Enhanced oxidation resistance of MoTaTiCrAl high entropy alloys by removal of Al

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ABSTRACT Refractory high-entropy alloys (HEAs) exhibit remarkable mechanical properties desired for high-temperature applications. However, their oxidation resistance at high temperatures received less attention. Recent work indicates that MoTaTiCrAl alloy exhibits excellent oxidation resistance, but the effects of Al and Cr remain unclear. In this work, we demonstrate that the addition of Al is unnecessary for preventing oxidation of the MoTaTiCrAl alloy and the removal of Al leads to a more oxidation resistant MoTaTiCr medium entropy alloy. Structural and chemical analyses indicate that the excellent oxidation resistance of MoTaTiCr is mainly associated with the formation of continuous CrTaO₄ oxide layer. The results indicate that complex oxides can be adopted as effective candidates for enhancement of oxidation resistance, in addition to typical strategy of forming Al₂O₃, Cr₂O₃ or SiO₂ barrier layer.

Keywords: high-entropy alloy, oxidation resistance, MoTaTiCr, high-temperature application

INTRODUCTION

Oxidation resistance is critical for high-temperature applications of structural alloys because the formation of oxides can lead to severe degradation of mechanical properties [1]. From conventional perspective of alloy design, the primary strategy to enhance oxidation resistance is to incorporate Al, Cr or Si, as these elements are expected to form stable and dense protective oxide layers (e.g., Al₂O₃, Cr₂O₃, SiO₂) that can prevent the diffusion of O²⁻ into the interior of alloys, leading to further

oxidation [1–3]. However, traditional alloys are typically composed of one or two principal elements, with minor amount of other elements added to tailor microstructures and properties. Along with such design strategy, only a small fraction of Al, Cr, or Si is added for improving the oxidation resistance. The development of high-entropy alloys (HEAs), which are composed of five or more elements in (near) equimolar compositions, provides a new strategy for designing high-temperature alloys [4–8]. Instead of the formation of complex intermetallic phases, many HEAs form solid solutions in a wide compositional range and exhibit excellent phase stability, such that tuning of compositions and thus properties becomes possible in a vast range [4–8]. This novel strategy for alloy design not only significantly increases the number of potential alloys for technological applications, but also represents a new perspective for the development of highly oxidation-resistant alloys because a larger amount of Al, Cr, or Si can be incorporated into these alloy systems without sacrificing their mechanical properties [9].

Refractory HEAs (RHEAs), containing elements of high melting temperatures, such as Mo, Ta, W, Nb, Hf, are demonstrated to possess excellent mechanical properties at both room and elevated temperatures [4,10,11]. Such properties imply that they are promising candidates for the applications as high-temperature structural alloys. Nonetheless, compared with the investigation on their mechanical properties, oxidation resistance of RHEAs received less attention [12]. Recently, (Mo, W)-(Nb, Ta, Ti, Zr, Hf)-(Cr, Al, Si) alloys were found to exhibit pro-

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misgiving oxidation resistance in the temperature range of 900–1100°C. Among the alloys, MoTaTiCrAl was reported to be one of the most oxidation-resistant HEAs [12–16]. Analyses on the oxide layer indicate that the formation of a complex CrTaO_4 oxide plays an important role in the enhanced oxidation resistance of the alloy system, because a dense CrTaO_4 layer can inhibit outward diffusion of the constituent elements [13–15]. Although HEAs typically refer to alloys having at least five elements, suitable selection of elements is more important than solely increasing the number of elements in designing RHEA [9,15,17].

In this study, we demonstrate that MoTaTiCr, the derivative of MoTaTiCrAl RHEA, exhibits better oxidation resistance. By evaluating the oxidation behavior of MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl, we found that although the addition of Al into MoTaTi can result in increased oxidation resistance, the Al-free alloy MoTaTiCr was more resistant to oxidation as characterized by the smallest mass change and thinnest oxide layer during isothermal exposure at high temperatures in air. It was found that CrTaO_4 with larger Pilling-Bedworth ratio (PBR) can serve as a better protective oxide layer, according to the observation that Mo oxide evaporated at high temperatures, leading to porous oxide layer.

