

A new strategy to intrinsically protect refractory metal based alloys at ultra high temperatures

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Abstract

Poor oxidation resistance represents one of the main shortcomings of refractory metal based alloys. This work shows an innovative way to intrinsically protect such materials. Our approach relies on the alloying with Cr and Ta allowing the formation of CrTaO₄. The CrTaO₄ scale formed on the novel refractory equiatomic high entropy alloy Ta-Mo-Cr-Ti-Al reveals a unique combination of the following properties: (i) easy formation in a wide temperature range from 500°C to 1500°C, (ii) excellent adherence after cooling, (iii) low growth rates, and (iv) wide stability range of the stoichiometric composition that suppresses the formation of non-protective oxides.

Keywords: High temperature materials, Refractory high entropy alloys, Oxidation resistance, Protective oxides, CrTaO₄

1 Introduction

Because of their high melting temperatures, refractory metal (RM) based alloys have been considered for decades as potential candidates to substitute Ni-base superalloys in gas turbines aiming at a substantial increase of the turbine thermodynamic efficiency. Unfortunately, refractory metals exhibit poor oxidation resistance forming, depending on temperature, either quickly growing non-protective or volatile oxides causing a fast disintegration of the material [1]. To the best of our knowledge, so far no oxide scale was established on refractory metal-based materials that guarantees protective properties in air in a temperature range from 500°C up to 1500°C [1, 2]. Recently introduced Refractory High Entropy Alloys (RHEAs) may enable a breakthrough towards higher operating temperatures as they possess exceptionally attractive mechanical properties [3, 4]. However, none of the RHEAs reported in the literature forms continuous protective oxides such as Al₂O₃, Cr₂O₃ or SiO₂ known to insure the required enduring oxidation resistance in a wide temperature range [5-8]. Most of RHEAs form complex oxides which possess rather moderate protective properties [9-11]. It should, however, be mentioned that some of them, e.g. CrNbO₄ and especially CrTaO₄, exhibit significant protectiveness during high temperature oxidation [11]. In fact, these oxides were observed in different alloy systems such as Cr-Ta and Cr-Nb [12-15]. Recently, the beneficial effect of the complex oxides CrNbO₄ as well as CrTaO₄ was found in studies investigating high temperature oxidation behavior of RHEAs. Butler et al. explained the nearly parabolic kinetics by the formation of CrNbO₄ on the RHEA Nb-Ti-Zr-Cr [11]. Remarkable protectiveness of CrTaO₄ was recently reported by Lo et al. while studying the oxidation behavior of the RHEA based on the alloy system Al-Si-Ti-Cr-Nb-Mo-Ta [16]. Apparently, these complex oxides seem to offer a unique opportunity to provide reasonable protectiveness for RHEAs.

In this paper, we present experimental proof that RHEAs can be intrinsically protected by a thermally growing scale consisting of complex oxide(s) which provides protectiveness not only at temperatures beyond the thermal capability of the best Ni-base superalloys (> 1200°C), but also prevents from the so-called “peesting” phenomenon, i.e. the fast disintegration of the metallic substrate due to intergranular oxidation at moderate temperatures (around 500 to 800°C) for which RM alloys are well-known [17, 18].

The chemical composition of the equiatomic RHEA Ta-Mo-Cr-Ti-Al investigated in this study was chosen on the basis of the following considerations: (i) Ta and Mo were selected to ensure a high melting point and to provide good mechanical strength, (ii) Cr and Al were added to ensure the oxidation resistance, and (iii) Ti (in addition to Al) should reduce the alloy density. On grounds of the chemical composition, this alloy includes 60 at.% of refractory metals, i.e. Ta, Mo and Cr. According to our thermodynamic calculations, the solidus temperature of the alloy is about 2100°C. In contrast to other approaches for RM-based materials where intermetallic phases like silicide (in e.g. Mo- and Nb-based alloys) containing passivating elements (e.g. Si in Mo- and Nb-based alloys) are utilized to protect other non-protective microstructural parts, the (almost) single-phase solid solution form of RHEAs ensures a homogeneous distribution and activity of passivating elements throughout the surface. No further microstructural optimization and manipulation of the oxides scale is needed (e.g. viscosity of the scale by adding B to Mo-based materials).

