Study on substitution of Ni with Ni$_3$Al on structure and properties of W–6Ni$_3$Al–4Co alloys by two-step sintering process

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Abstract

Herein, the effect of substitution of Ni with Ni$_3$Al and two-step sintering on the phase transformation, microstructure evolution, and properties of W–6Ni–4Co alloys were evaluated. The results show that the reaction products of Ni$_3$Al and Co include (Ni, Co)$_3$Al$_4$ to Co$_2$Al$_9$ during the two-step sintering process. When Ni was substituted by Ni$_3$Al, the densification temperature was reduced. The distribution of W phase turned from stripes to network, and the grain size increased with an increase in the sintering temperature. The Ni$_3$Al substituted sample sintered at 1500 °C for 20 min displayed a combination of high densification parameter, microhardness, and strength because of denser microstructure of the alloy.

1. Introduction

High density tungsten alloys can be used as functional materials, such as high-voltage contact and heating unit of electron microscope, because of good conductivity of heat and electricity [1–3]. Owing their superb mechanical properties, they can also be used as structural materials, such as bullet core, gyroscope, and first wall of nuclear reactor [4–6]. The W–Ni–Me (e.g. W–Ni–Fe, W–Ni–Cu, W–Ni–Co, and W–Ni–Mn) series alloys are widely used in war industry, spaceflight, and nuke industry [7–11]. In our earlier works [12–14], the W–Ni–Cu alloy and W–Ni–Co alloy prepared by liquid phase sintering and two-step sintering have been investigated. The two-step sintering refined the grains of W–Ni–Cu alloy and W–Ni–Co alloy by forming W skeleton structure during the solid phase sintering, while the grain growth occurred because of solution re-precipitation of W in binder during the liquid phase sintering. This issue has also been experienced by other researchers [13]. Thus, two-step sintering is a process with practical engineering value.

Apart from the sintering process, the binder modification is also an effective method for regulating structure and properties of W–Ni–Me series alloys. Zhu et al [15] reported a new W–Ni–Cu–Sn heavy alloy fabricated via high–energy ball milling–assisted vacuum sintering. The tensile strength of the obtained alloy was comparable to the conventional sintered W–Ni–Cu alloys but with 250 °C–300 °C lower sintering temperature. Chen et al [16] reported about sintering behavior of the W–Ni–Co alloy and suggested that a transition from solid to liquid phase occurs during sintering as the Ni/Co ratio changes from 9 to 2.3. Sengupta et al [17] also reported the effect of NiB substitution for Ni on densification, structure, and properties of 90W–6Ni–2Fe–2Co alloys. The substitution of NiB for Ni resulted in enhanced densification at relatively less sintering temperature. These works establish that binder modification can be a novel avenue for new W alloys.

Ni$_3$Al is a compound with closely-packed L1$_2$ structure, and in general, is used as high temperature alloy [14]. It forms a liquid phase at $\sim$1293 °C, and accordingly, it is imperative to investigate the role of Ni$_3$Al substitution in the W–Ni–Me series alloys. Herein, an attempt is made to evaluate the effect of Ni$_3$Al substitution for Ni on the phase transformation, microstructure evolution and properties of W–6Ni–4Co alloys by two-step sintering process.
2. Experimental

