Microstructural development in nanostructured AlCoCrFeNi–ZrO₂ high-entropy alloy composite prepared with mechanical alloying and spark plasma sintering methods

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Abstract
In this research, ZrO₂-reinforced AlCoCrFeNi high-entropy alloy (HEA) composites were fabricated using mechanical alloying (MA) and spark plasma sintering (SPS) methods. It was found that after 30 h of milling a body-centered cubic (BCC) solid solution structure with an average particle size of 54 μm for HEA sample and 46 μm for HEA-10 wt% ZrO₂ could be obtained. The addition of 10 wt% ZrO₂ particles to Al–Co–Cr–Fe–Ni system resulted in finer particle size during the mechanical alloying process. Consolidation of MA-processed HEA powders with SPS method at 1000 °C was led to the formation of a combination of FCC and BCC phases due to the high heating rate of SPS process and limited time for the completion of BCC to FCC phase transformation. With the aid of Rietveld refinement analysis, it was found that the addition of zirconia particles has a restrictive effect on the grain growth of HEA phases during SPS. Interestingly, it was observed that while the weight percentage of FCC phase was almost similar in HEA and HEA-ZrO₂ composites, after the addition of zirconia reinforcements the content of BCC phase was decreased. It is well known that the introduction of hard ceramic particles to metal matrices can enhance the interfaces in the composite samples and facilitate the outward diffusion of aluminum from the BCC phase. Thus, the content of BCC phase was decreased in the HEA-based composite samples compared to the pure HEA sample.

1. Introduction
In 2004, a novel approach for alloy design was proposed by Yeh et al [1], termed as 'high-entropy alloys' (HEAs), due to the high configurational entropy of these alloys that obtained from a random mixing of elements [2]. HEAs consist of at least five principal elements [3, 4], each having an atomic percentage between 5 and 35 [5]. Studies have shown that HEAs possess high-entropy effects, sluggish diffusion, severe lattice distortion and cocktail effect [3, 6, 7]. These effects make HEA alloys a great candidate for a variety of applications including tools, molds, dies, mechanical parts and furnace parts [8]. High entropy of mixing in multi-element alloy systems such as HEAs generally leads to the formation of FCC or BCC solid solution structures [3, 9].

Among various HEAs, AlCoCrFeNi system has been widely investigated due to its exceptional properties [10–21]. A variety of techniques such as arc melting and casting [17, 18], suction casting [19], Bridgman solidification [20], electro-spark deposition [21], and spark plasma sintering (SPS) [10, 11] have been utilized for the fabrication of this alloy. This alloy shows a BCC structure in all processing routes, except for powder metallurgy methods, in which both of BCC and FCC structures were observed. The reason for the formation of this dual structure can be attributed to the solid-state processes which can occur during sintering [22].

The BCC structured HEAs usually exhibit high strength and low ductility while HEAs with the FCC structure have low strength and high ductility. Therefore, a mixture of FCC-BCC structures will have balanced mechanical properties. AlCoCrFeNi alloy with FCC and BCC structures possess excellent properties such as...
high hardness (625 HV), improved compressive strength (1907 MPa) and exceptional phase stability that provide an ideal matrix for the development of MMCS [10].

Al is the major alloying element in most of the HEAs. Chou et al. [23], reported that Al_{1}CoCrFeNi alloys possess FCC structure with x up to 0.375, a mixture of FCC + BCC structures with x between 0.5 to 1.0 and BCC structure with x higher than 1.25. Transition elements are also commonly used in HEAs that can change the structure of these alloys [24]. For example, Wang and Zhang [18], showed that increasing Co element with FCC structure in AlCoCrFeNiTi_{0.5} alloy to more than x = 1 lead to the appearance of FCC phase, and with the increase of cobalt weight percentage, the content of the FCC phase also enhances and, the compressive strength slightly decreases. Praveen et al. [25] showed that CoFeNi and CoCuFeNi alloys formed by MA exhibit a single-phase FCC structure. It has been argued that the reference structure in these alloys is Ni, where other elements are dissolved. The complete solubility of Co–Ni and Cu–Ni and sufficient solubility of Fe in Ni stabilize the FCC structure in these alloys. Therefore, whenever these elements come together, it is more likely to reach the HEA FCC structure except for a few cases where Al is present in a greater amount.

