM-BSE imaging. In the silicide, micro-cracks are also present, as indicated with yellow arrows in Fig. 4.5 a and b. The cracks also reach into the solid solution (see Fig. 4.5 c).

In the AC state, tiny dark precipitates of $(\text{Ti},\text{Mo})_5\text{Si}_3$ are observed in the bright solid solution regions, as marked with red arrows in Fig. 4.5 b. Also, tiny bright precipitates of $(\text{Mo},\text{Ti},\text{Si})_{\text{ss}}$ are detected in dark $(\text{Ti},\text{Mo})_5\text{Si}_3$, as indicated with blue arrows in Fig. 4.5 b. But, they appear in very localized regions and are not as widespread as $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates in the solid solution. The phase boundary density in the AC samples is about $0.60\ \mu\text{m}^{-1}$, as judged from Fig. 4.5 b. Figure 4.5 d shows the typical morphology of the HT sample in a $150\ \mu\text{m}^2$ frame, as obtained by SEM-BSE imaging. The strong contrast relates again to the two mentioned phases. Compared to the AC microstructure, the HT microstructure is coarser. This is due to the heat treatment at $1600\ ^\circ\text{C}$ for 150 hours. The corresponding phase boundary density is $0.23\ \mu\text{m}^{-1}$, from Fig. 4.5 d.

The local distribution of plastic strain in the microstructure is presented with kernel average misorientation (KAM) maps post-processed from recorded EBSD data. These maps indirectly hint at the geometrically necessary dislocation densities. Figure 4.6 depicts a color-coded KAM map of the AC microstructure partitioned into two phases: a) solid solution and b) silicide. The other phase is depicted in pure white. The majority of the grains have low plastic strain close to zero, presented in dark blue color. In some regions,

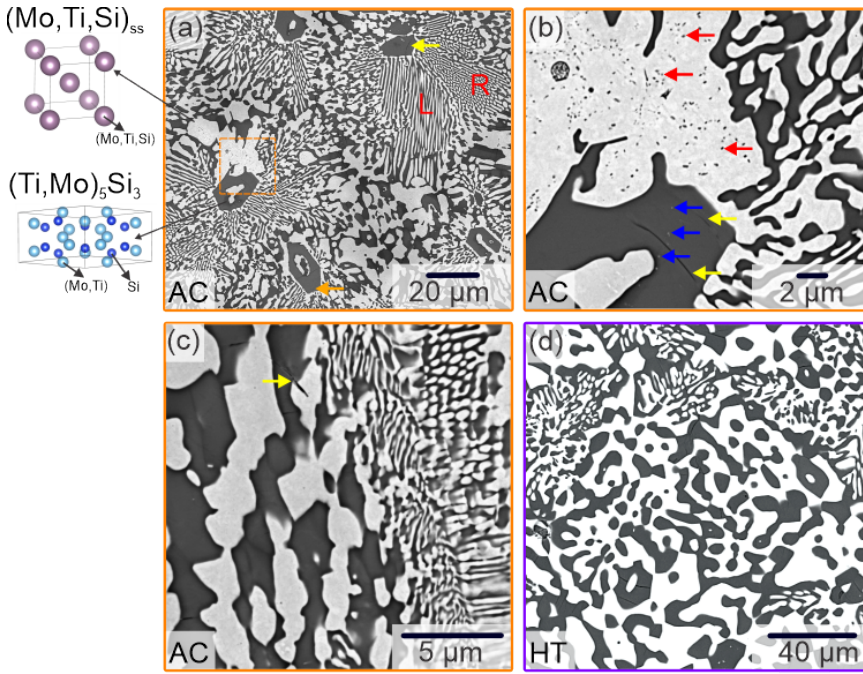


Figure 4.5.: The initial microstructure of a eutectic Mo-20Si-52.8Ti alloy in AC and HT states is presented by SEM-BSE images. The bright phase corresponds to the solid solution, and the dark phase corresponds to silicide in AC and HT conditions. (a) Overview of various eutectic morphologies in the AC state: lamellar, rod, and equiaxed morphologies, as well as primary solidified phases. The letters L and R indicate the lamellar and the rod colony morphologies. (b) The magnified region of two phases contains precipitates in both phases, labeled with red and blue arrows. Cracks in the silicide matrix are highlighted with yellow arrows. (c) Magnified region of AC sample showing cracks from the silicide reaching into the solid solution. (d) Microstructure of an HT state sample.

the solid solution of the AC sample has a pre-existing plastic strain, presented with lighter blue regions. One of these regions is marked with an orange arrow in Fig. 4.6 a. The silicide, shown in Fig. 4.6 b, barely shows regions of plastic strain accumulation. It is here suggested that the solid solution accumulates strain during sample cooling because of the difference in the CTE between the two phases. The CTE difference results in plastic deformation in the mechanically softer phase, which is the solid solution matrix. As a result, the solid solution deforms and accommodates the plastic strain, whereas the silicide stays strain-free. As the CTE of silicide is anisotropic and differs in c- and a-directions, the resulting plastic strain varies in adjacent solid solution regions.

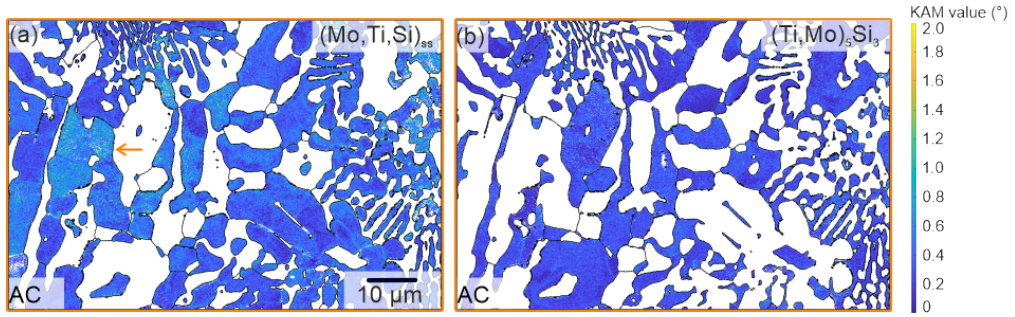


Figure 4.6.: Local distribution of plastic strain in the microstructure are presented with electron back scatter diffraction (EBSD)-kernel average misorientation (KAM) maps in Mo-20Si-52.8Ti AC state for (a) The solid solution phase and (b) The silicide phase. Each pixel in the KAM maps is color-coded with the appropriate KAM range shown in the figure legend on the right. The orange arrow in Fig. 4.6 a highlights a solid solution grain with a higher KAM value, appearing bright with yellow pixels.

To visualize how the plastic strain is accumulated in the AC state, STEM-BF investigations were performed by preparing a TEM lamella from the solid solution regions containing higher KAM value. Representative results are shown in Fig. 4.7. It shows the two-beam condition TEM-BF image of the same dislocations imaged using the $\vec{g}$ of $(10\bar{1})$, $(11\bar{2})$ and $(\bar{1}21)$ respectively. Figure 4.7 a shows dislocations acquired in the two-beam condition STEM-BF using the $\vec{g}$ $(10\bar{1})$. Numerous dislocations (appearing as dark lines) are observed in solid solution of the AC state (Fig. 4.7 a). This finding is in good agreement with the observations of the higher plastic strains in the KAM maps in Fig. 4.6 a, in the solid solution. The dislocations are detected in close vicinity to $(\text{Ti,Mo})_5\text{Si}_3$ precipitates. These precipitates may act as obstacles to dislocation motion and pin the dislocations.

To determine $\vec{b}$ of the dislocations, the same region containing dislocations is tilted to a different crystallographic excitation conditions ($\vec{g}(10\bar{1})$, $\vec{g}(\bar{1}21)$ and $\vec{g}(11\bar{2})$) to establish the Invisibility criterion ($\vec{g} \cdot \vec{b} = 0$). This technique is described in the experimental section 3.4.4. In Figure 4.7 b, the dislocation marked 1 and 2 are invisible when imaged with $\vec{g}(11\bar{2})$, accordingly $\vec{b}$ can be determined to be $\frac{1}{2}[111]$. The Invisibility criterion, $\vec{g} \cdot \vec{b} = 0$ performed for the solid solution are summarized in Table 4.3. Majority of dislocations visible in Fig. 4.7 a are parallel to each other. They do not become invisible with the analyzed two-beam conditions because their $\vec{b}$ lies in a different direction and the chosen $\vec{g}$ for the Invisibility criterion does not work in the current case.

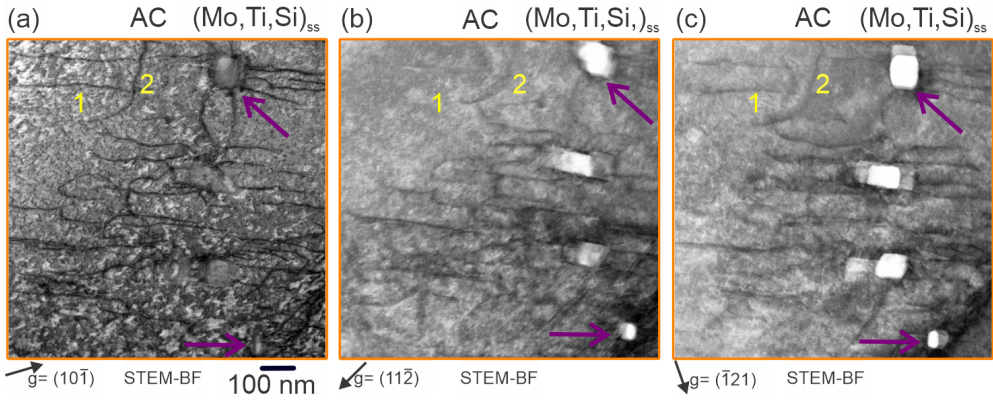


Figure 4.7.: Determination of dislocation character in the solid solution of a eutectic Mo-20Si-52.8Ti in AC state. Imaging of dislocations from [111] zone-axis (ZA) by two-beam condition STEM-BF technique with the $\vec{g}$ of (a) $(10\bar{1})$, (b) $(11\bar{2})$, and (c) $(\bar{1}21)$. The purple arrows indicate the position of the same silicide precipitates in all three images. The dislocations are enumerated with yellow color to indicate that their character is found out. The $\vec{g}$ is annotated in each STEM-BF image with a black arrow on the bottom left. The black spots in Fig. A.1 a-c are from the Ga^+ ion beam damage and not edge-on dislocations.

Table 4.3.: Invisibility criterion, $\vec{g} \cdot \vec{b}$ of selected two-beam conditions in solid solution of AC state

$\vec{g} \cdot \vec{b}$	Burgers vector, $\vec{b}$			
$\vec{g}$	$\frac{1}{2}[111]$	$\frac{1}{2}[\bar{1}11]$	$\frac{1}{2}[1\bar{1}1]$	$\frac{1}{2}[\bar{1}1\bar{1}]$
$(10\bar{1})$	0	-1	0	1
$(11\bar{2})$	0	-1	-1	2
$(\bar{1}21)$	1	2	-1	0

To evaluate the mobility of dislocations, the screw or edge character of the two dislocations is determined. They are characterized by the dislocation line direction ($\vec{u}$), the angle (θ) between $\vec{u}$ and $\vec{b}$. These dislocation descriptors and the acting slip planes with respect to the crystallographic space conditions of the selected region are tabulated in Table 4.4. The angle θ between $\vec{u}$ and $\vec{b}$ of dislocation 1 is 98.4° . Thus, the dislocation 1 has mainly edge character. The angle θ between $\vec{u}$ and $\vec{b}$ of dislocation 2 is 60.0° , dislocation 2 has mixed character.

A second region was analyzed for the characterization of dislocations in the solid solution of the AC sample, shown in Fig. A.1 in the Appendix section. There is a small overlap

Table 4.4.: Line direction for dislocations: 1 and 2 in solid solution of AC sample, see Fig. 4.7

No	Line direction ($\vec{u}$)	$\theta = \cos^{-1}(\vec{u} \cdot \vec{b})$	$\vec{u} \times \vec{b}$	Slip plane
1	$[\overline{0.22} \ 0.43 \ \overline{0.36}]$	98.4°	$(\overline{0.40} \ 0.07 \ 0.33)$	$(\overline{1}01)$
2	$[\overline{0.23} \ 0.76 \ \overline{0.30}]$	62.0°	$(\overline{0.53} \ 0.26 \ 0.26)$	$(\overline{2}11)$

of Fig. A.1 with Fig. 4.7. Firstly, dislocations are imaged in the solid solution using the $\vec{g}$ (10 $\bar{1}$) shown in Fig. A.1 a. Similar to the previous observations, (Ti,Mo)₅Si₃ precipitates are embedded by many dislocations. After that, the same region containing dislocations is tilted to another two-beam conditions: $\vec{g}(\overline{2}11)$ and $\vec{g}(1\overline{1}0)$ to establish the Invisibility criterion. All the dislocations visible in the Fig. A.1 a are invisible in Fig. A.1 b and Fig. A.1 c. The $\vec{b}$ of the dislocations in the above area is $\frac{1}{2}[111]$. In a silicide grain, no single dislocation is observed, but on some occasions, an array of dislocations is observed (shown in Fig. A.2 in the Appendix section). The whole overview of the prepared FIB lamella for the TEM characterization of the AC sample is shown in Fig. A.3 in the Appendix section.

4.3. Mesoscale evolution of crept samples

Figure 4.8 displays SEM-BSE images of the two phases of a eutectic Mo-20Si-52.8Ti alloy, by applying compressive creep stress at 1200 °C to the sample in the vertical direction (compression direction CD given in a). The images relate to samples that are crept to various ε_t : a & b) 0.2%, c & d) 1.3%, e & f) 10% and g & h) 20%, as determined in section 4.1 (Table 3.2 and Fig. 4.3). The area fractions of the two phases: solid solution and silicide, are found to be equal in proportion, $\approx 50\%$ among the different creep strains. The area fractions of the phases do not vary much, within an error of $\pm 3\%$. The upper row in Fig. 4.8 provides the microstructure after 0.2% with different magnifications. In the Fig. 4.8 b, precipitates of silicide in solid solution (marked with red arrows) and solid solution in silicide (marked with blue arrows) are visible, with an increased number density when compared to the AC state, provided in Fig. 4.5. Thus both phases tend to precipitate in the other phase during creep deformation. At 0.2%, a precipitate-free zone (PFZ) is observed in solid solution grains near the original two-phase interface (refer

Fig. 4.8 b). The PFZ does not have a uniform width, but it changes from 350 nm to 900 nm in the same grain. A PFZ is detected in all the crept samples in solid solution.

The silicide precipitates (dark) in solid solution matrix (bright) show a bimodal distribution: larger precipitates with edge lengths ranging from 200 nm to 500 nm (marked with red double headed dashed arrows in Fig. 4.8 b and small ones with edge lengths ranging from 50 nm to 100 nm (marked with red arrow in Fig. 4.8 b). The large precipitates are also present in the AC sample. Thus they stay the same during cooling after arc melting. While the small precipitates nucleate during the creep test. They appear lighter than the former (red arrow in Fig. 4.8 b). In the same manner, solid solution precipitates (bright) also show two different sizes: larger precipitates with edge lengths from 200 nm to 400 nm (marked with double headed dashed blue arrow in Fig. 4.8 b) and smaller ones with edge lengths from 50 nm to 150 nm (indicated with blue arrow in Fig. 4.8 b). Similarly, the latter form during the creep test and former during cooling after arc melting.

Furthermore, cracks are detected in the silicide. These cracks reach into solid solution (marked with yellow arrows) also noted in Fig. 4.8 a and g. As a function of creep strain, the precipitate sizes in both phases are different in different grains. This might result from minor variations in the solute content, i.e., Si in the solid solution and Mo in the silicide, respectively. Creep stress has led to enhanced precipitation and fine distribution of precipitates during the creep test. The quantification of precipitates is performed in the section 4.5. As it is difficult to draw inferences on the deformation of the two phases in response to the applied creep strain from the SEM-BSE images alone, EBSD-KAM maps are used.

The plastic strain in the two phases is depicted by the maximum KAM value in the solid solution and silicide phases, plotted for different creep strains in Fig. 4.9 a) and b). The initial maximum KAM values seem to drop gradually from AC to 1.3% in the solid solution in Fig. 4.9 a. This might indicate the activation of softening mechanisms, such as dynamic recovery or dynamic recrystallization, leading to plastic strain reduction. After reaching the creep minimum at 1.3%, the plastic strain increases in the solid solution, as shown by an increase in the KAM value at 10%. With increasing creep strain, the KAM value remains same from 10% to 20%. This saturation might hint at dynamic recovery in solid solution at 20%.

In the silicide, the KAM values presented in Fig. 4.9 b are constant within the given error bars, even though the error bars do not support this information. With these

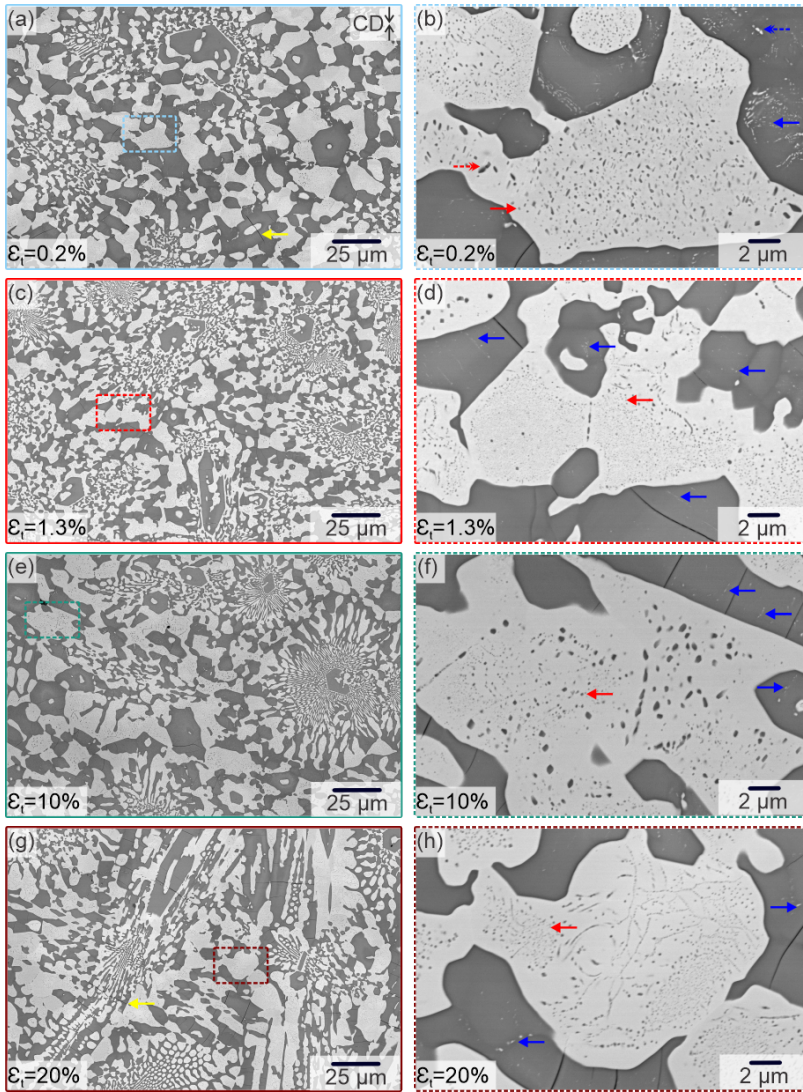


Figure 4.8.: Distribution of the two phases in a eutectic Mo-20Si-52.8Ti alloy characterized by SEM-BSE imaging. The images show samples crept to total strains, ϵ_t , of (a, b) 0.2%, (c, d) 1.3%, (e, f) 10%, and (g, h) 20% at 1200 °C in compression. The left column shows the microstructure at lower magnification, and the right column shows higher-magnification images. Red arrows indicate individual silicide precipitates in the solid solution, while blue arrows indicate solid-solution precipitates in the silicide. Yellow arrows in (a) and (g) indicate cracks extending from the silicide into the solid solution. CD denotes the compression direction, as shown in (a), and is the same for all crept samples.

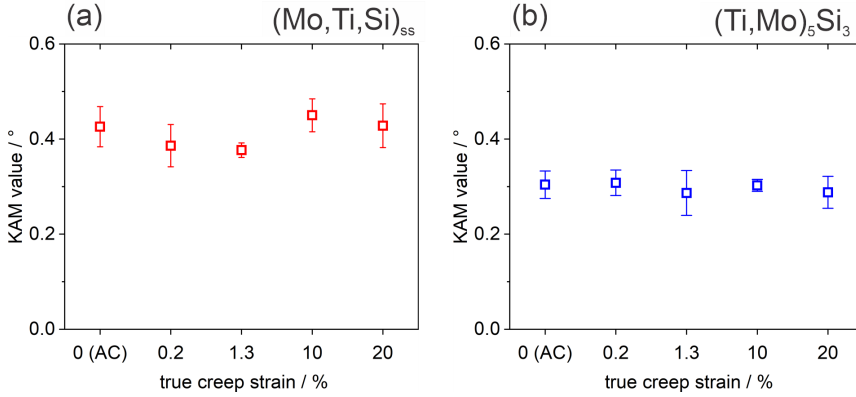


Figure 4.9.: Plastic strain in the AC and crept samples plotted with the maximum phase KAM value as a function of ε_t in (a) The solid solution and (b) The silicide. The solid solution and silicide values are plotted in red and blue squares respectively.

small increases, a clear trend cannot be attributed to silicide as a function of true creep strain. These almost constant KAM values and the quite large error bars may point to inhomogeneous deformation of silicide within the analyzed region, and in-depth mesoscale strain analysis at the grain-level across various creep strains can reveal more information. The same is done in the next paragraphs.

To get a more detailed understanding of plastic strain accumulation, KAM distributions of solid solution and silicide are illustrated in Fig. 4.10, for five different regions and two different creep conditions. In addition to the AC state, 0.2% is chosen to study the state just before the creep minimum. In the solid solution, the KAM distributions of the sample with 0.2% shift by a constant value from higher values (AC) to the left, indicating plastic strain reduction. In the silicide, the KAM values mainly shift to the right, but the shift depends on the individual area. This hints at deformation of the silicide already at 0.2%.

The plastic strain due to creep deformation in both phases is visualized as KAM maps in Fig. 4.11 to 4.14. The top and bottom images belong to solid solution and silicide respectively. The respective other phase is plotted in white. In the solid solution of 0.2% sample, the KAM map in Fig. 4.11 a shows sub-grain boundaries (marked with purple arrows in Fig. 4.11 a). These boundaries with misorientation angles of 2° to 5° are observed within the grains of the solid solution. The sub-grain boundaries appear as line features with light green color, present within the grain. These observations combined

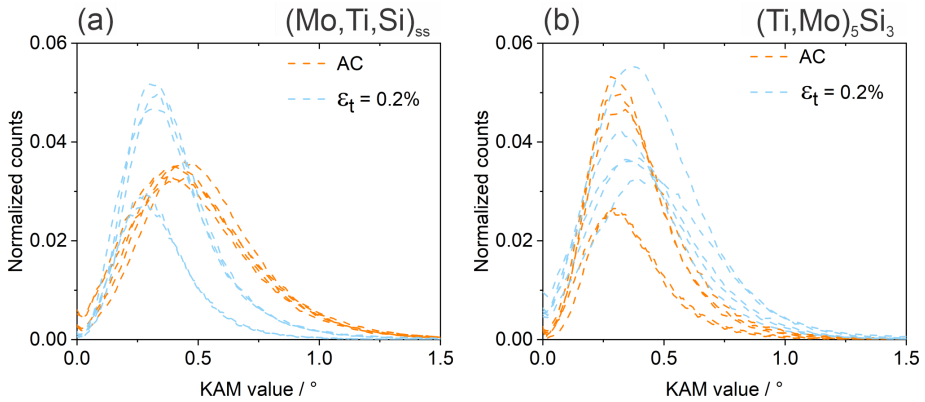


Figure 4.10.: Plastic strain in AC and 0.2% samples plotted as KAM distributions in (a) The solid solution and (b) The silicide at 5 different locations. The KAM distributions of AC and 0.2% sample are plotted in orange and turquoise lines, respectively.

with the KAM value reduction presented in Fig. 4.9 a and the reduction in plastic strain (KAM distributions) shown in Fig. 4.10 a support the occurrence of dynamic recovery in the solid solution. In the 0.2% sample, deformation of the silicide is evident (gray arrow in Fig. 4.11 b) by the lighter blue colored grains. This finding is related to the shift of the KAM distributions to higher values for many silicide grains in Fig. 4.10 b.

At creep minimum (1.3%), both phases start to deform simultaneously (red arrows in Fig. 4.12 a and b), accumulating creep strain. For the sample of 1.3% sample, solid solution grains have more green and yellow color pixels (see Fig. 4.12 a) than silicide grains with mostly dark blue pixels (see Fig. 4.12 b). The solid solution accumulates higher strain compared to the silicide in this sample. Furthermore, silicide grains initiate sub-grain boundary formation in some small lamellar grains at 1.3% (purple arrows in Fig. 4.12 b). These results suggest the beginning of dynamic recovery in silicide already at 1.3%.

For the creep states beyond creep minimum (10% and 20%), both phases show sub-grain boundaries with misorientation angle between 2° and 5° . Subsequently, partitioning of individual grains into sub-grains occur. In the 10% sample, sub-grain boundaries are observed, but they do not fully extend throughout the visible area of the solid solution grains (see Fig. 4.13 a). Similarly, silicide grains form sub-grain boundaries and they also end up within the grains, without forming well-defined sub-grains, is noted in the 10%

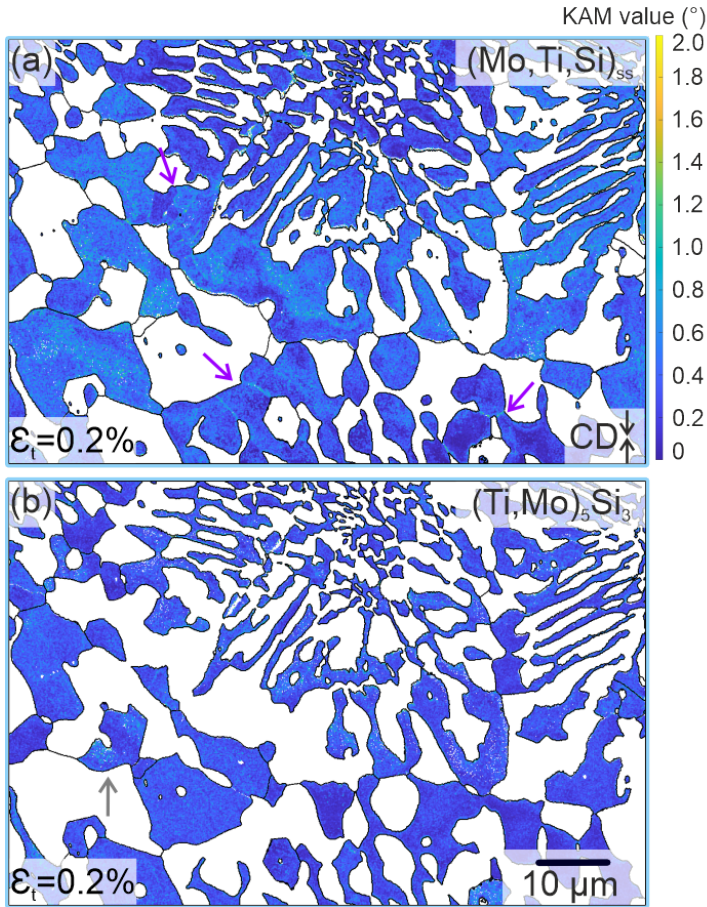


Figure 4.11.: Plastic strain in 0.2% sample depicted as KAM maps in (a) The solid solution and (b) The silicide.

sample (refer Fig. 4.13 b). These observations of sub-grain boundary formation imply the start of dynamic recovery, at 10% in both phases.

