Influence of Heat Treatment on Microstructure and Mechanical Properties of Ni-Fe-Co Ternary Alloy Prepared via Spark Plasma Sintering

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Abstract. The use of nickel-based superalloys has extended to different fields such as turbines, rocket motors, chemical equipment, space vehicles and power plants due to their excellent mechanical properties. This study investigates the effect of heat treatment on the microstructure and microhardness of spark plasma sintered Ni-Fe-Co ternary alloy. 50wt.% Ni and varying percentages of Fe and Co powders were milled and fabricated by Spark Plasma Sintering (SPS) technique at a temperature of 900 °C, pressure and holding time were kept at 50 MPa and 10 min respectively. The sintered compacts were heat-treated at 1000 °C, soaked for 1 hr and quenched in distilled water for 5 min. Subsequently, the sintered and heat-treated samples were characterized by scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) and X-ray Diffraction (XRD) to determine the microstructural evolution and phase transformation accompanying the process. XRD results revealed the evolution of strengthening phases in the heat treated of the samples. The as-sintered and heat-treated compacts Vickers hardness was also investigated before and after the heat treatment. The results show a general improvement in the microstructure after the heat treatment which translated to the observed increase in the hardness of the heat-treated samples.

1. Introduction

Superalloys are materials of special interest for applications in corrosive and elevated temperature due to their high strength, excellent resistance to wear, fatigue and creep. Generally, most of the superalloys used in power generation and aerospace industries are Ni, Fe and Ni-Fe based [1, 2]. Ni-Fe-Co ternary alloys are specifically developed for usage in the turbine hottest and high pressure region e.g. the combustor [3]. Ni-Fe-Co ternary alloys are of use in other industrial applications which include power plants, chemical plants, petrochemical plants, and reciprocating engines because of their excellent combination of mechanical properties such as high hardness, strength, good wear resistance, corrosion resistance and hot resistance [4]. Even though Ni-Fe-Co possesses excellent mechanical properties, thermal treatment can be employed to alter the microstructure to produce enhanced strength, hardness, ductility and creep resistance [5-8]. In hardening, the alloy is heated to a temperature high enough to
promote the formation of supersaturated solid solution, hold at that temperature and then quenched in distilled water to a suitable rate to allow martensitic transformation to take place.

Spark plasma sintering (SPS) technique has the advantage of low sintering temperature, short sintering time and lower pressure relative to conventional powder metallurgy processes like hot pressing and hot isostatic pressing [9-11]. The short sintering time for consolidation of powders during SPS process inhibits microstructure coarsening thus retaining nearly the grain size of the starting powder and achieving enhanced mechanical properties. Hence, SPS technique overcomes the challenges of grain coarsening and poor mechanical properties encountered during the production of nickel-based superalloy using the conventional production route.

Several works have been conducted on the heat treatment of Ni-based superalloys [6, 12, 13]. However, few studies are available in the literature on the properties exhibited by Ni-Fe-Co ternary alloy due to solution treatment of this alloy. Hence, in this study, Ni-Fe-Co powder with varying composition of Fe and Co was consolidated through SPS technique and the effect of heat treatment (hardening) on the microstructure, phase evolution and mechanical properties of the sintered alloy were evaluated.

2. Experimental Procedure

2.1 Powder preparation

Ni, Fe and Co powders with characteristics shown in Table 1 were used as starting materials. Each powder was milled in a high-energy planetary ball mill (Retsch, PM 400, Germany) with steel balls and vial as the grinding media for particle size reduction. Milling was done for 15hrs at a vial rotation speed of 350rpm and ball to powder ratio of 10:1. To prevent powder agglomeration, wet milling was employed using ethanol as the suspension media. The milled powder mixture having composition Ni-20Fe-30Co (wt.%) and Ni-20Fe-30Co (wt.%) were separately mixed by subjecting the powders to translational and rotational motion in a turbula mixer at 49 rpm for 8 h. The ad-mixed powders were analysed with the use of scanning electron microscope (SEM) incorporated with energy dispersive x-ray spectroscopy to check its morphology and elemental composition. The SEM micrograph and the EDS of the milled powders are shown in Figure 1.