EXPERIMENTAL SECTION

As the elements used in this study have significantly different melting temperatures, in order to guaranty chemical homogeneity of the fabricated samples, the equimolar MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl alloys were produced by powder compaction followed by arc melting the powder tablets. Pure metal powders were accurately weighted and fully mixed at equal atomic ratios. For safety, small Al pellets, instead of Al powder, were used. The purity of all metal powders and Al pellets is more than 99.9%. The mixed powders were placed in a tablet mold and compacted at room temperature under a pressure of 300 MPa for 3 min. The tablets were then arc-melted in Ar atmosphere using a water-cooled copper crucible. The ingots were flipped over and remelted for at least four times to ensure chemical homogeneity. Samples with a dimension of 2.5 mm × 2.5 mm × 1 mm were cut from the ingots and polished by using P300 to P5000 SiC papers. The crystal structures and microstructures were characterized by using X-ray diffraction (XRD) (Bruker D8) and scanning electron microscopy (SEM) (Phenom XL), respectively. Chemical analysis was carried out by using energy-dispersive X-ray (EDX) spectrum attached to SEM. Oxidation tests were

conducted by exposing the samples in air for 10 h at temperatures ranging from 500 to 1000°C. Quantitative evaluation of oxidation resistance was performed by using a thermogravimetric analyzer (TGA) (STA 449F3) to measure the mass change as a function of isothermal exposure time, during which the samples were heated at a rate of 20°C/min from room temperature to 1000°C and held at 1000°C for 5 h in air.

RESULTS AND DISCUSSION

Microstructure of as-cast alloys

Fig. 1a presents the XRD patterns of the as-cast MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl alloys. For each alloy, the patterns exhibit only one set of diffraction peaks, which are identified to be a single-phase solid solution having a body-centered cubic (BCC) structure. This is expected because their physical and thermal parameters, such as atomic size difference, mixing enthalpy, and mixing entropy (Table 1), are all within the previously proposed range for the formation of solid solution [18,19]. With the addition of Al and Cr, the Bragg peaks shift towards higher diffraction angle, indicating the shrinkage of lattice parameters that are calculated to be 0.323, 0.321, 0.319, and 0.318 nm for MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl, respectively. The overall compositions of the alloys are confirmed to be close to equimolar ratio (Table 2). Microstructures of the as-cast alloys are shown in Fig. 1b–e. As can be seen, they all exhibit dendrite microstructures. The average sizes of the dendrite arms are 40, 7, 20, 6 μm for MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl, respectively. The formation of the dendritic microstructures can be attributed to non-equilibrium solidification [20]. Chemical analyses indicate that the bright dendritic core is rich in elements of higher melting temperatures such as Ta and Mo, while the dark interdendritic region is rich in elements such as Al, Cr and Ti that have lower melting temperatures (Table 2).

Oxidation resistance

The oxidation resistance of the alloys was first qualitatively evaluated by observing the changes in sample appearance upon isothermal exposure for 10 h at temperatures ranging from 500 to 1000°C in air. Fig. 2a shows the evolution of appearance for the samples with increasing exposure temperature. For ternary MoTaTi alloy, the sample turns black at 700°C, suggesting obvious oxidation. With the increase of exposure temperature, the shape of sample gradually turns to be rounded and finally

Figure 1 XRD patterns of the studied alloys (a) and microstructures observed by SEM for MoTaTi (b), MoTaTiAl (c), MoTaTiCr (d), and MoTaTiCrAl (e), respectively.

Table 1 Summary of atomic size difference (δ), mixing enthalpy (ΔH_{mix}), and mixing entropy (ΔS_{mix}) for MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl

	MoTaTi	MoTaTiAl	MoTaTiCr	MoTaTiCrAl
δ	2.91	2.55	5.93	5.50
ΔH_{mix} (kJ mol ⁻¹)	-3.5	-15.5	-5.5	-13.8
ΔS_{mix} (J K ⁻¹ mol ⁻¹)	9.13	11.53	11.53	13.38

becomes irregular at 1000°C. This demonstrates that MoTaTi underwent severe oxidation so that the entire bulk sample was oxidized at 1000°C. In comparison to MoTaTi, the MoTaTiCr, MoTaTiAl, and MoTaTiCrAl alloys exhibit much better oxidation resistance at high

temperatures. With increasing exposure temperature, only color changes can be seen. This suggests that merely thin oxide layers were formed on their surfaces even at a temperature as high as 1000°C.