After 20%, sub-grains are visible in the solid solution (see Fig. 4.14 a). A few solid solution grains accumulate higher strain even without the formation of sub-grain boundaries. This indicates that some grains in solid solution undergo dynamic recovery and few continue to deform at 20%. In contrast, sub-grain boundaries and low angle grain boundaries with 5° to 15° misorientation, appearing as white lines in Fig. 4.14 b, are predominantly detected in the silicide. These two boundaries may intersect and may form junctions (marked with J in Fig. 4.14 b), leading to formation of distinct sub-grains in the silicide

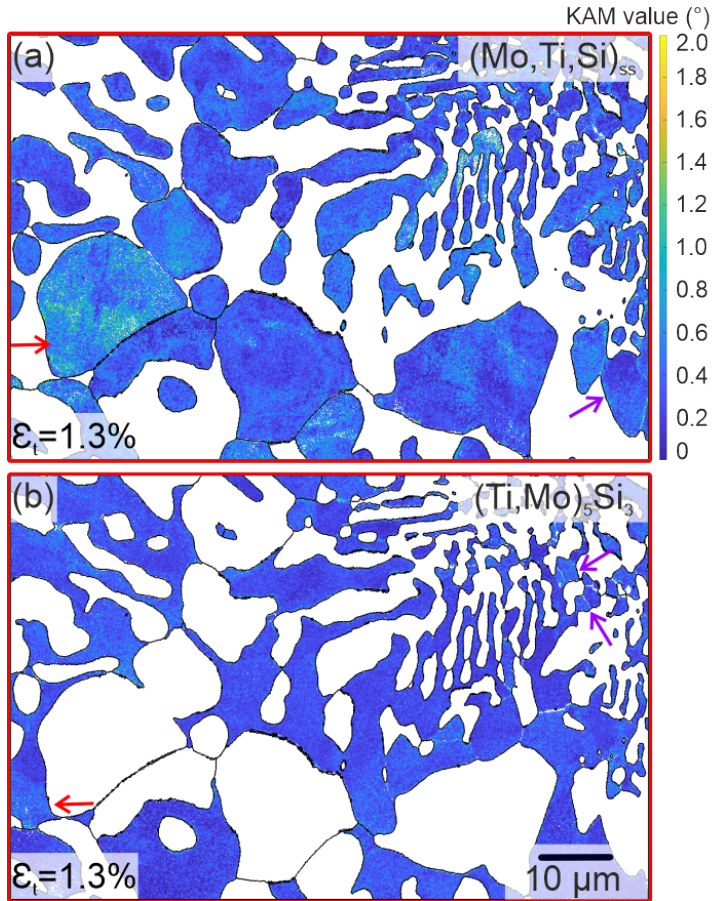


Figure 4.12.: Plastic strain in 1.3% sample shown as KAM maps in (a) The solid solution and (b) The silicide.

phase. These results support the completion of dynamic recovery in the silicide phase as most of the silicide grains have lower strain at 1.3%. In addition, the KAM values of AC and 20% are similar. The possibly small reduction in the KAM value from 10% to 20% in the silicide would be in line with dynamic recovery (Fig. 4.9 b)

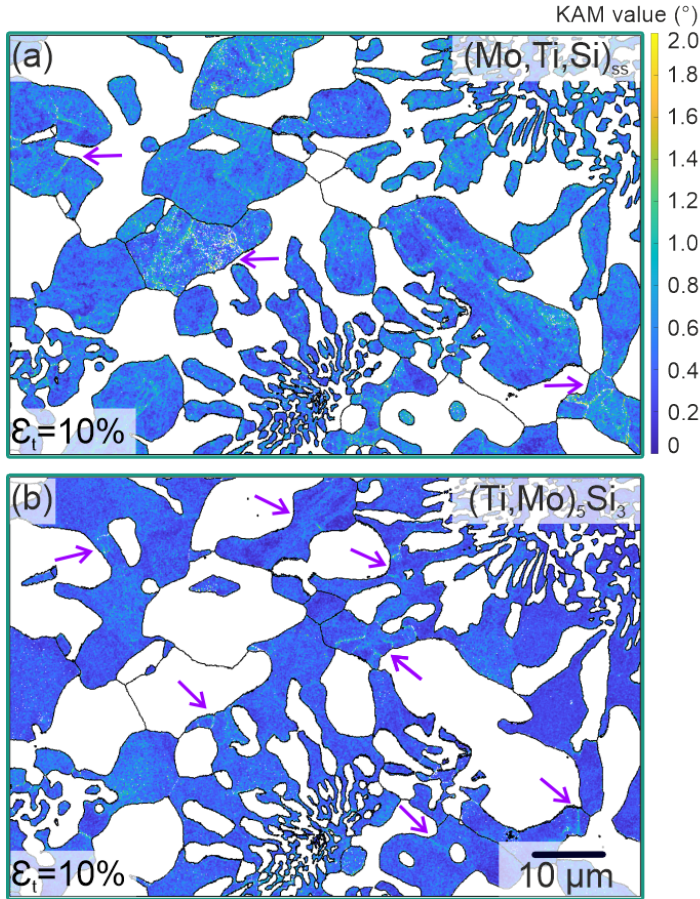


Figure 4.13.: Plastic strain in 10% sample represented as KAM maps in (a) The solid solution and (b) The silicide.

4.4. Evolution of dislocations as a function of creep strain

A FIB lamella was cut out of the selected sample region and the two-beam condition TEM/STEM BF imaging is performed in both phases of a eutectic Mo-20Si-52.8Ti alloy to decipher the dislocation-precipitate interactions and understand the evolution of microstructure as a function of creep strain on the micro scale using TEM. One of the fundamental objectives is to understand the acting slip system in the two phases: solid solution and silicide.

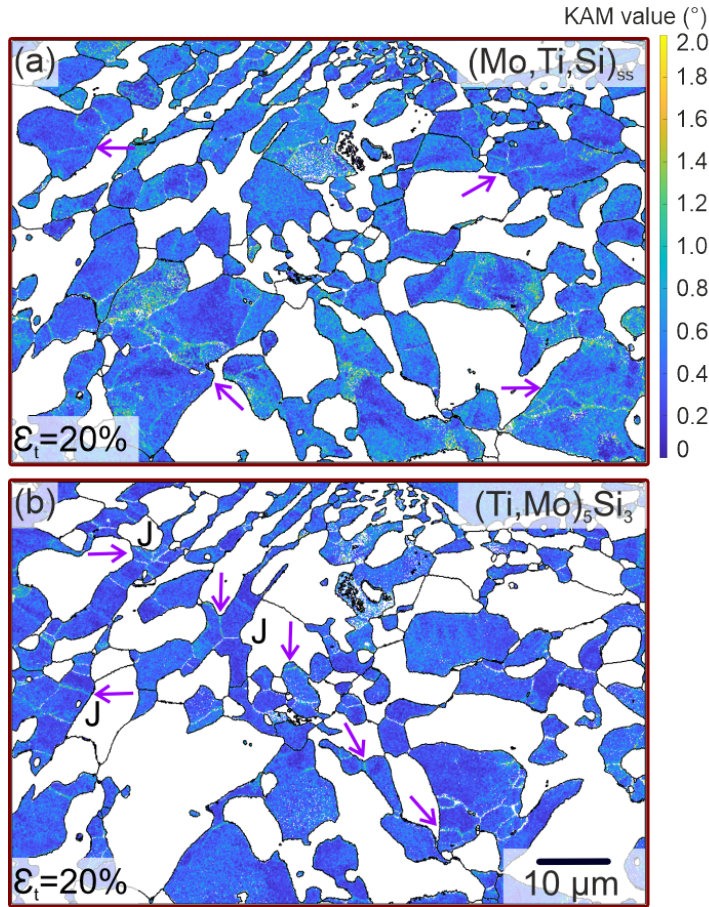


Figure 4.14.: Plastic strain in 20% sample depicted as KAM maps in (a) The solid solution and (b) The silicide.

4.4.1. Creep-induced dislocations in the solid solution

Figure 4.15 depicts the in-plane dislocations in the solid solution of 0.2% sample. Figure 4.15 a shows the accumulation of dislocations at $(\text{Ti,Mo})_5\text{Si}_3$ precipitates. These precipitates obstruct the glide motion of dislocations and act as obstacles. So, dislocations accumulate at precipitate-matrix interface. Generally, there are three possible dislocation-precipitate interactions. The dislocations can either cut through the precipitates or form Orowan loops around the precipitates. At sufficiently high temperature where diffusion is prominent, dislocation can climb over the precipitate, see section 2.3. Fig. 4.15 b

denotes the higher magnification image of the region marked in Fig. 4.15 a. It shows a dislocation lying next to two silicide precipitates. They appear to be sheared by the gliding dislocation. There is a small noticeable translation between two precipitates (shown with red arrow in Fig. 4.15 b). The gliding dislocation from the solid solution matrix may have cut through the $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitate and thus sheared by dislocation. The translation of two halves are not distinct because the silicide precipitate is not perfectly in the plane of TEM lamella and slightly inclined to foil plane. This cutting event can be understood as follows: the gliding direction of the dislocation is from right to left of the image. The dislocation enters the precipitate from the right, shears the precipitate, and leaves it from the left. Even though silicide precipitate has an edge length of 100 nm, the cutting event might have occurred through the semi-coherent interface, which contains matching planes between silicide precipitate and solid solution matrix (see section 2.2 and 2.4). The shearing of the precipitate might have occurred due to a localized increase in stress, and dislocations must glide to accommodate creep strain, forcing it to shear the precipitate. In addition, the precipitate is inclined to the TEM lamella. Due to the projection effect of 3-D volume into 2-D area for the TEM/STEM images, the step at the matrix-precipitate interface is barely visible.

Figure 4.15 c displays another solid solution grain that contains $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates in various morphologies: cuboidal, cube and triangular. The two cuboidal (marked CB) precipitates share a common boundary, which is noted. Moiré contrast is not observed at interface possibly because the interface is edge-on and thickness of the precipitate is same as the solid solution matrix. Therefore, no interference of lattice planes can be expected in this case. Among other silicide precipitates, one triangular precipitate (marked T in Fig. 4.15 c) shows Moiré contrast at the two interfaces (yellow arrows) and third interface (turquoise) does not show any Moiré contrast. The interfaces that show Moiré contrast are not lying edge-on but inclined to the foil plane. Hence the interface, which show Moiré contrast are semi-coherent type. The identification of type of $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitate from the Moiré contrast have been shown in section 4.5 and hence the $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitate are semi-coherent. There is another smaller precipitate (marked C in Fig. 4.15 c) which has a cube morphology with an edge length of 30 nm, which is significantly smaller in size compared to the surrounding larger precipitates. It displays Moiré contrast around the periphery and is possibly semi-coherent. This implies that silicide precipitates might have nucleated during primary creep at 0.2%. Thus silicide precipitates may nucleate as

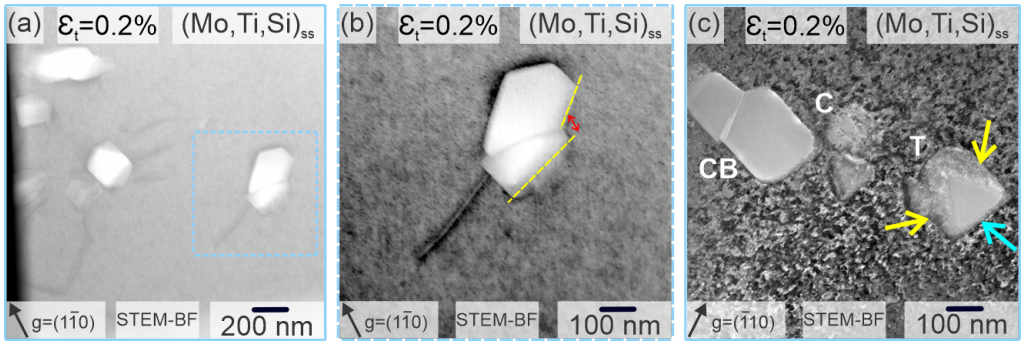


Figure 4.15.: Dislocation imaging under the two-beam condition from [111] ZA STEM-bright-field (BF) technique in the solid solution of a eutectic AC Mo-20Si-52.8Ti alloy crept to 0.2% (a) Dislocations in a specific grain, with inset showing: (b) Dislocation cut through a $(\text{Ti, Mo})_5\text{Si}_3$ silicide precipitate and (c) $(\text{Ti, Mo})_5\text{Si}_3$ silicide precipitates exhibiting Moiré contrast. The black spots in Fig. 4.15 c are due to Cu redeposition and Ga^+ beam damage.

a semi-coherent interface with solid solution matrix. The observation of small and large silicide precipitates in Fig. 4.8 b support the bimodal distribution at 0.2%. Comparatively, a lesser number of dislocations are seen from AC to 0.2% in solid solution matrix.

The dislocations in the solid solution of 1.3% sample is shown in Fig. 4.16 a. There are only two dislocations present in that particular grain and silicide precipitates appear as cubes, with an edge length of 75 ± 10 nm is visible. The most striking feature is that these precipitates with cubic morphology seem to grow from 0.2% to 1.3%. The dislocations ending at the solid solution-precipitate interface is seen. Figure 4.16 b-d depict the in-plane dislocations present in the two solid solution grains in 10% sample. b and d are from the same grain but from different regions within the FIB lamella. The number of dislocations are seven, ten and nine in three images. The number of dislocations tend to increase from 1.3% to 10%. The silicide precipitate with cube morphology and edge length of 260 nm has coarsened, as a function of creep strain (Fig. 4.16 b).

Furthermore, hexagon-shaped silicide precipitates are also visible in Fig. 4.16 d. The interaction of the precipitates with dislocations is shown in Fig. 4.16 d. In this image, the dislocation line appears discontinuous at the silicide precipitate (marked with yellow dashed line) to the left and right of it. This is because the contrast from the dislocation gets overlapped with the precipitate. As a result, the diffraction contrast is prominent from the precipitate and the intensity from the dislocation is lost. These dislocation-precipitate interactions are possible climb evidences.

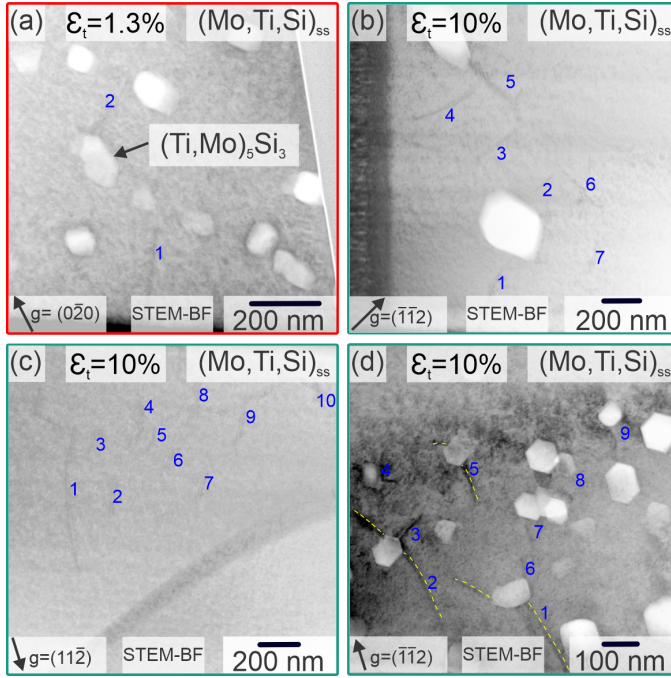


Figure 4.16.: Dislocation imaging under two-beam condition STEM-BF technique in the solid solution of a eutectic Mo-20Si-52.8Ti alloy, at (a) 1.3%, (b) 10%, (c) 10%, and d) 10%. The annotated lines in the image depict the position of dislocation trajectory.

The dislocations accumulated in the solid solution of 20% is shown in Fig. 4.17. The same region containing dislocations is imaged using the three two-beam conditions: $\vec{g}(\bar{1}21)$, $(\bar{1}01)$ and $(\bar{2}\bar{3}1)$ respectively, as seen in Fig. 4.17 a-c. The dot product of the selected two beam conditions are shown in Table 4.5. Numerous short segments of dislocations are observed in Fig. 4.17 a. The dislocations are numbered to find out the $\vec{b}$. The character of dislocations numbered: 17 and 28 could be determined. The dislocation 17 and 28 are invisible when imaged using $\vec{g}(\bar{2}\bar{3}1)$ and $\vec{g}(\bar{1}21)$. Hence, the $\vec{b}$ of the dislocations 17 and 28 are $\frac{1}{2}[\bar{1}11]$ and $\frac{1}{2}[11\bar{1}]$, respectively. The dislocations: 4,5,6 are invisible when they are imaged with $\vec{g}(\bar{1}21)$. Therefore, $\vec{b}$ of those dislocations is identified as $\frac{1}{2}[111]$.

The line direction of these dislocations are evaluated using the two surface analysis from [138] and the dislocation descriptors are denoted in Table 4.6. The angle θ between $\vec{u}$ and $\vec{b}$ for dislocations: 17 and 28 are 81.7° and 91.8° respectively. Hence, the dislocation 28 has an edge character, and dislocation 17 has an orientation close to the edge character.

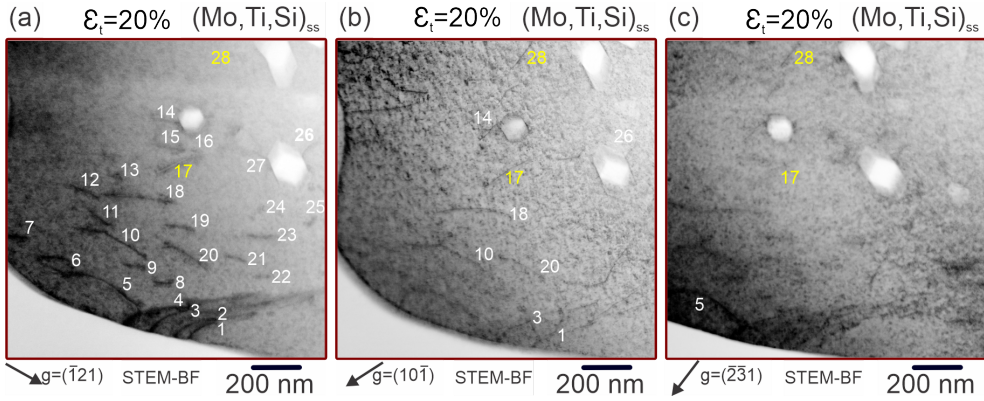


Figure 4.17.: Dislocation imaging under two beam condition STEM-BF technique in the solid solution of a eutectic Mo-20Si-52.8Ti alloy at 20% imaged using different diffraction vectors (a) $\vec{g}(\bar{1}21)$ from [101] ZA (b) $\vec{g}(10\bar{1})$ from [101] ZA and (c) $\vec{g}(\bar{2}31)$ from [102] ZA

Table 4.5.: Invisibility criterion, $\vec{g} \cdot \vec{b}$ of selected two beam conditions in solid solution of Fig. 4.17 for dislocations: 17 and 28

$\vec{g} \cdot \vec{b}$	Burgers vector, $\vec{b}$			
$\vec{g}$	$\frac{1}{2}[111]$	$\frac{1}{2}[\bar{1}\bar{1}1]$	$\frac{1}{2}[1\bar{1}\bar{1}]$	$\frac{1}{2}[\bar{1}1\bar{1}]$
$(\bar{1}21)$	1	2	-1	0
$(10\bar{1})$	0	-1	0	1
$(\bar{2}31)$	-2	0	2	-3

Figure 4.18 shows the dislocations in the other two grains of the solid solution in 20% sample. Fig. 4.18 a shows many curved dislocations in the solid solution interacting with silicide precipitates. The majority of the dislocations have a curved appearance. The θ between $\vec{b}$ and $\vec{u}$ changes with the $\vec{u}$ (Fig. 4.18 a). At 20%, they have lost their pure

Table 4.6.: Line direction of dislocations: 17 and 28 in solid solution at 20% of Fig. 4.17

No	$\vec{u}$	$\cos^{-1}(\vec{u} \cdot \vec{b})$	$\vec{u} \times \vec{b}$	Slip plane
17	$[0.24 \ 0.78 \ 0.31]$	81.7°	$[0.55 \ 0.035 \ 0.51]$	$(\bar{1}0\bar{1})$
28	$[1.65 \ 1.10 \ 0.66]$	91.8°	$[0.22 \ 1.15 \ 1.37]$	(011)

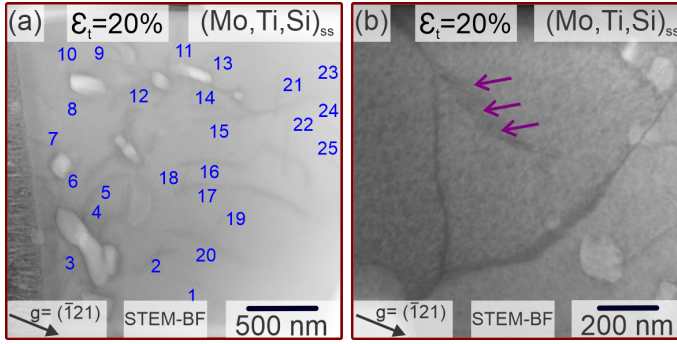


Figure 4.18.: Dislocation imaging under two-beam condition ($\bar{1}21$) from [101] ZA STEM-BF technique in the solid solution of a eutectic Mo-20Si-52.8Ti alloy at 20% (a) Bowing of dislocation around silicide precipitate, (b) Initiation of sub grain boundary formation. The purple arrows indicate the array of dislocations.

character and become mixed dislocations with rounded morphology. Individual dislocations tend to arrange themselves into sub-grain boundaries, and sub-grain formation is also seen in Fig. 4.18 b.

4.4.2. Creep-induced dislocation activity in the silicide

Figure 4.19 depicts the dislocations in the silicide matrix of 0.2% sample. Each individual sub-figure, a to c, displays the presence of dislocations in three different grains. In Fig. 4.19 a, a high number density of $(\text{Mo, Ti, Si})_{ss}$ precipitates with dislocations is visible. They act as a frequent obstacle to dislocations gliding in the silicide. Similar to SEM-BSE images in Fig. 4.8 b, there is a bimodal distribution of solid solution precipitates. One type of precipitate appears as cuboids and rods. Other type appears significantly finer. The first type of precipitates, which appear dark (marked with red arrows in Fig. 4.19 d), are coarser, with an aspect ratio ranging from 2.75 to 10. The second type of precipitates that appear less darker (marked with blue arrows in Fig. 4.19 d) have polygonal morphology, and the smallest precipitate measured is 10 nm. They might have probably precipitated from matrix during primary creep. The characterization of solid solution precipitates are analyzed in section 4.5.2.

Similarly, the other two grains also show the dislocations with solid solution precipitates in Fig. 4.19 b and c. In comparison to dislocations in solid solution, the majority of dislocations are straight. These images directly confirm that silicide accumulated

part of the creep strain by the generation of dislocations and support the EBSD-KAM results in Fig. 4.10 b and Fig. 4.11 b. In contrast, the solid solution precipitates are not widespread, and they are distributed heterogeneously in the silicide.

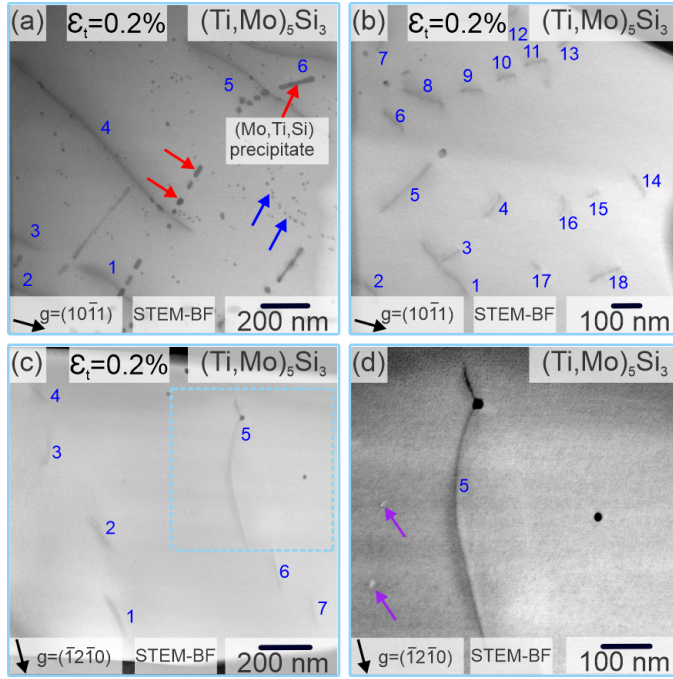


Figure 4.19.: Dislocation imaging under two-beam condition using the STEM-BF technique in the silicide of a eutectic Mo-20Si-52.8Ti alloy at 0.2% (a) First grain using $\vec{g}(10\bar{1}1)$ from $[2\bar{1}13]$ ZA (b) Second grain (c) Third grain using $\vec{g}(\bar{1}2\bar{1}0)$ from $[10\bar{1}3]$ ZA and (d) Magnified region of a precipitate pinning a dislocation in the third grain. Solid solution precipitates are indicated by red arrows, while purple arrows indicate either nano-precipitates or dislocation loops.

The STEM-BF image in Fig. 4.19 d shows the high magnification image of the region marked in turquoise in Fig. 4.19 c. It shows a dislocation pinned by $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate. In addition, bowing of the dislocation above and below the precipitate is noted. But there is a small change in contrast of the dislocation above the precipitate (appearing as dark) and below the precipitate (appearing slightly less dark). This might be due to small changes in the deviation parameter (s), the diffraction vector (g), and the thickness of the region. Furthermore, some localized regions of a few nanometers with bright contrast (marked with purple arrows in Fig. 4.19 d) are noted, but it is not clear from the current investigations whether they are nano-precipitates or dislocation loops lying edge-on. The

acquisition of diffraction patterns from that region did not reveal any additional spots as the selected area has a larger proportion of matrix selected even though the smallest SAD aperture ($10\ \mu\text{m}$) is used. STEM-EDXS was not performed in the particular region.

Figure 4.20 shows the presence of dislocations in the silicide matrix of 1.3%. In addition to dislocations, alternate bright-dark bands are visible in Fig. 4.20 a. These are bending contours. Solid solution precipitate is also visible in Fig. 4.20 a. The interaction of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate with the gliding dislocations is seen in Fig. 4.20 b and bowing of dislocations around the precipitate is observed. Growth of the $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitates with increasing creep strain is visible in Fig. 4.20 b. For instance, the aspect ratio of two solid solution precipitates are 1.5 and 1 in Fig. 4.20 b. The lowest aspect ratio is 2.75 at 0.2% (Fig. 4.19 a), whereas it dropped to 1 and 1.5, based on a few precipitates at 1.3%. The growth of precipitates as a function of creep strain is therefore inferred.

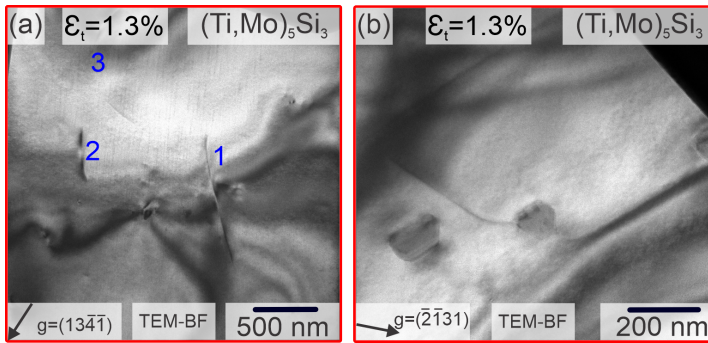


Figure 4.20.: Dislocation imaging under two-beam condition using TEM-BF technique in the silicide of a eutectic Mo-20Si-52.8Ti alloy at 1.3% (a) Dislocations within a grain and (b) Interaction of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate with dislocation in another silicide grain.

Figure 4.21 displays in-plane dislocations in the silicide matrix at 10%. Both in-plane and inclined dislocations are visible in Fig. 4.21 a. Additionally Figure 4.21 b shows a snapshot of dislocation interacting with $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate. The dislocation is gliding from left to right, and the top part of the dislocation has surmounted the precipitate, while the bottom segment is still behind it. Possibly, the dislocation may be undergoing climb rather than cutting, as the precipitate remained unchanged and no bifurcation of the $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate is observed. The solid solution precipitate has an edge length of 200 nm and an aspect ratio of 2.6. Growth of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitates with increasing creep strain is comprehended from 10% sample as well.

