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Enhancing the plasticity of HfZrTiCr_x alloys by forming single phase solid solutions via reducing Cr content

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ABSTRACT

The solid solution design strategy bolsters the comprehensive mechanical properties of high/medium entropy alloys (H/MEAs), yet its utilisation within hexagonal close-packed (HCP) H/MEAs remains notably limited. Here, exploring the impact of reduced Cr content ($x = 0.3, 0.1$, and 0) from the $\text{HfZrTiCr}_{0.5}$ prototype alloy, our study successfully obtained a novel HCP single phase MEA and investigated the relationship between microstructure and mechanical properties. Decreasing Cr content led to the diminishing presence of the Laves phase, culminating in a single HCP phase solid solution at $x = 0.1$. The Laves phase, arising from negative enthalpy between Cr and other elements and lower atomic radius of Cr, acted as crack initiation sites, resulting in brittle fracture ($x = 0.5$) alloy and limited plasticity strain of 3.5% ($x = 0.3$). Conversely, the $\text{HfZrTiCr}_{0.1}$ alloy exhibited impressive combined yield strength (1360 MPa) and plasticity strain (14.5%), attributed to prominent solid solution strengthening and enhanced dislocation movement within the solid solution structure. These findings offer insights into manipulating Cr content to form HCP solid solution structures, potentially broadening solid solution alloy design strategies for superior mechanical properties in HCP H/MEAs.

ARTICLE HISTORY

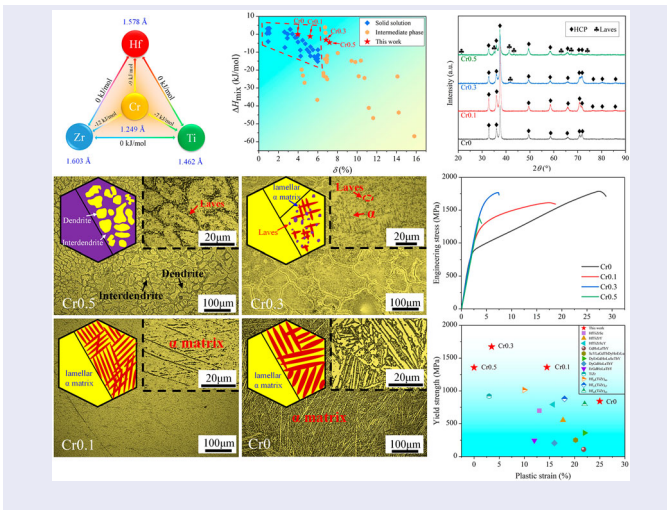
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1. Introduction

To pursuit high-performance metal materials with exceptional strength and plasticity is a long-standing challenge for metallurgists. Owing to the principal element that often existed in traditional alloys, to optimise their mechanical properties inevitably relies on regulating trace alloying elements, which have gradually encountered the limitation due to the finite principal elements employed [1,2]. In the past two decades, high entropy alloys (HEAs) [3,4], alloys composed of five or more principal elements in equal or near-equal atomic ratio, have developed rapidly and exhibited outstanding properties such as high strength [5], toughness [6], corrosion resistance [7] and elevated temperature oxidation resistance [8]. Stemming from the concept of HEAs, medium entropy alloys (MEAs), such as CoCrNi [9] and TiZrVNb [10] have also shown promising mechanical properties and garnered extensive research interest. From a thermodynamic perspective, a high mixing entropy in H/MEAs contributes to lowering the Gibbs free energy of the system and inhibiting intermetallic compound formation. This favours the formation of solid solution structure, thereby significantly enhancing the performance of the alloy [11–13]. However, higher mixing entropy doesn't guarantee easier solid solution formation. For instance, the TiVCrZrNbMoHfTaW alloy, comprising nine elements in equal atomic ratio with an ideal/expected entropy was up to $2.2R$ (where the high entropy alloys are defined as those with mixing entropy of more than $1.5R$), still formed intermetallic compounds [14]. As a result, the consideration of other physical properties of alloying elements, such as mixing enthalpy (ΔH_{mix}), atomic radius difference (δ), and valence electron concentration (VEC), becomes crucial in forming H/MEA solid solution structures. Following the Hume-Rothery rule, an empirical formula $-15 < \Delta H_{\text{mix}} < 5$ kJ/mol, $\delta < 6.6\%$ has been derived as a criterion for the formation of solid solution structures in H/MEAs [15,16].

Recent research highlights that H/MEAs exhibiting a solid solution structure possess distinctive concentration fluctuation characteristics, fostering significant cross-slip within the material, thereby endowing the alloy with robust and tough properties [17,18]. Conversely, when alloy ΔH_{mix} and δ fall outside the solid solution criteria, there's a possibility of forming intermetallic compounds. Although these phases might enhance the alloy's strength by impeding dislocation movement, they can become sources of crack formation, severely compromising the alloy's plasticity, as seen in the aforementioned TiVCrZrNbMoHfTaW alloy [14]. Interestingly, utilising natural-mixing characteristics among refractory elements, a new refractory high entropy alloy $\text{Ti}_{38}\text{V}_{15}\text{Nb}_{23}\text{Hf}_{24}$, meeting the solid solution criteria, displayed over 20% tensile ductility strain in its as-cast state [14]. Furthermore, the strategy of inhibiting or eliminating intermetallic compounds to obtain a solid solution structure and subsequently enhance plasticity has been frequently employed in body-centered cubic (BCC) and face-centered cubic (FCC) high entropy alloys [19–21]. For instance, by reducing Cr content, the phase constitution of $\text{ZrNbTaHf}_{0.2}\text{Cr}_x$ alloy shifted from BCC + Laves phases to a single BCC phase, leading to a significant increase in compressive plasticity from zero to fracture-free behaviour [20]. Additionally, in a CoCrFeNi alloy with single FCC structure, reducing Nb content decreased the presence of Laves phase, ultimately resulting in its disappearance at 2.5 at.% Nb. The alloy adhered to the $\Delta H_{\text{mix}}\text{-}\delta$ criteria, exhibiting a single solid solution structure with promising mechanical properties: yield strength of 317 MPa and plastic strain of 19.2% [21]. Evidently, adjusting alloy elements to minimise or eliminate intermetallic compounds in favour of promoting a solid solution structure proves advantageous in enhancing alloy plasticity. However, there are limited reports on H/MEAs with HCP structure, particularly regarding improving mechanical properties by regulating intermetallic compounds.

Hence, this paper adopted the solid solution structure design strategy, utilising the brittle alloy $\text{HfZrTiCr}_{0.5}$ as the prototype. By decreasing the Cr content, efforts were made to diminish and ultimately eliminate the Laves phase, aiming to facilitate the formation of a single-phase HCP solid solution structure. Moreover, the investigation focused on exploring the evolution of microstructure morphology and Laves phase within the alloys, while delving into the mechanism underlying enhanced plasticity. This study is beneficial to broaden the application of solid solution design strategy and to develop high strength and high toughness HCP H/MEAs.

2. Experimental

High purity (99.9 wt.%) Hf, Zr, Ti, and Cr particles were carefully chosen as raw materials for the preparation of HfZrTiCr_x alloys ($x = 0.5, 0.3, 0.1$ or 0) using vacuum arc melting. The resulting samples were labelled as Cr0.5, Cr0.3,

Cr0.1, and Cr0, respectively. Prior to melting, the furnace underwent evacuation to 5×10^{-3} Pa, followed by backfilling with high purity argon (99.99 N) to reach 0.05 MPa. Then, pure Ti ingot was molten to gather residual oxygen in the furnace. To ensure compositional homogeneity, the ingots underwent at least four cycles of flipping and re-melting, aided by an electromagnetic stirrer. Samples were wire-cut along the radial quarter of the ellipse-shaped ingots for analysis of crystal structure, microstructure observation, and mechanical property testing, as shown in Figure 1. Noting that, the polished surfaces of the samples extracted from the arc-melted ingot that for microstructure observation show no obvious porosity defection. Moreover, the porosity (P) of the sample can be determined by the measured density (ρ_{meas}) obtained by the Archimedes' displacement method and the theoretical density (ρ_{theor}) calculated by the formula, $\rho_{\text{theor}} = \frac{\sum C_i A_i}{\sum \frac{C_i A_i}{\rho_i}}$ (where A_i , ρ_i are the atomic weight and density of element i , respectively), $P = (1 - \rho_{\text{meas}}/\rho_{\text{theor}}) \times 100\%$. One can estimate that all the porosities of the samples are around 1% according to the density values listed in Table 1, indicating that there are almost no porosities in the samples. The alloy's composition and elemental distribution in each region were determined using energy-dispersive spectrometry (EDS).

The crystal structure was characterised via X-ray diffraction (XRD) utilising Cu K α radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA, scanning within the range of 20° – 90° at a rate of 4° per minute. Before microstructure observation, the samples were mechanically ground on 400 #, 800 #, 1200 # and 2000 # sandpapers and progressively polished on a polishing cloth with $3 \mu\text{m}$ and $1 \mu\text{m}$ diamond suspensions and $0.04 \mu\text{m}$ colloidal silica by using automatic grinding & polishing machine (TRUER, Smoothneer-6). After polishing to achieve a mirror-like surface, the samples were etched using an etchant solution

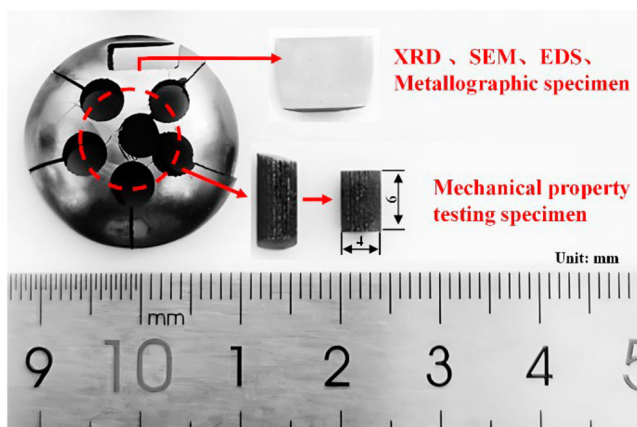


Figure 1. Schematic diagram of the samples derived an arc-melting ingot for compression tests and microscopic inspection.

Table 1. The mixed enthalpy, atomic radius differences, as well as measured and theoretical densities of the studied alloys.

Alloy	ΔH_{mix} (kJ·mol ⁻¹)	δ (%)	ρ_{meas} (g/cm ³)	ρ_{theor} (g/cm ³)
HfZrTiCr _{0.5}	-4.57	7.19	8.15	8.24
HfZrTiCr _{0.3}	-3.09	6.84	8.18	8.28
HfZrTiCr _{0.1}	-1.17	5.22	8.22	8.32
HfZrTi	0	3.97	8.23	8.35

composed of 3% HF, 15% HNO₃, and 82% H₂O. The polished samples were examined using a field emission scanning electron microscope (FESEM, Zeiss Sigma 500) equipped with an EDS detector, while the etched samples were analysed using the optical microscope (OM, Zeiss Axio Imager M2 m). For uniaxial compressive tests at room temperature, specimens with dimensions set at Φ 4 mm $\times$ 6 mm were tested using a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ on a computer-controlled Instron mechanical testing machine (INSTRON-4206). Before conducting the compressive tests, a thin Teflon foil was placed between the compression faces and silicon carbide dies to minimise friction.

3. Results and discussions

3.1. Impact of Cr content on alloy phase constituents

According to the empirical formation criterion, where $-15 < \Delta H_{\text{mix}} < 5 \text{ kJ/mol}$ and $\delta < 6.6\%$, numerous H/MEAs have been successfully predicted to form solid solution structure [22–24]. In predicting the phase constituents of the studied alloys based on ΔH_{mix} and δ , Figure 2(a) provides the mixing enthalpy and atomic radius of the component elements extracted from References [25,26]. Notably, zero mixing enthalpy and similar atomic radius among Hf,

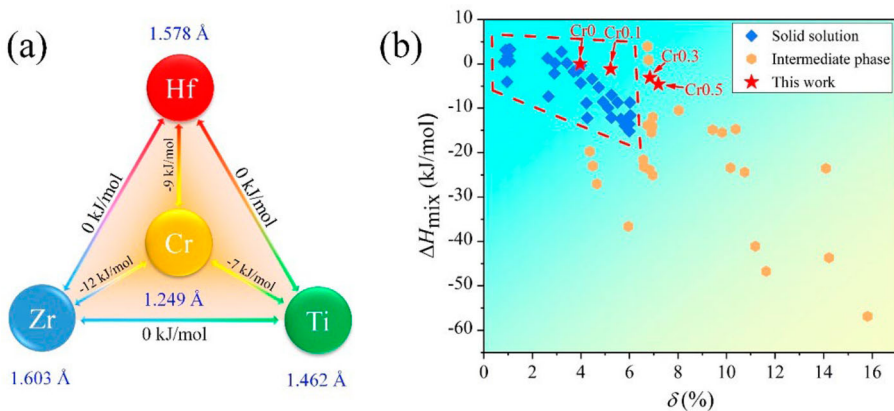


Figure 2. (a) Mixing enthalpies and atomic radii of Hf, Zr, Ti, and Cr. (b) ΔH_{mix} - δ diagram plots depicting the HfZrTiCr_x ($x = 0.5, 0.3, 0.1$ or 0) alloys alongside relevant H/MEAs [26,27].

Zr and Ti indicate easy formation of solid solution alloys. However, the introduction of Cr induces substantial fluctuations in ΔH_{mix} and δ of the alloys, due to the larger negative mixing enthalpy between Cr and Hf, Zr, Ti, as well as the comparatively smaller atomic radius of Cr, suggesting a propensity for intermetallic compound formation within the alloys. Detailed calculations of ΔH_{mix} and δ for each alloy (as listed in Table 1) reveal that all alloys fall within the specified criterion for ΔH_{mix} , but not for δ . Alloys with higher Cr content, such as Cr0.5 and Cr0.3, exhibit elevated δ values at 7.19% and 6.84%, respectively, exceeding the criterion range, indicating a potential for intermetallic compound formation. Conversely, alloys Cr0.1 and Cr0 with relatively low Cr content or without Cr exhibit δ values within the solid solution criterion, suggesting a tendency towards solid solution structure formation. Moreover, a ΔH_{mix} - δ diagram is generated, plotting the data for ΔH_{mix} and δ of the studied alloys alongside relevant H/MEAs [26,27], as shown in Figure 2(b). As the Cr content decreases, the HfZrTiCr_x alloys values transition from the intermediate phase zone (Cr0.5 and Cr0.3 alloys) to the solid solution zone (Cr0.1 and Cr0 alloys).

In order to validate the accuracy of the solid solution criterion prediction, XRD analysis was conducted to examine the phase constituents of the studied alloys, as shown in Figure 3. The findings revealed that the prototype alloy Cr0.5 comprised two phases: the HCP and Laves phases. As the Cr content decreased, the diffraction peaks corresponding to the HCP phase persisted across all alloys, while the intensity of the diffraction peaks associated with the Laves phase gradually diminished (observed in the Cr0.3 alloy) until its complete disappearance in the Cr0.1 and Cr0 alloys. This XRD observation

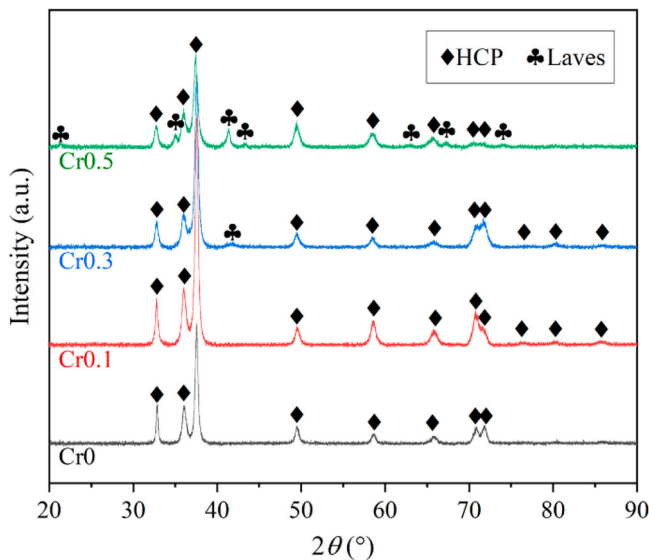


Figure 3. XRD curves of HfZrTiCr_x ($x = 0.5, 0.3, 0.1$ or 0) alloys.

actually aligns with the predicted outcomes, indicating that alloys Cr0.5 and Cr0.3, with an atomic radius difference beyond the range of the solid solution criterion, contain intermetallic compounds. Conversely, Cr0.1 and Cr0 alloys, meeting the solid solution criterion, achieved a single-phase HCP solid solution structure. The reduction and disappearance of the Laves phase correlate with the decrease in Cr content in the alloy, corroborated by previous literature [20,28], indicating Cr's inclination towards forming the classic AB_2 ($B = \text{Cr}$) Laves phase. The formation of ordered phase is facilitated by the substantial negative mixing enthalpy between Cr element and Hf, Zr and Ti elements. Furthermore, the ratio of the atomic radii, R_A/R_B (where A represents alloying elements with larger atomic radii such as Hf, Zr, Ti in our study work, and B represents Cr element), significantly influences the stability of the Laves phase, favouring its formation within the range of 1.03 to 1.67 (especially around the ideal value of 1.225) [29]. In our studied alloys, the calculated ratios of atomic radii between Hf, Zr, Ti and Cr were 1.263, 1.283, and 1.171, respectively. These values, closely approximating 1.225, indicate that the presence of Cr tends to facilitate the formation of Laves phase in the studied alloys.

3.2. Microstructure evolution and elements distribution

Figure 4 shows the metallographic structure of the studied alloys HfZrTiCr_x ($x = 0.5, 0.3, 0.1$, or 0), and the corresponding SEM images and EDS mappings are displayed in Figure 5. The prototype alloy $\text{HfZrTiCr}_{0.5}$ exhibited a distinctive dendrite structure (Figure 4(a)). EDS mapping revealed Hf, Zr and Ti-rich regions within the dendrites, whereas the interdendritic regions exhibited an enrichment of Cr elements (Figure 5(a4), marked as yellow arrow). These observations, coupled with XRD results, suggest that the dendrites constituted an HCP phase rich in Hf, Zr, and Ti, while the interdendritic regions comprised a Cr-rich Laves phase. During the solidification process of the alloy, elements with higher melting points (Hf, Zr, and Ti), capable of mutually dissolving, solidified firstly, forming dendrites. Meanwhile, Cr element, having a lower melting point, was excluded from the solidifying phase and combined with residual Hf, Zr and Ti atoms to form interdendrites. As the Cr content decreased to $x = 0.3$, the dendritic structure vanished, giving way to equiaxed crystals with an average grain size of approximately $140\text{ }\mu\text{m}$ (Figure 4(b)). Upon closer inspection (top right of Figure 4(b)), numerous fine lamellar structures and micron-scale particles dispersed randomly throughout the matrix were observed. EDS mapping confirmed these particles as Cr-rich Laves phase (Figure 5(b4), marked as yellow arrow). Further reduction in Cr content led to significant alterations in the equiaxed crystal microstructure. The micron-scale particles disappeared, and the length of the fine lamellar structures increased (Figure 4(c)). EDS mapping indicated a uniform distribution of Cr element within the matrix, suggesting that a small amount of Cr solute element can entirely

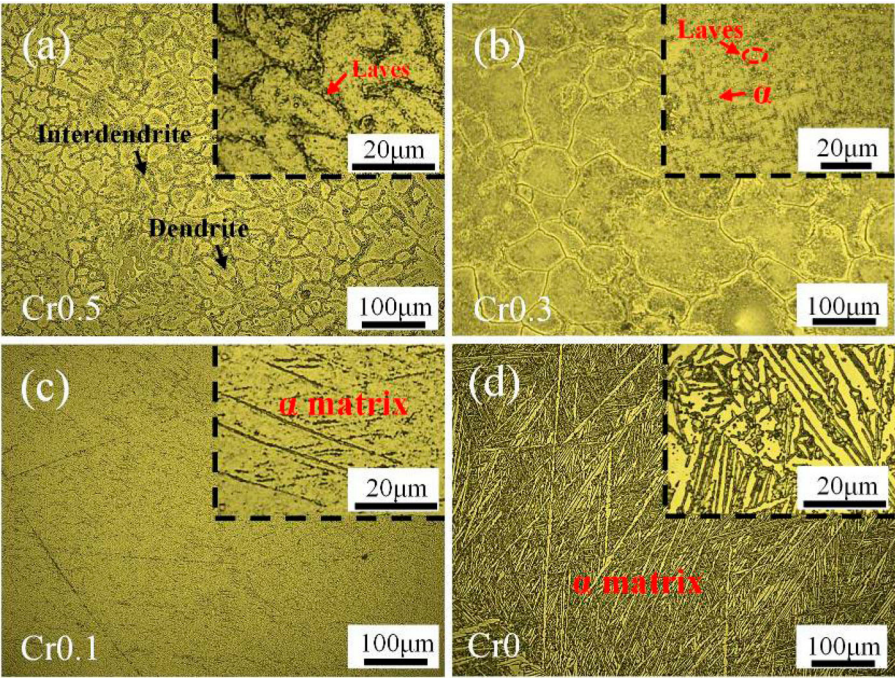


Figure 4. Optical micrographs of the studied alloys. (a) HfZrTiCr_{0.5}, (b) HfZrTiCr_{0.3}, (c) HfZrTiCr_{0.1}, and (d) HfZrTi.

dissolve into the HfZrTi matrix, forming the HfZrTiCr_{0.1} solid solution alloy (Figure 5(c)). In the absence of added Cr, the lamellar structure within the

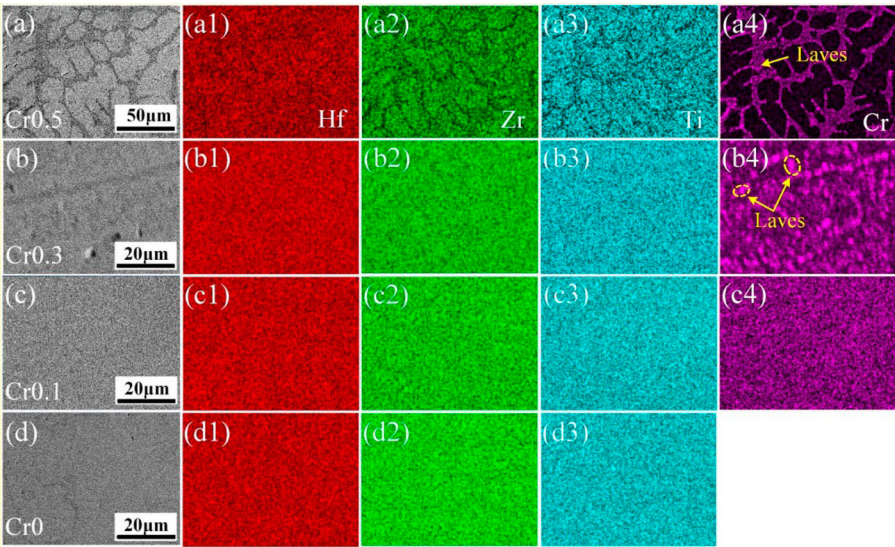


Figure 5. SEM and EDS mapping images of (a) HfZrTiCr_{0.5}, (b) HfZrTiCr_{0.3}, (c) HfZrTiCr_{0.1}, and (d) HfZrTi MEAs.

equiaxed crystal broadened, lengthened, and permeated the entire grain (Figure 4(d)). Elements within the HfZrTi alloy were uniformly distributed, showcasing a typical solid solution structure (Figure 5(d)).