Quantitative characterizations were then performed by measuring the mass change as a function of isothermal exposure time at 1000°C in air for 5 h. As shown in Fig. 2b, dramatic mass change can be seen for MoTaTi even after a short exposure time. The tendency continues until the end of test. After 5 h of exposure, the mass gain is as high as 21.8 mg cm⁻², indicating the low oxidation resistance of MoTaTi at 1000°C. The behavior is consistent with the sample appearance changes shown in Fig. 2a. Addition of Cr, i.e., MoTaTiCr, substantially decreases the mass changes upon isothermal exposure. Only slight mass gain can be seen in the first hour of isothermal exposure. After that, the mass gain curve reaches to a plateau without obvious increase. At 5 h, the mass gain is as low as 0.93 mg cm⁻². Addition of Al, i.e., MoTaTiAl, also decreases the mass changes upon isothermal exposure, and the mass gain after 5 h is 2.39 mg cm⁻², significantly smaller than MoTaTi alloy but larger than that of MoTaTiCr alloy. However, simultaneous incorporation of Cr and Al into MoTaTi does not further improve the oxidation resistance in terms of mass gain. As shown in Fig. 2b, although the MoTaTiCrAl shows a similar overall behavior as that of MoTaTiCr, the mass gain at 5 h is higher (1.39 mg cm⁻²) than that of MoTaTiCr. This indicates that the MoTaTiCr medium entropy alloy possesses better oxidation resistance than its HEA counterpart. Furthermore, the comparison between MoTaTiCr and MoTaTiAl suggests that the incorporation of Cr plays a more important role than Al for the enhancement of oxidation resistance in MoTaTiCrAl.

Formation and microstructure of oxide layer

Fig. 3 shows the XRD spectra of the surface layers from which oxidation products can be revealed. Fig. 4 presents the cross-section back scattering images of the alloys after isothermal exposure in air at 1000°C for 10 h, along with the corresponding chemical analyses by EDX mapping. In the case of MoTaTi, the XRD spectrum and SEM images were taken on a sample oxidized at 900°C.

The oxides of MoTaTi are mainly composed of TiO₂ and MoTiTa₈O₂₅ (Fig. 3). As shown in Fig. 4a, the oxide layer is ~160 μm in thickness and appears to be porous. EDX mapping indicates that oxygen distribution in the oxide layer is non-uniform. Chemical analysis along the black line in Fig. 4a indicates that Mo concentration is substantially reduced compared with that in non-oxidized

Table 2 Compositions (at.%) of MoTaTi, MoTaTiAl, MoTaTiCr, and MoTaTiCrAl measured by EDX

Alloy	Region	Mo	Ta	Ti	Cr	Al
MoTaTi	Overall	32.17	33.62	34.21	–	–
	Bright	34.80	39.35	25.86	–	–
	Dark	29.57	23.59	46.84	–	–
MoTaTiAl	Overall	24.65	23.90	27.00	–	24.45
	Bright	27.61	27.30	23.30	–	21.79
	Dark	23.50	20.01	29.09	–	27.40
MoTaTiCr	Overall	24.34	24.63	28.51	22.52	–
	Bright	32.83	34.63	19.56	12.99	–
	Dark	13.41	13.27	36.30	37.03	–
MoTaTiCrAl	Overall	19.73	19.70	22.27	18.67	19.63
	Bright	25.23	26.37	16.50	12.60	19.30
	Dark	18.39	18.81	20.60	17.93	24.26

Figure 2 (a) Changes of sample appearances after 10 h isothermal exposure in air at different temperatures, and (b) mass gain curves measured by TGA at 1000°C for MoTaTi, MoTaTiCr, MoTaTiAl, and MoTaTiCrAl alloys.

Figure 3 XRD patterns of the surface layers of the studied alloys after isothermal exposure in air for 10 h at 900°C for MoTaTi and 1000°C for MoTaTiAl, MoTaTiCr, and MoTaTiCrAl.

region (Fig. 5a, e). This suggests that Mo oxide could have formed but evaporated during oxidation, since MoO₃ is highly volatile at temperatures above 800°C [21–23]. The argument is in consistent with previous investigations [13–16]. Because the evaporation of Mo oxides creates porosity and thus additional pathways for oxygen diffusion, oxidation of region underneath oxide layer cannot

be prevented. This explains the severe oxidation of MoTaTi.

