

## Paragraph Ran in the Queries

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

**Content :**

### Introduction

In view of the rapid development of the aerospace, automotive, and energy industries, there is a great demand for high-performance materials with excellent mechanical properties [1], [2], [3], [4], [5], [6]. High entropy alloys (HEAs) are able to successfully enhance their mechanical and physical properties from the perspective of five or more elements in near-equi-molar ratios with high entropy, lattice distortion, sluggish diffusion, the cocktail effect, and the short-range order effect [7], [8], [9], [10], [11]. High entropy enforces the effect for stabilization of the elements to distribute in evenness and yield a stable solid solution structure such that excellent thermal stability and resistance to corrosion happen. The phase composition of HEAs can be affected by their manufacturing and processing methods [12], [13]. Lattice distortion simultaneously increases internal stress fields, which, in turn, will give rise to obstacles for dislocation movement and enhance the yield strength and hardness of materials [7], [14], [15], [16]. These properties enable HEAs to maintain excellent performance in harsh environments, under either high temperature conditions [10], [17], [18], [19], cryogenic temperature conditions [20], [21], [22], [23], or vacuum conditions [24], [25].

In recent years, research efforts have increasingly focused on enhancing HEAs to retain their mechanical and tribological properties in extreme environments, such as under high temperatures and/or high pressures. This involves sliding against different materials [26], or adding new elements like Al [27], Cu [28], [29], C [30], Cr [31], Ti [32], [33] and Mo [34], to existing mature HEA systems or adjusting the alloy's phase composition and structure to create variants like eutectic HEAs, with the goal of improving or expanding their performance in various conditions [35], [36], [37], [38]. This further underlines its importance in advanced alloys design, given the remarkable effects of vanadium on structural and mechanical properties in HEAs [39], [40], [41], [42], [43], [44]. Vanadium significantly enhances the structural morphology and mechanical properties of HEAs [45], [46], [47], [48]. Improvement in mechanical properties occurs due to lattice strain and enhanced resistance to dislocation movement promoted by solid solution strengthening. This has been discovered to enable enhancement in tensile strength and strain in HEAs, e.g., CrFeCoNi, by inclusion of this element, whereas on V<sub>x</sub>NbMoTa alloys, it enhances yield strength and ductility through

grain refinement [49], [50], [51], [52], [53]. Vanadium further promotes the transformation of phases and thus enhances their strengths [42], [52]. Vanadium forms fine precipitates in the alloy matrix, acting as barriers to dislocation motion and increasing strength and hardness. Studies demonstrate that vanadium-rich precipitates and the formation of core-shell-like structures in HEAs significantly enhance hardness, yield strength, and compressive properties [53]. Vanadium further improves the overall mechanical properties of the structures through grain boundary strengthening and mechanisms that refining structures are compatible with. The AlCrFe<sub>2</sub>Ni<sub>2</sub>V<sub>x</sub> alloy shows remarkable gains, with hardness increasing from 332.4 HV (AlCrFe<sub>2</sub>Ni<sub>2</sub>) to 590.7 HV (AlCrFe<sub>2</sub>Ni<sub>2</sub>V) and yield strength rising from 765 MPa to 1744.6 MPa [54]. Similar improvements in V<sub>x</sub>NbMoTa alloys are observed when the hardness increases from 332.4 HV (NbMoTa) to 590.7 HV (VNbMoTa), the yield strength increases from 1017 MPa to 1233 MPa, and the fracture strain increases from 9.2% to 29.0%, indicating a significant improvement in both strength and ductility [51]. The potential of the CuFeNiTiV HEA is well indicated by the measured ultimate compressive strength of 2441 MPa that the alloy has shown, clearly stating the business that vanadium, when appropriately added, plays a very important role [55]. However, studies on the high temperature mechanical properties of V-containing HEAs have been rarely reported.

The oxidation properties of HEAs are influenced by vanadium in a complex and multifaceted manner, with both positive and negative effects depending on the specific compositions and conditions [56]. In general, the addition of vanadium to HEAs results in a reduction in oxidation resistance due to the formation of volatile vanadium oxides during oxidation. This leads to the formation of large fissures in the oxide layer, which in turn facilitates a greater rate of oxidation by allowing oxygen to more easily penetrate the material. Conversely, the oxidation properties are significantly influenced by the composition of vanadium. For instance, vanadium was reported to increase the formation of a compact passive film in AlCoCrMo HEA coatings [57]. The optimum content of approximately 0.8 at.% of vanadium can lead the film to show a stable film with passivation of the film without much dissolution, hence reducing the corrosion rate and improving the overall durability of the passivated film. In CoCrFeMnNiV<sub>x</sub> HEAs, the presence of V influences microstructure and mechanical properties, which in turn has an impression on the overall oxidation behavior [42]. Similarly, in high entropy alloy systems such as CoCrFeNiV<sub>x</sub> [58], [59], TiZrNbCrV, and TiZrNbFeV [60], it has been proven that vanadium can enhance the stability and protective nature of the oxide layer. By stabilizing oxide mixtures, vanadium improves the high temperature mechanical properties of the alloys.

