



High-temperature sulfidation behavior of refractory TaMoCrTiAl(–3 W) high entropy alloys

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ABSTRACT

Despite the excellent sulfidation resistance of binary refractory metal–aluminum alloys, their rapid oxidation above 900°C remains a critical limitation for high-temperature applications. This study aims to bridge this gap by evaluating refractory high-entropy alloys (RHEAs), which offer the potential to simultaneously exhibit oxidation and sulfidation resistance. The high-temperature sulfidation behavior of TaMoCrTiAl and TaMoCrTiAl–3 W RHEAs was investigated in the temperature range of 800–1000°C at a sulfur vapor pressure of 1000 Pa. Kinetic measurements revealed diffusion-controlled mechanism. The sulfidation rates were found to be exceptionally low (k_p in the range of 10^{-13} – 10^{-11} g² cm⁻⁴ s⁻¹), outperforming pure molybdenum and conventional amorphous Al–Mo alloys, as well as the oxidation rates of standard chromia-formers. The superior corrosion resistance is attributed to the formation of complex, protective scales composed of a mixture of oxides (Al₂O₃, Cr₂O₃, TiTaO₄, TiO₂) and sulfides (CrS and refractory metal sulfides). The presence of highly protective oxides and sulfides in the scale provides a highly effective barrier against reagent transport, making these RHEAs promising candidates for structural applications in multi-oxidant, harsh environments.

1. Introduction

Materials in many branches of modern industry are exposed to sulfur-containing atmospheres at high temperatures [1,2]. However, to date, no alloys have been successfully developed to withstand simultaneous sulfidation and oxidation at temperatures exceeding 900°C. Conventional oxidation resistant alloys undergo accelerated degradation in sulfur-containing atmospheres [1–4]. This behavior is mainly attributed to the high concentration of point defects (mainly cation vacancies) in sulfides which are orders of magnitude higher than in the corresponding metal oxides [4]. Consequently, the diffusional transport of reagents across sulfide scales, which determines the overall reaction rate, is relatively rapid. Pure refractory metals demonstrate specific high resistance against sulfur attack with sulfidation rates comparable to the oxidation rates of chromia-forming alloys [2,4,5]. This situation generally results from lower point defect concentrations (and/or their

very low diffusivities) in refractory metal sulfides [4,5] than in common-metal-based counterparts. Thus, alloying with refractory metals considerably reduces the sulfidation rate of common principal metals, i. e. iron, cobalt and nickel [6–8].

Simultaneous additions of refractory metals and Al to conventional principal elements increase sulfidation resistance even further. For example, the sulfidation rate of Fe30Mo9Al alloy is comparable to that obtained for pure molybdenum [9,10]. Unfortunately, the mechanical properties of this alloy are rather poor and numerous cracks within metallic core have been observed during sulfidation. Up to date, the amorphous binary alloys Al–Mo, Al–Nb and Al–Ta demonstrate the most superior sulfidation resistance [11–20]. This resistance is attributed to the excellent protective properties of the thermally grown bilayer scale, which constitutes a diffusion barrier for the reactants. Generally, the outer layer constitutes Al₂S₃, whereas the inner layer consists of the refractory–metal sulfide. The presence of aluminum within the

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refractory–metal sulfide layer creates a doping effect. This reduces the native point defect concentration compared to pure metal sulfides, leading to a significantly lower degradation rate [11]. Although the sulfidation resistance of such alloys is very good, they undergo relatively fast oxidation above a certain critical temperature, despite the relatively high aluminum content [11,16–20]. For example, sputter-deposited Al–Mo binary alloys possess good resistance against oxidation up to 850°C, and silicon addition to such alloys increases their oxidation resistance merely to about 950°C [21]. It should be noted that addition of a second refractory metal to binary amorphous alloys only slightly increases their sulfidation resistance without improving oxidation resistance [22]. Additionally, replacing aluminum with chromium in a binary alloy has no beneficial influence when it comes to reducing the sulfidation rate in comparison with binary alloys consisting of a given refractory metal and aluminum [23].

Recently, refractory high-entropy alloys (RHEAs) have emerged as a promising materials class for high-temperature application in harsh environments [24–30]. Several RHEAs have been reported to retain high mechanical strength at temperatures approaching 1200–1400°C, making them promising structural material candidates for temperatures beyond the application range of Ni–base alloys [24–30]. In parallel, it has been demonstrated that selected RHEAs containing refractory metals together with chromium and aluminum exhibit outstanding oxidation resistance, in some cases [31–33] approaching that of classical alumina-forming alloys even at temperatures as high as 1400°C. In particular, alloys in the Ta–Mo–Cr–Ti–Al system have shown the ability to form protective, slow-growing rutile-structure complex oxide scales, making them highly attractive for extreme-environment applications [31,33]. Recent report [34] indicates that W addition may further improve its oxidation resistance. It has been shown, namely, that the beneficial effect of W on oxidation resistance is primarily attributed to two factors. First, W can reduce the solubility and diffusivity of oxygen in the alloy matrix. Second, W can be incorporated into the rutile oxide scale, where it acts as a dopant and reduces the concentration of oxygen vacancies, leading to lower oxygen transport rates through the scale. The beneficial effect of W on oxidation resistance via decreasing the solubility and diffusivity of oxygen can be rationalized from both thermodynamic and experimental perspectives. The W–O equilibrium phase diagram [35] indicates a negligible solubility of oxygen in W, even at elevated temperatures. Furthermore, similar beneficial effects of W additions on oxidation resistance have been reported in other high-entropy alloys and Fe-based alloys [36,37], where W doping was shown to reduce oxidation rates. Given that TaMoCrTiAl contains refractory metals and aluminum, such alloys are possibly the materials that combine sulfidation and oxidation resistance at temperature clearly above 900°C.

The aim of this work is to verify the above-mentioned assumption by studying sulfidation behavior of TaMoCrTiAl and TaMoCrTiAl–3 W in the temperature range between 800 and 1000°C.

2. Materials and methods

The investigated alloys were produced from high-purity elemental granules (Ta 99.9%, Ti 99.7%, Mo 99.97%, Cr 99.94%, Al 99.9%) or powder (W 99.9%) using an arc melting furnace (AM/0.5, Edmund Bühler GmbH). The elements were weighed to achieve the target compositions: the TaMoCrTiAl alloy contained 20 at% of each principal element, while the W-modified alloy was prepared with 19.4 at% of each principal element and 3 at% of W. Arc melting was performed under an argon atmosphere (~0.6 atm) in a water-cooled copper mold, with each alloy button flipped and remelted at least five times to ensure compositional homogeneity. To remove the dendritic microstructure resulting from solidification, the alloys were subsequently homogenized for 20 h at 1500°C in a tube furnace (RHTC, Nabertherm GmbH) under flowing argon. Heating and cooling were performed at 100 K/h, and spongy titanium was used as a getter to minimize oxygen and nitrogen

partial pressures inside the tube. The chemical compositions of the synthesized alloys were verified using the ICP-OES method. The analyzed elemental concentrations (at%) were determined as follows: Ta (20.3), Mo (20.3), Cr (19.7), Ti (20.4), and Al (19.2) for the TaMoCrTiAl alloy; and Ta (19.5), Mo (19.7), Cr (19.4), Ti (19.4), Al (18.6), and W (3.0) for the TaMoCrTiAl–3 W alloy. Coupons for high-temperature sulfidation tests were sectioned from the homogenized alloy buttons and ground sequentially with SiC papers up to 2500 grit. The samples were then ultrasonically cleaned in ethanol to remove surface contaminants. The resulting coupons had approximate dimensions of $8 \times 8 \times 3$ mm³.

Both the alloy with and without W addition consist of a body-centered cubic (BCC) ordered B2 matrix with C14-type Laves phase (Cr₂Ta) decorating the grain boundaries. The addition of 3 at% W does not alter the phase constitution but leads to a pronounced grain refinement, reducing the average grain size from ~1000 µm to ~200 µm, as shown in Fig. 1. In addition, the volume fraction of the C14 Laves phase decreases from ~1.5% to ~0.7%, as estimated by image analysis. Further details on the microstructure and phase constitution of these alloys are provided in [34,38].

The sulfidation experiments were carried out in a He–S₂ gas mixture under isothermal–isobaric conditions at temperatures ranging from 800 up to 1000°C and sulfur vapor pressure equal to 1000 Pa. The reaction atmosphere flowed through the reaction chamber at a rate equal to 10 ml/min. All sulfidation tests, recorded up to 100 h, have been carried out in a microthermogravimetric apparatus enabling the mass changes of a given sample to be monitored continuously in a well-defined test environment with accuracy in mass change the order of 10^{−6} g. The sulfidation experiments were performed without interruption of the sulfur supply thanks to the application of two sulfur boilers. The desired sulfur vapor pressure in the reaction chamber of the microthermogravimetric apparatus was achieved by mixing sulfur vapor with high-purity helium (99.999%). In the resulting He–S₂ gas mixture, the sulfur partial pressure was controlled by both the helium flow rate and the temperature of the liquid sulfur, under a total pressure of 10⁵ Pa. This procedure ensures stable sulfur pressure in the reaction chamber, in a range from 5×10^4 –10^{−2} Pa.

At this point, the presence of oxygen in the sulfidation apparatus is worth explaining. In this type of experiment, helium is used as a protective gas for inner mechanical and electronic parts of the microbalance head, as well as a carrying medium for transporting sulfur vapors to the reaction chamber, where a given sample is investigated. Although the purity of helium used in those experiments was high (99.999%), the gas still contains approximately 1 ppm of both oxygen and water vapor as impurities. This means that at the applied temperatures, under thermodynamic equilibrium conditions, the oxygen pressure remains in the range of 10^{−16} to 10^{−13} atm. This is sufficient to form oxide phases.

Details concerning the utilized microthermogravimetric apparatus, as well as the experimental procedure, were described elsewhere [39].