2 Material and methods

The equiatomic RHEA Ta-Mo-Cr-Ti-Al was manufactured by arc melting. The elements Ta, Mo, Cr, Ti and Al possess nominal purities of 99.9, 99.96, 99, 99.8 and 99.9 %, respectively. All these elements were mixed and placed in the vacuum chamber of an AM/0.5 arc melting furnace by Edmund Bühler GmbH (Germany). The furnace chamber was alternately pumped down to a pressure of $5 \cdot 10^{-2}$ mbar and flooded with Ar up to ambient pressure for three times. A high vacuum of $1 \cdot 10^{-4}$ mbar was finally established. The value of the working Ar pressure for the melting operation was around 600 mbar. The manufactured ingots were flipped, remelted for at least five times and cast into a water-cooled, rod-shaped Cu mold with a diameter of 12 mm and a length of 60 mm. A homogenization treatment was performed in an Ar atmosphere at 1500 ° for 20 h. The heating and cooling rate were 250 K/h each.

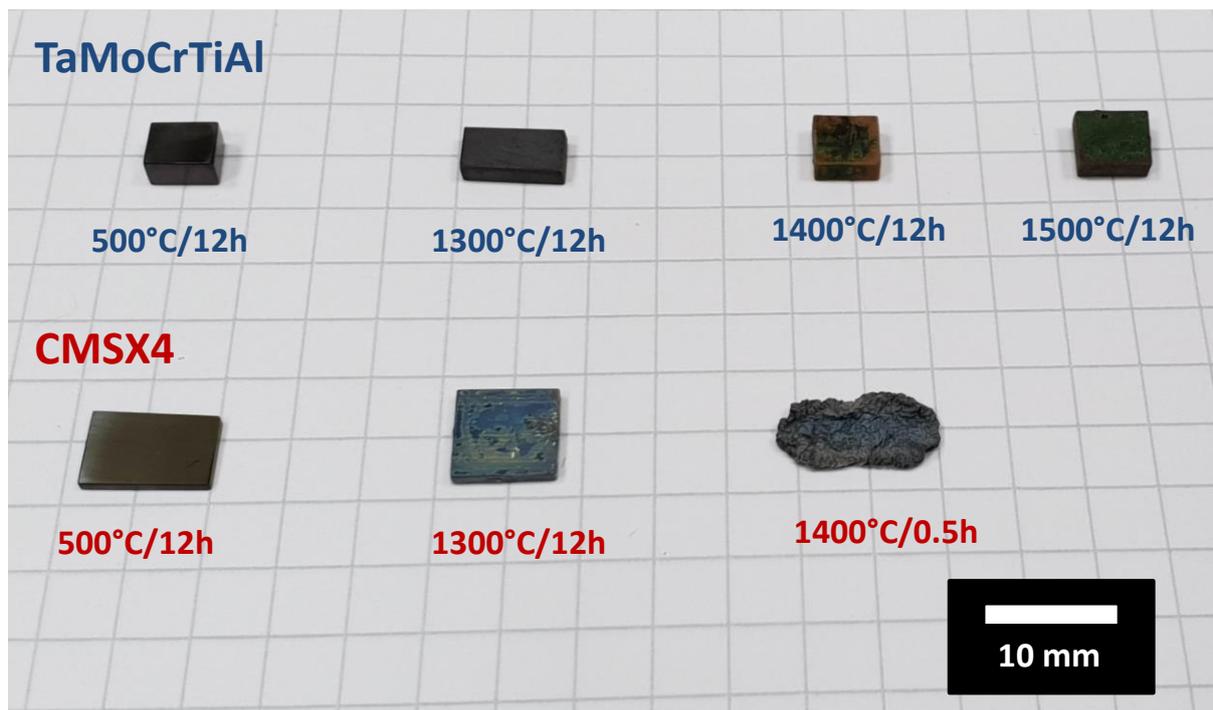
To perform oxidation tests on the RHEA Ta-Mo-Cr-Ti-Al, the ingots were cut by electrical discharge machining (EDM) to dimensions of 5 mm x 5 mm x 2 mm, polished up to grit P1200 and finally ultrasonically cleaned in ethanol directly before high temperature exposure. The samples of the Ni-based alloy CMSX-4 for the comparative studies (provided by Dr. Julian Mueller, Micro- and Nanoanalytics Group, Institute of Materials Science, University of Siegen) were prepared analogously. Oxidation tests were performed isothermally in a Rubotherm thermogravimetric system at 500°C, 1000°C, 1300°C, 1400°C and 1500°C for 12 hours in air. The crystal structures of the oxides formed were analysed using X-ray diffraction (XRD). The XRD measurements were conducted using an X'Pert Pro MPD diffractometer operating in Bragg-Brentano geometry with Cu-K α radiation. To study the oxide morphology, a Focused Ion Beam - Scanning Electron Microscope (FIB-SEM) DualBeam system of type FEI Helios Nanolab 600 was utilized which is equipped with backscatter electron (BSE) imaging, energy dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD).

