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Phase formation criteria assessment on the microstructure of a new refractory high entropy alloy

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ABSTRACT

This work focuses on the evaluation of various parametric models for the formation of solid solution phases in high entropy alloys. The actual observation of MoWHfZrTi microstructure, along with the theoretical suggestions for single phase selection is discussed. The micro-segregated obtained structure is explained in terms of introducing a possible mechanism based on the estimation of thermodynamic parameters and further analysis of the experimental evidence upon solidification. High values of both micro and macro hardness characterize the synthesized system, indicating a solid solution strengthening mechanism.

1. Introduction

High Entropy Alloys (HEAs) have triggered a new interest in materials design philosophy. Presenting intriguing properties [1–5] and unique microstructural features [6–8] these new systems have gradually opened a new frontier in the metallic materials field [9]. Phase stability is vitally important for HEAs, but understanding this phenomenon is quite complex [10]. However, the ability to predict phase formation/selection, based on the fundamental thermodynamic properties of the constituent elements, would greatly benefit the capacity for further alloy exploration.

Thus, the relationship between physicochemical and thermodynamic parameters of the alloying components in HEAs seems to influence the design concept lately [11]. Towards this direction, several prediction models concerning phase formation criteria in HEAs have gradually been introduced [12–16]. For example, the evaluation of thermodynamic parameters such as atomic size difference, enthalpy of mixing and entropy of mixing [12] seem to be dominant factors in determining the formation of stable solid solution phases.

Moreover, a new model based on the use of high-throughput computation of the enthalpies of formation of binary compounds in HEAs systems, predicts the specific combinations of elements most likely to form single-phase high entropy alloys [13]. Additionally, a novel method for rapidly predicting the formation and stability of undiscovered single phase HEAs has been developed, using Miedema's model as a basis. The introduction of parameter, phi, suggests the presence of stable solid solutions at the systems' melting temperature [14].

Perhaps the most critical weakness of the parametric approaches is that most of them are fitted to experimentally obtained data [17]. Indeed, careful assessment of the actual microstructural features is necessary before conclusions are drawn about the characteristics and stability of the corresponding structures [18]. It is undoubtable that the task of HEAs phase selection will add immeasurably to understanding phase formation in high entropy systems, and to our ability to predict complex microstructures in multicomponent alloys.

In this present effort, a new – in terms of composition – refractory $Mo_{0.85}W_{0.85}Hf_{1.1}Zr_{1.6}Ti_{0.6}$ alloy was produced and tested in order to assess whether the predicting models can indeed forecast the observed final microstructures. The system, as a new refractory high entropy alloy, is expected to show improved properties (mechanical, wear, oxidation etc. response) at both ambient and elevated temperatures. It is also important to mention that, irrespectively of the final result (single phase, dual solid solutions, intermetallic phase formation or combinations of them) the HEA approach in designing a new alloy system is of extreme importance as it promises novelty in the designing perception and uniqueness on the microstructural outcome.

2. Results and discussion

This paper presents an analysis of this aspect. Specifically, $Mo_{0.85}W_{0.85}Hf_{1.1}Zr_{1.6}Ti_{0.6}$ high entropy alloy was prepared by melting pure metallic powders and wires in an arc furnace with a non-consumable W-electrode, under a protective argon atmosphere. Two re-melting

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efforts followed the initial stage of preparation in order to achieve a better distribution of the elements in the final structure.

Various phase formation criteria were estimated in an initial effort to correlate theoretical prediction evidence with actual microstructural findings. In particular, estimations of atomic size difference, enthalpy of mixing, entropy of mixing, enthalpy of formation and phi parameter data were evaluated and compared with the presented morphological features of the examined refractory system.

A Bruker D8 Advance X-ray diffractometer was used for crystal structure examination, while a JEOL 6510 LV SEM equipped with both backscatter electron (BSE) and energy dispersive spectroscopy (EDS) detectors further characterized the resultant structure of the high entropy alloy.

