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Effect Of Milling Time And Sintering Temperature On Mechanical Behavior Of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High Entropy Alloy Through Mechanical Alloying

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This research work focuses on the effect of milling time and sintering temperature on mechanical behavior of advanced high-entropy alloys (HEAs) through mechanical alloying. Mechanical alloying gives uniform dispersion of materials. Raw materials, including powders with an average particle size of 40 µm, were processed via high-energy ball milling (HEBM) for up to 30 hours. The milled HEA powders were consolidated and sintered at two distinct temperatures such as 600°C and 800°C. The mechanical properties of the synthesized HEAs were evaluated through density measurements, hardness testing and compression tests. Density was measured using Archimedes' principle, revealing a relative porosity of 7% and a relative density of 95% after 30 hours of milling. The Vickers micro hardness values were measured as 400 ± 5 $HV_{0.3}$ for samples sintered at 600°C and 700 ± 6 $HV_{0.3}$ for those sintered at 800°C. Similarly, the ultimate compressive strength was recorded as 245 ± 5 MPa for samples sintered at 600°C and 300 ± 5 MPa for those sintered at 800°C. Phase analysis was conducted using Electron Backscattered Diffraction (EBSD), which confirmed the presence of mixed body-centered cubic (BCC) and face-centered cubic (FCC) phases in the sintered samples at both temperatures.

Keywords: High Entropy Alloy; Sintering; Hardness; Compressive strength; Phase analysis

Introduction

High-Entropy Alloys (HEAs) are emerging materials with excellent potential for demanding applications such as space systems and gas turbine engines, including components like compressors, combustion chambers, exhaust nozzles, and gas turbine cases. Since the pioneering work on HEAs in 2004 [1], research in this field has grown linearly, driven by their remarkable properties. Yeh et al.[2] and other researchers categorized HEAS based on their elemental configuration into low, medium and high entropy categories. High entropy alloys typically consist of five or more principal elements present in equimolar or non-equimolar concentrations, with each element contributing 5% to 35% of the total composition.

HEAs have been successfully synthesized using a variety of techniques, including friction stir processing [3], vacuum arc melting [4], vacuum induction melting [5], Infiltration techniques [6], gas atomization [7] and mechanical alloying [8]. Among these methods, mechanical alloying stands out as a highly promising technique for synthesizing HEAs due to its ability to achieve uniform dispersion of elements throughout the alloy matrix [9-12]. The effect of age treatment on the microstructure and micro hardness of $Al_{0.3}CrFe_{1.5}MnNi_{0.5}$ HEAs was reported by Tsao et al.[4]. The effect of electromagnetic stirring on microstructure and properties of $Al_{0.5}CoCrCuFeNi$ HEAs has been investigated by Yanyan Du et al. [5]. The effect on infiltration route and gas atomization techniques on mechanical properties of HEAs reported by Mileiko et al. [6] and Yang et al. [7].

Al and Cr have low density and good yield strength. Iron (Fe), zinc (Zn) and nickel (Ni) have higher densities. The yield strength of iron (Fe), zinc (Zn), and nickel alloys depends on the alloy composition and processing methods. Al, Cr, Fe, Ni, and Zn can be used to make high entropy alloys (HEAs) with a variety of properties including strength, ductility, and corrosion resistance