3 Results and discussion

The results of the oxidation tests performed on the equiatomic RHEA Ta-Mo-Cr-Ti-Al at 900°C, 1000°C and 1100° were presented and discussed in ref. [19]. In the current study, the range of temperature is expanded to 500°C, 1300°C, 1400°C and 1500°C. To quantitatively assess the oxidation resistance of our alloy, analogous experiments were carried out with the single crystalline Ni-based superalloy CMSX-4. Figure 1a compares macroscopic images of the alloy Ta-Mo-Cr-Ti-Al and the alloy CMSX-4 oxidized continuously for 12h at 500°C, 1300°C, 1400°C and 1500°C. Obviously, both alloys maintain their original shape, particularly, the sharp edges of the cuboids are still visible at temperatures up to 1300°C indicating excellent oxidation resistance. Beyond that, the alloy CMSX-4 starts to melt at 1400°C. The alloy Ta-Mo-Cr-Ti-Al shows, on the contrary, a remarkable resistance to corrosion attack even at temperatures up to 1500°C. It is noteworthy that the color of the outer oxide scale changes from gray (1300°C) to greenish orange (1400°C) and finally to green (1500°C). XRD investigations in combination with EDS analysis of the sample surface (results are not shown here) reveal that the outer layer consists of TiO₂, Cr₂O₃ and Al₂O₃. While the color of TiO₂ may change depending on dopant from yellow to orange [20], Cr₂O₃ and Al₂O₃ usually exhibit green [21] and gray color [22], respectively. Detailed microstructural investigations of the sample surfaces show that the ratio of these oxides and,

consequently, the oxide color varies depending on the oxidation temperature. Moreover, the color of the scale and, thus, the ratio of TiO_2 , Cr_2O_3 and Al_2O_3 may even change within one sample (see, e.g. the surface of the sample after oxidation at 1400°C , Fig. 1a). The results of oxidation tests performed in our earlier study at 1000°C revealed that the outer scale did not change markedly in terms of the constituting oxides and their ratio even after extended oxidation up to 300h [19]. We thus anticipate a similar behavior at the higher temperatures tested here, although experimental proof should be left for future work.

However, the most remarkable finding was made at the lower end of the temperature range at 500°C , neither pesting that is typical of some refractory metal-based phases (e.g. MoSi_2) [17] nor pesting-like phenomenon (accelerated formation of simple oxides with unfavorable volumetric expansion) often observing in RHEAs [23] occur. It should also be pointed out that the same holds true for our alloy when tested at the higher end of the pesting regime, i.e. at 900°C , see ref. [19]. A deeper insight into the protective properties of the oxide scales is given in Figs. 1b and 1c. Apparently, the oxide layers formed on the alloy CMSX-4 tend to be prone to spallation during cooling indicating the development of high stresses in the oxide scales. The oxide layer formed on the alloy Ta-Mo-Cr-Ti-Al, however, yields no indications of macroscopic cracks and remains perfectly adherent.