The evolution of the microstructure morphologies in these alloys is closely associated with both the type and concentration of the added solute, influencing the changes in crystal morphology and intergranular microstructure. Schematic diagrams depicting the microstructure morphologies for the studied alloys, with decreasing Cr content, are presented in Figure 6. Initially, the reduction in solute Cr content from $x = 0.5$ to 0.3 prompted a shift in the alloy's microstructure from dendrites (Figure 6(a)) to equiaxial crystals (Figure 6(b)). This transition was instigated by alterations in the degree of constitutional supercooling at the solidification interface. According to the constitutional supercooling criterion expressed as $\frac{G_L}{R} < \frac{m_L \cdot C_0}{D_L} \cdot \frac{(1 - k_0)}{k_0}$ (where G_L represents the liquid phase gradient, R is crystalline growth velocity, m_L is the liquidus slope, C_0 denotes solute concentration, D_L stands for solute diffusion coefficient, and k_0 is solute partition coefficient), a decrease in solute concentration leads to a reduction in the degree of supercooling. Consequently, this reduction

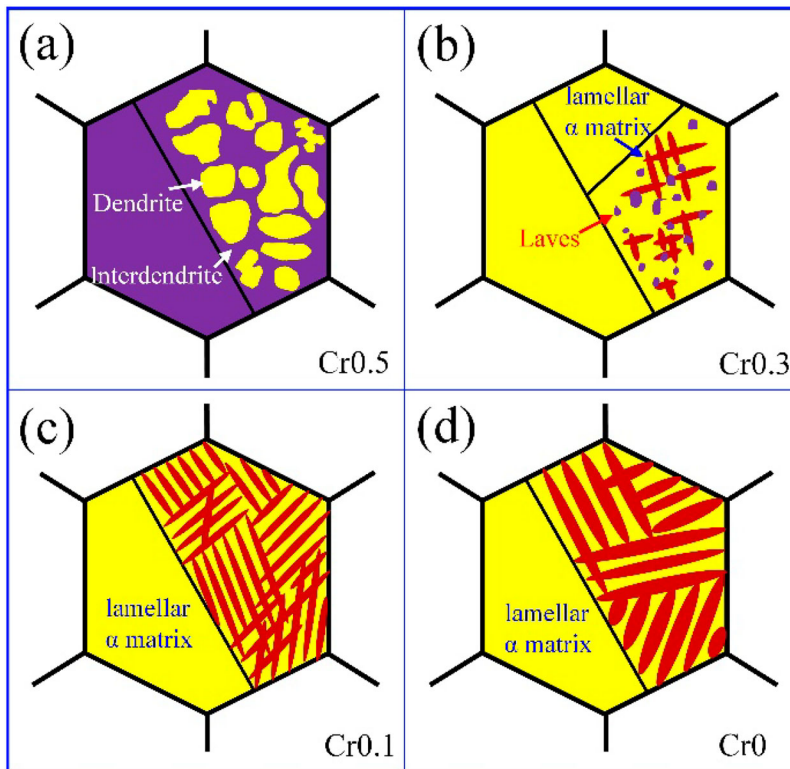


Figure 6. Schematic diagram of the microstructure morphology evolution for the studied alloys.

in supercooling fosters a morphological shift from dendritic to equiaxed crystals.

Furthermore, the solute Cr content significantly influences the intergranular microstructure morphology of the alloy following solid-state phase transformation. The phase continuous cooling transition process in HfZrTi-based H/MEAs shares similarities with titanium alloys. Specifically, at lower cooling rate [30,31], both alloy types typically form the primary α phase with an HCP structure, along with residual β phase with a BCC structure, and the secondary α phase. However, during rapid quenching, metastable phase like α' with an HCP structure, α'' with an orthogonal structure, and ω with an HCP structure are formed, yet these phases are thermodynamically unstable and decompose upon heating [32–34]. In the present work, samples were taken from arc-melted button ingots and slowly cooled with a cooling rate of about 2.5 °C/s as reported in the literature [35], indicating a continuous cooling transition at lower cooling rate during cooling. Combining the HCP phase identified through XRD analysis and the observed lamellar structure from OM results, it is inferred that the alloys contain a matrix with secondary α phase. This α phase, exhibiting a lamellar structure, is obtained through the diffusion transformation of high temperature β phase, possessing a substantial aspect ratio, akin to what is commonly found in titanium alloys [36]. When Cr content was $x = 0.3$, the growth of the lamellar structure was hindered by small Laves phase particles, characterised by relatively reduced length and width (Figure 6(b)). As the Cr content decreased further, the Laves phase vanished, disappeared, resulting in a lamellar structure characterised by a large length-to-width ratio (Figure 6(c)). Without adding Cr element, the width of the lamellar structure increased (Figure 6(d)). This widening is attributed to the weaker refining effect on the lamellar α structure in alloys with lower Cr content, aligning with findings reported in literatures [37,38]. Moreover, analysing the morphology evolution of Cr-rich Laves phases can be facilitated by examining the distribution of Cr element, as elaborated in the subsequent sections.

As observed from the EDS mapping images (Figure 5), as Cr content decreased, the concentrated distribution of Cr in the format of network-like dendrites noticeably transformed to discrete particles and eventually to a uniform dispersion in the matrix. The schematic diagrams depicting their distribution throughout the solidification and cooling phases of the alloys are displayed in Figure 7. In the initial stage (Figure 7(I)), all studied alloys existed in a liquid state when the temperature surpassed the liquidus T_L . For alloys with higher Cr alloy, primary dendrites rich in Hf, Zr, and Ti formed first below T_L . Subsequently, Cr-rich interdendrites were generated in the remaining liquid phase above the solidus temperature T_S (Figure 7(II)). During subsequent cooling, owing to the notably negative mixing enthalpy and atomic radius difference between Cr and other elements within the alloy, the

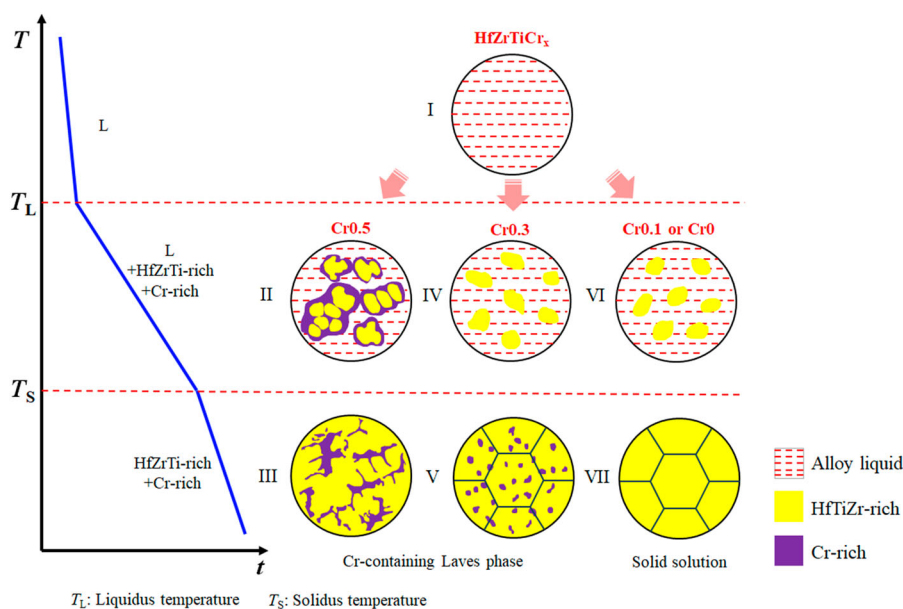


Figure 7. Schematic diagram of elements distribution in the alloys during the solidification and cooling processes.

precipitation of Laves phase containing Cr occurred within the interdendritic regions (Figure 7(III)). Upon reducing the Cr content, dendrite formation ceased during solidification, replaced by the emergence of equiaxed crystals (Figure 7(IV)). Following this transition, numerous granular Cr Laves phases precipitated during subsequent cooling (Figure 7(V)). When the Cr content was further diminished to $x = 0.1$, insufficient Cr remained to combine with the alloying elements to form Laves phase. Consequently, the Cr element became uniformly dispersed throughout the matrix (Figure 7(VII)). At this stage, the alloy represented a single-phase solid solution structure, indicating the maximum solid solubility of Cr in HfZrTi to be 3.2 at.% ($x = 0.1$). The solidification and cooling processes of the HfZrTi alloy closely resemble those of Cr0.1, as displayed in Figure 7(VI and VII).

3.3. Microstructure-mechanical properties relationship

As described previously, the reduction in Cr content within the HfZrTiCr_x ($x = 0.5, 0.3, 0.1$ or 0) alloys results in the diminishing presence of Laves phase, transitioning from a continuous network to particle-like structures, finally promoting the formation of a solid solution. The remarkable alteration in microstructure significantly influences the mechanical properties of the alloys. To elucidate this relationship, the compressive properties of these alloys were assessed and the stress-strain curves are shown in Figure 8, accompanied by yield strength, compressive strength and plastic strain values

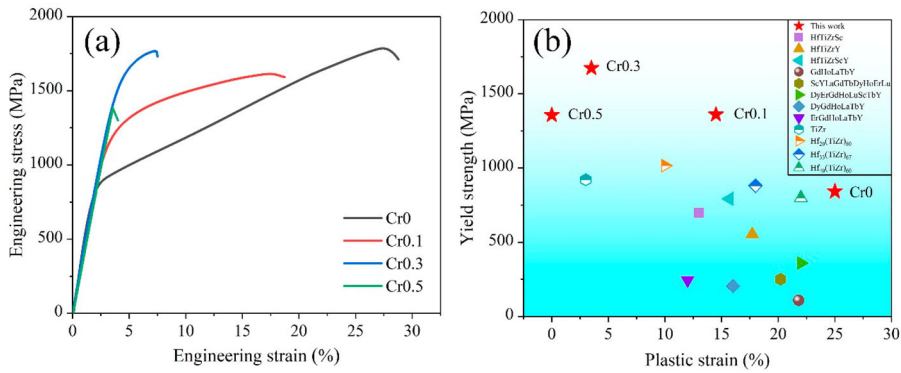


Figure 8. (a) Compressive stress–strain curves of the studied alloys. (b) Comparison diagram of yield strength and plastic strain among the studied alloys and other HCP-structured H/MEAs [27,48–51].

tabulated in Table 2. Notably, the HfZrTiCr_{0.5} alloy exhibited brittle fracture at 1356 MPa, before yielding. In many H/MEAs containing Cr element, the presence of brittle and hard Laves phase tends to initiate crack formation, limiting the plasticity of the alloy [39–41]. Particularly in the HfZrTiCr_{0.5} alloy studied here, the Laves phase existed in a continuous network, facilitating cracks propagation along this network, resulting in brittle fracture. As the Cr content decreased, the plasticity of the HfZrTiCr_{0.3} alloy improved, evidenced by an increase in strain to 3.5% and a yield strength of 1673 MPa. The enhanced mechanical properties primarily stem from the random distribution of Laves phase particles in the matrix. This random dispersion impedes crack propagation within the matrix, enhancing the alloy's plasticity. Furthermore, the hindrance of dislocation movement due to the presence of Laves phase contributes to the improved strength of the alloy [42]. Continued reduction in Cr content led to a significant increase in plastic strain for the HfZrTiCr_{0.1} alloy, reaching 14.5%, attributed to the absence of the brittle and hard Laves phase. Despite the partial loss of yield strength due to the absence of precipitation strengthening, the substantial lattice distortion caused by Cr resulted in high lattice friction, enabling the alloy to maintain a yield strength of 1360 MPa. Without Cr addition, the plastic strain of the HfZrTi alloy increased to 25%, while the yield strength decreased significantly to 842 MPa.

Among the studied alloys, the HfZrTiCr_{0.1} alloy, characterised by a solid solution structure and minimal Cr addition, showcased an excellent combination of strength and plasticity. Primarily, the enhanced yield strength resulted predominantly from solid solution strengthening [43–45]. The introduction of the Cr element, with a smaller atomic radius, induced substantial lattice distortion, creating increased lattice friction that impeded dislocation movement. Additionally, the considerable negative mixing enthalpies between Cr and Hf, Ti, Zr might induce uneven element distribution within the alloy due to

Table 2. The yield strength (σ_y), compressive strength (σ_b) and plastic strain (ϵ_p) comparison among the studied alloys and other HCP-structured H/MEAs.

Alloys	σ_y (MPa)	σ_b (MPa)	ϵ_p (%)	References
HfZrTiCr _{0.5}	–	1356	0	This work
HfZrTiCr _{0.3}	1673	1766	3.5	This work
HfZrTiCr _{0.1}	1360	1611	14.5	This work
HfZrTi	842	1785	25	This work
HfZrTiSc	698	1598	13	[48]
HfZrTiY	554	1010	17.7	[49]
HfZrTiScY	793	1300	15.7	[49]
GdHoLaTbY	108	880	21.8	[27]
ScYLaGdTbDyHoErLu	251	1197	20.2	[50]
ErGdHoLaTbY	245	869	12	[51]
DyGdHoLaTbY	205	863	16	[51]
DyErGdHoLuScTbY	360	850	22	[51]

substantial differences for elements in their binding capacities. This concentration fluctuation, verified in CoCrFeNiPd HEA [17] and CoCrNi-3W MEA [18], leads to pronounced dislocation pile-up and tangling. Both the hindered dislocation motion and dislocation pile-up contribute significantly to augmenting the alloy's strength. Furthermore, the advantageous solid solution structure supports the alloy's plasticity due to reduced atom affinity within the solid solution, facilitating easier atom diffusion within the lattice. This diffusion behaviour alleviates stress concentration, diminishes barrier to dislocation slip and grain boundary slip, thereby enhancing the alloy's plasticity [46]. Moreover, atoms within a solid solution can move and rearrange more freely, decreasing the internal resistance of the alloy under stressed, making it more deformable [47]. Comparatively, the Cr_{0.1} alloy, with heightened lattice distortion, faces challenges in atom diffusion compared to the Cr₀ alloy, leading to reduced dislocation and grain boundary slips and resulting in some loss of plasticity. Conversely, in contrast to alloys containing Laves phase (Cr_{0.5} and Cr_{0.3}), the Cr_{0.1} alloy demonstrates superior ductility due to its homogeneous structure, favouring dislocation sliding. In addition, the HfZrTiCr_{0.1} alloy exhibited outstanding mechanical properties among reported HCP-structured H/MEAs, evident in the yield strength and plastic strain comparison diagram (Figure 8) and Table 2. This underscores the effectiveness of the strategy to eliminate Laves phase and promote solid solution formation in enhancing mechanical properties of HCP H/MEAs.

4. Conclusion

This study focused on the HfZrTiCr_x ($x = 0.5, 0.3, 0.1$, or 0) alloys, revealing significant insights. The alloys' phase constituents shifted from a mix of HCP and Laves phases (Cr_{0.5} and Cr_{0.3}) to a sole HCP phase (Cr_{0.1} and Cr₀), aligning with solid solution criteria for H/MEAs. This transformation was influenced by Cr content, driven by its negative enthalpies of mixing with the other elements

and smaller atomic radius. Decreasing Cr content altered crystal morphology from dendritic to equiaxed grains, resulting in the transition of the Laves phase from networks to particles and ultimate disappearance. The lamellar secondary α phase also transformed, thinning and elongating with diminishing Cr content. Laves phase substantially enhanced alloy strength but reduced plasticity. As Cr decreased, plastic strain increased (3.5% to 25%) due to a solid solution structure promoting dislocation and grain boundary slip, offsetting deformation resistance. The $\text{HfZrTiCr}_{0.1}$ alloy, with minimal Cr, showcased an outstanding balance between yield strength (1360 MPa) and plasticity (14.5%).

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Data availability statement

Data will be made available on request.

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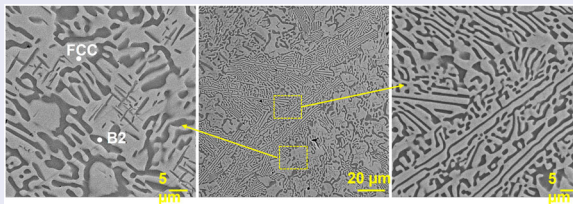
Design of a nickel–cobalt based eutectic high entropy alloy (NiCo)_{1.7}AlCrFe with hierarchical microstructural length scales

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ABSTRACT

A combined nickel–cobalt-based eutectic high entropy alloy (Ni-Co-based HEA) has been designed based on the valence electron concentration (VEC) value. The microstructure of the developed alloy consists of a face-centered cubic (FCC) and ordered cubic (B2) structure, which was validated using CALPHAD. The microstructure is hierarchical with length scales in micrometers (lamellar eutectic morphology) and nanometers (B2 length scale). B2 phase precipitation was observed in the supersaturated FCC primary phase. The orientation relationship (OR) between the phases exhibited a strong Kurdjumov-Sachs (KS) type OR, typical of FCC/BCC interface structures. This EHEA displayed good yield strength at room temperature and strain rate insensitivity in the 10^{-3} – 10^{-1} strain rate range.



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Introduction

The subject of alloy design has been transformed by high entropy alloys (HEAs), a novel class of multi-component alloys [1–3]. To achieve a stable single phase generally, four or five components are added in an equiatomic concentration corresponding to the maximization of the configuration entropy of the system [4, 5]. Due to their high thermal stability, HEAs have surpassed several traditional materials in high-temperature attributes, such as oxidation and creep behavior [6]. Single-phase FCC or BCC structure formed due to the high configurational

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entropy caused by mixing equal proportions of different elements results in either high strength (BCC) or high ductility (FCC) phase at a single stage of alloy design [7]. As a result, researchers have attempted to develop HEAs with non-equiatomic proportions, which could cause phase separation resulting in dual-phase (FCC + BCC) and improving mechanical performance [8]. Guo et al. [9] proposed a mixture rule based on valence electron concentration (VEC) to generate a dual-phase microstructure and gave an empirical approximation that the VEC value must be in the range of 6.87–8 to achieve FCC + BCC phases. If the two components melt at varying temperatures, the casting of HEAs leads to elemental segregation and defects. Eutectic high entropy alloys (EHEAs) have been proposed to eliminate segregation-related flaws and provide an excellent balance between strength and ductility.

EHEAs can be designed to have both HEA and eutectic properties and can be used as good castable materials [10]. As eutectic alloys are acknowledged to have superior properties in terms of strength and toughness, there is a constant need to develop new EHEAs and improve existing ones. The remarkable mechanical properties of nickel and cobalt-based EHEAs have inspired this design approach [10, 11]. Because of its high Al and Cr content, the vastly studied Ni-base (AlCoCrFeNi_{2,1}) EHEA has outperformed copper alloys, which are currently employed as propeller materials, in aspects of seawater corrosion resistance. [12–15]. Furthermore, the EHEAs exhibit good damping capabilities and have a high potential to be used as a functional material. Moreover, load-bearing applications and alternate soft and hard phases offer a promising solution for high-temperature mechanical response [11]. In EHEAs, the switch between hard and soft phases can cause a massive magnetoresistance effect [11, 16]. As a result, designing new EHEAs will always result in some unique mechanical and functional features.

Strategy for alloy development

The present investigation has developed an EHEA with nickel and cobalt as the base elements in equiatomic proportion along with an equiatomic proportion of other constituent elements such as Al, Cr, and Fe. As several EHEAs contain expensive refractory elements like Nb and V, the study focuses on removing the expensive elements and designing an EHEA using the traditional five elements (Ni, Co, Al, Cr, Fe, with Ni and Co serving as base elements). The present experimental alloy was designed to have a VEC of 7.7, which was our imposed experimental constraint, such that it is equivalent to the Ni_{2,1}-base EHEAs. Table 1 shows the morphology and structure achieved in several EHEAs with non-equiatomic Ni and Co proportions. The table shows that a different combination of (FCC/L12 and BCC/B2) microstructures can be obtained by varying the alloy compositions. Most of the developed alloys either increased Ni or decreased Co or vice versa to achieve such eutectic microstructures. The present work successfully developed an equiatomic Ni, Co

Table 1. List of Cobalt and Nickel-containing eutectic high entropy alloys with non-equiatomic base elements.

Nos	Alloy Composition	Morphology	Structure	Reference
1	AlCoCrFeNi _{2,1}	Eutectic	(FeCoCr)-FCC + (AlNi)-B2	[10]
2	Al _{1,2} CrCuFeNi ₂	eutectic	(FeCr)-FCC + ((NiCu)Al)CrFe)-B2	[27]
3	AlCo _{0,2} CrFeNi _{2,8}	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[16]
4	AlCo _{0,4} CrFeNi _{2,6}	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[16]
5	AlCo _{0,6} CrFeNi _{2,4}	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[16]
6	AlCo _{0,8} CrFeNi _{2,2}	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[16]
7	Al ₁₆ Co ₄₁ Cr ₁₅ Fe ₁₀ Ni ₁₈	eutectic	(FeCoCrNi)-FCC + (AlNi)-rich BCC	[28]
8	V ₁₀ Cr ₁₅ Mn ₅ Co ₁₀ Ni ₂₅ Fe _{25,3} Nb _{9,7}	eutectic	(Fe,Cr)-rich FCC + Nb-rich Laves	[29]
9	Al _{19,3} Co ₁₅ Cr ₁₅ Ni _{50,7}	eutectic	Al-poor FCC + Al-rich B2	[30]
10	Fe ₂₀ Co ₂₀ Ni ₄₁ Al ₁₉	eutectic	(Fe,Co)-rich L1 ₂ + (AlNi)-B2	[31]
11	Zr _{0,6} CoCrFeNi _{2,0}	eutectic	FCC + Ni ₇ Zr ₂	[32]
12	Nb _{0,74} CoCrFeNi _{2,0}	eutectic	FCC + (Co,Ni) ₂ Nb	[32]
13	Al ₁₇ Co _{14,3} Cr _{14,3} Fe _{14,3} Ni _{40,1}	eutectic	L1 ₂ + B2	[33]
14	Al ₁₇ Co _{28,6} Cr _{14,3} Fe _{14,3} Ni _{25,8}	eutectic	FCC + B2	[33]

approach such that both elements acts as the base element in the individual FCC/BCC phases in order to exploit the benefits of Ni or Co base alloys.