The effect of milling time and sintering temperatures on mechanical properties of composites investigated and reported by earlier studies [8-15]. The milling parameter such as ball to powder ratio and milling speed influence the final properties of prepared HEAs. This parameter is important in ball milling, a process that breaks down materials into smaller particles. A higher BPR increases the number of collisions between the balls and the powder, which lowers the powder particles. A higher BPR can improve the mechanical properties and wear resistance of the HEAs. Milling speed can significantly influence the crystallite size of the final product. The ball to powder ratio (BPR) dependent morphology and microstructure of tungsten powder refined by ball milling has been investigated Wu et al. [16]. Synthesis and characterization study of Al10Cr25Co20Ni25Fe20 High-Entropy alloy powders through mechanical alloying has been investigated by Jeyasimman et al. [8]. The effect of compaction pressure, sintering temperature and recovery heat treatment temperature of powder metallurgical Fe-20Mn-5Si-5Ni-8Cr shape memory alloy has been investigated by Bakrudeen et al. [13]. Effect of milling time on structural, mechanical and tribological behavior of a newly developed Ti-Ni alloy has been investigated by Nabila Bouchareb et al. [15]. Mamoun Fellah et al. [17] has been investigated and reported the effect of milling time on structural and mechanical properties of nanostructured hiped alpha alumina. Effects of mechanical ball milling time on the microstructure and mechanical properties of Mo2NiB2-Ni cermets has been investigated by Zhang et al.[18]. Yang et al. [19] investigated the effects of milling time and sintering temperature on the mechanical properties of 8 wt% WC/AlCoCrFeNiTi0.5 high entropy alloy matrix composite. Sintering at higher temperatures improves the mechanical properties of materials, such as strength, fracture, and fatigue behaviors. The impact of the final sintering temperature on the microstructure and dielectric properties of $Ba_{0.75}Ca_{0.25}Tio_3$ perovskite ceramics has been investigated by Feliksik et al [20]. There is always need of new composition of HEAs with superior mechanical properties through high energy ball milling in materials research community. These variant HEAs will be required in industries and aerospace sectors for high temperature applications. Moreover, there is limited works available effect of milling time and sintering temperatures on mechanical properties of high entropy alloys.

This research work focuses on examining the effect of milling time and sintering temperature on the mechanical behavior of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High-Entropy Alloy (HEA) synthesized through mechanical alloying.

Materials and Methods

In this study, $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High-Entropy Alloy (HEA) was synthesized using pure elemental powders (average particle size ~40 µm and >95% purity), sourced from SRL Chemicals, Mumbai, India. The synthesis process involved the following steps: Elemental powders of Al, Cr, Ni, Fe, and Zn were weighed, each contributing 20 g to the alloy composition. The powders were mixed and subjected to high-energy ball milling (HEBM) for up to 30 hours. Tungsten carbide balls and vials were used as equipment. Ball-to-powder ratio (BPR) is maintained at 10:1. Powder samples were collected every 5 hours of milling to analyze the effect of milling time on the alloy's properties.The milled powders were compacted into cylindrical shapes with 10 mm diameter and 15 mm height using a uni-axial compression testing machine. Green compacts were sintered at two distinct temperatures 600°C and 800°C, for 3 hours in a tubular furnace. After sintering, the samples were gradually cooled to room temperature. The density of the composites, prepared with varying milling times and sintering temperatures, was evaluated using Archimedes' principle [13-14]. Porosity was calculated based on the relationship between theoretical (determined from elemental densities) and sintered density (measured using Archimedes' principle).Vickers micro hardness of the sintered HEA samples was measured using a micro hardness testing machine under a load of 500 g with a dwell time of 15 seconds. The tests were conducted on samples prepared with various milling times and sintering temperatures. Compression tests were carried out on sintered HEA samples using a universal testing machine with a maximum capacity of 40 tons. The range of compression tests from 0 to 2 % strain. These tests provided insights into the ultimate compressive strength and deformation behavior of the material. Phase analysis was conducted using Electron Backscattered Diffraction (EBSD). A JEOL JSM 7600F Field Emission Gun Scanning Electron Microscope (FEG SEM) was utilized to identify the crystallographic phases and analyze the microstructure of the sintered HEAs.