The phase composition of the corrosion scales formed on the exposed alloys was analyzed by X-ray diffraction (XRD) using a Seifert PAD II diffractometer in Bragg–Brentano geometry. Measurements were performed with Cu Kα₁ radiation ($\lambda = 0.15406$ nm), employing a step size of 0.01° and a scan rate of 1°/min to ensure high angular resolution. Microstructural and compositional characterization, including surface morphology, cross-sectional features, and elemental distribution, was carried out using scanning electron microscopy (SEM) (JEOL JSM–6400 and Zeiss MERLIN) and field-emission electron probe microanalyzer (FE–EPMA) (JXA–iHP200F), both equipped with energy-dispersive X-ray spectroscopy (EDS). A WDS (wavelength-dispersive spectroscopy) detector is used in EPMA for quantitative chemical analysis. Subsurface chemical analysis was performed on selected specimens using Auger electron spectroscopy (AES) with a PHI 710e/680 Hybrid Auger Nanoprobe. Depth profiles were obtained by argon ion sputtering at an acceleration voltage of 3 kV and a beam current of 3 µA. Nanoscale structural and chemical characterization of the scale was conducted on one selected sample using scanning transmission electron microscopy

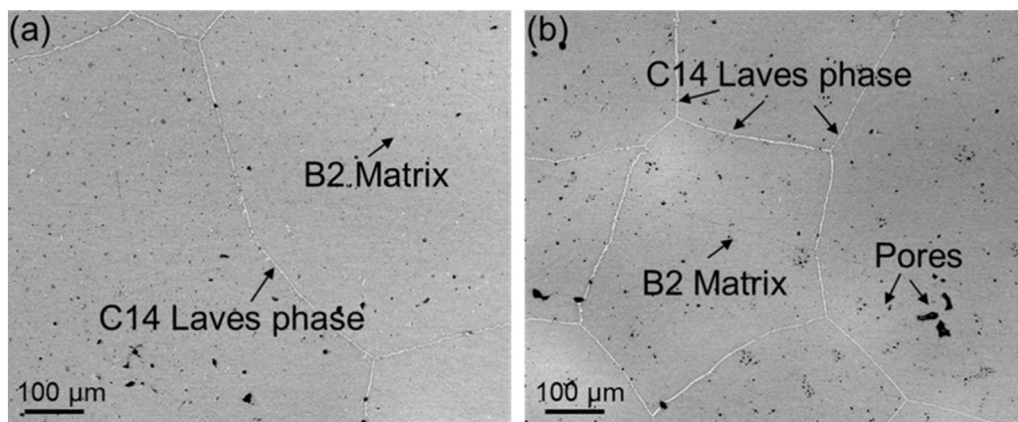


Fig. 1. BSE images taken from cross-sections of the homogenized alloys: (a) TaMoCrTiAl, (b) TaMoCrTiAl-3 W.

(STEM). Cross-sectional lamellae were prepared by focused ion beam (FIB) milling in a Zeiss Auriga workstation and thinned using Ga ions at 30 kV. STEM analysis was performed on a Talos F200X (Thermo Fisher Scientific) operated at 200 kV. Microstructural characterization included bright-field (BF) and dark-field (DF) imaging, selected area electron diffraction (SAED), as well as high-angle annular dark-field

(HAADF) imaging to resolve nanoscale structural and compositional features.

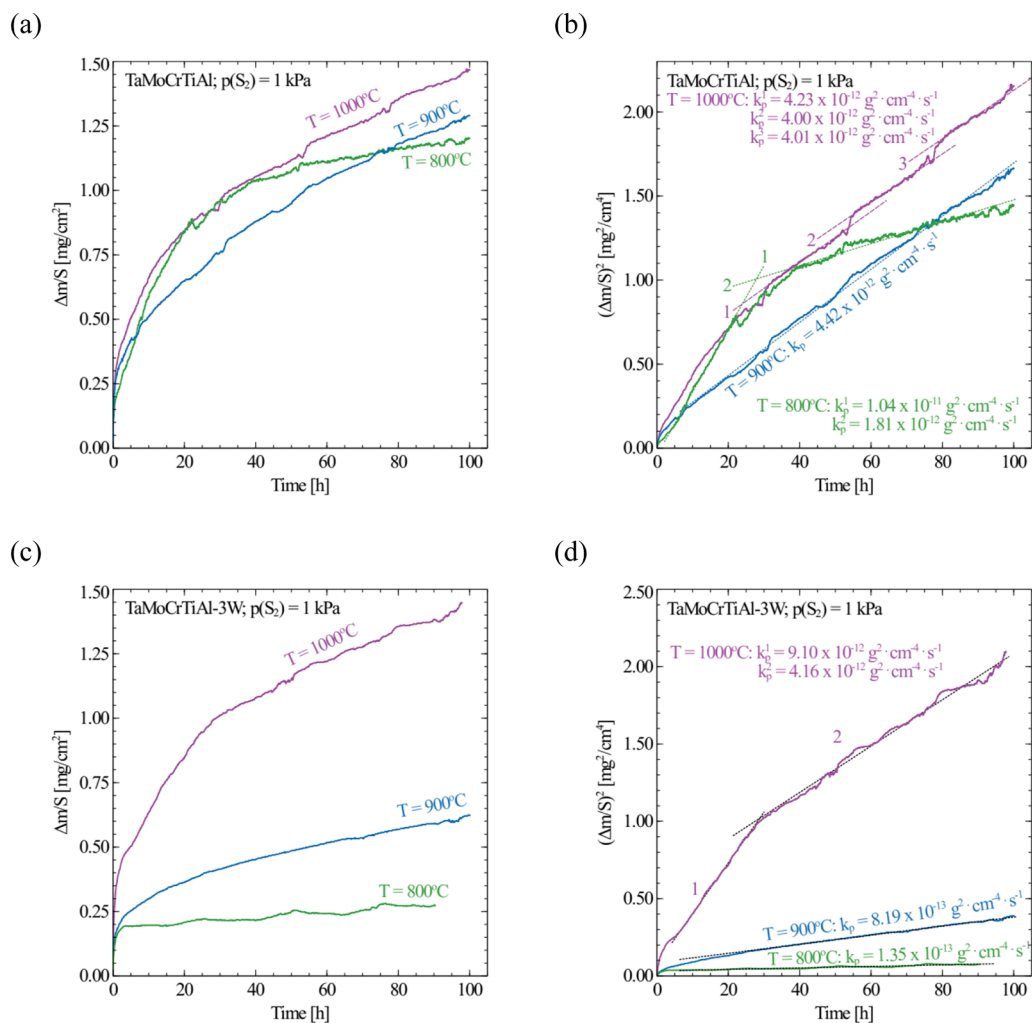


Fig. 2. Reaction kinetics obtained between 800 and 1000°C for 1 kPa sulfur vapor pressure, and $< 10^{-11}$ Pa oxygen pressure. (a) TaMoCrTiAl, linear system of coordinates, (b) TaMoCrTiAl, parabolic system of coordinates, (c) TaMoCrTiAl-3 W, linear system of coordinates, (d) TaMoCrTiAl-3 W, parabolic system of coordinates.

3. Results

3.1. Isothermal sulfidation experiments between 800 and 1000°C

The reaction kinetics of TaMoCrTiAl and TaMoCrTiAl-3 W high-entropy alloys obtained at different temperatures are presented in Fig. 2. The mass change versus time curves for the TaMoCrTiAl alloy samples recorded at 900 and 1000°C showed significant similarities in shape and slope. In contrast, the kinetics recorded at 800°C stand out. During the initial period up to approximately 40 h, it follows the trend recorded at 1000°C, but after this point, the slope noticeably decreases. Regardless of the shape of the resulting curves, the relative differences in the final mass gains between individual samples do not exceed 20%. However, cross-sectional analyses later clearly show a pronounced increase in corrosion-layer thickness with increasing temperature. The apparent similarity in mass gains could be attributed to microstructural defects. In addition, after an initial period lasting from about 5–20 h (Fig. 2(b)), the process approximately follows the parabolic rate law, indicating that it is diffusion controlled. The parabolic rate constant calculated for steady sulfidation stages is comparable for the three applied temperatures and is of the order of $10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$. This value is relatively low, suggesting that the formed scales exhibit good protective properties. Fig. 2(c),(d), in turn, show TaMoCrTiAl-3 W alloy sulfidation kinetics under analogous conditions. From the data illustrated in Fig. 2(c),(d) it suggests that sulfidation temperature has a significant influence on the reaction rate, which increases along with temperature. The variation in the parabolic rate constant with increasing sulfidation time is mainly attributed to the influence of edge effects (more pronounced at lower temperatures) and the presence of internal porosity in the alloy. In the early stages of sulfidation, these features can provide additional pathways for sulfur ingress and accelerate the initial reaction kinetics, resulting in a relatively higher apparent parabolic rate constant. In the case of W-modified alloy, as in the previous case, after an initial reaction period, the process can be described by parabolic kinetics. However, at the highest tested temperature, the parabolic sulfidation rate constant is comparable to the values obtained for the TaMoCrTiAl alloy, whereas at 800°C it assumes a lower value the order of $10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$.

According to X-ray diffraction analysis, the scales grown on the studied alloys are heterogenous and their surfaces are composed of mainly oxide phases, such as $(\text{Cr,Al})_2\text{O}_3$, TiTaO_4 and TiO_2 (Fig. 3). Several low-intensity peaks that are difficult to index were also detected, and are likely associated with sulfide phases, primarily CrS. Due to their low concentration in the scale (<2%—detection limit of the

method), these phases could not be definitively identified by XRD. Nonetheless, EPMA, EDX, and particularly subsequent TEM analyses (shown later in this section) confirm their presence.

Surface morphologies of the studied alloys after high-temperature corrosion tests are illustrated in Fig. 4. Outside the grain boundary areas, the scale surface is practically flat and homogeneous. For both alloys, significant corrosion-product formation is observed primarily along the grain boundaries, which protrude above the relatively flat grain interiors. This effect is particularly visible at the lowest applied temperature and becomes minor as temperature increases. This indicates that grain boundary diffusion is predominant at lower temperatures, while lattice diffusion becomes more prominent as temperature increases. Additionally, in the case of the TaMoCrTiAl alloy, the size and density of the faster-growing scale areas appear to be greater. This phenomenon is associated with the lower volume fraction and smaller size of the Cr_2Ta Laves phase located on grain boundaries in the TaMoCrTiAl-3 W alloy compared to the undoped TaMoCrTiAl alloy, as shown in Figs. 1, 5, and 6.

During Cr_2Ta sulfidation, the formation of both tantalum and chromium sulfides is generally expected. However, according to literature data, the diffusion coefficient of chromium in Cr_2Ta [40] is several orders of magnitude greater than that of tantalum. This significantly faster diffusion is the primary reason chromium reaches the scale surface to react with sulfur and form CrS. Although XRD results did not explicitly identify the chromium sulfide phase within the corrosion product layer, its presence can be anticipated based on the EDX analysis and TEM observations described later in this section.

