Influence of zirconium addition on the microstructure, thermodynamic stability, thermal stability and mechanical properties of mechanical alloyed spark plasma sintered (MA-SPS) FeCoCrNi high entropy alloy

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Abstract: Equiatomic FeCoCrNi (Zr₀) and non-equiatomic FeCoCrNiZr_{0.4} (Zr_{0.4}) high-entropy alloys (HEAs) Received 25 May 2018 were synthesised by mechanical alloying and spark plasma sintering. XRD analysis verified the Revised 24 August 2018 formation of FCC and BCC solid solution phases in both alloys after 30 h of ball milling. While the SPS FeCoCrNi alloy contains both FCC and BCC solid solution phases, the FeCoCrNiZr_{0.4} presents an FCC solid solution. The thermodynamic analysis showed that FeCoCrNiZr_{0.4} is more stable with respect to the FeCoCrNi alloy. The phase stability of FeCoCrNiZr_{0.4} was revealed up to ~800°C. The shear strength and hardness of the FeCoCrNi HEA improved with Zr addition. plasma sintering; thermal Failure analysis of the shear punch tested samples revealed a ductile fracture with dimple stability; mechanical structure for FeCoCrNi and a brittle fracture with a smooth featureless surface for FeCoCrNiZr_{0.4}.

1. Introduction

High-entropy alloys (HEAs) are physically defined by their configurational energy leading to exceptional properties well described in the very recent past as dependent on the so-called core effects related to the severe lattice distortion and sluggish diffusion [1-5]. Depending on their composition, HEAs can exhibit enhanced structural stability at elevated temperatures, high-temperature oxidation resistance and exceptional mechanical properties [6-13].

HEAs have been mostly produced using liquid phase methods like arc and induction melting. Recently, HEAs production through solid state and gas phase processing methods such as mechanical alloying (MA) and sputtering was reported [3]. Obviously, the microstructural evolution in HEAs is directly related to the production route and to the employed processing parameters. Powder metallurgy is a low-cost and high-efficiency technique for the production of many non-equilibrium materials [14]. In this regard, many HEAs, like FeCoCrNi, can be made using MA and subsequent consolidation processes [15]. For a given alloy composition, MA offers a material with desired microstructural and mechanical properties, and therefore, it is believed to be a very attractive method. In order to investigate the improvement of FeCoCrNi HEAs properties, the effect of alloying elements addition like Mn [16], Al [17] and Ti [18] on the microstructural features have been investigated. Detailed studies show that the addition of these elements leads to a considerable increase in the yield strength and a strong decrease in plastic strain. The addition of refractory metals HEAs can simultaneously increase the mechanical properties and decrease the materials' density. In the present study, Zr was selected as the alloying element revealing similar physical features to Ti, i.e. both elements have an HCP crystal structure, have a high melting temperature and a good corrosion resistance. The difference between the radius of the Zr atom and the other constituent atoms as well as the negative enthalpy of the mixing have an important role in controlling the phase formation in HEAs [19]. In spite of advancement in the synthesis methods, characterisation, sintering and mechanical behaviour analysis of HEAs, the role of the thermodynamic aspect on their formation has been hardly

investigated. Moreover, the synthesis, characterisation and mechanical properties of FeCoCrNiZr_{0.4} HEA have not been reported.

In this study, a new FeCoCrNiZr_{0.4} HEA was developed using MA and spark plasma sintering (SPS). The microstructural features were investigated, and physical properties including melting point, difference of mixing entropy and enthalpy, difference of atomic size and concentration of valance electrons were studied and compared with the thermodynamic criteria for HEAs formations. The thermodynamic aspects of phase formation were studied based on the Miedema model and compared with experimental results. The thermal stability of FeCoCrNiZr_{0.4} HEA was investigated up to 1100°C. Finally, the effect of Zr addition was studied using shear punch testing (SPT) and Vickers microhardness measurements. SPT is recognised as an alternative method for a standard tensile experiment for evaluating the tensile and shear strength of materials with limited material availability.