The acting slip plane in the silicide is determined by accessing the specific two-beam conditions where the dislocations are visible and ruling out the $\vec{b}$ whose dot product is zero using the invisibility criterion ($\vec{g} \cdot \vec{b} = 0$). The same region containing dislocations in Fig. 4.21 a are imaged using the diffraction vectors: $\vec{g}(12\bar{3}1)$, $\vec{g}(11\bar{2}2)$ and $\vec{g}(\bar{3}000)$ of the hexagonal silicide, see Fig. A.5. By accessing these four $\vec{g}$, three out of six $\vec{b}$ of $1/3\langle 11\bar{2}3 \rangle$ are excluded and dot product of other two doesnot become zero with the investigated $\vec{g}$. Due to restrictions in the tilting of the goniometer, the $\vec{g}$ of $(1\bar{1}0\bar{2})$, $(03\bar{3}0)$ and $(3\bar{3}00)$ could not be accessed. The remaining possibilities are $1/3[11\bar{2}3]$ and other three $1/3\langle 11\bar{2}0 \rangle$. The clear identification of acting slip plane is not possible from the above analysis. The $\vec{g} \cdot \vec{b} = 0$ of different planes in hexagonal silicide are represented in Table 4.7.

Table 4.7.: Invisibility criterion $\vec{g} \cdot \vec{b}$ product of hexagonal silicide, $(\text{Ti},\text{Mo})_5\text{Si}_3$

$\vec{g} \cdot \vec{b}$	Burgers vector directions, $\vec{b}$									
$\vec{g}$	[0001]	$\frac{1}{3}[11\bar{2}0]$	$\frac{1}{3}[\bar{1}210]$	$\frac{1}{3}[2110]$	$\frac{1}{3}[11\bar{2}3]$	$\frac{1}{3}[\bar{1}2\bar{1}3]$	$\frac{1}{3}[\bar{2}113]$	$\frac{1}{3}[1123]$	$\frac{1}{3}[\bar{1}213]$	$\frac{1}{3}[\bar{2}11\bar{3}]$
$12\bar{3}1$	1	3	2	-1	4	11/3	0	2	3	-2
$123\bar{1}$	-1	3	2	-1	2	5/3	-2	4	1	0
$11\bar{2}2$	2	2	1	-1	4	11/3	1	0	3	-3
$1\bar{1}0\bar{2}$	-2	0	-1	-1	-2	-7/3	-3	2	-3	1
$03\bar{3}0$	0	3	3	0	3	3	0	3	3	0
$3\bar{3}00$	0	0	3	3	0	1	3	0	3	3
$\bar{3}000$	0	-1	1	2	-1	-1	2	-1	1	2

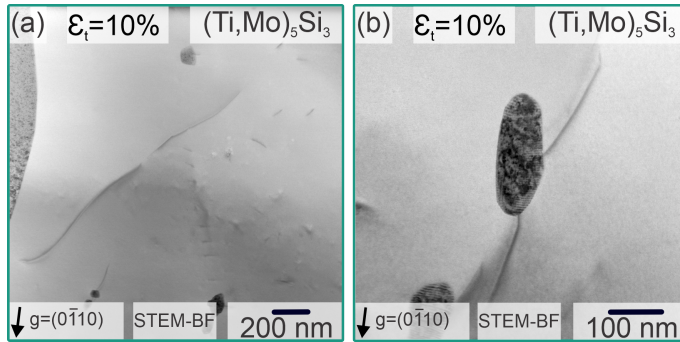


Figure 4.21.: Dislocation imaging under two-beam condition $\vec{g}(0\bar{1}10)$ from $[2\bar{1}\bar{1}3]$ ZA using STEM-BF technique in the silicide of a eutectic Mo-20Si-52.8Ti alloy at 10% (a) Dislocations within a grain and (b) Interaction of a $(\text{Mo},\text{Ti},\text{Si})_{ss}$ precipitate with a dislocation.

Figure 4.22 illustrates an array of dislocations in 20% sample. Figure 4.22 a depicts the junction of three arrays of dislocations and Figure 4.22 b shows the whole array of dislocations in the vertical direction. In addition to this, individual dislocations are also seen in Fig. 4.22 b. The formation of array of dislocations within a silicide grain partitions the grain into sub-grains. Similar findings of sub-divisions of silicide grains into sub-grains is also observed in KAM maps shown in Fig. 4.14 d. The misorientation angle of the boundary is found out by measuring the spacing between dislocations using ImageJ software and substituting the magnitude of possible hcp $\vec{b}$ [49] into the read-shockley model [150].

$$\theta = \frac{b}{D} \quad (4.1)$$

where θ is the misorientation angle

b is the magnitude of the Burgers vector

D is the spacing between dislocations

The misorientation angles vary from 0.3° to 1° . So, the array of dislocations is sub-grain boundaries.

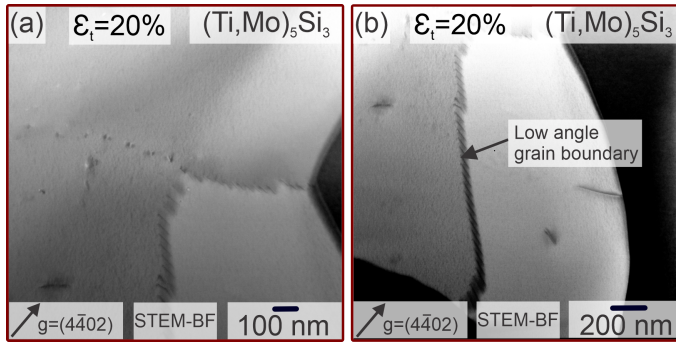


Figure 4.22.: Dislocation imaging under two-beam condition $\vec{g}(4402)$ from $[2\bar{1}\bar{1}6]$ ZA using the STEM-BF technique in the silicide of a eutectic Mo-20Si-52.8Ti alloy at 20% (a) Array of dislocations within a grain forming triple junction and (b) Whole vertical array of dislocations in the triple junction.

4.5. Precipitation as a function of creep strain

The following sections give a complete account of precipitate characterization by determining the local chemical composition, crystal structure and type of the interface in the precipitates of both phases.

4.5.1. Silicide precipitates in solid solution matrix

Figure 4.23 a shows the STEM-HAADF image of $(\text{Ti},\text{Mo})_5\text{Si}_3$ silicide precipitates in the solid solution matrix of the AC sample. The silicide precipitates exhibit a darker contrast compared to the bright solid solution matrix. To rule out any compositional overlap of the precipitate with the matrix, STEM-EDXS is done on the region in which precipitates have dimensions larger than FIB lamella thickness of 80 nm. Two precipitates of the silicide are visible, marked P1 and P2 in Fig. 4.23 a. The P1 precipitate has edge lengths of 90 nm and 80 nm, respectively, while the P2 precipitate has edge lengths of 60 nm and 40 nm, respectively. The elemental mapping of the precipitates from STEM-EDXS is depicted in Fig. 4.23 b-d. Line scans across the two precipitates are shown in Fig. 4.24 a and b.

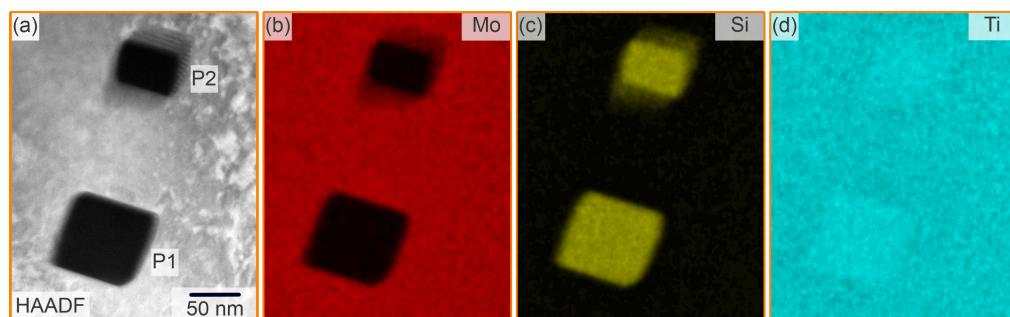


Figure 4.23.: Local chemical composition of $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates in the $(\text{Mo},\text{Ti},\text{Si})_{ss}$ matrix of the AC sample, analyzed by STEM-energy dispersive x-ray spectroscopy (EDXS) elemental mapping. (a) STEM-high angle annular dark field (HAADF) image of the precipitates, (b) Mo map, (c) Si map and (d) Ti map. Elements are color-coded as follows: Mo in red, Si in yellow, and Ti in turquoise. P1 is the larger precipitate and P2 is the smaller precipitate.

The silicide precipitates, shown in Fig. 4.23 a & b, are rich in Ti and Si, but depleted in Mo, as indicated by these elemental maps and line scans. The local chemical composition

of the precipitate are tabulated in Table 4.8. The Si content of the two precipitates are 38.5 and 38.7 at.% respectively, which is slightly higher than the expected stoichiometric concentration, 37.5 at.% from M_5Si_3 composition. Despite the size difference, both precipitates exhibit nearly identical compositions. This suggests that both have a similar thickness in the solid solution matrix.

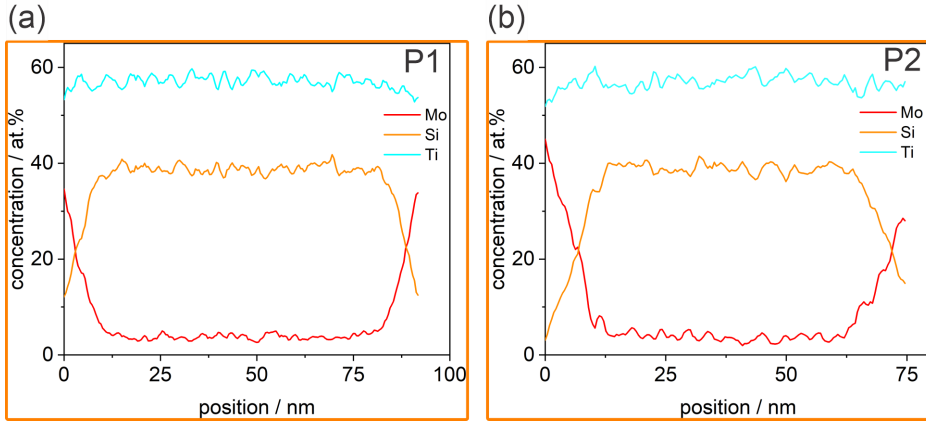


Figure 4.24.: STEM-EDXS line profile of local chemical composition of $(Ti,Mo)_5Si_3$ precipitates in $(Mo,Ti,Si)_{ss}$ matrix of AC sample, as shown in Fig. 4.23 a. (a) P1 and (b) P2. Mo, Si and Ti are plotted in red, yellow and turquoise respectively.

Figure 4.25 shows the STEM-BF image of silicide precipitate in the solid solution matrix. The matrix is aligned to the $[111]$ zone axis and the diffraction pattern is taken around the precipitate. The strong spots correspond to the solid solution matrix and weaker spots correspond to the silicide precipitate. The crystal structure of the precipitate is identified as hexagonal, with zone axis of $[4\bar{2}23]$. The orientation relationship (OR) of silicide precipitate with the solid solution matrix is identified by aligning the matrix grain to two different zone axes, and the OR is analyzed.

Table 4.8.: Local chemical composition of silicide precipitate in AC state of solid solution matrix

Precipitate	Mo in at. %	Si in at. %	Ti in at. %
P1	4.1 ± 0.5	38.5 ± 0.7	57.4 ± 0.7
P2	4.0 ± 0.8	38.7 ± 0.9	57.3 ± 0.7

Figure 4.26 shows the zone-axis alignment of solid solution to two different zone axis: $[111]$ and $[101]$ respectively. Analogous to crystal structure determination, the solid solution spots are brighter and weak satellite spots are from silicide precipitate in both images (Fig. 4.26). By indexing the spots, the OR between the matrix and precipitates is obtained by following the stereographic projections method [122]. Figure 4.26 shows the diffraction pattern of $[2\bar{1}10]$ zone-axis. There are a multitude of spots around the weak precipitate reflections. These spots could indicate double diffraction events. Both phases exhibit an OR and the results are presented in Table 4.10. For instance, $(010)_{(\text{Mo,Ti,Si})_{\text{ss}}}$ aligns with first-order prismatic plane, $(01\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3}$. In other two cases, $(010)_{(\text{Mo,Ti,Si})_{\text{ss}}}$ aligns with second-order prismatic planes: $(\bar{1}2\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3}$, $(11\bar{2}0)_{(\text{Ti,Mo})_5\text{Si}_3}$ and $(\bar{2}110)_{(\text{Ti,Mo})_5\text{Si}_3}$. The silicide precipitates show a preference to align along the prismatic planes.

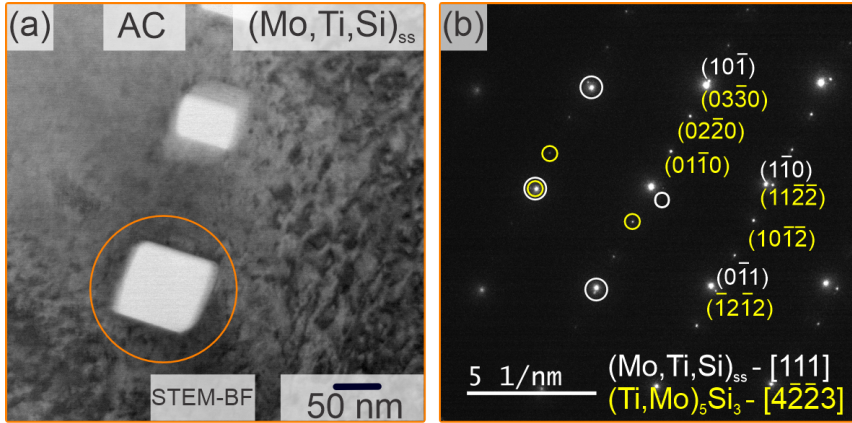


Figure 4.25.: $(\text{Ti,Mo})_5\text{Si}_3$ precipitate in the solid solution matrix of the AC sample (a) STEM-BF image (b) Selected area electron diffraction (SAED) pattern of $(\text{Ti,Mo})_5\text{Si}_3$ precipitate aligned along the $[111]$ ZA of the $(\text{Mo,Ti,Si})_{\text{ss}}$. The orange circle indicates the area selected by the SAD aperture. Diffraction spots corresponding to the solid solution matrix and silicide precipitate are marked in white and yellow, respectively.

Figure 4.27 a shows a $(\text{Ti,Mo})_5\text{Si}_3$ silicide precipitate in the solid solution of AC state. The Moiré contrast is seen extending on the top and bottom interfaces of the precipitate. This is because the precipitate is not perfectly lying edge-on the TEM lamella plane, but slightly inclined to the foil plane. It is observed that Moiré fringes occur perpendicular to the $\vec{g}$. To ascertain the occurrence of the Moiré fringes due to translation, the fringe spacing in the TEM-BF image and the interplanar spacings are compared. The relation

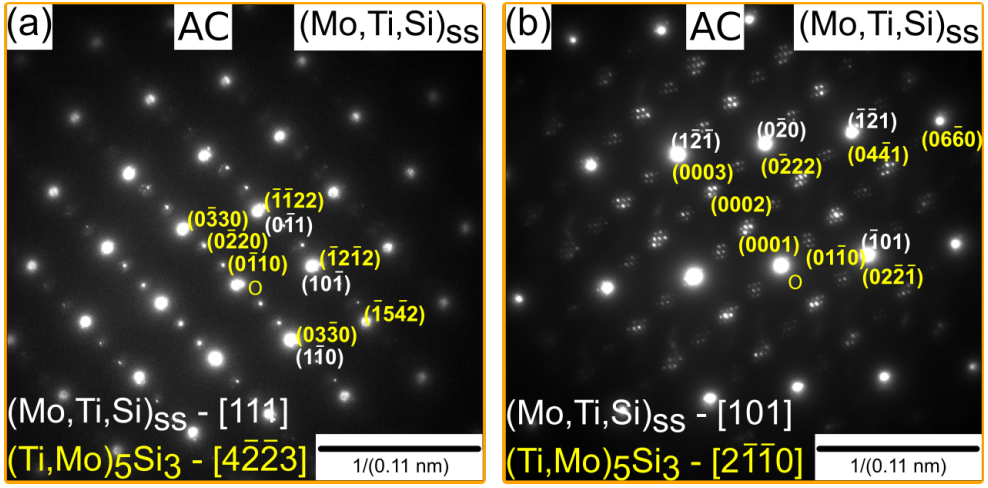


Figure 4.26.: SAED patterns of (Ti,Mo)₅Si₃ precipitate in the (Mo,Ti,Si)_{ss} matrix of the AC sample. (a) Pattern aligned along the [111] ZA. (b) Pattern aligned along the [101] ZA. Diffraction spots corresponding to the (Mo,Ti,Si)_{ss} matrix and (Ti,Mo)₅Si₃ precipitates are annotated in yellow and white, respectively.

Table 4.9.: Crystallographic orientation relationships between matrix and precipitate phases

Matrix	Crystallographic orientation relationships	
	Direction	Plane
(Mo,Ti,Si) _{ss}	$[111]_{(\text{Mo,Ti,Si})_{ss}} \parallel [\bar{4}2\bar{2}3]_{(\text{Ti,Mo})_5\text{Si}_3}$	$(\bar{1}10)_{(\text{Mo,Ti,Si})_{ss}} \parallel (01\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3}$
	$[101]_{(\text{Mo,Ti,Si})_{ss}} \parallel [2\bar{1}\bar{1}0]_{(\text{Ti,Mo})_5\text{Si}_3}$	$(010)_{(\text{Mo,Ti,Si})_{ss}} \parallel (01\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3}$
	$[102]_{(\text{Mo,Ti,Si})_{ss}} \parallel [1\bar{1}0\bar{4}]_{(\text{Ti,Mo})_5\text{Si}_3}$	$(010)_{(\text{Mo,Ti,Si})_{ss}} \parallel (\bar{1}2\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3}$
	$[101]_{(\text{Mo,Ti,Si})_{ss}} \parallel [10\bar{1}0]_{(\text{Ti,Mo})_5\text{Si}_3}$	$(010)_{(\text{Mo,Ti,Si})_{ss}} \parallel (11\bar{2}0)_{(\text{Ti,Mo})_5\text{Si}_3}$
	$[102]_{(\text{Mo,Ti,Si})_{ss}} \parallel [01\bar{1}3]_{(\text{Ti,Mo})_5\text{Si}_3}$	$(010)_{(\text{Mo,Ti,Si})_{ss}} \parallel (\bar{2}110)_{(\text{Ti,Mo})_5\text{Si}_3}$
(Ti,Mo) ₅ Si ₃	$[101]_{(\text{Mo,Ti,Si})_{ss}} \parallel [11\bar{2}6]_{(\text{Ti,Mo})_5\text{Si}_3}$	
	$[10\bar{1}3]_{(\text{Ti,Mo})_5\text{Si}_3} \parallel [0\bar{1}2]_{(\text{Mo,Ti,Si})_{ss}}$	$(\bar{1}2\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3} \parallel (100)_{(\text{Mo,Ti,Si})_{ss}}$
	$[10\bar{1}6]_{(\text{Ti,Mo})_5\text{Si}_3} \parallel [001]_{(\text{Mo,Ti,Si})_{ss}}$	$(\bar{1}2\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3} \parallel (010)_{(\text{Mo,Ti,Si})_{ss}}$

between interplanar spacing and lattice parameter in cubic and hexagonal lattices [151] are used for calculation. The lattice parameters of the two phases reported in Ref. [16] and OR obtained in the current thesis in Table 4.10 are substituted into the equations below:

$$d_{tm} = \frac{d_1 d_2}{|d_1 - d_2|} \quad (4.2)$$

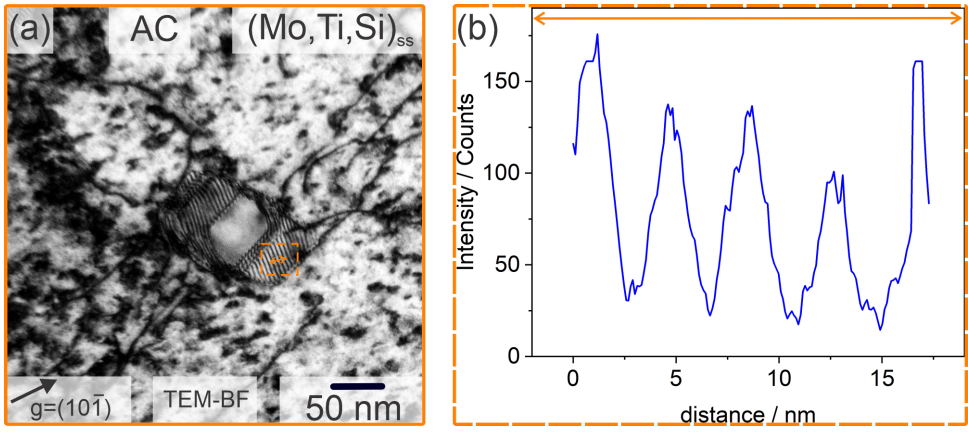


Figure 4.27.: (Ti,Mo)₅Si₃ precipitates in the solid solution matrix of AC sample showing Moiré contrast. (a) High magnification TEM-BF image and (b) Intensity profile measured perpendicular to the Moiré fringes.

Relation between interplanar spacing and lattice parameter in cubic and hexagonal lattices

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (4.3)$$

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right) \quad (4.4)$$

Table 4.10.: Calculated interplanar spacings in solid solution and silicide phases

No	Solid solution in nm	Silicide in nm
1	$d_{\{110\}} = 0.224$	$d_{\{0001\}} = 0.197$
2	$d_{\{112\}} = 0.129$	$d_{\{10\bar{1}0\}} = 0.640$
3	$d_{\{123\}} = 0.085$	$d_{\{11\bar{2}0\}} = 0.370$
4	$d_{\{100\}} = 0.317$	$d_{\{10\bar{1}1\}} = 7.500$
5		$d_{\{11\bar{2}2\}} = 27.580$

The fringe spacing obtained from the TEM-BF image is 4.3 nm, whereas the value calculated for translational Moiré fringe spacing between the second-order prismatic plane, $(\bar{1}2\bar{1}0)_{(\text{Ti,Mo})_5\text{Si}_3}$ and $(010)_{(\text{Mo,Ti,Si})_{\text{ss}}}$ is 2.2 nm. Other plane combinations for the solid

solution and silicide phases were evaluated, but the above selected planes (from OR shown in Table 4.10) yield the fringe spacing closest to experimental observations, while all alternatives produce larger spacings. The calculated interplanar spacings do not match the observed values, likely due to the misfit at the interface that alters the Moiré fringe spacing through the accumulation of misfit dislocations, an effect not captured in Equation 4.2. Hence, the Moiré fringe spacing observed is not a pure translational Moiré but includes a combination of rotational and translational contributions. A gradual bending of fringes is noticed above the top interface of the precipitate.

$$\delta = \frac{2(a_p - a_m)}{(a_p + a_m)} \quad (4.5)$$

Here, a_p is the lattice parameter of the silicide precipitate, $a_p = 7.419 \text{ \AA}$. a_m is the lattice parameter of the solid solution matrix, $a_m = 3.167 \text{ \AA}$. Silicide precipitate exhibits an absolute misfit (δ) of 0.8033 or 80.33%. The Moiré fringe analysis combined with misfit value, indicates a semi-coherent interface between solid solution matrix and silicide precipitate. Imaging misfit dislocations or interfacial dislocations at the semi-coherent interface, however, falls beyond the scope of the current thesis. In AC state, the silicide precipitates show Moiré contrast with the solid solution matrix as shown in Fig. 4.27 a. There is no change in the type of interface with increasing creep strain. Even at higher creep strains of 20%, silicide precipitates still exhibit Moiré contrast and retain the nature of the interface (Fig. 4.17 a).

Figure 4.28 illustrates the STEM-HAADF images of $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates in the solid solution matrix as a function of the creep strain. The silicide precipitates appear darker relative to the brighter solid solution matrix, as STEM-HAADF images show Z-contrast. In the 0.2% sample, the silicide precipitates have both cube and cuboidal morphologies with rounded corners, as visible in Fig. 4.28 a. In addition, hexagonal and quadrilateral morphologies are also seen. In some cases, when the precipitate center lies outside the thickness of the TEM lamella, the precipitates appear triangular or rhombus-like, which are truncation and projection effects. At 1.3%, a large number of silicide precipitates are seen in Fig. 4.28 b, compared to Fig. 4.28 a. This indicates that more silicide precipitates have nucleated at 1.3%.

At creep strains exceeding creep minimum (e.g., 10%), a large silicide precipitate lying on a sub-grain boundary (marked with blue arrows in Fig. 4.28 c) is observed, with no

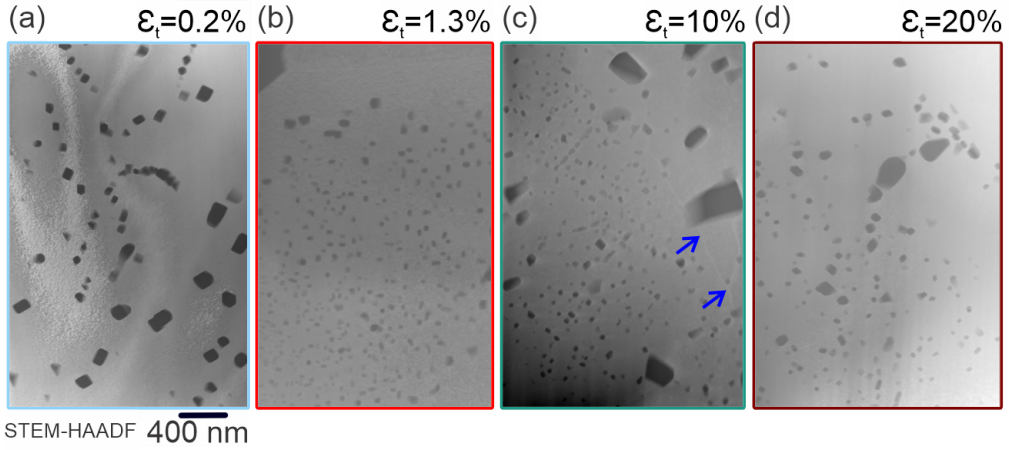


Figure 4.28.: Precipitation of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in $(\text{Mo,Ti,Si})_{\text{ss}}$ matrix, as observed in STEM-HAADF images, crept at (a) 0.2% (b) 1.3% (c) 10% and (d) 20%. The STEM-HAADF images show the Z-contrast. The silicide precipitates appear darker with respect to the solid solution matrix.

smaller precipitates in the surrounding regions. This suggests that smaller precipitates near the larger one have dissolved. The growth of larger precipitates at the expense of surrounding smaller ones is known as Ostwald ripening. In 10% sample, coarsening of silicide precipitates occurs, compared to 1.3% sample (see Fig. 4.28 b and Fig. 4.28 c). In 20% sample, coarsening of precipitates is seen in Fig. 4.28 d. It is worth noting that these results are based on different samples, which may have different initial precipitate size distributions; the size of the precipitates differs between the 10% and 20% samples.

The precipitate distributions are quantified in terms of area fraction, number density, size distributions and cumulative frequency distributions, as defined in section 3.5 to distinguish the precipitation sequence (nucleation, growth and coarsening). These parameters are calculated from STEM-HAADF images shown in Fig. 4.28. Figure 4.29 a shows the area fraction of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in the solid solution as a function of ε_t . In the AC state, the area fraction of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates is minimal, 1.4%. The area fraction of silicide precipitates increases to 5% in 0.2% samples. It gradually increases from 9% to 12% in 1.3% and 10% respectively. The area fraction of precipitates increases with increasing creep strain. Due to significantly lower statistics, the precipitates at 20% are not quantified.

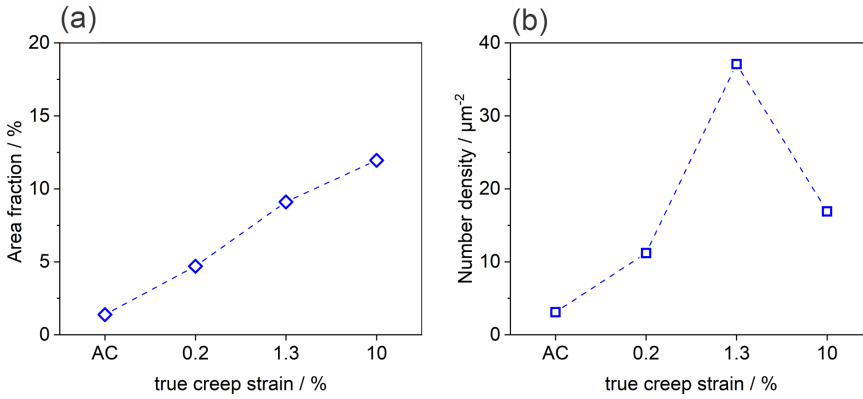


Figure 4.29.: Quantification of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in the solid solution of AC and crept samples, with increasing ε_t (a) Area fraction and (b) Number density.