Nowadays, most of the HEAs are produced by vacuum arc melting technology, which usually leads to the fabrication of small samples and simple geometries [26, 27]. As a widely used solid-state processing route, mechanical alloying can easily fabricate nanocrystalline materials with good homogeneity from elemental powders [28]. Almost any material can be produced by this method, including ductile metal alloys, brittle intermetallic compounds and composites [29]. In addition, SPS can be employed for the consolidation of MA-processed powders to high densities. During the SPS process, pulsed currents lead to the formation of spark plasma at the particle-particle interfaces in short periods causing almost instant heating of the powder particles. This leads to the completion of the sintering in a shorter time compared to conventional sintering methods. Therefore, the time available for grain growth in SPS is very short, which helps to preserve the nanostructure of MA-processed powders [30].

In research conducted by Wei et al. [10], AlCoCrFeNi alloy was synthesized by mechanical alloying. The MA-processed powder with FCC structure exhibited good phase stability until 500 °C and transformed to FCC phase above 500 °C. Then, the as-milled powder was consolidated by spark plasma sintering at 900 °C which leads to formation of both FCC and BCC solid solution structures. The development of AlCoCrCuFe and NiCoCrCuFe alloys using mechanical alloying and spark plasma sintering was also investigated [25]. It was found that the as-milled powders contain simple FCC and BCC phases. The bulk specimens after SPS showed FCC and BCC phases with Cu-rich FCC and sigma phases. The hardness for AlCoCrCuFe and NiCoCrCuFe samples were reported to be 770 ± 10 HV and 400 ± 10 HV, respectively.

Metal matrix composites (MMCs) reinforced with carbide, nitride and oxide particles have attracted significant attention [31]. The addition of hard ceramic particles to these MMCs offers a wide range of improved mechanical properties, such as hardness, toughness, wear, and compressive strength compared with the base metals and alloys [32, 33]. So far, few researches have been conducted on HEA-based composites especially AlCoCrFeNi matrix composites. Nevertheless, a careful adjustment of sintering conditions, reinforcement type and quantity can open the door to a new generation of metal-matrix composites based on HEAs [34].

In a research conducted by Yang et al. [35, 36] effect of nano-Al_{2}O_{3} on the mechanical properties of Al_{0.4}FeCrCoNi_{1.2}Ti_{0.3} and Al_{0.4}FeCrCo_{0.5}Ni_{1.2}Ti_{0.3}, high-entropy alloys were studied. The deformation twins in this composite were high and the fracture toughness (2250 MPa), plastic tension (20%) and hardness (743 HV) of Al_{0.4}FeCrCoNi_{1.2}Ti_{0.3} + 12 wt% Al_{2}O_{3} composite was improved. Riva et al. [34] investigated the thermal and mechanical properties of Al_{2}CoCrFeNi + 2 wt% nano-diamonds composite and compared to the Al_{2}CoCrFeNi alloy. The results showed that this composite is unsuitable due to low electrical conductivity for use as a thermoelectric material and nano-diamonds negatively affected mechanical properties by increasing the brittleness of the sample. Praveen et al. [37] studied the phase evolution of oxide (33 wt% Y_{2}O_{3} – 67 wt% Ti) dispersed AlCoCrFe high entropy alloy during mechanical alloying and spark plasma sintering. According to their report, the MA-processed powders were transformed from BCC phase to BCC with a small amount of chromium carbide and sigma phases after spark plasma sintering. A slight increment in the hardness of samples was reported after the SPS process of these samples.