2. Experimental procedure

2.1 Materials and sample preparation

FeCoCrNiZr_x (with $x = 0$ and 0.4) quasi-equilibrium HEA powders were produced with a Fritsch P7 planetary ball mill. The elemental powders of Fe, Ni, Co, Cr and Zr (with particle size ≤ 60 μm , purity higher than 99.5% from Merck Co, Germany) were mixed in equiatomic ratio. MA was carried out up to 50 h with 0.3wt% stearic acid as a process control agent at 350 rev min^{-1} using hardened chromium steel balls with a 10:1 ball to powder weight ratio and under argon atmosphere. The hardened chromium steel vessel had 120 cm^3 volume. The filling factor was 40%. The ball sizes are listed in Table 1. The phase composition and morphology of the powders were checked at regular intervals of 10 h during the milling. The ball milled powders were annealed at different temperatures in the range 400-1000°C at 5°C min^{-1} heating rate in argon atmosphere. The powders were characterised using X-Ray diffractometry (Philips Xpert-MPD) with Cu α radiation ($\lambda = 1.542 \text{ \AA}$). The chemical composition and microstructure of the powders were analysed by scanning electron microscopy (SEM) (Philips XL30 SERIES) equipped with an energy dispersive spectrometer (EDS) (SERON-ALS2300C) and transmission electron microscopy (TEM) (Philips, operated at 150 kV). Thermal analysis was carried out at 5°C min^{-1} heating rate in argon atmosphere by differential scanning calorimetry (DSC, Linsis, Germany). Thermodynamic analysis of the process was carried out using the Miedema model. Subsequently, the ball milled powders were consolidated using SPS (KPFVT Company) at 900°C under 45 MPa pressure for 6 min in argon atmosphere.

2.2. Investigation of mechanical properties

Hardness measurements

The Vickers microhardness of cross-sectioned and polished samples was measured using a load of 300 g. The average and standard deviation of at least 10 indentations are reported.

Shear punch test

In order to investigate the effect of Zr addition on the mechanical properties of the FeCoCrNi high-entropy alloy, the yield and ultimate shear strength (USS) were evaluated by SPT at a crosshead speed of 0.2 mm min^{-1} at room temperature. A schematic view of the SPT setup is shown in Figure 1. Three tests were conducted in each condition. During the test, the applied load, P , was measured as a function of the punch displacement r [20]. The average shear stress was calculated using Equation (1) [21]:

$$\tau = \frac{P}{2\pi tr_{avg}} \quad (1)$$

where t is the specimen thickness and r the average radii of the punch and die ($r_{avg} = (r_{punch} + r_{die})/2$); with $r_{punch} = 1.5 \text{ mm}$ and $r_{die} = 1.54 \text{ mm}$. In the present work, polished surface specimens of

500 ± 20 µm thickness were used. The correlation between the shear and tensile yield and ultimate strength data was calculated by Equations (2) and (3) [21]:

$$\sigma_{0.02} = \alpha \tau_{1.00} \text{ where } \alpha = 1.77 \quad (2)$$

$$\sigma_{UTS} = \beta \tau_{USS} \text{ where } \beta = 1.80 \quad (3)$$

With σ_{UTS} , τ_{USS} , $\sigma_{0.02}$ and $\tau_{1.00}$, the ultimate tensile strength (UTS), USS, estimated 0.02% tensile yield point and 1.00% SPT normalised yield point, respectively. The mechanical properties such as USS and shear yield stress (SYS or 1.00% offset) were calculated from the SPT curves as (1) primary deviation from linearity along the elastic loading line, considered as ≈0% strain offset; (2) 1% offset in the shear strain γ , described using the pure shear approximation and (3) 1% offset in the normalised displacement δ_n [20,22].