The number density of precipitates per unit area is shown in Figure 4.29 b. Since TEM images are projected images of a 3-dimensional volume, the number density per unit volume has to be reported. However, the thickness of the FIB lamella is not measured in the present work. Since all the TEM lamella are prepared to a final thickness of 80 nm or less, the precipitate parameters can be compared among different creep strains. Figure 4.29 b shows the number density of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in the solid solution with increasing ε_t . The starting number density of silicide precipitates in solid solution of AC sample is 3 precipitates per μm^2 and it increases to 11 precipitates per μm^2 in 0.2% samples. The number density of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates peaks at the creep minimum, 1.3%, and after that, there is a drop in number density. It reduces by half from 37 to 18 precipitates per μm^2 as the ε_t increases from 1.3% to 10%. The reason for the different trends in area fraction and number density is Ostwald ripening. Also, the statistics obtained from the TEM-FIB lamella are a minuscule fraction and may not be statistically significant. If the chosen region contains abnormally large precipitates, these can substantially influence the area fraction and number density. The area fraction and number density don't have any error bars because they are from a TEM lamella with two different grains. The reported values give the combined values of three FIB TEM lamellae windows.

The size distributions of the silicide precipitates, obtained from STEM-HAADF images as a function of ε_t are shown in Fig. 4.30. The silicide precipitates in AC have a narrow size distribution. At 0.2%, the silicide precipitates undergo growth, as evidenced by

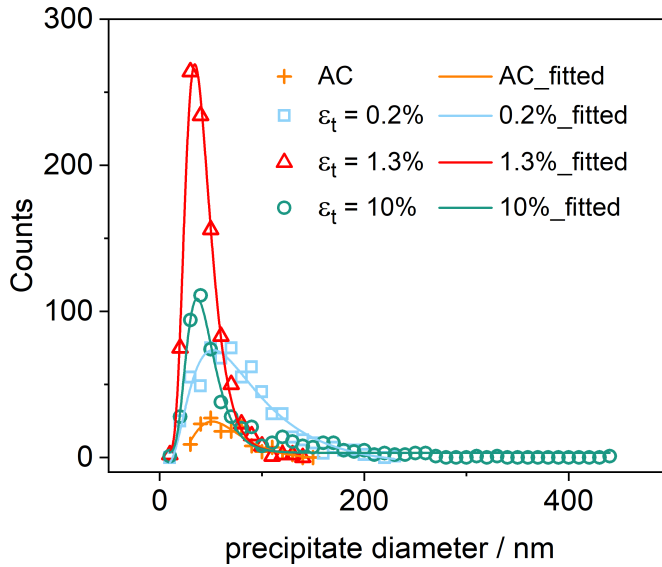


Figure 4.30.: Quantification of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates within the $(\text{Mo,Ti,Si})_{\text{ss}}$ matrix, as a function of ε_t , based on STEM-HAADF imaging. Precipitate size distributions are fitted to a log-normal function.

broadening of the distribution. In comparison to the AC distributions, precipitates in 0.2% sample have higher intensity and wider distributions, implying precipitate growth. At the creep minimum ($\varepsilon_t = 1.3\%$), the silicide precipitate distribution shifts to left with even higher intensity. This hints at the nucleation of new precipitates. At higher strains ($\varepsilon_t = 10\%$) surpassing creep minimum, the size distribution of precipitates broadens. It extends up to the range of 500 nm. It signifies the coarsening of precipitates with increasing creep strain. The mean values of log-normal distributions also follow the same trend as size distributions. Firstly, the mean value increases from AC to 0.2%, then drops from the 0.2% to 1.3%, and then tends to increase again at 10%.

The size distribution of silicide precipitates is quantified using the cumulative frequency distribution (CFD). To evaluate the change of precipitate size across different creep strains, different quantities: d_{25} , d_{50} , and d_{90} are chosen. The subscript denotes that subscript% of particles have a diameter less than or equal to that particular value. For example, d_{90} denotes that 90% of total particles have their diameter less than d_{90} value. The d_{90} values of AC, 0.2%, 1.3% and 10% samples are compared in Table 4.11. The CFD is used to quantify how the precipitate distributions fall when the initial 25%, 50%, and 90% of the precipitates are considered. If the d_{90} value is taken into account, the value increases

slightly from 102 nm in AC to 124 nm in 0.2% true creep strain. Then it drops significantly to 67 nm at 1.3% and increases steeply to 155 nm in the 10% sample. The d_{50} and d_{25} also follow the same trend, but the relative change is small.

Table 4.11.: Quantification of silicide precipitates in solid solution matrix as a function of true creep strain from STEM-HAADF images.

Sample condition	Mean value of log-normal Distribution	d_{25} (nm)	d_{50} (nm)	d_{90} (nm)
AC	63 ± 5	46	61	102
0.2%	78 ± 6	49	71	124
1.3%	39 ± 1	31	40	67
10%	42 ± 1	36	49	155

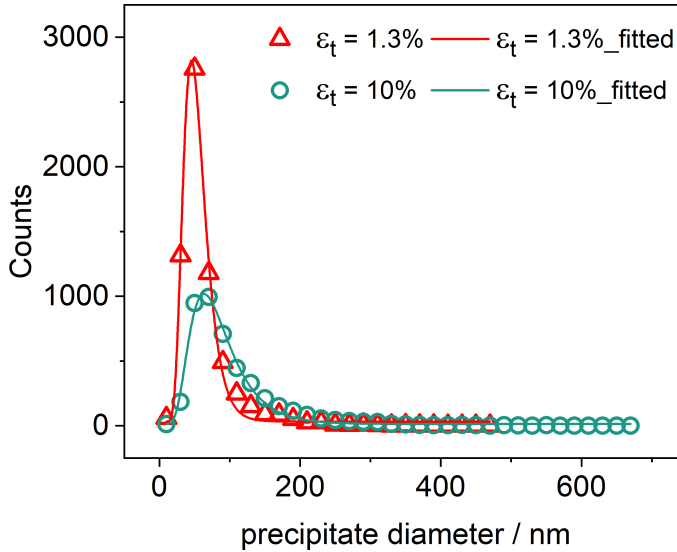
To ascertain the reduction in the number density from creep minimum ($\varepsilon_t = 1.3\%$ to $\varepsilon_t = 10\%$) and to mitigate the limited statistics of TEM results, 20 BSE images from 20 different solid solution grains are acquired. The results are also compared in terms of area fraction, number density per unit area, and CFD. Within the error bars, the detected area fraction of samples at 1.3% and 10% samples are constant and above 9%. The saturation of the area fraction and drop in number density values signify the onset of coarsening in solid solution at 10%. Hence, the creep minimum at 1.3% is due to a high number density of precipitates, and coarsening seems to lead to an increase in creep rate. The direct consequence of coarsening is the increase in interparticle spacing, and this has an implication on the mean free path of dislocations. The number density of silicide precipitates in 1.3% and 10% samples is 15.4 and 7.4 per μm^2 respectively and the values are tabulated in Table 4.12. At creep strains beyond the creep minimum, the number density at 10% is half of the 1.3%. Even though the TEM number densities are higher in absolute values, the SEM number densities also exhibit the same trend as the TEM number densities.

The size distributions of precipitates in 1.3% and 10% samples are also compared and shown in Fig. 4.31. The mean value of the distributions in samples at 1.3% and 10% samples is 51 nm and 77 nm, respectively. The precipitate distribution shifts to the right, comparatively, and spreads to higher size distribution up to 700 nm. Table 4.13 displays the d_{25} , d_{50} , and d_{90} values of CFD in 1.3 % and 10% samples respectively. The d_{90}

Table 4.12.: Number density of $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates in solid solution matrix from SEM-BSE images

Sample condition	Area fraction in %	Number density per μm^2
$\varepsilon_t = 1.3\%$	8.7 ± 2.0	15.4 ± 7.0
$\varepsilon_t = 10\%$	9.5 ± 2.4	7.4 ± 5.0

value in the 10% sample (168 nm) is 1.75 times higher than d_{90} value in 1.3% sample (96 nm). The other two parameters (d_{25} and d_{50}) are also 1.5 times higher in 10% sample than 1.3% sample.

**Figure 4.31.:** Quantification of $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates within $(\text{Mo},\text{Ti},\text{Si})_{\text{ss}}$ matrix in crept ($\varepsilon_t = 1.3\%$ and $\varepsilon_t = 10\%$) samples, based on SEM-BSE images. The precipitate size distributions are fitted to a log-normal function.**Table 4.13.:** Quantification of silicide precipitate SEM-BSE images as a function of creep strain

Sample Condition	$\bar{d}$ in nm	d_{25} in nm	d_{50} in nm	d_{90} in nm
$\varepsilon_t = 1.3\%$	51 ± 1	28.0	47.2	96.2
$\varepsilon_t = 10\%$	78 ± 1	44.5	68.2	168.5

Figure 4.32 illustrates the SEM-BSE images of silicide precipitates in the solid solution of 1.3% and 10% samples. In 1.3% sample, abnormal growth of the silicide precipitates (indicated with blue arrows) is observed and size disparity exists between nano precipitates and sub-micron precipitates. Furthermore, the nano precipitates are absent in the vicinity of sub-micron precipitates. In the 10% sample, due to higher strains and comparatively longer duration of high-temperature exposure, the Ostwald ripening is more pronounced. This might be the reason for the increase in the area fraction of silicide precipitates with the increasing ε_t in Fig. 4.29 a.

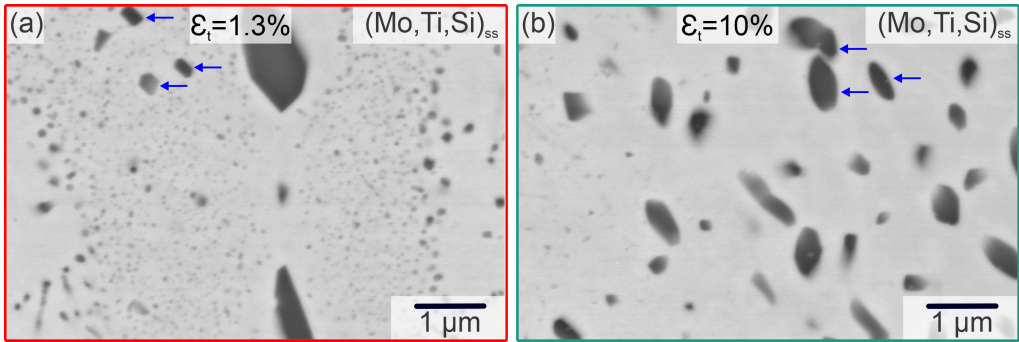


Figure 4.32.: Precipitation of $(\text{Ti},\text{Mo})_5\text{Si}_3$ in $(\text{Mo},\text{Ti},\text{Si})_{\text{ss}}$ matrix, shown by SEM-BSE images of a eutectic Mo-20Si-52.8Ti alloy at (a) $\varepsilon_t = 1.3\%$ (b) $\varepsilon_t = 10\%$. Blue arrows indicate abnormally grown silicide $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates within the solid solution matrix.

4.5.2. Solid solution precipitates in silicide matrix

The accurate local chemical composition of the solid solution precipitates in the 0.2% could not be determined because their dimensions are small (10 nm to 50 nm) compared to FIB lamella thickness (≈ 80 nm). If the precipitates have smaller dimensions than the matrix, the overlapping chemical information from the matrix would be obtained. At creep minimum ($\varepsilon_t = 1.3\%$), the solid solution precipitates are observed at the bottom of the FIB lamella. There is an overlap of the matrix with the precipitate composition. Hence the local chemical composition of solid solution precipitates in the silicide is determined in a 10% sample, where the precipitates are large.

Figure 4.33 a shows the STEM-HAADF image of solid solution precipitates in the silicide matrix at 10%. The solid solution precipitate appears bright relative to the dark silicide

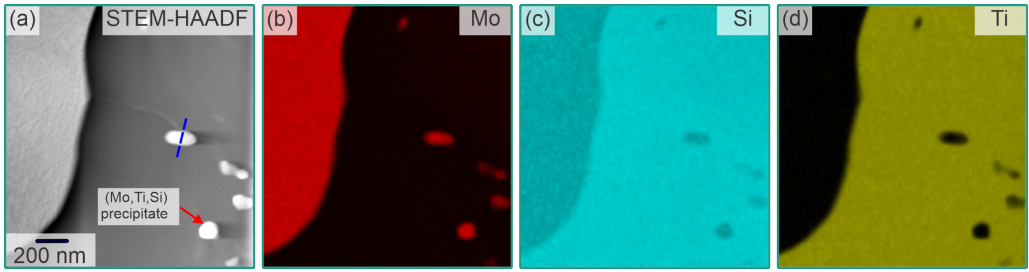


Figure 4.33.: Local chemical composition of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitates in the silicide matrix at 10%, analyzed by STEM-EDXS elemental mapping. (a) STEM-HAADF image of the precipitate, (b) Mo map, (c) Si map and (d) Ti map. Elements are color-coded as follows: Mo in red, Si in yellow, and Ti in turquoise.

matrix, exhibiting Z-contrast. The STEM-EDXS elemental mapping of the solid solution precipitates is depicted in Fig. 4.33. The precipitates are rich in Mo and Ti but depleted in Si. The average chemical composition of the solid solution precipitate in at.% is Mo - 49.0 ± 2.3 , Si - 5.7 ± 2.1 and Ti - 45.3 ± 0.9 . According to Pandat thermodynamic calculations reported in Ref. [16], the solid solution has 2.7 at.% of Si and the remaining content equally shared by Mo and Ti.

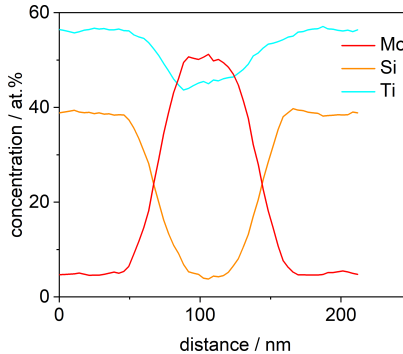


Figure 4.34.: Local chemical composition of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitates in the silicide matrix at 10% shown in Fig. 4.33 a, obtained by STEM-EDXS line profiling. Mo, Si and Ti are plotted in red, yellow and turquoise respectively.

Figure 4.35 shows the diffraction patterns of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate, when the silicide matrix is aligned to the zone axis. Figure 4.35 a shows the diffraction pattern of $[10\bar{1}3]$ zone axis. The brighter spots are from the silicide matrix, and the additional weak spots are from the solid solution precipitate. The spots from the solid solution precipitate are not observed in the diffraction pattern in $[10\bar{1}3]$ zone axis because the spots from the solid

solution precipitate and the silicide matrix overlap. So, distinct spots are not observed in Fig. 4.35 a.

In contrast, when the silicide matrix is indexed to a higher-order zone axis ($[10\bar{1}6]$), weak spots from the solid solution precipitate are also observed in Fig. 4.35 b, in addition to silicide reflections. Additionally, splitting of spots at higher reflections is noted (marked with orange arrows in Fig. 4.35 b). The crystal structure of the precipitate is identified as body-centred cubic (bcc). Figure 4.36 shows the TEM-BF image of the solid solution in the silicide matrix. It shows Moiré contrast, which indicates that the precipitates could be semi-coherent with the matrix. At 10%, the solid solution precipitate shows the Moiré contrast, see Fig. 4.21 b. Similar to silicide precipitates in solid solution, solid solution precipitates in silicide also retain the semi-coherent interface with increasing creep deformation.

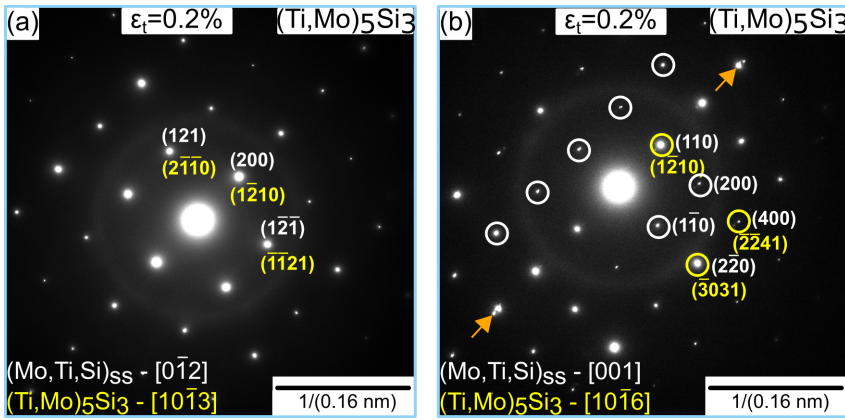


Figure 4.35.: SAED patterns of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitates in $(\text{Ti,Mo})_5\text{Si}_3$ matrix at 0.2% (a) Pattern aligned along the $[10\bar{1}3]$ ZA, and (b) Pattern aligned along the $[10\bar{1}6]$ ZA. Diffraction spots corresponding to the silicide matrix and the solid solution precipitates are annotated in yellow and white, respectively.

Figure 4.37 shows the solid solution precipitates in the silicide matrix in 1.3% and 10%. The number density of solid solution precipitates in the silicide are 72 precipitates per μm^2 . They decrease from 21 precipitates per μm^2 at the creep minimum (1.3%) to 3 precipitates per μm^2 in 10% sample. The solid solution precipitate increases in size with increasing creep strain from 1.3% to 10%. Despite limited particle statistics, the results reveal a reduction in solid-solution precipitate number density after the creep

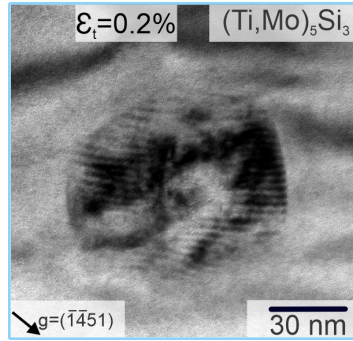


Figure 4.36.: High magnification TEM-BF image of $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitate in the $(\text{Ti,Mo})_5\text{Si}_3$ matrix at 0.2%, showing Moiré contrast. The $[10\bar{1}6]$ ZA is used to set the two-beam condition.

minimum, consistent with coarsening. Analogous to silicide precipitates in solid solution matrix, the solid solution precipitates also coarsen with increasing creep strain.

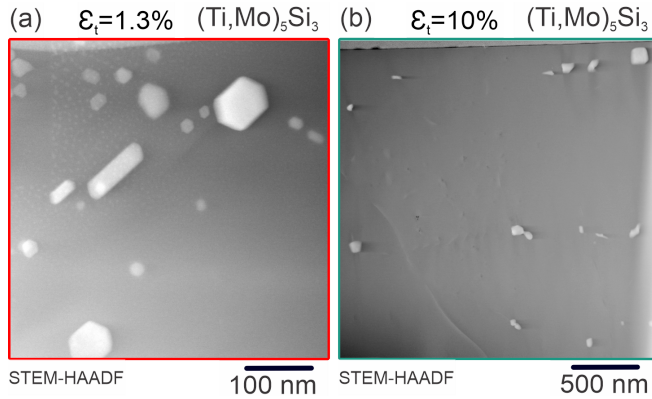


Figure 4.37.: Precipitation of $(\text{Mo,Ti,Si})_{\text{ss}}$ in $(\text{Ti,Mo})_5\text{Si}_3$ matrix, illustrated by STEM-HAADF images at (a) $\varepsilon_t = 1.3\%$ and (b) $\varepsilon_t = 10\%$ respectively.

4.5.3. Change of matrix's chemical composition with precipitation and its effect on solid solution strengthening

Figure 4.38 depicts the change in the composition of all three elements (Mo, Si and Ti) in the solid solution matrix, with the precipitation of silicide as a function of ε_t . In AC state, the silicide precipitates are Ti-rich (57.4 at.%), with 38.5 at.% Si and a significant

Mo content (4.1 at.%) in the solid solution matrix. Figure 4.38 a shows the variation of Si content with increasing creep strain. In AC state, the Si content in the solid solution is 2.14 at.%. The Si content drops gradually with increasing creep deformation from AC to 10% samples. This is because precipitation of silicide occurred with increasing creep strain. At 20%, the Si content increases from 10% to 20%. The STEM-HAADF images in Fig. 4.28 c and d show that some silicide precipitates have grown abnormally with respect to tiny precipitates surrounding them and the occurrence of Ostwald ripening. The same has been observed in SEM-BSE images of Fig. 4.32 b. This might have contributed to increased Si content in the solid solution matrix of 20% sample.

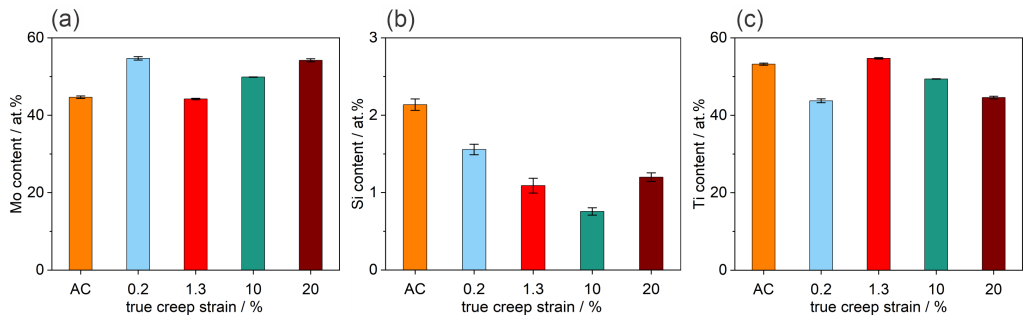


Figure 4.38.: Change in the local chemical composition of the (Mo,Ti,Si)_{ss} matrix by precipitation of (Ti,Mo)₅Si₃ with increasing ε_t , based on STEM-EDXS analysis (a) Mo content (b) Si content and (c) Ti content.

The variation of Mo and Ti contents is shown in Fig. 4.38 a and c respectively. At the beginning of the creep test ($\varepsilon_t = 0.2\%$), there is an increase in Mo content and a decrease in Ti content because of (Ti,Mo)₅Si₃ precipitates. The reason for the increase in former's value is not clear. At the creep minimum ($\varepsilon_t = 1.3\%$), the Mo content drops and Ti content increases. From the creep minimum onwards, there is a gradual reduction in the Ti content and a simultaneous increase in the Mo content. From the area fractions and number densities in section 4.5.1, at 10%, precipitates are in the coarsening stage, and this led to an increase in Mo content and vice versa for Ti.

Figure 4.39 displays the variation in concentration of constituent elements in the silicide matrix after the precipitation of solid solution, with increasing creep deformation. The Mo content drops from AC to 1.3% and increases again from 1.3% to 10% and it stays constant until 20% (Fig. 4.39 a). As a function of creep strain, the Ti and Si content remains unaffected with the formation of solid solution precipitates (Fig. 4.39 b and c). In

10% sample, the solid solution precipitates are Mo-rich (49.0 at.%), with 45.3 at.% Ti and a significant Si content (5.7 at.%) in the silicide matrix.

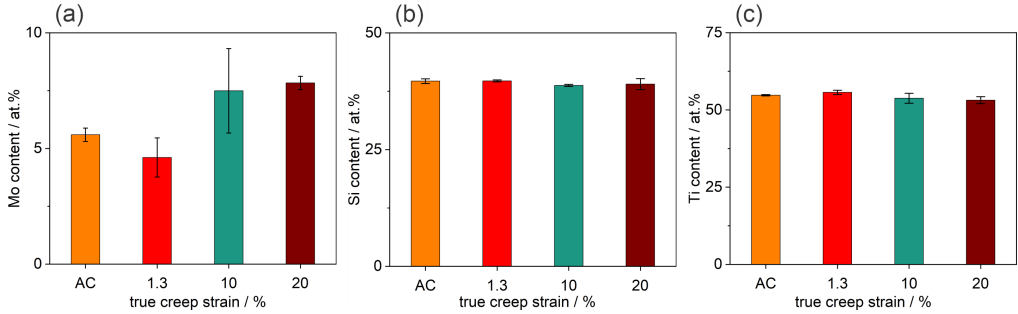


Figure 4.39.: Change in the local chemical composition of the $(\text{Ti,Mo})_5\text{Si}_3$ matrix after precipitation of $(\text{Mo,Ti,Si})_{\text{ss}}$ as a function of ε_t , based on STEM-EDXS analysis (a) Mo content (b) Si content and (c) Ti content.

4.6. Effect of temperature on precipitation without application of creep stress

A eutectic AC sample was heat treated at 1200 °C for an hour (referred as ht sample) to ascertain whether precipitates form due to applied creep strain or solely due to annealing. Figure 4.40 presents TEM-BF and STEM-BF, showing the silicide precipitates in two grains of the solid solution matrix. The silicide precipitates in Fig. 4.40 a exhibit a peculiar contrast, distinct from the strain contrast (coffee-bean contrast). The line of no-contrast is not clearly visible, and the strain lobes on either side appear asymmetric. In the AC and crept samples, the precipitates showed Moiré contrast at the semi-coherent interface (see Fig. 4.27 and Fig. 4.15 c). A change in strain contrast from coffee-bean contrast to the skewed contrast is interpreted to result from a shift in interfacial type from coherent to semi-coherent, as described in Ref. [143]. Figure 4.40 b illustrates the varied morphologies of precipitates, including cube, cuboid, and hexagonal shapes.

Figure 4.41 shows the STEM-HAADF images of solid solution precipitates within the silicide matrix of the ht sample. These precipitates exhibit a variety of morphologies, ranging from elongated platelets to polygonal shapes. Figure 4.41 b depicts a high magnification image of the region highlighted in Fig. 4.41 a. Similar to the silicide precipitates in solid

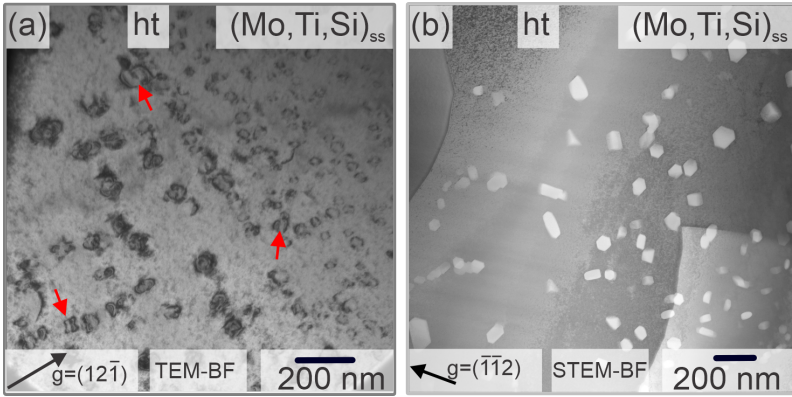


Figure 4.40.: Precipitation of $(\text{Ti,Mo})_5\text{Si}_3$ within $(\text{Mo,Ti,Si})_{\text{ss}}$ matrix in an AC sample heat-treated at 1200 °C for 1 h (ht sample), observed under two-beam conditions (a) TEM-BF image taken with $\vec{g}=(12\bar{1})$ from $[113]$ ZA (b) STEM-BF image with $\vec{g}=(\bar{1}12)$ from $[111]$ ZA. The red arrows indicate asymmetric strain contrast associated with $(\text{Ti,Mo})_5\text{Si}_3$ precipitates.

solution matrix, solid solution precipitates also form in a silicide matrix. The solid solution precipitates display Moiré contrast across their entire width, indicating that they could be semi-coherent with the silicide matrix. In contrast, Figure 4.36 exhibits Moiré contrast only along part of the semi-coherent interfaces, suggesting a possible difference in interface character due to creep deformation. In total, precipitates are found to form due to annealing.