Figs. 5 and 6 present cross-sections of TaMoCrTiAl and TaMoCrTiAl-3 W samples tested at temperatures of 800 and 900°C, respectively. The surface of the samples investigated at 800°C (Fig. 5(a) and (b)), except for the grain boundary areas, is covered with a thin layer of reaction products. The flat, thin scale (about 2 μm in thickness at 900°C, see Fig. 6) has a bilayer structure (Fig. 5(b)), in which the outer part consists of a mixture of TiO_2 and $(\text{Cr,Al})_2\text{O}_3$ oxides and CrS sulfide. The inner part on the other hand is primarily composed of rutile-structured TiTaO_4 containing metallic molybdenum inclusions. Below the scale, there is an internal corrosion zone with a thickness comparable to both scale layers combined. In contrast, in the grain boundary areas, the scale is locally significantly thicker and consists mainly of the CrS phase. The distinct growth of the scale in these areas correlates with the presence of the Cr_2Ta phase (intermetallic Laves phase) decorating the grain boundaries in the studied alloys. During corrosion process, the Cr-rich Laves phase provides a favorable local source of Cr for the formation of CrS. Consequently, CrS is preferentially formed in the vicinity of the Laves phase. The above-average increase in the thickness of the product layer, composed mainly of chromium sulfide, results from the relatively rapid diffusion of chromium in the intermetallic phase [40], facilitating the transport of this element to the surface.

Essentially the same scale structure was observed on the alloys tested at 900°C (Fig. 6), with the difference that the individual layers of the bilayer scale were significantly thicker, and the outgrowths forming over the grain boundaries in the substrate were much more extensive. Additionally, the presence of isolated alumina (Al_2O_3) precipitates was confirmed in the internal corrosion zone. The nearly identical structure and thickness of the scales forming on the alloys both with and without the addition of tungsten confirm that its presence in the alloy has no significant effect on the kinetics or the scale formation mechanism of intergranular corrosion, which, to some extent, contradicts the results obtained from TGA. The observations conducted on the cross-sections correlate well with the surface morphology observations of the tested samples (Fig. 4), where the rapid growth of scales in the grain boundary areas is clearly visible.

The chemical composition analysis performed using the EDX technique in the grain boundary area of the TaMoCrTiAl alloy (without tungsten addition) tested at 900°C, shown in Fig. 7, clearly demonstrates that chromium and sulfur dominate in the area of the scale thickening

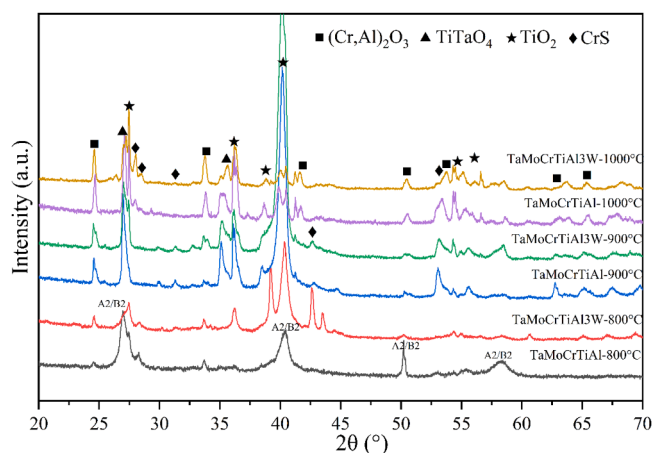


Fig. 3. X-ray diffraction patterns received from TaMoCrTiAl and TaMoCrTiAl-3 W alloys after 100 h of reaction in sulfidizing-oxidizing conditions at sulfur vapor pressure equal to 1 kPa and temperatures ranging from 800°C to 1000°C.

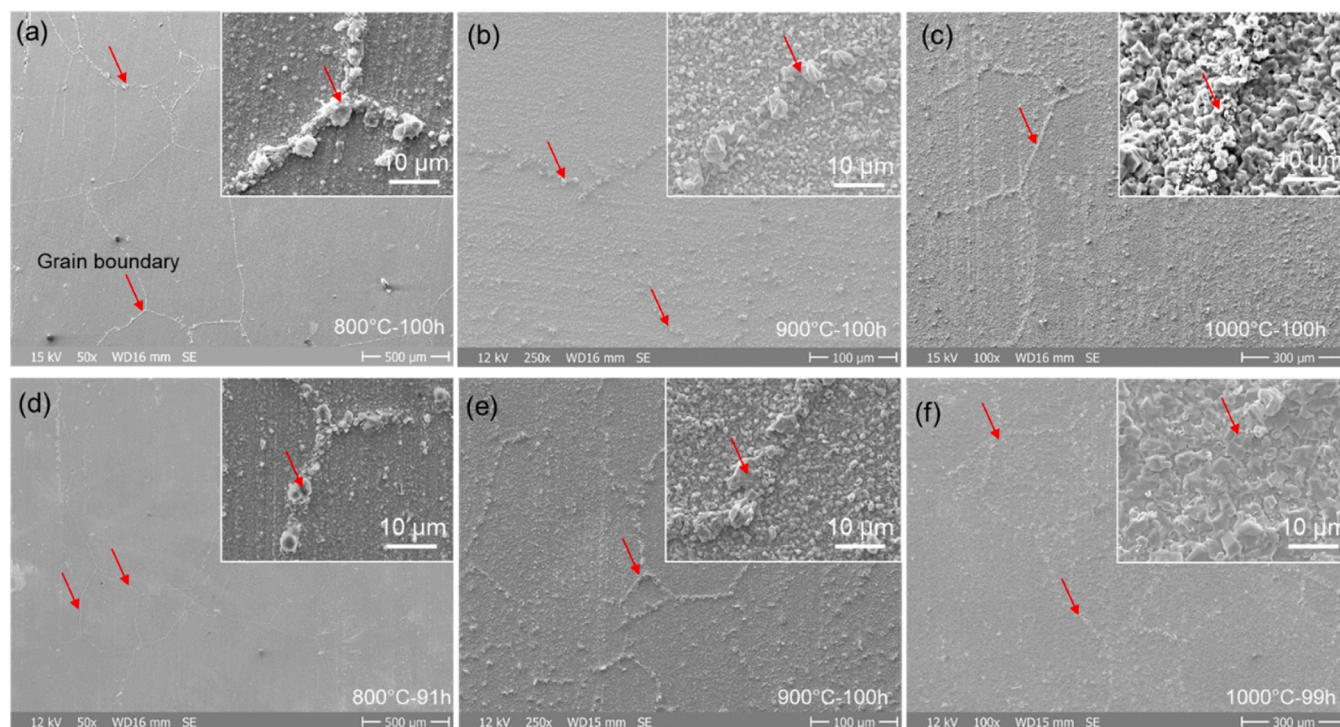


Fig. 4. SEM surface images of (a), (b), (c), TiMoCrTiAl and (d), (e), (f), TaMoCrTiAl-3 W alloys after corrosion tests. Red arrows indicate grain boundary regions. The inserted images at right corner are taken at higher/same magnification highlighting the grain boundary regions.

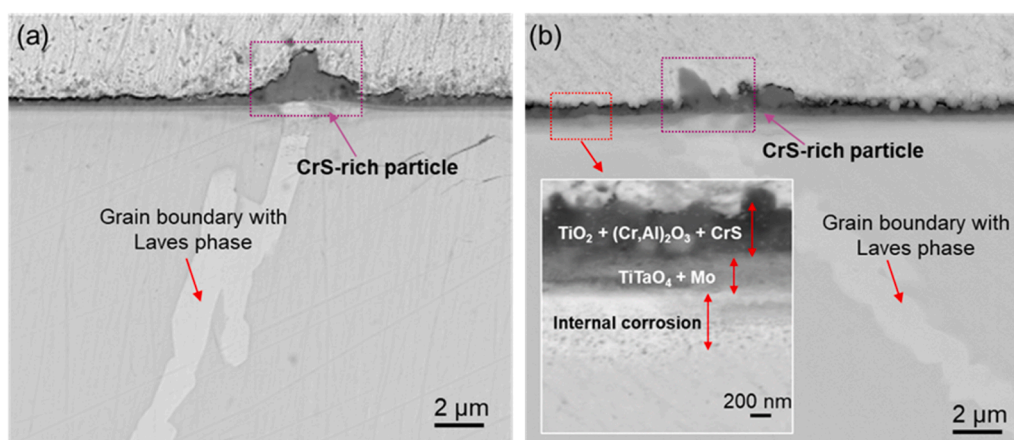


Fig. 5. Cross-section of the (a) TaMoCrTiAl and (b) TaMoCrTiAl-3 W alloys tested at 800°C under 1 kPa sulfur vapor pressure.

directly above the grain boundary, accompanied by aluminum, titanium, and oxygen. In contrast, the thin, flat scale growing over the alloy grains is mainly composed of titanium, aluminum, molybdenum, and oxygen. These analyses also confirm that the grain boundary area is enriched in chromium and tantalum—the primary components forming the Cr_2Ta Laves phase.

In turn, EPMA elemental mapping (Fig. 8) performed on the tungsten-containing alloy sample tested at 900°C in two different surface areas reveals that the scale growing over the grain boundary area contains a significant amount of titanium in the outer layer, in addition to sulfur and chromium located in the inner part of the scale. Tantalum and chromium are primarily located in the precipitates constituting the Laves phase. The presented maps also show that Mo and Ta practically do not migrate from the metallic substrate into the scale. Conversely, maps produced in an area far from the grain boundary confirm the layered structure of the scale. In the outer part of the scale, layers rich in

chromium, titanium, sulfur, and oxygen were identified using this technique. The inner part of the scale contains elements such as tungsten, molybdenum, and tantalum—the latter two being practically absent in the scale at 800°C—as well as sulfur and oxygen, forming the internal corrosion zone. In contrast to sulfidation–oxidation reaction at lower temperatures, the scale formed at 1000°C on both alloys (Fig. 9) exhibits a similar microstructure, but with increased overall thickness, followed by a zone showing features characteristic of internal corrosion. A distinctive difference is the presence of a discontinuous Al_2O_3 layer located between the middle rutile-structured TiTaO_4 layer and the internal corrosion zone, which consists of a mixture of refractory metals, alumina, and sulfides. Cross-sectional observations further confirm that the scale thickness is essentially identical for both alloys in regions away from grain boundaries (Fig. 9).