3. Results and discussion

3.1 Powder synthesis

Figure 2 depicts the XRD patterns of FeCoCrNi (Zr₀) powder for different milling times. The diffraction peaks of the principal individual elemental powders are observed in the diffraction pattern after 0 h. The peak intensity of the individual elements decreased after 10 h of milling and the peaks corresponding to the elemental nickel and cobalt are barely visible indicating the beginning of solid solution formation [18,23]. After 30 h of milling, only the most intensive diffraction peaks can be resolved, indicating the presence of a solid solution. Owing to the close atomic radius of the constituent elements, the formation of a solid solution of randomly distributed elements with regular compact structure is expected at this stage [24]. The magnified diffraction pattern in the range of 64° < 2θ < 66° shows a shift of the chromium peak to higher 2θ values by increasing the milling time. This can be explained by the dissolution of smaller iron atoms in the chromium structure, promoting the formation of BCC phase in the Zr₀ alloy. Moreover, an FCC solid solution formation is confirmed by the investigation of the other diffraction peaks.

As a matter of fact, longer ball milling of the alloy resulted in a more homogenous solid solution and was accompanied with peak broadening (see Figure 2). The observed broadening of the diffraction peak can be explained by the nanostructured nature of powder during the longer period of milling, as well as by the developed lattice strain caused by deformation during MA [16,24]. The solid solution formation during MA is governed by two phenomena, namely, the mixing entropy and the non-equilibrium MA process, both favouring the formation of a solid solution over intermetallic phases. The higher the number of alloying elements in the system is, the greater the mixing entropy, and the faster the random diffusion between different elements results. High mixing entropy reduces the phase separation and favours the formation of solid solution phase over intermetallic compounds and other ordered phases. The MA process promotes the formation of solid solution phases by increasing the solubility in the solid state by increasing the stored energy in the microstructure. High-entropy effect is the first important core effect because of its role in the enhancement of possibility of solid solution phase formation having simple microstructure by minimising the Gibbs free energy of formation [25]. According to maximum entropy production principal, high entropy of mixing tend to stabilise the solid solution phases than intermetallic phases [2]. The decrease in grain size during ball milling is accompanied with an increase in grain boundary area, or an increase in the total interface energy, hence increasing strain energy due to the developed nanostructure [24].

The XRD patterns of the Zr₀ and Zr_{0.4} HEAs after 50 h of MA are shown in Figure 3. The XRD pattern of the Zr_{0.4} alloy after milling is slightly different from that of Zr₀ one near the main diffraction peak. The intensity of the solid solution diffraction peak is increased and the peak is shifted to a lower 2θ angle. This is attributed to the distortion of crystal lattice and the consequent increase of the lattice parameter due to the dissolution of larger Zr atomic radius [19]. As shown in Figure 3, there is no indication of any diffraction peak corresponding to intermetallic phases in the

FeCoCrNiZr_{0.4} HEA powder after 50 h MA. The results can be attributed to two reasons: (1) the appropriate concentrations of component Zr element and (2) the solid solubility extension during MA.

In order to define the host or solvent and solute elements in each of the solid solution phases in the Zr_{0.4} HEA, the lattice parameters of the BCC and FCC phases are measured and compared with those of the constituent elements. The lattice parameter of the BCC phase is measured to be 2.8827 Å, which is very close to that of elemental chromium, (2.8797 Å). The slightly larger lattice parameter of the BCC phase can be explained by the fact that the Cr atoms in the BCC structure are partly substituted with larger Zr and Fe atoms with their atomic radius equal 1.26, 1.6 and 1.28 Å, respectively. Similarly, the matching lattice parameters of FCC phase (3.5225 Å) and Ni (3.5238 Å) supports the idea that the FCC solid solution phase is formed by dissolution of Fe, Co or Zr in Ni.

In order to further verify the evolved solid solution phase and the corresponding microstructure after 50 h of MA, a TEM analysis was performed (Figure 4). Figure 4 shows a bright field image of agglomeration of particles with different thicknesses which appeared in different grey levels. The particle sizes were measured using Image J software. While the particles sizes variation was recorded to be in the range of 5 and 50 nm, the average particle size showed to be around 12 nm, which is close to the value obtained from the XRD peak broadening by the Scherrer equation (Table 2) [22].

The analysis of the SAED pattern (Figure 4 (b)) confirms the results obtained from the XRD analysis verifying the formation of FeCoCrNiZr_{0.4} solid solution with crystalline size of about 12 nm (Figure 4(a)).