Zirconia (ZrO_{2}) is an attractive material in various industrial applications due to its unique properties such as high hardness, improved wear resistance, high elastic modulus and high melting point [38–40]. ZrO_{2} is a ceramic material that has a thermal expansion coefficient close to metals and metal alloys, which results in better adhesion of reinforcement particles and matrix. Also, this material has not destructive phase transformations in the sintering temperature of AlCoCrFeNi HEA. Conducted researches on the effects of adding zirconia to aluminum, copper, magnesium, and their alloys show the ability of this ceramic particle to improve the mechanical and wear properties of these composites [41–44]. According to the interesting properties of ZrO_{2} particles in MMCS, in this study, ZrO_{2}-reinforced AlCoCrFeNi composites were synthesized by the MA method and consolidated by SPS technique and the influences of zirconia reinforcement introduction on the mechanical
alloying stages, sintering behavior and microstructural aspects of AlCoCrFeNi matrix composite were investigated.

2. Material and methods

The characteristics of starting materials are presented in table 1. Figure 1 shows SEM images of the starting materials. The starting powders with and without zirconia reinforcements were subjected to mechanical alloying. The MA process was performed at room temperature in a planetary ball mill at a rotational speed of 250 rpm and ball to powder weight ratio of 10:1 under a high purity argon atmosphere. The milling was continued up to 50 h while in various intervals (0, 10, 20, 22, 28, 30, 40 and 50 h) small amount of powder was taken out and analyzed. To prevent excessive welding in the vial, 0.5 wt% of stearic acid powder was used as the process control agent. The carbon content of milled powders was measured by Carbon/Sulfur Analyzer-ELTRA ELEMENTRAC Cs-d-2000. A commercial TC-436-DR (Leco, USA) oxygen analyzer was used for the oxygen analysis.

In this research, four systems were studied which shown in table 2. The prepared powders were consolidated using SPS at 1000 °C for 5 min with the heating rate of 20 °C min⁻¹ under 30 MPa pressure in a vacuum. The phase identification of the powders and sintered samples was performed using x-ray diffraction (XRD) (XRD, D-500, Siemens (Germany) CuKα radiation: λ = 0.154 nm at 20 kV and 30 mA). Each pattern was collected with a step size of 0.02°. X-ray diffraction pattern was corrected for Kα and instrumental errors. The crystallite size and lattice strain of MA-processed powders after different milling times were calculated by Scherrer’s formula after eliminating the instrumental and the strain contributions. Scanning electron microscopy (FESEM, TESCAN MIRA3, Czech Republic) equipped with an energy dispersive spectroscopy (EDS) unit was used for morphological studies. Bulk density and porosity percentage were calculated according to ASTM C373-14a standard. In this study, zirconia reinforcement particles were introduced to AlCoCrFeNi HEA matrix in two different ways: (i) zirconia particles were ball-milled with Al, Co, Cr, Fe, and Ni elements up to 50 h and (ii) zirconia particles were mixed for 1 h with prepared HEA powder. The results of density measurements on the sintered samples showed that the porosity of all samples is less than 5% which confirms the success of densification process. Moreover, to obtain crystallographic information of related phases and quantitative analysis of SPS-processed samples through Rietveld refinement technique, Material Analysis Using Diffraction

Table 1. % Purity and particle size of starting materials.

|       | Al  | Co  | Cr  | Fe  | Ni  | ZrO₂ |
|-------|-----|-----|-----|-----|-----|------|
| % Purity | >99.0 | >99.0 | >99.0 | >99.0 | >99.8 | >99.0 |
| Particle size | ~3–5 μm | <45 μm | <0.315 mm | <45 μm | ~14 μm | ~5 μm |
| Company | Xinji Guangyuan | Merck | Merck | Merck | Aldrich | Aldrich |

Figure 1. SEM images of the starting materials, (a) Al, (b) Co, (c) Cr, (d) Fe, (e) Ni and (f) ZrO₂ particles.
(MAUD) software was used which works through the least-squares method. Instrumental broadening was removed using a defect-free silicon sample. Due to better accuracy for the calculation of crystallite size and lattice strain, a pseudo-Voigt (pV) function with asymmetry was used. In all refinements, ‘Sig.’ and ‘R’ values were less than 2 and 10, respectively. Also, the backgrounds of patterns were eliminated with a polynomial function of degree 4. A similar approach to the measurement of crystallite size and lattice strain is widely used by other researchers [45–48].