The four important parameters that define the theory of alloy design are size difference δ %, mixing enthalpy ΔH_{mix} , the entropy of mixing ΔS_{mix} , and valence electron concentration (VEC). Understanding the possible reciprocation between these critical factors for phase selection is the goal of a HEA. The configurational entropy influences phase stability at higher temperatures [5]. Zhang et al. [17, 18] proposed using atomic size difference and mixing enthalpy ΔH_{mix} as a valuable tool for alloy design. ΔH_{mix} determines whether the atoms want to attract one another to form a single phase or repel each other to phase separate, and it is strongly influenced by the interaction parameters (Ω).

When the enthalpy of mixing (ΔH_{mix} , a negative interaction parameter) is low, and the atomic size difference is small, single-phase solid solutions are preferred (low misfit). Specifically, for single-phase solid solution, the formation energy and size difference lies in the range of $-15 \text{ kJ/mol} < \Delta H_{\text{mix}} < 5 \text{ kJ/mol}$ and $0 < \delta < 5$, respectively [19]. If the atoms in the constituents start repelling each other, it represents a positive interaction parameter, which can widen the miscibility gap in the phase diagram even further. During casting, if $\delta > 8$ and $\Delta H_{\text{mix}} < -15 \text{ kJ}$, HEAs can form metallic glass, as stated by Inoue [20]. As a result, the two-parameter (ΔH_{mix} vs. δ) approach, as shown in Tables 2 and 3, provides a deeper understanding of alloy design than the one-parameter (ΔS_{mix}) approach. Guo et al. [9] also introduced the concept of the VEC parameter, which extends the Hume-Rothery rule applied to a multi-component

Table 2. Enthalpy of mixing ΔH_{mix} of the constituent elements in its binary form.

ΔH_{mix}	Al	Co	Cr	Fe	Ni
Al	-	-19	-10	-11	-22
Co	-19	-	-7	-1	0
Cr	-10	-7	-	-1	-7
Fe	-11	-1	-1	-	-2
Ni	-22	0	0	-2	-

system. Table 3 lists the critical parameters of HEA alloy design for the present study. The abbreviation r_i , r_j , c_i , c_j stands for the atomic radius and concentration of i^{th} and j^{th} element in the alloy system.

The obtained value of parameters follows the phase separation rule. The size difference was obtained to be 12.75, which is very high for the alloy to be sustained as a single phase; thus, phase separation is expected. The ΔH_{mix} (−33 kJ/mol) falls within the range provided by Inoue for the formation of a multi-phase alloy. Table 4 highlights the parameters obtained for several other Ni/Co-based HEAs whose values lies in the range obtained for the (NiCo)_{1.7}AlCrFe except the Co lean HEAs. Most of the alloys mentioned in Table 1 are non-equiatomic. Either they are rich in Co or Ni. The VEC values range from 7.45 to 7.65 in the five-element (Al, Co, Cr, Fe, Ni) system, as shown in Table 4. Guided by the above calculation, the alloy design is based on constraining (1) VEC to 7.7, similar to AlCoCrFeNi_{2.1}, and (2) maintaining an equiatomic ratio of Ni-Co and Cr-Fe-Al for designing an FCC/BCC type high entropy alloy.

Materials & methods

After validating through a theoretical approach without further thinking, we prepared the alloy with the nominal composition AlCrFe(NiCo)_{1.7} (each of Al, Cr, Fe as 15.62 at. % and Ni, Co as 26.56 at. %) by vacuum arc-melting from the pure elemental constituents. X-ray diffraction experiments were carried out utilising (Rigaku, SmartLab SE) Cu-K α radiation to identify phases and estimate lattice parameters. The microstructure was characterised using a scanning electron microscope (FEG-SEM – TESCAN, MIRA 3 FEI). Correlative EBSD and EDS have been exploited to investigate the orientation relationship and the local composition of individual phases.

Results & discussion

The X-ray diffraction pattern from the as-cast material (Figure 1a) shows prominent FCC peaks. The $\sin^2\theta_1:\sin^2\theta_2:\sin^2\theta_3 \dots$ considering the high-intensity peak was found to be 3:4:8:11:12:16 (green), indicating the FCC structure of one

Table 3. HEA parameter obtained for (NiCo)_{1.7}AlCrFe.

(NiCo) _{1.7} AlCrFe		
δ %	$100\% \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\sum_{j=1}^n c_j r_j} \right)^2}$	12.75
ΔH_{mix}	$\sum_{i=1, i \neq j}^n \Omega_{ij} c_i c_j = \sum_{i=1, i \neq j}^n 4\Delta H_{\text{mix}} c_i c_j$	−33.64 kJ/mol
ΔS_{mix}	$-R \sum_{i=1}^n c_i \ln c_i$	13.078 J/mol/k
VEC	$\sum_{i=1}^n c_i (\text{VEC})_i$	7.7

Table 4. HEA parameter obtained for Ni/Co-based HEAs.

Alloys	δ %	ΔH_{mix}	ΔS_{mix}	VEC
AlCo _{1.9} CrFeNi	12.84	−30.05	13.03	7.47
AlCoCrFeNi _{2.1}	11.49	−36.26	12.91	7.70
AlCo _{0.2} CrFeNi _{2.8}	7.47	−40.49	11.34	7.79
AlCo _{0.4} CrFeNi _{2.6}	8.94	−39.33	11.96	7.76
AlCo _{0.6} CrFeNi _{2.4}	10.03	−38.16	12.40	7.73
AlCo _{0.8} CrFeNi _{2.2}	10.87	−36.99	12.74	7.69
Al ₁₆ Co ₄₁ Cr ₁₅ Fe ₁₀ Ni ₁₈	12.32	−30.77	12.32	7.78
Al ₁₇ Co _{14.3} Cr _{14.3} Fe _{14.3} Ni _{40.1}	12.84	−31.55	12.42	7.48
Al ₁₇ Co _{28.6} Cr _{14.3} Fe _{14.3} Ni _{25.8}	12.85	−30.97	13.01	7.62

of the constituent phases. The remaining peaks could exhibit the ratio 2:4:6:10 (red), suggesting a phase with BCC structure; however, a superlattice peak was also detected. The superlattice peak obtained at 31° is the (100) peak of the BCC phase, indicating an ordered B2 phase instead of the anticipated disordered BCC phase. The microstructure of the as-cast material in Figure 1 (b, c, d) shows exquisite eutectic lamellar morphology as well as a primary phase with a second phase in the form of a plate-like precipitate. B2 phase precipitation

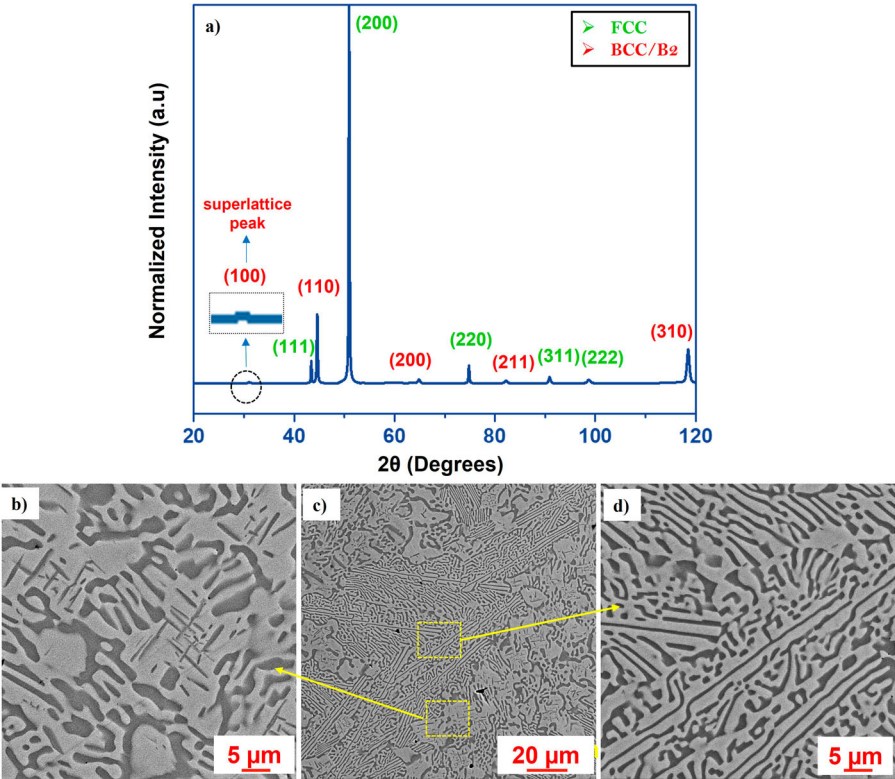


Figure 1. (a) X-ray diffraction pattern from the as-cast specimen; microstructure revealing (b) secondary phase precipitating from a primary phase. (c) eutectic plus primary phase, (d) lamellar morphology.

was observed in the supersaturated FCC primary phase, which is in a nano-metric length scale. The FCC phase was measured to have a volume percentage of $65 \pm 2\%$, while the ordered B2 phase occupied the rest, with a volume percentage of $35 \pm 3\%$.

To understand the orientation relationship and volume fraction of the individual phases, EBSD was performed on the as-cast specimen on the plane normal to the solidification direction, as shown in Figure 2. The FCC phase has a similar orientation; however, the B2 phase forms different variants in different grains, according to the inverse pole figure (IPF) map (Figure 2a). The solidification sequence is as follow: the primary FCC phase solidifies first, with B2 phase precipitating inside the FCC matrix and the remaining liquid in the inter-dendritic regions leads to eutectic morphology. The volume fraction of the FCC phase is higher than that of the B2 phase, as shown in the phase map (Figure 2b). The interface of these lamellae strongly determines the slip transmission and further determines the deformation texture. Thus, the pole figure analyses (Figure 2c) were done at the FCC/B2 interface and showed a strong correlation between the close-packed plane and the close-packed direction. A strong Kurdjumov-Sachs (KS) type orientation relationship (OR) exists where one of the poles matches exactly [21]. This could be attributed to the fact that the FCC phase that forms first serves

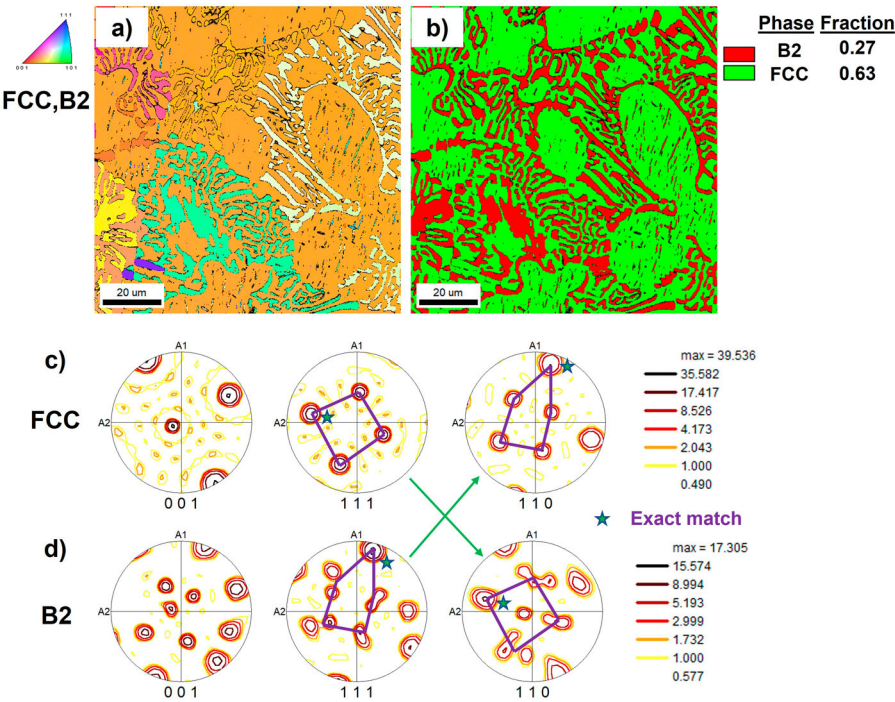


Figure 2. (a) IPF map, (b) phase map, and (c) pole figures representing the orientation relationship between FCC and ordered B2 phase.

as a nucleating site for the FCC phase present in the lamellar eutectic, whereas the B2 phase evolves in the eutectic, maintaining the Kurdjumov-Sachs (KS) type of orientation relationship.

To find out the elemental segregation between phases, correlative EDS was done on the same region where the EBSD was performed. The mapping was done on the lamellae and the primary dendritic phase for all elements Al, Co, Cr, Fe, and Ni. In contrast to the B2 phase, the FCC phase is deficient in Al and Ni and rich in Co, Cr, and Fe, as seen in [Figure 3](#). The nominal compositions of the FCC and B2 phases are listed in [Table 5](#).

CALPHAD (CALculation of PHase Diagrams) database was utilised to validate the theoretical-based approach of alloy design and predict the formation of the FCC and B2 phases. CALPHAD is being extensively used to design high performance HEAs [22]. As illustrated in [Figure 4](#), CALPHAD was used to estimate the equilibrium volume fraction of distinct phases as well as the eutectic melting point of the alloy system. Thermo-Calc software was used in conjunction with the thermodynamic database for high entropy alloy (TCHEA-v2.1) [23] Gibbs energy database to calculate the volume fraction of equilibrium phases as a function of temperature. The computed volume fraction is nearly identical to the phase fraction estimated from EBSD maps. According to thermodynamic calculations, the alloy solidifies with the FCC and B2 phases because all three phases are in equilibrium at 1360°C.

Compression tests at various strain rates at room temperature were performed to decipher the mechanical behavior of Ni-Co-based EHEA. The true stress vs. true strain plots at strain rates of 10^{-3} , 10^{-2} , and 10^{-1} are shown in [Figure 5](#). At room temperature, the yield strength (Y_s) was found to be 718 ± 16 MPa, and there was no substantial change in yield strength as a function of strain rate, indicating that the material is strain-rate insensitive in this domain until 25% strain. Furthermore, the material has a high strain hardening rate that is roughly similar to all strain rates. The insensitivity to the strain rate is attributed to the slow deformation. If the deformation occurs slowly, say at a strain rate of 10^{-2} s^{-1} or less, the heat generated inside the specimen can be dissipated at the same rate to the surroundings by natural cooling, resulting in no overall change in sample temperature. Under these conditions, a compression

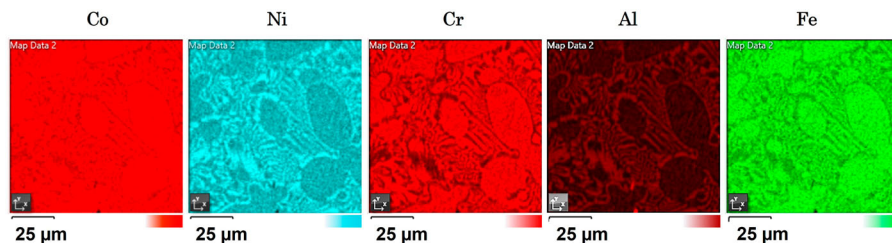


Figure 3. EDS mapping of the as-cast EHEA showing Co, Ni, Cr, Al, and Fe.

Table 5. EDS analysis of the constituent phases in the Eutectic microstructure.

Phases	Element (At. %)					Total
	Co	Ni	Al	Fe	Cr	
Nominal	26.56	26.56	15.62	15.62	15.62	100
Measured	26.60	26.30	15.10	15.80	16.20	100
FCC	30 ± 0.45	24 ± 0.33	8 ± 0.78	19 ± 0.88	19 ± 1.05	100
B2	26 ± 0.72	26 ± 0.39	19 ± 1.12	14 ± 0.55	15 ± 0.98	100

test may be termed isothermal. However, if the deformation occurs at a higher strain rate, such as in a split Hopkinson pressure bar (SHPB) test, there may not be enough time for the heat to escape, and the specimen temperature will rise in proportion to the degree of strain-induced. A compression test is considered adiabatic if the strain rate is high enough that no heat is lost throughout the test. Most metals harden through the formation of dislocations, which multiply as the rate of deformation increases [24, 25]. This leads to increased work hardening and, as a result, stress increases with strain. As shown in Figure 5, the strain hardening rate decreases monotonously with a constant slope. In addition, at high deformation rates, a part of the deformation energy is

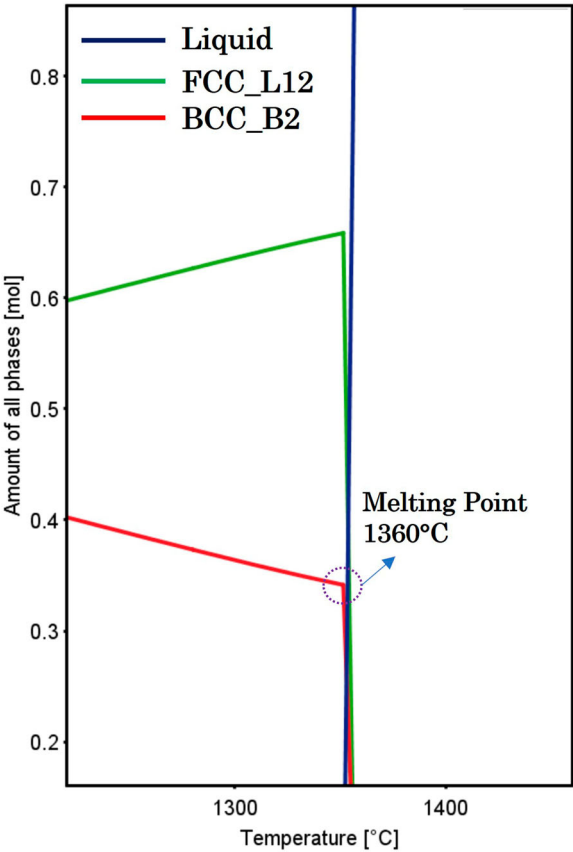


Figure 4. Calculated phase fraction plot of (NiCo)_{1.7}FeCrAl alloy as a function of temperature using CALPHAD.

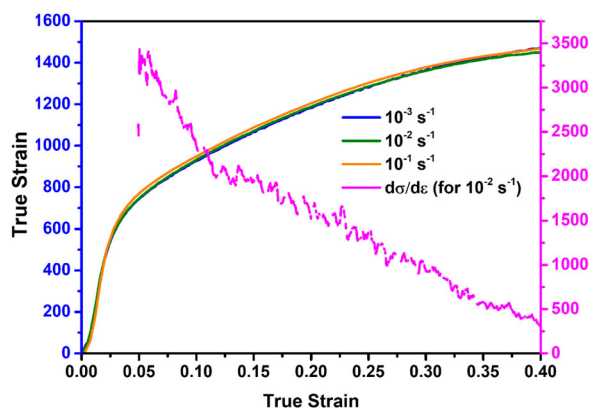


Figure 5. Room temperature compression behavior of as-cast Ni-Co-based eutectic high entropy alloy at different strain rates and the corresponding strain hardening rate at 10^{-2} s^{-1} .

converted into heat, which softens the material, and creates a competition between work-hardening and thermal softening. If the hardening and softening effects balance, it results in overlapped flow curves at different strain rates. Also, the hierarchical microstructure with hard and soft laminates and hard precipitate in a soft matrix can give rise to different deformation micromechanisms, which is our future scope of interest [26].

Conclusions

A Ni-Co-based eutectic high entropy alloy was designed utilising analytical calculations and Thermo-Calc. The microstructure consists of alternating fine lamellar morphology with alternating FCC and ordered B2 phases with a plate-like B2 phase as the primary phase. The FCC phase was low in Al, and the B2 phase was high in Al. A Kurdjumov-Sach orientation relationship was found between the FCC and B2 phases at the interface, credited to its unique microstructural properties with alternate soft and hard phases. The material displayed a very high strain hardening rate and was strain rate insensitive at varied strain rate intervals.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Interstitial-oxygen induced and magnetically driven HCP-to-FCC transformation in CoCrFeNiO_x high-entropy alloy: a first-principles study

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ABSTRACT

We report the influences of oxygen interstitials and magnetisms on phase stability and structural transformation of CoCrFeNi high-entropy alloy (HEA) from first-principles calculations. It is found the formation of oxygen interstitials is energetically favourable to occur in face-centred cubic (FCC) CoCrFeNiO_x HEA as compared with that in hexagonal close-packed (HCP) one, and at those octahedral sites neighbouring with more Cr or less Ni. Meanwhile, it is determined the HEA prefers FCC over HCP phases when the oxygen concentration exceeds 4.2 and 5.1 at.% with and without considering its magnetisms, respectively. The HCP-to-FCC structural transformation in CoCrFeNiO_x HEA could be magnetically driven, accompanied by the significant changes in the atomic magnetic moments in the HEA, particularly with an oxygen interstitial concentration larger than 2.7 at.%. Furthermore, the HCP-to-FCC transformation under hydrostatic pressure in CoCrFeNi and CoCrFeNiO_x HEAs is investigated from generalised stacking fault energies, and it is revealed that the synergy effects of oxygen interstitials and magnetisms could facilitate the transformation in CoCrFeNiO_x HEA. The coupled interstitials-induced and magnetically driven structural transformation paves a new avenue for the application of HEAs.

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1. Introduction

High-entropy alloys (HEAs) have attracted much attention because of their outstanding mechanical properties [1–4], and further improvement on the strength and ductility of these alloys has been carried out by micro-alloying [5–7]. In particular, interstitial alloying has been proved to be much promising in improving the mechanical properties of HEAs, which are mainly attributed to the effects of interstitials on the phase stability and dislocation activities in HEAs [8,9].

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Interstitial carbon, nitrogen, hydrogen, and oxygen have been reported to strongly affect the mechanical properties of HEAs. Previous experimental studies indicated that carbon, nitrogen, and hydrogen interstitials were effective in simultaneously improving the strength and ductility of face-centred cubic (FCC) CoCrFeMnNi HEA and its sub-systems [10–15]. Remarkably, oxygen interstitials with a content of 2.0 at.% were also found to substantially enhance the tensile strength and ductility of body-centred cubic (BCC) TiZrHfNb HEA [16]. It is suggested that the significantly enhanced mechanical properties were attributed to the changes in dislocation slips and multiplications, and the competitions among stacking faults, deformation twinning, and structural transformation as affected by the interstitials under different loading conditions [16,17].

The influences of interstitials on the magnetic and structural properties of HEAs are of much interest as well, which are found to be closely related to interstitial alloying in HEAs. Previous work revealed that the formation of a metastable dual-phase structure could be an efficient strategy to overcome the strength–ductility trade-off in FeMnNiCoCr HEA [18], and the related phase transformation can be tailored by varying the concentration of magnetic constituent alloy elements and alloying interstitials [19,20]. It was found that the Al and Si micro-alloying elements significantly affected the saturation magnetisation of FeCoNi medium entropy alloy [21–24]; and the magnetic behaviours of CoFeMnNi HEAs could be affected by Al, Cr, Ga, and Sn doping in the HEAs [25]. However, to the best of our knowledge, the effects of interstitials on magnetic properties of HEAs have not been exploited. To further promote the structural and functional applications of HEAs, it is of urgent need to have an insight into the influence of interstitials on the phase stability and magnetic properties of HEAs. Particularly, it is of great interest to figure out why and how much oxygen interstitials could alter the mechanical and magnetic properties of HEA, as oxygen is abundant in nature which makes the oxygen-free materials difficult and expensive. Furthermore, understanding the effects of oxygen interstitials on the phase stability is much more important for alloy design and for tuning the mechanical and magnetic properties of HEAs. Nevertheless, investigations on the phase stability, mechanical, and magnetic properties of HEAs containing oxygen interstitials are incomplete.