SEM images of the starting powder mixture and mechanical alloyed FeCoCrNiZr_{0.4} powder are presented in Figure 5(a–d). Before MA, the starting powder is characterised by granular particles which are less than 60 µm in size. After 50 h of MA, the powder shows a wide range of the particle size distribution. The particles are typically in the form of semi-spherical agglomerates with size less than 1 µm. This is mainly related to the repeated plastic deformation and fracture due to particle impact in ball mill and the consequent joining of the fractured surfaces [26] (shown in Figure 5(d)).

Figure 6 shows the EDS area and point analysis conducted on the FeCoNiCr and FeCoCrNiZr_{0.4} powders after 50 h of MA. The chemical composition of the synthesised powders is in good agreement with the targeted values. The slightly increased Fe content is due to the milling contamination from the milling balls and vial, whereas the slightly decreased amount of nickel is attributed to the adhesion of nickel powder to the walls of the chamber due to the soft character of the material.

3.2. Investigation of the criteria for HEA formation

Formation of HEAs is typically determined by competing factors like a difference in atomic sizes (d), mixing enthalpy ΔH_{mix} and mixing entropy ΔS_{mix} [27,28]. According to Miedema model

$$\Delta H = \sum_{i=1, i \neq j}^n 4\Delta H_{\text{mix}}^{ij} c_i c_j \quad (4)$$

where n is the number of components in the alloy, $\Delta H_{\text{mix}}^{ij}$ is the mixing enthalpy of the binary alloy, and c_i and c_j are the atomic percentages of i and j elements, respectively.

King et al. [27] presented a novel method for the prediction of HEA formation basing on the Gibbs free energy due to the formation of a disorder solid solution phase and the largest Gibbs free energy due to the formation of binaries from the constituent mixture, respectively.

Another parameter that influences the structural stability of a solid solution phase is the valence electron concentration (VEC) of the alloy which is related to the fact that in solid solutions atoms form a common d band. FCC phase is expected to be formed for $VEC \geq 8$, and the possibility of BCC phase formation is increased for $VEC \leq 6.67$. FCC and BCC both stabilises at an intermediate value ($6.87 \leq VEC < 8$). These values of VEC are for reference which can vary for different alloy system [28,29].

The values of the physical and thermodynamic variables, calculated for the alloy systems and the parameters that allow the prediction of HEA formation, are summarised in Table 3. Alloy system containing elements with a small difference in enthalpy of mixing shows a single solid solution phase even at high temperature [30,31]. On contrary, the alloys with the higher difference in enthalpy of mixing for unlike pairs have more than two phases. They all suggest the formation of an HEA, with both BCC and FCC solid solution phases in both alloy systems, which is in agreement with the XRD results.

3.3. Thermodynamic investigation

In order to extend the phase formation investigation, a thermodynamic analysis was performed.

ΔH calculations

The formation enthalpy of a crystallite solid depends on the chemical contribution related to the mixing of two different metals, on the elastic contribution due to the atomic size mismatch of solute and solvent, and on the structural contribution caused by different arrangements of valence electron of elements with a different VEC [32,33].

According to the Miedema model, calculation of $\Delta H^{chem}(AB)$ follows Equation (5) [34,35].

$$\Delta H^{chem}(AB) = c_A c_B \left(f_B^A \Delta H^{inter}(A \text{ in } B) + f_A^B \Delta H^{inter}(B \text{ in } A) \right) \quad (5)$$

where c is the concentration of A and B elements in the binary system. ΔH^{inter} and f_B^A are well known and defined in [34].