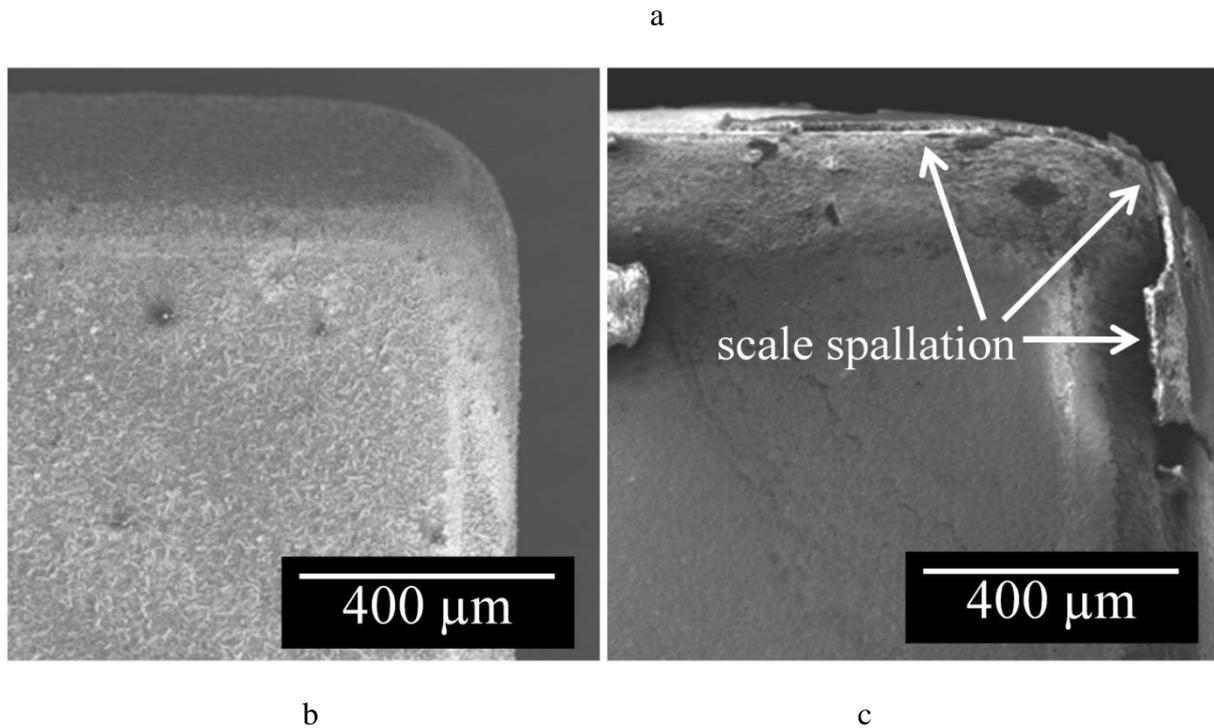


Fig. 1: Qualitative comparison of the oxidation behavior of the equiatomic HEA Ta-Mo-Cr-Ti-Al with the Ni-based alloy CMSX-4. **a**, macroscopic micrographs of the alloys oxidized at 500°C, 1300°C, 1400°C and 1500°C. **b**, view of a sample edge of the alloy Ta-Mo-Cr-Ti-Al oxidized at 1300°C for 12h. **c**, view of a sample edge of the alloy CMSX-4 oxidized at 1300°C for 12h.

To assess the oxidation kinetics in detail, specific mass change of the alloy Ta-Mo-Cr-Ti-Al was recorded continuously at temperatures of 1000°C, 1300°C, 1400°C and 1500°C. Note that temperatures greater than 1200°C are beyond the current maximum metal temperature of Ni-base superalloys in gas turbine applications. The oxidation curves exhibit the following remarkable features at all temperatures: (i) very moderate mass gains indicating slow growth rates and (ii) no signs of spallation suggesting well-adhering oxide scales. Further, no signs of evaporation of Mo and Ta oxides were detected. Numerous studies report on the excellent oxidation resistance of Ni-based superalloys in a wide temperature range, see e.g. [24, 25]. The results of the oxidation experiments on the alloy CMSX-4 reveal even lower specific mass change compared to those of our HEA - only 0.32 mg/cm² was recorded after 12h of oxidation at 1300°C. However, beyond this temperature, this alloy cannot be used/tested due to incipient melting (see Fig. 1a).