Result and Discussion

Fig. 1 illustrates the relationship between milling time and the relative density and porosity of the $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ high-entropy alloy (HEA) samples. The findings reveal a clear trend where both properties improve with extended milling durations. For samples milled for 5 hours, the relative density was 84%. With increased milling time, the relative density showed a steady rise, reaching 95% after 30 hours of mechanical alloying (MA). The improvement in density is attributed to better particle refinement and homogeneous mixing, promoting enhanced densification during sintering. The relative porosity of the samples was 17% after 5 hours of milling. As milling time increased, the porosity gradually decreased, achieving a 7% relative porosity after 30 hours of MA. The reduction in porosity is linked to improved compaction and reduced void spaces, consistent with earlier studies [15]. Fig.2 presents the Vickers micro hardness values $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ high-entropy alloy (HEA) samples as a function of milling time, with measurements taken for samples sintered at 600°C and 800°C. The results demonstrate a significant improvement in hardness with both increased milling time and sintering temperature. Vickers micro hardness values for sintered samples at 600°C for 330 ± 3 $HV_{0.3}$, 342 ± 2 $HV_{0.3}$, 350± 3 $HV_{0.3}$ 355 ± 3 $HV_{0.3}$, 381 ± 3 $HV_{0.3}$ and 399 ± 3 $HV_{0.3}$ for 5 h, 10 h, 15 h, 20 h, 25 h and 30 h MA respectively. Vickers micro hardness values for sintered samples at 800°C for 558 ± 2 $HV_{0.3}$, 641 ± 3 $HV_{0.3}$, 658 ± 3 $HV_{0.3}$, 671 ± 3 $HV_{0.3}$, 671 ± 3 $HV_{0.3}$, 684 ± 3 $HV_{0.3}$ and 698 ± 3 $HV_{0.3}$ for 5 h, 10 h, 15 h, 20 h, 25 h and 30 h MA respectively. Hardness values consistently increased with milling time, attributed to structural refinement, including grain size reduction and improved homogeneity of the HEA matrix. Prolonged mechanical alloying promoted particle refinement and a more uniform distribution of alloying elements. Higher sintering temperatures (800°C) resulted in significantly higher hardness values compared to 600°C, primarily due to enhanced densification and reduced residual porosity. At low sintering temperature, high porosity leads to low strength specimen. At high sintering temperature, changes in structure and size reduction of porosity makes the bond formation between powders clearer. The strength increased with increasing in bonding formation between particles [21]. Therfore sintering at 800°C, beyond the porosity reduction and increase in density, hardness improvements happened. In our earlier study [8], the obtained hardness value of AlCrCoNiFe HEAs was 305± 5 $HV_{0.5}$. Praveen et al. [22] investigated the effect of molybdenum and niobium on CoCrFeNi HEA and reported the hardness value was 570 HV and Liu et al. [23] developed CrMnFeCoNi HEA and obtained the hardness value 526 HV. These results were in good agreement with this research work. Fig.3 depicts the compressive strength of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ high entropy alloys (HEAs) sintered at 600°C and 800°C. The data provides insight into the mechanical behavior under compressive loading and highlights the influence of sintering temperature. The ultimate compressive strength was 245 ± 5 MPa obtained for samples sintered at 600°C and 300 ± 5 MPa for those sintered at 800°C. The increase in ultimate compressive strength for samples sintered at 800°C can be attributed to better densification and improved particle bonding, resulting in a more robust microstructure. The total elongation was 6.18 % for sintered sample at 600°C and 6.87 % for sintered sample at 800°C. The slight increase in total elongation with higher sintering temperature suggests that elevated sintering promotes not only strength but also the capacity to undergo plastic deformation, which is likely due to reduced residual porosity and improved inter-particle cohesion. In compression strength measurement, the results obtained for conventional sintering (245 ± 5 MPa and 300± 5 MPa for sintering temperature at 600°C and at 800°C) were good agreement with earlier study (246 ± 5 MPa and 305± 5 MPa for sintering temperature at 1000°C and at 1200°C) [8]. Fig.4 presents the Electron Backscattered Diffraction (EBSD) analysis of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ high entropy alloys (HEAs) samples sintered at 600°C and 800°C. The analysis provides insights into the phase distribution and dominant crystal structures. The analysis revealed that the body-centered cubic (BCC) phase is more dominant than the face-centered cubic (FCC) phase in the sintered samples. This is primarily attributed to the dissolution of aluminum (Al) and zinc (Zn), which have FCC structures and lower melting points (660°C and 419°C respectively), into the chromium (Cr) and iron (Fe) matrix, which are characterized by high-melting-point BCC phases (1538°C and 1907°C, respectively). At the sintering temperatures used (600°C and 800°C), the BCC phase was more stable and prevalent due to the higher melting points and stronger bonding tendencies of Cr and Fe. A bi-phase alloy (BCC + FCC) can form at higher sintering temperatures, as the increased thermal energy promotes phase co-existence and stabilization of FCC phases. These findings align with earlier studies [8], where the predominance of the BCC phase at moderate sintering temperatures was similarly observed in HEAs. Bi-phase structure (BCC + FCC) were obtained in the earlier study AlCrCoNiFe HEA synthesized by mechanical alloying [8] and AlCoCrFeNi HEA developed by mechanical alloying and followed by spark plasma sintering [24]. These results were in good agreement with this present research work.