$\Delta H^{elastic}$ is obtained using Equation (6) [34] by employing the mechanical and structural parameters listed in Table 4:

$$\Delta H^{elastic}(AB) = c_A c_B \left(c_B \Delta H^{elastic}(A \text{ in } B) + c_A \Delta H^{elastic}(B \text{ in } A) \right) \quad (6)$$

The structural contribution to the mixing enthalpy results from the electron charge arrangement of the elements with different VEC during alloying. The structural contribution to the enthalpy is considered only for transition-transition solid solutions such as Fe-Ni, Co-Cr and Ni-Co in FeCoNiCr and FeCoCrNiZr_{0.4} alloy systems due to the presence of free electrons in the d orbitals. The structural enthalpy of the solid solution depends on the number of valence electrons of each atom ($\langle z \rangle$), i.e. the sum of the electrons present in the outer s and d orbital. Figure 7 depicts the variation of this structural enthalpy for BCC, FCC and HCP crystalline structures as a function of the number of valence electrons. In amorphous alloys, the structural and elastic enthalpies are dramatically decreased [36].

ΔG evaluations and discussion

The Gibbs free energy change of formation is calculated for all possible intermetallic compounds, solid solutions and amorphous phases in the FeCoNiCr and FeCoCrNiZr_{0.4} systems. Since the MA process was performed at room temperature, the temperature for all calculations was considered to be 298 K. Table 5 compares the calculated Gibbs free energy of formation of the FeCoNiCr and FeCoCrNiZr_{0.4} solid solutions and amorphous phases. It is clear that the formation of solid solution phases is thermodynamically more favoured compared to an amorphous phase. Moreover, the addition of Zr substantially lowered the ΔG of the solid solution as well as amorphous alloy.

Owing to the potential formation of intermetallic compounds, the Gibbs free energy changes as a consequence of possible binary intermetallic compounds formation. So, it was calculated for each mole of the system and the results were compared with the solid solution formation. The Gibbs free energy changes for the binary intermetallic compounds are summarised in Table 6. It is evident that the Gibbs free energy of formation of the intermetallic compounds containing zirconium is more negative compared to the other intermetallic compounds, which is due to the large difference in atomic radius and electronegativity of Zr with the other alloying elements. The solid solution multielement phase is more stable than any binary intermetallic compounds and multi-element amorphous phase in both alloy systems. Moreover, FeCoCrNiZr_{0.4} phase is more stable than FeCoCrNi. This is in good agreement with the results of X-Ray diffraction patterns, TEM and thermodynamic criteria.

3.4. Thermal behaviour

Figure 8 shows the result of DSC and gross weight curves for the FeCoCrNiZr_{0.4} powder milled for 50 h. The long exothermic line from 25 to 750°C is associated with the release of internal stresses, such as structural deformation, lattice strain, etc. The exothermic peak over 800°C is related to the energy release during the phase transformation process. The gross weight curve (black line in Figure 8) shows the weight change for the 50 h milled powder. The weight loss increases up to 600°C. The behaviour changes for higher temperatures. While the weight loss is explained by the evaporation of process controlling agent, the weight increase is attributed to the oxidation of the surface of the powder [37].

The mechanically alloyed FeCoCrNiZr_{0.4} HEA powder was annealed at the similar heating rate used in the DSC. The diffraction pattern presented in Figure 9 shows a very good thermal stability at temperatures up to 800°C, implying the retention of the solid solution structures, while the FeCoCrNi high entropy alloy retained the solid solution structure only up to 600°C [15]. However, around 850°C, the transformation from FCC/BCC solid solutions to an FCC/sigma phase can be observed. The formed sigma phase can be FeCr or intermediate CoCr phase with a tetragonal structure, confirming the results reported in previous studies [18,38]. At an annealing temperature 1000°C, the FCC solid solution is found to be the main phase. The increased intensity of the XRD peaks at this temperature is also related to the coarser morphology evolved during the annealing. The phase transformation, under different annealing temperatures, is due to the presence of metastable supersaturated solid solution phases, which evolve into the stable phases in the final stages of annealing [24]. The performed analyses in this study allowed verifying that FeCoCrNiZr_{0.4} high-entropy alloy powder sustained the solid solution structure both after milling and during annealing stages. Therefore, the application of MA for the synthesis of FeCoCrNiZr_{0.4} highentropy alloy showed to be successful. The acquired solid solution phase powder also exhibited excellent structural stability in argon at 800°C.