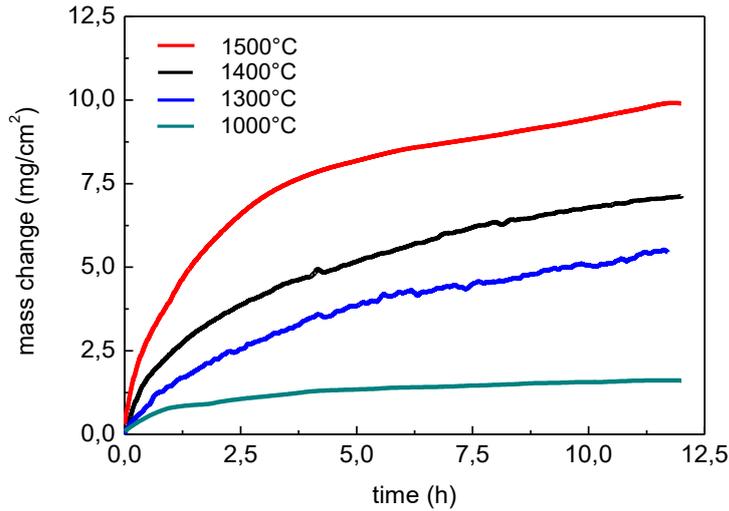
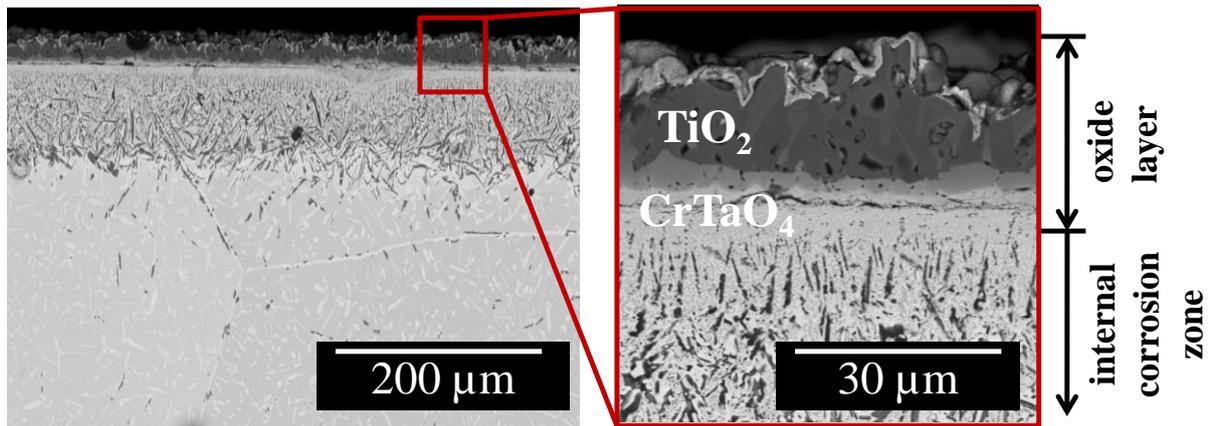
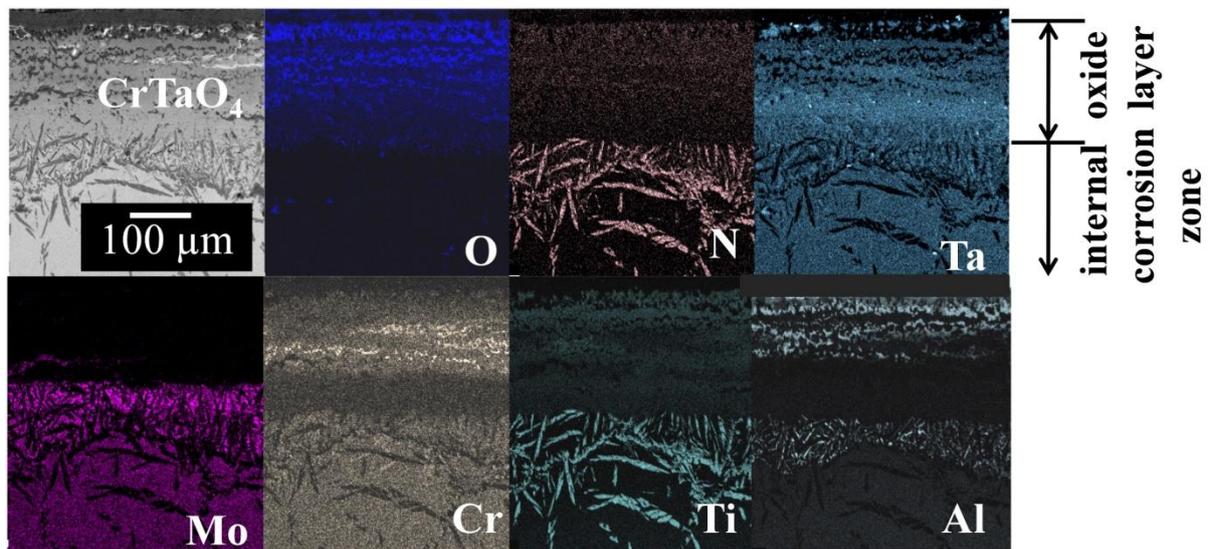


Fig. 2: Mass change of Ta-Mo-Cr-Ti-Al during isothermal oxidation at 1000°C, 1300°C, 1400°C and 1500°C.

