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Paper Title: The effect of changing constituents on tensile mechanical properties of HfNbTaTiZr high entropy alloy: A molecular dynamics study

Content :

Introduction

The high-entropy alloy (HEA) has been gaining more attention lately due to its exceptional properties such as high strength, significant hardness, and excellent wear resistance [1,2]. Apart from conventional alloys, a HEA consists of a minimum of four or five constituent elements, each present in a molar ratio ranging from 5 % to 35 % [3]. To construct HEAs, a wide range of materials have been used in recent times. Despite the vast number of possible combinations of four or five constituent elements, it is possible to identify five primary groups of metallic HEAs [4], which are FCC-Cantor Alloys, BCC-Refractory Alloy, HCP-HEAs, Light Elements Alloy-HEAs, and the HEAs that possess valuable functional properties [5]. Among these, the BCC refractory HEAs are distinguished from other materials by their outstanding high-temperature strength, oxidation resistance, and corrosion resistance properties has gained significant attention. These alloys primarily consist of refractory elements such as tungsten, tantalum, molybdenum, zirconium, hafnium, vanadium, and niobium, each present in the range of 5 %–35 % [6].

The current research focused on the refractory HEA, which is constructed by the elements from the I, V, and VI groups of the periodic table [7]. The various mechanical properties of HfNbTaTiZr system has been experimentally studied by the researchers. The tensile creep behavior of HfNbTaTiZr refractory HEA has been demonstrated by Liu et al. [8] at 1250 °C and suggested that the creep rate of the alloy was controlled mainly by Ta element. Another study by Zherebtsove et al. [9] examined the microstructure and mechanical properties of HfNbTaTiZr-HEA during cold rolling. While increasing the thickness strain to 15 % the microhardness was increased and came to a plain stage at the interval of 15–40 % strain, afterword the microhardness again increased with the thickness strain. The elastic moduli at higher temperatures ranging from 293 K to 1100 K were also explored by Laplanche et al. [10]. Microhardness was strongly increased after aging the HfNbTaTiZr-HEA at 600 °C and a second HCP phase particles were formed in the BCC matrix after the process of annealing at 600 °C and 800 °C [11]. The HfNbTaTiZr-HEA is being used in dual-phase alloys [12] and reinforced high entropy composites [13,14]. Dissimilarity in thermal expansion coefficient can lead to thermal stresses during solidification, which potentially might affect the composite strength [15].

Therefore, this study also aims to understand the thermal expansion coefficient (TEC) and elastic moduli at specific temperatures.

Though it is difficult to find hafnium (Hf) that is pure due to its high reactivity in the ambient atmosphere [4], also as both hafnium and tantalum are high price elements [16,17], it is difficult to experimentally study the effect of all the elements on mechanical properties of HfNbTaTiZr-HEA. Adding to that, a more sophisticated and costlier experimental setup is necessary for high temperature inspections. Moreover, there is lack of studies that show the effect of changing the ratio of all five constituent elements of HfNbTaTiZr-HEA on the mechanical properties, especially the stress-strain behavior. Hence, the current research focused on molecular dynamics (MD) simulation to study the effect of changing composition on stress-strain behavior in the present study. The current study shows the effect of changing the Nb, Ta, Ti, and Zr elements from 0 to 30 % on stress-strain behavior of the HfNbTaTiZr-HEA and also gives an insight into the fracture that occurred during the uniaxial tensile test. Overall, how the changes in the atomic level interaction and crystal structure affect the macroscopic properties of HEA are investigated. This level of detail is difficult to achieve experimentally making our findings particularly valuable. Also, the understanding can contribute to the design of new HEA with more tailored properties for various engineering applications such as nuclear or aerospace industries. TEC was also investigated for the equimolar alloy and for the optimized alloys which are discussed in the later section of this article.

Individual elastic behavior of the single elements

The ideal stress-strain behavior of the individual constituent elements was tabulated for comparison purposes. Table 2 gives the comparison of Elastic Moduli of individual HEA elements where ‘Ta’ has exhibited the value of C_{11}, and Young's Modulus among the other constituents of HfNbTaTiZr-HEA elements of this group. The BCC crystal of ‘Ta’ mainly contributes to its high strength and modulus by limiting the pathways for movement of dislocations that require high stress to deform plastically. On the contrary, ‘Zr’ exhibits the lowest elastic Moduli as well as the C_{11} value, when compared to BCC and FCC structures, Zr's hexagonal close-packed (HCP) structure has fewer slip systems. The prismatic planes make plastic deformation more easier in ‘Zr’ that lower the Critical Resolved Shear Stress (CRSS) and also lowers tensile strength and ductility [24]. Moreover, the experimental results of the different groups of researchers also confirmed that the ‘Ta’ exhibits the highest Young's Modulus when compared to other constituent elements of the HfNbTaTiZr-HEA

Effects on ultimate tensile strength (UTS)

The effect of changing constituents and their respective composition were studied to explore their effects on UTS. Fig. 2 demonstrates how the UTS property of the

HfNbTaTiZr-HEA changes when Nb, Ta, Ti, and Zr percentages are changed individually.The tensile strength of the material was 1.1 GPa for Nb0 meaning there are only four elements in the alloy and increased to 3.8 GPa when Nb is added to HEA of 10 % *i.e.* simply by adding Nb can make the alloy stronger. The tensile strength is raised here as a result of the 'Nb' addition is mainly of solid solution strengthening effect [42]. A small amount of Nb can disrupt the regular arrangement of atoms in the host material and impede the mobility of the dislocations and cause plastic deformation. In other words, when a high-strength element Nb (*i.e.* 12.08 GPa) is added to a lower-strength $Hf_{0.4}Nb_{0.0}Ta_{0.2}Ti_{0.2}Zr_{0.2}$-HEA alloy (*i.e.*, 1.1 GPa), it increases the strength initially. However, the alloy's strength falls as the 'Nb' content increases, specifically for the cases of Nb20 and Nb30. The mismatch between 'Nb' and the base metal also grows as 'Nb' content rises due to the difference in atomic size and crystal structure. Additionally, at a certain point, increasing the 'Nb' level in the alloy might prevent the development of a homogeneous solid solution, lowering the alloy's strength.