In this work, motivated by the limited studies on oxygen interstitials in the widely reported equatomic CoCrFeNi quaternary alloys (CoCrFeNi HEA, as commonly referred in literature), we performed comprehensive first-principles calculations on FCC and HCP phases of CoCrFeNi containing oxygen interstitials (denoted as CoCrFeNiO_x hereafter), which could provide an accurate and efficient way to understand the interstitial alloying in HEAs at atomic scales [26–28]; Specifically, we aim to elucidate the energetics of interstitials, and the changes in the magnetic properties as well as the HCP-to-FCC phase transformation in the HEAs. Moreover, the influences of oxygen interstitials on deformation twinning and HCP-to-FCC transformation in CoCrFeNi and

CoCrFeNiO_x HEAs under applied pressures are further elucidated by using generalised planar fault energy (GPFE) curves. The results obtained in this work are of significance in the structural and functional applications of HEAs.

2. Computational methods

Special quasirandom structure (SQS) method was employed to simulate CoCrFeNi HEAs with atoms randomly distributed in the lattice [29], and both HCP (1#) and FCC(1#) supercells that containing 108 atoms (denoted as Cr₂₇Co₂₇Fe₂₇Ni₂₇) were generated with the ATAT software package [30]. Periodic boundary conditions were applied to all the configurations used in this work, as shown in Figure 1. Meanwhile, the HCP-to-FCC phase transformation in the HCP(1#) structure was also simulated by shifting selected atom layers along the specified directions to generate another FCC structure denoted as FCC(2#) [31], as shown in Figure 2. Consequently, the phase stability of HEAs with HCP and FCC(2#) structures could be well compared, and they were further employed for the calculation of energetics and phase stability after oxygen interstitials were introduced into them. Additionally, another HCP(2#) supercell consisting of 18 (0001) atom layers aligned in [10–10] and [–12–10] directions was generated to compute the stacking fault energy (SFE) and generalised stacking fault energy curves, since the HCP structure was energetically favourable over FCC structure at 0 K [19,32,33] (also based on our first-principles calculation results). Structural relaxation was performed and lattice distortion was allowed to minimise the interatomic Hellmann–Feynman forces. For the relaxed HEA systems in equilibrium, the octahedron sites were randomly occupied by the oxygen atoms (denoted as Cr₂₇Co₂₇Fe₂₇Ni₂₇O_x) with a content $x/(108 + x)$ less than 8 at.%.

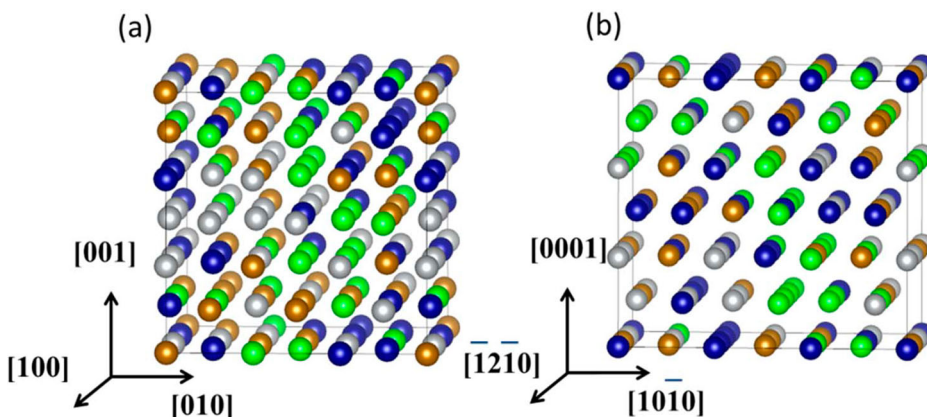


Figure 1. The supercells of FCC (1#) and HCP CoCrFeNi HEAs used in the calculation of solution energy of oxygen interstitials. Configurations of Co₂₇Cr₂₇Fe₂₇Ni₂₇ HEA in (a) FCC (1#) structure, and (b) HCP(1#) structure.

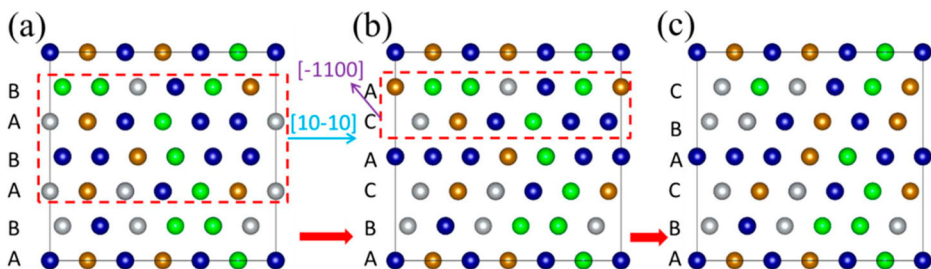


Figure 2. Schematic diagram of HCP-to-FCC transformation based on the initial configuration of HCP HEA: supercells with (a) initial HCP(1#) structure, (b) the transition state, (c) FCC (2#) structure. The thin arrow represents the direction that the atomic layers marked within the red dashed regions are shifted.

First-principles calculations were performed by using the Vienna *ab initio* Simulation Package (VASP) [34,35], and generalised gradient approximation (GGA) was used for exchange–correlation functionals [36]. The plane-wave energy cutoff was set to be 500 eV, and a gamma centred k-point mesh of $1 \times 1 \times 1$ generated using Monkhorst–Pack [37] algorithm was employed for FCC(1#) supercell. It was found that the k-point mesh as large as $3 \times 3 \times 3$ did not much affect the computational results, whereas that of $2 \times 2 \times 3$ or $2 \times 3 \times 1$ were used to calculate the total energy of the HCP(1#) and FCC(2#) supercells, or the stacking fault energy of the HCP(2#) supercell, respectively. The total energy and force tolerances were set to be 1.0×10^{-4} eV/atom and 1.0×10^{-2} eV/Å, respectively. For the calculation on the stability of HCP and FCC phases in HEAs, both magnetic and nonmagnetic states were considered by turning on and off the spin polarisation, respectively.

3. Results and discussion

3.1 . Site preference of interstitial oxygen in CoCrFeNi HEA

The preference of interstitial oxygen at the octahedral sites in FCC and HCP HEAs is determined by calculating the solution energy E_{sol} of the interstitials with the following relation,

$$E_{sol} = E_{HEA-O} - E_{HEA} - E_O \quad (1)$$

where E_{HEA-O} and E_{HEA} are energies of alloy systems with and without interstitial oxygen, respectively, and E_O is the total energy of one single oxygen atom in an O_2 molecule, which can be obtained as $E_O = E_{O_2}/2$ with E_{O_2} being the energy of the O_2 molecule. In this work, 108 octahedral sites in each supercell are attempted for interstitial oxygen to fit into, and the solution energy is calculated by Eq.(1) after the systems are fully relaxed. Figure 3(a) and 3(b) show the histogram of E_{sol} for FCC(1#) and HCP CrCoFeNiO_x HEAs. Meanwhile, E_{sol} for FCC(2#) HEA transformed from its counterpart with a HCP phase is also

computed, and its distribution is shown in Figure 3(c). Owing to the chemical disorder in the HEAs, E_{sol} at different octahedral sites fluctuate significantly, with the differences between the highest and the lowest values of E_{sol} being larger than 2.0 eV. The results suggest that the stability of oxygen interstitials in HEAs is highly dependent on local atomic environment.

The averaged E_{sol} ($\pm$ standard deviation) of interstitials in the HEAs with HCP, FCC(1#) and FCC(2#) structures are -0.455 (± 0.370), -0.746 (± 0.432) and -1.045 (± 0.417) eV, respectively, suggesting that HEA containing interstitial oxygen in an FCC phase is more stable than that in an HCP phase at 0 K, and also implying that the interstitials-induced HCP-to-FCC transformation could occur in the HCP HEAs containing interstitial oxygen. Although the calculations are performed at 0 K, considering that the solution energy for interstitial oxygen is generally large, it is suggested that at elevated temperatures the influences of thermal excitations and diffusion of oxygen as well as the local chemical environment of octahedral interstitials could have substantial impacts on the physical properties of HEAs.

Particularly, the influence of local chemical ordering of oxygen-centred octahedron on the solution energy is characterised. The chemical ordering is quantitatively measured by the local concentration of a constituent alloy element in the octahedron with total 6 oxygen-coordinated metal atoms in the first nearest neighbour (1NN) shell. Figure 3(d) and 3(e) show the solution

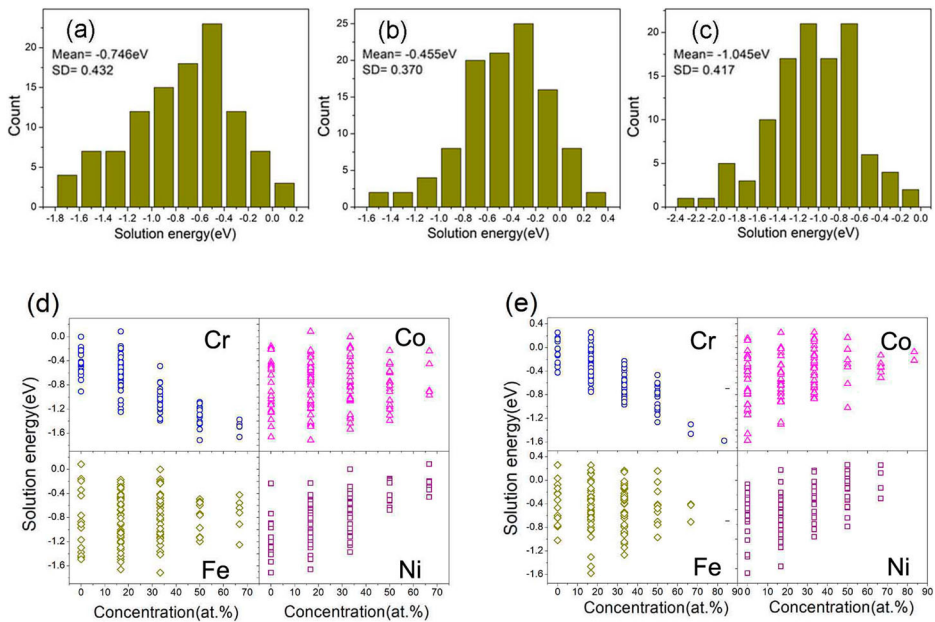


Figure 3. Histogram plots with mean and standard derivative (SD) for solution energy of interstitial oxygen in (a) FCC(1#), (b) HCP, and (c) FCC(2#) CoCrFeNiO_x HEAs; and the relations between the solution energies of oxygen interstitials and the local concentrations of oxygen-coordinated alloy elements for (d) FCC (1#), and (e) HCP HEAs.

energies of the interstitials at the sites surrounded by Cr, Co, Fe, and Ni atoms with different concentrations, respectively. From Figure 3, it is found that in both HCP and FCC CoCrFeNiO_x HEAs, a relatively lower solution energy occurs when more Cr atoms are coordinated with the interstitial oxygen, and the octahedral sites containing more oxygen-coordinated Ni atoms are found to be unstable with higher or even positive solution energy. Interestingly, similar effects for Co are found in HCP HEAs. On the contrary, the effects of local concentration of Fe on the solution energy of oxygen interstitials are limited in both HCP and FCC HEAs. Based on the facts that among those bonds formed between oxygen and the coordinated metal atoms, Cr-O bond is strong and Ni-O bond is weak, it is expected that the solution energy of interstitials at the Cr-rich octahedral site is relatively low [38], suggesting that the interstitial oxygen is more likely to segregate in the octahedral sites with Cr-rich local chemical environment.

3.2. Phase stability of CrCoFeNiO_x HEAs with various concentrations of oxygen interstitials

The phase stability of CrCoFeNiO_x HEAs containing different concentrations of oxygen interstitials is quantitatively analyzed. The analysis should be based on the comparison on the total energy of HCP and FCC(2#) HEAs containing oxygen interstitials, which excludes the influences of chemical disorder on the total energy of HEAs because of the identical configurations of chemical disorder in the HCP and FCC(2#) structures. Firstly, one oxygen atom is placed at an interstitial site where the solution energy is the lowest in the original supercell. Subsequently, another oxygen atom is placed at an interstitial site where the solution energy is the second lowest in the original supercell, thereby forming the configuration of HEA containing two oxygen in CrCoFeNiO_x. So on and so forth, the configurations containing three, four, and five oxygen atoms can be constructed. Figure 4(a) and 4(b) presents the total energies E_{HCP} (E_{FCC}) of the HCP (FCC(2#)) systems with different contents of oxygen interstitials, without and with considering their magnetic states, respectively. It is found that the difference in total energy between HCP and FCC(2#) phases ($\Delta E = E_{FCC} - E_{HCP}$) decreases with increasing oxygen concentration, and the difference becomes smaller when the local magnetisms of atoms are taken into account. Obviously, CoCrFeNiO_x HEA prefers the FCC structure over the HCP structure when the oxygen concentration exceeds 4.2 and 5.1 at.%, with and without considering the local magnetisms of atoms, respectively. Thus, it is determined that an interstitials-induced HCP-to-FCC transformation in CoCrFeNiO_x HEA could occur at 0 K at a critical content of interstitial oxygen of 4.2-5.1 at.%.

To further elucidate the effects of oxygen interstitials and magnetisms on phase stability of CrCoFeNi HEAs, the total energies of HCP and FCC Cr₂₇-Co₂₇Fe₂₇Ni₂₇ HEA supercells at different volumes are determined by using

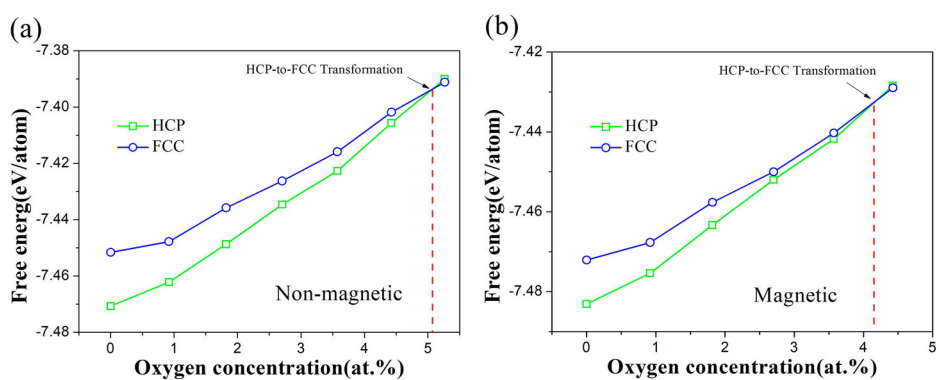


Figure 4. The influence of concentration of oxygen interstitials on the total energy of HCP and FCC (2#) HEAs (a) without, and (b) with considering their magnetic states.

non-spin-polarised (NSP) and spin-polarised (SP) calculations, which are also compared with those of $\text{Cr}_{27}\text{Co}_{27}\text{Fe}_{27}\text{Ni}_{27}\text{O}_5$ HEA supercell. As displayed in Figure 5, for CrCoFeNi , the HCP phase is preferable over the FCC phase in both SP and NSP states, while the FCC phase is favourable in HEAs under volume dilatation. Moreover, it is found the magnitude of volume dilatation that induces an HCP-to-FCC transformation in the NSP state is higher than

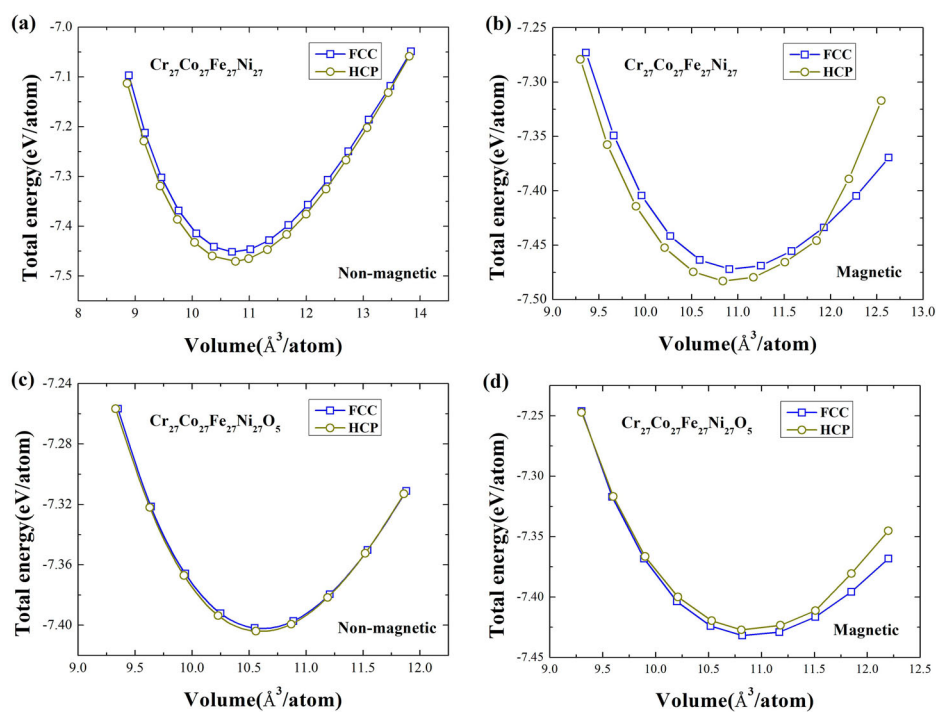


Figure 5. Total energy versus volume curves for non-spin-polarised and spin-polarised $\text{Cr}_{27}\text{Co}_{27}\text{Fe}_{27}\text{Ni}_{27}$ and $\text{Cr}_{27}\text{Co}_{27}\text{Fe}_{27}\text{Ni}_{27}\text{O}_5$ in HCP and FCC structures.

that in the SP state. Thus, it is concluded that the magnetisms tend to promote the HCP-to-FCC transformation in CrCoFeNi HEA at 0 K. In other words, the magnetism of HEA could stabilise the FCC phase. These findings agree well with the experimental results and the aforementioned results that there is a co-existence of HCP and FCC phases in CrCoFeNi HEA at specific pressures [39]; The magnetically driven HCP-to-FCC transformation predicted in this work also agrees with that previously studied by Niu et al. [19]. The total energy of $\text{Cr}_{27}\text{Co}_{27}\text{Fe}_{27}\text{Ni}_{27}\text{O}_5$ at an equilibrium state indicates HCP structure is preferable in the NSP state, whereas the FCC structure is preferable in the SP state. Moreover, on the basis of equilibrium state, the HCP-to-FCC transformation might occur in the NSP state under volume dilatation, and FCC-to-HCP might occur in the SP state under volume compression.

3.3. Magnetic properties of CoCrFeNi and CoCrFeNiO_x HEAs

The results described above indicate that local magnetism significantly affects the phase stability of CoCrFeNiO_x HEA. Thus, the influences of local magnetisms of atoms on the interstitials-induced HCP-to-FCC transformation in CoCrFeNiO_x HEA are further elucidated by the identification of the local magnetic moments of individual atom in FCC and HCP HEAs containing interstitial oxygen with various concentrations, which are shown in Figure 6(a) and 6(b), their averaged values are summarised in Figure 6(d) and 6(e), respectively. In the FCC and HCP HEAs without interstitial oxygen, the local magnetisms of Cr and Fe are antiferromagnetic-like while those of Ni and Co are ferromagnetic-like, which are well consistent with the results reported by Zuo et al. [25]. As shown in Figure 6(a) and 6(b), in the FCC and HCP HEAs containing oxygen interstitials, the local magnetisms of Ni, Co, and Cr are not much affected by the content of oxygen. On the contrary, the local magnetism of Fe in HCP HEAs varies with the addition of oxygen, and the Fe atoms particularly change from an antiferromagnetic-like to a ferromagnetic-like ordering behaviour when the content of oxygen exceeds 2.7 at.%. In the FCC HEAs containing oxygen interstitials, the antiferromagnetic-like ordering behaviour of Fe atoms is not much affected by the content of interstitial oxygen. With the suppressed magnetic frustration of Fe only in FCC HEAs containing interstitial oxygen, it is well explained that the difference in total energy between FCC and HCP HEAs is reduced when their magnetic states are considered in the total energy calculations, as shown in Figure 6(c). The results thus demonstrate that the local magnetisms of Fe play an important role in the interstitial oxygen-induced HCP-to-FCC transformation in CoCrFeNiO_x HEAs. Moreover, the magnitude of the averaged local magnetic moments of Cr and Fe increases with increasing concentration of interstitials in the HCP HEAs, while those of Ni and Co vary slightly with the interstitials content, as shown in Figure 6(e). In addition, the magnetic moment of atoms in HCP HEAs, in

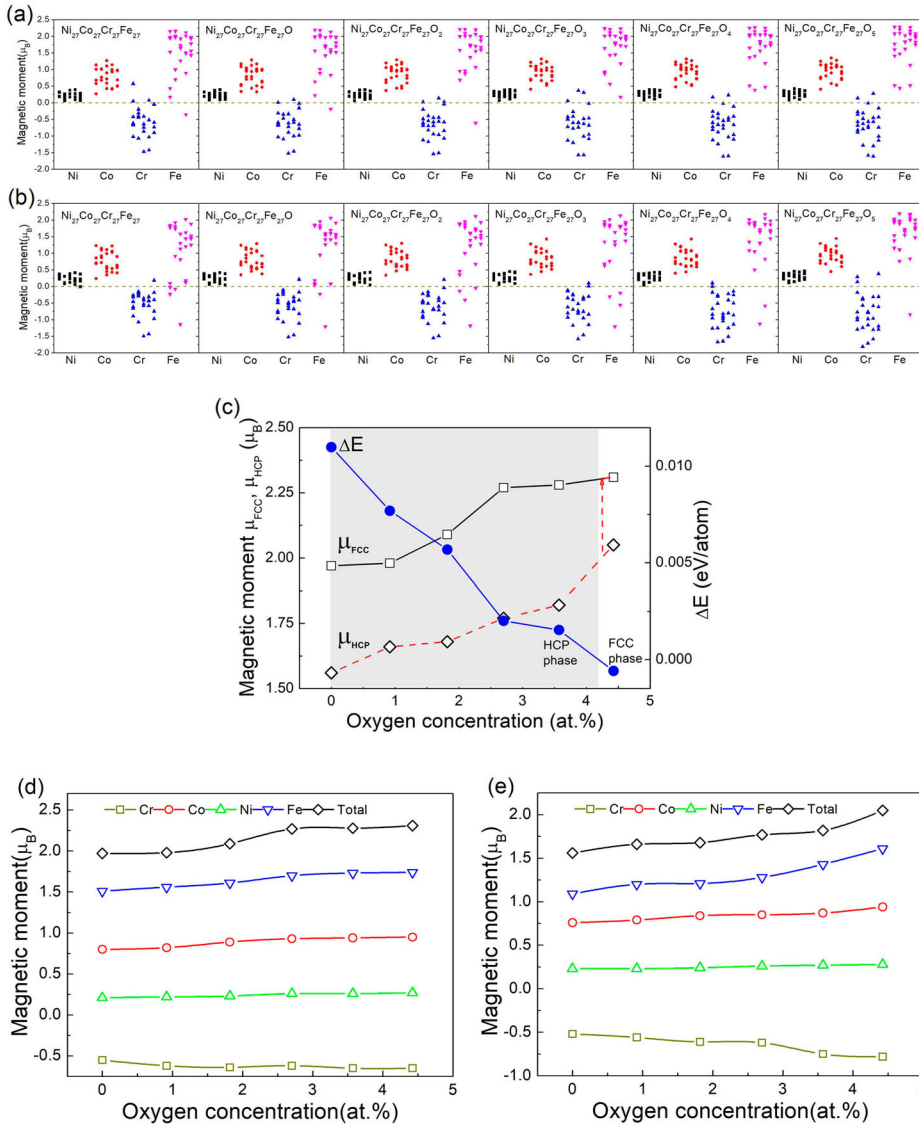


Figure 6. Effects of concentrations of interstitial oxygen on the magnetic moments of local magnetisms of constituent alloy elements in (a) FCC, and (b) HCP CoCrFeNiO HEAs. (c) The changes in the total energy difference ($\Delta E = E_{\text{FCC}} - E_{\text{HCP}}$) between FCC and HCP HEAs, and the atomic magnetic moments μ_{FCC} and μ_{HCP} of FCC and HCP HEAs, respectively, with increasing contents of interstitial oxygen. The relations between the averaged atomic magnetic moments of Cr, Co, Ni, and Fe in (d) FCC (2#) and (e) HCP CrCoNiFe HEAs containing oxygen interstitials and the content of oxygen. The ‘total’ atomic magnetic moment refers to that averaged over all atoms in the system and is equivalent to the magnetisation of HEAs.

equivalent to the magnetisation of HEAs, exhibits a sudden increase to that in FCC HEAs when the content of interstitial oxygen is larger than 4.2 at.%, as indicated by the red dash arrow shown in Figure 6(c), close to which the HCP-to-FCC phase transformation occurs (when $\Delta E = E_{\text{FCC}} - E_{\text{HCP}}$ becomes

zero). It is thus suggested that the structural transformation could be accompanied by significant changes in the atomic magnetic moments in the HEAs, and the transformation could be magnetically driven.