3.5. Consolidation by SPS

The alloyed powders (50 h mechanical alloyed powders) were densified using SPS at 900°C under 45 MPa pressure for 6 min (Figure 10). The XRD patterns of the densified HEA powders, presented in Figure 11, clearly show that the SPS process alters the phase composition of the as-milled FeCoCrNiZr_{0.4} powder by facilitating the phase transformation from a non-stable BCC to a stable FCC phase. Formation of the non-equilibrium BCC phase during MA is the result of a non-equilibrium state typically induced by a large density of defects and strains. It is mainly attributed to the short sintering time of SPS process and to the limited diffusion rate in the close-packed crystal structure of an FCC phase.

3.6. Mechanical properties

The Vickers microhardness of the materials was measured along a polished cross-section. The microhardness of FeCoCrNi and FeCoCrNiZr_{0.4} were measured to be 622 ± 6 and 828 ± 6 HV, respectively. The fairly high hardness associated with the synthesised HEA materials is mainly related to the material processing steps and the solid solution nature of the materials. During MA, a high density of dislocations is formed which results in dislocation induced back stress, hindrance to dislocation motion and dislocations pile up. Furthermore, the hardness is also improved by the interaction between the solution atoms and dislocations. So, increase in hardness can be contributed to large solution hardening in distorted lattice. In the case of quaternary and quinary equiatomic BCC alloys, the majority of the same elements are found in the second nearest cell. While the majority of the same atoms are found in the first nearest neighbouring cell in case of quaternary and quinary FCC. Because larger number of unlike pairs between centre atoms and dissimilar atoms in the first cell would provide larger distortion and hence this suggest that BCC solid solution would have larger solution hardening effect than FCC solid solution by the same set of elements with same proportions [39]. The higher hardness of FeCoCrNiZr_{0.4} is partially attributed to the presence of Zr atoms with a higher atomic radius which results in an increased distance between slip planes, impeding an easy slip of planes in the FCC structure of FeCoCrNiZr_{0.4}. The overall effect was due to the combination of solid solution strengthening; grain boundary strengthening favoured by the retention of nanostructured grain size, precipitation hardening and Orowan dislocation bypass mechanism.

The shear punch tests results on the FeCoCrNi and FeCoCrNiZr_{0.4} HEA are presented in Figure 12. It is clear that the addition of Zr to FeCoCrNi alloy increased the shear load of the material. Similar to the stress–strain curve during uniaxial tensile testing, the displacement–load curve during SPT testing shows a linear elastic behaviour up to the yield point, which is followed by a plastic flow in ductile materials. In the conducted experiments, failure occurred at a normal displacement of about 1 mm.

The mechanical properties such as USS and SYS were calculated from the SPT curves. In this method, the deviation point is referred to as the SYS and the stress corresponding to the maximum is considered as the USS. The tensile yield and ultimate strength can be calculated using relationships (1) and (2). Figure 13 presents a comparison of tensile yield and ultimate strength of the two materials. The addition of Zr improved the yield and ultimate strength of the FeCoCrNi alloy from 418 ± 10 MPa and 486 ± 10 MPa to 453 ± 10 MPa and 570 ± 10 MPa. Despite the absence of BCC phase, when compared to FeCoCrNi alloy, tensile strength in FeCoCrNiZr_{0.4} increased. It can be explained by the presence of Zr atoms, with a higher atomic radius, which results in an increased distance between slip planes, and therefore impeding an easy slip of planes in the FCC structure of FeCoCrNiZr_{0.4}. In addition, enhanced grain boundary strengthening and solid solution strengthening can be responsible for such behaviour. This is in a good agreement with the microhardness data. The following mechanisms have been reported through which solution atoms can interact with dislocations:

- Elastic interaction: due to the interaction between the elastic stress field of solution atoms and linear dislocation cores.
- Modulus interaction: interaction between solution atoms and dislocations due to local variations of crystals shear modulus.
- Low-range order interaction: due to the non-equilibrium spontaneous order of solution atoms.
- Stacking fault interaction: separation of solution atoms in the continuous dislocations shape stacking fault regions.