The oxide and sulfide designations shown in Figs. 5–9, proposed based on chemical composition studies, are only indicative in nature,

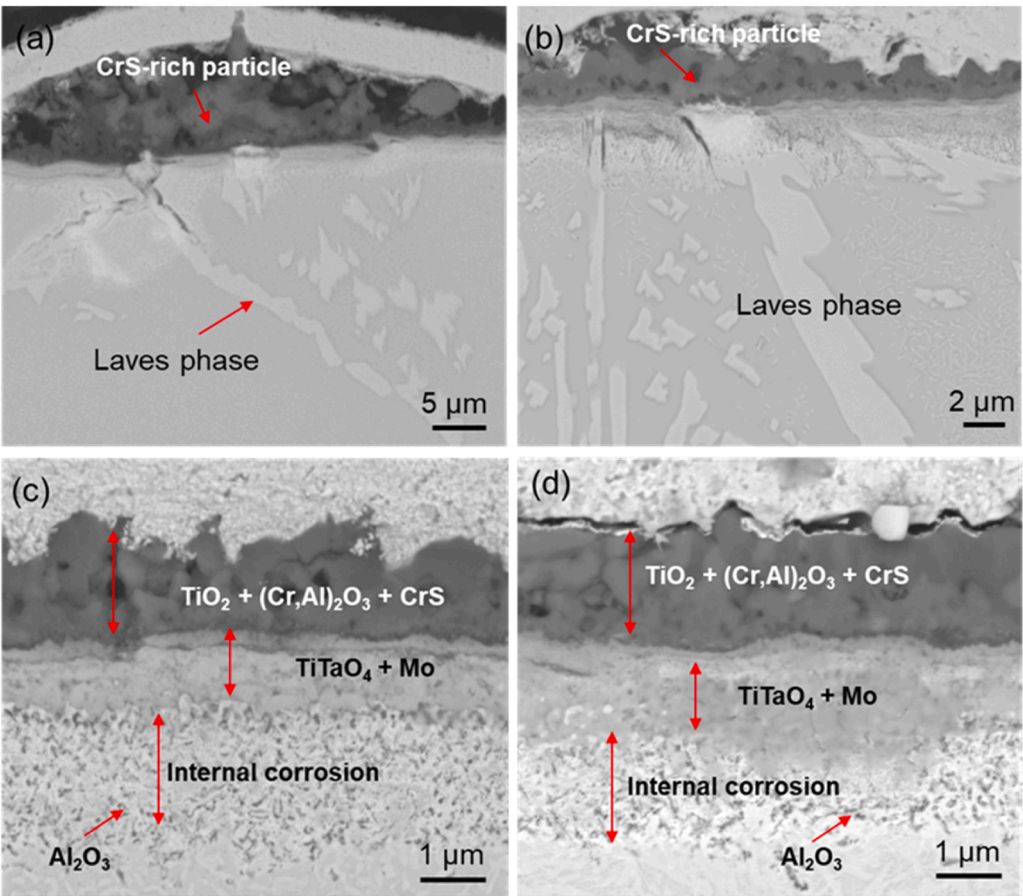


Fig. 6. Cross-section of (a), (c) TaMoCrTiAl and (b), (d) TaMoCrTiAl-3 W alloys tested at 900°C under 1 kPa sulfur vapor pressure. Panels (c) and (d) were acquired at locations away from grain boundaries and at the same magnification, revealing very similar corroded layer thicknesses.

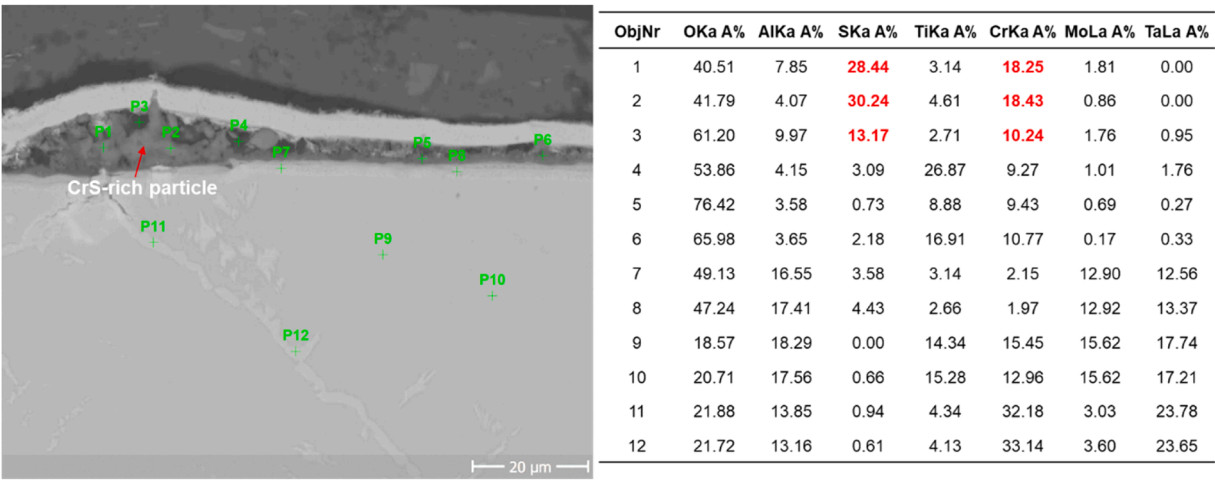


Fig. 7. SEM cross-section image of a grain boundary region of TaMoCrTiAl alloy tested at 900°C with EDX chemical composition analysis. Results highlighted in red corresponds to the presence of CrS phase.

and therefore complementary studies were conducted using STEM-EDX and SAED techniques of TaMoCrTiAl-3 W after corrosion at 1000°C. Fig. 10 presents a general TEM-HAADF image and corresponding EDS maps of the corrosion scale, while detailed chemical compositions and phase identification via SAED at the surface layer/inner TiTaO₄ layer interface and inner TiTaO₄ layer/internal corrosion zone interface are shown in Figs. 11 and 12, respectively. The multilayered structure of the corrosion scale is clearly resolved in the high-magnification HAADF

image, with interfaces roughly delineated by the dashed white lines in Fig. 11. Discontinuous Al₂O₃ layer, located at the inner TiTaO₄ layer/internal corrosion zone interface, is occasionally observed to extend into the inner TiTaO₄ layer. EDS mapping and SAED further confirm the formation of CrS within the surface layer, in addition to rutile TiO₂ and the solid solution (Cr, Al)₂O₃ (Fig. 11). The (Cr,Al)₂O₃ in the surface layer exhibits chemical gradient, with Al enrichment toward the internal interface. Precipitation

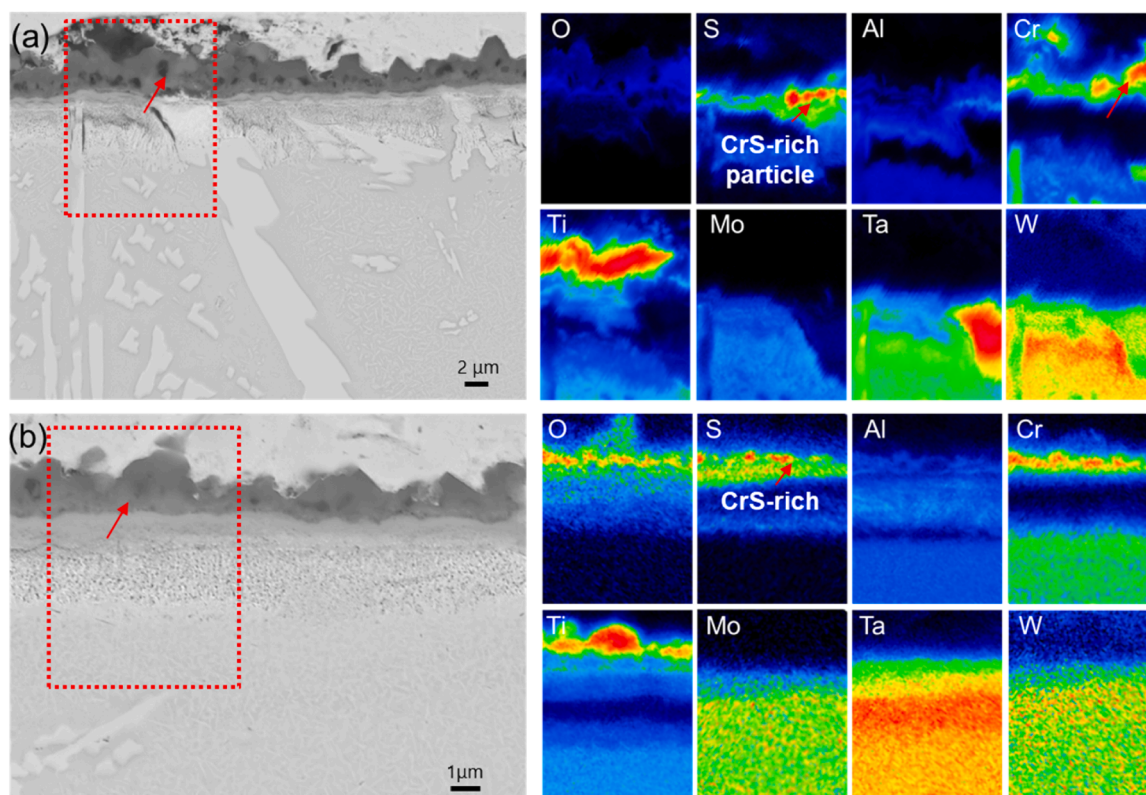


Fig. 8. EPMA elemental maps of the regions marked by dashed rectangles of TaMoCrTiAl-3 W alloy tested at 900°C: (a) region above a grain boundary containing large Cr_2Ta Laves-phase particle; (b) region above the grain interior.

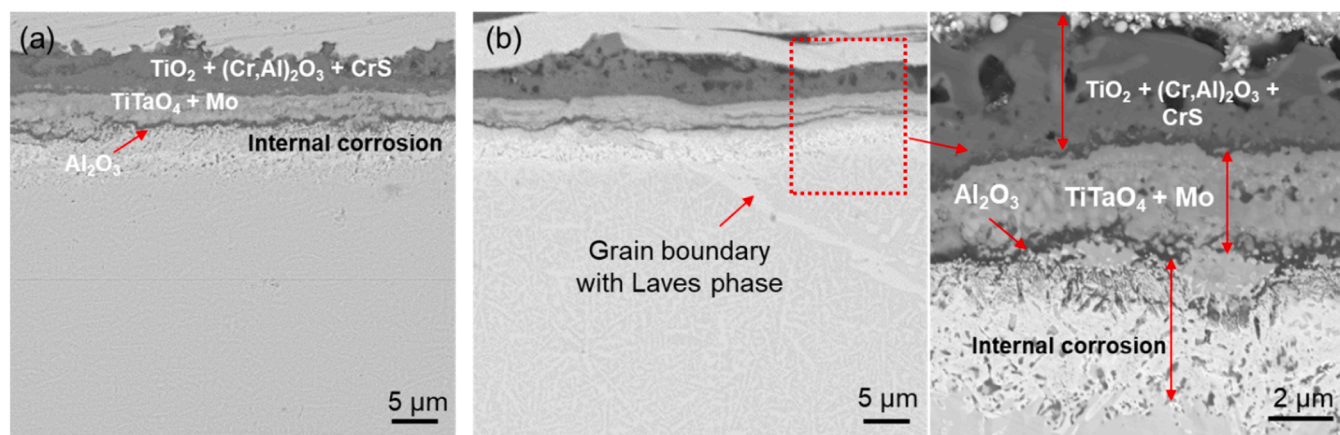


Fig. 9. SEM cross-section images of (a) TaMoCrTiAl and (b) TaMoCrTiAl-3 W alloy after corrosion in sulfidizing-oxidizing conditions at 1000°C.

of metallic Mo particles within the inner TiTaO_4 layer, as well as Al_2O_3 precipitates, is also confirmed by SAED (Fig. 12). TEM-HAADF imaging and EDS elemental mapping of the internal corrosion zone (Fig. 13) reveal that it primarily consists of unoxidized Mo and Ta, together with Al_2O_3 precipitates, and minor CrS and TiS phases.

