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Microstructure and wear behavior of a refractory high entropy alloy

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The microstructure, hardness and wear behavior of a refractory high-entropy $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ alloy of equi-atomic composition were evaluated. The alloy was prepared by vacuum arc melting and presented optimal empirical parameters for the formation of a solid solution phase. The lattice parameter $a = 3.1867$ Å for the quinary alloy was determined with high-energy X-ray diffraction. The alloy's Vickers micro hardness was estimated as $HV_{0.5} = 7576 \pm 201$ MPa, while its Rockwell B hardness took a value of 97 ± 4 HRB. The exceptional hardness in this alloy is greater than any individual constituent, suggesting the operation of a solid-solution-like strengthening mechanism. The alloy's wear behavior was also studied and analyzed under different experimental conditions. The volume loss and wear rate were determined, accompanied by SEM images and EDS analysis of the wear tracks and debris, proposing some possible wear mechanisms for each case. Finally, the wear behavior of $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ was compared with that of a commercial superalloy (Inconel 718), proving the supremacy of the high entropy alloy concerning its wear resistance.

1. Introduction

With the fast development of new technologies and theories for exploring advanced materials, the number of constituent principal elements for metallic alloys has increased from one to three or more. With more than three or four principal elements, the alloys were intuitively thought to be complex. Conventional alloy strategy leads to an enormous amount of knowledge about alloys based on one component, but to very little or no knowledge about alloys containing several main components in approximately equal proportions [1].

Nevertheless, High Entropy Alloys (HEAs), a brand new category of metallic materials, appeared to be a new effort in materials science and engineering, which attracted great interest. The first publications appeared not quite 10 years ago [2,3] and HEAs are being considered for a wide range of functional and structural applications [4].

The standard definition of a HEA is an alloy that contains at least five major metallic elements ($N \geq 5$), each one with a concentration between 5–35 at.% [4,5]. The lower limit of five elements is imposed because it is considered to be the point at which the mixing entropy is high enough to counterbalance the mixing enthalpy in most alloy systems and thus ensure the formation of solid solution phases [4]. The idea behind this definition is that compositional complexity may not necessarily lead to microstructural complexity (i.e., compound formation) due to the influence of entropy. Specifically, it is suggested that disordered solid solutions might remain stable relative to ordered intermetallic compounds in alloys with high total entropies of mixing (ΔS_{mix}).

Perhaps the most significant benefit of HEAs has little to do with the magnitude of entropy. The major benefit of HEAs is that they stimulate the study of compositionally complex alloys not previously considered. This suggests an astronomical number of compositions, giving great potential for discoveries of scientific and practical benefit. Supporting this view, a wide array of HEA microstructures has been produced, including single phase, multiple phase, nanocrystalline and even amorphous alloys [6].

Since the introduction of the HEA concept, the most commonly used alloying elements were transition metals such as (fcc)-type Cu, Al, Ni; (bcc)-type Fe, Cr, Mo, V and (hcp)-type Ti, Co [7–12]. However, from 2010 onwards, some efforts have been pursued to explore new HEAs based on refractory constituents [13–21].

Because of their unique multi-principal element composition, HEAs can possess special properties. These include high strength/hardness, outstanding wear resistance, exceptional high-temperature strength, good structural stability, good corrosion oxidation and creeping resistance [22–27].

Some of these properties are not seen in conventional alloys, making HEAs attractive in many fields. The fact that HEAs can be used at high temperatures broadens their spectrum of applications even further. Moreover, the fabrication of HEAs does not require special processing techniques or equipment, which indicates that their mass production can be easily implemented with the existing equipment and technologies [28].

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Table 1
Chemical composition of $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ alloy prepared by vacuum arc melting.

Alloy ID	Composition	Mo	Ta	W	Nb	V
$Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$	at.%	20	20	20	20	20
	wt.%	15.87	29.93	30.41	15.37	8.43

Table 2
The crystal lattice parameter, a_{mix}, of $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ HEA.

Metal	Mo	Ta	W	Nb	V	Theoretical value a_{mix}	Experimental value a_{mix}
a (Å)	3.15	3.31	3.16	3.3	3.02	3.1827	3.1867

Moving towards this direction, several high-entropy refractory alloys with promising combinations of microstructure and properties have been reported in literature. For example, $Ta_{20}Nb_{20}Hf_{20}Zr_{20}Ti_{20}$ [29,30] exhibited promising combinations of room temperature and elevated temperature mechanical properties. Both single phase bcc disordered structures of $Nb_{25}Mo_{25}Ta_{25}W_{25}$ and $V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$ [31,32] also showed improved mechanical behavior over a wide temperature range, while $Hf_{25}Nb_{25}Ti_{25}Zr_{25}$ high entropy alloy [33] presented excellent structural stability and tensile properties. In addition, HfMoTaTiZr and HfMoNbTaTiZr [34] demonstrated improved strength at high temperatures, while retaining reasonable toughness at room temperature and $Ti_{20}Zr_{20}Hf_{20}Nb_{20}V_{20}$ [15] exhibited considerable strengthening and homogeneous deformation.