Table 1: Particle size and purity of starting powders.

| MATERIALS   | PARTICLE SIZE (µm) | PURITY (%) | SUPPLIER               |
|-------------|--------------------|------------|------------------------|
| Nickel (Ni) | ≥0.5 to 30         | 99.5       | WEAR TECH PTY (LTD)    |
| Iron (Fe)   | <44                | 99.9       | WEAR TECH PTY (LTD)    |
| Cobalt (Co) | <44                | 99.9       | WEAR TECH PTY (LTD)    |

2.2 Sintering of powder mixtures

The mixed powders were compacted by spark plasma sintering (SPS) technique using machine model HHPD 5, FCT Germany. Predetermined weight of the mixed powder was poured into a graphite die with a diameter of 20 mm and sintered at 900 °C in a vacuum. The Optical Pyrometer was used to measure the sintering temperature which was implanted in the SPS apparatus at 3 mm from the top of the sample surface. The pressure was maintained at 50 MPa and heating rate of 150 °C/min throughout the whole process. The sintering temperature was 900 °C with dwell time of 10 min. After the completion of the sintering process, the compacted sample was removed at room temperature. The sintered samples were sand blasted to remove graphite impurities.
2.3 Heat treatment
To study the effect of heat treatment on microstructural and mechanical properties, hardening of the sintered Ni-20Fe-30Co and Ni-15Fe-35Co samples was carried out at a temperature of 1000 °C in a muffle furnace. The compacts were held for 1 hour and quenched in distilled water for 5 minutes.

2.4 Relative density
To study the effect of heat treatment on the as-sintered alloy, a densitometer which employs Archimedes' principle was used to determine the density. The densitometer uses deionised water as the immersion liquid and automatically calculates the density of the sintered compact by comparing its weight in water and air using Archimedes' principle. The average of five measurements done on each sample was recorded as the density value. The relative density was determined by comparing the measured and theoretical density of the sintered sample.

2.5 Microstructural Characterization
The microstructure of the as-sintered and heat-treated polished surface was examined using SEM (JSM-7600F, Joel, Japan) incorporated with EDS facilities (Oxford X-max). The phases prior and after heat treatment were analyzed by XRD (PANalytical Empyrean model) with Cu kα radiation at 40kV and 20mA and analysed Xpert High Score software.

2.6 Hardness
Hardness testing was done using a Vickers hardness tester (FUTURE-TECH FM 800). The as-sintered and heat-treated samples were subjected to a load of 300 gf for a dwelling time of 10 seconds. The recorded hardness in HV for each compact is the average of 10 indentations.
3. Results and Discussion

3.1 Powder characterization

The SEM micrographs of the mechanically milled powders are shown in Figure 1. The powder particles were observed to be flattened out into sheets due to ball-ball and ball-wall of the vial interaction during the milling operation for 15 hrs. This resulted in severe plastic deformation of the powder particles. According to Karimbeigi et al. [14] and Rominiyi et al. [15], particle disintegration takes place at longer milling time as a result of fracturing and welding cycle induced by strain hardening of the materials.

3.2 Microstructure

The SEM (EBSD) micrographs of the sintered and heat-treated samples are shown in Figure 2. Similar microstructures comprising light and dark grey phases were observed in Figure 2a and b. These phases were revealed by the EDS analysis of the microstructures to be Ni and Co-Fe rich phases respectively. As, were observed in as-sintered Ni-20Fe-30Co (Figure 2a) and Ni-15Fe-35Co (Figure 2b). In addition to this, few pores were observed. This may be as a result of the sintering temperature (900 °C), which caused poor metallurgical bonding between the powders particle [16]. After solution treatment for 2 hrs and quenching with distilled water to room temperature, the microstructure of the heated-treated samples presented Figure 2c and d showed a more refined and homogeneous distribution of these phases.

![Figure 2](image-url)

**Figure 2.** SEM micrograph of Ni-20Fe-30Co sample as-sintered (a) Ni-20Fe-30Co (b) Ni-15Fe-35Co and heat treated (c) Ni-20Fe-30Co (d) Ni-15Fe-35Co.