3.2. Scale evolution at 1000°C of TaMoCrTiAl-3 W

Short-term experiments in sulfidizing-oxidizing conditions (1–10 h) were performed on TaMoCrTiAl-3 W to track the early-stage formation and evolution of the corrosion scale and to elucidate the underlying corrosion mechanisms. Fig. 14 shows representative cross-sectional SEM images together with corresponding AES depth profiles. After 5 h of reaction, the characteristic multilayered corrosion scale structure

observed after long-term exposure (Fig. 9) is already well developed. In contrast, after only 1 h of exposure (Fig. 14(a)), the scale is limited to two distinct regions. AES depth profiling confirms that the surface layer already contains TiO_2 , $(\text{Cr,Al})_2\text{O}_3$, and CrS. The formation of CrS on the sample surface during this initial stage is evidenced by the concurrent high concentrations of Cr and S with negligible contributions from other elements. Within the surface layer, TiO_2 is predominantly located in the mid-region, followed by a $(\text{Cr,Al})_2\text{O}_3$ solid-solution layer that gradually transitions from Cr-rich to Al-rich, terminating in a nearly pure Al_2O_3 layer at the interface, which is consistent with previous TEM observations. Beneath the surface layer, no TiTaO_4 layer is detected after 1 h. Instead, a bright-contrast region, which can be identified as the internal corrosion zone, is observed. AES analysis reveals enrichment in S together with Ta and Mo, which can be attributed to the rapid outward

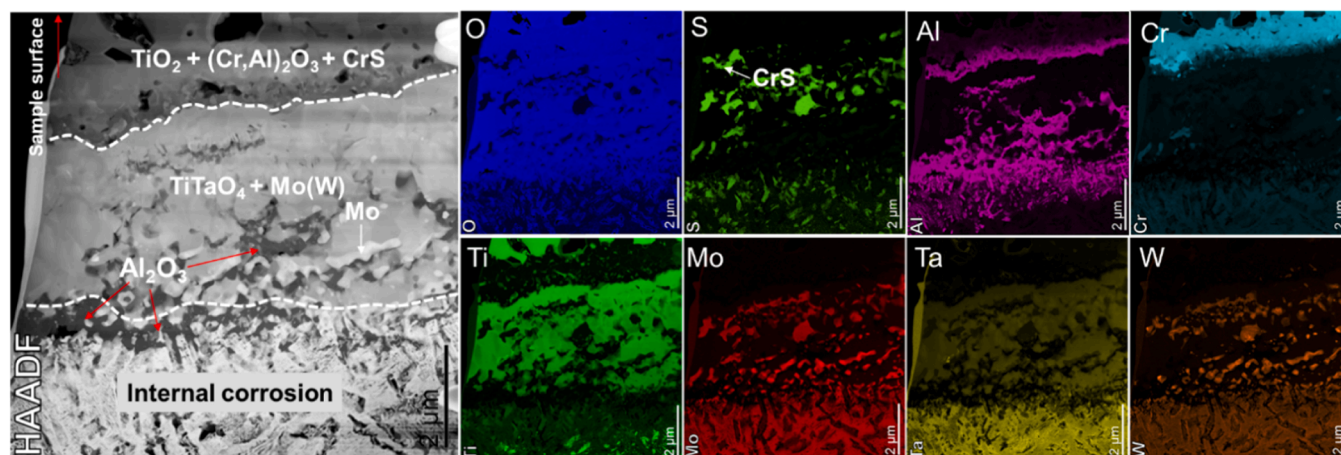


Fig. 10. General TEM-HAADF image and EDS mapping of TaMoCrTiAl-3 W after reaction at 1000°C (the white dashed lines roughly denote the boundaries of different regions).

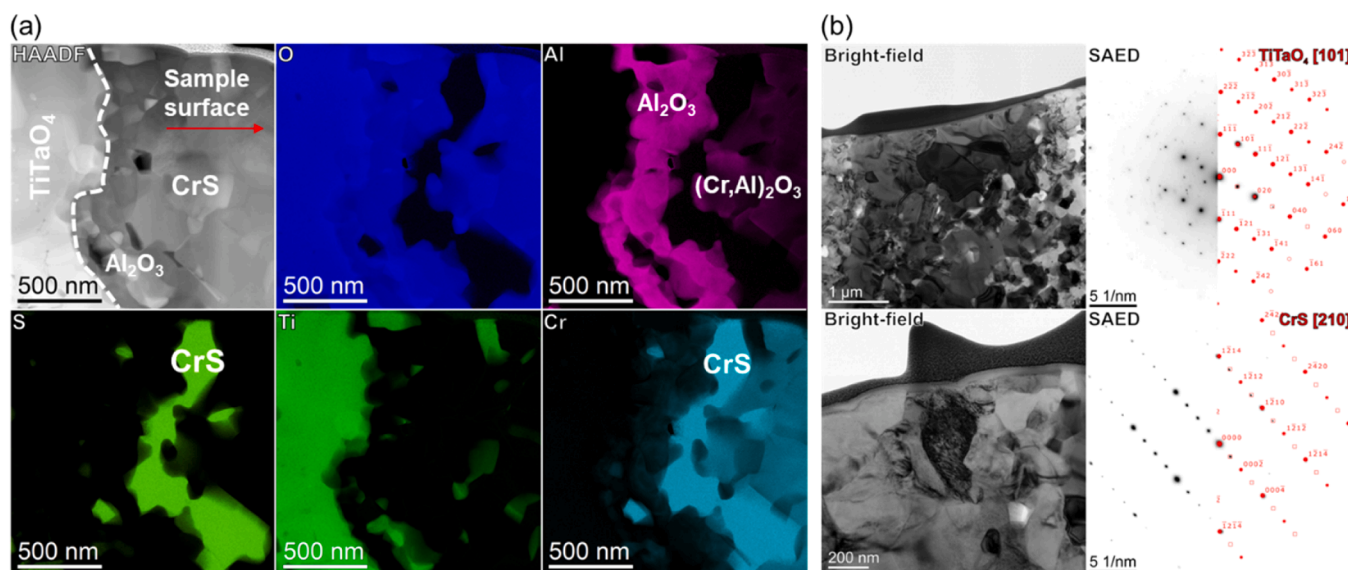


Fig. 11. TEM results of TaMoCrTiAl-3 W after reaction at 1000°C. (a) HAADF image and EDS mapping located near the surface layer/inner TiTaO₄ layer interface, (b) BF images and SAED of TiTaO₄ and CrS phases.

diffusion of Ti, Cr, and Al during initial surface-scale formation, leading to a subsequent depletion of the alloy surface region of these elements. At this stage, no distinct Al₂O₃ precipitates are present within the internal corrosion zone.

After 5 and 10 h exposure, CrS sulfides are observed not only at the surface but also within the inner region of the outer corrosion layer, as evidenced by the sulfur depth profiles obtained from AES measurements in Fig. 14 (b) and (c). Concurrently, the formation of the inner TiTaO₄ layer becomes apparent, as indicated by the appearance of a second oxygen peak in the AES depth profiles. This layer also contains a substantial amount of Mo, consistent with previous TEM observations of metallic Mo inclusions. Compared to the 1 h condition, the sulfur concentration within the internal corrosion zone decreases markedly after 5 and 10 h exposure. In addition, the total corroded layer thickness increases only slightly, from approximately 10–12 µm. These observations reveal that the multilayered corrosion scale effectively suppresses inward sulfur transport, resulting in strongly reduced inward sulfur (and oxygen) fluxes and correspondingly low corrosion kinetics.

The 10 h sample was further examined by EPMA, and the results are shown in Fig. 15. The EPMA elemental maps confirm the general multilayered structure and the associated chemical composition of the

corrosion scale. The TiTaO₄-based inner layer exhibits a compositional gradient, with increasing Ta content toward the internal corrosion zone, a phenomenon that is also confirmed by the AES depth profile in Fig. 14 (c). The elemental maps reveal strong elemental partitioning of O, S, and metallic elements across the scale, indicating coupled sulfidation-oxidation processes governing scale formation and growth during exposure.

4. Discussion

All the above-described results of morphology, chemical, and phase composition analyses performed on the scales formed on the tested alloys during the investigation process lead to interesting conclusions regarding the reasons for such a significant improvement in their heat resistance.

In both TaMoCrTiAl and TaMoCrTiAl-3 W alloys, growth of the corrosion scale containing mostly titanium, chromium and aluminum lowers the content of these components at the alloy surface, thereby simultaneously increasing the contribution of tantalum and molybdenum in this region, resulting in favorable conditions for the formation of sulfides from both those metals, leading to an internal corrosion zone.