The W, Ni₃Al, and Co powders were used as raw materials. Table 1 summarizes the average size, processing route, and shape of W, Ni₃Al, and Co powders. The characteristics of W and Co powders were the same as that of [12]. Ni₃Al was prepared by fine grinding after self-propagation synthesis. Figure 1 shows the morphology of these powders. The reduced tungsten powder had polyhedron morphology, while the Tri-nickel aluminide, which was produced by self-propagation synthesis, resulted in irregular morphology. Cobalt, which was produced by electrolysis, resulted in arborization morphology. The alloy compositions were mass weighed and ball mixed by a planetary ball mill (XQM-0.4 A) for 20 h under argon atmosphere. A grinding medium produced by cemented carbides with size 5 mm, 8 mm, and 10 mm was used an ball to powder weight ratio was 3:1. To study the densification response and properties, cuboid samples (length: 30 mm, width: 7 mm, and height: 3.5 mm) were firstly pressed at 476 MPa using a uniaxial press, and then, sintered via two-step sintering process in a MoSi₂-heated tubular furnace (GSL-1700X-II). All the samples were sintered in flowing Ar atmosphere at 20 ml min⁻¹. The two-step sintering curves and technological parameters are shown in figure 2 and table 2, respectively. For the two-step sintering, the temperature and soaking time were 1450 °C and 1500 °C for 20 min, respectively. The heating rates was 8 °C min⁻¹ and 5 °C min⁻¹ while the cooling rates were 4 °C min⁻¹ and 10 °C min⁻¹, respectively. The samples were cooled inside the furnace to room temperature. The sintered samples for density and mechanical property tests were wet polished in pregrinder using a series of 400 meshes, 800 meshes, and 1500 meshes metallographic sandpaper, followed by cloth polishing using a 0.03 μm Al₂O₃ suspension. The sample size was 25 mm × 6 mm × 3 mm.

The density of green body and sintered samples was obtained via Archimedes principle. The samples for density testing were wax-sealed to prevent the distilled water into pores of the samples. To include the effect of Ni₃Al and two-step sintering on the densification of W–6Ni₃Al–4Co alloy, the densification parameter was calculated as follows:

| Element | Mass fraction (wt%) | Average size (μm) | Preparation method |
|---------|---------------------|-------------------|--------------------|
| W       | 90                  | 3                 | Reduction          |
| Ni₃Al   | 6                   | 25                | Self-propagating   |
| Co      | 4                   | 5                 | Electrolysis       |

Figure 1. SEM images of W, Ni₃Al, and Co: (a) W, (b) Ni₃Al, and (c) Co.

Table 1. Characteristics and mass fraction of W, Ni₃Al, and Co powders.
where $D$ is the densification parameter of W–6Ni3Al–4Co alloy under different sintering process. $\rho_S$, $\rho_G$, and $\rho_T$ are the sintered density, green compact density, and theoretical density, respectively.

To understand the phase evolution of W–6Ni3Al–4Co alloy, differential thermal analyzer (DTA) was used. The 60Ni–40Co, 60Ni3Al–40Co, and 90W–6Ni3Al–4Co compacts were heated to 1600 °C at a constant rate of 8 °C min$^{-1}$ in a DTA unit (TGA/DSC1).

The micrographs and quantitative analysis of sintered samples were obtained with scanning electron microscope (JSM-6700F) equipped with energy disperse spectroscopy in the backscattered electron (BE) mode. The fracture morphology was observed by another scanning electron microscope (JSM-6390LV). The average grain size was measured using the line intercept method, ignoring sub grain boundary in W–6Ni3Al–4Co alloys under different two-step sintering. The phase determination was performed for sintered samples using x-ray Diffractometer (D8 ADVANCEX). Micro hardness tester (HVS-1000) was used to evaluate the average hardness of W–6Ni3Al–4Co alloys. The loads and holding times were 100 g and 20 s, respectively. The hardness values for each sample were an average of five testing points taken at different locations on the whole micrographs. For measuring the compressive strength, cylindrical pellets samples (diameter: 1.5 mm and height 3 mm) were processed by a linear cutting machine. Compressive strength and flexural strength of the sintered samples was obtained using a mechanical tester (MP-200). The loading rates were 0.08 mm min$^{-1}$ and 0.5 mm min$^{-1}$, respectively.

3. Results and discussion

3.1. Phase evolution of W–6Ni3Al–4Co alloys

Figure 3 compares x-ray diffraction patterns of the sintered samples at different two-step sintering processes. The alloying of Ni3Al and Co clearly occupies main status in W–6Ni3Al–4Co alloys during the two-step sintering process. This phenomenon is different from the one in W–6Ni–4Co alloys, which is composed of W, NiW, and Co3W [12]. This is because Ni and Co completely dissolve and react with W under solid phase and liquid sintering [12], while Ni is prone to be replaced by Co in the Ni3Al–Co system under the same process [14]. (Ni, Co)$_3$Al$_4$ is a partial replacement product and Co$_2$Al$_7$ is the complete replacement product. While W element dissolves in Ni–Co solid solution in W–6Ni–4Co alloys under same conditions, which forms a great contribution to improve the alloying of W, Ni, and Co, and promote the formation of intermetallic phases [12].
The volume fraction of phase is calculated by using equation (2) [12], as listed in table 3.