3. Results and discussion

3.1. Mechanical alloying of Al–Co–Cr–Fe–Ni system in the presence and absence of zirconia reinforcements

In figures 2(a), (c), (e), (g), (i) the morphological changes of Al–Co–Cr–Fe–Ni powder mixture after 10, 20, 30, 40 and 50 h of MA are presented. Generally, during the MA process, three main mechanisms, including (i) plastic deformation, (ii) cold welding and (iii) fracture, govern the morphological changes [49]. During the first 10 h of milling (figure 2(a)), severe plastic deformation and cold welding of powder particles occurred and coarse particles with an average size of 12 μm were formed. With the increment of the milling time to more than 10 h, the density of dislocations increases which leads to further work hardening in the particles and facilitates their fracture. With increasing the milling time to 20 h (figure 2(c)), the tendency of fracture of particles enhances, so the average particle size decreased from 12 to 9 μm. With increasing of the milling time to 30 h, equiaxed particles were created. Here, after 30 h of milling (figure 2(e)), the mechanism of cold welding between particles was dominant and, as a consequence, the average particle size was increased from 9 μm to 54 μm. Also, equiaxed particles were evolved at this stage. After 40 h of milling (figure 2(g)), a further reduction in the average particle size (36 μm) was observed, and the powder particle size distribution was more uniform. After milling for 50 h (figure 2(i)), the particle size decreased from 36 to 23 μm, but the morphology of the powder particles did not change.

In figures 2(b), (d), (f), (h), (j), SEM images of Al–Co–Cr–Fe–Ni + 10 wt% ZrO2 powders after mechanical alloying for different times have been represented. It is seen that after 10 h of MA (figure 2(b)), plastic deformation and cold welding mechanisms occurred, but due to introduction of hard zirconia particles, the fracture of welded particles happens more frequently which leads to smaller particle size (9 μm) compared to the unreinforced HEA powder system. With increasing the milling time to 20 h (figure 2(d)), the work hardening of ductile particles in the presence of ZrO2 particles was increased and, as a consequence, the average particle size was reduced from 9 to 4 μm. With the continuation of the MA process up to 30 h, the composite powder particles morphology reached a steady-state and equiaxed particles with an average size of 46 μm were obtained (figure 2(f)). After 40 and 50 h of MA for Al–Co–Cr–Fe–Ni + 10 wt% ZrO2 system, equiaxed particles with an average size of 23 and 14 μm (figures 2(h), (j)) were formed, respectively.

Figure 3 shows the variation of the average particle size of the mixed powders with milling time. It is seen that with the increment of milling time to 20 h, the average particle size of milled powders decreases which shows that the fracture mechanism governs the milling process. However, with further milling of powders to 30 h the average particle size increases which shows that a considerable amount of cold welding occurs in the system. The continuation of the milling process up to 50 h, leads to further particle size reduction which confirms that the rate of fracture is higher than that of cold welding in this stage. The results showed that the addition of hard ceramic particles such as ZrO2 into Al–Co–Cr–Fe–Ni HEA system has a considerable effect on reducing the particle size during the MA process (milling agent effect) [49]. As a result, the powder particles easily break down and become finer particles.

The nominal composition of each element in Al–Co–Cr–Fe–Ni HEA system was selected to be 20 at%. According to the results of EDS analysis in figure 4, after the MA process for 20 and 30 h, the composition of reinforced and unreinforced HEA powder did not considerably change. The reason for the slightly lower

### Table 2. Samples description in this research.

| Sample number | Composition | Preparation method | Sample code |
|---------------|-------------|---------------------|-------------|
| 1             | AlCoCrFeNi  | 30 h MA + SPS at 1000 °C for 5 min | HEA         |
| 2             | AlCoCrFeNi + 10 wt% ZrO2 | Reinforcement and HEA matrix mechanically alloyed for 30 h + SPS at 1000 °C for 5 min | H10Z–30 h |
| 3             | AlCoCrFeNi + 5 wt% ZrO2 | HEA matrix MA-processed for 30 h and mixed for 1 h with 5 wt% ZrO2 | H5Z–1 h    |
| 4             | AlCoCrFeNi + 10 wt% ZrO2 | HEA matrix MA-processed for 30 h and mixed for 1 h with 10 wt% ZrO2 | H10Z–1 h   |

