High-temperature Mechanical Properties and Microstructure of ZrTiHfNbMo$_x$ (x=0.5, 1.0, 1.5) Refractory High Entropy Alloys

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Abstract: Refractory high entropy alloys (RHEAs), with excellent properties at high temperature, have several applications. In this work, the ZrTiHfNbMo$_x$ (x=0.5, 1.0, 1.5) alloys were prepared by arc melting. All these alloys form body centered cubic (BCC) structure without other intermediate phases. The Mo element contributes to the strength of alloys at high temperature, but too much of Mo decreases the plasticity severely and enhances the strength. The ZrTiHfNbMo$_x$ alloy, whose compressive stress is 1099 MPa at 800°C, is a promising material for high-temperature applications.

1. Introduction
In recent years, RHEAs were proposed due to their extraordinary properties in the high temperature application field[1-3]. Contrasted with the traditional superalloys, RHEAs contain more than five elements with near equal mole ratios (5%-35%) and form the single microstructure [4, 5]. Because the elements of RHEAs are in the group IV, V and VI with the melting point over 1650 °C, the operating-temperature range of these alloys are more than Al-Ni superalloy [6, 7]. The special performances of RHEAs including high configurational entropy, sluggish diffusion, the severe lattice distortion and unique cocktail effect [8-11] contribute to the high strength even in the extreme conditions, which become promising candidates in high temperature materials field.

2. Experimental
The ZrTiHfNbMo\(_x\) (x=0.5, 1.0, 2.0) alloys were prepared by arc melting under the purified argon atmosphere, and the cooling system employed the water-cooled copper crucible. The as-cast crystalline structure was investigated by X-ray diffractometer (XRD, D8 advance) with \(K_x\) radiation. The high temperature compressive performances were performed on a Gleeble-3500 thermal simulator, each alloy was heated 800\(^\circ\)C and 900\(^\circ\)C in turns, the heating rate was setting as 300\(^\circ\)C/min and the holding time was 3 minutes. A scanning electron microscope (SEM, HITACHI4800) was adopted to analyze the microstructure with the secondary electron image.

3. Results and discussion

3.1. Crystal structure and microstructure analysis
The X-ray diffraction patterns of these as-cast ZrTiHfNbMo\(_x\) alloys are shown in the figure 1. According to the analysis through JADE 5.0 software, all the major peaks of these alloys are consistent with the single phase of body center cubic without any other precipitated phase. The diffraction peaks are sharp, which indicates that these alloys have high crystallinity. With the increase of Mo content (the radius of Mo element is apparently smaller than other element), the diffraction peak shift to the low theta due to the crystal lattice become smaller.

![X-ray diffraction patterns of the RHEAs](image)

**Figure 1.** X-ray diffraction patterns of the RHEAs

3.2. High temperature compression performance analysis
The compressive stress-strain curves of ZrTiHfNbMo\(_x\) alloys at high temperature are displayed in the figure 2. The process of stress follows that increase rapidly, reduction and remaining a stable value with the deformation increase. The high-temperature stress of the ZrTiHfNbMo\(_{0.5}\) alloy is relatively poor, which is 585 MPa at 800\(^\circ\)C and 288 MPa at 900\(^\circ\)C. When adjusting the content of Mo element, the stress of ZrTiHfNbMo alloy is 1099 MPa at 800\(^\circ\)C and 804 MPa at 900\(^\circ\)C. The Mo element has the highest melting point and strength among these elements, which contributes to the properties of softening resistance. As the Mo content continues to increase, the stress of ZrTiHfNbMo\(_{2.0}\) alloy is 1155 MPa at 800\(^\circ\)C, and 897 MPa at 900\(^\circ\)C, but the strain is less than 15% at 800\(^\circ\)C contrasted with
the strain of ZrTiHfNbMo$_{0.5}$ and ZrTiHfNbMo alloy more than 40%, respectively. The excessive Mo element made the lattice distortion increase and the dislocation slides difficultly even at high temperature. As the high temperature could provide much more energy, then it would promote the movement of dislocation, vacancy and grain boundary, which could decrease the stress.

The compression scanning electron microscopics of ZrTiHfNbMo$_x$ alloys at high temperature are shown in the figure 3. Compared the figure 3(a) and (b) with the figure 3(d) and (e), the size of grains become larger and the intercrystalline crack is more serious as the temperature increases, part of the dendrites were fused. The fracture feature of ZrTiHfNbMo$_{2.0}$ alloys is the river-like appearance in the figure 3(c), which reveals that the poor plasticity at 800°C.

![Figure 2](image2.png)

**Figure 2.** High-temperature compressive stress-strain curves of these alloys: (a) Mo$_{0.5}$; (b) Mo$_{1.0}$; (c) Mo$_{2.0}$

![Figure 3](image3.png)

**Figure 3.** The high-temperature fracture scanning electron microscopics of ZrTiHfNbMo$_x$ alloys. Mo$_{0.5}$: (a) at 800°C and (d) at 900°C; Mo$_{1.0}$: (b) at 800°C and (e) at 900°C; Mo$_{2.0}$: (c) at 800°C and (f) at 900°C;
4. Conclusion
In this paper, the ZrTiHfNbMo$_x$ (x=0.5, 1.0, 2.0) refractory HEAs were melted and the high-temperature properties were analyzed. These alloys formed the body centered cubic structure without other phases. The high temperature stress of these alloys is enhanced with the Mo element increase (Mo content from 0.5 to 1.0). The strength of ZrTiHfNbMo$_{2.0}$ enhances a few and their plasticity decreases rapidly as the Mo element continues to increase, and the fracture displays the river-like appearance at 800 °C. The reasonable content of Mo element is contributed to the high temperature mechanical properties, and the HEAs with balance between strength and plasticity at high temperature can be acquired through controlling the Mo content addition.

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