Figure 3a shows exemplary cross-sectional micrographs of oxidized samples of the alloy Ta-Mo-Cr-Ti-Al at 1300°C and 1500°C obtained by SEM in BSE mode. Further in-depth microstructural investigations employing energy dispersive X-ray spectroscopy, X-ray diffraction and transmission electron microscopy (not shown here) techniques confirm the formation of an outermost TiO_2 layer and an underlying continuous CrTaO_4 -based layer (appears light gray in contrast) with embedded Cr_2O_3 and Al_2O_3 particles on the alloy Ta-Mo-Cr-Ti-Al. Al_2O_3 and Cr_2O_3 cannot provide reliable oxidation protectiveness as they do not form fully continuous scales. TiO_2 , in general, does not possess protective properties. Obviously, the formation of the CrTaO_4 -based oxide layer accounts for the high oxidation resistance of Ta-Mo-Cr-Ti-Al. Considering the experimental results presented above, we believe that the oxidation mechanism at 1000°C as described in our recent study [19] also holds true for the temperatures relevant for this study. According to Mueller et al. [19], the formation and the growth of the CrTaO_4 -based oxide is governed by the inward (solid-state) diffusion of oxygen through this scale, thus determining the steady-state oxidation kinetics discussed in the next paragraph in the context of Fig. 4. The oxide CrTaO_4 , which possesses the rutile-type crystal structure, seems to exhibit the remarkable feature that this oxide is able to solve substantial amount of other elements, e.g. Ti and Al (see the EDX mappings in Fig. 3b). Other elements seem to participate in the constitution of CrTaO_4 rather than forming their own oxides, hence, potentially suppressing the formation of non-protective and fast growing oxides such as e.g. TiO_2 and Ta_2O_5 . Similar features were reported in literature. Based on the results of the X-ray single crystal investigations, Petersen and Mueller-Buschbaum concluded that metal cations in the CrTaO_4 are randomly distributed in the rutile-type structure [26]. Further, Kirnbauer et al. stated that the entropy effect in $(\text{Al,Cr,Nb,Ta,Ti})\text{O}_2$ high-entropy oxide thin films may lead to a significant stabilization of the rutile structure [27]. It should be mentioned that nitrogen (in addition to oxygen) diffuses inward through the CrTaO_4 scale contributing to the formation of a pronounced zone of internal corrosion (see Fig. 3a).



a



b

Fig. 3: Oxide scales formed on the alloy Ta-Mo-Cr-Ti-Al after 12h oxidation. **a**, cross-section after oxidation at 1300°C. **b**, cross-section and EDX analysis after oxidation at 1500°C

Based on the results presented in Fig. 2, the parabolic oxidation constants k_p were calculated according to the equation (1). Fig. 4 compares the determined parabolic growth rate constants of CrTaO_4 to those of the well-known and widely applied protective oxides Al_2O_3 [28], Cr_2O_3 [28], and SiO_2 [29]. While chromia-forming alloys are often used, their thermal capability is limited to temperatures below 1050°C, as gaseous CrO_3 evaporates above this critical temperature resulting in a continuous mass loss and unacceptable corrosion rate [30]. While silica exhibits low growth rates at very high temperatures, protective scales form only at temperatures above 800°C. At lower temperatures, due to sluggish diffusion the slow growth rate of SiO_2 prevents the development of a continuous layer leading to the formation of mixed non-protective oxides [31]. This effect and the additional risk that Si at the concentrations required for a reliable SiO_2 formation often embrittles alloys by the formation of intermetallic compounds, i.e. silicides, explains, why till date no structural high temperature alloys rely on the protective properties of SiO_2 (marked as dashed lines in Fig. 4) [32]. As Al_2O_3 is stable in

a wide temperature range even in aggressive environments, such as wet air or sulfidizing environments, many technical components, including turbine blades, are protected by Al_2O_3 scales [33].