\[ V_i = \frac{A_i}{\sum_{j=1}^{n} A_j} \% \]  

where \( A_i \) presents the area of diffraction peaks of W, (Ni, Co)\(_3\)Al\(_4\) and Co\(_2\)Al\(_9\) phases, respectively; \( V_i \) is the volume fractions of W, (Ni, Co)\(_3\)Al\(_4\), and Co\(_2\)Al\(_9\) phases, respectively. The volume fractions of (Ni, Co)\(_3\)Al\(_4\) and Co\(_2\)Al\(_9\) phases in the alloy sintered at 1200 °C for 30 min were 6.77% and 1.23%, and the relative volume fractions of (Ni, Co)\(_3\)Al\(_4\) phase to Co\(_2\)Al\(_9\) phase was 5.05. While those for sintering at 1450 °C for 20 min under two-step sintering were 8.53% and 2.75%, and the relative volume fractions for those decreased to 3.10. The higher solid phase sintering temperature clearly improved both the partial replacement reaction and complete replacement reaction in the Ni\(_3\)Al–Co ternary system. The relative volume fractions of the alloy sintered at 1500 °C for 30 min increased to 7.64, and the volume fractions of two phases were 8.41% and 0.77%. This is because complete replacement reaction of Co\(_2\)Al\(_9\) phase was restrained by the liquid phase sintering. To understand the densification mechanism of W–6Ni\(_3\)Al–4Co alloys during the two-step sintering process, it is important to evaluate the phase changes that occur in the premixed W–6Ni\(_3\)Al–4Co powder compacts during thermal cycling.

To compare the effect of Ni\(_3\)Al and Ni on the associated phase changes, DSC analysis was conducted separately for the 60Ni–40Co, 60Ni\(_3\)Al–40Co, and 90W–6Ni\(_3\)Al–4Co alloys. The DSC curves are presented in figure 4. For the 60Ni–40Co compaction, an endothermic peak was found at 1462.4 °C. According to the Ni–Co binary phase diagram in figure 5, an infinite solid solution with face-centered cubic structure can be formed because of the narrow spacing of solid phase line and liquid phase line, which illustrates that 1462.4 °C could be the melting point of the Ni–Co solid solution component. For the 60Ni\(_3\)Al–40Co compaction, an endothermic peak was also found at 1455.2 °C. It can be inferred that 1455.2 °C is the melting point of (Ni, Co)\(_3\)Al\(_4\) phase according to Ni\(_3\)Al–Co ternary system [14] and x-ray diffraction patterns. As shown in figure 5(c), there were two minor endothermic peaks in the thermal analysis curve of 90W–6Ni\(_3\)Al–4Co compaction at 1502.3 °C and 1548.4 °C. As shown in x-ray diffraction patterns in figure 4, W, Ni\(_3\)Al, and Co did not react, and reaction of Ni\(_3\)Al and Co was restrained by W, which improved the formation temperature of (Ni, Co)\(_3\)Al\(_4\) phase to Co\(_2\)Al\(_9\) phase. Therefore, 1502.3 °C and 1548.4 °C may be the melting point of (Ni, Co)\(_3\)Al\(_4\) phase to Co\(_2\)Al\(_9\) phase in the

![Figure 3](image-url)

Figure 3. XRD patterns of W–6Ni\(_3\)Al–4Co alloys via different sintering processes. (a)-1200 °C, 30 min; (b)-1450 °C, 20 min; (c)-1500 °C, 20 min.

| Sample no. | Volume fraction of phases/% |
|------------|----------------------------|
|            | W   | (Ni, Co)\(_3\)Al\(_4\) | Co\(_2\)Al\(_9\) |
| a          | 92  | 6.77          | 1.23            |
| b          | 88.72 | 8.53          | 2.75            |
| c          | 90.82 | 8.41          | 0.77            |
90W–6Ni3Al–4Co compaction. These results indicate that the densification of 90W–6Ni3Al–4Co alloy can be improved by alloying of Ni3Al and Co, while the alloying of Ni3Al and Co was restrained by W under 1502.3 °C.

