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Observation of a refractory metal matrix containing Zr-Ti- rich precipitates in a $\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ high entropy alloy

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Abstract:

Refractory metal high entropy superalloys (RMHES) offer potentially superior strength at elevated temperatures and lower densities than Ni-based superalloys. However, concerns exist over their ductility as their microstructures comprise fine distributions of refractory metal solid solution precipitates within a Zr- and Ti-rich ordered matrix. Consequently, identifying methodologies to invert this arrangement is critical. Here, we show that removal of Al from the $\text{AlMo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ RMHES, enables a microstructure to be obtained comprising Zr-Ti-rich disordered precipitates within a refractory metal matrix. This observation represents a significant development for the field and may help guide future alloy design.

Keywords: High Entropy Alloy; Microstructural formation; Phase transformations

The development of more efficient aeroengines for long-haul aviation necessitates higher turbine entry temperatures and, consequently, materials capable of withstanding these increasingly hostile operating conditions. The current materials of choice, Ni-based superalloys, are reaching the limit of their capability [1,2]. As such, the recent discovery of Refractory Metal High Entropy Superalloys (RMHES) has attracted significant attention, as they offer higher melting points, enhanced strength at elevated temperatures and lower densities than commercial Ni-based superalloys [3,4].

Similarly to Ni-based superalloys, RMHES, such as $\text{AlMo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$, exhibit dual phase intragranular microstructures consisting of a solid solution phase and a related ordered superlattice phase. However, unlike the face centred cubic based Ni-superalloys, RMHES consist of a body centred cubic (bcc) solid solution, typically rich in refractory metal (RM) elements, and an associated B2 superlattice phase, which tends to be enriched in Zr, Ti and Al [1,5-10]. In addition, the configuration of these phases in RMHES is inverted with respect to that of Ni-base superalloys, such that the matrices are the ordered B2 phase within which nanoscale cuboidal and plate-like particles of the bcc phase reside [1,11]. Consequently, there are concerns relating to the ductility and fracture toughness of these alloys, resulting in significant efforts to achieve a direct microstructural analogue to Ni-base superalloys, i.e. a RM-rich bcc solid solution matrix, reinforced by intermetallic precipitates.

To date, attempts to invert the microstructure of these alloy through variations in both processing routes and composition have had limited success [5,12]. A microstructural inversion has been achieved through a specific series of heat treatments applied to $\text{Al}_{0.5}\text{NbTa}_{0.8}\text{Ti}_{1.5}\text{V}_{0.2}\text{Zr}$ [12]. However, it is not evident that this approach is applicable to a wider range of alloys and, critically, the inverted microstructure may only be stable at lower temperatures. A number of compositional variants of $\text{AlMo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ have been studied but all of these alloys had microstructures that were predominantly a Zr-rich B2 phase, with no evidence of microstructural inversion [5].

In contrast, recent work investigating the simplified constituent system, Ti-Ta-Zr, has shown that a microstructure consisting of a RM-rich bcc matrix with intragranular Ti- and Zr-rich bcc particles can be produced by varying the ratio of Ta:Zr [13]. These observations suggest that the study of simplified systems may facilitate the identification of routes by which microstructural control may be achieved in more complex RMHES. It should be noted that the alloys investigated in reference [13] did not contain Al and, therefore, the ordered B2 phase was not present in any of the microstructures produced. However, the observed elemental partitioning supports the hypothesis that compositional modification may be able to facilitate microstructural inversion in more complex RMHES.

Here, this concept is extended through the characterisation of the microstructure and phase constituents of $\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$, which differs from the exemplar RMHES, $\text{AlMo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$, by the absence of Al. The nanoscale phase constituents in RMHES such as $\text{AlMo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ are believed to form through a process involving a spinodal decomposition, due to the miscibility gaps between the refractory metal elements and Zr [5], and the ordering of the Zr-rich phase caused by Al. Therefore, by removing Al, the microstructure would be expected to comprise two bcc phases, with a Zr- and Ti-rich matrix containing refractory metal rich particles, and act as a base for further studies relating to the influence of varying elemental ratios.