Vanadium greatly affected microstructure, mechanical properties, wear resistance, friction coefficient, worn microstructural characteristics, and oxide layer development of HEAs [61], [62], [63], [64]. All these features reveal composition-dependent impacts on

wear mechanism and application optimization. Mpofu et al. [61] explored the effect of vanadium content on the friction and wear performance of AlCrFeCuNi HEAs synthesized via arc melting, finding that the coefficient of friction (CoF) increased with V content. The CoF is about 0.42 for the alloy with 5% V compared to 0.38 for the reference alloy. This increase in friction is attributed to solid-solution strengthening and the formation of a body-centered cubic (BCC) phase. Liao et al. [57] investigated the effect of V on AlCoCrMoV<sub>x</sub> HEA coatings prepared by laser cladding, showing that with optimal V content (x=0.8), the specific wear rate was lowest at  $0.630 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ , with improved corrosion resistance. Liu et al. [63] studied the impact of V on VAlTiCrW HEA films, demonstrating that V addition reduced the friction coefficient to 0.15 at 800°C and maintained a low wear rate of  $1.97 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$  at 700°C. Another study investigated the effect of V additions on flame-sprayed AlCoCrFeMo HEA coatings, finding that AlCoCrFeMoV HEA coatings formed face-centered cubic (FCC) phases and spinel-type oxides, with 18% higher average microhardness and 46% higher nano-hardness compared to AlCoCrFeMoW coatings [64]. These coatings also demonstrated the lowest wear rate ( $21 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ ) and superior erosion resistance, showing that V addition enhances wear and erosion resistance through higher hardness and strain hardening ability.

Very recently, we have successfully developed a new V-containing Al<sub>0.5</sub>CrFeNiV<sub>0.5</sub> HEA, which exhibits very good mechanical and tribological properties in a wide temperature range [65]. This study is specifically extended to investigate the influence of V content in Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs considering four different V additions. We have examined the microstructure and high temperature properties, including in-situ oxidation, compressive strength, and friction and wear responses of these Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs. There are four main research objectives of this paper: (i) to understand how vanadium affecting the phase composition of Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs; (ii) to investigate the impact of vanadium on the in-situ oxidation behavior of Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs at 700 °C; (iii) to study how vanadium affecting the mechanical properties of Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs at both room and elevated temperatures; (iv) to examine the effect of vanadium content on the wear properties of Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEA in a wide temperature range.

## Mechanical properties

The mechanical properties of cast Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs were investigated utilizing Vickers hardness testing, nanoindentation, and compression testing. Based on ten separate measurements, the calculated average Vickers hardness for V<sub>0.25</sub>, V<sub>0.5</sub>, V<sub>0.75</sub>, and V<sub>1.0</sub> are  $520 \pm 17.2 \text{ HV}$ ,  $570.5 \pm 28.8 \text{ HV}$ ,  $592 \pm 27.6 \text{ HV}$ , and  $608 \pm 31.1 \text{ HV}$ , respectively, as depicted in Fig. 7(a) and (b) show the distribution of nano-hardness for Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs. It can be seen that the trend is consistent with the Vickers hardness, both increasing with the rise in vanadium content. The nano-hardness results

for the V<sub>0.25</sub> alloy mainly fall within the range of 6-8 GPa, corresponding to the hardness of the BCC matrix phase, with a small fraction, about 7%, reaching 11-13 GPa, corresponding to the vanadium-rich phase. For V<sub>0.75</sub> and V<sub>1.0</sub> alloys, more than 15% and 20% of the nanoindentation results exceed 11 GPa, respectively, due to the increase in vanadium-rich phases as the vanadium content rises.

The mechanical properties of vanadium-containing Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs are significantly influenced by vanadium content and resulting microstructural phases. Alloys V<sub>0.25</sub> and V<sub>0.5</sub> consist of BCC phases combined with (Al,Ni)-rich B<sub>2</sub> phase, while alloys with V<sub>0.75</sub> and V<sub>1.0</sub> consist of BCC phases combined with V-rich phases. Increasing vanadium content enhances compressive strength from 2476±30 MPa at V<sub>0.25</sub> to 3241±40 MPa at V<sub>1.0</sub> and increases nano-hardness from 8.05 GPa to 11.35 GPa, but reduces ductility from 34% to 22%. At elevated temperatures (600°C, 700°C, and 800°C), V<sub>0.5</sub> and V<sub>0.75</sub> alloys exhibit the best combination of high compressive strength and ductility, with V<sub>0.75</sub> showing exceptional high temperature stability. The BCC + (Al,Ni)-rich B<sub>2</sub> phase alloys (V<sub>0.25</sub> and V<sub>0.5</sub> [65]) balance strength and ductility, while BCC+V-rich phase alloys (V<sub>0.75</sub> and V<sub>1.0</sub>) enhance hardness and strength but reduce ductility. For high temperature friction applications, V<sub>0.5</sub> and V<sub>0.75</sub> alloys are optimal, with V<sub>0.5</sub> offering superior modulus of elasticity and balanced properties and V<sub>0.75</sub> maintaining high strength under thermal stress.

In general, the enhancement of mechanical strength of Al<sub>0.5</sub>CrFeNiV<sub>x</sub> HEAs by increasing the vanadium content is likely attributed to the combined strengthening mechanisms of solid solution strengthening, precipitation strengthening, and grain refinement strengthening [19], [66], [69], [70]. Namely, (i) solid solution strengthening: vanadium atoms cause lattice distortion when they substitute into the BCC lattice because they are larger than the matrix atoms as evident from XRD analysis in Fig. 1. This distortion impedes the dislocation motion and leads to increased hardness and strength; (ii) precipitation hardening: formation of the Laves phase (VAl<sub>2</sub>) introduced at higher vanadium contents caused random distribution of intermetallic precipitates within the matrix as evident from OM and SEM microstructure analysis in Fig. 2 and Fig. 3. These precipitates can act as barriers to dislocation movement and thus further enhance strength; and (iii) grain refinement strengthening: vanadium addition refines the grain structure by inhibiting grain growth during solidification and increases the number and area of grain boundaries as evident from OM in Fig. 2 and SEM microstructures in Fig. 3, which thus impedes dislocation motion and enhances the mechanical strengths. These insights are crucial for designing HEAs for applications requiring high strength and wear resistance across varying temperatures.