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Figure 2. (a), (c), (e), (g), (i) SEM micrographs of Al–Co–Cr–Fe–Ni powders in the absence of ZrO\textsubscript{2} reinforcements; (a) 10 h, (c) 20 h, (e) 30 h, (g) 40 h, and (i) 50 h. (b), (d), (f), (h), (j) SEM micrographs of Al–Co–Cr–Fe–Ni powders in the presence of 10 wt\% ZrO\textsubscript{2} reinforcements; (b) 10 h, (d) 20 h, (f) 30 h, (h) 40 h, and (j) 50 h.
detection of Al in this HEA system in EDS analysis can be attributed to the higher x-ray absorption of heavy elements such as Cr, Co, and Fe which leads to the lower detection of light elements like aluminum. Considering the limitations of EDS method for the quantitative analysis of light elements such as carbon and oxygen, and due to the probability of atmospheric oxidation during SEM-EDS analysis, the contents of these elements in MA-processed HEA powders were directly assessed. According to the measurements, it was found that MA-processed HEA powder which milled for 20 h contains about 0.56 wt% carbon and 1.29 wt% oxygen and for 30 h milled HEA powder about 0.73 wt% carbon and 1.64 wt% oxygen exist in the powder mixture.

The variation of phase constituents of both reinforced and unreinforced HEA powder systems during the MA process from 0 h to 50 h was investigated with XRD technique (figure 5). It is seen that while the starting mixture is composed of alloying elements, with increasing milling time to 10 h, the intensities of related peaks Figure 3. Variation of the average particle size of the milled HEA and HEA + 10 wt% ZrO2 powders with milling time.

Figure 4. EDS analysis of (a), (c) Al–Co–Cr–Fe–Ni powder in the absence of ZrO2 reinforcements after, (a) 20 h, (c) 30 h of milling. (b), (d) Al–Co–Cr–Fe–Ni powder in the presence of 10 wt% ZrO2 reinforcements after, (b) 20 h, (d) 30 h of milling.

6

Mater. Res. Express 6 (2019) 1265b5 M Ghanbariha et al
were decreased which indicates the starting of dissolution in the system. After 20 h of MA, the related peaks of Al, Co, and Ni are almost disappeared. Also, the intensities of peaks related to Fe and Cr are further decreased. The lower alloying rate in Fe and Cr elements can be attributed to the higher melting point of these elements [50]. Finally, after the MA process for 28 h, new peaks related to BCC solid solution \((110), (200),\) and \((211)\) were evolved. The lattice parameters of this structure after 28 h of MA were determined to be 2.898 Å for the unreinforced system and 2.891 Å for the reinforced system. Increment of milling time to 50 h only broadened the width of BCC peaks due to refinement of crystallite size and enhancement of lattice strain.

The variations of crystallite size and lattice strain with milling time for the HEA powders with and without ZrO\(_2\) reinforcement have been presented in figures 6(a), (b). As shown in this figure, the crystallite size in the BCC phase is refined as the milling duration increases, reaching 5 nm after 30 h MA. Further increase of the milling time has no considerable influence on the crystallite size which indicates that the equilibrium between crystallite refinement and cold welding has been achieved. The lattice strain of AlCoCrFeNi alloy powders increases gradually as the milling time prolongs and reaches 2% when the milling time is 50 h. Generally, the increment in lattice strain is caused by the size mismatch effect among the elements, increased grain boundary fraction and mechanical deformation. In the HEA + 10 wt% ZrO\(_2\) powder with increasing milling time, crystallite size decreased and reached 5 nm after 30 h MA (figure 6(b)). Increasing milling time to 40 h has no vital influence on the crystallite size. However, after MA for 50 h, the crystallite size slightly decreases and reaches to 4 nm. The lattice strain of AlCoCrFeNi + 10 wt% ZrO\(_2\) powder increases gradually as the milling time prolongs and reaches 1.94% when the milling time is 50 h. The lattice parameters of Al–Co–Cr–Fe–Ni system during MA in the presence and absence of ZrO\(_2\) reinforcements were calculated from XRD patterns. It is seen that the lattice parameter of HEA powder with and without ZrO\(_2\) reinforcement increased with the increase in milling time. According to figure 6(c), it seems that with the diffusion of Al and Ni elements, the structure is progressing towards a structure with a higher lattice parameter.
3.2. Spark plasma sintering of Al–Co–Cr–Fe–Ni HEA system reinforced with zirconia particles