The fluctuation of magnetic moment can be further analyzed using the mean square deviation (MSD), and the obtained MSD of the magnetic moments of local magnetisms of Co, Cr, Fe, and Ni in FCC and HCP structured CoCrFeNiO_x HEAs are displayed in Figure 7. It is found that the fluctuations of magnetic moments for Co and Ni are not much influenced by the addition of oxygen. However, the MSD of Cr and Fe are severely affected when the concentration of oxygen interstitial exceeds 2.7 at.%.

In particular, as shown in Figure 6(e), the enhanced atomic magnetic moments of Cr and Fe in the HCP phase indicate the instability of local atomic structures of HCP HEA with high concentrations of interstitial oxygen, in consistent with that determined by the total energy calculation, as shown in Figure 6(c). Thus, the unstable local atomic structure, which tends to form the local FCC stacking sequence, could be responsible for the HCP-to-FCC phase transformation in HCP CoCrFeNiO_x HEAs. Since the interstitial oxygen is usually coordinated with more Cr or Fe atoms at the octahedral sites (as discussed in Section 3.1), the increase in x could be accompanied by the obvious changes in the magnetic moments of Cr and Fe, i.e. the increases in magnetic moments with increasing x , as shown in Figure 6(e). Meanwhile, as shown in Figure 6(c), the increase in x results in an HCP-to-FCC transformation at $x \sim 4.2$ at.%, where lattice instability should occur during such structural transformation.

3.4. The influence of interstitial oxygen and magnetisms on deformation mechanisms in HEAs

To explore the mechanisms of pressure-induced reversible structural transformation between the FCC and HCP phases in the CoCrFeNi and

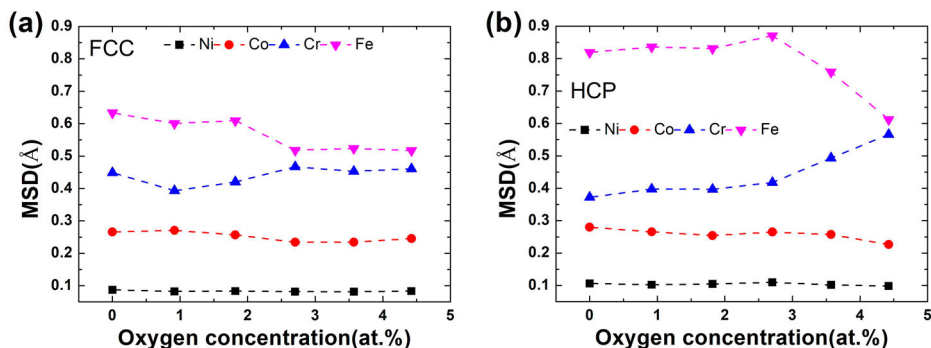
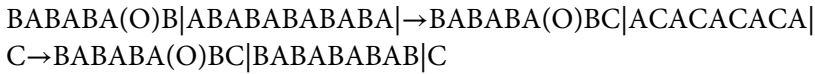


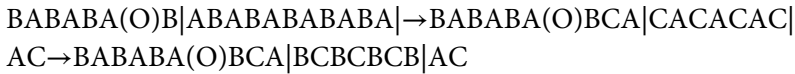
Figure 7. The mean square deviation of the magnetic moments of local magnetisms of constituent alloy elements in (a) FCC, and (b) HCP CoCrFeNiO_x HEAs containing different concentrations of interstitial oxygen.

CoCrFeNiO_x HEAs, the GPFE curves are utilised in this work, which could be convenient to generate planar faults resulting from the operation of partial dislocations in HCP HEAs [31]. The HCP supercell presented in Figure 2(a) is used for further calculations, which possesses a stacking sequence of ... BABABABABABABABA ... with A and B representing the (0001) slip plane. The displacement of the 8th-18th atomic layers for one partial along [10-10] direction leads to the supercell containing two I_2 intrinsic stacking faults, and the stacking sequence could become BABABAB-CACACACACAC (denoted as SC1). Moreover, the supercell with twin fault (denoted as SC2) and FCC fault (denoted as SC3) are obtained by shifting atoms on the 9th -17th and the 10th -16th layers along [01-10] and [-1100] directions in the SC1 model, respectively. The evolutions of stacking sequence during deformation twinning and HCP-FCC transformation are described as follows:

(i) Deformation twinning:



(ii) HCP-FCC transformation:



The mechanisms of deformation-induced reversible structural transformation between the FCC and HCP phases in CrCoFeNi HEAs can be investigated from the GPFE curves determined for the HCP HEAs. The stacking fault energy is calculated as $\gamma_{isf} = (E_{isf} - E_0)/2S_0$ [34], where E_{isf} and E_0 are the total energies of faulted and pristine supercells, respectively, and S_0 is the area of the stacking fault. In the calculation, atomic positions are allowed to relax only in the direction perpendicular to the glide plane.

The calculated GPFE curves for HCP CoCrFeNi HEA under the NSP condition are displayed in Figure 8, where the stacking fault energy (γ_{isf}), twinning fault energy (γ_t) and FCC fault energy (γ_{fcc}) are defined as the three local minima at the end of a GPFE curve, respectively; While the local maxima at the curve prior to reaching those three minima are named as unstable stacking fault energy (γ_{usf}), unstable twinning fault energy (γ_{ut}) and unstable FCC fault energy (γ_{ufcc}), respectively. The energy barrier for the formation of a specified fault can be determined, and it is straightforward that the energy barrier for the formation of an FCC fault ($\Delta U_F = \gamma_{ufcc} - \gamma_{isf}$) is larger than that of a twinning fault ($\Delta U_T = \gamma_{ut} - \gamma_{isf}$), implying that the deformation twinning is energetically favourable over HCP-to-FCC transformation to occur in the HEA under the NSP condition.

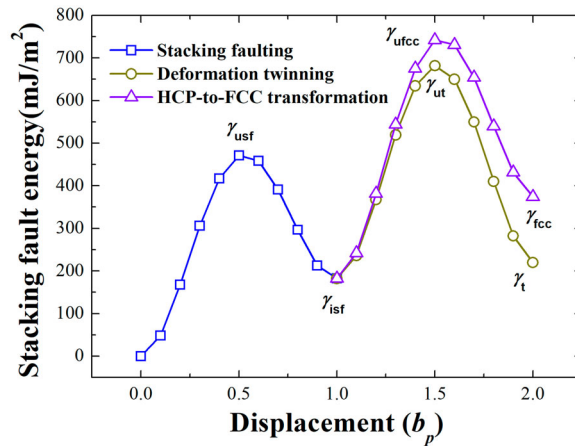


Figure 8. Generalised planar fault energy curves obtained from first-principles calculations of HCP CrCoFeNi HEA. $b_p = a_0/3[-1100]$; a_0 is the lattice constant.

To determine the influence of magnetisms on deformation mechanisms of HCP CoCrFeNiO_x HEA, the GSFE curves with and without considering magnetisms are calculated for CoCrFeNi and CoCrFeNiO_x HEAs, where the interstitial oxygen are located between the 6th and 7th atomic layers and with Cr-rich nearest neighbours. The obtained stacking fault energies γ_{usf} , γ_{isf} , γ_{ut} and γ_{ufcc} are summarised in Table 1, which can be found to decrease by taking into account of the influences of interstitial oxygen or magnetisms. The reductions are more noticeable when the influences of interstitial oxygen or magnetisms are both considered. The reduced γ_{usf} , γ_{isf} and γ_{ufcc} indicate that CoCrFeNi HEA could prefer the FCC stacking sequence when there exist interstitial oxygen and magnetisms in it. Although the energy barrier for deformation twinning is relatively lower than that for HCP-to-FCC transformation, the difference in energy barrier between deformation twinning and HCP-to-FCC transformation is reduced when there exist oxygen interstitials and magnetisms in the HEAs.

The competition between deformation twinning and HCP-to-FCC transformation in CrCoFeNiO_x HEAs under hydrostatic pressures P are further analysed from an energetics perspective. The relative volume dilatation of supercell caused by the negative (positive) P can be measured by the lattice strain $e > 0$ (< 0) at each side of the supercell, as follows: $\eta = (V - V_0)/V_0 = (1 + e)^3 - 1$, where

Table 1. The effects of magnetism and interstitial oxygen on stacking fault energies of HCP CoCrFeNi and CoCrFeNiO_x HEAs.

Stacking fault energies		γ_{usf}	γ_{isf}	γ_{ut}	γ_{ufcc}
Non-magnetic	Cr ₂₇ Co ₂₇ Fe ₂₇ Ni ₂₇	471	182	682	742
	Cr ₂₇ Co ₂₇ Fe ₂₇ Ni ₂₇ O	262	109	406	442
Magnetic	Cr ₂₇ Co ₂₇ Fe ₂₇ Ni ₂₇	287	75	359	398
	Cr ₂₇ Co ₂₇ Fe ₂₇ Ni ₂₇ O	230	59	311	347

η is the volumetric strain, V_0 and V are the volumes of supercell before and after the application of hydrostatic pressure, respectively.

The computations are performed on the same HCP CrCoFeNi model system to exclude the effects of chemical disorder, and the energy barriers for the formation of twin faults and FCC faults (ΔU_T and ΔU_F) are determined from the GPFE curves. Figure 9 presents the relationship between the applied lattice strain e and the energy barriers ΔU_T and ΔU_F for the formation of twin faults and FCC faults, respectively. Firstly, it is found that the energy barriers decrease with increasing applied hydrostatic pressure $P < 0$, which results in volume dilatation of the supercell. From Figure 9(a), it is found that when the strain exceeds a critical value of 8.2% for the CrCoFeNi HEA in the NSP state, the energy barrier for the formation of twin faults (ΔU_T) is higher than that (ΔU_F) of FCC faults. The results indicate that the slips of partial dislocations with a Burgers vector $b_2 = a_0/3[-1100]$ in the formation of FCC fault on the basal plane (0001) are more prevalent during the deformation process in HCP CrCoFeNi HEA under volume dilations with $e > 8.2\%$, leading to an HCP-to-FCC allotropic transformation. For the CrCoFeNi HEA in the SP state, the same conclusion holds while the critical value of strain (e_c) is found to be 7.9%. Similarly, in the case of CrCoFeNiO_x HEA, those critical values of strains for HEA in the NSP

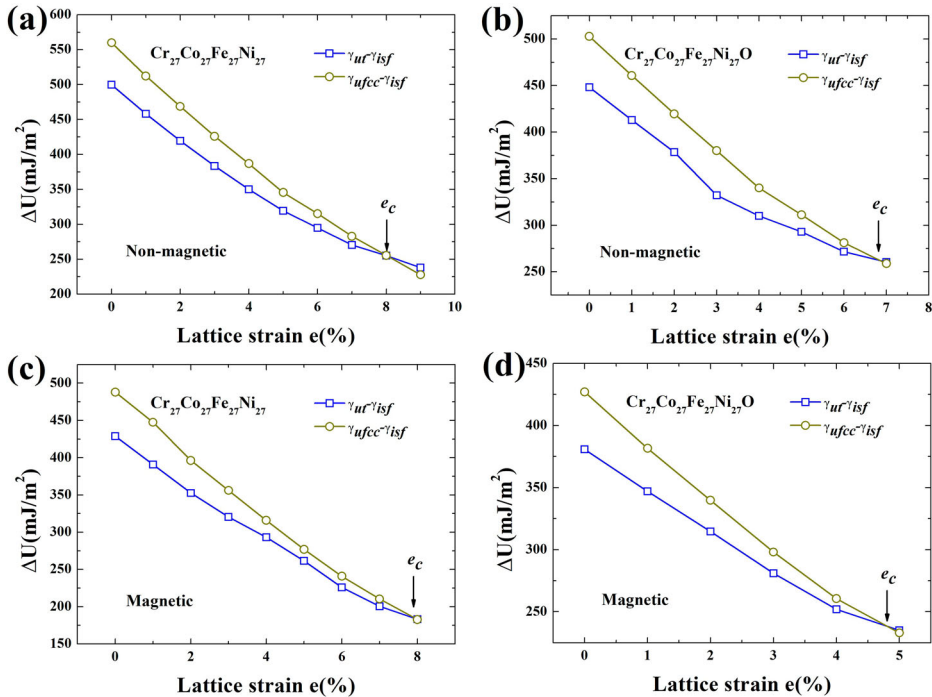


Figure 9. The energy barriers for the formation of twin faults ($\Delta U_T = \gamma_{ut} - \gamma_{isf}$) and FCC faults ($\Delta U_F = \gamma_{ufcc} - \gamma_{isf}$) under the loading conditions of hydrostatic pressures as measured by the lattice strain e in HCP CrCoFeNiO_x HEAs. The arrow marks the critical applied strains e_c for the transformation.

and SP state are found to be 6.8% and 4.8%, respectively. Thus, it is suggested that the GPFE curves shown in Figure 9 could well characterise the reversible structural transformation between HCP and FCC phases in CrCoFeNi and CrCoFeNiO_x HEAs under hydrostatic pressures, and the results well explained the HCP-to-FCC phase transformation that could be induced by the oxygen interstitials and driven by the magnetisms of local chemical environment.

3.5. The influence of interstitial oxygen and magnetisms on the structural transformation in HEAs under applied pressures

To simulate the HCP-to-FCC transformation as affected by the magnetisms in CoCrFeNiO_x HEAs, the lattice strains can be applied to the HCP and FCC HEAs with different oxygen concentrations (<5 at.%). As a result, the critical lattice strain required to drive the structural transformation in CoCrFeNiO_x HEAs can be determined with and without considering the magnetisms in the HEAs. The obtained results are presented in Figure 10(a), and it is found that there exists a dual-phase region in this phase diagram. It has been observed from previous experimental studies that the co-existence of HCP and FCC phases in CoCrFeNi HEA is responsible for its enhanced mechanical strength and ductile [17,18]. Since the magnetic and non-magnetic states of CoCrFeNiO_x HEAs can be alternated by thermal activation or applied magnetic fields, the resulting coexistence of non-magnetic HCP phase and magnetic FCC phase in the alloy is of significance in tuning its magnetic and mechanical properties.

Furthermore, taking Co₂₇Cr₂₇Fe₂₇Ni₂₇O₃ HEA as an example, the changes in magnetic moments of HCP HEA under different lattice strains are computed, as shown in Figure 10(b). It is found that when the lattice strain exceeds ~4 at.% the magnetic moment of HCP HEA varies slightly, which is close to that of FCC

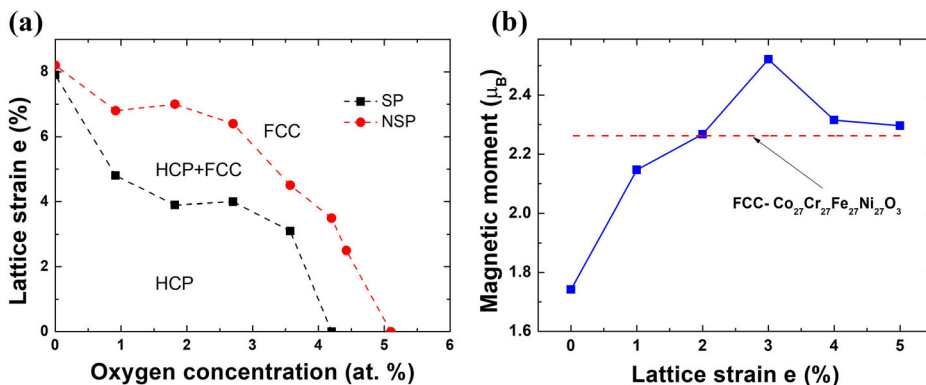


Figure 10. (a) Competition between HCP and FCC phases in CoCrFeNiO_x HEA under external loading conditions of volume compression or dilatation, and (b) the magnetic moment of HCP Co₂₇Cr₂₇Fe₂₇Ni₂₇O₃ under different loading strains, the red dot line is the magnetic moment of FCC Co₂₇Cr₂₇Fe₂₇Ni₂₇O₃ which is at an equilibrium state.

HEA at an equilibrium state. It is thus suggested that the HCP phase of $\text{Co}_{27}\text{-Cr}_{27}\text{Fe}_{27}\text{Ni}_{27}\text{O}_3$ could transform to the FCC phase under a lattice strain of ~ 4 at.%, in consistent with that indicated in Figure 9(d). Thus, it is remarkable to confirm that the structural transformation is accompanied by the magnetic transition in CoCrFeNiO_x HEAs.

The influences of interstitial oxygen and magnetisms on phase transformations in HEA, as revealed above, have some implications on the structural and functional applications of HEAs. On the one hand, the coupled magnetisms and structural transformation in HEAs can be well applied to improve the mechanical properties of HEAs by finely tuning the constituent alloy elements with different magnetism or through applying external magnetic fields or pressures [19,40–46]. On the other hand, the HEAs could be considered as promising candidates for magnetic refrigeration applications with a giant magnetocaloric effect [47–52] since the structural transformation could have a significant contribution to the magnetic entropy changes in the HEAs for magnetocaloric applications [47,48].

4. Conclusions

In summary, first-principles calculations are performed to elucidate the effects of interstitial oxygen, magnetisms, and pressures on the phase stability and structural transformation in CoCrFeNiO_x HEA. First, it is found that the oxygen interstitials tend to occupy the octahedral sites in FCC HEA. Second, it is determined that in the HEAs the FCC phase is energetically favourable over the HCP phase when oxygen concentration exceeds 4.2 and 5.1 at.%, with and without considering its magnetism, respectively. Third, the structural transformation in CoCrFeNiO_x HEA is accompanied by significant changes in the atomic magnetic moments in the HEAs, and the transformation could be magnetically driven. Fourth, the volume dilatation required for the HCP-to-FCC transformation in CoCrFeNi HEA could be reduced with the synergy effects of oxygen interstitials and magnetisms. The coupled interstitials-induced and magnetically driven structural transformation paves a new avenue for the structural and functional application of HEAs.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Microstructure and mechanical properties of Al–Co–Cr–Fe–Ni–(Nb–Ti) high entropy alloys

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ABSTRACT

The structure and mechanical properties of non-equiatomic $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Nb}_4$, $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Nb}_2\text{Ti}_2$ and $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Ti}_4$ high entropy alloys (HEAs) were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), hardness and tensile testing. TEM and XRD analyses revealed the formation of $\gamma''\text{-Ni}_3\text{Nb}/\gamma$ (FCC), double FCC and $\gamma'\text{-Ni}_3\text{Al}/\gamma$ (FCC) structure for as-cast $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Nb}_4$, $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Nb}_2\text{Ti}_2$ and $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Ti}_4$ HEAs, respectively. The hardness and yield strength values were found to increase with the addition of Nb while the ductility of alloys increased with the increase in Ti concentration, significantly. The as-cast $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Ti}_4$ alloy exhibited an excellent combination of ultimate tensile strength of 844 MPa and an elongation of 29.8% due to the coherent phase relation between γ' precipitates and γ matrix. The fractured surfaces of as-cast $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Nb}_4$, $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Nb}_2\text{Ti}_2$ and $\text{Al}_8\text{Co}_{30}\text{Cr}_{18}\text{Fe}_9\text{Ni}_{31}\text{Ti}_4$ HEAs showed typical dimple type ductile fracture under tension test.