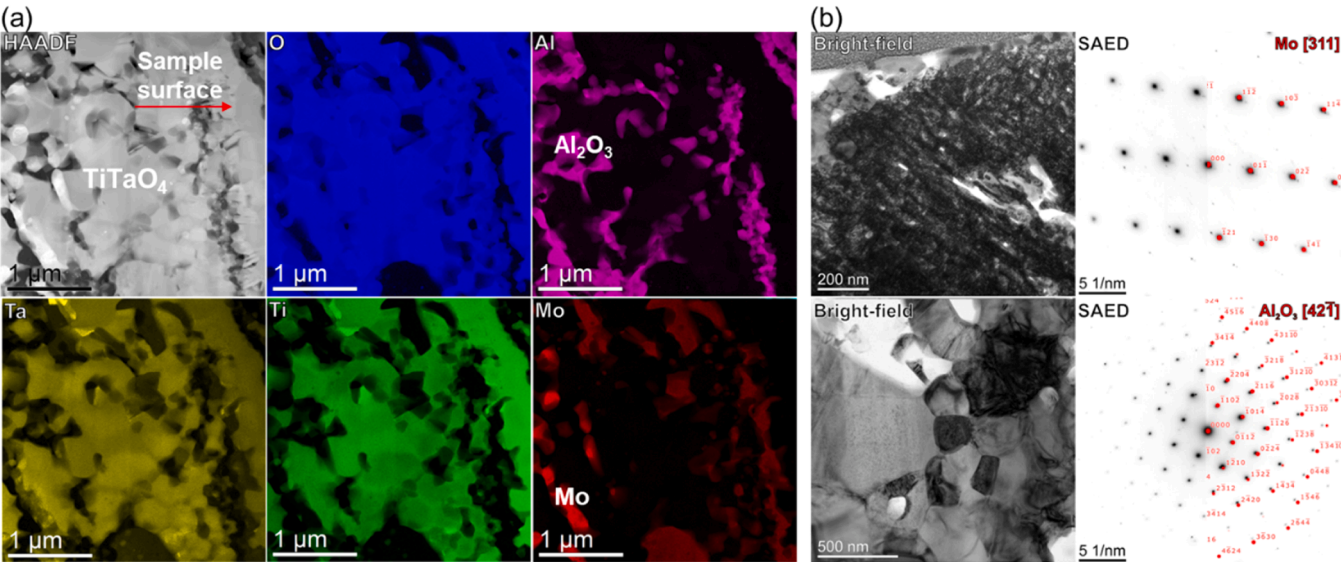


Fig. 12. TEM results of TaMoCrTiAl-3 W after reaction at 1000°C. (a) HAADF image and EDS mapping located near inner TiTaO₄ layer/internal corrosion region interface, (b) BF images and SAED of metallic Mo and Al₂O₃ precipitates within this layer.

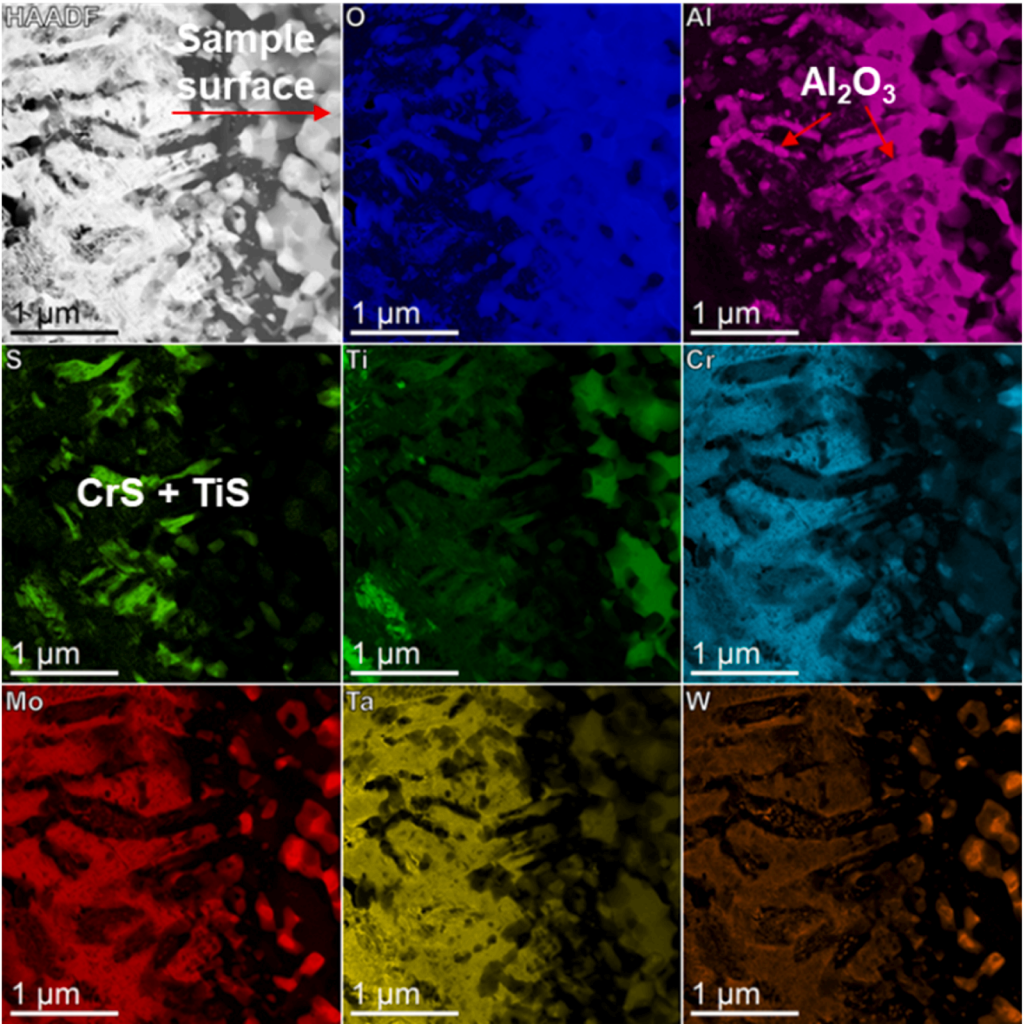


Fig. 13. TEM-HAADF imaging and EDS elemental mapping of the internal corrosion zone of TaMoCrTiAl-3 W after reaction at 1000°C for 100 h.

Fig. 16 schematically represents the evolution of the reaction product layers formed on the studied alloys during the first 10 h of corrosion

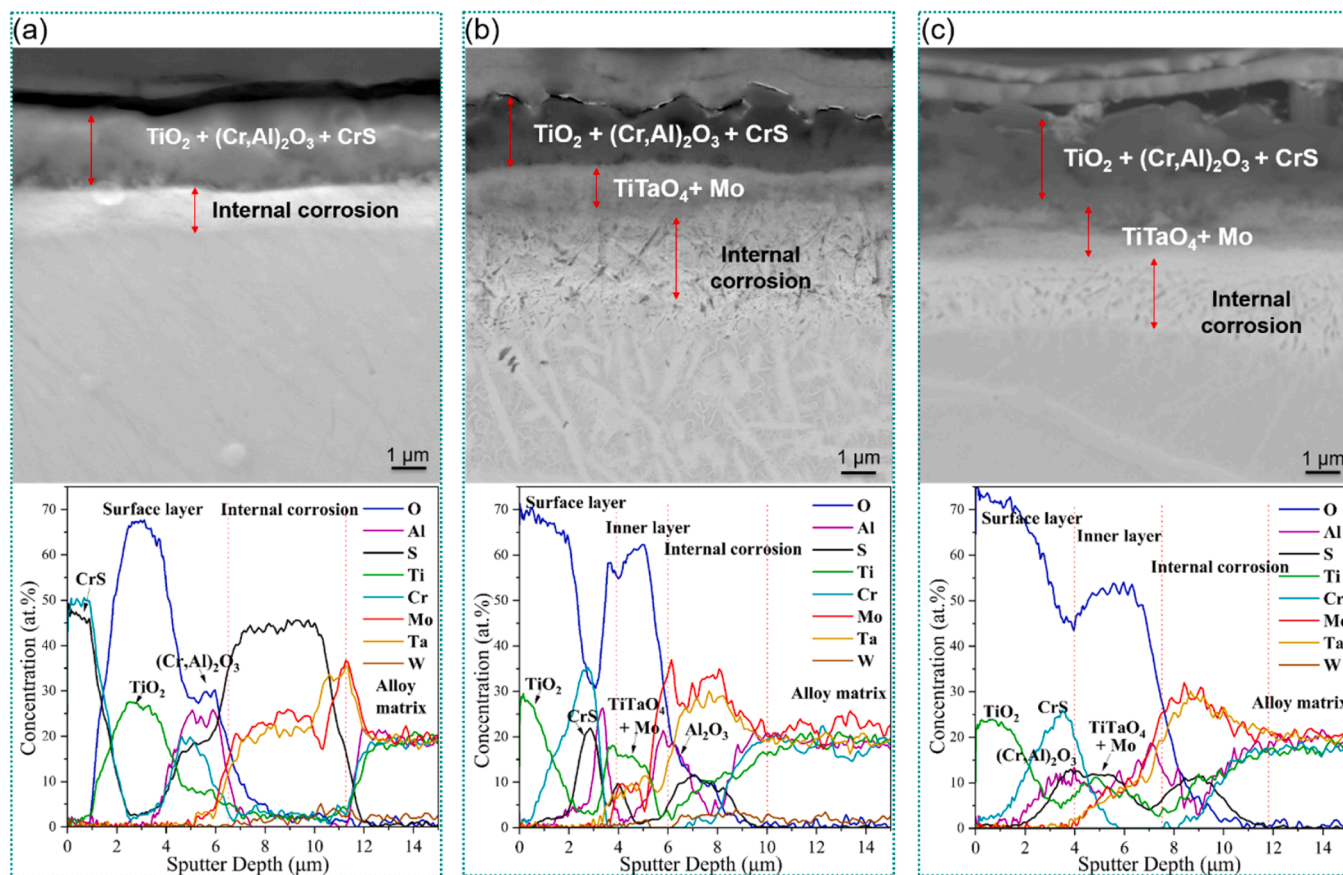


Fig. 14. Cross-sectional SEM images (top row) and corresponding AES depth profiles (bottom row) of TaMoCrTiAl-3 W after reaction for (a) 1 h, (b) 5 h, and (c) 10 h. Note that the sputter depths are calibrated using a standard SiO₂ reference; the actual layer thickness may differ due to variations in the sputter rate of the constituent materials.