Figure 7 shows the variation of SPS temperature and punch displacement against sintering time during the SPS process of the HEA samples. In this study, samples were sintered at 1000 °C with 5 min holding time and heating rate of 20 °C min⁻¹. The consolidation process of these samples can be divided into three distinct zones. At the start of the SPS process, a pressure of 10 MPa was uniaxially applied to the powders. Therefore, in zone 1, from room temperature to 900 °C, due to particles’ rearrangements, initial compaction occurs. With the increment of temperature from 900 to 1000 °C, the first considerable displacement happened (zone 2). With the
enhancement of uniaxial pressure from 10 to 30 MPa at the peak temperature of 1000 °C, the main part of the consolidation process occurred in zone 3.

Figure 8 illustrates the XRD patterns of SPS-processed samples. The indexing of the peaks in the XRD patterns of all sintered samples revealed that these samples consist of both FCC and BCC phases. In order to understand the appropriate method for the addition of zirconia reinforcement particles to the HEA matrix, two approaches have been utilized: (1) zirconia particles were mixed for 1 h with the pre-prepared HEA powder, and (2) zirconia particles were added to the batch of starting elements and ball-milled for 30 h. According to the XRD patterns represented in figure 8(e), it is seen that in the H10Z–30 h (HEA + 10 wt% ZrO2–30 h) sample the peaks related to zirconia phase are not detected and new peaks are evolved at 33 and 38 degrees. In this sample, due to long milling time (30 h), the density of dislocations considerably increased which facilitates the interdiffusion of zirconia particles with light elements such as aluminum. Thus, as seen in the XRD pattern of H10Z–30 h, the ZrO2 peaks in the sample shift to the higher angles which confirm the interaction of zirconia reinforcements with light and mobile elements. This hypothesis was also confirmed by the EDS result presented in figure 12(d). However, as can be seen in figures 8(c), (d), in the samples prepared from mixing pre-prepared HEA powder with ZrO2 particles (H5Z–1 h and H10Z–1 h), the ZrO2 peaks can be easily detected. A comparison of XRD patterns of HEA powder (figure 8(a)) and SPS-processed HEA sample (figure 8(b)) shows that after the SPS process on the prepared HEA powder (MA-processed powder for 30 h) the stability of FCC phase is enhanced. In AlCoCrFeNi HEA system, FCC phase has higher stability at elevated temperatures [51] but because of sluggish diffusion in HEAs, it also remains at room temperature.

To better understand the influences of ZrO2 addition on the phase constituents and weight percentage of phases in HEA-based composites, Rietveld refinement analysis was utilized. In figures 8(f)–(h), detailed scans for (111) plane of FCC phase and (110) plane of BCC phase were represented for HEA, H5Z, and H10Z samples, respectively. The results obtained from the Rietveld refinement analysis are summarized in table 3. The estimated crystallite size for the prepared HEA powder was about 5 nm. It is seen that the crystallite size of the HEA sample after the SPS process increases to about 38 nm for FCC phase and 80 nm for BCC phase. Interestingly, it was found that the addition of reinforcement particles has a restrictive effect on the grain growth of HEA phases during SPS. For example, in the HEA sample reinforced with 10 wt% zirconia particles, the crystallite size of FCC and BCC phase was reached to 21.582 nm and 78.631 nm, respectively which are lower than the values obtained for pure HEA sample. Also, according to the results provided in table 3, it is seen that while the weight percentage of FCC phase is almost constant in HEA and HEA-based composites, with the increment of zirconia the content of BCC phase decreases in the SPS processed. To confirm the stability of zirconia reinforcements during the SPS process, the XRD patterns of monoclinic and tetragonal zirconia phases were plotted and compared with H5Z–1 h and H10Z–1 h samples. It is seen that the peaks of monoclinic zirconia are clearly in accordance with the initial peaks of samples. Therefore, it can be concluded that the monoclinic zirconia phase remained stable in both of H5Z–1 h and H10Z–1 h samples.