### 3.2. Microstructure of W–6Ni3Al–4Co alloys

Figure 6 compares the effect of sintering process on the microstructure of W–6Ni3Al–4Co alloys. The microstructure evolution of W–6Ni3Al–4Co alloys sintered at the temperature of 1200 °C, 1450 °C, and 1500 °C is shown in the figure. The average grain size was measured by the intercept method. To analyze the elemental and phase distribution, EDS analysis of W–6Ni3Al–4Co alloy was performed at 1500 °C for 20 min (see figure 7). The microstructure was composed of white W phase, light gray binder phase, dark gray binder phase, and black

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**Figure 4.** DTA analysis of 60Ni–40Co, 60Ni3Al–40Co and 90W–6Ni3Al–4Co green bodies. (a)–60Ni–40Co; (b)–60Ni3Al–40Co; (c)–90W–6Ni3Al–4Co.

**Figure 5.** Ni–Co binary phase diagram.
pores. As shown in figure 6(a), white W phase of the alloy sintered at 1200 °C for 30 min exhibited stripes, which is similar to that of W–6Ni–4Co alloy in same conditions. However, the pore volume of W–6Ni3Al–4Co alloy was less than that of W–6Ni–4Co alloy, and the distribution of pores was non-uniform. The average grain size of
W–6Ni3Al–4Co alloy sintered at 1200 °C for 30 min was 2.77 μm, which is more than that of W–6Ni–4Co alloy in same conditions. This is because the microhardness and strength of Ni3Al powder was higher than that of Ni powder, restraining its deformation and fragmentation, which hindered the process of ball milling refinement and increased the particle size of Ni3Al powder and grain size of the alloy sintered. At 1450 °C for 20 min, white W phase of alloy began to connect into network, and the pores decreased, and the average grain size was 3.99 μm, which is more than that of W–6Ni–4Co alloy in same conditions (see figure 6(b)). This is caused by the densification effect of Ni3Al above 1293 °C. Moreover, Ni3Al liquid phase can be the medium for W grain growth. The densification parameter of alloy at 1500 °C for 20 min was the largest, and the average grain size was 4.37 μm (figure 6(c)).

To compare the densification parameter of W–6Ni3Al–4Co and W–6Ni–4Co alloys under two-step sintering process, figure 8 shows histogram of densification parameter of W–6Ni3Al–4Co and W–6Ni–4Co alloys. The W–6Ni3Al–4Co alloy under solid phase sintering at 1200 °C for 30 min was more compact, which can be observed in figure 6. However, the densification parameters of W–6Ni3Al–4Co alloy at 1450 °C and 1500 °C were lower than those of W–6Ni–4Co alloy. These results can be attributed to the thermal expansion behaviors of (Ni, Co)3Al4 phase and Co2Al9 phase, which prevented the shrinkage. Hence, the densification process was slow.

3.3. Mechanical properties of W–6Ni3Al–4Co alloys

Figure 9 shows microhardness, bending strength, and compressive strength of W–6Ni3Al–4Co alloy under different sintering processes. The data is shown in table 4. The yield strength and compressive toughness were calculated by true stress-strain curves of the compressive test. The microhardness of alloy at 1200 °C was the lowest, but was higher than that of W–6Ni–4Co alloy at 1200 °C. The microhardness increased to 518.3 HV with increase in sintering temperature to 1450 °C because of the densification strengthening effect and structure reinforcement effect of network W phase in alloy under two-step sintering at 1450 °C for 20 min. At 1500 °C, the W phase began to grow, and the microstructure was compact, improving its microhardness. The microhardness of alloy at 1500 °C was 529 HV, which is less than that of W–6Ni–4Co alloy in same conditions. The variation trend of compressive strength was similar to that of microhardness. The compressive strength of alloy at 1500 °C for 20 min was highest with the value of 1312 MPa. This can be attributed to densification during liquid phase sintering, enhancing the densification strengthening effect. The yield strength, compressive toughness, and bending strength also reached highest at 1121 MPa, 140 J cm−2, and 558 MPa at 1500 °C for 20 min. Thus, the mechanical properties of W–6Ni3Al–4Co alloy under different sintering processes were closely related with densification. Figure 10 shows the true stress-strain curves of the compressive test. The plastic deformation of alloys at 1200 °C, 1450 °C, and 1500 °C were 50%, 57%, and 57.8%, respectively, which are higher than those of W–6Ni–4Co alloy, indicating a better ductility. This is because ductility of the alloys depends on their porosity and pore distribution, suggesting an important role of densification and uniformity of microstructure on the ductility.