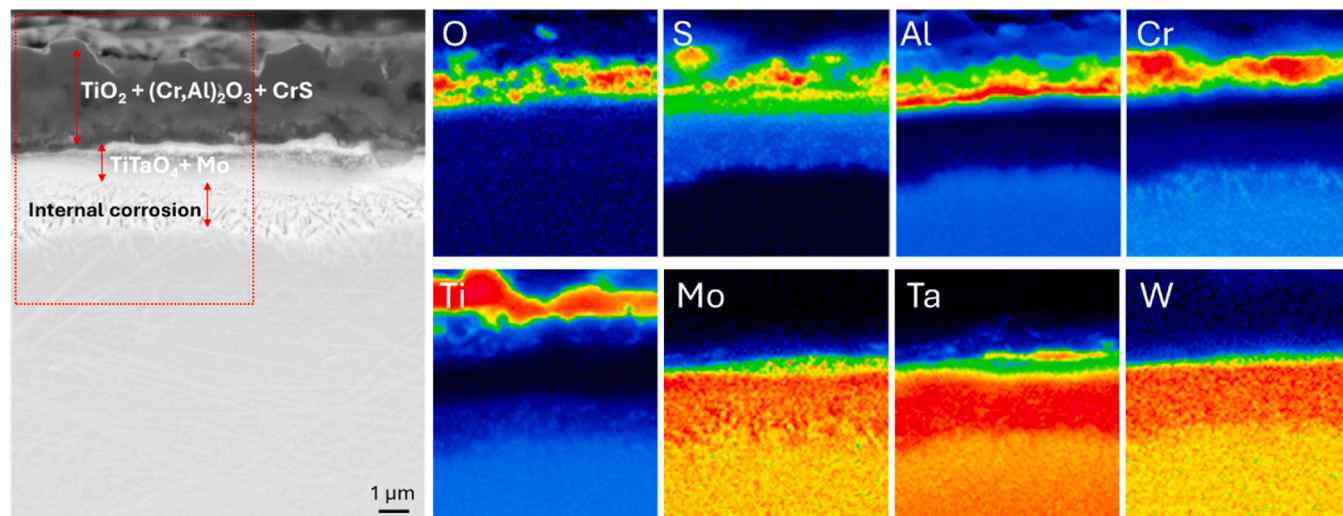


Fig. 15. EPMA elemental maps of the regions marked by dashed rectangles of TaMoCrTiAl-3 W alloy tested at 1000°C for 10 h.

process. The observed morphology of the scales and the mechanism of their growth are to a certain degree comparable with those formed on multicomponent alumina- and chromia-forming alloys in oxidizing-sulfidizing environments [41]. As a rule, traditional oxidation resistant alloys are, already in the initial reaction stage in an oxidizing-sulfidizing environment, covered with a protective Al₂O₃ or Cr₂O₃ layer. In the subsequent reaction stage, sulfur diffuses inward

along grain boundaries and precipitates as sulfides along these boundaries. Once these grain-boundary sulfides reach the alloy surface, rapid sulfide growth can initiate catastrophic degradation because of sulfide corrosion [41]. However, for the alloys investigated in this work, such rapid degradation does not occur even after 100 h of exposure. This suggests that, in addition to the protective Al₂O₃ and Cr₂O₃ layers, other scale constituents act as effective diffusion barriers for reactive species,

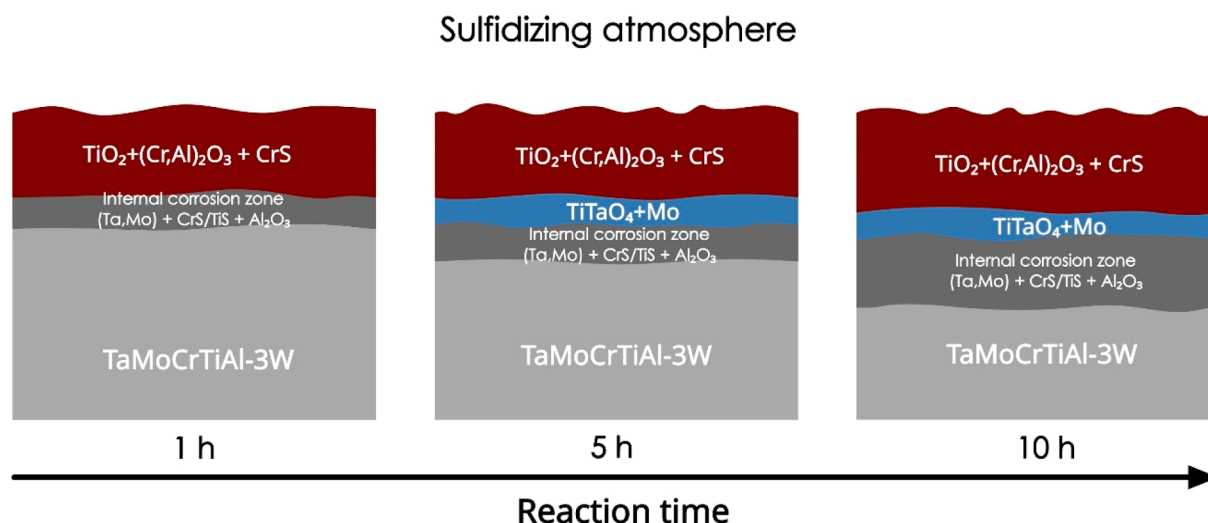


Fig. 16. Schematic representation of progressive development of corrosion scales on TaMoCrTiAl and TaMoCrTiAl-3 W alloys at high temperatures.

which are typically absent in the corrosion scales of conventional alloys.

After the reaction proceeds for five hours, the inner scale layer forms, consisting of TiTaO_4 with metallic Mo inclusions. TiTaO_4 and the oxides of Cr—and especially Al—grow extremely slowly. Because certain sulfides can grow very rapidly, they may dominate the scale and constitute nearly 100% of corrosion products when their formation are preferred. This is the case with another high-entropy alloy (AlCoCrNiSi) [42], in which both nickel and chromium sulfide formed extremely rapidly. On the other hand, the currently studied TaMoCrTiAl and TaMoCrTiAl-3 W alloys contain refractory metals, whose sulfides possess exceptionally good protective properties, and thus, grow very slowly on the tested samples. As a consequence, these sulfides constitute a barrier against sulfur corrosion, and the resulting oxides are visible in analytical results due to the very low thickness of the corrosion products. The explanation presented above was fully confirmed by the chemical and phase composition analyses performed on the formed scales, described in the previous paragraph.

Starting from the surface layer, TiO_2 could assume such a role to a certain extent. It demonstrates predominant disorder in the anion sublattice [43], and thus, hinders outward metallic diffusion of the individual alloy components to a large degree. At the same time, this oxide exhibits very low decomposition oxygen partial pressure comparable to that of aluminum oxide, which significantly reduces oxygen activity under these layers, resulting in the oxidation of other metals becoming practically impossible. There is a lack of literature data on the structure of point defects and their mobility in relation to TiTaO_4 , making it difficult to precisely determine its role in corrosion control. The presence of all these oxides in the scale is also important as it pertains to the possibility of volatile oxide formation, e.g., molybdenum oxide, MoO_3 . Relatively large molybdenum concentration on the surface of amorphous Al-Mo alloys, and their consequent rapid degradation due to MoO_3 evaporation [41], limited the temperature range, in which these alloys can be used. In the case of the investigated refractory alloys, molybdenum in higher concentrations is only located below the scale surface, i.e. at a location where oxygen activity is low enough to inhibit significant degradation associated with MoO_3 formation. Importantly, no signs of volatile Mo and W oxide formation were observed during the tests. This is primarily due to unfavorable thermodynamic conditions during the high-temperature experiments, inhibiting formation of those phases. This conclusion is further supported by microstructural observations, as no evidence of volatile product formation was detected in the scale. As previously mentioned, oxides containing aluminum and chromium, i.e. Al_2O_3 , Cr_2O_3 and $(\text{Al,Cr})_2\text{O}_3$ also constitute an excellent barrier against reagent transport through the scale. This is due to both

the low point defect concentration in those materials, as well as the predominant disorder existing in the cation sublattice, which hinders inward lattice diffusion of sulfur [43].

The presence of titanium sulfide in the internal corrosion zone also may contribute to the heat resistance of the studied alloys. As shown in Fig. 17, the decomposition pressure of TiS is the lowest among all sulfides of metals presented in the studied alloys. This means that sulfur diffusing even in very small amounts into the metal core will react first with titanium. This reaction should potentially maintain the sulfur activity under the scale at a relatively constant level insufficient to support the growth of other metal sulfides, thus protecting these metals from sulfidation. However, because the kinetic of TiS formation is extremely low [44] the potential for sulfur consumption will decrease with time, leading to an increase of sulfur concentration in the surface layer of the alloy. This process will enable the sulfidation of subsequent metals in the alloy. Theoretically, according to the data presented in Fig. 17, aluminum should be the next metal to be sulfidized. However, aluminum concentration under the scale layer is significantly lower than the nominal one due to its oxidation, resulting in the formation of relatively large amounts of aluminum oxide, as well as due to its slow diffusion in the alloy, which makes it difficult to equilibrate. As a result, instead of aluminum sulfide, chromium sulfide is formed, particularly in regions containing the Cr_2Ta Laves phase. Under favorable conditions, CrS sulfide can form at a rate approximately four orders of magnitude faster than that observed for TiS [4]. This means that sulfur activity can be stabilized approximately at a level corresponding to the dissociation pressure of CrS, which blocks the formation of sulfides of other metals.

The sulfidation rate constant of the TaMoCrTiAl alloy, at 1000°C , is about two orders of magnitude lower than those obtained for pure niobium and molybdenum, as well as the Al-(34–46)Mo amorphous alloys—the best materials developed to date [8,11], whose values are comparable, as shown in Fig. 18. It is particularly important to emphasize that such high resistance against sulfur attack at high temperatures, as demonstrated by the TaMoCrTiAl-3 W alloy studied in this work, has not been reported in the literature. The parabolic sulfidation rate constant of the Al-(34–46)Mo alloys, is approximately an order of magnitude higher than that obtained for the TaMoCrTiAl-3 W under similar conditions.

The scales formed on Al-(34–46)Mo and TaMoCrTiAl(3 W) alloys differ fundamentally, despite analogous test conditions. In practice, all investigated alloys were exposed to atmospheres containing high sulfur vapor pressures ($\sim 10^3$ Pa) along with minor oxygen partial pressures (10^{-14} – 10^{-11} Pa), mainly originating from impurity in the helium used in the measurements as an auxiliary gas. This means that corrosion of both