Table 1 presents the calculated parameters of the refractory system, regarding atomic size difference, enthalpy of mixing and entropy of mixing as proposed by Guo et al. [12]. The estimated values for $Mo_{0.85}W_{0.85}Hf_{1.1}Zr_{1.6}Ti_{0.6}$ high entropy alloy were determined as $\delta = 7.05$, $\Delta H_{mix} = -6.39$ kJ/mol and $\Delta S_{mix} = 12.9$ J/K, all ranging within the proposed literature limits. On the other hand, the Troparevsky et al. model [13] suggests the formation of several binary solutions with some ΔH_f values of the binary components escalating outside the recommended boundaries for single phase solid solution formation ($-138 < \Delta H_f < 37$ meV/mol) in a 5 component system. Possible phase segregation phenomena could be spotted in this case. Moreover, according to King et al. [14] the derived values of parameters δ and Φ (using www.alloyASAP.com platform as a calculation tool) were determined as 6.309 and 1.456, respectively, both lying within the proposed ranges for solid solution formation, but also being very close to their marginal limits. As such, some possible deviations from the theoretical response could be expected.

To sum up, all the aforementioned proposed prediction models, provide some first clues about the possible phase selection speculations, but do not guarantee a single phase solid solution formation. It is of high priority to further examine the actual alloy microstructure, in order to receive acceptable data about the real structural mechanisms of the synthesized alloy.

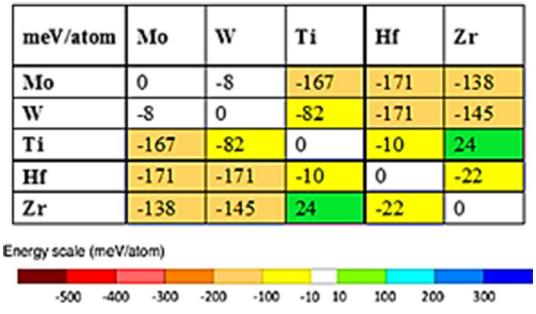
Therefore, Fig. 1 presents the X-ray spectrum of $Mo_{0.85}W_{0.85}Hf_{1.1}Zr_{1.6}Ti_{0.6}$ high entropy alloy. The presence of different crystal structures is evident, as two BCC and one HCP based lattices are formed. According on these findings, a first indication about a phase segregation formation is established, verifying the predictions of Troparevsky et al. [20] proposed model and King's et al. [21] uncertainty in forming a single solid solution.

Further analysis of the presented microstructure was conducted by SEM examination, as depicted in Fig. 2. The alloy exhibits dark and bright areas (as a sign of possible segregation tendency), while the final structure is significantly refined (<10 μm). A rather equiaxed – especially for the primary W–Mo enriched grains – microstructure was observed, which may raise questions on the establishing for growth driving force conditions (temperature gradients, undercooling rate) ahead of the solidifying fronts, as they may alter the involved segregation mechanisms.

A detailed approach to the microstructural findings also led to elemental mapping and line scan analysis (Fig. 2), both verifying the segregation of W and Mo within the bright areas and Zr and Ti within the darker areas. The distribution of Hf seems to be uniformly spread along the final structure.

The presence of such segregation phenomena in various refractory high entropy alloys is widely criticized by many researchers [19–23]. For example, Stepanov et al. [21] and Senkov et al. [23] linked the observed micro-segregation in their systems with non-equilibrium solidification within the temperature range between the liquidus-solidus temperatures. As proposed, this tendency is also associated with an increase in the difference in the melting temperatures of the alloying elements. Another approach [20] relates segregation formation with the cooling rate upon solidification. Specifically, depending on the position

Table 1
Calculated values of atomic size difference, enthalpy of mixing, entropy of mixing, enthalpy of formation and phi parameter, according to different proposed prediction models for the initial and actual composition of the examined alloy after specific elemental point analysis.

System	Guo et al. [12]			Troparevsky et al. [13]	King et al. [14]	
	δ	ΔH_{mix} [kJ/mol]	ΔS_{mix} [J/K·mol]	ΔH_f [meV/atom]	δ	Φ
$Mo_{0.85}W_{0.85}Hf_{1.1}Zr_{1.6}Ti_{0.6}$	7.05	−6.39	12.9		6.309	1.456

		Estimations based on King et al. model [14]					
		δ	H_{max}	H_{ss}	Φ	S_{mix}	T_m [K]
Actual alloy composition (point EDS analysis)	Dark area Mo = 13.74 at.% W = 0 at.% Hf = 20.65 at.% Zr = 44.16 at.% Ti = 21.45 at.%	5.13	−10.88	2.66	1.99	10.72	2271
	Light area Mo = 25.39 at.% W = 33.80 at.% Hf = 18.25 at.% Zr = 17.39 at.% Ti = 5.18 at.%	7.36	−24.26	−3.45	1.62	12.32	2912