XRD analysis on MoTaTiAl indicates the formation of Al₂O₃, as well as TiO₂ and MoTiTa₈O₂₅ (Fig. 3). The oxide layer has an average thickness of ~35 μm, which is much less than that in MoTaTi. This is consistent with the better oxidation resistance of MoTaTiAl, and confirms that the addition of Al into MoTaTi is helpful for the enhancement of oxidation resistance. As revealed by SEM/EDX (Fig. 4b), the microstructure of oxide layer duplicates that of non-oxidized region. However, large porosity can be observed both in the oxide layer and at the wavy interface between oxide layer and non-oxidized alloy. According to EDX mapping (Fig. 4b), the formation of porosity can be ascribed to the evaporation of Mo oxides during oxidation, because the concentration of Mo is significantly reduced in the oxide layer (Fig. 5b and f). It can be seen that there is Al enrichment at the top of oxide layer, while Ti enrichment is observed at the interface between oxidized and non-oxidized regions. Therefore, it is possible that upon oxidation, Al₂O₃ was formed as the top layer, but incapable to form a continuous layer. This argument is further supported by the significant concentration variation of Al and Ti in the oxide layer in contrast to the much more uniform distribution of Ta (Fig. 4b). This indicates that even though Al addition can help to increase oxidation resistance of

Figure 4 Cross-section images and the corresponding chemical analyses by EDX mappings after isothermal exposure in air for 10 h at 900°C for MoTaTi (a), and 1000°C for MoTaTiAl (b), MoTaTiCrAl (c), and MoTaTiCr (d).

Figure 5 Chemical analyses by EDX line scan along the black line shown in Fig. 4. (a, e) MoTaTi; (b, f) MoTaTiAl; (c, g) MoTaTiCrAl; (d, h) MoTaTiCr. The panels from (e–h) show the relative concentration of each constituent elements without taking oxygen into account.

MoTaTi, formation of Al_2O_3 cannot result in a dense layer as an effective barrier against further oxidation.

As indicated by XRD analysis (Fig. 3), the addition of Cr into MoTaTiAl results in the formation of CrTaO_4

that has been considered effective to prevent oxidation of RHEA by inhibition of outward cation diffusion [14]. Other oxides in MoTaTiCrAl are mainly TiO_2 and Al_2O_3 . As shown in Fig. 4c, the distribution of Ta and Cr mat-

ches quite well, confirming the formation of CrTaO_4 . However, neither Ti nor Al is distributed evenly across the surface, suggesting that they fail to form a continuous layer. In addition, it can be seen that the concentration reduction in Mo (Fig. 5c and g) creates voids where both Ta and Al are depleted (Fig. 4c). This indicates that neither CrTaO_4 nor Al_2O_3 continuously cover the surface, and the discontinuity leaves pathway for oxygen diffusion into the region underneath the oxide layer. This is supported by the similar distribution of Ti and O in the interior of the alloy that implies possible internal oxidation.

Surprisingly, the removal of Al from MoTaTiCrAl to MoTaTiCr results in a continuous CrTaO_4 layer (Fig. 3), as confirmed by the coincident distribution of Cr, Ta, and oxygen. TiO_2 and $\text{MoTiTa}_8\text{O}_{25}$ have also been identified in MoTaTiCr (Fig. 3). EDX mapping indicates that TiO_2 forms in the outer-most layer and mainly in the Ti-rich region of the alloy. This can be attributed to its large thermodynamic driving force of formation than that of CrTaO_4 [15]. In the oxide layer, the reduction in Mo concentration still happens but is only significant near the top of the oxide layer (Fig. 5d and h). This clearly demonstrates that the formation of a continuous CrTaO_4 layer is the primary reason for the remarkable oxidation resistance of MoTaTiCr. In addition, the results also indicate that Al_2O_3 is not a prerequisite for enhancing oxidation resistance in the MoTaTi-(Cr, Al) alloy system.

DISCUSSION

As shown in Fig. 5, there is Mo reduction in the oxide layers in all of the studied alloys, which can be ascribed to the evaporation of Mo oxide that is volatile at high temperature [14,15,22,23]. This can be clearly seen from the variation of relative concentration without taking oxygen into account. In the case of MoTaTiCr, the formation of CrTaO_4 can effectively suppress the escape of Mo, as the reduction of Mo is only significant at the very top of oxide layer (Fig. 5h) and the relative concentration of Mo quickly becomes the same as that of non-oxidized alloy. For the other three alloys, however, Mo reduction is constant across the entire oxide layer. The reduction of Mo relative to the amount in non-oxidized region is more than 70%. Therefore, it is reasonable to conclude that the escape of Mo upon oxidation leads to underestimated mass gain in TGA measurement, in particular, for MoTaTi, MoTaTiAl, and MoTaTiCrAl.