Conclusion

The following conclusions were drawn from the study:

1. The equimolar $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ high-entropy alloy (HEA) was successfully developed through 30 hours of mechanical alloying (MA).
2. The mechanical properties of the HEA were analyzed for various milling times (5 h, 10 h, 20 h, and 30 h), revealing significant improvements with extended milling time.
3. After 30 hours of MA, the relative density of the HEA reached 95%, while the relative porosity was reduced to 7%, reflecting increased densification.
4. Maximum Vickers micro hardness value 400 ± 3 $HV_{0.3}$ and 700 ± 3 $HV_{0.3}$ were obtained for sintered samples at 600°C and 800°C. The hardness increased with both milling time and sintering temperature due to structural refinement and densification.
5. The ultimate compressive strength was 245 ± 5 MPa obtained for samples sintered at 600°C and 300 ± 5 MPa for those sintered at 800°C. The increased compressive strength at higher sintering temperatures was attributed to improved densification.
6. Electron Backscattered Diffraction (EBSD) analysis showed the presence of a bi-phase structure (BCC + FCC). The BCC phase was the dominant phase, comprising >95% of the microstructure, while the FCC phase constituted a smaller portion (< 5%).

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Figures

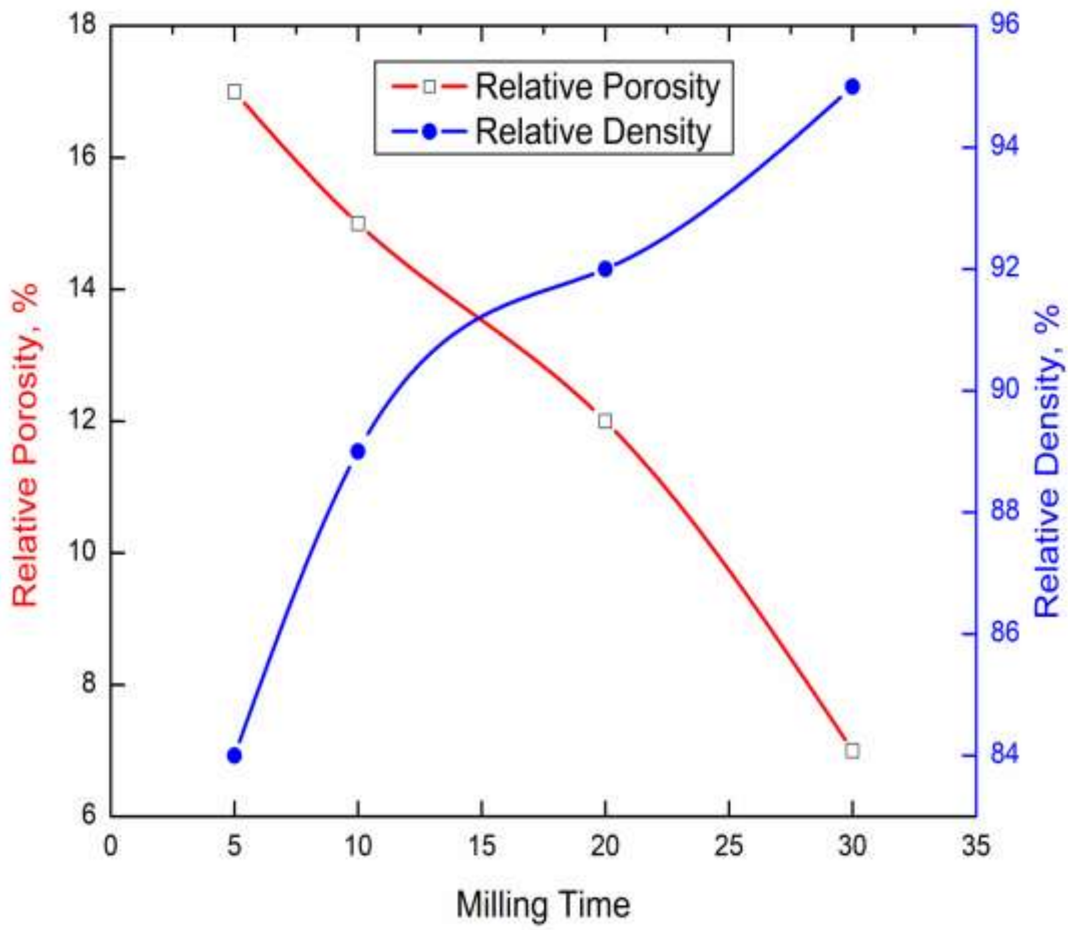

Fig. 1 Relative density and porosity of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High entropy alloy.