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1. Introduction

Regarding their remarkable and unique properties such as high strength and hardness [1–3], excellent corrosion and oxidation resistance [4,5], superior high temperature mechanical properties [4–6], magnetic properties [7] and impressive thermal stability [8], high entropy alloys (HEAs) have attracted much attention. Since their discovery by Cantor et al. [9] and Yeh et al. [10], much effort has been given to understand the concept of HEAs and numerous types of HEA systems were discovered with impressive properties. HEAs may have intermetallic or even amorphous phases, together with solid solution phases due to differences in the atomic sizes and electronegativities between constituent elements, valence electron configuration (VEC) and elemental compositions. Among the HEA systems, Al–Co–Cr–Fe–Ni system has attracted

much attention due to the formation of wide range of microstructures and corresponding mechanical properties [11–17]. The equimolar AlNiCoFeCr HEA was reported as a very brittle HEA with nearly zero ductility due to the spinodal decomposition of BCC and B2 phases [17]. The effect of secondary alloying elements with minor concentration on the microstructure and mechanical properties has also been investigated. It has been shown that the addition of Ti, Nb or Mo results in the formation of secondary phase and thus precipitation strengthening that improves the mechanical properties. It was reported that AlCoCrFeNiTi_{0.5} HEA showed a compressive yield strength of 2.2 GPa with a compressive plasticity of 23.3% at room temperature with the addition of Ti element [18]. Malathi et al. [19] stated that the addition of Nb improves the yield and maximum strengths due to its effect on the grain structure and solid solution phases. HEAs with single FCC structure exhibit high ductility with low strength while the alloys with single BCC structure show high hardness and yield strength but their ductility is low. The formation of intermetallic phases such as Laves, L1₂ and B2 improves the strength and ductility of the HEA alloys, significantly. It was reported that the addition of Nb into the CoCrFeNi HEA leads to the formation of an ordered Nb-enriched Laves phase embedded in the FCC solid solution matrix [20]. However, laves phase is known as a brittle phase thus the formation of L1₂ and B2 phases in the HEAs serves the excellent combination of strength and ductility. The precipitation of coherent Ni₃(Al, Ti) L1₂ structured phase in FCC (γ) matrix offers effective strengthening in superalloys [21]. Due to the similarity of L1₂ type Ni-, Al-, Ti- rich γ' precipitates embedded in γ matrix to the precipitation strengthened Ni-based super alloys, these HEAs are named as high entropy superalloys (HESAs) [22,23]. The volume fraction of the L1₂ phase precipitated in single-crystal Ni-based superalloys was reported as 65–70% [24]. The L1₂-strengthened HEAs and complex HEAs were also reported previously [25–29]. Yang et Al. [29] stated that the precipitation of the L1₂ phase in Al₇(Fe, Co, Ni)₈₆Ti₇ HEA improves the tensile yield strength and elongation up to 1028 MPa and 47.8% at room temperature, respectively. The formation of the L1₂ phase in the interdendritic regions of the as-cast Co_{37.6}Ni_{35.4}Al_{9.9}Mo_{4.9}Cr_{5.9}Ta_{2.8}Ti_{3.5} HEA was also reported previously [30]. Zhao et Al. [31] reported that the co-addition of Al and Nb enables the desired formation of the coherent L1₂ precipitates in the Al–Co–Cr–Fe–Nb–Ni system. Besides the L1₂ phase, D022-ordered γ'' -Ni₃Nb phase is the other well-known precipitate in the γ matrix used to enhance the strength of superalloys, such as Inconel 718 [32]. We previously studied the microstructure and mechanical properties of CoCrFeNi and CoCrFeNiTi_{0.5}Al_{0.5} HEA [33]. We reported that the crystal structure of CoCrFeNi HEA has changed from FCC to a mixture of FCC and double BCC structures by the addition of Ti and Al in CoCrFeNiTi_{0.5}Al_{0.5} HEA. The compression test revealed that CoCrFeNiTi_{0.5}Al_{0.5} HEA yields at 1997 MPa and fractures at 2344 MPa with a cleavage mode [33]. It has been reported that

equiatomic or near equiatomic HEAs tend to form brittle intermetallics, such as B2-type NiAl and other sigma phases. However, the non-equiatomic HEAs with high Ni/Al ratio promote the formation of ductile L1₂ phases. Here we focused on three different non-equiatomic Al–Co–Cr–Fe–Ni–(Ti/Nb) HEAs and investigated the effect of Nb and Ti on the phase formation, microstructure and mechanical properties of Al–Co–Cr–Fe–Ni HEAs.

2. Material and methods

The alloy ingots with nominal compositions of Al₈Co₃₀Cr₁₈Fe₉Ni₃₁Nb₄ (RA01) Al₈Co₃₀Cr₁₈Fe₉Ni₃₁Nb₂Ti₂ (RA02) and Al₈Co₃₀Cr₁₈Fe₉Ni₃₁Ti₄ (RA03) alloys were prepared using high purity elements (0.999 Al, Co, Cr, Fe, Ni, Nb, and Ti, by weight) by Edmund Bühler MAM-1 vacuum arc melter with Turbomolecular pumping system HVT52/G under an Ar atmosphere. The alloy ingots with a mass of 3–5 g were cast three times to ensure chemical homogeneity. The alloys were then cast into 4 mm diameter copper moulds via suction casting for tension tests. The structural analysis and phase stability of the as-cast alloys were investigated by XRD (D8 Advance Bruker) using Cu K α radiation. The microstructures of the as-cast alloys and their fractured surfaces after tension tests were examined using SEM (FEI 430 NanoSEM-30 kV). The elemental distribution analysis was carried out using Energy-dispersive X-ray Spectroscopy detector (EDS) inserted in FEI Nova NanoSEM 430 SEM. The microstructure of as-cast alloys was examined using transmission electron microscopy (TEM) using JEOL JEM-2100F microscope at 200 kV. TEM samples were prepared using a focused ion beam (FEI-Nova 600i FIB). The Vickers microhardness tests of the as-cast alloys were performed using a load of 10 kgf due to the ASTM E92 standard using a microhardness tester (InnovaTest Nexus 7501) at room temperature. At least 10 indentation measurements were taken for each specimen, and then the average Vickers Hardness (HV) values with standard deviations were calculated. The HV values were also converted into MPa by multiplying by 9.807 for convenience. The tensile test specimens of as-cast alloys were prepared due to ASTM E8/E8M standard using Instron 5582 mechanical testing machine. Tension tests were operated with a crosshead speed of 1 mm/min.

3. Results and discussion

Table 1 shows the calculated thermophysical parameters such as the enthalpy of mixing (ΔH_{mix}), the entropy of mixing ΔS_{mix} , the valance electron

Table 1. Thermophysical parameters of HEAs.

Alloy	ΔH_{mix} (kJ mol ⁻¹)	ΔS_{mix} (J K ⁻¹ mol ⁻¹)	δ (%)	VEC	Expected crystal structure
RA01	–11.11	13.14	4.69	8.04	FCC
RA02	–11.59	13.37	4.83	8.02	FCC
RA03	–11.75	13.14	4.98	8.00	FCC

concentration (VEC) and atomic size difference (δ) [34] of the alloys. The VEC values (>8.00) and δ values ($<6.6\%$) of three alloys suggest a single FCC solid solution phase formation [35,36]. The ΔH_{mix} values of the alloys calculated based on the binary ΔH_{mix} values of atomic pairs [37] were listed in Table 2. All alloys have medium-negative ΔH_{mix} values in the range of $-22 \text{ kJ mol}^{-1} \leq \Delta H_{\text{mix}} \leq 7 \text{ kJ mol}^{-1}$ corresponding to a single solid solution [35,38].

The microstructure of the as-cast RA01, RA02 and RA03 alloys is shown in Figure 1. SEM micrographs of all alloys exhibit dendritic (D) and interdendritic (ID) regions that are typical microstructures of many HEAs. The RA01 alloy has coarse dendritic and interdendritic regions (Figure 1a) in comparison to RA02 (Figure 1b) and RA03 (Figure 1c) alloys. The higher melting temperature of Nb than other alloying elements results in the reduction of undercooling during solidification and thus the coarser grains. SEM images of RA03 alloy in Figure 1(c) illustrate the equiaxed shape second phase embedded in the dendritic matrix. Table 3 shows the EDS analysis results of alloys and specifically for dendritic and interdendritic regions. EDS analysis reveals the segregation of Nb and Ti elements in the interdendrites due to their high negative ΔH_{mix} . Cr and Fe segregate into dendritic regions of all alloys due to their moderate ΔH_{mix} to form solid solution phases [37]. EDS mapping of RA01 alloy indicates partitioning of Nb in the interdendritic regions. The elemental analysis of RA03 alloy reveals the Al pile-up at dendritic regions and minor increase in Ni and Ti at interdendritic regions. The EDS elemental distribution maps of alloys are illustrated in Figure 2. EDS maps confirm the segregation of Nb and Ti through interdendritic regions, while Cr and Fe pile-up at dendritic regions for RA01, RA02 and RA03 HEAs. Ni partitioned to the equiaxed regions embedded in the dendritic matrix of RA03 alloy.

Microstructural analysis was performed for as cast RA01, RA02 and RA03 alloys using TEM in bright field (BF) and selected area diffraction (SAED) modes. The BF images in Figure 3(a,b) indicate crystal embedded in the matrix of RA01 alloy. The BF image (Figure 3b) with corresponding SAED pattern taken reveal the formation of $\gamma''\text{-Ni}_3\text{Nb}$ crystal in the matrix. The corresponding EDS map also confirmed the partitioning of Nb due to $\gamma''\text{-Ni}_3\text{Nb}$ crystals. Presumably, the excess Nb is accommodated by interdendritic segregation and, the contrast and feature difference are due to $\gamma''\text{-Ni}_3\text{Nb}$ particles.

Table 2. ΔH_{mix} of the binary systems in kJ.mol^{-1} [37].

Al	Co	Cr	Fe	Ni	Nb	Ti	
	-18.8	-9.9	-11.1	-22.3	-18.2	-29.5	Al
		-4.5	-0.6	-0.2	-24.5	-28.3	Co
			-1.5	-6.7	-7.2	-7.5	Cr
				-1.6	-15.7	-16.8	Fe
					-29.9	-34.5	Ni
						2.0	Nb
							Ti

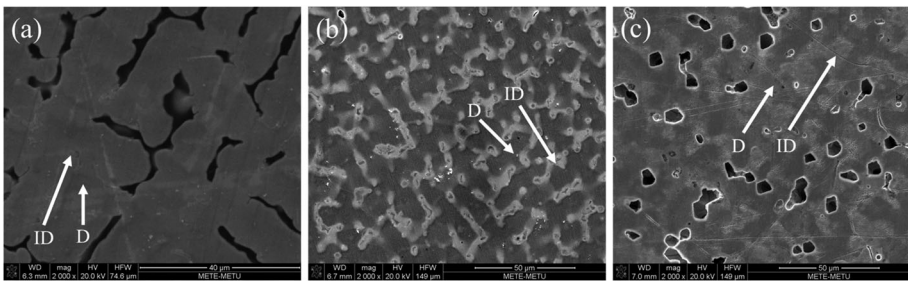


Figure 1. SEM images of the as-cast (a) RA01, (b) RA02 and (c) RA03 HEAs.

Figure 4(a,b) indicate the BF images of RA02 alloy which has both Ti and Nb. The inset SAED pattern corresponding to BF image in Figure 4(b) indicates the FCC structure. As a difference from the RA01 alloy, Nb and Ti segregate through interdendritic regions instead of partitioning. The BF images of RA03 alloy are given in Figure 5(a,b). Figure 5(b) displays the crystal particles embedded in the matrix, with its corresponding inset CBED along at $[01\bar{1}]$ zone axis of an ordered $L1_2$ (FCC) γ' -Ni₃Al precipitates. RA03 alloy has the highest Ti concentration which facilitates the formation and stabilisation of the $L1_2$ phase. The γ' -Ni₃Al precipitates in the γ matrix are similar to the precipitation strengthening mechanism that occur in superalloys.

The XRD patterns of the as-cast RA01, RA02 and RA03 alloys are shown in Figure 6. XRD analysis of the as-cast alloys shows FCC (γ) phase and the overlapped main peaks of the other intermetallic γ , γ' -Ni₃Al and γ'' -Ni₃Nb phases, because their lattice parameters are identical. It has been previously reported that Co and Ni are the FCC stabilisers, thus their high concentrations promote the formation of the FCC phase in the alloys [39]. The XRD pattern of RA01 alloy indicates the crystalline peaks due to FCC and γ'' -Ni₃Nb. Ma et al. [40] previously reported the formation of BCC and Laves phases in the AlCoCrFeNiNb_x ($x = 0.1, 0.25, 0.5$ and 0.75) HEAs. Here, we did not observe the formation of BCC or Laves phases. It may be due to the different concentrations of the alloying elements. With increase in Nb content of the alloy, FCC peaks shift to lower Bragg angles due to the lattice strain induced by the larger atomic size of Nb in the alloy. The lattice parameters of FCC and γ'' -Ni₃Nb

Table 3. Chemical composition of the as-cast RA01, RA02 and RA03 alloys in at.%.

	RA01			RA02			RA03		
	D	ID	Overall	D	ID	Overall	D	ID	Overall
Al	3.2	2.9	9.1	4.9	4.2	9.0	7.2	0.5	7.7
Co	31.9	32.3	29.0	31.8	29.0	30.1	30.9	31.9	29.6
Cr	16.9	12.5	17.8	18.5	15.2	17.3	18.7	18.4	18.1
Fe	8.9	6.8	9.1	10.1	7.6	9.1	10.0	8.9	9.2
Ni	36.3	26.1	30.4	32.7	30.5	30.7	30.4	34.9	31.3
Nb	2.8	19.4	4.5	0.8	9.7	2.4	–	–	–
Ti	–	–	–	1.2	3.7	2.1	2.7	5.2	4.1

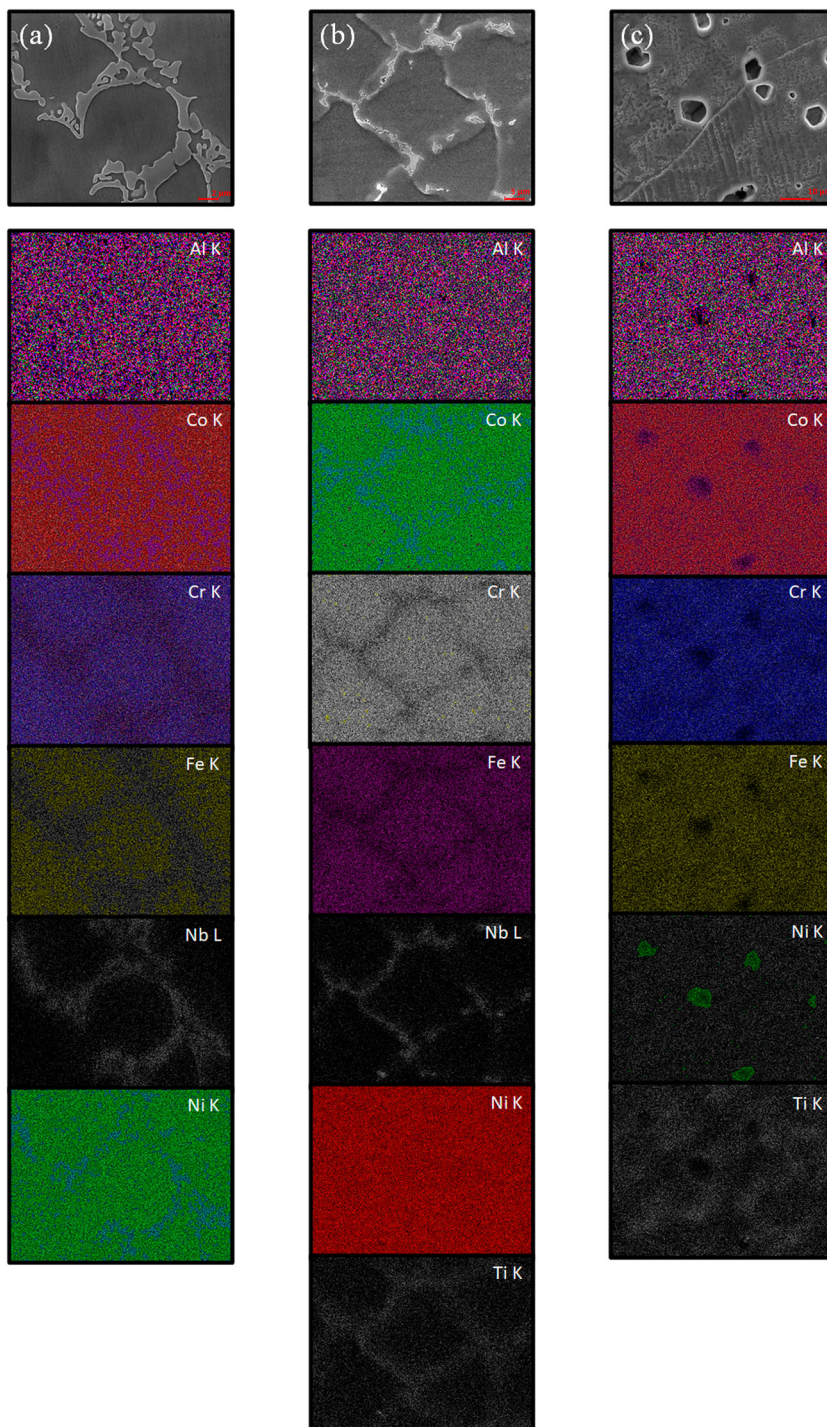


Figure 2. EDS maps according to elemental distributions of the as-cast (a) RA01, (b) RA02 and (c) RA03 HEAs.

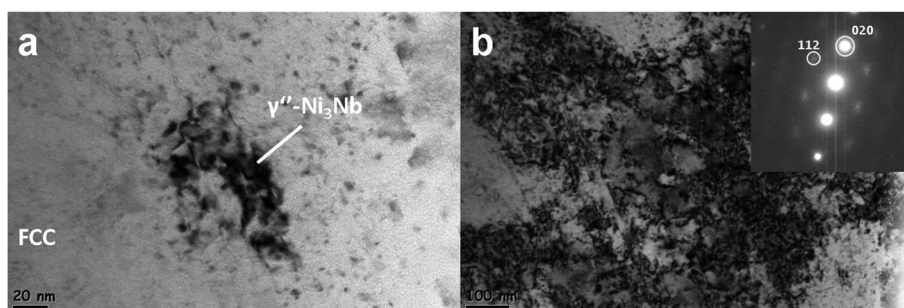


Figure 3. (a) and (b) BF images of as-cast RA01 HEA at different magnification. Inset figure in (b) indicates the corresponding SAED taken from γ'' -Ni₃Nb crystal at $[20\bar{1}]$ zone axis.

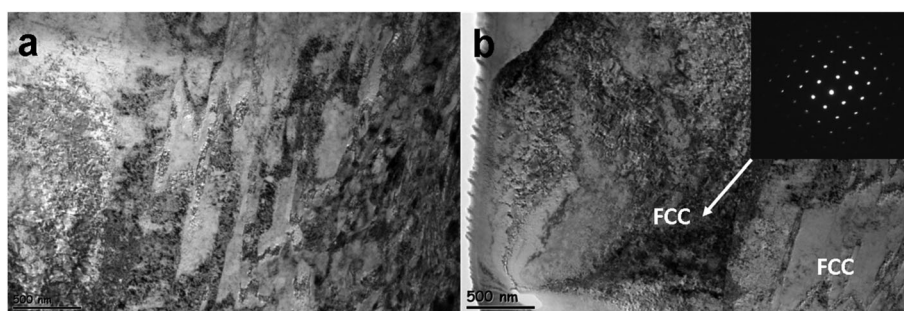


Figure 4. (a) and (b) BF images of as-cast RA02 HEA at different magnification. Inset figure in (b) indicates the corresponding SAED taken from γ crystal at $[011]$ zone axis.

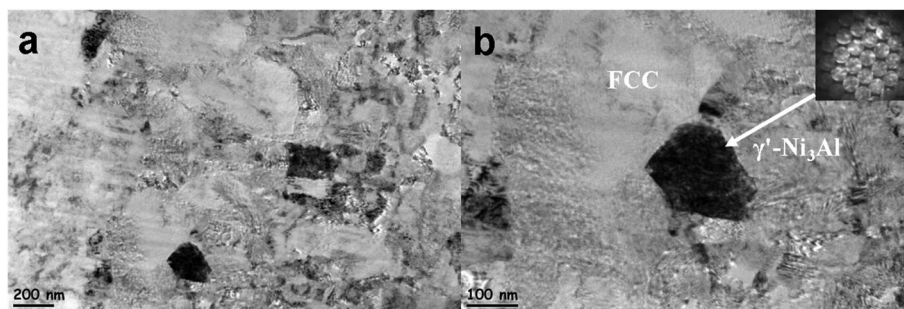


Figure 5. (a) and (b) BF images of as-cast RA03 HEA at different magnification. Inset figure in (b) indicates the corresponding CBED taken from γ' -Ni₃Al at $[01\bar{1}]$ zone axis.

phase for RA01 alloy were determined as 0.3592 and 0.3590 nm, respectively. The XRD pattern of RA02 alloy indicates strong FCC peaks and overlapped second FCC phase. TEM analysis of RA02 also indicate the dominant FCC structure. The corresponding lattice parameters of (FCC)₁ and (FCC)₂ phases of RA02 alloy were determined as 0.3597 and 0.3592 nm, respectively. The XRD analysis pattern of RA03 alloy indicates the coexistence of FCC and γ' -Ni₃Al phases with the lattice parameters of 0.3589 and 0.3587 nm, respectively.

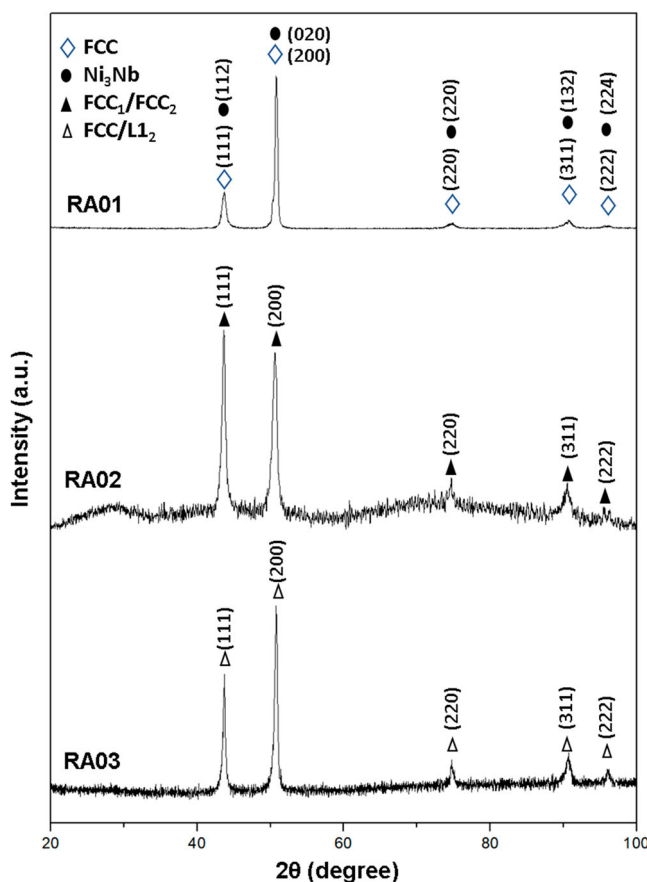


Figure 6. XRD patterns of the as-cast RA01, RA02 and RA03 HEAs.