3.7. Fractography after SPT

SEM was used to investigate the features on the fracture surfaces of the punched-out SPT discs. Figure 14(a,b) shows the sheared surfaces after SPT of FeCoCrNi and FeCoCrNiZr_{0.4} high entropy alloys, respectively. While the fracture of FeCoCrNi alloy created a rough surface with the appearance of dimples, the shear fracture in FeCoCrNiZr_{0.4} was mainly characterised with a fairly smooth surface with less plastic deformation, implying a reduced ductility of the FeCoCrNi alloy upon the addition of Zr.

4. Conclusions

In the present work, MA and SPS were used for the synthesis and densification of FeCoCrNiZr_{0.4} and FeCoCrNi HEAs. The effects of Zr addition on the microstructural, thermal and mechanical properties of the FeCoCrNi(Zr_{0.4}) HEAs were studied.

- (1) The equiatomic multicomponent FeCoCrNi and FeCoCrNiZr_{0.4} high entropy alloy powders with FCC and BCC solid solution structures were synthesised successfully after 50 h of MA. The observed Shift of the peaks was an indication of the crystal lattice distortion and the consequent increase of the lattice parameter by adding of Zr element. XRD characterisation revealed that the spark plasma sintered FeCoCrNi contained both FCC and BCC solid solution phases, whereas the FeCoCrNiZr_{0.4} alloy is an FCC solid solution.
- (2) Combined FCC and BCC solid solution phase formation for both FeCoCrNi and FeCoCrNiZr_{0.4} high-entropy alloy powders were confirmed by examining variables such as atomic size difference, the VEC and changes in dissolution enthalpy and entropy.
- (3) Thermodynamic analysis using Miedema model confirmed the formation of a solid solution FeCoCrNi and FeCoCrNiZr_{0.4} phase, which was calculated to be more stable than the intermetallic and amorphous phases. The addition of Zr increased the stability of the HEA solid solution. The thermodynamic analysis results were in full agreement with the experimental results.
- (4) Thermal analysis of the alloys showed good thermal stabilities of FeCoCrNiZr_{0.4} high entropy alloy powders at high temperatures up to 800°C, and the retention of solid solution nanostructures. Also, it is found that the adding of Zr to FeCoCrNi high entropy alloy led to increase thermal stability.
- (5) The UTS and microhardness of the FeCoCrNi HEA were found to improve significantly upon adding Zr from 486 ± 10 to 570 ± 10 MPa and 622 ± 6 to 828 ± 6 HV.

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Table 1. Characteristic of balls that were used for MA.

Material	Diameter (mm)	Weight (g)	Number
Chromium steel (hardened)	20	31	3
Chromium steel (hardened)	16	16	2
Chromium steel (hardened)	8	5.5	5

Table 2. Structural characteristics of the FeCoCrNiZr_{0.4} and FeCoCrNi HEAs powders.

	FeCoCrNi		FeCoCrNiZr _{0.4}	
	FCC	BCC	FCC	BCC
Crystallite size (nm)	12.8	8.3	13.19	8.85
Lattice strain (%)	0.441	0.565	0.417	0.59
Lattice parameter (nm)	3.5102	2.8704	3.5225	2.8827
Theoretical density (g/cm ³)	8.218		8.063	

Table 3. Values of physical and thermodynamic variables calculated for the alloy systems.

Alloy	T _m (°C)	ΔH _{mix} (kJ/mol)	ΔS _{mix} (J/mol K)	δ (Å)	VEC	Ω	Φ
FeCoCrNi	1598.75	−3.75	11.52	0.99	8.25	4.91	1.46
FeCoCrNiZr _{0.4}	1622.12	−10.72	13.01	7.72	7.86	1.96	1.17

Table 4. The mechanical and structural properties required to calculate the Gibbs free energy change [36,37].