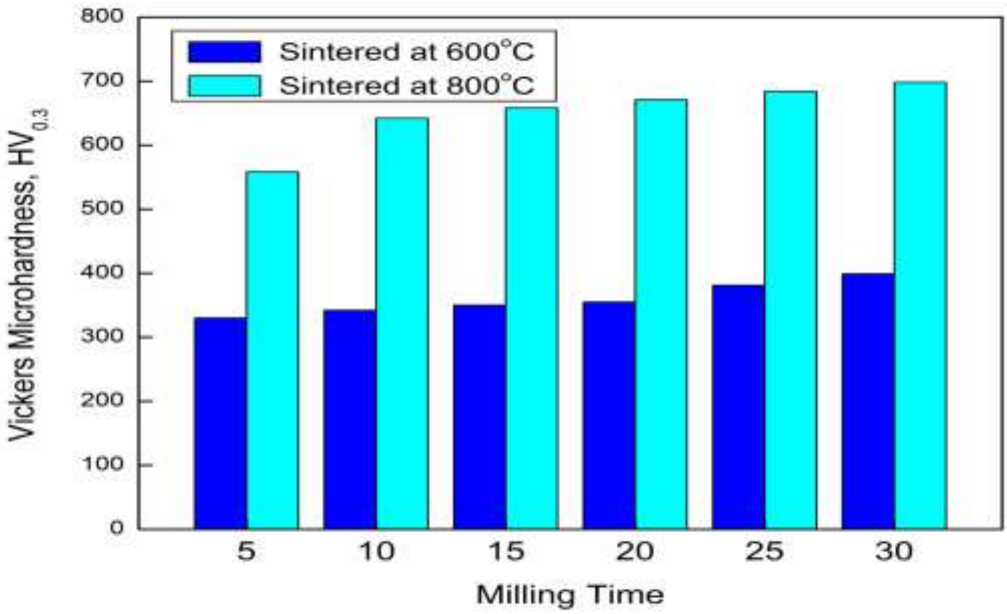

Fig.2. Vickers micro hardness of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High entropy alloy sintered at 600°C and 800°C temperatures

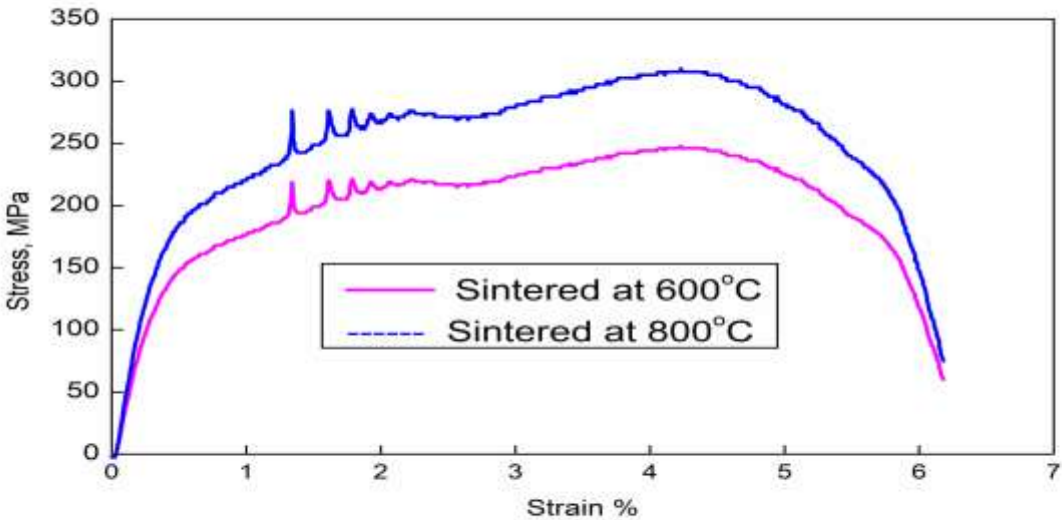

Fig.3 Compressive strength of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High entropy alloy sintered at 600°C and 800°C temperatures