The Vickers microhardness tests were carried out on as-cast RA01, RA02 and RA03 alloys. The hardness values were determined as 291 ± 55 HV (2854 ± 539 MPa), 294 ± 11 HV (2833 ± 108 MPa) and 274 ± 10 HV (2687 ± 91 MPa) for as-cast RA01, RA02 and RA03 alloys, respectively. The hardness values are higher for the Nb-rich RA01 and RA02 alloys than the Ti-rich RA03 alloy. The engineering stress–strain curves of as-cast RA01, RA02 and RA03 alloys at room temperature are given in Figure 7. The resulting mechanical properties, namely yield strength (σ_y), ultimate tensile strength (σ_{UTS}) and tensile fracture strain (ϵ_f) of alloys were summarised in Table 4. RA01 alloy presents the highest σ_y with lowest ductility. The precipitation of γ'' -Ni₃Nb precipitates in γ -matrix strengthened the alloy and enhanced the σ_y and σ_{UTS} . Regarding highest strength values, RA01 has the lowest ductility. With the addition of Ti and the presence of two coherent FCC phases, RA02 alloy has higher ductility but lower strength than RA01 alloy. RA03 alloy exhibits the highest ϵ_f of 29.76% thus highest ductility with the highest σ_{UTS} of 844 MPa in comparison to other alloys. With the increase in Ti concentration, γ'

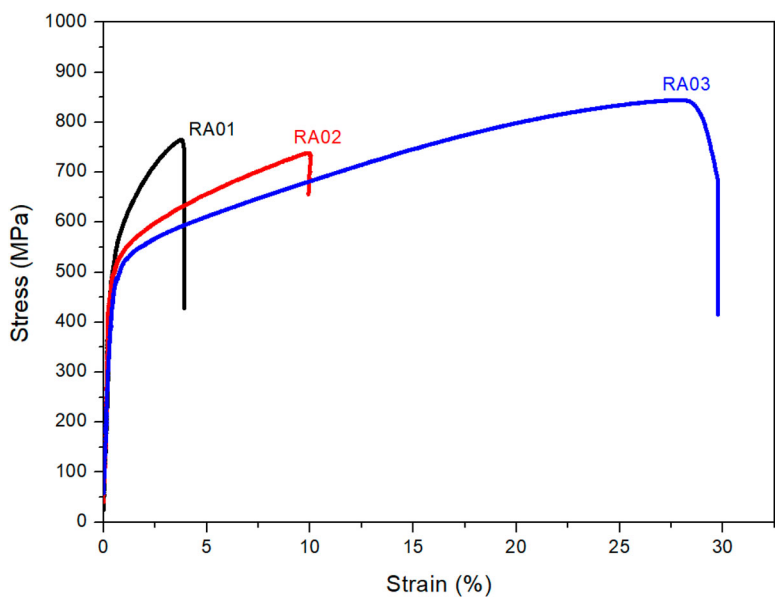


Figure 7. Engineering tensile stress-strain curves of the as-cast RA01, RA02 and RA03 alloys at room temperature.

Table 4. The yield strength (σ_y), ultimate tensile strength (σ_{UTS}) and tensile fracture strain values (ϵ_f) of RA01, RA02 and RA03 HEAs.

Alloy	σ_y (MPa)	σ_{UTS} (MPa)	ϵ_f (%)
RA01	568	765	3.90
RA02	494	738	9.97
RA03	486	844	29.76

phase precipitate in γ matrix. The lattice misfit of γ'/γ is smaller than that of γ''/γ because both γ' and γ have the same FCC structure, thus γ'' -Ni₃Nb precipitates have more strengthening effect than γ' -Ni₃Al precipitates in the γ matrix. It is interesting to note that even the ductility is increasing significantly with Ti content, strength values of the alloys are not decreasing sharply. Thus

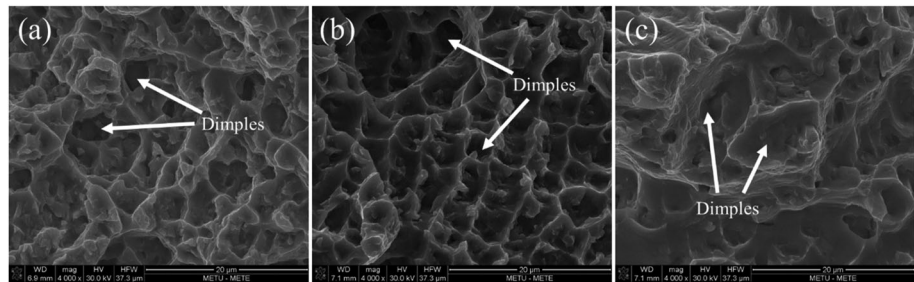


Figure 8. SEM images of fractured surfaces of (a) RA01, (b) RA02 and (c) RA03 alloys after tensile test at room temperature.

the excellent combination of ductility and strength was achieved in RA03 HEA. The σ_{UTS} and ϵ_f (%) of RA03 alloy are higher than the value of 786 MPa and 12, previously reported by Daoud et. al. [41] for $Al_{10}Co_{25}Cr_{17}Fe_{17}Ni_{36}Ti_6$ HEA. RA03 alloy is a candidate alloy with high potential for high entropy superalloys (HEAS).

Figure 8(a–c) indicate the SEM images of the fracture surfaces of RA01, RA02 and RA03 alloys after tensile testing at room temperature. The fracture morphology of the alloys consists of uniform dimples typical of plastic deformation. The size and the depth of the dimples are the largest for RA03 alloy in Figure 8(c) which is consistent with its highest ductility observed during tensile loading.

4. Conclusion

The structure and mechanical properties of $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_4$, $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_2Ti_2$ and $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ HEAs were investigated using XRD, SEM, TEM, hardness and tensile testing. The following conclusions can be derived as follows:

- The TEM and XRD analyses indicate double phase formation for $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_4$, $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_2Ti_2$ and $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ HEAs. TEM and XRD analysis revealed the formation of γ'' - Ni_3Nb precipitates in γ -matrix, double FCC phase and γ' - Ni_3Al precipitates in γ -matrix of as-cast $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_4$, $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_2Ti_2$ and $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ HEAs, respectively.
- The hardness and the yield strength values were increased by increasing the Nb content.
- The highest σ_y were achieved in $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Nb_4$ due to precipitation of γ'' - Ni_3Nb in γ -matrix.
- Ti addition facilitates the formation of γ' crystals and thus improves the ductility of the alloy significantly.
- The tensile test revealed an excellent combination of high strength and ductility in $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ HEA. $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ HEA alloy exhibited an excellent combination of ultimate tensile strength of 844 MPa and an elongation of 29.8% due to the coherent phase relation between γ' precipitates and γ matrix.
- SEM analysis of fracture surfaces of alloys also showed high-density dimple-like structure that reveals ductile fracture mode. The larger sizes of the dimples confirm the higher ductility of $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ HEA.
- $Al_8Co_{30}Cr_{18}Fe_9Ni_{31}Ti_4$ alloy has high potential to serve as a high entropy superalloy (HESA).

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Small-scale deformation behaviour of the AlCoCrFeNi_{2.1} eutectic high entropy alloy

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ABSTRACT

Novel methods to probe and evaluate the mechanical properties of High entropy alloy are gaining popularity to accelerate the development of new material for structural application and for establishing the physics-based mechanical property models. Nanoindentation techniques are predominantly suitable for evaluating the properties of materials in which deformation volumes can be cautiously controlled, and indentation can be applied to probe the properties of specific phases or features present within the microstructure. The current investigation is based on the plastic deformation response of Eutectic High Entropy Alloy, AlCoCrFeNi_{2.1}, using experimental and computational approaches. In this paper, the plastic deformation of eutectic high entropy alloy AlCoCrFeNi_{2.1} is investigated using nanoindentation over a broad range of strain rates at room temperature to probe the mechanical properties of Eutectic High Entropy Alloy, AlCoCrFeNi_{2.1} and also to understand its elasto-plastic behaviour of BCC and FCC phase present in the alloy. In order to capture the deformation mechanism of material under the tip of the nano-indenter as well as to predict the load variation with depth, molecular dynamic simulation is performed. A characteristic load-depth curve has also been generated from the developed model, which is in good agreement with the experimental one. These findings will lead to understanding the phase-specific contribution to bulk mechanical response of multicomponent alloys and aid in designing structural materials with high fracture toughness.

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1. Introduction

In recent times, high entropy alloys (HEAs) have attracted the attention of many researchers and industries due to their excellent mechanical properties.

HEAs are relatively new materials developed last decade [1–4]. HEAs do not have any dominating elements compared to conventional ones; all the elements present in these alloys have an equal or near-equal ratio. These principal elements are termed significant elements, and besides these principal elements, HEAs may contain minor elements to enhance their properties, each less than five atomic percent [5]. Unlike conventional alloys, the mixing entropies of these alloys are much higher. Due to the higher mixing entropy effect, it makes possible to have several opportunities with promising desirable properties like high hardness [6,7], excellent thermal stability [8], good fatigue resistance characteristics [9], excellent wear resistance [10–13], high-temperature properties. Therefore, high entropy alloy is considered a suitable and potential material for functional and structural applications. The primary attention is to develop HEA with a single phase during the initial phases. This results in the trade-off between strength & ductility [14–18]. Hence, a lot of effort is made to develop HEA with both hard & soft phases. To achieve ductility along with strength, eutectic high entropy alloys (EHEAs) are studied to overcome the shortcomings of single-phase HEAs. These alloys are comprised of two solid-solution phases, which can be a mixture of BCC and FCC or HCP and FCC to take advantage of ductility of FCC phase and strength of BCC phase or HCP phase. However, significant studies in these alloys are inclined to design and evaluate the alloy's microstructure, thermodynamics and strength. Minimal studies on the mechanical behaviour of HEAs are reported at micro or nano-scales [16,17]. Nanoindentation is considered a suitable technique to study the mechanical properties of small-sized samples [18].

Therefore, assessing the mechanical properties at a specific location using small volumes is quite informative for the material designer as in most case, due to the constraint of sample size and shape it is difficult to determine properties using the conventional macro experiments. Nanoindentation is also considered an efficient technique to evaluate the creep properties of metals. Unlike uniaxial creep tests that involve sample size and cost, nanoindentation creep is quite convenient and used to investigate the creep performance of HEAs [19]. The indenter is commonly used for probing the surface area Berkovich three-sided pyramid indenter or a four-sided pyramid Vickers indenter. In the present study, we have used Berkovich indenter in place of Vickers indenter as the Berkovich indenter has a sharp pointed tip compared to the 0.5 μm slight offset of the Vickers indenter.

Moreover, using the Berkovich indenter, it is convenient to probe several points on the sample's surface through a line, point, or grid method. Nevertheless, Vickers and Berkovich indenters both provide satisfactory results, accepted by the ISO/FDIS 14577-1 standard [20,21]. In recent times, Molecular dynamics has been used to investigate the deformation behaviour of HEA at the atomic level [22–25].

This study uses a nano indentation technique to investigate the micro-mechanical properties of eutectic AlCoCrFeNi_{2.1} high entropy alloy. Furthermore, the numerical model based on molecular dynamic simulation is used to understand the deformation behaviour. The simulated force-displacement curve is compared with data from actual nanoindentation tests.

2. Materials, experimental and molecular dynamic simulation details

2.1. Synthesis of HEA using Vacuum Induction Melting

The alloy was prepared by the Vacuum Induction Melting (VIM) route in rectangular ingots. The required weight of pure metals is charged into a VIM furnace having an alumina crucible. The melting was carried out around 1600–1750°C. The temperature was monitored using K-type thermocouple installed in the furnace and the melting process was performed under an argon atmosphere. The electromagnetic stirring action was carried out to achieve homogeneity of the melt. The chemical composition of as-cast material was measured using Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry and reported in Table 1. The chemical composition of the individual phases B2 and L1₂ were determined using FESEM-EDS and reported in Table 1. The multiple readings of EDS analysis were taken, and the average value was reported. The EDS analysis of the sample exhibit that the material under investigation comprised of five principal elements (i.e. having atomic % greater than 5) and satisfied the criteria of high entropy alloy [26].

2.2. Equipment and indentation procedure

The test was performed on a Fischerscope H100C table-mounted indentation machine equipped with a Berkovich indenter and *in situ* optical microscope facility. The Fischerscope H100C is a computer-controlled measuring system for microhardness testing and measuring of material parameters as per ISO 14577. Similar to uniaxial tensile tests, nanoindentation experiments can be performed either in load or displacement control. The tests were performed for four different load condition i.e. 200, 300, 400 and 1000 mN for both the phases separately. The maximum load capacity of the equipment is 1000 mN.

Using the method proposed by Oliver and Pharr [27–29] data obtained from Berkovich indenters can be analyzed. The Berkovich indenter has a total

Table 1. Chemical compositions in at% and wt.% in the as-cast EHEA, AlCoCrFeNi_{2.1}.

Element at% (wt.%)	Al	Co	Cr	Fe	Ni
Nominal	16.90 (8.8)	16.41 (18.67)	16.44 (16.50)	16.36 (17.63)	33.89 (38.40)
B2 (BCC)	24.26 (13.05)	14.04 (16.47)	7.78 (8.05)	11.21 (12.47)	42.71 (49.95)
L1 ₂ (FCC)	7.69 (3.82)	17.46 (18.95)	21.87 (20.9)	19.12 (19.68)	33.85 (36.59)

included angle (plane to edge) of 142.31 degree and a half angle of 65.351 degree. Using an aspect ratio of 1:8, the Berkovich indenter is designed to have the same depth to area ratio as the Vickers indenter (micro indentation standard). The generated load-depth curve for each load was analyzed for both phases to determine the material's indent properties. For each, the specified total time was 75 s. Out of the total time, 30 s were allotted for the loading process, 15 s for dwelling & the remaining 30 s for the unloading part. While working with Berkovich indenter, the standard load-controlled test for indenting the individual sample generally comprised three parts: loading, holding at the peak and unloading. Loading and unloading of trapezoidal loading function lasted for 60 s, and the dwelling part lasted for 15 s with maximum applied load was up to 1000 mN. The nano-indenter is equipped with a high-resolution actuator to force an indenter into the test surface and a high-resolution sensor to continuously measure the resulting penetration.

Following the model and concept for nanoindentation developed by Oliver and Pharr, [30] the load-depth data obtained during unloading were best fitted to below Equation (1),

$$P = B(h - h_f)^m \quad (1)$$

where P is the applied load, h is the penetrated depth, h_f is the final depth after complete unloading, while B and m are the best fit empirically determined parameters. The unloading stiffness S , i.e. slope of the unloading curve at maximum depth, is then found by differentiating the above Equation (1), i.e.

$$S = \frac{\partial P}{\partial h} = Bm(h_{max} - h_f)^{m-1} \text{ at } h = h_{max} \quad (2)$$

For the given geometry of the indenter from Oliver and Pharr method 1992, the contact depth, h_c is provided by Equation (3),

$$h_c = h - 0.75 \times \frac{P}{S} \quad (3)$$

Then from Equation (3), the projected contact area, A_c can be calculated as

$$A_c = 24.56 h_c^2 \quad (4)$$

Further, the reduced Young's modulus, E_r is calculated by Equation (5),

$$E_r = \frac{\sqrt{\pi}}{2} \times \frac{S}{\sqrt{A_c}} \quad (5)$$

From the obtained value of E_r the elastic modulus, E can be evaluated as

$$E = (1 - \nu^2) \left[\frac{1}{E_r} - \frac{1 - \nu_{in}^2}{E_{in}} \right]^{-1} \quad (6)$$

6) where E_{in} and ν_{in} are the elastic modulus & Poisson's ratio for the Berkovich indenter. Finally, the hardness, H of the material can be determined by using the Equation (7),

$$H = \frac{P}{A_c} \quad (7)$$

The used equipment for this test was 'Fischerscope[®]H100C' with table-mounted and Berkovich indenter as in- tool situ optical microscopy facility with maximum load capacity of 1000 mN. So, the highest load was also operated to check the material's response at the tip of the indenter, like crack propagation, and to find the material's fracture toughness. But there were no cracks found at this load. Hence, to find the fracture toughness of the given material, a load greater than 1 N should be used in future work.

The generated load-depth curve for each load was analyzed for both phases to determine the material's indent properties. For each, the specified total time was 75 s. Out of the total time, 30 s were allotted for loading process, 15 s for dwelling & the remaining 30 s for unloading part.

2.3. Computational details

LAMMPS software has been chosen to perform the MD simulations of the nanoindentation process [31]. Figure 1 depicts the initial configuration of AlCoCrFeNi_{2.1} Eutectic HEA of B2 phase and L1₂ phase. The dimensions and total atoms of the simulation box are $15 \times 15 \times 15 \text{ nm}^3$ and 318,028

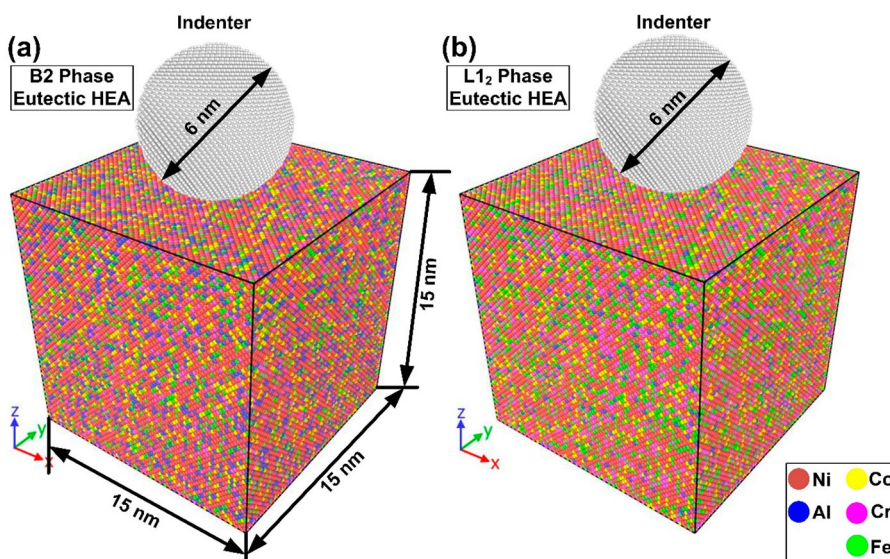


Figure 1. Initial configuration of AlCoCrFeNi_{2.1} Eutectic HEA of B2 phase and L1₂ phase specimens with indenter of radius 3 nm.

atoms, and the chemical compositions of both specimens (B2 phase and L1₂ phase HEA) are reflected, as per Table 1. Periodic boundary conditions in x and y directions and the shrink-wrapped boundary condition in the z -direction (i.e. nanoindentation direction) are preferred to carry out the nanoindentation process. The bottom portion of the specimen up to 1.5 nm has been fixed before the nanoindentation process. The time step of 2 fs has been considered. The Embedded Atom Method (EAM) potential is chosen for the interatomic interactions of Al, Co, Cr, Fe and Ni [32]. Energy minimisation has been performed through the conjugate-gradient technique. The specimen is then equilibrated at room temperature using a Nose–Hoover thermostat [33]. The nanoindentation process has been performed with a virtual spherical indenter of a 3 nm radius. The indenter is placed above the specimen at the height of 0.5 nm. It travels towards the specimen with pre-set (depth and velocity) up to a depth of 1 nm with a velocity of 40 m/s during nanoindentation [34]. The force acting on the atoms of the specimen through the indenter tip is given as [31]:

$$F(r) = -K(r - R)^2 \quad (8)$$

where F means Repulsive force among atoms at distance r and indenter tip, R and K are the radius of the indenter and force constant.

OVITO software has been used to visualise and analyse both specimens [35]. Dislocation analysis (DXA) is performed for the dislocation type's identification and their density [36]. Common neighbour analysis (CNA) is implemented to identify the structural variation and defects evolution [37]. Displacement vector (DV) is done for the atom movement relative to the initial atom position during the nanoindentation process.

3. Results and discussion

3.1. Experimental results obtained from nanoindentation

Nanoindentation uses a small indenter tip to evaluate the load versus penetration relationship. Compared to conventional mechanical testing, the benefit of this technique is that material parameters can be obtained from a tiny volume in the range of tens of nanometers to micrometers. A given load was applied for both the phases separately, and the data obtained from the machine was used to plot the load versus time graph. The material in the current study has two phases, namely B2 and L1₂, with BCC and FCC-ordered crystal structures, respectively. During the loading, the applied load on the indenter was the function of time and continuously increased with it. Figure 2(a) shows the loading history of the nanoindentation test for AlCoCrFeNi_{2,1} material, where p–q represent the loading part with increasing load till it reached the maximum displacement for the allotted time of 30 s.

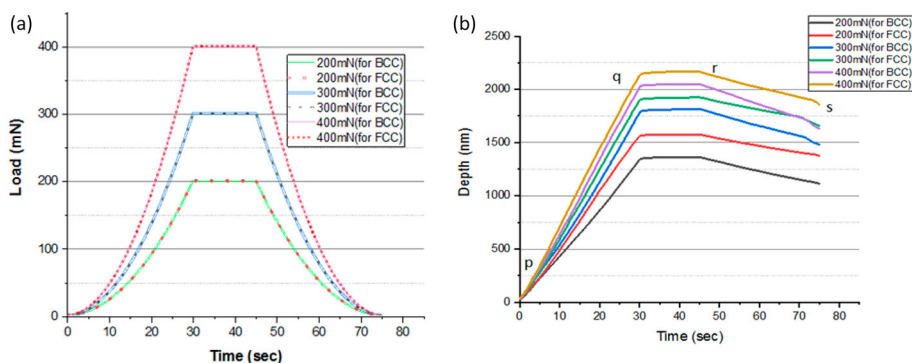


Figure 2. (a) represents the loading and unloading history, and (b) depicts penetration depth history.

Further, the line between points q and r shows the dwell time of 15 s for which the load was kept constant, and then, r–s represent the unloading part through which the elastic recovery of the material can be noticed as the depth keeps on reducing. Moreover, the unloading curve is not parallel to the load axis. Here, the loading and unloading times were kept equal, 30 s. Figure 2(b) shows the depth history of indentation for $\text{AlCoCrFeNi}_{2.1}$, and it is noted from the plot that the penetrated depths for both phases are quite different. For a given load, the maximum penetration depth for the B2 phase (BCC ordered) is relatively less than that of the L_{12} phase (FCC ordered). In Figure 2(b), p–q represents the loading time, q–r shows the dwelling time, and r–s represents the test's unloading time.

Figure 3(a) shows the dwell time behaviour of the material $\text{AlCoCrFeNi}_{2.1}$ for both phases. It is important to note that the depth of penetration, though very slowly, increases during the dwell time. This phenomenon of the time-dependent deformation experienced by the material when the load was kept constant can be related to 'creep'. Nanoindentation test is well-known for

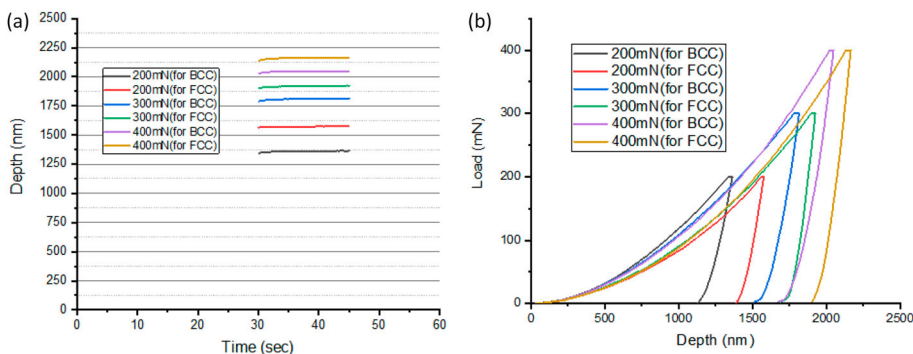


Figure 3. (a) represent the creep phenomenon, and (b) represent the load-depth curve for $\text{AlCoCrFeNi}_{2.1}$ EHEA.

generating the continuous load-depth characteristic curve. In this plot, the load is assigned on the y -axis, while the depth is on the x -axis. Figure 3(b) clearly, shows the load-depth curve for both phases. On the top of all the curves a small horizontal line can be seen, which is nothing but the dwell time, and finally, the unloading curve can see the elastic recovery of the material. In this test, a given load was applied to the material for both phases separately to generate the characteristic load-depth curves. And thereby, a significant comparison can be made on the material's response at the tip of the indenter, as the penetrated depth corresponding to a given load in the case of the B2 phase lesser than that of the $L1_2$ phase. Hence, the indenter faced more resistance to penetrate the B2 phase than the $L1_2$ phase for an applied load.