3.3. Microstructural evaluations

Figure 9 illustrates FESEM-EDS results of AlCoCrFeNi sample after the SPS process at 1000 °C. It is seen that this sample consists of 4 major phases including FCC (bright), BCC1 (dark grey), BCC2 (grey) and Al-rich (black) phases. According to the EDS results, FCC phase contains higher Cr, Fe, and Co and lower Al and Ni amounts (figure 9(b)), while the BCC phases (BCC1 and BCC2) have higher Al and Ni weight percentages and lower Cr, Fe, and Co contents. With the comparison of the EDS analysis results of BCC1 (figure 9(c)) and BCC2 (figure 9(d)) phases, it was found that the content of Al in BCC1 is slightly higher and the weight percentages of Ni is lower than that of BCC2. Also, a small fraction of fine black points detected as Al-rich phase can be found in the microstructure of this sample. According to figure 9(e), AlCoCrFeNi HEA sample mainly consists of FCC phase.

Figure 10 presents the FESEM-EDS results of the sintered HEA + 5 wt% ZrO2–1 h (H5Z–1 h) composite sample. In this sample, despite ZrO2 reinforcement particles (distinguished with white color), in the HEA matrix, four different contrasts can be observed. (i) FCC matrix which is rich in Fe, Cr, and Co elements (figure 10(b)), (ii) BCC phase which contains high values of Al and Ni (figure 10(c)), (iii) Cr-rich (figure 10(d)), and (iv) Al-rich phases. In this sample, it was not easy to find BCC2 phase in the microstructure. However, in some parts of the sample small fractions of Cr-rich and Al-rich phases can be identified. The formation of Cr-rich phase was also reported by other researchers such as Moravcik et al [27] in HEA systems. Cr is the element that strongly increases the thermodynamic driving force for σ phase formation and Cr element has an important effect on the acceleration of the precipitation rate of σ phase [14]. Figure 10(e) shows the phase fraction of HEA + 5 wt% ZrO2–1 h sample. In accordance with the Rietveld refinement results, FCC phase has a higher volume fraction in this sample.
Figure 8. (a)–(e) XRD patterns of the SPS-processed samples, (f)–(h) the detailed scans for the peak of (111) of FCC phase and (110) of BCC phase; (f) HEA, (g) HEA + 5% ZrO$_2$-1 h, and (h) HEA + 10% ZrO$_2$-1 h composites and (i) XRD patterns of monoclinic and tetragonal zirconia phases.
Table 3. Structural data of HEA + x ZrO₂ (x = 0, 5 and 10) obtained from Rietveld refinement.

| ZrO₂ (Wt%) | FCC | BCC | FCC | BCC | FCC | BCC |
|------------|-----|-----|-----|-----|-----|-----|
|            | 0   | 5   | 10  | 0   | 5   | 10  |
| Crystal system | Fm-3m | Im-3m | Fm-3m | Im-3m | Fm-3m | Im-3m |
| Unit cell dimensions a = b = c (nm) | 0.3603 | 0.2883 | 0.3584 | 0.2883 | 0.3591 | 0.2878 |
| Crystallite size (nm) | 38.213 | 80.045 | 24.341 | 79.712 | 21.584 | 78.631 |
| Phase fraction (wt%) | 55.85 | 44.15 | 55.29 | 39.71 | 58.89 | 31.11 |

Figure 9. (a) SEM images of the SPS-processed AlCoCrFeNi, result of EDS analysis taken from (b) FCC phase, (c) BCC₁ phase, (d) BCC₂ phase, and (e) phase fraction.