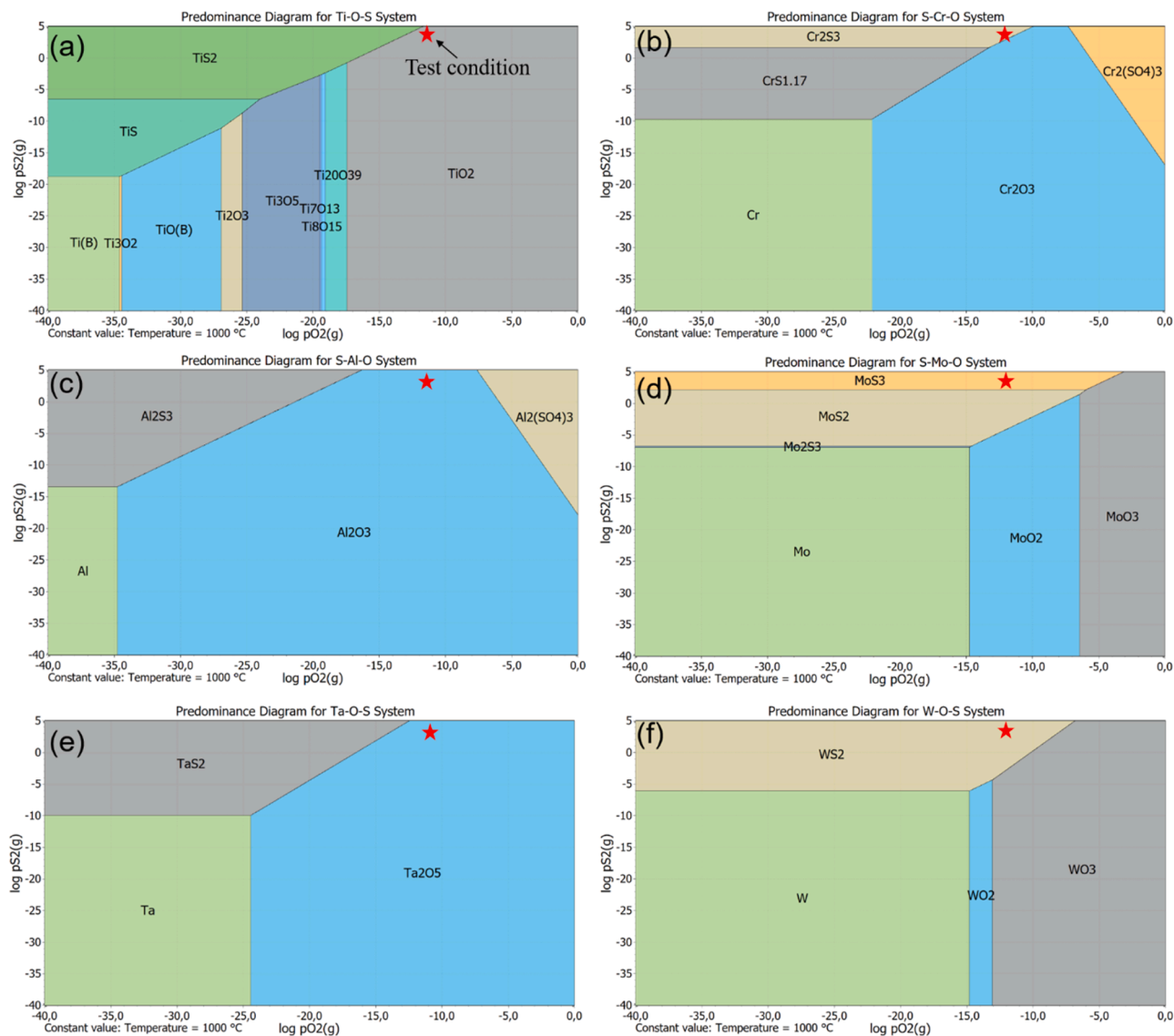


Fig. 17. Predominance diagrams for (a) Ti–O–S, (b) Cr–O–S, (c) Al–O–S, (d) Mo–O–S, (e) Ta–O–S and (f) W–O–S at 1000°C calculated using HSC Chemistry 9. The red star marks the experimental conditions, characterized by sulfur vapor pressure of $\sim 10^3$ Pa and minor oxygen partial pressures of 10^{-14} to 10^{-11} Pa.

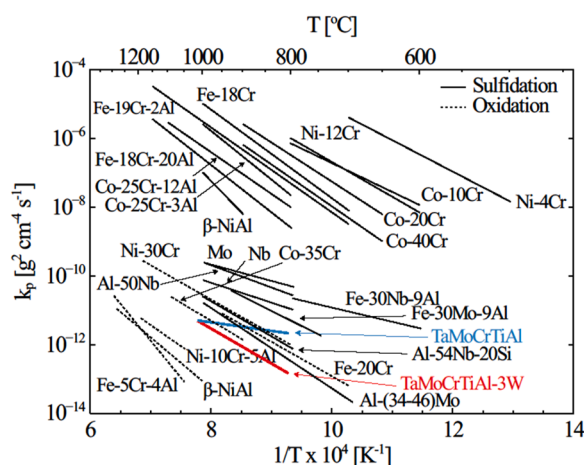


Fig. 18. Temperature dependence of the sulfidation rate constants received from the alloys studied in this work presented on the background of analogous results obtained for several binary and ternary alloys, and refractory metals [41].

types of materials was not studied in pure sulfidizing atmospheres, but rather under mixed sulfidizing–oxidizing conditions. Nevertheless, in the case of Al–(34–46)Mo alloys, scales were composed exclusively of sulfides and consist of two layers. The inner layer was molybdenum disulfide, MoS_2 , doped with aluminum, while the outer layer was aluminum sulfide, Al_2S_3 . The excellent protective properties of these scales are primarily due to the low concentration of point defects in the inner layer and, to some extent, their lower chemical diffusion coefficient compared to the diffusion coefficients of most metal sulfides [5].

On the other hand, the scales growing on the surface of TaMoCrTiAl and TaMoCrTiAl–3 W alloys have a different and generally more complex oxide–sulfide structure (Figs. 9 and 10). The surface layer of the scales is built of TiO_2 and $(\text{Cr}, \text{Al})_2\text{O}_3$ oxides, as well as a minor amount of chromium sulfide, CrS. The formation of mixed oxide–sulfide surface scales can be rationalized by the thermodynamic stability of the relevant phases under the tested conditions, as illustrated by the predominance diagrams in Fig. 17. At a sulfur vapor pressure of $\sim 10^3$ Pa and oxygen partial pressures of 10^{-14} – 10^{-11} Pa, Al_2O_3 and TiO_2 are thermodynamically favored over their sulfides, whereas Cr (and Mo) preferentially forms sulfides. It is worth noting that AlCoCrNiSi high-entropy alloy, also containing chromium and aluminum but without any refractory

metals, during sulfidation under similar conditions and in the same apparatus was covered with a multi-layered scale composed exclusively of sulfides [42]. Moreover, obtained scales were very thick and devoid of any oxide inclusions.

Doping the alloys with 3 at% W improves corrosion resistance in sulfidizing-oxidizing conditions primarily by suppressing the rapid growth of CrS along grain boundaries, where the Cr₂Ta Laves phase is located. Although the overall mass gain of TaMoCrTiAl–3 W alloys remains lower, the corrosion scale thickness is largely comparable outside the grain-boundary regions. Incorporation of W cations into the rutile-structured TiO₂ or TiTaO₄ oxides may reduce the inward flux of O and S anions. This conclusion follows directly from the analysis of the defect situation in the oxide of the TiO₂ type doped with tungsten. The predominant defects in TiO₂ within the temperature and oxygen pressure range used in this work are doubly ionized oxygen vacancies [45]. Substitutional incorporation of tungsten into the TiO₂ crystal lattice results in a decrease of the native defect concentration. This is possible for two reasons. Firstly, the dopant concentration in the alloy is several orders of magnitude higher than the concentration of doubly ionized oxygen vacancies, so the effect of dopant introduction should be visible. Secondly, the ionic radius of tungsten (0.64 Å) is comparable to that of a titanium ion in the correct crystal lattice position in TiO₂ (0.6 Å), which allows for substitutional incorporation of the dopant. Additionally, it should be emphasized that the presented experiments were conducted at temperatures above the Tammann's temperature, which means that lattice diffusion determines the formation of TiO₂ and TaTiO₄ oxides, and therefore, the effect of doping will be visible in the corrosion test results. Unfortunately, although the predominant defects in TiO₂ within the tested temperature and oxygen pressure range are doubly ionized oxygen vacancies, this oxide exhibits a complex defect structure, containing, among others, quadruply ionized titanium vacancies [45]. Under the experimental conditions, the concentration of these defects is slightly lower than the concentration of doubly ionized oxygen vacancies. Consequently, the tungsten dopant is hypothesized to reduce the concentration of oxygen vacancies, while simultaneously increasing the concentration of titanium vacancies. The final effect of the tungsten dopant is therefore not obvious and depends largely on its concentration in the TiO₂ crystal lattice. Therefore, one can expect at most a small effect of the addition of tungsten on slowing down the corrosion rate of the alloy containing the addition of this element.

It should be added that the discrepancy between the observed mass changes of the alloy samples investigated in this work and the thickness of the scales forming on them most likely results from several different factors. Firstly, a substantial amount of corrosion products forms along the grain boundaries of the tungsten-free sulfidized alloy, and their thickness is several times greater than that of the scale on the flat grain surfaces. Secondly, the observed difference may result from a varying contribution of individual phases within the scale, which are characterized by different densities.

At the current stage of research, these appear to be the only plausible explanations for the aforementioned discrepancies, as no scale spallation was detected during the experiments. Furthermore, the observed effects are not related to the formation of volatile oxides. The latter conclusion is supported by the fact that throughout the entire duration of the experiments, the corrosion process strictly followed the parabolic rate law (Fig. 2d).

In summary, a combined effect of both oxides and sulfides can be expected in the studied alloys, thereby enhancing their capacity to limit oxidation and sulfidation reactions. It is worth noting that this phenomenon can have practical significance, as sulfur and oxygen concentrations analogous to those in this work resemble many industrial atmospheres [41].

5. Summary and conclusions

TaMoCrTiAl and TaMoCrTiAl–3 W high-entropy alloys demonstrate

excellent resistance to corrosion under mixed sulfidizing–oxidizing conditions, with partial pressures of sulfur vapor and oxygen equal to 1000 Pa and < 10[−] Pa, respectively, up to 1000°C. Under these conditions, the corrosion rates of both alloys—and particularly TaMoCrTiAl–3 W—are lower than the sulfidation rates of pure molybdenum or highly resistant to sulfidation amorphous Al–Mo alloys, as well as the oxidation rates of chromia-forming alloys. The investigated alloys derive their high corrosion resistance from the formation of surface oxide–sulfide scales composed of Al₂O₃, Cr₂O₃, TiTaO₄, TiO₂, and CrS along with CrS/TiS in the internal corrosion zone. These constituents act as a diffusion barrier on the surface as well as entrap sulfur that has migrated into the alloy core, significantly reducing the overall corrosion rate. This performance positions tested alloys as the most resistant materials currently known to sulfur attack taking place in presence of small amount of oxygen.

CRedit authorship contribution statement

Grzegorz Smola: Writing – review & editing, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation. **Chongchong Tang:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Björn Schäfer:** Writing – review & editing, Investigation. **Michael Dürrschnabel:** Writing – review & editing, Investigation. **Carsten Schroer:** Writing – review & editing, Resources. **Paul Gokelaere:** Writing – review & editing, Investigation. **Bronislava Gorr:** Writing – review & editing, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Zbigniew Grzesik:** Writing – original draft, Validation, Project administration, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability

Data will be made available on request. The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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