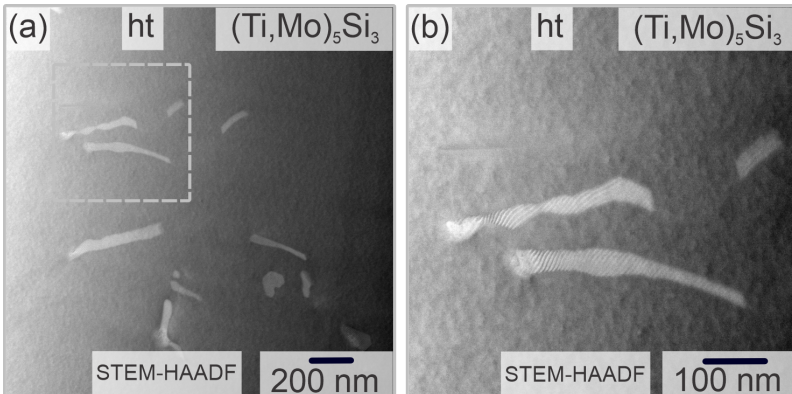


Figure 4.41.: Precipitation of $(\text{Mo,Ti,Si})_{\text{ss}}$ in $(\text{Ti,Mo})_5\text{Si}_3$ matrix, observed by STEM-HAADF imaging in ht sample (a) Overview of a grain showing the distribution of precipitates and its (b) Higher magnification image highlighting the morphology of the $(\text{Mo,Ti,Si})_{\text{ss}}$. The STEM-HAADF images exhibit Z-contrast, with the $(\text{Mo,Ti,Si})_{\text{ss}}$ precipitates appear brighter than the surrounding silicide matrix due to their higher average atomic number.

5. Understanding the creep deformation mechanism of the alloy

This chapter discusses the dominant creep deformation mechanisms and the reasons for creep-minimum in a eutectic Mo-20Si-52.8Ti alloy. They are analyzed in detail, assessing creep strain partitioning among individual phases and the effect of precipitation on both phases. Additionally, the implications of the precipitation and its role are elucidated in the following paragraphs.

5.1. Dislocation climb controlled creep mechanism

In the previously tested stress ranges, which are 50 to 200 MPa at 1200 °C [16, 23], an n value of 3.5 was obtained, consistent with dislocation climb-controlled creep. By testing an extended stress range, a differentiation into two regimes is now possible: (i) for 15 to 100 MPa, n values are 1.7 and 2.0 in the AC and HT conditions, respectively, and (ii) n value of 5.3 is obtained for both conditions between 100 to 200 MPa. The present differentiation is, thus, consistent with the expectation of lower stresses favoring diffusional creep and higher stresses favoring dislocation-climb controlled creep respectively. However, the microstructural mockup of a eutectic alloy requires more detailed considerations of the effective creep behavior, as the constituting phases are loaded at (i) different T_{hom} , (ii) different stresses by load partitioning and (iii) complex microstructural changes occur.

An n value of 1.7 to 2.0 at stresses below 100 MPa suggests significant contribution of diffusional creep. This is reasonable given the high T_{hom} for the alloy of 0.74 (1200 °C) and the high phase boundary density of $0.60 \mu m^{-1}$ in the AC condition. Diffusional creep happens by either lattice diffusion or grain boundary diffusion. The slightly lower n value for HT condition may be a result of the lower phase boundary density of $0.23 \mu m^{-1}$,

which reduces the influence of boundary diffusion. In this case, Coble creep is to be expected, where the creep rate can be expressed by following the original formulation on single-phase materials [88, 89, 90, 152, 153]:

volume diffusion

$$\dot{\epsilon}_{NH} \propto \frac{\sigma}{d^2} \quad (5.1)$$

phase boundary diffusion

$$\dot{\epsilon}_C \propto \frac{\sigma}{d^3} \quad (5.2)$$

dislocation climb controlled

$$\dot{\epsilon}_{BZ} \propto \frac{\sigma^8}{\sqrt{d}} \quad (5.3)$$

15 MPa yields $\sigma^{1.7}/d^{-2.6}$ and 200 MPa yields $\sigma^{5.3}/d^{-2.1}$ ($\dot{\epsilon}_{min} \propto \sigma^n/d^p$). Here the n value is obtained from slope of $\dot{\epsilon}_{min}$ as function of σ (see Fig. 4.2) and p value from the slope of $\dot{\epsilon}_{min}$ as a function of d . This is consistent with volume and phase boundary diffusional creep deformation at low stresses and an increasing proportion of dislocation mediation for increased stresses. However, even at 200 MPa the diffusional contribution to creep is still significant. In the case of eutectic alloy, intra-colony phase boundaries and colony boundaries can serve as fast diffusion paths. In the present case, the colony mockup remains stable even up to high strains suggesting a homogeneous deformation of the entire material. Thus, it is reasonable to propose that diffusion progresses along intra-colony boundaries to be the dominant diffusion path in the present case. Consistently, the microstructural length scale of choice corresponds to the lamellar width.

By assuming a transition to dislocation climb-controlled creep at 100 MPa, the n value of 5.3 for both microstructural conditions, which is consistent with the n of the solid solutions, is in the same stress range. No significant contribution of diffusion to creep is identified for the matrix (single phase, bcc) solid solution alloys, which might be attributed to the large grain size and the significantly lower T_{hom} . The literature data on creep of monolithic Ti_5Si_3 (see Fig. 4.2 c) suggests, that this silicide phase may possess the lowest creep resistance. However, the addition of Mo to form $(\text{Ti},\text{Mo})_5\text{Si}_3$ will have an impact on the solid solution strengthening of this phase and also lowers the T_{hom} of $(\text{Ti},\text{Mo})_5\text{Si}_3$ from 0.62 to 0.60 (see Table 4.1). Furthermore, Srinivasan et al [19] investigated the 3-dimensional interconnectivity of two phases by focused ion beam (3-D) tomography. The two phases appear disconnected in 2-D but in 3-D, the phases are connected in the thickness dimensions. They found that both phases form a

continuous, interpenetrating network. It follows that both phases are involved in the creep deformation. The correlative EBSD and TEM investigations of the samples presented here were crept at 1200 °C and 100 MPa, which is the transition between mainly diffusional creep dominated and dislocation climb-controlled creep mechanisms, revealed that this is truly the case.

Likewise, a transition in n value is identified in Al-alloys [154] and a near- α Ti-6Al-2Sn-4Zr-2Mo alloy [94] by testing an extended range. Despite the interaction of dislocations with precipitates in both phases, the obtained n values are relatively lower (5.3), compared to 10 or higher in precipitation hardening systems like Al alloys [154], T91 steel [83] and single-crystal, nickel-base super alloys [155]. This might be due to the occurrence of dynamic recovery in the solid solution at 0.2% sample (see Fig. 4.11 a) and also dynamic recovery in silicide lamella at the creep minimum ($\varepsilon_t = 1.3\%$) (see Fig. 4.12 b), which leads to a reduction of overall stress in the alloy. Hence, the n value of eutectic Mo-20Si-52.8Ti do not compare with other precipitation hardening systems. In the classical sense, an n value of 1.7 and 2 indicate interface-reaction controlled diffusional creep and grain boundary sliding, as determined in yttria stabilized zirconia and alumina composites [147, 148, 149]. But the observation of dislocation activity within the grains of both phases hints on a dislocation-based mechanism, which excludes the possibility of grain boundary sliding. The nature of interfaces and the role of interfacial dislocations in the crept samples is not performed in this work, and this analysis would require significant experimental effort.

The characterization of dislocations in 20% sample is shown in Fig. 4.17. The presence of edge dislocations has been confirmed by determining the character of two dislocations. The other dislocations in 20% sample are also probably of edge character because they exist as short line segments. The presence of screw dislocations as long lines and edge dislocations as short segments, is attributed to higher elastic strain energy of edge dislocations than screw dislocations [33, 35, 41]. The presence of edge dislocations and determination of their character confirms the dislocation-climb controlled creep mechanism in the solid solution. Three possible climb evidences of dislocations around the solid solution precipitates have been found in the silicide (Fig. 4.19 d, Fig. 4.20 b and Fig. 4.21 b). The climb of dislocations around solid solution precipitate has been characterized in silicide using WBDF technique (see Fig. A.5). The formation of jogs in the dislocations has not been observed because of micro-scale investigations performed in

the current thesis. If the jogs form as atomic steps, high-resolution transmission electron microscopy (HRTEM) investigations can provide insights into the jog formation at the atomic scale. The observation of a PFZ in the solid solution of crept samples in Figs. 4.8 a-h, located near the phase boundary and absence of precipitates, indicates the occurrence of diffusional process [156]. Unwin et al. [156] reported that the width and properties of the PFZ can be explained by considering the vacancy and solute concentration profile at the boundary. In addition, they concluded that both the width and its variation depend on the structure and misorientation of the boundary. Similarly, width of PFZ in Mo-20Si-52.8Ti alloy depends on the structure and misorientation of the two-phase interface.

5.2. Individual contributions to creep minimum

5.2.1. Deformation of individual phases

During arc melting process, a eutectic Mo-20Si-52.8Ti alloy solidifies at high cooling rates. During the cooling of the ingot, the silicide has an anisotropy in the coefficient of thermal expansion (CTE) of 2.7 from the c-axis to the a-axis [18]. To accommodate this strain during cooling, the solid solution preferentially deforms due to its 48 slip systems [35, 46] and accommodates plastic strain. Ramdoss et al. [157] have measured the hardness of the individual phases of a eutectic Mo-20Si-52.8Ti by nanoindentation. The silicide has a hardness of 12.8 ± 1.7 GPa and solid solution has a hardness of 5 ± 1 GPa. Raja et al. [20] measured the hardness and reduced elastic modulus of the solid solution and silicide phases of eutectic, Mo-20Si-52.8Ti alloy synthesized by directional solidification. The silicide has a hardness 16 ± 0.8 GPa and reduced elastic modulus of 204 ± 10 GPa. Whereas solid solution has lower hardness of 6 ± 0.1 GPa and reduced elastic modulus of 157 ± 4 GPa. It has to be noted that reduced elastic modulus reported in the previous study includes the elastic modulus of the phase and indenter material as well as poisson's ratio of phase and indenter. So, the solid solution preferentially takes up strain. Generally, intermetallic compounds have higher hardness compared to metals and alloys [33]. Both phases constitute equal proportions in area, $\approx 50\%$ area fractions.

In AC state, higher plastic strain is observed in solid solution compared to silicide from EBSD-KAM maps (compare Fig. 4.6 a and b). A large number of dislocations is

observed in the AC condition of $(\text{Mo,Ti,Si})_{\text{ss}}$ matrix (see Fig. 4.7 a), while only a few dislocations arranged as low angle grain boundaries are found in $(\text{Ti,Mo})_5\text{Si}_3$ matrix (see Fig. A.2). The reason for that is that both phases have different CTE. The CTE of the $(\text{Mo,Ti,Si})_{\text{ss}}$ phase is unknown, to the best of our knowledge. However, the CTE of Mo and Ti are $5.1 \times 10^{-6} \text{ K}^{-1}$ and $8.9 \times 10^{-6} \text{ K}^{-1}$, respectively [158, 159]. A rough estimation by a linear rule of mixture based on the atomic fractions yields $6.6 \times 10^{-6} \text{ K}^{-1}$ for Mo-40Ti. In contrast to that, the CTE of Ti_5Si_3 is anisotropic with $5.8 \times 10^{-6} \text{ K}^{-1}$ and $17.0 \times 10^{-6} \text{ K}^{-1}$ in $\langle 11\bar{2}0 \rangle$ and $\langle 0001 \rangle$ direction [160]. This can be assumed to be also the case for $(\text{Ti,Mo})_5\text{Si}_3$. This ultimately leads to internal stresses especially in the $(\text{Ti,Mo})_5\text{Si}_3$ due to its high anisotropy in the CTE [160] and at the interfaces of the $(\text{Mo,Ti,Si})_{\text{ss}}$ and $(\text{Ti,Mo})_5\text{Si}_3$. As a result of these internal stresses, microcracking occurs in the $(\text{Ti,Mo})_5\text{Si}_3$ matrix preferentially perpendicular to $\langle 0001 \rangle$, as previously reported in Refs. [19, 25]. Besides the formation of microcracks, dislocations in $(\text{Mo,Ti,Si})_{\text{ss}}$ matrix at the interface with $(\text{Ti,Mo})_5\text{Si}_3$ is caused by the plastic deformation of the ductile solid solution during cooling.

In 0.2% sample, deformation of the silicide is observed from EBSD-KAM maps (Fig. 4.11 b) and KAM distributions (Fig. 4.10 b). Imaging of dislocations in three distinct silicide grains in 0.2% sample, reinforces evidence of silicide deformation during transient creep (Fig. 4.19 a to c). A macroscopic plastic strain of 0.2% can only be achieved if both phases deform plastically; a single phase with an area fraction of just 50% cannot by itself account for the total observed plastic strain. Due to the prior plastic strain in AC state, the solid solution undergoes dynamic recovery during creep testing at 1200°C in the 0.2% sample, forming low-angle grain boundaries and subdividing the original grains into subgrains. The observation of low-angle grain boundaries in the solid solution grains in 0.2% sample unambiguously confirms dynamic recovery (refer Fig. 4.11 a). Therefore, dynamic recrystallization is excluded.

At the creep minimum ($\varepsilon_t = 1.3\%$), the solid solution accumulates the creep strain again after dynamic recovery, and both phases accumulate the creep strain together simultaneously. In the same manner, accumulation of dislocations is observed in both solid solution and silicide grains (Fig. 4.16 a and Fig. 4.20). This leads to an increase in creep rate after the creep minimum. Simultaneous deformation of two phases leading to acceleration of creep rate after creep minimum has also been observed in NiAl-Mo directionally solidified fibers [96, 120] and two phase Fe-Al and Fe-Al₂ intermetallic [113, 114]. After reaching

the $\dot{\epsilon}_{min}$ in 1.3% sample, a few dislocations are present in $(\text{Mo,Ti,Si})_{ss}$ matrix and dislocation activity in $(\text{Ti,Mo})_5\text{Si}_3$ matrix is noted. The presence of only a few dislocations in $(\text{Mo,Ti,Si})_{ss}$ can be attributed to annihilation of dislocations during the transient creep deformation, due to dynamic recovery. A significant contribution of diffusion creep at this stage has to be taken into account, as the previous analysis of n value has shown. In 10% sample, dislocation activity is observed in both phases, as shown by Fig. 4.16 b-d in solid solution and Fig. 4.21 in silicide. Creep deformation will predominantly accumulate by dislocation slip, with dislocation climb being the creep rate-determining mechanism. In contrast to earlier investigations [16], it is concluded here that creep deformation in the stress range of 100 to 200 MPa is carried by both phases in the eutectic alloy. At higher strains exceeding creep minimum, in 10% and 20% samples, the formation of sub-grain boundaries is observed in both phases (Fig. 4.13 and 4.14). The occurrence of sub-grain formation is similar to class M alloys that exhibit an n value of 5, leading to dynamic recovery during creep [59, 60, 161].

The acting slip planes of edge dislocations in the AC state of the solid solution, shown in Fig. 4.7, are $(\bar{1}01)$ and $(\bar{2}11)$, respectively. In addition, the acting slip planes at 20%, shown in Fig. 4.17, are $(\bar{1}0\bar{1})$ and (011) , respectively. In bcc metals and alloys, slip on $\{110\}$, $\{112\}$, and $\{123\}$ planes is widely reported [36, 46]. Based on the Invisibility criterion analysis in the silicide matrix at 10%, shown in Fig. A.5, pyramidal slip could be ruled out; however, unambiguous identification of the slip plane has not been accomplished in this work. Kishida et al. [22] reported that the critical resolved shear stress (CRSS) for prismatic slip $\{1\bar{1}00\}\langle 0001 \rangle$ is considerably lower than that of pyramidal slip $\{2\bar{1}\bar{1}2\}\frac{1}{3}\langle 2\bar{1}\bar{1}3 \rangle$ at all temperatures, but is comparable to twinning $\{2\bar{1}\bar{1}8\}\langle 8\bar{4}43 \rangle$ in single-crystal Ti_5Si_3 under compression tests. Thus, prismatic slip is likely.

5.2.2. Precipitation strengthening in both phases

In the AC state, the precipitation of silicide in solid solution matrix and solid solution in silicide matrix is noted in Fig. 4.5 b. The formation of precipitates in the solid solution and silicide matrix phases (i) further impedes dislocation movement and/or (ii) changes the matrix's T_{hom} . The significant drop in the creep rate during the transient stage of creep is associated to the formation of a large number of small $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in the $(\text{Mo,Ti,Si})_{ss}$ matrix, seen in Fig. 4.8 b and $(\text{Mo,Ti,Si})_{ss}$ precipitates in silicide

matrix, shown in Fig. 4.8 b. They are observed by TEM from 0.2% onwards, Fig. 4.15 a in solid solution matrix and Fig. 4.19 a in silicide matrix. Not only the crystal structure but also the local chemical composition of silicide and solid solution precipitates have been investigated (see section 4.5). The goal was to ascertain the role of precipitation on the shape of the creep curve. Firstly, the silicide precipitates in the solid solution are compared for the different crept states. The number density calculations from STEM-HAADF images yielded a peak density of 37 precipitates per μm^2 for creep minimum ($\dot{\epsilon}_{min} = 1.3\% \epsilon_t$). It has dropped to 17 precipitates per μm^2 in 10% sample. The number density at 10% is half of 1.3%. But the area fraction of silicide precipitates has slightly increased from 9% at 1.3% to 12% at 10%. As discussed before, the areal density resembles the volume density when the TEM foil thickness is similar.

These number densities and area fractions from STEM-HAADF images have been correlated with decent statistics from SEM-BSE images, containing at least 4,500 precipitates for these two creep strains ($\epsilon_t = 1.3\%$ and $\epsilon_t = 10\%$). The number density in the 10% sample (7.4 ± 5 precipitates per μm^2) is half that of 1.3% sample (15.4 ± 7 precipitates per μm^2) (refer Table 4.12). Considering the error bars, the area fractions of 1.3% and 10% samples remained approximately the same, 9% (see Table 4.12). The mean values of log-normal silicide precipitate distributions and CFD parameters (d_{25} , d_{50} and d_{90}) are 1.4 times higher in 10% sample than in 1.3% sample (see Table 4.13). The saturation of area fraction, the halving of number density, and the shift in size distribution towards larger precipitate sizes confirm the onset of coarsening after the creep minimum ($\epsilon_t = 1.3\%$) in the solid solution. All these findings support the coarsening of the silicide precipitates in solid solution matrix via Ostwald ripening with increasing creep strain. The thickness of the TEM lamella has not been measured with either convergent beam electron diffraction (CBED) [162, 163] or EELS [164] method. Despite this, the STEM-HAADF number densities are only 2.3 times higher than SEM densities. Given that the dimensions of precipitates are 30 nm or larger, the evaluation of number density per unit area remains reasonable. These values are not orders of magnitude higher than those from SEM measurements, but are instead slightly overestimated.

Even though quantification of solid solution precipitates in silicide matrix has not been performed, a high number density of solid solution precipitates has been observed in the 0.2% sample (see Fig. 4.19 a). An increase in the size of solid solution precipitates with increasing ϵ_t is depicted in the 1.3% and 10% samples (see Fig. 4.37). These combined

findings, initially high number density and growth of solid solution precipitates as a function of ε_t , suggest a conventional precipitation sequence of nucleation, growth until creep minimum, and coarsening thereafter, which can also be expected in the silicide as well. Lifshitz and Slyozov [109] stated that a decrease in precipitate number density with aging time indicates coarsening, governed by an inverse dependence on aging time, $1/t$, where t is the duration of the aging treatment. Based on the above reasoning, the anticipated number density of silicide precipitates in solid solution of 20% sample would be smaller than 10% sample.

5.2.3. Implications of precipitation

In the previous section, the coarsening of silicide precipitates in solid solution is assessed. Precipitation can lead to change in the inter-particle spacing, reduction in the solid solution strengthening due to precipitation of solute and associated change in T_{hom} of creep test. This section systematically examines all these aspects in detail.

Inter-particle spacing

An implication of the coarsening process is the increased inter-particle spacing, which directly affects the mean free path of the dislocations. The mean planar surface-to-surface separation or interparticle spacing (λ_p) for precipitates becomes a relevant parameter, especially when the separation is not negligible compared to particle dimensions [54, 165], and is applied here.

$$\lambda_p = 1.25r\sqrt{\frac{2\pi}{3f}} - 2r\sqrt{\frac{2}{3}} \quad (5.4)$$

Here λ_p is the interparticle spacing, r is the diameter of the precipitates, f is the volume fraction. For simplicity, the area fraction is assumed to be equivalent to the volume fraction. By substituting the d_{90} values and area fractions from the Tables 4.12 and 4.13 into interparticle spacing equation, the calculated interparticle spacings in the solid solution are 216 nm for 1.3% and 356 nm for 10% samples. In solid solution, the planar interparticle spacing in the 10% sample is 1.65 times higher than the 1.3% sample. Orowan [77] proposed a relationship correlating the λ_p and τ_{or} required to form Orowan loops around the particles. The most simplified form of this relationship is given in Equation 2.10. The Orowan shear stress is calculated in the current thesis by substituting $G_{Mo} = 123$ GPa

and $b = \frac{\sqrt{3}}{2} a_{(\text{Mo,Ti,Si})_{\text{ss}}}$ into Equation 2.10. The calculated values τ_{or} are shown in Table 5.1. The increased interparticle spacing in 10% led to a reduction in the τ_{or} (47 MPa) for the formation of Orowan loops than in 1.3% (79 MPa). In precipitation hardening systems, the threshold stresses are some fraction of Orowan stresses [72, 80]. In the same manner, the solid solution precipitates have also undergone growth as a function of creep strain, larger planar inter-particle spacing and reduction in stress required for the Orowan stress can also be anticipated in the silicide.

Table 5.1.: Interparticle spacing (λ_p) and Orowan shear stress (τ_{or}) in the solid solution phase

crept condition	λ_p in nm	τ_{or} in MPa
1.3%	216	79
10%	356	47

Loss of solid solution strengthening & reduction in homologous temperature

Si acts as a solid solution strengthener in Mo-Si binary system. In solid solution of a eutectic Mo-20Si-52.8Ti alloy, the precipitate of $(\text{Ti, Mo})_5\text{Si}_3$ leads to depletion of Si in Fig. 4.39 b. Si depletion progresses continuously from 2.1 ± 0.1 at.% in the AC condition to 0.7 ± 0.1 at.% at 10%, see Fig. 4.38 b. In this case, precipitation hardening contributes to matrix strengthening rather than the loss of solid solution strengthening. In the same manner, Mo is also depleted from silicide matrix when precipitation of solid solution occurs during creep. The Mo content decreases from 5.6 ± 0.3 at.% in AC to 4.6 ± 0.8 at.% in 10% sample, see Fig. 4.39 a. Within the error margins, the values are comparable, indicating that solid solution strengthening in the silicide matrix is largely retained.

Obert et al. [23] have previously shown that the T_{hom} significantly affects the creep resistance of Mo-Si-Ti alloys. This is because various designed Mo-Si-Ti alloys have different solidus temperatures, and this affects the T_{hom} . The creep resistance of a eutectic Mo-20Si-52.8Ti alloy (investigated in this thesis) is compared by Obert et al. [23] to Mo-21Si-43.4Ti alloy that is composed of eutectic regions and solid-state transformed regions containing $(\text{Mo,Ti,Si})_{\text{ss}}$ and $(\text{Mo,Ti})_5\text{Si}_3$. At the same test temperature of 1200 °C as in the present work, the latter (Mo-21Si-43.4Ti) has a lower $\dot{\epsilon}_{min}$. However, the T_{hom} for this alloy at 1200 °C is 0.68 because of its higher T_s . When this alloy was tested at 1316 °C

(corresponding to T_{hom} 0.74), the $\dot{\epsilon}_{min}$ is the same as for a eutectic Mo-20Si-52.8Ti alloy at the same T_{hom} . Furthermore, Obert et al. [23] demonstrated that the increased creep rate is not solely attributed to the presence of $(\text{Mo,Ti})_5\text{Si}_3$, as it has been postulated previously [16]. The creep resistance depends on the T_s of the alloy.

The literature data for monolithic Ti_5Si_3 [166] presented in Fig. 4.2 do not fully reflect the creep resistance of the $(\text{Ti,Mo})_5\text{Si}_3$ phase present in a eutectic alloy due to the additional Mo dissolved in the $(\text{Ti,Mo})_5\text{Si}_3$ phase and the expected increase in solid solution strengthening that comes with it. Furthermore, the T_{hom} decreases with the addition of Mo in $(\text{Ti,Mo})_5\text{Si}_3$. At a test temperature of 1200 °C, T_{hom} of this phase is 0.67, which is lower than that of the $(\text{Mo,Ti,Si})_{ss}$ phase being 0.74 (Table 4.1). This suggests, that the creep deformation is initially carried by the $(\text{Mo,Ti,Si})_{ss}$ due to higher T_{hom} . EBSD-KAM maps of the solid solution in the AC state further support this finding. As shown in Fig. 4.6 a, the solid solution has undergone preferential deformation compared to the silicide. The formation of $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in the $(\text{Mo,Ti,Si})_{ss}$ matrix in the transient creep regime changes the chemical composition of the matrix phase. This leads to a decrease in T_{hom} to 0.64 at 1.3%. In case of the Mo-21Si-43Ti alloy investigated by Obert et al. [23], a difference in the creep rate of one order of magnitude was observed by changing T_{hom} from 0.68 to 0.74. A similar effect is expected here. The formation of precipitates also changes the local composition of the $(\text{Mo,Ti,Si})_{ss}$ and, thus, the T_{hom} at which the solid solution is tested. For 1200 °C, this means that by increasing the Mo content by 6.2 at.%, while decreasing Ti and Si by 4.9 and 1.3 at.% respectively, the T_{hom} decreases significantly from 0.74 to 0.64. Such a significant decrease in T_{hom} will have an impact on the decrease in the creep rate during the transient creep regime.

The occurrence of a $\dot{\epsilon}_{min}$ results from a balance between hardening and recovery processes dominant in the transient and tertiary creep regimes, respectively. This has been demonstrated for several different alloying systems in the past [167, 168, 169, 170]. Interestingly, both solid solution alloys (Mo-40Ti and Mo-3Si-40Ti) do not exhibit a $\dot{\epsilon}_{min}$. On the contrary, they have a distinct steady state creep regime with more than 20% of the true plastic strain, see Fig. 4.1. They also show no evidence of a dominant diffusional creep mechanism as indicated by the n value (Fig. 4.2). The latter may be influenced by the relatively large grain size compared to the fine eutectic microstructure in a eutectic alloy and a lower T_{hom} . It is worth mentioning here, that the two solid solution alloys

have similar creep resistance even though the T_{hom} is significantly different, 0.69 vs. 0.61 for Mo-3Si-40Ti and Mo-40Ti, respectively. Although the difference in T_{hom} is caused by the addition of Si to Mo-40Ti, the formation of precipitates appears to increase the creep resistance to fully compensate for this difference. Analogous to the decrease in the transient creep regime due to the change in T_{hom} by the precipitation of $(Ti,Mo)_5Si_3$ in the $(Mo,Ti,Si)_{ss}$ matrix, the increased creep rate in the tertiary creep regime could be attributed to the formation of $(Mo,Ti,Si)_{ss}$ precipitates in the $(Ti,Mo)_5Si_3$. CALPHAD calculations suggest that T_{hom} at a test temperature of 1200 °C remains constant at 0.67 by changing the chemical composition of the $(Ti,Mo)_5Si_3$ phase from 1.3% to 10% true strain. This clearly indicates, that in contrast to the change in T_{hom} of $(Mo,Ti,Si)_{ss}$, no significant effect or contribution to the formation of a $\dot{\epsilon}_{min}$ is to be expected in the $(Ti,Mo)_5Si_3$ matrix.

Recently, Obert et al. [23] have reported that the true total strain to reach the $\dot{\epsilon}_{min}$ increases with decreasing applied true stress for Mo-21Si-43.4Ti in the stress range of 100 to 300 MPa. They have also shown that this alloy has the same creep behavior as a eutectic alloy studied here by performing creep tests at the same T_{hom} . These results indicate that the applied stress accelerates the formation of precipitates, since the $\dot{\epsilon}_{min}$ occurs at shorter times as the applied stress increases. However, the formation of $(Ti,Mo)_5Si_3$ precipitates without stress at 1200 °C for the appropriate creep test duration has not been investigated in this thesis. At 1200 °C and 100 MPa true stress, the $\dot{\epsilon}_{min}$ for the eutectic alloy is reached after 0.5 h. As shown in Fig. 4.30, the particle size decreases from 102 nm in the AC condition to 67 nm at 1.3% sample, and then increases to 155 nm at 10% sample (representing 2.5 hours of creep). This initial reduction in precipitate size indicates the nucleation of new precipitates during the early stages of creep, which also accounts for the drop in d_{90} at the $\dot{\epsilon}_{min}$ ($\epsilon_t = 1.3\%$). It appears that the equilibrium condition in the $(Mo,Ti,Si)_{ss}$ is reached before or at the $\dot{\epsilon}_{min}$, taking into account the reduced amount of dissolved Si observed by STEM-EDXS, as discussed earlier. As a result, the $(Ti,Mo)_5Si_3$ precipitates begin to coarsen (compare Fig. 4.28 b and c). The coarsening process is further corroborated by SEM-BSE images shown in Fig. 4.32.