$$\left(\frac{\Delta m}{A}\right)^2 = k_p \cdot t \quad (1)$$

Surprisingly, while the growth rates of CrTaO_4 are only marginally higher than those of Al_2O_3 at temperatures up to 1300°C , they become competitive beyond that limit. Furthermore, the oxide CrTaO_4 seems to be unprecedentedly stable and protective over a wide temperature range from 500°C to 1500°C . While the formation of a dense and protective Al_2O_3 layer can be easily realized on Ni-based alloys even at low Al concentrations [24], no dense alumina scale could be obtained on RM-based alloys so far. Moreover, the high Al concentrations required for Al_2O_3 scale formation lead to the appearance of undesired, brittle phases [34]. On the negative side, our equiatomic alloy Ta-Mo-Cr-Ti-Al is brittle below 1000°C . Furthermore, the integrity of the metallic substrate is a matter of concern if thermal cycling is applied. Our very recent studies, though, show that non-equiatomic alloys based on the system Ta-Mo-Cr-Ti-Al even with substantial amounts of Cr and Al are ductile at room temperature. Mechanical properties of Ta-Mo-Cr-Ti-Al alloys are, however, beyond the scope of this work and will be presented and discussed in a follow-up paper.

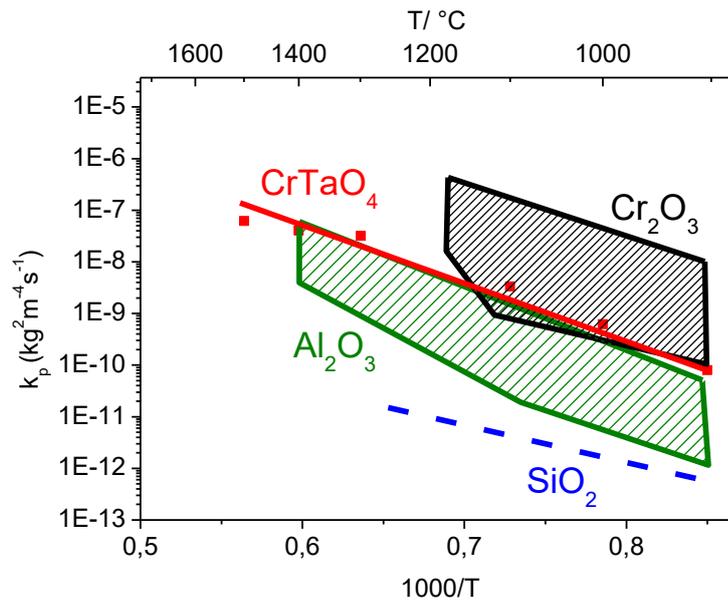


Fig. 4: Comparison of the parabolic oxidation constants of CrTaO_4 on Ta-Mo-Cr-Ti-Al with those of approved protective oxides Cr_2O_3 , SiO_2 and Al_2O_3 , after [28] and [29]

It is by no means surprising that the excellent high-temperature corrosion resistance of the CrTaO_4 is poorly explored since the rather high Ta concentrations employed here are not common in high temperature structural alloys. Though the oxide CrTaO_4 was occasionally observed in selected Ni-based superalloys [35], the formation of this oxide on the RHEA Ta-Mo-Cr-Ti-Al reveals its unique beneficial properties clearly. Overall, our approach reveals a new way to protect RM-based alloys provided they contain sufficient concentrations of the refractory elements Ta and Cr. This concept described might pave the way to develop a new

class of high melting point, oxidation resistant RHEA being able to serve as novel structural materials for operation at ultrahigh temperatures beyond 1300°C.

4 Conclusions

Our contribution clearly shows that the oxide CrTaO₄ formed on the equiatomic high entropy alloy Ta-Mo-Cr-Ti-Al possesses protective properties. The oxide CrTaO₄ possesses a number of unique properties that are highly important for the development of new RM-based high temperature structural materials: (i) the oxide CrTaO₄ forms in a wide temperature range from 500°C to 1500°C exhibiting low growth rates, (ii) CrTaO₄ seems to possess high adhesive properties (iii) since the oxide CrTaO₄ is prone to solve other metallic components, a harmful competition between oxides can be avoided, (iv) the protectiveness of RM-based alloys can be realized if alloys contain required concentrations of Cr and Ta.

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