The hardness values obtained in nanoindentation test with Berkovich type indenter are shown in Table 2. And to comprehend the tabulated data, it is also plotted in Figure 4(a). Here the hardness values obtained were in GPa unit. In Figure 4(a), two different symbols and colours have been chosen to clearly distinguish the two phases in terms of their hardness values at other loads. It can be depicted from the graphical data also that the B2 phase (BCC ordered) has a higher range of hardness to varying loads than that of $L1_2$ phase (FCC ordered).

The Young's modulus values obtained in the nanoindentation test with Berkovich type indenter are shown in Table 3. And to comprehend the tabulated data, it is also plotted in Figure 4(b). Here the values obtained were in GPa unit. In Figure 4(b), two different symbols and colours have been chosen to distinguish the two phases clearly in their elastic modulus values at different loads. Figure 5 shows the optical images of EHEA $AlCoCrFeNi_{2.1}$, having two phases with mark of indenter in nanoindentation test: (a) at 400 mN load on $L1_2$ phase, (b) at 1000 mN load on B2 phase. Figure 6 shows FESEM images of EHEA $AlCoCrFeNi_{2.1}$, depicting two different phases and measured edge value of the indenter's impression in nanoindentation test.

The data obtained from the nanoindentation technique has been analyzed to manifest the elasto-plastic behaviour of the material. In Table 4 the elastic recovery of the material for both phases is exhibited. Also, the properties like wear resistance, elastic energy, plastic energy, etc., have been evaluated for the load of 200 mN. Since the current material had a dual phase, it was essential

Table 2. Hardness of $AlCoCrFeNi_{2.1}$.

Data No.	B2 Phase (BCC)				$L1_2$ Phase (FCC)			
	H(Gpa) Loads (mN)							
	200	300	400	1000	200	300	400	1000
1	3.95	3.02	3.47	3.21	3.31	2.95	3.55	3.27
2	3.41	3.35	3.46	3.28	2.91	3.31	3.12	3.2
3	3.93	3.34	3.45	3.29	2.93	2.93	3.13	3.21
Average	3.76	3.23	3.46	3.26	3.05	3.07	3.26	3.22
Standard Deviation	0.31	0.19	0.01	0.04	0.22	0.21	0.25	0.04

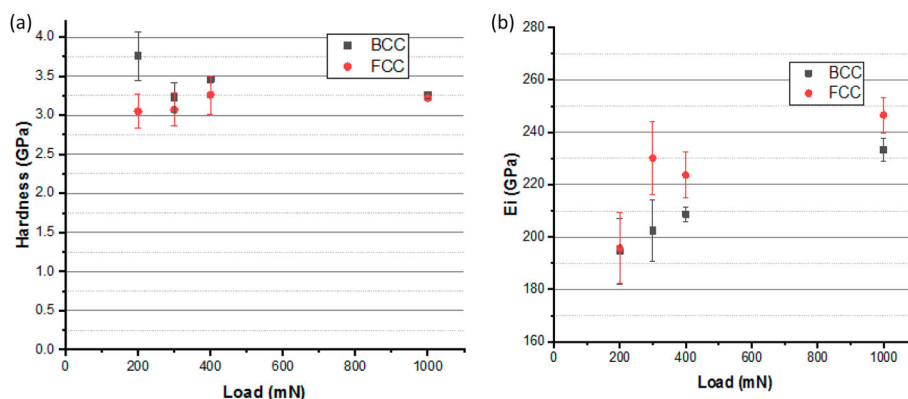


Figure 4. (a) represents the nanoindentation hardness values, and (b) represents the elastic modulus of AlCoCrFeNi_{2.1} EHEA, respectively.

Table 3. Young's modulus for AlCoCrFeNi_{2.1}.

Data No.	B2 Phase (BCC)				L1 ₂ Phase (FCC)			
	Ei (Gpa) Loads (mN)							
	200	300	400	1000	200	300	400	1000
1	203.12	210.94	211.13	233.28	180.12	239.42	213.56	253.48
2	180.04	189.08	209.45	228.85	203.86	214.13	229.46	240.01
3	200.33	207.26	205.62	237.80	203.30	237.00	227.91	246.27
Average	194.50	202.43	208.73	233.31	195.76	230.18	223.64	246.59
Standard Deviation	12.59	11.70	2.82	4.47	13.55	13.95	8.76	6.74

to keep the indenter at a very much localised place (individually in both the phases) to compare their obtained mechanical properties. The average hardness of B2 phase (BCC ordered) and L1₂ phase (FCC ordered) at a load of 200 mN is 3.76 and 3.05 GPa, respectively. To study the elasto-plastic behaviour of the material by calculating and analyzing the elastic recovery from the provided data of the test in terms of elastic and plastic energy. The wear resistance of

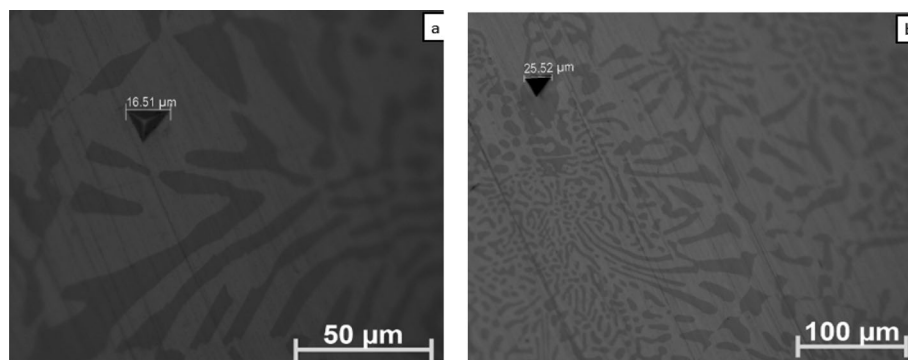


Figure 5. Optical images of EHEA AlCoCrFeNi_{2.1}, showing two phases with mark of indenter in nanoindentation test: (a) at 400 mN load on L1₂ phase, (b) at 1000 mN load on B2 phase.

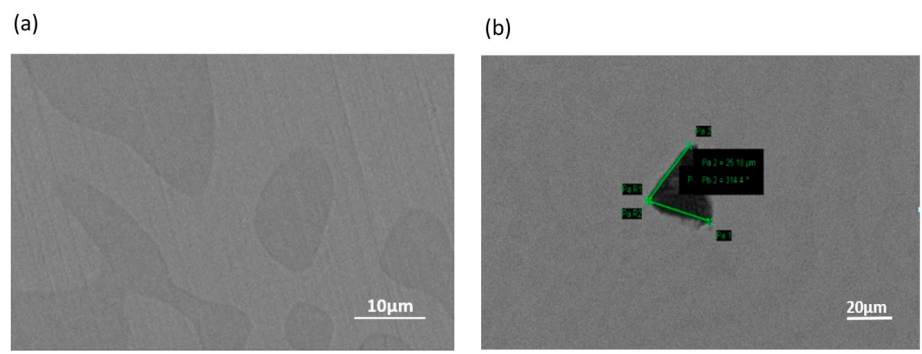


Figure 6. SEM images of EHEA AlCoCrFeNi_{2.1}, (a) showing two different phases and (b) measured edge value of the indenter's impression in nanoindentation test.

Table 4. Mechanical properties determined in nanoindentation test for (load = 200 mN).

	Hardness, H (GPa)	Reduced Young's modulus, E _r (GPa)	Elastic energy, U _e (nJ)	Plastic energy, U _p (nJ)	Total energy, U _t (nJ)	Wear resistance, H/E _r	Elastic recovery, U _e /U _t
B2(BCC)	3.766 ± 0.3	185.67 ± 1.35	17.84 ±	82.18 ±	100.02 ±	0.0203	0.178
L1 ₂ (FCC)	3.050 ± 0.2	185.685 ±	0.73	0.83	0.76	0.01643	0.154
		1.34	15.83 ±	86.86 ±	102.70 ±		
			1.31	0.66	0.53		

the material for both the phases was calculated by dividing the hardness and reducing young's modulus (or effective elastic modulus). FE-SEM images have been taken with much precaution to find the exact dimensions of the impression made by the indenter for a particular load.

3.2. Computational (MD) results

Figure 7 depicts the load vs. indentation depth, hardness vs. indentation depth and dislocation vs. indentation depth plots for the AlCoCrFeNi_{2.1} Eutectic HEA specimens. The load-indentation depth for both phases (i.e. B2-black line and L1₂-red line) of Eutectic HEA specimens is shown in Figure 7(a). At the initial stages, the load is linearly proportional to the depth of 0.04 nm for both phases. After that, the load is diminished for the B2 phase HEA and continuously increases for the L1₂ phase concerning indentation depth. Correspondingly, the deviation in the linearity of the load-depth plot signifies plastic deformation initiation in the specimens. Another indication for the instigation of plastic deformation in the p-h plot is that both phases of HEA specimens release the stored energy in stacking faults form at the intermediate of the indenter tip and the specimen surface area. As depth increases, displacement of the atoms has taken place in both phases of the specimens beneath the indenter surface. Overall, the

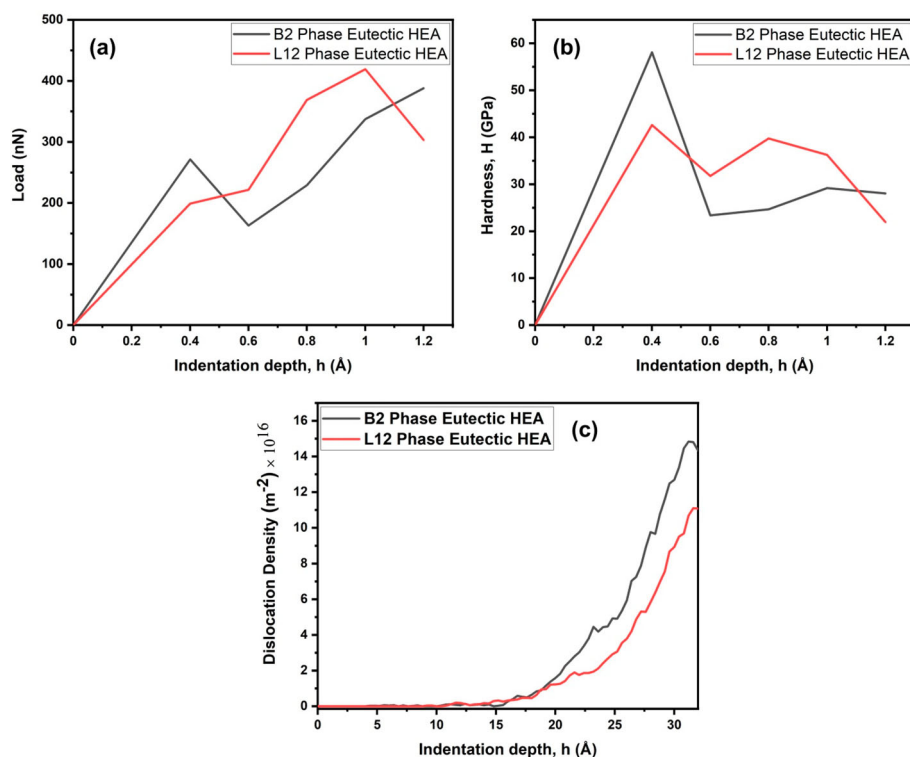


Figure 7. Represents the plots of (a) Load-Indentation depth, (b) Hardness-Indentation depth and (c) Dislocation density-Indentation depth during the nanoindentation deformation process on both phases (B2 and L1₂) of eutectic HEA.

B2 phase HEA exhibits a higher load-bearing capacity than the L1₂ phase HEA as per Figure 7(a). Figure 7(b) shows the H-h plots for both phases of AlCoCrFeNi_{2.1} Eutectic HEA specimens. The hardness (H) is calculated from the following Equation (7), where A_c equals $\pi(2R-h)h$. In which R means indenter radius, and h means depth of indentation. The B2 phase HEA shows the highest hardness values than the L1₂ phase HEA as evident from Figure 7(b), due to the formation of Stair-rod and Hirth dislocations. These dislocations have sessile nature during the nanoindentation deformation process. Figure 7(c) shows the plot of overall dislocation density and indentation depth for both phases of HEA. The dislocation density is lower at the initial stage for B2 phase HEA compared to L1₂ phase HEA. As the indenter depth increases, the evolution of the dislocation also increases for both phases. Finally, at the end of the nanoindentation process, the B2 phase HEA depicts a higher dislocation density than the L1₂ phase, as shown in Figure 7(c).

Figure 8 illustrates the deformation behaviour of the B2 phase HEA specimen during the nanoindentation process through the atomic snapshots of CNA, DXA, DV and colour-coding. Figure 8(a1–a5) illustrates the

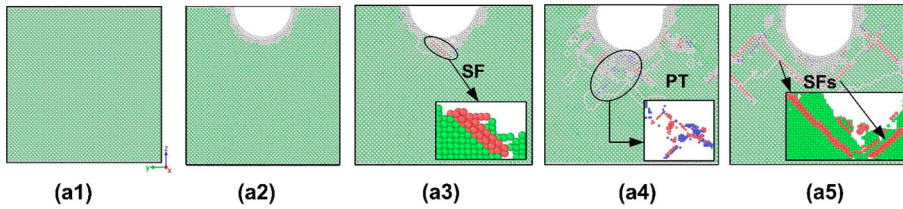
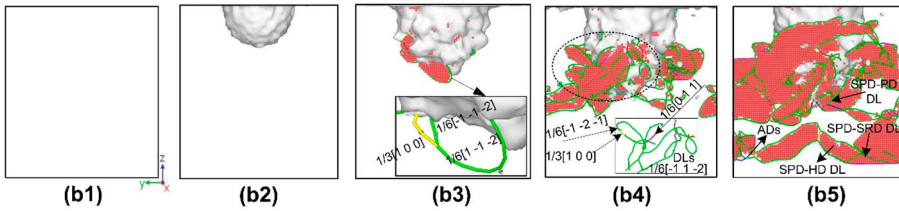
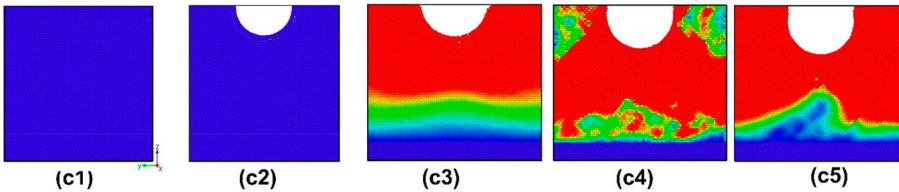
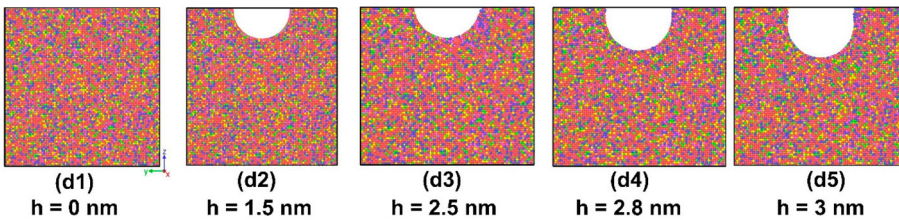
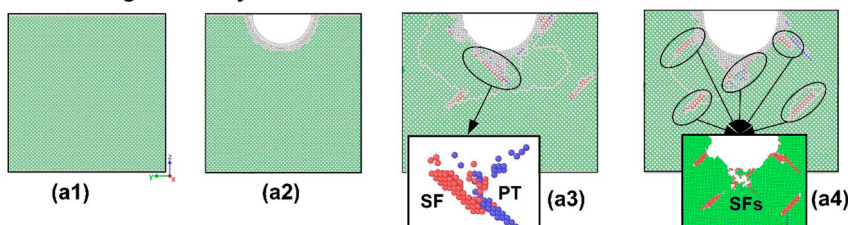
Common Neighbor Analysis**Dislocation Analysis****Displacement Vector Analysis****Color Coding Analysis**

Figure 8. Illustrates the atomic snapshots of B2 phase eutectic HEA by CNA, DXA and DV analysis during the nanoindentation deformation process.

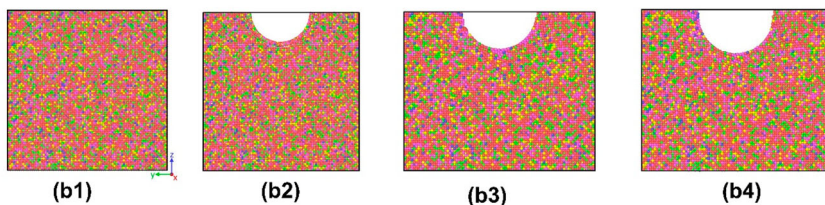
deformation behaviour under the nanoindentation process through CNA analysis; Figure 8(b1–b5) by dislocation analysis (DXA); Figure 8(c1–c5) through displacement vector analysis (DV); and Figure 8(d1–d5) by colour-coding analysis. Figure 8(a1–d1) illustrates the initial configuration of the B2 phase HEA specimen with various features at 0 nm depth. The initial mark of indenter is noticed on the specimen at 1.5 nm depth, and it's the indication for the commencing of plastic deformation as per Figure 8(a2–d2). The stacking faults are formed at 2.5 nm depth due to dislocations generation and their motion, as shown in the inset of Figure 8(a3–b3). The dislocations are generated in the specimen by releasing the excess energy through the slip process of close-packed planes. The Hirth partial dislocation is formed

from the Shockley partial dislocation as displayed with the burger vector in the inset of Figure 8(b3). As the indenter moves towards the specimen surface, the indentation depth gradually increases in the B2 phase HEA specimen as per Figure 8(a4–d4). The phase transformation (PT) occurs in the specimen at this stage, as shown in Figure 8(a4). Correspondingly, the dislocations generation is also higher at this stage. The Stair-rod partials, dislocation entanglements, and Shockley partial dislocations loops (DLs) are displayed with burger vectors in the inset of Figure 8(b4). Increase in indentation depth from 2.8 to 3 nm, the dislocations generation and propagation also increased and leads to more stacking faults have been created in the

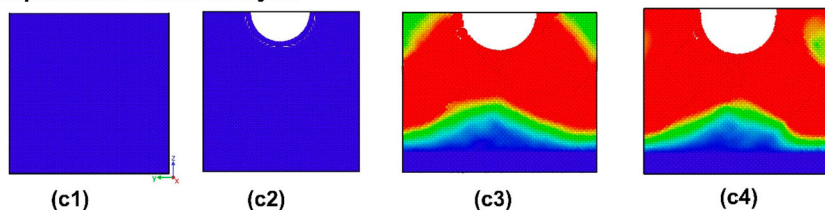
Common Neighbor Analysis



Color Coding Analysis



Displacement Vector Analysis



Dislocation Analysis

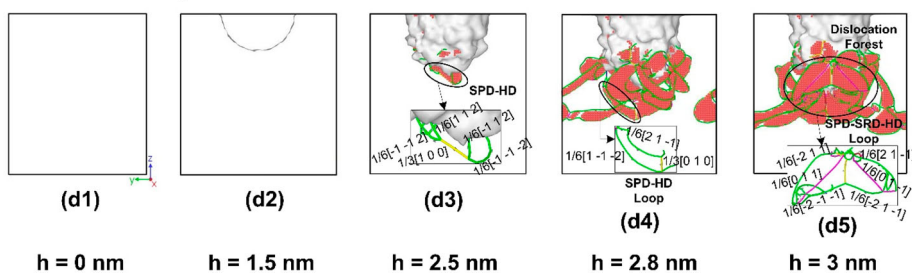


Figure 9. Illustrates the atomic snapshots of L12 phase eutectic HEA by CNA, DXA and DV analysis during the nanoindentation deformation process.

specimen as per Figure 8(a5–b5). All types of dislocations (ADs), dislocation loops, and dislocation entanglements are generated at the indentation depth of 6 nm. As well, the Stair-rod partial dislocations (SRD) and Hirth partial dislocations (HD) are obtained from the Shockley partial dislocations (SPD). The partial dislocations such as Hirth, Frank and Stair-rod dislocations are rising due to Shockley's partial dislocation reaction concerning indentation depth. These dislocations have sessile nature and promote improving the hardness of the specimen through strain hardening phenomena.

Figure 9(a–d) illustrates the deformation behaviour of $L1_2$ phase HEA specimen during the nanoindentation process through the atomic snapshots of CNA, DXA, DV and colour-coding features. The deformation mechanism of $L1_2$ phase HEA specimen is analogous to B2 phase HEA specimen under nanoindentation process except that the generation of partial dislocations such as Hirth, Frank and Stair-rod dislocations are less in quantity and it causes a reduction in hardness. Overall, the $L1_2$ phase HEA specimen exhibits low hardness than the B2 phase eutectic HEA specimen. Fig. S1 (in Supplementary material) depicts slip lines with dislocations motion in B2 and $L1_2$ phase EHEA specimens. The $L1_2$ phase EHEA (FCC) specimen has exhibited lower hardness owing to ease dislocation motion and new dislocations generation and motion. Subsequently, multiple slip lines are formed in the specimen, leading to a ductile phenomenon during nanoindentation loading. On the other hand, the B2 phase EHEA (BCC) specimen has shown greater hardness due to the high hindrance to dislocation motion. Consequently, the minimum slip lines are generated in the specimen during nanoindentation loading [38,39].

4. Conclusions

The plastic deformation behaviour of $\text{AlCoCrFeNi}_{2.1}$ HEA is investigated at small length scale using the nanoindentation technique and via MD nanoindentation simulation. It helps to identify the phase-specific contribution to the mechanical load. Nano-indentation is a very efficient and effective technique to study the elasto-plastic behaviour of materials. The microstructure is comprised of eutectic lamellae $L1_2$ phase and B2 phase. It is observed both experimentally and through computational study that B2 phase exhibited higher hardness than $L1_2$ phase. The partial dislocations such as Hirth and Stair-rod partials increase the hardness of the specimen by strain hardening phenomena because these partial dislocations have sessile nature, and these dislocations are examined clearly with dislocation analysis. The B2 phase showed higher wear resistance compared to the $L1_2$ phase. The $L1_2$ phase is deformed by forming multiple slip lines and significant material pile up during small scale. Proper knowledge of the mechanical properties of a multi-phase material is vital for advanced material design and application.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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