Threshold stresses

The presence of precipitates in Mo-based alloys, such as known for TZM (Mo-0.5Ti-0.08Zr-(0.02-0.04)C in wt.%) [171] and MHC (Mo-(0.8-1.4)Hf-(0.005-0.15)C in wt.%)

[172], not only increases the strength relative to Mo, but also increases the creep resistance of these alloys. In addition, it has been suggested that solid solutions capable of second phase precipitation within the grains can possess an intrinsic threshold stress (σ_0) for creep by pinning the dislocations to these obstacles [173, 174, 175]. This σ_0 must be subtracted from the applied stress (σ) to obtain an “effective stress” for creep ($\sigma - \sigma_0$). The pinning of dislocations at $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates in a AC condition of the eutectic alloy can be seen in Fig. A.1 a. The σ_0 value was calculated by plotting $\dot{\epsilon}^{1/n}$ as function of σ on a linear axis and data were extrapolated linearly to $\dot{\epsilon}$ value of zero [175, 176]. Here n value is 5.3, obtained from Norton plot shown in Fig. 4.2. This procedure was applied only to stresses between 100 and 200 MPa since the main contribution of diffusional creep is at lower σ , σ_0 was determined to be 34 MPa. Interestingly, the exact same σ_0 was observed for the Mo-3Si-40Ti alloy, again indicating the same creep mechanism being active in both these alloys. The n value for both alloys decreases to 4 after applying the “effective stress” to the Norton plot, still supporting dislocation climb controlled creep in this stress regime. It is worth noting that the threshold stress is similar to the stress regime associated to diffusion creep. Hence pinning of dislocations supports creep deformation by diffusion.

The extensive pinning of dislocations by solid solution and silicide precipitates in both phases has been observed in section 4.4. These results imply the existence of threshold stresses. The calculation of threshold stresses is performed in precipitation hardened Al-alloys [82], single-crystal, nickel-base superalloys [6], and ODS steels [83]. The existence of threshold stresses in a Mo-Si-Ti eutectic alloy could also be found by producing the same alloy without any precipitates and conducting creep tests. However, in the present thesis, the alloy without any precipitates is not synthesized. So the possibility of finding threshold stresses is excluded. Hence, the experimental creep rate cannot be calculated.

5.3. Combined reason for creep minimum

Based on the previous discussion, the formation and coarsening of $(\text{Ti},\text{Mo})_5\text{Si}_3$ and $(\text{Mo},\text{Ti},\text{Si})_{\text{ss}}$ precipitates in solid solution and silicide phases seem to be the primary reason for the $\dot{\epsilon}_{\min}$ in a eutectic alloy. While the Mo-3Si-40Ti alloy showed only extended state creep, the main difference is that the solid solution alloy has a composition of Mo-3Si-40Ti, and the composition of the solid solution in a eutectic alloy is Mo-3Si-50Ti. The

10 at.% difference in Ti content changed the creep behaviour of alloy drastically from extended secondary steady state creep to a creep minimum. In addition to the composition difference, grain size differences are also noted. The single phase of Mo-3Si-40Ti has relatively large, coarse grains compared to the solid solution in the eutectic alloy. Another reason for the creep minimum could be the recovery and low-angle grain boundary formation observed in both phases of the eutectic alloy. The KAM maps displayed in Fig. 4.13 and 4.14 confirm the formation of low-angle grain boundaries (marked with purple arrows) in both the solid solution and silicide phases. However, the same observation was made for the Mo-3Si-40Ti alloy. This would exclude at least the single-phase behavior of the solid solution for creep strain accumulation and confirm the creep strain partitioning among both phases. However, the two phases may interact to form a distinct minimum. Also, the creep behavior of monolithic Ti_5Si_3 with respect to the creep curves is unknown, since no such data was reported by any. For example, see Refs. [146, 166]. Furthermore, other microstructural changes could influence the creep behavior, but phase boundary density remains constant during the entire creep process at 1200 °C and 100 MPa. The slight variation of the phase boundary density can be attributed to minor local variations in the microstructure depending on the position of the specimens within the ingot after casting. The variations in the cooling rate affect the lamellae spacing and therefore the phase boundary density. Therefore, the microstructure at 1200 °C can be assumed to be robust against coarsening at least in the time period of the conducted creep experiments.

The creep minimum is explained in the following manner, accompanied by a schematic diagram shown in Fig. 5.1. In the AC state, most grains in the solid solution contain silicide precipitates, whereas solid solution precipitates in the silicide are sporadic (Fig. 5.1 a). The prior dislocation density in the solid solution leads to dynamic recovery at 0.2 %. To compensate for this, the silicide accommodates part of the deformation by accumulating creep strain with generation of dislocations (Fig. 5.1 b). This is also important for maintaining geometrical compatibility between the phases. Moreover, 3-D FIB tomography have revealed that the individual phases are connected along the thickness direction [19]. Subsequently, the nucleation of silicide precipitates in solid solution during transient creep helps retain strength. Likewise, solid solution precipitates also form within the silicide. During nucleation, a high density of precipitates can be expected. Both the pre-existing precipitates from the AC state and those formed during

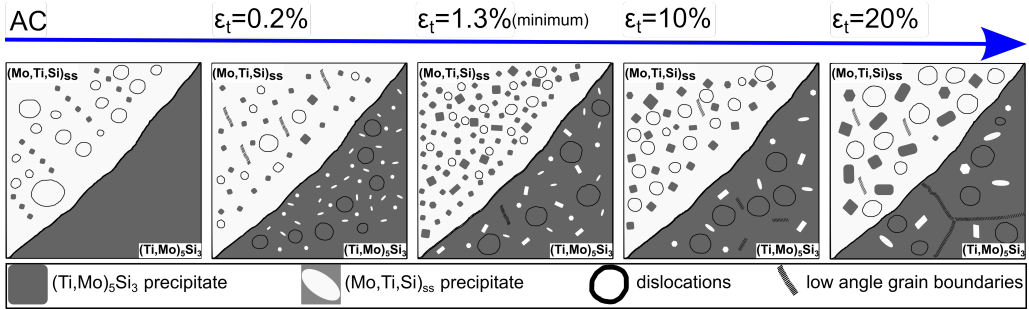


Figure 5.1.: Schematic of microstructural evolution during creep of eutectic AC Mo-20Si-52.8Ti alloy at 100 MPa and 1200°C

creep result in effectively reduced interparticle spacing, which impedes the motion of gliding dislocations. This contributes to precipitation strengthening in both phases until the creep minimum (Fig. 5.1 c). At the creep minimum ($\epsilon_t = 1.3\%$), the solid solution continues to accumulate plastic strain following dynamic recovery, and both phases begin to deform concurrently. Precipitation is more pronounced in the solid solution, likely due to its higher prior dislocation density. Due to their higher elastic strain energy, dislocations can act as favorable heterogeneous nucleation sites for precipitates [177]. During creep deformation, additional solid solution precipitates may also nucleate along dislocations, effectively pinning them. Meanwhile, the small silicide grains begin to undergo dynamic recovery. The precipitation process proceeds through nucleation, growth, and subsequent coarsening of the precipitates.

At the creep minimum, the growth stage of the precipitates is complete, and coarsening begins with increasing creep strain. This coarsening leads to an increase in interparticle spacing. The drop in precipitate number density, saturation of area fraction, and increase in precipitate diameter collectively reduce the resistance to dislocation glide at 10% (Fig. 5.1 d). As coarsening progresses at 20%, the number density of particles decreases, thereby increasing the interparticle spacing (Fig. 5.1 e). Since the interparticle spacing is inversely proportional to Orowan stress, this results in a reduction in the Orowan stress. The direct implication of precipitate coarsening is increased spacing between obstacles, allowing dislocations to glide more freely. With fewer obstacles in their path, dislocations no longer require climb to bypass precipitates. As a result, creep rate accelerated again.

5.4. Role of precipitates in the two phases

The formation of precipitates is caused by the non-equilibrium state that occurs after casting, resulting in a supersaturated solid solution of Si. The Si content determined by STEM-EDXS is (2.3 ± 0.4) at.% in the AC condition, while the thermodynamic equilibrium CALPHAD calculation by Pandat suggests a Si content of less than 0.1 at.% in the Mo-Si-Ti system at RT. This agrees well with the Si content in the binary Mo-Si system determined in Ref [178]. At the test temperature of 1200 °C, the maximum Si content dissolved in Mo increases to 1 at.% according to CALPHAD. A similar Si content of (1.2 ± 0.5) at.% at 1.3% was determined by STEM-EDXS in this work. The latter condition corresponds to 0.5 h of exposure at 1200 °C and 100 MPa applied stress. In contrast to earlier observations by Jain and Kumar [179] in ternary Mo-Si-B alloys, where the slow diffusion of Si in Mo even at 1200 °C for 300 h prevents the formation of Mo-rich silicides, the presence of Ti in the solid solution promotes the formation of $(\text{Ti},\text{Mo})_5\text{Si}_3$ precipitates. This is not surprising when the interdiffusion coefficient of Ti and Mo at 1250 °C being in the order of $4 \times 10^{-15} \text{ m}^2/\text{s}$ is considered [180], while for Si in Mo at the much higher temperature of 1600 °C it is less than $10^{-16} \text{ m}^2/\text{s}$ [181]. At 1200 °C, this suggests that Ti inter-diffusion has a greater influence than Si diffusion for silicide precipitation in solid solution.

The local chemical compositions of the silicide precipitate in AC state, as obtained from STEM-EDXS in the present work, is Mo : 4.1 ± 0.5 , Si : 38.5 ± 0.7 and Ti : 57.4 ± 0.7 (in at.%). Schliephake et al. [16] analyzed the chemical composition of individual phases from the CALPHAD calculations as follows: $(\text{Mo},\text{Ti},\text{Si})_{\text{ss}}$ as Mo: 47, Si: 3 and Ti: 50 and hexagonal silicide as Mo: 7, Si: 38 and Ti: 55. The measured silicide precipitate composition agrees well with both the CALPHAD predictions [16] and binary Ti_5Si_3 from Ti-Si phase diagram [15]. According to this diagram, Ti_5Si_3 is a congruently melting compound with a Si content from 35 to 39 at.%. In the same manner, the local chemical composition of solid solution precipitate in 10% sample is measured to be Mo : 45.6 ± 1.1 , Si : 5.9 ± 2.1 and Ti : 48.7 ± 2.8 (in at.%). This composition contains a higher Si content than predicted by CALPHAD values, which might indicate that the precipitate has not reached its equilibrium composition. It is important to note that, before interpreting the chemical composition of the precipitates, the lamella thickness should

be measured to avoid any overlap between matrix and precipitate. However, this measurement was not performed in the current study, which may affect the accuracy of the reported compositions. The thickness of the matrix has not been investigated in the current thesis. The crystal structures of the individual phases: bcc solid solution and hexagonal silicide, have been confirmed by SAED pattern analysis, and their structures have also been determined through XRD measurements [16].

In the present study, silicide precipitates within solid solution and solid solution precipitates within silicide are observed at AC state. Both precipitates retain their semi-coherent interface even after coarsening in 10% sample. In classical precipitation hardening alloy systems, such as Al-4 wt.%Cu alloys, the metastable precipitates nucleate and successively lose their coherency with the matrix [52, 55, 143]. In Al-Cu alloys, the precipitation sequence involves the formation of Guinier-Preston zones (Cu clusters), followed by coherent θ'' , then semi-coherent θ' , and finally incoherent θ precipitates during isothermal aging. The final stable precipitate θ is incoherent with the Al-matrix [51]. This transformation illustrates the gradual loss of precipitate coherency that accompanies precipitate growth and coarsening.

In contrast, the Mo-Si-Ti alloy system studied here exhibits a peculiar behavior. Stable precipitates of silicide in solid solution and solid solution in silicide, nucleate directly and undergo growth and coarsening while maintaining semi-coherent interfaces. This suggests a distinct thermodynamic and interfacial evolution, likely driven by the reduction of interfacial energy without passing through metastable coherent states. The coarsening of precipitates is driven by the system's tendency to reduce the interfacial energy between the precipitate and the matrix. Additionally, Ostwald ripening occurs due to differences in chemical potential between small and large precipitates [17, 107]. Smaller precipitates dissolve preferentially, while larger ones grow, leading to a more thermodynamically stable microstructure.

Legros et al. [182] investigated pipe diffusion along individual dislocation in an aluminum thin-film system containing silicon precipitates using in-situ TEM heating experiments. They reported that Si pipe diffusivity was up to three orders of magnitude higher than bulk diffusion at T_{hom} ranging from 0.61 to 0.82. This finding is particularly surprising given that previous studies typically observed significant pipe diffusion only near $0.5T_m$. However, a similar enhancement in pipe diffusivity may be expected in both phases of the current system, namely, Si diffusion in the solid solution and Mo diffusion in

the silicide, which could account for the accelerated coarsening of precipitates observed during the creep exposure.

Burger [183] proposed an OR between the hcp and the bcc crystal, being $[11\bar{2}0]_{\text{hcp}} \parallel [111]_{\text{bcc}}$ and $(0001)_{\text{hcp}} \parallel \{110\}_{\text{bcc}}$. Based on this relationship, 12 different variants of hcp crystal can form from a single bcc crystal. Raja et al. [20] have observed the following orientation relationship between bcc and hexagonal phases in the Mo-Si-Ti eutectic system as : $(123)_{(\text{Mo,Ti,Si})_{\text{ss}}} \parallel (0001)_{(\text{Ti,Mo})_5\text{Si}_3}$ and the direction remains the same as Burger's OR. In the current case, the OR between the matrix and precipitates in both phases is different from the phase OR reported between bcc and hcp phases by Burger [183] and OR between solid solution and silicide by Raja et al. [20]. This may be attributed to interface deformation, which leads to a loss of semi-coherency and, consequently, weakens the OR. Other non-basal plane OR have also been reported in Refs. [184, 185].

5.5. Unexpected results

Cutting of precipitates

In some metallic materials, the formation of anti-phase boundary has been observed when dislocations cut through the ordered compounds such as γ' L_{12} in Al (fcc) γ matrix [75, 186, 187] and B2 (ordered bcc) in A2 matrix [188]. When a matrix dislocation with a larger $\vec{b}$, such as $\langle 110 \rangle$, shears a coherent γ' precipitate, it results in the formation of an anti-phase boundary [189]. Whereas a dislocation with a partial dislocation, $\frac{1}{6}\langle 112 \rangle$ cuts through the γ' precipitate, it leads to the formation of a stacking fault [186, 187]. In the present work, a dislocation from solid solution (bcc) has been observed to cut through the hexagonal silicide precipitate (Fig. 4.15 b), despite the significant crystallographic differences between the two phases.

Cutting of a silicide precipitate has been observed at 0.2% in one precipitate. Even though this might be a rare occurrence, the observation of this event hints at a possible cutting interaction. Seidman et al. [74] reported a size-dependent transition in dislocation-precipitate interaction from cutting of Al_3Sc to Orowan looping, in fcc Al- L_{12} Al_3Sc alloys. Similarly, Heilmaier et al. [76] observed an analogous transition from weakly coupled, shearing of γ' precipitates to strong coupling with Orowan by-passing in wrought

IN 100 nickel-base superalloy, as a function of γ' precipitate size. Couzinié et al. [188] reported the shearing of B2 precipitates in bcc matrix of $\text{Al}_{0.5}\text{NbTa}_{0.8}\text{Ti}_{1.5}\text{V}_{0.2}\text{Zr}$ refractory high entropy alloy, suggesting weak coupling of dislocations. The shearing observed in the current study may indicate weakly pair-coupled dislocations before the creep minimum and strong pair-coupling leading to Orowan looping after the creep minimum due to the continuous growth of the precipitates. This requires further study. First-principles density functional theory (DFT) calculations might provide more insights into the energetics of the cutting event by calculating anti-phase boundary and determining whether the cutting mechanism is energetically feasible or not.

6. Summary & Outlook

Summary

In the present study, the creep deformation mechanism at 1200 °C of a eutectic, two-phase, Mo-20Si-52.8Ti (in at.%) alloy was systematically investigated using correlative electron microscopy techniques, including electron backscatter diffraction (EBSD), focused ion beam (FIB), and scanning transmission electron microscopy (STEM). The two phases correspond to solid solution and silicide, respectively. The macroscopic creep behavior of the alloy was directly correlated with the underlying micro- and mesoscale deformation mechanisms. The key findings of this study are summarized as follows:

From the Norton plot (true minimum creep rate plotted as a function of creep stress), an apparent stress exponent, n value of 1.7 was observed at low stresses (<100 MPa), indicating diffusional creep, whereas n value of 5.3 at higher stresses(>100 MPa) suggested a dislocation-climb controlled creep mechanism. SEM-BSE images revealed the formation of a precipitate-free zone near two-phase interfaces in the solid solution, consistent with the operation of diffusion and thus diffusional creep. Furthermore, the characterization of dislocations by TEM confirmed the presence of edge dislocations in the solid solution of crept samples, providing strong evidence for dislocation climb-controlled creep at higher stress levels. In the silicide phase, three distinct dislocation–precipitate interaction events were imaged, each indicative of possible dislocation climb. The combined evidence of edge dislocations in the solid solution and climb-related interactions in the silicide confirms that dislocation climb is the dominant creep mechanism under high-stress conditions.

The macroscopic creep response at 1200 °C of a eutectic alloy exhibited a distinct minimum. During the transient creep stage, mutual precipitation occurred in the solid solution and silicide, with each phase precipitating into the other, in addition to silicide

precipitates in solid solution matrix at AC state. The observed work hardening up to the creep minimum is attributed to the nucleation and growth of these precipitates, which acted as additional obstacles to dislocation motion in both phases. Beyond the creep minimum, coarsening of the precipitates led to increased interparticle spacing and reduced obstacle density, facilitating easier dislocation glide. This coarsening, particularly of silicide precipitates within the solid solution matrix, was evidenced by a saturation in area fraction and a reduction in number density of precipitates. Following the creep minimum, dynamic recovery occurred in both phases, contributing to the creep rate acceleration. Creep strain accumulation in both the solid solution and silicide was primarily accommodated by dislocation plasticity, as confirmed by EBSD-KAM maps indicating localized plastic strain and by TEM imaging, which revealed dislocation accumulation in both phases as a function of creep strain. Collectively, these observations demonstrate that the characteristic shape of the creep curve is governed by a precipitation hardening mechanism, involving an initial strengthening due to precipitate formation followed by softening driven by precipitate coarsening and dynamic recovery.

The local chemical composition and crystal structure of the hexagonal silicide and bcc solid solution precipitates in both phases were characterized by STEM-EDXS and TEM SAD pattern analysis. The silicide precipitate exhibited a slightly higher Si content, 38.5 at.% compared to stoichiometric composition. Their formation is driven by the higher Si solubility in the solid solution close to solidus temperatures, with excess Si precipitating as silicide upon cooling after casting. Analogous to the solid solution, Mo supersaturation led to precipitation of the solid solution within the silicide during creep deformation. The solid solution precipitate exhibited a higher Si content of 5.8 at.% Si compared to the equilibrium composition. Both solid solution and silicide precipitates displayed Moiré contrast and could be semi-coherent with their respective matrices. No change in the interface type was observed, and the precipitates remained semi-coherent throughout the increasing creep deformation.

This study provides a comprehensive understanding of the creep mechanisms and macroscopic response of a two-phase Mo-Si-Ti eutectic alloy, offering new insights into the deformation behavior of each constituent phase and their interactions at the micro- and mesoscale. By correlating the creep behavior with microstructural evolution, this work advances the fundamental knowledge of eutectic alloy behavior under creep conditions and assesses the alloy's potential for structural applications in extreme environments. The

findings suggest that targeted alloy design-specifically, reducing the Si content could suppress precipitate formation, thereby avoiding the acceleration of creep rate associated with precipitate coarsening. This strategy may help maintain a prolonged steady-state creep regime and improve long-term mechanical stability. The correlative electron microscopy approach combining EBSD, FIB and TEM offers a robust template for studying similar multi-phase systems.

Outlook

In future work, the development of suitable phase-field models could provide a reliable framework for understanding dislocation–precipitate interactions and offer fundamental insights into dislocation climb mechanisms. Moreover, the findings of this study may serve as an impetus for the creep testing of advanced high-temperature structural materials, particularly for demanding applications in the energy and aerospace industries.

Since a eutectic alloy microstructure is composed of two phases, TEM bulk specimen preparation via dimpling followed by ion milling is recommended to obtain bulk electron-transparent specimens. This approach enables analysis over a comparatively larger area of analysis, thereby improving the statistics of dislocations and precipitate quantification. In addition, isothermal heat treatments at creep temperatures should be conducted to ascertain whether the temperature or applied strain predominantly influences precipitation in two matrices.

Although the present study confirmed dislocation-based creep deformation mechanisms, the precise identification of either jogged edge or jogged screw dislocations remains inconclusive. Future work focusing on the unambiguous characterization of these dislocation types will provide clearer insights into dominant deformation mechanisms. Additionally, a detailed investigation of interfacial deformation during creep is necessary to better understand the role of interfaces in the mechanical response of a two-phase eutectic alloy.

A. Appendix

Figure A.1 (in the Appendix section) shows the two-beam condition TEM-bright field (BF) images of the dislocations in the solid solution of the AC sample. Dislocations appear as black lines observed throughout the analyzed area in Fig. A.1a. Dislocations are pinned by $(\text{Ti,Mo})_5\text{Si}_3$ precipitates in Fig. A.1a. These precipitates act as obstacles to dislocation motion and pin the gliding dislocations. The precipitates were semi-coherent with the matrix showing typical Moiré contrast. The precipitate showed moiré contrast on both sides of the precipitate (marked with red arrow in Fig. A.1a) because it is inclined to the foil plane, and this is the reason for the appearance of Moiré contrast, above and below the precipitate. The observed contrast is Moiré contrast, as the appearance of fringes changed with the different g-vectors. If the contrast is due to the interfacial dislocations, the contrast would not change. So, the contrast is not from the interfacial dislocations.

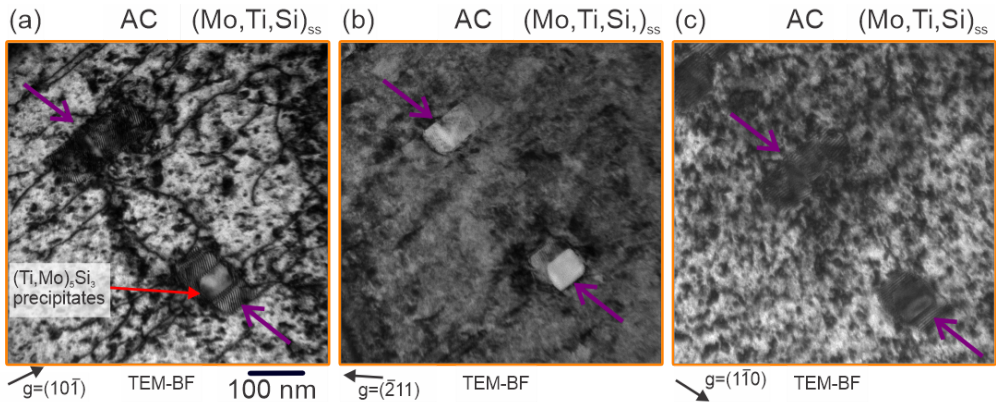


Figure A.1.: Identification of Burgers vector in the solid solution of eutectic Mo-Si-Ti alloy in AC state using two beam condition TEM-BF technique. Dislocations were imaged using diffraction vector of a) $(10\bar{1})$ b) $(\bar{2}11)$ c) $(1\bar{1}0)$. The g-vector direction was annotated in all the two-beam condition TEM/STEM images used in the thesis. The black spots in Fig. A.1 c are from Cu redeposition and Ga^+ beam damage spots.

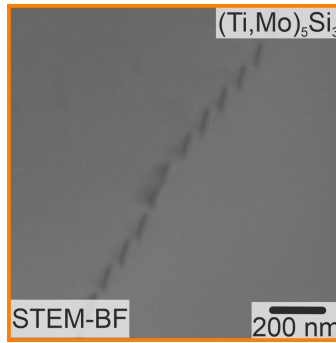


Figure A.2.: Imaging of an array of dislocations in the silicide of a eutectic Mo-20Si-52.8Ti in AC state by STEM-BF technique.