Previous studies of alloys within the MoNbTaTiZr quinary system have focused on equiatomic compositions and have identified the presence of two bcc phases [10,14]. Similarly, multiple bcc phases have been reported in other RMHEAs alloys, see Table 1 in reference [15]. However, the majority of these materials were characterised in the as-cast condition or following annealing in a multi-phase field [14,16-23]. As such, their microstructures were typically dendritic or dominated by the remnants of solidification induced segregation. Critically, very few studies have succeeded in homogenising a material of this type in a single bcc phase field from which a well distributed dispersion of fine-scale particles could be formed, e.g. NbTiVZr [24], which is essential for generating the microstructure desired for RMHES.

The present work shows that $\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ can be successfully homogenised in a single bcc phase field and that the fine-scale microstructure produced surprisingly comprises of a Zr-Ti-rich bcc particles within a refractory metal rich bcc matrix.

A 40g ingot of $\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ was fabricated by arc melting from elemental metals under an inert Ar atmosphere, that had been gettered by Ti prior to the melting the alloy. To enhance macroscopic homogeneity, the ingot was inverted and re-melted five times. The

ingot was subsequently homogenised at 1500°C for 24hr within a quartz tube that had been evacuated to a pressure of 8.9×10^{-7} bar and backfilled with 99.999 % purity Ar to create an inert atmosphere. Following the thermal treatment, the sample was cooled at 20°C/min to 1000°C and finally furnace cooled to room temperature. This initial cooling rate is the same as, or faster than, those used in other studies of AlMoNbTaTiZr RMHES [3,5,12,25] and, therefore, should produce microstructures that are directly comparable. The bulk composition of the alloy was determined from solution heat treated material at a certified external laboratory and found to be 11.5Mo-23.2Nb-24.6Ti-12.7Ta-27.9Zr.

Material for scanning electron microscopy (SEM) analysis was prepared using standard metallographic techniques, which concluded with a final polishing step using a buffered 0.06 µm colloidal silica solution. Back scattered electron (BSE) images and energy dispersive X-ray (EDX) elemental distribution maps were acquired using a Zeiss GeminiSEM 300 with an Oxford Instruments X-Max^N 50 detector. Higher resolution analysis of the fine-scale features within the alloy was performed using an FEI Talos F200X Scanning Transmission Electron Microscope (STEM), operated at 200kV and equipped with a Super EDX detector.

In the as-cast condition, Figure 1, the alloy exhibited a dendritic microstructure and associated solidification induced microsegregation. EDX elemental distribution mapping showed distinct variations in partitioning between the two regions, with the dendrites being enriched in Ta and Mo, whilst the interdendritic regions were enriched in Ti, Nb and Zr, consistent with data from MoNbTaTiZr [14,16]. It is vitally important to remove this microsegregation prior to assessing phase equilibria or studying microstructural evolution [4,26]. As such, the ingot was heat treated at 1500°C for 24 hours. The BSE image obtained after this heat treatment and the associated EDX elemental distribution maps are shown in Figure 2. The EDX elemental distribution maps were obtained under the same conditions as Figure 1 and showed an even contrast, indicating that the dendritic segregation had been eliminated.

Despite the apparent macroscopic homogeneity of the alloy following heat treatment, closer inspection of the microstructure revealed a number of micron scale features, somewhat similar to those observed in NbTiVZr [24]. Figure 3a shows a characteristic image of these features acquired from a region near to a grain boundary. Along the grain boundary a relatively coarse, dark BSE contrast phase was observed, immediately surrounded by a bright contrast matrix phase. Within the matrix, a large number of round precipitates were observed, all of which exhibited dark contrast but that suddenly decreased in size when ~30 – 40 µm away from the grain boundary. The larger precipitates, within 30 µm of the grain boundary, had diameters of approximately 5 - 10 µm and, along with the grain boundary phase, contained evidence of internal sub-structure, Figure 3b. The composition of these two dark-contrast regions were found to be very similar from EDX analysis and, therefore, it was concluded they were the same phase. Quantitative compositional data obtained from this dark contrast phase, in addition to the surrounding bright contrast matrix, are shown in Table 1. The precipitate phase was found to be significantly enriched in Zr and depleted in Ta and Mo. EDX analysis also indicated the presence of O and N in some regions of the microstructure. However, as a result of the inherently high inaccuracy when analysing the concentration of light elements using EDX, the O and N concentrations were not included in the quantitative analysis reported in Table 1.