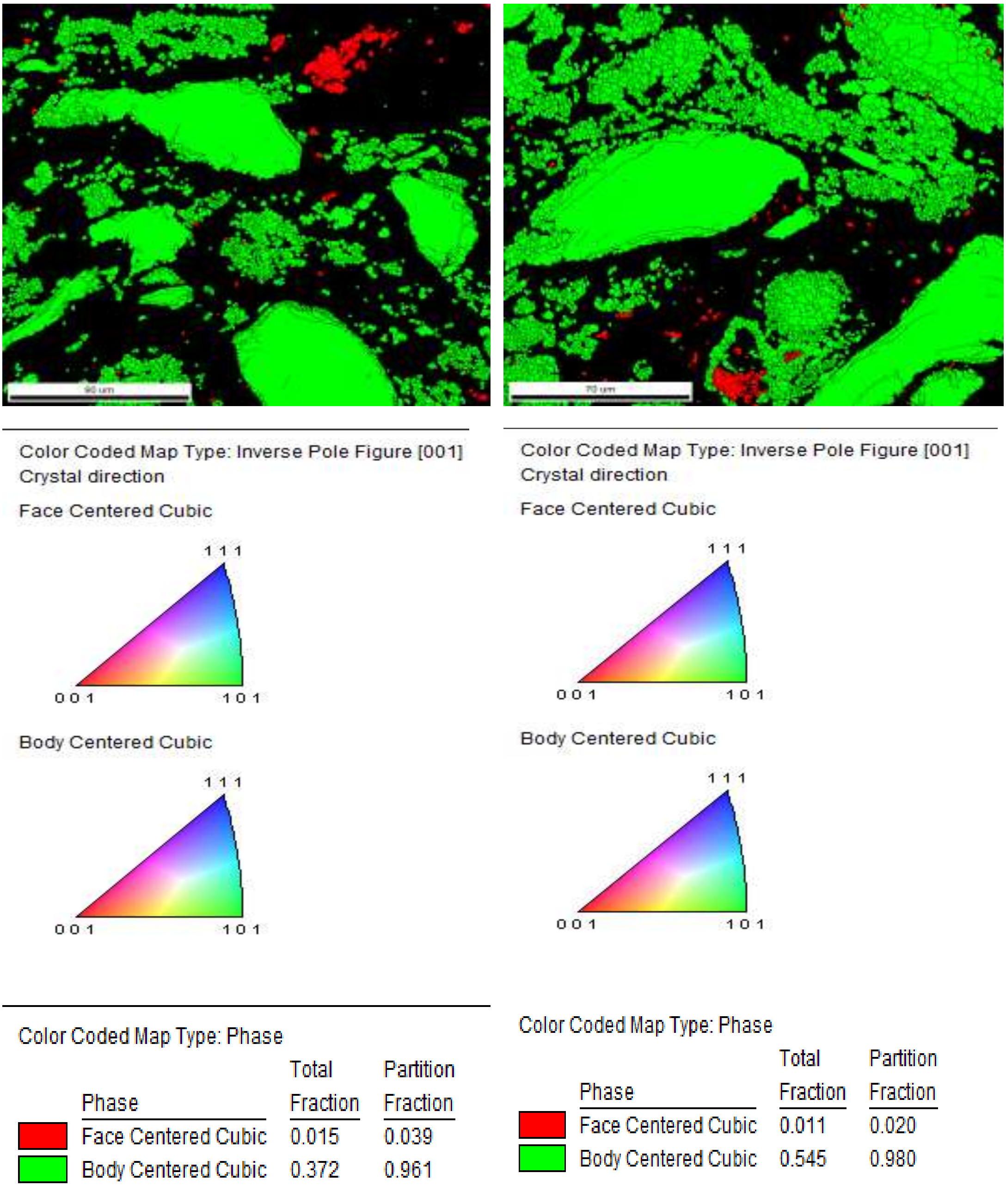

Fig.4. EBSD analysis of $Al_{20}Cr_{20}Ni_{20}Fe_{20}Zn_{20}$ High entropy alloy sintered (a) at 600°C (b) 800°C