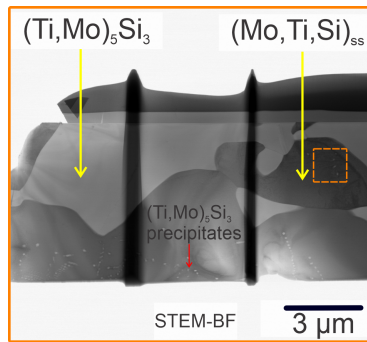


Figure A.3.: Overview of the whole TEM specimen prepared by focused ion beam (FIB) shown by STEM-BF image. The solid solution and silicide appear with dark and bright grey contrast respectively. The presence of silicide precipitates in the solid solution is indicated by red arrow. The orange inset is the region investigated in Fig. 4.7

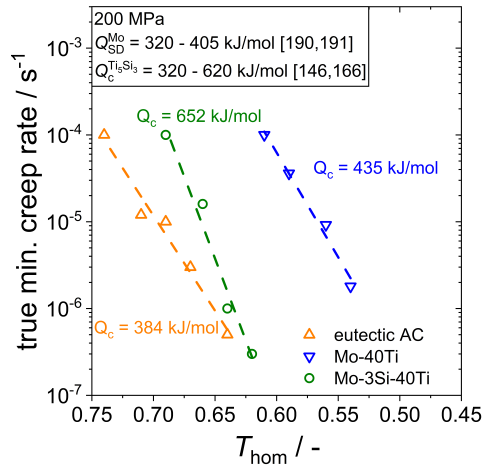


Figure A.4.: Activation energy of eutectic Mo-20Si-52.8Ti, Mo-40Ti and Mo-3Si-40Ti alloys, illustrated by Arrhenius plot at 200 MPa. Data of Ti_5Si_3 is taken from Ref. [146, 166]. Data for activation energy of Mo is taken from Refs. [190, 191]. Figure adapted with permission from Thota et al. [99]

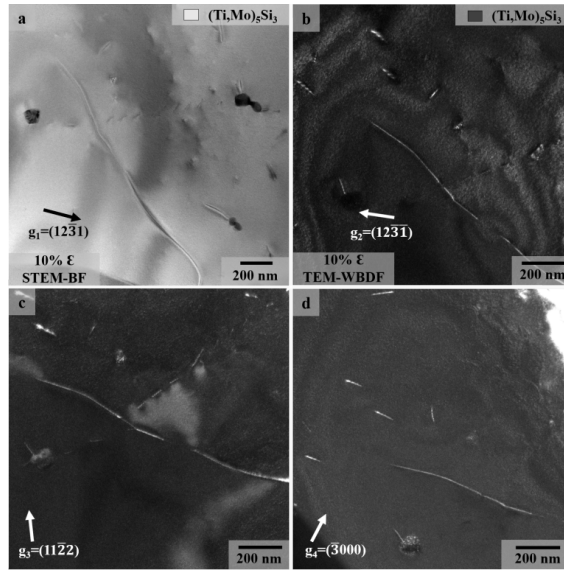


Figure A.5.: Imaging of in-plane dislocations under two beam condition in the silicide of a eutectic Mo-20Si-52.8Ti alloy at 10% true creep strain using different diffraction vectors (a) TEM-BF image with $\vec{g}(12\bar{3}1)$ (b) Weak beam dark field (WBDF) image with $\vec{g}(12\bar{3}1)$, (c) WBDF image with $\vec{g}(11\bar{2}2)$ and (d) WBDF image with $\vec{g}(3000)$. Reproduced with permission from Ref. [192]

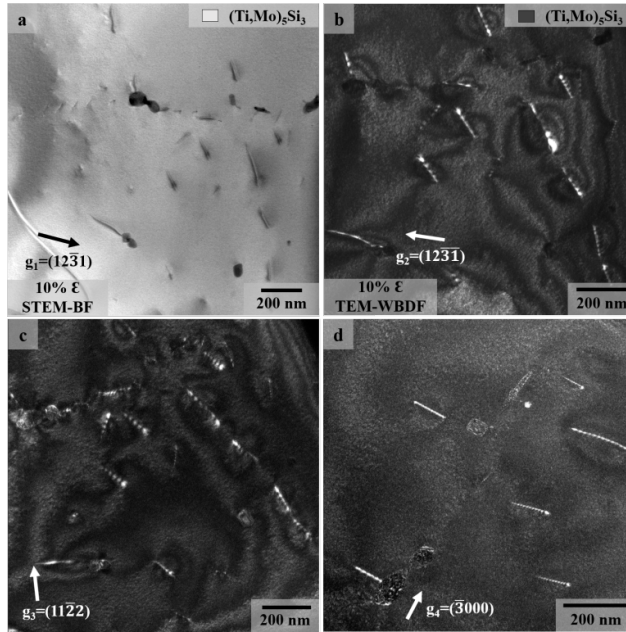


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Table A.1.: Invisibility criterion $\vec{g} \cdot \vec{b}$ of $\{112\}$ in solid solution, (Mo,Ti,Si)_{ss}

$\vec{g} \cdot \vec{b}$	Burgers vector, $\vec{b}$			
$\vec{g}$	$\frac{1}{2}[111]$	$\frac{1}{2}[\bar{1}\bar{1}1]$	$\frac{1}{2}[1\bar{1}\bar{1}]$	$\frac{1}{2}[\bar{1}1\bar{1}]$
112	2	1	1	0
$\bar{1}12$	1	2	0	-1
$1\bar{1}2$	1	0	2	-1
$11\bar{2}$	0	-1	-1	2
$1\bar{1}\bar{2}$	-1	-2	0	1
$\bar{1}1\bar{2}$	-1	0	-2	1
$\bar{1}\bar{1}2$	0	1	1	-2
$\bar{1}\bar{1}\bar{2}$	-2	-1	-1	0
211	2	0	1	1
$\bar{2}11$	0	2	-1	-1
$2\bar{1}1$	1	-1	2	0
$21\bar{1}$	1	-1	0	2
$2\bar{1}\bar{1}$	0	-2	1	1
$\bar{2}1\bar{1}$	-1	1	-2	0
$\bar{2}\bar{1}1$	-1	1	0	-2
$\bar{2}\bar{1}\bar{1}$	-2	0	-1	-1
121	2	1	0	1
$\bar{1}21$	1	2	-1	0
$1\bar{2}1$	0	-1	2	-1
$12\bar{1}$	1	0	-1	2
$1\bar{2}\bar{1}$	-1	-2	1	0
$\bar{1}2\bar{1}$	0	1	-2	1
$\bar{1}\bar{2}1$	-1	0	1	-2
$\bar{1}\bar{2}\bar{1}$	-2	-1	0	-1

Table A.2.: Invisibility criterion $\vec{g} \cdot \vec{b}$ of $\{110\}$ in solid solution, (Mo,Ti,Si)_{ss}

$\vec{g} \cdot \vec{b}$	Burgers vector, $\vec{b}$			
$\vec{g}$	$\frac{1}{2}[111]$	$\frac{1}{2}[\bar{1}11]$	$\frac{1}{2}[1\bar{1}1]$	$\frac{1}{2}[11\bar{1}]$
110	1	0	0	1
$\bar{1}10$	0	1	-1	0
$1\bar{1}0$	0	-1	1	0
$\bar{1}\bar{1}0$	-1	0	0	-1
101	1	0	1	0
$\bar{1}01$	0	1	0	-1
$10\bar{1}$	0	-1	0	1
$\bar{1}0\bar{1}$	-1	0	-1	0
011	1	1	0	0
$0\bar{1}1$	0	0	1	-1
$01\bar{1}$	0	0	-1	1
$0\bar{1}\bar{1}$	-1	-1	0	0

Table A.3.: Visibility criterion $\vec{g} \cdot \vec{b}$ of $\{200\}$ in solid solution, (Mo,Ti,Si)_{ss}

$\vec{g} \cdot \vec{b}$	Burgers vector, $\vec{b}$			
$\vec{g}$	$\frac{1}{2}[111]$	$\frac{1}{2}[\bar{1}11]$	$\frac{1}{2}[1\bar{1}1]$	$\frac{1}{2}[11\bar{1}]$
200	1	-1	1	1
$\bar{2}00$	-1	1	-1	-1
020	1	1	-1	1
$0\bar{2}0$	-1	-1	1	-1
002	1	1	1	-1
$00\bar{2}$	-1	-1	-1	1

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List of Publications

Journal articles

- [1] H. Thota, D. Schliephake, A. Kauffmann, H. Wu, A. Pundt, M. Heilmaier, and Y. M. Eggeler. The Creep-Induced Micro- and Nanostructural Evolution of a Eutectic Mo-Si-Ti Alloy at 1200°C. *Advanced Engineering Materials*, page 2301909, 2024. <https://doi.org/10.1002/adem.202301909>.
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- [3] D. Schliephake, S. R. Ramdoss, R. J. Vikram, G. Falcão, F. Galgon, H. Thota, F. Hinrichs, C. Zenk, A. Kauffmann, Y. M. Eggeler, S. Suwas, R. Schwaiger, and M. Heilmaier. Microstructure and mechanical properties of a laser-based directed energy deposited Mo-Si-Ti alloy. *Journal of Materials Science*, 60:18246–18260, 2025. <https://doi.org/10.1007/s10853-025-11158-0> , my contribution: performed FIB milling for TEM lamella preparation and STEM-EDXS.
- [4] H. Thota, D. Schliephake, A. Kauffmann, H. Wu, A. Pundt, M. Heilmaier, and Y. M. Eggeler. Origin of the creep minimum in a eutectic Mo-20Si-52.8Ti alloy with emphasis on precipitation effects. (*under preparation*).

Conference contributions

- [1] H. Thota, D. Schliephake, A. Kauffmann, H. Wu, A. Pundt, M. Heilmaier, and Y. M. Eggeler. Creep-induced microstructural evolution of the eutectic Mo-Si-Ti alloy by correlative electron microscopy. *BIO Web Conf.*, 129:23022, 2024.

Bibliography

- [1] N. Dolšak and A. Prakash. Different Approaches to Reducing Aviation Emissions: reviewing the Structure-Agency Debate in Climate policy. *Climate Action*, 1(1):2, 2022. <https://doi.org/10.1007/s44168-022-00001-w>.
- [2] T. M. Pollock and S. Tin. Nickel-Based Superalloys for Advanced Turbine Engines: Chemistry, Microstructure and Properties. *Journal of Propulsion and Power*, 22(2):361–374, 2006. <https://doi.org/10.2514/1.18239>.
- [3] R. C. Reed. *The Superalloys: Fundamentals and Applications*. Cambridge University Press, Cambridge, First edition, 2006. <https://doi.org/10.1017/CB09780511541285>.
- [4] D. R. Gaskell and D. E. Laughlin. *Introduction to the Thermodynamics of Materials*. CRC Press, Boca Raton, Sixth edition, 2017. <https://doi.org/10.1201/9781315119038>.
- [5] J. H. Perepezko. The Hotter the Engine, the Better. *Science*, 326(5956):1068–1069, 2009. <https://doi.org/10.1126/science.1179327>.
- [6] M. McLean. Nickel-base superalloys: Current status and potential. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 351(1697):419 – 433, 1995. <https://doi.org/10.1098/rsta.1995.0044>.
- [7] W. Martienssen and H. Warlimont. *Springer Handbook of Condensed Matter and Materials Data*. Springer Berlin Heidelberg, 2005. <https://doi.org/10.1007/3-540-30437-1>.

- [8] T. C. Chou and T. G. Nieh. Kinetics of MoSi₂ pest during low-temperature oxidation. *Journal of Materials Research*, 8(7):1605–1610, 1993. <https://doi.org/10.1557/JMR.1993.1605>.
- [9] E. S. Jones, Capt. J. F. Mosher, R. Speiser, and J. W. Spretnak. The Oxidation of Molybdenum. *Corrosion*, 14(1):20–26, 01 1958. <https://doi.org/10.5006/0010-9312-14.1.20>.
- [10] D. M. Berczik. Method for enhancing the oxidation resistance of a molybdenum alloy, and a method of making a molybdenum alloy. *US Patent 005595616A*, 1997.
- [11] D. M. Berczik. Oxidation resistant molybdenum alloy. *US Patent 005693156A*, 1997.
- [12] P. Jéhanno, M. Heilmaier, and H. Kestler. Characterization of an industrially processed Mo-based silicide alloy. *Intermetallics*, 12(7):1005–1009, 2004. <https://doi.org/10.1016/j.intermet.2004.03.006>.
- [13] D. Schliephake, M. Azim, K. von Klinski-Wetzel, and M. Heilmaier. High-Temperature Creep and Oxidation Behavior of Mo-Si-B alloys with High Ti contents. *Metallurgical and Materials Transactions A*, 45(3):1102–1111, 2014. <https://doi.org/10.1007/s11661-013-1944-z>.
- [14] J. Perepezko, M. Krüger, and M. Heilmaier. Mo-silicide Alloys for High-Temperature Structural Applications. *Materials Performance and Characterization*, 10(2):122–145, 2021. <https://doi.org/10.1520/MPC20200183>.
- [15] T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak. *Binary Alloy Phase Diagrams*. ASM International, Ohio, Second edition, 1990. 3-volume set.
- [16] D. Schliephake, A. Kauffmann, X. Cong, C. Gombola, M. Azim, B. Gorr, H. J. Christ, and M. Heilmaier. Constitution, oxidation and creep of eutectic and eutectoid Mo-Si-Ti alloys. *Intermetallics*, 104:133–142, 2019. <https://doi.org/10.1016/j.intermet.2018.10.028>.
- [17] D. A. Porter, K. E. Easterling, and M. Y. Sherif. *Phase Transformations in Metals and Alloys*. CRC Press, Boca Raton, Third edition, 2009. <https://doi.org/10.1201/9781003011804>.

-
- [18] J. H. Schneibel and C. J. Rawn. Thermal expansion anisotropy of ternary titanium silicides based on Ti_5Si_3 . *Acta Materialia*, 52(13):3843–3848, 2004. <https://doi.org/10.1016/j.actamat.2004.04.033>.
- [19] A. S. Tirunilai, F. Hinrichs, D. Schliephake, M. Engstler, F. Mücklich, S. Obert, G. Winkens, A. Kauffmann, and M. Heilmaier. Phase Continuity, Brittle to Ductile Transition Temperature, and Creep Behavior of a Eutectic Mo–20Si–52.8Ti Alloy. *Advanced Engineering Materials*, 24(11):2200918, 2022. <https://doi.org/10.1002/adem.202200918>.
- [20] V. Raja Jothi, S. K. Aramanda, D. Schliephake, A. Kauffmann, A. Choudhury, M. Heilmaier, and S. Suwas. Unveiling the Intricacies of a Ductile-Phase Toughened Intermetallic: An In-Depth Exploration of a Eutectic Mo–Si–Ti Alloy and its Mechanical Behavior. *Advanced Engineering Materials*, page 2301843, 2024. <https://doi.org/10.1002/adem.202301843>.
- [21] G. Frommeyer, R. Rosenkranz, and C. Lüdecke. Microstructure and properties of the refractory intermetallic Ti_5Si_3 compound and the unidirectionally solidified eutectic Ti– Ti_5Si_3 alloy. *International Journal of Materials Research*, 81(5):307–313, 1990. <https://doi.org/10.1515/ijmr-1990-810501>.
- [22] K. Kishida, M. Fujiwara, H. Adachi, K. Tanaka, and H. Inui. Plastic deformation of single crystals of Ti_5Si_3 with the hexagonal D_{8h} structure. *Acta Materialia*, 58(3):846–857, 2010. <https://doi.org/10.1016/j.actamat.2009.09.062>.
- [23] S. Obert, A. Kauffmann, and M. Heilmaier. Characterisation of the oxidation and creep behaviour of novel Mo-Si-Ti alloys. *Acta Materialia*, 184:132–142, 2020. <https://doi.org/10.1016/j.actamat.2019.11.045>.
- [24] S. Obert, A. Kauffmann, S. Seils, T. Boll, S. Kauffmann-Weiss, H. Chen, R. Anton, and M. Heilmaier. Microstructural and chemical constitution of the oxide scale formed on a pesting-resistant Mo-Si-Ti alloy. *Corrosion Science*, 178:109081, 2021. <https://doi.org/10.1016/j.corsci.2020.109081>.

- [25] S. Obert, A. Kauffmann, S. Seils, S. Schellert, M. Weber, B. Gorr, H. J. Christ, and M. Heilmaier. On the chemical and microstructural requirements for the pesting-resistance of Mo-Si-Ti alloys. *Journal of Materials Research and Technology*, 9(4):8556–8567, 2020. <https://doi.org/10.1016/j.jmrt.2020.06.002>.
- [26] M. Weber, B. Gorr, H. J. Christ, S. Obert, A. Kauffmann, and M. Heilmaier. Effect of Water Vapor on the Oxidation Behavior of the Eutectic High-Temperature Alloy Mo-20Si-52.8Ti. *Advanced Engineering Materials*, 22(7):2000219, 2020. <https://doi.org/10.1002/adem.202000219>.
- [27] S. Obert. *Characterisation of the Oxidation and Creep Behaviour of Novel Mo-Si-Ti Alloys*. PhD thesis, Karlsruher Institut für Technologie (KIT), 2021. <https://doi.org/10.1016/10.5445/IR/1000133636>.
- [28] G. I. Taylor. The Mechanism of Plastic Deformation of Crystals. Part I. Theoretical. *Proceedings of the Royal Society A*, 145(855):362–387, 1934.
- [29] E. Orowan. Zur Kristallplastizität. III. Über den Mechanismus des Gleitvorganges. *Zeitschrift für Physik*, 89:634–659, 1934.
- [30] M. Polanyi. Über eine Art Gitterstörung, die einen Kristall plastisch machen könnte. *Zeitschrift für Physik*, 89:660–664, 1934.
- [31] D. Kuhlmann-Wilsdorf and H. G. F. Wilsdorf. Dislocation Movements in Metals. *Science*, 144(3614):17–25, 1964. <https://doi.org/10.1126/science.144.3614.17>.
- [32] G. E. Dieter. *Mechanical Metallurgy*. McGraw-Hill, New York, Third edition, 1986.
- [33] D. Hull and D. J. Bacon. *Introduction to Dislocations*. Butterworth-Heinemann, Oxford, Fifth edition, 2011. <https://doi.org/10.1016/C2009-0-64358-0>.
- [34] W. Cai and W. D. Nix. *Imperfections in Crystalline Solids*. Cambridge University Press, Cambridge, 2016. <https://doi.org/10.1017/CB09781316389508>.
- [35] P. M. Anderson, J. P. Hirth, and J. Lothe. *Theory of Dislocations*. Cambridge University Press, New York, Third edition, 2017. <https://doi.org/10.1017/9780511977732>.

-
- [36] J. W. Christian. Some surprising features of the plastic deformation of body-centered cubic metals and alloys. *Metallurgical Transactions A*, 14(7):1237–1256, 1983. <https://doi.org/10.1007/BF02664806>.
- [37] T. Imura, K. Noda, H. Matsui, H. Saka, and H. Kimura. Direct Measurement of Mobility of Dislocations in High-Purity Molybdenum. In *Dislocations in Solids*, pages 287–292. University of Tokyo Press, 1985.
- [38] W. Sigle. High-resolution electron microscopy and molecular dynamics study of the $(a/2)[111]$ screw dislocation in molybdenum. *Philosophical Magazine A*, 79(5):1009–1020, 1999. <https://doi.org/10.1080/01418619908210343>.
- [39] V. Vitek. Core structure of screw dislocations in body-centred cubic metals: relation to symmetry and interatomic bonding. *Philosophical Magazine*, 84(3-5):415–428, 2004. <https://doi.org/10.1080/14786430310001611644>.
- [40] V. Vitek and V. Paidar. Non-planar Dislocation Cores: A Ubiquitous Phenomenon Affecting Mechanical Properties of Crystalline Materials. In *Dislocations in Solids*, volume 14, pages 439–514. Elsevier, Amsterdam, 2008. [https://doi.org/10.1016/S1572-4859\(07\)00007-1](https://doi.org/10.1016/S1572-4859(07)00007-1).
- [41] H. J. Kaufmann, A. Luft, and D. Schulze. Deformation mechanism and dislocation structure of high-purity molybdenum single crystals at low temperatures. *Crystal Research and Technology*, 19(3):357–372, 1984. <https://doi.org/10.1002/crat.2170190312>.
- [42] F. Wang, G. H. Balbus, S. Xu, Y. Su, J. Shin, P. F. Rottmann, K. E. Knipling, J. C. Stinville, L. H. Mills, O. N. Senkov, I. J. Beyerlein, T. M. Pollock, and D. S. Gianola. Multiplicity of dislocation pathways in a refractory multiprincipal element alloy. *Science*, 370(6512):95–101, 2020. <https://doi.org/10.1126/science.aba3722>.
- [43] M. H. Yoo. Slip, twinning, and fracture in hexagonal close-packed metals. *Metallurgical Transactions A*, 12(3):409 – 418, 1981. <https://doi.org/10.1007/BF02648537>.

- [44] H. Numakura, Y. Minonishi, and M. Koiwa. $\langle \bar{1}\bar{1}23 \rangle \{10\bar{1}1\}$ slip in titanium polycrystals at room temperature. *Scripta Metallurgica*, 20(11):1581 – 1586, 1986. [https://doi.org/10.1016/0036-9748\(86\)90399-6](https://doi.org/10.1016/0036-9748(86)90399-6).
- [45] H. Numakura, Y. Minonishi, and M. Koiwa. $\langle \bar{1}\bar{1}23 \rangle \{10\bar{1}1\}$ slip in zirconium. *Philosophical Magazine A: Physics of Condensed Matter, Structure, Defects and Mechanical Properties*, 63(5):1077 – 1084, 1991. <https://doi.org/10.1080/01418619108213938>.
- [46] J. W. Christian and S. Mahajan. Deformation twinning. *Progress in Materials Science*, 39(1):1–157, 1995. [https://doi.org/10.1016/0079-6425\(94\)00007-7](https://doi.org/10.1016/0079-6425(94)00007-7).
- [47] G. I. Taylor. Plastic strain in metals. *Journal of the Institute of Metals*, 62:307–324, 1938.
- [48] W. F. Hosford. *Mechanical Behavior of Materials*. Cambridge University Press, Cambridge, Second edition, 2005. <https://doi.org/10.1017/CB09780511810930>.
- [49] P. G. Partridge. The crystallography and deformation modes of hexagonal close-packed metals. *Metallurgical Reviews*, 12(1):169–194, 1967. <https://doi.org/10.1179/mtlr.1967.12.1.169>.
- [50] M. De Graef and M. E. McHenry. *Structure of Materials: An Introduction to Crystallography, Diffraction and Symmetry*. Cambridge University Press, Cambridge, Second edition, 2012. <https://doi.org/10.1017/CB09781139051637>.
- [51] R. E. Reed-Hill. *Physical Metallurgy Principles*. University Series in Basic Engineering. Van Nostrand Reinhold Company, New York, Second edition, 1973.
- [52] C. Laird and H. I. Aaronson. Mechanisms of formation of θ and dissolution of θ' precipitates in an Al–4% Cu alloy. *Acta Metallurgica*, 14(2):171–185, 1966. [https://doi.org/10.1016/0001-6160\(66\)90298-7](https://doi.org/10.1016/0001-6160(66)90298-7).
- [53] A. Kelly and R. B. Nicholson. Precipitation hardening. *Progress in Materials Science*, 10(3):149–391, 1963. [https://doi.org/10.1016/0079-6425\(63\)90010-0](https://doi.org/10.1016/0079-6425(63)90010-0).

- [54] J. W. Martin. *Micromechanisms in Particle-Hardened Alloys*. Cambridge University Press, Cambridge, 1980.
- [55] E. Nembach. *Particle Strengthening of Metals and Alloys*. Wiley–Interscience, New York, 1996.
- [56] B. Reppich, H. Bügler, R. Leistner, and M. Schütze. Creep Behaviour of Die-Cast Al–Si–Cu alloys. In *Proceedings of the 2nd International Conference on Creep and Fracture of Engineering Materials and Structures*, pages 279–297, Swansea, 1984. Pineridge Press.
- [57] B. Reppich. Particle strengthening. In *Plastic Deformation and Fracture of Materials*, volume 6 of *Materials Science and Technology*, pages 312–357. Wiley-VCH, Weinheim, 1996.
- [58] B. Wilshire and R. W. Evans. *Creep Behaviour of Crystalline Solids*. Pineridge Press, Swansea, 1985.
- [59] O. D. Sherby and P. M. Burke. Mechanical behavior of crystalline solids at elevated temperature. *Progress in Materials Science*, 13:323–390, 1968. [https://doi.org/10.1016/0079-6425\(68\)90024-8](https://doi.org/10.1016/0079-6425(68)90024-8).
- [60] M. E. Kassner and M. T. Pérez-Prado. Five-power-law creep in single phase metals and alloys. *Progress in Materials Science*, 45(1):1–102, 2000. [https://doi.org/10.1016/S0079-6425\(99\)00006-7](https://doi.org/10.1016/S0079-6425(99)00006-7).
- [61] A. K. Mukherjee, J. E. Bird, and J. E. Dorn. Experimental Correlations for High-Temperature Creep. Technical Report UCRL-18526, The Detroit Materials Engineering Congress of American Society for Metals, Detroit, October 1968.
- [62] A. K. Mukherjee, J. E. Bird, and J. E. Dorn. Experimental correlations for high-temperature creep. *Transactions of the Metallurgical Society of AIME*, 245(6):1795–1799, 1969. <https://doi.org/10.1557/mrs2003.191>.
- [63] F. H. Norton. *The Creep of Steel at High Temperatures*. McGraw-Hill Book Company, New York, 1929.
- [64] B. Ilschner. *Hochtemperatur-Plastizität: Warmfestigkeit und Warmverformbarkeit metallischer und nichtmetallischer Werkstoffe*, volume 23 of *Reine und angewandte*

- Metallkunde in Einzeldarstellungen*. Springer-Verlag, Berlin, 1973. <https://doi.org/10.1007/978-3-642-80708-4>.
- [65] M. F. Ashby. A first report on deformation-mechanism maps. *Acta Metallurgica*, 20:887–897, 1972. [https://doi.org/10.1016/0001-6160\(72\)90082-X](https://doi.org/10.1016/0001-6160(72)90082-X).
- [66] H. J. Frost and M. F. Ashby. A second report on Deformation-Mechanism maps. Technical report, Division of Applied Physics, Harvard University, August 1973. <https://doi.org/10.21236/AD0769821>.
- [67] J. Weertman. Theory of Steady-State Creep in Metals based on Dislocation Climb. *Journal of Applied Physics*, 26:1213–1217, 1955. <https://doi.org/10.1063/1.1721875>.
- [68] J. Weertman. Dislocation Climb Theory of Steady-State Creep. *Transactions of the American Society of Metals*, 61:680–694, 1968.
- [69] J. Weertman. High temperature creep produced by dislocation motion. In *Rate Processes in Plastic Deformation of Metals*, pages 315–336. ASM, Materials Park, 1975.
- [70] J. Weertman. *Mechanics and Materials Interlinkage*. Wiley, New York, 1999.
- [71] J. Harper and J. E. Dorn. Viscous creep of aluminum near its melting temperature. *Acta Metallurgica*, 5(11):654–665, 1957. [https://doi.org/10.1016/0001-6160\(57\)90144-4](https://doi.org/10.1016/0001-6160(57)90144-4).
- [72] J. S. Zhang. *High Temperature Deformation and Fracture of Materials*. Woodhead Publishing / Elsevier, Cambridge, 2010. <https://doi.org/10.1533/9780857090805>.
- [73] J. Friedel. *Dislocations*, volume 3 of *International Series of Monographs on Solid State Physics*. Pergamon Press, Oxford, 1964.
- [74] D. N. Seidman, E. A. Marquis, and D. C. Dunand. Precipitation strengthening at ambient and elevated temperatures of heat-treatable Al(Sc) alloys. *Acta Materialia*, 50(16):4021–4035, 2002. [https://doi.org/10.1016/S1359-6454\(02\)00201-X](https://doi.org/10.1016/S1359-6454(02)00201-X).

- [75] Y. M. Eggeler, J. Müller, M. S. Titus, A. Suzuki, T. M. Pollock, and E. Spiecker. Planar defect formation in the γ phase during high temperature creep in single crystal CoNi-base superalloys. *Acta Materialia*, 113:335–349, 2016. <https://doi.org/10.1016/j.actamat.2016.03.077>.
- [76] M. Heilmaier, U. Leetz, and B. Reppich. Order strengthening in the cast nickel-based superalloy IN 100 at room temperature. *Materials Science and Engineering: A*, 319-321:375–378, 2001. [https://doi.org/10.1016/S0921-5093\(01\)00989-3](https://doi.org/10.1016/S0921-5093(01)00989-3).
- [77] E. Orowan. Discussion on internal stresses. In *Symposium on Internal Stresses in Metals and Alloys*, pages 451–453. Institute of Metals, London, 1948.
- [78] A. Cui, X. Wang, and Y. Cui. Multiscale modelling of precipitation hardening: a review. *Journal of Materials Science: Materials Theory*, 8(1):13, 2024. <https://doi.org/10.1186/s41313-024-00066-6>.
- [79] W. Blum and B. Reppich. Creep of particle-strengthened alloys. In *Creep Behaviour of Crystalline Solids*, Pineridge Series on Progress in Creep and Fracture, pages 83–135. Pineridge Press, Swansea, 1985. <https://doi.org/10.1002/crat.2170211015>.
- [80] M. E. Kassner. Chapter 8 - Creep Behavior of Particle-Strengthened alloys. In *Fundamentals of Creep in Metals and Alloys*, pages 167–188. Butterworth-Heinemann, Boston, Third edition, 2015. <https://doi.org/10.1016/B978-0-08-099427-7.00008-6>.
- [81] D. McLean. On the threshold stress for dislocation creep in particle-strengthened alloys. *Acta Metallurgica*, 33(4):545–553, 1985. [https://doi.org/10.1016/0001-6160\(85\)90018-5](https://doi.org/10.1016/0001-6160(85)90018-5).
- [82] E. A. Marquis and D. C. Dunand. Model for creep threshold stress in precipitation-strengthened alloys with coherent particles. *Scripta Materialia*, 47(8):503–508, 2002. [https://doi.org/10.1016/S1359-6462\(02\)00165-3](https://doi.org/10.1016/S1359-6462(02)00165-3).
- [83] S. Spigarelli, E. Cerri, P. Bianchi, and E. Evangelista. Interpretation of creep behaviour of a 9Cr–Mo–Nb–V–N (T91) steel using threshold stress concept. *Materials Science and Technology*, 15(12):1433–1440, 1999. <https://doi.org/10.1179/026708399101505428>.

- [84] R. Lagneborg. Bypassing of dislocations past particles by a climb mechanism. *Scripta Metallurgica*, 7(6):605–613, 1973. [https://doi.org/10.1016/0036-9748\(73\)90222-6](https://doi.org/10.1016/0036-9748(73)90222-6).
- [85] D. J. Srolovitz, M. J. Luton, R. Petkovic-Luton, D. M. Barnett, and W. D. Nix. Diffusionally modified dislocation–particle elastic interactions. *Acta Metallurgica*, 32(7):1079–1088, 1984. [https://doi.org/10.1016/0001-6160\(84\)90011-7](https://doi.org/10.1016/0001-6160(84)90011-7).
- [86] J. H. Schröder and E. Arzt. Weak Beam Studies Of Dislocation/dispersoid Interaction In An ODS Superalloy. *Scripta Metallurgica*, 19(9):1129–1134, 1985. [https://doi.org/10.1016/0036-9748\(85\)90022-5](https://doi.org/10.1016/0036-9748(85)90022-5).
- [87] E. Arzt and D. S. Wilkinson. Threshold stresses for dislocation climb over hard particles: the effect of an attractive interaction. *Acta Metallurgica*, 34(10):1893–1898, 1986. [https://doi.org/10.1016/0001-6160\(86\)90247-6](https://doi.org/10.1016/0001-6160(86)90247-6).
- [88] F. R. N. Nabarro. Steady-state diffusional creep. *Philosophical Magazine*, 16:231–237, 1967. <https://doi.org/10.1080/14786436708229736>.
- [89] C. Herring. Diffusional Viscosity of a Polycrystalline Solid. *Journal of Applied Physics*, 21(5):437–445, 1950. <https://doi.org/10.1063/1.1699681>.
- [90] R. L. Coble. A model for boundary diffusion controlled creep in polycrystalline materials. *Journal of Applied Physics*, 34(6):1679–1682, 1963. <https://doi.org/10.1063/1.1702656>.
- [91] Y. Q. Jiang, Y. C. Lin, C. Phaniraj, Y. C. Xia, and H. M. Zhou. Creep and creep-rupture behavior of 2124-T851 aluminum alloy. *High Temperature Materials and Processes*, 32(6):533–540, 2013. <https://doi.org/10.1515/htmp-2012-0172>.
- [92] H. Mughrabi and U. Tetzlaff. Microstructure and High-Temperature Strength of Monocrystalline Nickel-Base Superalloys. *Advanced Engineering Materials*, 2(6):319–326, 2000. [https://doi.org/10.1002/1527-2648\(200006\)2:6<319::AID-ADEM319>3.0.CO;2-S](https://doi.org/10.1002/1527-2648(200006)2:6<319::AID-ADEM319>3.0.CO;2-S).
- [93] D. Mukherji, H. Gabrisch, W. Chen, H. J. Fecht, and R. P. Wahi. Mechanical behaviour and microstructural evolution in the single crystal superalloy SC16.