The finer scale precipitates, found at distances $>30\text{ }\mu\text{m}$ from the grain boundary, had diameters of $<1\text{ }\mu\text{m}$ and did not exhibit evidence of sub-structure within them. In addition, the morphology of these precipitates appeared to elongate, becoming more lath-like, at greater distances from the grain boundary, Figure 3c. This lath morphology was observed for precipitates across the remaining grain interior along with regions that did not contain any precipitates, as shown in Figure 3d. Given the relatively fine length scale of all of these precipitates, it is believed that they formed during cooling from 1500°C and were not present during the homogenisation heat treatment.

Table 1: Averaged quantitative EDX compositions from regions of type A & B in Figure 3 and regions C, D, E & F in Figure 4. The errors are the standard deviation within the measurements obtained from each region.

Element	SEM EDX		STEM EDX			
	Region A	Region B	Region C	Region D	Region E	Region F
Ti	24.4 ± 0.4	29.4 ± 1.8	30.7 ± 0.1	27.2 ± 1.2	30.8 ± 0.8	12.5 ± 1.1
Zr	17.8 ± 0.6	55.8 ± 0.7	21.7 ± 0.4	10.4 ± 0.1	58.2 ± 1.4	85.1 ± 1.5
Nb	28.9 ± 0.3	10.2 ± 1.4	30.8 ± 1.3	37.4 ± 0.5	8.9 ± 0.2	2.0 ± 0.5
Mo	15.1 ± 0.4	1.8 ± 0.4	10.9 ± 0.3	15.8 ± 0.6	1.3 ± 0.4	0.0
Ta	13.7 ± 0.2	2.8 ± 0.6	6.0 ± 0.7	9.2 ± 0.2	0.9 ± 0.2	0.4 ± 0.1

Higher resolution characterisation of the fine-scale features observed within region C of Figure 3 was achieved through high angle annular dark field (HAADF) STEM imaging, an example of which is given in Figure 4. The HAADF image contained relatively large areas of intermediate contrast (region C), which did not appear to have undergone a microstructural decomposition, surrounded by regions that had broken down to form dark contrast precipitates in a bright contrast matrix (regions D-F). These precipitates had a rounded square cross section, in keeping with the corresponding SEM micrographs in Figure 3c. Since the TEM foil was extracted at 90° to the surface imaged in Figure 3, the common morphology of the precipitates suggested that these features were roughly cuboidal in three-dimensions rather than being cross sections of an elongated lath.

The elemental distribution maps from both the constituent alloying elements and the interstitial elements O and N are shown in Figure 4. These maps indicated that the undecomposed areas (e.g. region C) had a composition intermediate between those of the matrix and precipitate phases in the surrounding material. Within the surrounding material, the matrix phase (region D) was enriched in the refractory metals Nb, Mo and Ta, whilst the precipitates were enriched in Zr. However, the maps also indicated that two compositionally distinct precipitate phases were present in these regions, one enriched in Ti (region E) and the other depleted in Ti (region F). Quantitative compositional data from these phases are given in Table 1 and it can be seen that the Ti enriched precipitates (region E) had a higher refractory content than those depleted in Ti (region F) as well as a similar overall chemistry to the larger dark contrast precipitates observed near the grain boundary in Figure 3 (region B). Notably, both of the precipitate phases contained elevated concentrations of O compared to the surrounding matrix. However, these concentrations were well below the solubility limits in elemental Ti and Zr, suggesting that O was

accommodated in the solid solution rather than in the form of oxides. Although, the preferential partitioning of O to the precipitates may well indicate that it has a role in stabilising these phases.

Selected Area Diffraction Patterns (SADPs) acquired from each of the different regions are shown in Figure 4. Regions C, D and E were all found to have a bcc crystal structure with similar lattice parameters of $\sim 3.33 \text{ \AA}$. These SADPs were all acquired from a single tilt condition suggesting that these phases were coherent and well aligned in a cube-cube orientation relationship. The similarity between these crystal structures and the intermediate composition of region C, compared to those of regions D and E, suggests that this phase may be the parent phase that had not yet decomposed. These observations are consistent with previous studies of the AlMoNbTaTiZr system, which reported the formation of a Ti- and Zr- rich phase and a refractory metal rich phase [1,5,11]. However, here, in the absence of Al, the Ti- and Zr- rich phase is found to have a bcc structure, which is in contrast to studies on AlMoNbTaTiZr alloys where this phase was reported to have an ordered B2 structure. This observation appears to be consistent with the suggestion that the primary role of Al in these alloys is to promote the ordering of the Ti- and Zr- rich phase [5].