3.3 Phase Analysis

The X-ray diffraction analysis results of the admixed powder, as-sintered and heat-treated alloys are presented in Figure 3. The diffraction pattern of the admixed powder consisted of the peaks of Ni, Fe, Co and C. The peak of C observed, though weak, may be as a result of the release of carbon into the milled powder during stainless steel ball-ball and ball-wall of the vial interaction that characterized the milling operation. The predominance of peaks corresponding to that of ordered B2 structure of CoFe (BCC) and (γ′) FeNi3 (BCC) with few peaks of γNiFe (FCC) [17] was observed in the diffraction patterns.
of as-sintered samples (Figure 3a and b). This confirmed the compositions of the light and dark grey regions in the microstructure of the as-sintered samples (Figure 2a and b) to be a combination of FeNi$_3$ (BCC) and $\gamma$NiFe (FCC) and CoFe (BCC) phases respectively. $\gamma$NiFe phase exists as a high temperature phase, its presence in the sintered samples can be ascribed to the fast cooling rate of the SPSed samples which prevented its transformation to a more stable phase of FeNi$_3$. The weak peak of Fe$_3$C observed was as a result of the interaction of ingressed C during the milling operation and the elemental Fe in the admixed powder.

The diffraction patterns of the heat-treated samples showed in Figure 3a and b revealed the presence of trapped high-temperature FCC phases such as $\gamma$(Ni,Fe), $\gamma$(Co,Fe) and orthorhombic, Fe$_3$C after solution treatment as the dominant phases. This can be attributed to the dissolution of the low temperature intermetallics such as ($\gamma'$) FeNi$_3$ and CoFe and subsequent quenching during the heat treatment at 1000 °C. This is in agreement with the results of the study conducted by Turchanin et al. [18]. Furthermore, narrower and higher intensities of the peaks were observed in heat-treated samples relative to the as-sintered samples. This can be attributed to the occurrence of grain refinement within the matrix of the heat-treated samples.

Figure 3. XRD patterns of (a) Ni-20Fe-30Co (b) Ni-15Fe-35Co

3.4 Relative density and hardness

Figure 4a showed the variation of the relative density of the as-sintered and heat-treated samples. The as-sintered Ni-20Fe-30Co and Ni-15Fe-35Co has a relative density of 84.2% and 87% respectively. These relative density values were found to increase to 86 % and 89 % respectively as the samples were heat-treated. Improvement in the densities of the heat-treated samples can be attributed to their close-structure dominated matrix compared to the pronounced open-structure that controlled the matrix of the as-sintered samples.

The microhardness test carried out before and after solid solution treatment of the investigated alloy indicated that the hardness of Ni-20Fe-30Co sample increased from 174.59 to 210.09 HV while an improvement in hardness from 198.45 to 298.09 HV was obtained for Ni-15Fe-35Co sample (Figure 4). It can also be observed that as the wt.% Co increased, the hardness value increased. This can be attributed to its higher relative density [9] and the fact that Co might have reduced the solubility of Fe in the matrix, causing significant increase in the volume fraction of the $\gamma'$ phase [19]. Also, grain refinement due to solution treatment of the as-sintered samples increased the volume of the grain boundaries within the matrix. This created impediments to the dislocation movement, hence enhancing the mechanical properties of the heat-treated samples [20].
4. Conclusion
Heat treatment of Ni-Fe-Co ternary alloys was conducted. The impact of this operation on the microstructure, phase evolution and mechanical properties were investigated. The following were concluded from this work:

1. NiFe, FeNi$_3$ and FeCo were the predominant precipitates found in the as-sintered samples while $\gamma$(Ni,Fe), $\gamma$(Co,Fe) and orthorhombic, Fe$_3$C constituted the quenched solid solution in the heat-treated sample.

2. The relative density and microhardness values of the investigated alloy increases due to an increase in the volume of FeNi$_3$ and FeCo intermetallics precipitated as the wt.% Co increases in the as-sintered samples.

3. The predominance of FCC structure in the quenched solid solution was responsible for the increase in the relative density and hardness observed in the heat-treated samples. These also increased with increasing wt.% Co.

4. The outcome of this work shows that applications of post sintering heat treatment enhanced the precipitation of hardening phases which eventually improved the mechanical properties of the sintered alloys. This makes the developed material a potential candidate in the applications that require high temperature strength and hardness such as in the production of turbine discs in aero-engines.

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6. References
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