Figure 11 shows the fracture morphology of W–6Ni3Al–4Co alloys under bending test by using SEM. The fracture modes include binder phase rupture (I), W–W grain boundary separation (II), and W–binder phase interface separation (III). The porosity of alloy at 1200 °C was higher, reducing its strength (table 4). The main
fracture modes of alloy at 1200 °C were binder phase rupture (I) and W-binder phase interface separation (III). At 1450 °C, the densification parameter increased. The proportion of W-binder phase interface separation in this alloy increased. When the sintering temperature was increase to 1500 °C, the proportion of binder phase rupture increased, indiciting its better interfacial bonding strength.

Figure 12 presents the fracture morphology of W–6Ni3Al–4Co alloys under compressive test by using SEM. The ductile fracture (D) and brittle fracture (B) were the main fracture modes. At 1200 °C, the pores in alloy had uneven distribution, resulting in alternate fracture with step mode (see figure 12(a)). The main fracture mode in alloy at 1450 °C was ductile fracture (D), which was due to its dense microstructure, while brittle fracture (B) was observed around the pores (figure 12(b)). At 1500 °C, the ductile fracture (D) increased, demonstrating its excellent ductility. Thus, the properties of W–6Ni3Al–4Co alloys can be enhanced by increasing the sintering temperature.

| Sample no. | HV  | $\sigma_{bb}$/MPa | $\sigma_b$/MPa | $\sigma_{0.2}$/MPa | $A_t$/J·cm$^{-3}$ |
|------------|-----|------------------|----------------|-------------------|------------------|
| A          | 292.7 | 282              | 363.3          | 303.1             | 8.85             |
| B          | 518.3 | 464              | 711.3          | 512.7             | 33.92            |
| C          | 529.1 | 558              | 1312.1         | 1121.2            | 139.82           |

Figure 10. True stress–strain curves for compressive testing and schematic of yield strength and compressive toughness for W–6Ni3Al–4Co alloys via different sintering processes: (a) 1200 °C, 30 min; (b) 1450 °C, 20 min; (c) 1500 °C, 20 min.
3.4. Conclusion

The W–6Ni3Al–4Co alloys were prepared via solid phase sintering and two-step sintering. Ni was substituted by Ni3Al as a binder. The phase transformation, microstructure evolution, and strengthening and toughening were investigated. The results show that:

1. The alloying in W–6Ni3Al–4Co alloys mainly occurred in the Ni3Al–Co ternary system. The products include the (Ni, Co)3Al4 and Co2Al9 phases. The reaction temperature was reduced through Ni substituted by Ni3Al. The alloying of Ni3Al–Co ternary system was restrained by W under the temperature of 1502.25 °C. The grain size and densification parameter increased with the increase in sintering temperatures.

Figure 11. Fracture morphology for flexural testing of W–6Ni3Al–4Co alloys via different sintering processes: (a) 1200 °C, 30 min; (b) 1450 °C, 20 min; (c) 1500 °C, 20 min.

Figure 12. Fracture morphology for compressive testing of W–6Ni3Al–4Co alloys via different sintering processes: (a) 1200 °C, 30 min; (b) 1450 °C, 20 min; (c) 1500 °C, 20 min.
(2) The microhardness, bending strength, compressive strength, yield strength, and compressive toughness at 1500 °C for 20 min were the largest. Their maximum values were 529.1 HV, 558 MPa, 1312.14 MPa, 1121.22 MPa, and 139.82 J cm−2, respectively. The fracture modes under bending tests included binder phase rupture, W–W grain boundary separation, and W–binder phase interface separation, and those under compressive test include ductile fracture and brittle fracture.

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