The SADP from region F did not solely correspond to a bcc crystal structure. Instead, when oriented such that the beam was aligned to the [001] of the bcc phases, a more complex pattern was obtained containing reflections from two different phases. As can be seen from the accompanying key diagrams, one set of reflections within the SADP were consistent with the surrounding bcc matrix, whilst the remaining reflections corresponded to the $[\bar{1}2\bar{1}6]$ zone of a hexagonal close packed (hcp) structure. The identification of an hcp structure is also in keeping with the composition of these highly Zr enriched precipitates, given in Table 1 [27]. The orientation of these two sets of reflections is such that the $[110]_{\text{bcc}}$ is parallel to the $[10\bar{1}0]_{\text{hcp}}$, which would be consistent with the Burgers orientation relationship commonly found between phases with these structures in Ti alloys [28]. A nearly pure Zr phase has been previously reported in $\text{Al}_{0.5}\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ following heat treatment at 1400°C [5], but its crystallography was not established and its morphology of highly elongated needles 10s of μm in length was markedly different to that observed here. Zr rich phases have also been reported in NbTiVZr [24] and HfNbTaTiZr [29] following thermal treatment, and in the case of the HfNbTaTiZr were reported to have a bcc or hcp structure depending on the exposure temperature.

From the results presented here, it seems likely that $\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ resides in a single bcc phase field at 1500°C . Upon cooling, decomposition of this phase results in the formation of two compositionally distinct phases, both of which have a bcc crystal structure and similar lattice parameters. Such decomposition indicates the presence of a miscibility gap in the bcc Gibbs energy curve, which drives the formation of the lower temperature microstructure. The observation of untransformed regions, particularly towards the grain centers, suggests that the decomposition in this alloy took place by nucleation and growth, rather than through a spinodal process. However, this simply means that $\text{Mo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ lies outside the spinodal region and does not preclude the possibility that other related alloys could decompose spinodally. Thus, it would appear that depending on alloy composition, a two-phase microstructure can be produced in RMTiZr alloys by either spinodal decomposition or through nucleation and growth.

However, the observation of greatest significance arising from this study is the presence of a refractory metal-based bcc matrix containing Ti- and Zr-rich precipitates. This microstructural configuration is unexpected and opposite to those reported in similar alloys, such as $\text{AlMo}_{0.5}\text{NbTa}_{0.5}\text{TiZr}$ or $\text{CrMo}_{0.5}\text{NbTa}_{0.5}$, which typically comprise Ti- and Zr-rich matrices containing refractory metal-based particles [1,11,17,30]. This observation lends further support to the hypothesis that microstructural inversion of RMHES may be achievable through compositional modification. These results also indicate that the role of Al in the AlMoNbTaTiZr system is more complex than simply driving an ordering transformation of the Zr- and Ti-rich phase. Al appears to have a significant impact on the crystal structures present, the microstructural formation pathway and the occurrence of refractory metal-based matrix phase. Consequently, further studies will be required to better understand the role of Al in these multi-component alloys.

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Figure 1: BSE micrograph and corresponding EDX elemental distribution maps in the as cast condition.

Figure 2: BSE micrograph and corresponding EDX elemental distribution maps in the homogenised condition.

Figure 3: BSE micrographs following solution heat treatment and furnace cooling. a) Low magnification image identifying typical regions from which the higher magnification images shown in b) c) and d) were obtained. b) region containing the coarse phase formed near grain boundaries. c) fine-scale cuboidal phases in the near grain boundary region. d) phase formed with lath morphologies from the grain center.

Figure 4: HAADF image and corresponding STEM-EDX elemental distribution maps from material in the homogenised condition. SADPs from each phase identified are included with key diagrams corresponding to the SADP from region F.

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