Element	K (GPa)	G (GPa)	Molar volume	Φ^*	$n_{WS}^{1/3}$	Electronic structure
Fe	210	81.9	7.0822	4.39	1.77	[Ar] 3d6 4s2
Cr	240	90	7.2328	4.65	1.73	[Ar] 3d5 4s1
Co	215	82.1	6.5479	5.1	1.75	[Ar] 3d7 4s2
Ni	205.4	78.5	6.6041	5.2	1.75	[Ar] 3d8 4s2
Zr	97.5	36.8	13.96	3.4	1.39	[Kr] 4d2 5s2

Table 5. Gibbs free energy of formation of FeCoCrNi and FeCoCrNiZr_{0.4} solid solutions and amorphous phases for each mole of the system.

	FeCoCrNi		FeCoCrNiZr _{0.4}	
	Solution	Amorphous	Solution	Amorphous
ΔG (kJ/mol)	-12.68	8.13	-52.85	-37.6

Table 6. Calculated Gibbs free energy for the formation of all possible binary intermetallic compounds in the FeCoCrNi and FeCoCrNiZr_{0.4} systems at 298 K.

Intermetallic component	$\Delta G \left(\frac{kJ}{mol} \right)$	Intermetallic component	$\Delta G \left(\frac{kJ}{mol} \right)$
FeNi	-2.01	Ni ₂ Zr ₃	-34.25
FeNi ₃	-1.29	Ni ₄₂ Zr ₅₈	-36.42
Fe _{0.64} Ni _{0.36}	-1.72	Ni ₁₁ Zr ₉	-45.17
CoFe	-0.44	Ni ₇ Zr ₂	-33.52
Co ₃ Fe ₇	-0.29	FeZr ₃	-3.41
Co ₇ Fe ₃	-0.32	FeZr ₄	-2.15
CrFe	-2.12	FeZr ₂	-6.02
CrCo	-5.59	CoZr ₃	-12.11
Cr ₃ Ni ₂	-8.66	CoZr ₄	-9.67
Cr _{1.36} Fe _{0.52}	-1.45	CoZr ₂	-17.81
Ni ₂ Cr	-8.05	Co ₅ Zr	-16.61
NiZr	-43.65	Co ₂ Zr	-30.88
Ni ₇ Zr ₂	-32.39	Co ₁₁ Zr ₂	-15.53
Ni ₃ Zr	-36.17	Co ₅ Zr	-18.43
Ni ₅ Zr	-24.39	Co ₂₃ Zr	-3.84
NiZr ₂	-17.17	ZrFe ₂	-12.31

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Figure 1. Schematic of the shear-punch setup.

Figure 2. XRD patterns of the FeCoCrNi HEA powders as a function of the milling time.

Figure 3. XRD patterns of the FeCoCrNi and FeCoCrNiZr_{0.4} HEAs powders after 50 h MA.

Figure 4. TEM images of the FeCoCrNiZr_{0.4} powder after 50 h of MA. (a) Bright Field (BF) and (b) SAEDP.

Figure 5. SEM images of the FeCoCrNiZr_{0.4} alloy powders. (a and b) before and (c and d) after 50 h of MA.

	Ni	Fe	Co	Cr
Calculated (%)	25	25	25	25
Observed (%)	23	27.6	25.4	25.3

	Ni	Fe	Co	Cr	Zr
Calculated (%)	22.27	22.27	22.27	22.27	9.12
Observed (%)	21.8	24.9	23.1	21.2	9

Figure 6. EDS analysis resultage of (a) FeCoCrNi HEA powders and (b) FeCoCrNiZr_{0.4} HEA powders after 50 h MA.

Figure 7. Structural enthalpy according to the valence electrons.

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Figure 9. XRD of annealed FeCoCrNiZr_{0.4} high entropy alloy powders.

Figure 10. SPS FeCoCrNiZr_{0.4} HEA disc.

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Figure 12. Load vs. normalised displacement curves of the MASPS FeCoCrNi and FeCoCrNiZr_{0.4} HEA.

Figure 13. Comparison of yield tensile stress (YTS) and UTS of MA-SPS FeCoCrNi and FeCoCrNiZr_{0.4} HEA.

Figure 14. SEM micrographs of the shear failure surfaces of (a) FeCoCrNi and (b) FeCoCrNiZr_{0.4} HEAs.