- Acta Materialia*, 45(8):3143–3154, 1997. [https://doi.org/10.1016/S1359-6454\(97\)00005-0](https://doi.org/10.1016/S1359-6454(97)00005-0).
- [94] R. W. Hayes, G. B. Viswanathan, and M. J. Mills. Creep behavior of Ti-6Al-2Sn-4Zr-2Mo: I. the effect of nickel on creep deformation and microstructure. *Acta Materialia*, 50(20):4953–4963, 2002. [https://doi.org/10.1016/S1359-6454\(02\)00279-3](https://doi.org/10.1016/S1359-6454(02)00279-3).
- [95] G. B. Viswanathan, S. Karthikeyan, R. W. Hayes, and M. J. Mills. Creep behaviour of Ti-6Al-2Sn-4Zr-2Mo: II. mechanisms of deformation. *Acta Materialia*, 50(20):4965–4980, 2002. [https://doi.org/10.1016/S1359-6454\(02\)00280-X](https://doi.org/10.1016/S1359-6454(02)00280-X).
- [96] M. Dudová, K. Kuchařová, T. Barták, H. Bei, E. P. George, Ch. Somsen, and A. Dlouhý. Creep in directionally solidified NiAl-Mo eutectics. *Scripta Materialia*, 65(8):699–702, 2011. <https://doi.org/10.1016/j.scriptamat.2011.07.019>.
- [97] H. Munch. Master’s thesis, Friedrich-Alexander-Universität Erlangen–Nürnberg, Erlangen–Nürnberg, Germany, 1983.
- [98] W. Blum and A. Finkel. New Technique for Evaluating Long-Range Internal Back Stresses. *Acta Metallurgica*, 30(8):1705–1715, 1982. [https://doi.org/10.1016/0001-6160\(82\)90192-4](https://doi.org/10.1016/0001-6160(82)90192-4).
- [99] H. Thota, D. Schliephake, A. Kauffmann, H. Wu, A. Pundt, M. Heilmaier, and Y. M. Eggeler. The Creep-Induced Micro- and Nanostructural Evolution of a Eutectic Mo-Si-Ti alloy at 1200°C. *Advanced Engineering Materials*, page 2301909, 2024. <https://doi.org/10.1002/adem.202301909>.
- [100] A. Deschamps, Y. Bréchet, P. Guyot, and F. Livet. On the Influence of Dislocations on Precipitation in an Al-Zn-Mg alloy. *International Journal of Materials Research*, 88(8):601–606, 1997. <https://doi.org/10.3139/ijmr-1997-0113>.
- [101] M. Taneike, M. Kondo, and T. Morimoto. Accelerated coarsening of MX Carbonitrides in 12% Cr steels during Creep Deformation. *ISIJ International*, 41(Suppl):S111–S115, 2001. https://doi.org/10.2355/isijinternational.1.41.Suppl_S111.

- [102] T. Nakajima, S. Spigarelli, E. Evangelista, and T. Endo. Strain Enhanced Growth of Precipitates during Creep of T91. *MATERIALS TRANSACTIONS*, 44(9):1802–1808, 2003. <https://doi.org/10.2320/matertrans.44.1802>.
- [103] M. Hättestrand and H.O. Andrén. Influence of strain on precipitation reactions during creep of an advanced 9% chromium steel. *Acta Materialia*, 49(12):2123–2128, 2001. [https://doi.org/10.1016/S1359-6454\(01\)00135-5](https://doi.org/10.1016/S1359-6454(01)00135-5).
- [104] T. Nakajima, M. Takeda, and T. Endo. Accelerated coarsening of precipitates in crept Al–Cu alloys. *Materials Science and Engineering: A*, 387-389:670–673, 2004. <https://doi.org/10.1016/j.msea.2004.01.131>.
- [105] T. Nakajima, M. Takeda, and T. Endo. Strain Enhanced Precipitate Coarsening during Creep of a Commercial Magnesium Alloy AZ80. *MATERIALS TRANSACTIONS*, 47(4):1098–1104, 2006. <https://doi.org/10.2320/matertrans.47.1098>.
- [106] G. Eggeler. The effect of long-term creep on particle coarsening in tempered martensite ferritic steels. *Acta Metallurgica*, 37(12):3225–3234, 1989. [https://doi.org/10.1016/0001-6160\(89\)90194-6](https://doi.org/10.1016/0001-6160(89)90194-6).
- [107] C. Wagner. Theory of the aging of precipitates by dissolution (ostwald ripening). *Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie*, 65(7):581–591, 1961. <https://doi.org/10.1002/bbpc.19610650704>.
- [108] I. M. Lifshitz and V. V. Slyozov. The kinetics of precipitation from supersaturated solid solutions. *Soviet Physics Journal of Experimental and Theoretical Physics*, 8(3):331–339, 1959.
- [109] I. M. Lifshitz and V. V. Slyozov. The kinetics of precipitation from supersaturated solid solutions. *Journal of Physics and Chemistry of Solids*, 19(1-2):35–50, 1961. [https://doi.org/10.1016/0022-3697\(61\)90054-3](https://doi.org/10.1016/0022-3697(61)90054-3).
- [110] P. D. Portella. Ph.D. Dissertation, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany, 1984.
- [111] W. Blum and P. D. Portella. *Deformation of Multi-Phase and Particle Containing Materials*. Danmarks Tekniske Universitet, 1983. 4th Risø International Symposium on Metallurgy and Materials Science; 1983.

- [112] A. Dlouhý, K. Kuchařová, and J. Březina. Dislocation slip and deformation twinning interplay during high temperature deformation in γ -TiAl base intermetallics. *Materials Science and Engineering: A*, 319-321:820–826, 2001. [https://doi.org/10.1016/S0921-5093\(01\)01092-9](https://doi.org/10.1016/S0921-5093(01)01092-9).
- [113] A. Schmitt, K. S. Kumar, A. Kauffmann, and M. Heilmaier. Microstructural evolution during creep of lamellar eutectoid and off-eutectoid FeAl/FeAl₂ alloys. *Intermetallics*, 107:116–125, 2019. <https://doi.org/10.1016/j.intermet.2019.01.015>.
- [114] A. Schmitt, K. S. Kumar, A. Kauffmann, X. Li, F. Stein, and M. Heilmaier. Creep of binary Fe-Al alloys with ultrafine lamellar microstructures. *Intermetallics*, 90:180–187, 2017. <https://doi.org/10.1016/j.intermet.2017.07.016>.
- [115] A. Dlouhy, N. Merk, and G. Eggeler. A microstructural study of creep in short fibre reinforced aluminium alloys. *Acta Metallurgica et Materialia*, 41(11):3245–3256, 1993. [https://doi.org/10.1016/0956-7151\(93\)90054-V](https://doi.org/10.1016/0956-7151(93)90054-V).
- [116] M. Kamaraj. Rafting in single crystal nickel-base superalloys - an overview. *Sadhana*, 28(1-2):115–128, Feb 2003. <https://doi.org/10.1007/BF02717141>.
- [117] F. R. N. Nabarro. Rafting in superalloys. *Metallurgical and Materials Transactions A*, 27(3):513–530, 1996. <https://doi.org/10.1007/BF02651622>.
- [118] P. J. Henderson and M. McLean. Microstructural contributions to friction stress and recovery kinetics during creep of the nickel-base superalloy IN738LC. *Acta Metallurgica*, 31(8):1203–1219, 1983. [https://doi.org/10.1016/0001-6160\(83\)90182-7](https://doi.org/10.1016/0001-6160(83)90182-7).
- [119] G. B. Viswanathan, R. W. Hayes, and M. J. Mills. A study based on jogged-screw dislocations for high-temperature creep in Ti alloys. *Materials Science and Engineering: A*, 319-321:706–710, 2001. [https://doi.org/10.1016/S0921-5093\(01\)01048-6](https://doi.org/10.1016/S0921-5093(01)01048-6).
- [120] J. Albiez, I. Sprenger, C. Seemüller, D. Weygand, M. Heilmaier, and T. Böhlke. Physically motivated model for creep of directionally solidified eutectics evaluated for the intermetallic NiAl-9Mo. *Acta Materialia*, 110:377–385, 2016. <https://doi.org/10.1016/j.actamat.2016.02.024>.

- [121] L. Reimer. *Scanning Electron Microscopy: Physics of Image Formation and Microanalysis*. Springer, Berlin, Second edition, 2010. <https://doi.org/10.1007/978-3-642-08398-2>.
- [122] D. B. Williams and C. B. Carter. *Transmission Electron Microscopy*. Springer New York, Second edition, 2009. <https://doi.org/10.1007/978-0-387-76501-3>.
- [123] E. Rutherford. LXXIX. The scattering of α and β particles by Matter and the Structure of the Atom. *Philosophical Magazine*, 21(125):669–688, 1911. <https://doi.org/10.1080/14786440508637080>.
- [124] B. Fultz and J. M. Howe. *Transmission Electron Microscopy and Diffractometry of Materials*. Springer, Cham, Fifth edition, 2013. <https://doi.org/10.1007/978-3-642-29761-8>.
- [125] P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan. *Electron Microscopy of Thin Crystals*. Robert E. Krieger Publishing Company, Malabar, 1965.
- [126] M. De Graef. *Introduction to Conventional Transmission Electron Microscopy*. Cambridge University Press, Oxford, First edition, 2003. <https://doi.org/10.1093/acprof:oso/9780198555837.001.0001>.
- [127] S. J. Pennycook and P. D. Nellist. *Scanning Transmission Electron Microscopy: Imaging and Analysis*. Springer, New York, First edition, 2011. <https://doi.org/10.1007/978-1-4419-7200-2>.
- [128] J. I. Goldstein, D. E. Newbury, J. R. Michael, N. W. M. Ritchie, J. H. J. Scott, and D. C. Joy. *Scanning Electron Microscopy and X-Ray Microanalysis*. Springer, New York, Fourth edition, 2018. <https://doi.org/10.1007/978-1-4939-6676-9>.
- [129] K. Kanaya and S. Okayama. Penetration and energy-loss theory of electrons in solid targets. *Journal of Physics D: Applied Physics*, 5(1):43–58, Jan 1972. <https://doi.org/10.1088/0022-3727/5/1/308>.
- [130] L. A. Giannuzzi and F. A. Stevie. *Introduction to focused ion beams: Instrumentation, theory, techniques and practice*. Springer New York, 2005. <https://doi.org/10.1007/b101190>.

-
- [131] F. Bachmann, R. Hielscher, and H. Schaeben. Texture Analysis with MTEX – free and open source software toolbox. *Solid State Phenomena*, 160:63–68, 2010. <https://doi.org/10.4028/www.scientific.net/SSP.160.63>.
- [132] A. J. Schwartz, M. Kumar, and B. L. Adams. Electron backscatter diffraction in materials science. *Materials Science and Engineering: A*, 283(1-2):1–10, 2000. [https://doi.org/10.1016/S0921-5093\(00\)00609-4](https://doi.org/10.1016/S0921-5093(00)00609-4).
- [133] A. J. Schwartz, M. Kumar, B. L. Adams, and D. P. Field. *Electron Backscatter Diffraction in Materials Science*. Springer, Boston, Second edition, 2009. <https://doi.org/10.1007/978-0-387-88136-2>.
- [134] V. Randle. Recent Developments in Electron Backscatter Diffraction. *Advances in Imaging and Electron Physics*, 151:363–416, 2008. [https://doi.org/10.1016/S1076-5670\(07\)00405-3](https://doi.org/10.1016/S1076-5670(07)00405-3).
- [135] V. Randle. Electron backscatter diffraction: Strategies for reliable data acquisition and processing. *Materials Characterization*, 60(9):913–922, 2009. <https://doi.org/10.1016/j.matchar.2009.05.011>.
- [136] S. I. Wright, M. M. Nowell, and D. P. Field. A review of strain analysis using electron backscatter diffraction. *Microscopy and Microanalysis*, 17(3):316–329, 2011. <https://doi.org/10.1017/S1431927611000055>.
- [137] L. A. Giannuzzi and F. A. Stevie. A review of focused ion beam milling techniques for TEM specimen preparation. *Micron*, 30(3):197–204, 1999. [https://doi.org/10.1016/S0968-4328\(99\)00005-0](https://doi.org/10.1016/S0968-4328(99)00005-0).
- [138] A. Kelly and K. M. Knowles. *Crystallography and Crystal Defects*. Wiley, Hoboken, Third edition, 2020. <https://doi.org/10.1002/9781119961468>.
- [139] G. Cliff and G. W. Lorimer. The quantitative analysis of thin specimens. *Journal of Microscopy*, 103(2):203–207, 1975. <https://doi.org/10.1111/j.1365-2818.1975.tb01462.x>.
- [140] J. W. Edington. *Electron Diffraction in the Electron Microscope*, pages 1–77. Macmillan Education UK, London, 1975. https://doi.org/10.1007/978-1-349-02595-4_1.

- [141] M. F. Ashby and L. M. Brown. Diffraction contrast from spherically symmetrical coherency strains. *Philosophical Magazine, Series 8*, 8(91):1083–1103, 1963. <https://doi.org/10.1080/14786436308207338>.
- [142] M. F. Ashby and L. M. Brown. On diffraction contrast from inclusions. *Philosophical Magazine, Series 8*, 8(94):1649–1676, 1963. <https://doi.org/10.1080/14786436308207329>.
- [143] S. Iwamura and Y. Miura. Loss in coherency and coarsening behavior of Al₃Sc precipitates. *Acta Materialia*, 52(3):591–600, 2004. <https://doi.org/10.1016/j.actamat.2003.09.042>.
- [144] C. T. Rueden, J. Schindelin, M. C. Hiner, B. E. DeZonia, A. E. Walter, E. T. Arena, and K. W. Eliceiri. ImageJ2: ImageJ for the next generation of scientific image data. *BMC Bioinformatics*, 18(29):1471–2105, 2017. <https://doi.org/10.1186/s12859-017-1934-z>.
- [145] H. E. Garrett. *Statistics in Psychology and Education*. Longmans, Green and Co., London, Sixth edition, 1966.
- [146] K. Sadananda, C. R. Feng, R. Mitra, and S. C. Deevi. Creep and fatigue properties of high temperature silicides and their composites. *Materials Science and Engineering: A*, 261(1):223–238, 1999. [https://doi.org/10.1016/S0921-5093\(98\)01070-3](https://doi.org/10.1016/S0921-5093(98)01070-3).
- [147] M. Kini and A. H. Chokshi. The Influence of Titania on Creep in Superplastic Zirconia. *Journal of the American Ceramic Society*, 93(6):1725–1731, 2010. <https://doi.org/10.1111/j.1551-2916.2010.03617.x>.
- [148] R. Cano-Crespo, B. M. Moshtaghioun, D. Gómez-García, A. Domínguez-Rodríguez, and R. Moreno. High-temperature creep of carbon nanofiber-reinforced and graphene oxide-reinforced alumina composites sintered by spark plasma sintering. *Ceramics International*, 43(9):7136–7141, 2017. <https://doi.org/10.1016/j.ceramint.2017.02.146>.
- [149] H. Gopalan and A. H. Chokshi. Creep in alumina and carbon nanotube reinforced alumina composites. *Materials Science and Engineering: A*, 731:561–568, 2018. <https://doi.org/10.1016/j.msea.2018.06.091>.

-
- [150] W. T. Read. *Dislocations in Crystals*. McGraw-Hill Book Company, New York, 1953.
- [151] B. D. Cullity and S. R. Stock. *Elements of X-ray Diffraction*. Prentice Hall, Upper Saddle River, Third edition, 2001.
- [152] W. Blum and X. H. Zeng. A simple dislocation model of deformation resistance of ultrafine-grained materials explaining hall–petch strengthening and enhanced strain-rate sensitivity. *Acta Materialia*, 57:1966–1974, 2009. <https://doi.org/10.1016/j.actamat.2008.12.041>.
- [153] W. Blum and X. H. Zeng. Effects of sequential operation with heat treatment and mechanical deformation on the properties of ultrafine-grained materials. *Acta Materialia*, 59:6205–6213, 2011. <https://doi.org/10.1016/j.actamat.2011.05.032>.
- [154] A. B. Pandey, R. S. Mishra, A. G. Paradkar, and Y. R. Mahajan. Steady state creep behaviour of an Al-Al₂O₃ alloy. *Acta Materialia*, 45(3):1297–1306, 1997. [https://doi.org/10.1016/S1359-6454\(96\)00225-X](https://doi.org/10.1016/S1359-6454(96)00225-X).
- [155] C. M. F. Rae and R. C. Reed. Primary creep in single crystal superalloys: Origins, mechanisms and effects. *Acta Materialia*, 55(3):1067–1081, 2007. <https://doi.org/10.1016/j.actamat.2006.09.026>.
- [156] P. N. T. Unwin, G. W. Lorimer, and R. B. Nicholson. The origin of the grain boundary precipitate-free zone. *Acta Metallurgica*, 17(11):1363–1377, 1969. [https://doi.org/10.1016/0001-6160\(69\)90154-0](https://doi.org/10.1016/0001-6160(69)90154-0).
- [157] S. R. Ramdoss, A. Kauffmann, G. Winkens, D. Schliephake, F. Hinrichs, H. Thota, Y. M. Eggeler, F. Galgon, C. Zenk, R. Schwaiger, and M. Heilmaier. Strengthening contributions in a two-phase eutectic Mo-Si-Ti alloy. *under review*.
- [158] D. Low, T. Sumii, and M. Swain. Thermal expansion coefficient of titanium casting. *Journal of Oral Rehabilitation*, 28(3):239–242, 2001. <https://doi.org/10.1111/j.1365-2842.2001.00664.x>.

- [159] T. Spittel and M. Spittel. Part 3: Non-ferrous alloys – heavy metals. In H.P. Warlimont, editor, *Landolt-Börnstein – Group VIII: Advanced Materials and Technologies, Volume 2 C3: Metal Forming Data*, Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology – New Series, pages 1–668. Springer, Berlin, Heidelberg, 2015.
- [160] J. J. Williams, M. J. Kramer, and M. Akinc. Thermal expansion of Ti_5Si_3 with Ge, B, C, N, or O additions. *Journal of Materials Research*, 15(8):1780–1785, 2000. <https://doi.org/10.1557/JMR.2000.0257>.
- [161] F. A. Mohamed and T. G. Langdon. The transition from dislocation climb to viscous glide in creep of solid solution alloys. *Acta Metallurgica*, 22(6):779–788, 1974. [https://doi.org/10.1016/0001-6160\(74\)90088-1](https://doi.org/10.1016/0001-6160(74)90088-1).
- [162] P. M. Kelly, A. Jostsons, R. G. Blake, and J. G. Napier. The determination of foil thickness by scanning transmission electron microscopy. *physica status solidi (a)*, 31(2):771–780, 1975. <https://doi.org/10.1002/pssa.2210310251>.
- [163] S. M. Allen. Foil thickness measurements from convergent-beam diffraction patterns. *Philosophical Magazine A*, 43(2):325–335, 1981. <https://doi.org/10.1080/01418618108239412>.
- [164] T. Malis, S. C. Cheng, and R. F. Egerton. EELS log-ratio technique for specimen-thickness measurement in the TEM. *Journal of Electron Microscopy Technique*, 8(2):193–200, 1988. <https://doi.org/10.1002/jemt.1060080206>.
- [165] A. J. E. Foreman and M. J. Makin. Dislocation movement through random arrays of obstacles. *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, 14(131):911–924, 1966. <https://doi.org/10.1080/14786436608244762>.
- [166] R. Rosenkranz, G. Frommeyer, and W. Smarsly. Microstructures and properties of high melting point intermetallic Ti_5Si_3 and TiSi_2 compounds. *Materials Science and Engineering: A*, 152(1):288–294, 1992. [https://doi.org/10.1016/0921-5093\(92\)90081-B](https://doi.org/10.1016/0921-5093(92)90081-B).
- [167] S. Spigarelli, M. Cabibbo, E. Evangelista, and T. G. Langdon. Creep properties of an Al-2024 composite reinforced with SiC particulates. *Materials Science and*

- Engineering: A*, 328:39–47, 2002. [https://doi.org/10.1016/S0921-5093\(01\)01698-7](https://doi.org/10.1016/S0921-5093(01)01698-7).
- [168] E. I. Samuel, B. K. Choudhary, D. P. R. Palaparti, and M. D. Mathew. Creep deformation and rupture behaviour of P92 steel at 923K. *Procedia Engineering*, 55:64–69, 2013. <https://doi.org/10.1016/j.proeng.2013.03.220>.
- [169] M. D. Mathew, J. Vanaja, K. Laha, G. V. Reddy, K. S. Chandrashekhara, and K. B. S. Rao. Tensile and creep properties of reduced activation ferritic–martensitic steel EUROFER97 in the temperature range 300–823K. *Journal of Nuclear Materials*, 417:77–84, 2011. <https://doi.org/10.1016/j.jnucmat.2011.04.050>.
- [170] F. Xue, C. H. Zenk, L. P. Freund, S. Neumeier, and M. Göken. Understanding raft formation and precipitate shearing during double minimum creep in a γ' -strengthened single crystalline Co-base superalloy. *Philosophical Magazine*, 101:326–344, 2020. <https://doi.org/10.1080/14786435.2020.1836415>.
- [171] H. A. Calderon, G. Kostorz, and G. Ullrich. Microstructure and plasticity of two molybdenum-base alloys (TZM). *Materials Science and Engineering: A*, 160(2):189–199, 1993. [https://doi.org/10.1016/0921-5093\(93\)90447-M](https://doi.org/10.1016/0921-5093(93)90447-M).
- [172] C. Cui, H. Duan, X. Zhu, M. Wu, M. Fan, Q. Liu, Z. Tian, G. Zhu, S. Chen, Q. Li, S. Liu, Z. Li, H. Wang, and S. Wei. Microstructure and mechanical behavior of a novel eutectic high-entropy alloy strengthened by laves phase. *Journal of Alloys and Compounds*, 967:171716, 2023. <https://doi.org/10.1016/j.jallcom.2023.171716>.
- [173] Y. Li and T. G. Langdon. A unified interpretation of threshold stresses in the creep and high strain rate superplasticity of metal matrix composites. *Acta Materialia*, 47(12):3395–3403, 1999. [https://doi.org/10.1016/S1359-6454\(99\)00219-0](https://doi.org/10.1016/S1359-6454(99)00219-0).
- [174] Y. Li and T. G. Langdon. An examination of a substructure-invariant model for the creep of metal matrix composites. *Materials Science and Engineering A*, 265:276–284, 1999. [https://doi.org/10.1016/S0921-5093\(98\)00728-8](https://doi.org/10.1016/S0921-5093(98)00728-8).

- [175] Y. Li and T. G. Langdon. Creep behavior of an Al-6061 metal matrix composite reinforced with alumina particulates. *Acta Materialia*, 45(11):4797–4806, 1997. [https://doi.org/10.1016/S1359-6454\(97\)00132-8](https://doi.org/10.1016/S1359-6454(97)00132-8).
- [176] R. Lagneborg and B. Bergman. The stress/creep rate behaviour of precipitation-hardened alloys. *Metal Science*, 10(1):20–28, 1976. <https://doi.org/10.1179/030634576790431462>.
- [177] F. C. Larché. Nucleation and precipitation on dislocations. In *Dislocations in Solids*, volume 4, pages 135–153. North-Holland, Amsterdam, 1979.
- [178] P. Villars. Inorganic solid phases. SpringerMaterials (online database), 2015. https://materials.springer.com/isp/phase-diagram/docs/c_0107112.
- [179] P. Jain and K. S. Kumar. Dissolved Si in Mo and its effects on the properties of Mo–Si–B alloys. *Scripta Materialia*, 62(1):1–4, 2010. <https://doi.org/10.1016/j.scriptamat.2009.09.008>.
- [180] I. Thibon, D. Ansel, M. Boliveau, and J. Debuigne. Interdiffusion in the β Mo–Ti solid solution at high temperatures. *International Journal of Materials Research*, 89(3):187–191, 1998. <https://doi.org/10.3139/ijmr-1998-0034>.
- [181] D. M. Dimiduk and J. H. Perepezko. Mo–Si–B Alloys: Developing a Revolutionary Turbine-Engine Material. *MRS Bulletin*, 28(9):639–645, 2003. <https://doi.org/10.1557/mrs2003.191>.
- [182] M. Legros, G. Dehm, E. Arzt, and T. J. Balk. Observation of Giant Diffusivity Along Dislocation Cores. *Science*, 319(5870):1646–1649, 2008. <https://doi.org/10.1126/science.1151771>.
- [183] W. G. Burgers. On the process of transition of the cubic-body-centered modification into the hexagonal-close-packed modification of zirconium. *Physica*, 1(7):561–586, 1934. [https://doi.org/10.1016/S0031-8914\(34\)80244-3](https://doi.org/10.1016/S0031-8914(34)80244-3).
- [184] M. X. Zhang and P. M. Kelly. Crystallographic features of phase transformations in solids. *Progress in Materials Science*, 54(8):1101–1170, 2009. <https://doi.org/10.1016/j.pmatsci.2009.06.001>.

- [185] F. Liu, R. Xin, X. Wen, X. Gu, and Q. Liu. Four new orientation relationships of $\text{Mg}_{17}\text{Al}_{12}$ phase with magnesium matrix in Mg-8Al-0.5Zn alloys. *Journal of Magnesium and Alloys*, 11(12):4689–4695, 2023. <https://doi.org/10.1016/j.jma.2021.09.014>.
- [186] B. Décamps, M. Condat, P. Caron, and T. Khan. Dissociated matrix dislocations in a γ/γ' Ni-based single crystal superalloy. *Scripta Metallurgica*, 18(10):1171–1174, 1984. [https://doi.org/10.1016/0036-9748\(84\)90200-X](https://doi.org/10.1016/0036-9748(84)90200-X).
- [187] B. Décamps, S. Raujol, A. Coujou, F. Pettinari-Sturmel, N. Clément, D. Locq, and P. Caron. On the shearing mechanism of γ' precipitates by a single $\frac{a}{6}\langle 112 \rangle$ shockley partial in Ni-based superalloys. *Philosophical Magazine*, 84(1):91–107, 2004. <https://doi.org/10.1080/14786430310001621472>.
- [188] J-P. Couzinié, M. Heczko, V. Mazánová, O. N. Senkov, M. Ghazisaeidi, R. Banerjee, and M. J. Mills. High-temperature deformation mechanisms in a BCC+B2 refractory complex concentrated alloy. *Acta Materialia*, 233:117995, 2022. <https://doi.org/10.1016/j.actamat.2022.117995>.
- [189] G. Scheunemann-Frerker, H. Gabrisch, and M. Feller-Kniepmeier. Dislocation microstructure in a single-crystal nickel-based superalloy after tensile testing at 823 K in the [001] direction. *Philosophical Magazine A*, 65(6):1353–1368, 1992. <https://doi.org/10.1080/01418619208205609>.
- [190] J. W. Pugh. Tensile Properties of Molybdenum at Elevated Temperatures. *Transactions of the American Society for Metals*, 47:984, 1955.
- [191] H. J. Frost and M. F. Ashby. *Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics*. Pergamon Press, Oxford, 1982.
- [192] H. Wu. Identification of the creep-induced deformation mechanism of a eutectic Mo-Si-Ti alloy by means of electron microscopy. Master’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2022.

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INTRODUCTION

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