Exploring the bio-medical applications of refractory HEAs, they mainly focus on the application of protective coatings on Ti alloys and stainless steels (e.g. (TiZrNbHfTa)N and (TiZrNbHfTa)C) [35]. This project aims to increase the life duration and performance of the substrates, as long as these coatings are characterized by low elastic modulus, high chemical stability and corrosion-wear resistance to surrounding biological fluids. Specifically, Braic et al. [35] showed that the carbide coating (TiZrNbHfTa)C exhibited a high hardness of about 31 GPa, an improved friction behavior ($\mu = 0.12$) and a high wear resistance (wear rate $K = 0.2 \times 10^{-6} mm^3 N^{-1} m^{-1}$), when testing in SBFs. The applications of these coatings are mostly related to dental and orthopedic fields [36].

Finally, concerning the tribological properties of HEAs, the literature, so far, focuses mainly on using transition metals for the synthesis of the examined materials. For example, $Co_{1.5}CrFeNi_{1.5}Ti$ and $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$ [37] presented improved wear resistance due to their magnificent anti-oxidative characteristics. Actually, the addition of the alloying elements enhanced the wear behavior due to the formation of a smoother wear surface and finer debris of high hardness, which restricted the further plastic deformation and resulted in the construction of an oxidative film.

Wu et al. [38] also studied the adhesive wear behavior of $Al_xCoCrCuFeNi$ HEAs as a function of Al content. Researchers claimed that, for higher Al content, the worn surface is smooth and yields fine debris with oxygen content, which gives a large improvement in wear resistance. The reason for this is attributed to its high hardness, which not only resists plastic deformation and delamination, but also brings about the oxidative wear in which the oxide film could assist the wear resistance.

The present work is part of a wide effort to assess refractory high entropy alloys at both ambient and high temperatures. The experimental effort described in this manuscript is an initial attempt to ascertain the sliding wear response of a refractory high entropy $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ alloy at ambient temperatures which, at the best of the authors' knowledge, has not been addressed so far. The microstructure and the macro- and micro-hardnesses are also included. A comparison of the sliding wear response between this HEA and the commercial superalloy Inconel 718 is also attempted, in order to reveal the improved resistance of $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ towards that of a well-known alloy for such purposes.

2. Methods

2.1. Experimental procedure

The $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ high entropy alloy was prepared by vacuum arc melting of equi-molar mixtures of the corresponding elements. The raw materials were in the form of powders with a purity of over 99.5% each. Arc melting of the alloy was conducted on a water-cooled copper plate in an atmosphere of high purity argon. To achieve a homogeneous distribution of elements in the alloy, the samples were re-melted five times and flipped for each

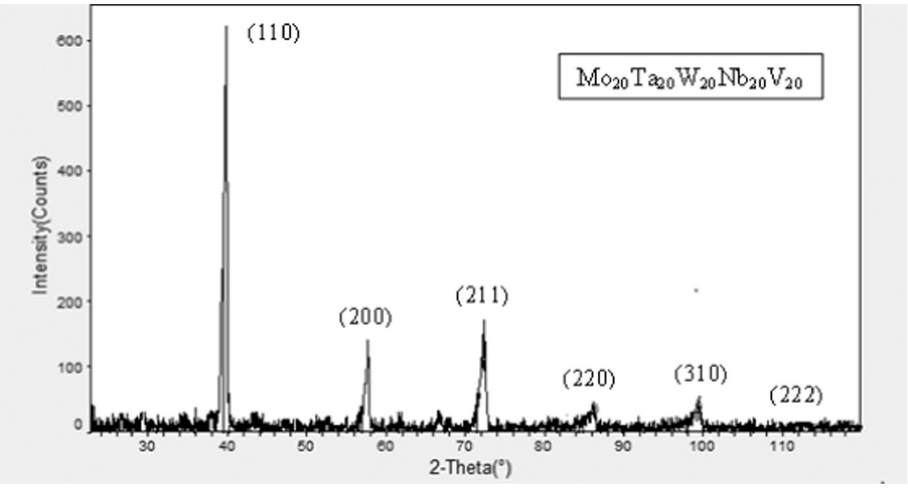

Fig. 1. X-ray diffraction pattern of the $Mo_{20}Ta_{20}W_{20}Nb_{20}V_{20}$ HEA. All peaks belong to the same bcc crystal lattice and their indexes are shown.