For the oxidation of metallic alloys, there are two extreme cases that can be expected [16]. In the first case, the oxide fails to form a continuous passive layer due to either oxide evaporation or crack formation induced by

volume mismatch between the oxide and the alloy. The discontinuity leads to easy oxidation of the alloy underneath the oxide layer. In the second case, a stable and dense surface oxide layer forms and retards oxygen diffusion through the layer, so that further oxidation is prevented. Hence, the compactness of oxides plays an important role in oxidation of alloys.

The volume change induced by the formation of oxide can be quantified by PBR [24,25], which is the ratio between the volume of oxide formed and the volume of the corresponding alloy, i.e., $\text{PRB} = V_{\text{oxide}}/V_{\text{alloy}}$. Dense oxide layers are expected if PBR is in the range of 1–2, beyond which the oxide layer can be discontinuous either due to small volume of oxides or the cracking of oxide layer induced by internal stress [24,25].

To gain insight into the origin of the oxidation resistance of MoTaTi-(Cr, Al) alloys, we estimated PBR of oxides observed from XRD analyses. In the estimation, the volumes occupied by each atom in the alloys are considered the same. In BCC lattice, the volume of every 2 atoms could be written as a^3 with a the lattice constant, and PBR can be written as [24]: $\text{PRB} = V_{\text{oxide}}/0.5za^3$, where V_{oxide} is the volume of oxide, z is the number of metallic atoms in one oxide cell. The estimated PBR values are summarized in Table 3. Apparently, $\text{MoTiTa}_8\text{O}_{25}$ has a too large PRB value to form a protective layer. This explains why MoTaTi can be easily oxidized. Although Al_2O_3 and TiO_2 show ideal PRB, they do not form a continuous layer, leading to the thick oxidized layer in MoTaTiAl. As mentioned above, oxidation in the alloy system is accompanied with evaporation of Mo oxide. This leaves voids and pores in the oxide layer composed of the mixture of different oxides. Such voids may cause break of originally protective Al_2O_3 that has a small PRB value. To compensate the volume mismatch between the oxide layer and non-oxidized alloy, the oxide of properly larger PRB is required. It is thus reasonable to assume that the formation of CrTaO_4 in MoTaTiCr plays such a role, so that a continuous and protective layer quickly forms. This assumption is supported by the fact that the reduction of Mo occurs mainly near the top of oxide layer (Fig. 5h).

Table 3 Calculated PBR for the oxides formed in the alloys

Alloy	$\text{MoTiTa}_8\text{O}_{25}$	TiO_2	CrTaO_4	Al_2O_3
MoTaTi	2.80	1.86	–	–
MoTaTiCr	2.92	1.94	2.01	–
MoTaTiAl	2.84	1.90	–	1.24
MoTaTiCrAl	2.95	1.96	2.02	1.29

CONCLUSION

In summary, we have fabricated MoTaTi, MoTaTiCr, MoTaTiAl and MoTaTiCrAl alloys by arc melting. All of the as-cast alloys exhibit a single-phase solid solution of BCC structure. Oxidation resistance of the MoTaTi-(Cr, Al) alloys was evaluated by isothermal exposure at high temperatures in combination with thermogravimetric analyses. It is found that Al addition is not a prerequisite for enhanced oxidation resistance of the MoTaTi-(Cr, Al) alloy system. Instead, MoTaTiCr is most resistant to oxidation among the four alloys. Microstructural characterizations by XRD and SEM/EDX suggest that the enhanced oxidation resistance of MoTaTiCr arises from the formation of CrTaO₄ that can compensate the volume mismatch between the oxide layer and non-oxidized alloy due to the escape of Mo oxide. The outstanding oxidation resistance of MoTaTiCr along with its remarkable mechanical properties [10] makes it a promising candidate for high-temperature applications.

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Conflict of interest The authors declare no competing interest.

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通过去除Al元素提高MoTaTiCrAl高熵合金的抗氧化性

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摘要 难熔高熵合金具有高温应用所需的优异力学性能,但其高温抗氧化性却很少受到关注.近期的研究表明,MoTaTiCrAl合金呈现较好的抗氧化性,但Al和Cr两种元素对提高抗氧化性的作用仍未得以阐明.本文发现,Al元素对防止MoTaTiCrAl合金的氧化是不必要的,去除Al元素反而能够获得更抗氧化的MoTaTiCr中熵合金.结构表征和成分分析表明,MoTaTiCr合金的抗氧化性主要是因为合金表面能够形成连续的CrTaO₄氧化层.本文结果说明,除了采用Al₂O₃, Cr₂O₃, SiO₂等典型氧化物作为保护层,在合金表面生成复杂氧化物也能有效提升难熔高熵合金的抗氧化性能.