The composition change of 'Ta' exhibits similar phenomena. The alloy's tensile strength is 2.1 GPa when 'Ta' is absent in the HEA and simply by adding 'Ta' (*i.e.,* Ta10), the strength increases to 3.9 GPa and further increase leads to gradual falls in the tensile strength for Ta20 and Ta30. The 'Nb' and 'Ta' both have a cubic structure (FCC and BCC respectively) and have a closer atomic radius (207 p.m. and 220 p.m.), as presented in Table 2, therefore they would have followed a similar trend in UTS properties during composition changes.

On the other hand, the addition of 'Ti' follows an opposite trend compared to 'Nb' and 'Ta'. When 'Ti' is absent, the $Hf_{0.4}Nb_{0.2}Ta_{0.2}Ti_{0.0}Zr_{0.2}$ -HEA alloy at its peak value of 4.3 GPa and suddenly dropped to 2.7 GPa due to the addition of 10 % of the referred element. Furthermore, it was observed that as the Ti % rises, so does the material's strength. It might be due to the initial addition of 'Ti' atoms occupying the substitutional position within the crystal lattice to form a solid solution. This can initially disrupt the orderly arrangement of atoms, causing lattice strain and potentially creating new defects. These defects can act as sites for crack initiation and propagation, leading to a decrease in strength. However, with the increasing addition of the element, the surrounding atoms can rearrange and accommodate the strain, leading to a stronger and more ordered structure. This results in an increased strength compared to the initial decrease. The addition of 'Zr' shows very similar effects on the HEA alloy as described for the 'Ti' element. It can be seen from Table 2 that the 'Ti' and 'Zr' both have the HCP crystal structure and closer atomic size difference (147 p.m. and 160 p.m. respectively) therefore it is expected they have similar effects on the properties.

To investigate the optimum UTS property for the best combination of constituent elements, their respective composition was analyzed using a surface and contour plot. Fig. 3 illustrates that among the four constituent elements (Nb/Ta/Ti/Zr) of HEA alloy:

Nb10, Ta10, and Ti0 exhibit the maximum tensile strengths and make them the most suitable for high-strength applications. The contour plot at the bottom confirms the same by indicating the green region for the maximum strength corresponding to Nb10, Ta10, and Ti0 composition.

Effects on modulus of elasticity (E)

The effects of material composition on modulus of elasticity are depicted in Fig. 4 and the results are identical with the composition variation on UTS. The highest observed value for the elastic modulus was recorded for the 'Nb' variation, specifically at Nb10, reaching 129.1 GPa. Similarly, while varying the 'Ta', it was found 137.7 GPa at Ta10. The reasons might be the same as discussed earlier for the UTS property.However, the addition of 'Ti' in HfNbTaTiZr-HEA decreases the modulus value from 137.3 GPa to 115.0 GPa for Ti0 and Ti10, respectively. Further addition of 'Ti' to the HfNbTaTiZr-HEA would increase the elastic modulus to 118 GPa at Ti = 30 %. A similar effect was observed for 'Zr' addition. The value of modulus of elasticity obtained for the HEA with four other constituent elements except 'Zr' was 133.6 GPa. Further addition of 'Zr' follows the lowest value (114 GPa) to a progressive increasing pattern but slowly similar to 'Ti'. In other words, when an HCP element (*i.e.,* Ti/Zr) was introduced to a BCC-HEA alloy the modulus was decreased initially and remained almost unchanged for a higher percentage.

Fig. 5 illustrates the combined effects of changing HEA constituents and compositions on Elastic Modulus through a surface-contour plot. It was found that 'Nb' at 10 % exhibits the maximum modulus of 137.7 GPa among all the combinations. Additionally, 'Ta' at 10 % and 'Ti' at 0 % could be an optimum choice for HEA materials when requiring a higher modulus, indicated by a green area in the contour plot.

Temperature effects of on optimized HEA compositions

From the above discussion, it was concluded that Nb10, Ta10, and Ti0 offer the best combination of UTS, Modulus of Elasticity, and %Elongation among all other compositions. Therefore, the temperatures of 300–1200 K at 300 K intervals are used to understand the effects of temperature. The purpose of this test is to comprehend the high-temperature behavior of these alloys while used as refractory or thermal shield material.

The UTS and modulus of elasticity of Nb10-HEA (i.e. $Hf_{0.30}Nb_{0.10}Ta_{0.20}Ti_{0.20}Zr_{0.20}$) alloys are 3.7 GPa and 137.7 GPa at room temperature, respectively (see in Fig. 8(a)). At a high-temperature exposure *e.g.* 1200 K, it shows the UTS value of 300 MPa and 8.35 GPa for modulus of elasticity. The values of UTS and modulus of elasticity steadily decrease as the temperature rises. This is brought on by thermal vibrations within the

lattice. An increase in thermal vibration promotes the dislocation's migration thus decreasing the strength of the materials [43].