In figure 11(a), FESEM images related to HEA + 10 wt% ZrO₂−1 h (H10Z−1 h) composite sample at different magnifications have been represented. Similar to previous samples, Fe–Cr rich FCC is the main phase of the microstructure and Al–Ni rich BCC phase (figure 11(b)) can be easily found in this sample. Also, the amount of cobalt element in the FCC phase was higher than that of the BCC phase. The result of EDS analysis
provided in figure 11(c), confirms the stability of zirconia particles during the SPS process. The formation of a small fraction of Al-rich phase (figure 11(d)) was also noticed. It is believed that a higher diffusion coefficient of aluminum compared to other elements of the HEA system can facilitate the formation of this Al-rich phase. Figure 11(e) shows the phase fraction of HEA + 10 wt% ZrO₂–1 h sample. The results showed that the phase fraction of FCC and BCC are higher than the other phases. It should be noted that initially prepared HEA powder is mainly consists of BCC phase. Also, the FCC phase is stable at elevated temperatures in this HEA system [51]. However, due to the high heating rate of SPS process, there is not enough time for the BCC to FCC phase transformation, and, as a consequence, a combination of FCC and BCC phases coexists in the SPS-processed samples.

Another important issue that should be considered is the formation of Al-rich phases in the interfaces of zirconia with the HEA matrix. It is well-known that the addition of hard particles to metal matrix composites can considerably increase the dislocations in the interfaces [52]. With the evolution of new interfaces and increment of dislocation density in the system, an appropriate condition for the diffusion of light elements such as aluminum toward interfaces is provided. Therefore, with the increment of zirconia particles which leads to the enhancement of interfaces in the composite samples, the higher amount of Al will be diffused out of BCC phase and, as a consequence, the weight fraction of BCC phase will be decreased in the composite samples. This observation is following the quantitative x-ray diffraction results provided in table 3.
In figure 12(a), the microstructure of HEA + 10 wt% ZrO₂−30 h (H10Z−30 h) sample at different magnifications have been provided. In the microstructure of this sample, despite FCC (figure 12(b)), BCC (figure 12(c)) and Al-rich phases, finely distributed zirconia particles (figure 12(d)) can also be detected. However, comparing the size of zirconia particles in this sample with H5Z−1 h and H10Z−1 h samples shows that MA process for 30 h considerably decreased the zirconia particle size. Also, as noticed in the XRD pattern of this sample (figure 8(c)), the content of reinforcements in this sample was lower than that of H10Z−1 h sample. The provided phase fractions result in figure 12(e) also confirms this finding.

4. Conclusions

In this study, a combination of mechanical alloying and SPS techniques were employed for the fabrication of AlCoCrFeNi−ZrO₂ composites. The main conclusions of the present work are given below:

(1) According to XRD and SEM results, the MA process of Al−Co−Cr−Fe−Ni powders for 30 h leads to the formation of BCC phase. The addition of zirconia particles to this milling system has a considerable effect on reducing the particle size during the MA process.
(2) With the SPS consolidation of the MA-processed AlCoCrFeNi powders at 1000 °C for 5 min, a combination of FCC and BCC phases have been formed. The reason for the evolution of this dual structure can be attributed to the high heating rate of the SPS process in which there is not enough time for the BCC to FCC phase transformation.

(3) With the increment of zirconia content, the weight percentage of BCC phase in the SPS-processed samples decreased while the content of FCC phase in HEA samples remained almost unchanged. It is well known that the addition of hard ceramic particles can enhance the interfaces in the composite samples and facilitates the outward diffusion of aluminum from the BCC phase and, as a consequence, the weight fraction of BCC phase will be decreased in the composite samples.

(4) Also, it was found that the addition of reinforcement particles has a restrictive effect on the grain growth of HEA phases during SPS.
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