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Properties and microstructural evolution of W-Ni-Fe alloy via microwave sintering

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The mechanical properties and microstructure evolution of 93W-4.9Ni-2.1Fe (wt.%) alloys were investigated via microwave sintering. The microwave sintering promoted the dissolution and diffusion of tungsten atoms in the matrix phase and strengthened sintering activity. With the increase of microwave sintering temperature, pores in the alloy were reduced and gradually eliminated, tungsten grains coarsened, the distribution of tungsten grains and matrix phase became more homogeneous, and the fracture mode transformed from intergranular fracture to tungsten transgranular cleavage fracture, respectively. The W-matrix interfacial bond strength of 93W-4.9Ni-2.1Fe was enhanced and the mechanical properties were significantly improved with the increase of sintering temperature.

1. Introduction

Tungsten heavy alloys are critical material for both military and civil applications because of their high density, high strength and good ductility [1,2]. These alloys are usually fabricated by conventional powder metallurgy (PM), which consumes too much sintering time and energy [3]. The average tungsten grain size generally varies from 20 μm to 60 μm, mechanical properties such as strength and ductility are low due to the coarse tungsten grain microstructure. Therefore, material researchers have been investigating and exploring new sintering technology to reduce grain size and refine microstructure to improve mechanical properties, such as employing mechanical alloying to increase powder activation and decrease sintering temperature [4], refining grain size by rare earth additions [5], plasma spraying [6], and laser sintering [7]. Microwave sintering provides a new technological innovation for sintering metal powders [8]. Microwave sintering has tremendous advantages over conventional sintering technique, such as heating by volumetric heating [9], a faster heating rate [10], short sintering time, finer microstructures, and improved mechanical properties. Therefore, the sintering technology of microwave has been widely applied in recent years. To date, material researchers have focused on ceramic materials sintered by microwave [11–13], which greatly enrich microwave sintering technology. However, tungsten heavy alloys fabricated by this technology has not been thoroughly investigated in the literature. The mechanical properties and microstructural evolution of 93W-4.9Ni-2.1Fe alloys sintered by microwave technology will be investigated mainly in this paper.

2. Experimental

Powders with the composition of 93W-4.9Ni-2.1Fe (wt.%) were milled in anhydrous ethanol in a planetary mixer (QM-1SP4 Nanjing, China) for 20 h at a speed of 200 rpm. The weight ratio of the balls to the powders mixture was 10:1. The extent of filling the planetary mixer with the powders, balls and anhydrous ethanol was about 50%. After dried in vacuum, the milled powders were mixed with 1 wt.% lubricant and 0.01 wt.% tungsten fibers. The tungsten fibers are 15 μm in diameter and 2–3 mm in length, which have little effect on the mechanical properties of final products can largely improve the degreasing efficiency and reduce deformation of the defatted samples. The mixture was consolidated into green tensile compacts (about 4.5 g) under a H41-25C type hydraulic presser. Fig. 1 shows the details of the green tensile specimen. After 800 °C pre-sintering treatment, the green compacts were sintered in a microwave furnace with frequency of 2.45 GHz (HAMiLab-V6) at the heating rate of 30 °C/min. Temperature is monitored using an infrared pyrometer (Raytek MM2MH, US). The whole sintering process was investigated at sintering temperatures 1250 °C, 1300 °C, 1350 °C, 1400 °C, 1450 °C and 1500 °C for 5 min in a flowing reducing atmosphere (10 vol.% H_2 and 90 vol.% N_2).

The density of the sintered specimen was characterized using Archimedes principle, and tensile strength and elongation were measured by a mechanical testing machine (INSTRON-8802) at a speed of 1 mm/min. Three samples were evaluated per condition. The tensile fracture morphology was observed by JSM-6360LV type scanning electron microscope (SEM) made by JEOL. The qualitative and quantitative analysis of elements were carried out by EDAX. The sintered specimens were polished by automatic polishing machine, and then, etched. The optical microstructure was observed with optical microscopy (MeF3A).

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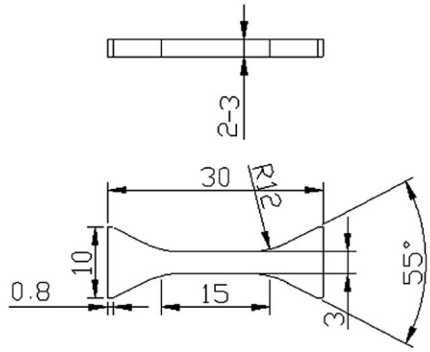

Fig. 1. The shape and dimension of the green tensile specimen.

3. Results and discussion

Fig. 2 shows the relative densities and mechanical properties of samples sintered at different temperatures for 5 min. As can be seen from Fig. 2(a) and (b), with the increase of sintering temperature from 1250 °C to 1500 °C, the relative density, elongation, tensile strength and hardness(HRC) were increased to maximum value of 98.8%, 16.4%, 1185.6 MPa and 42.1 (HRC) at 1500 °C, respectively. However, the hardness of sintered sample showed a slight decrease at 1450 °C.

Fig. 3 shows the fractures of 93W-4.9Ni-2.1Fe alloys sintered at different temperatures for 5 min via microwave sintering. It was clearly seen that many pores existed in Fig. 3(a), (b) and (c), which resulted in samples sintered at 1250 °C to 1350 °C failing under a lower stress.

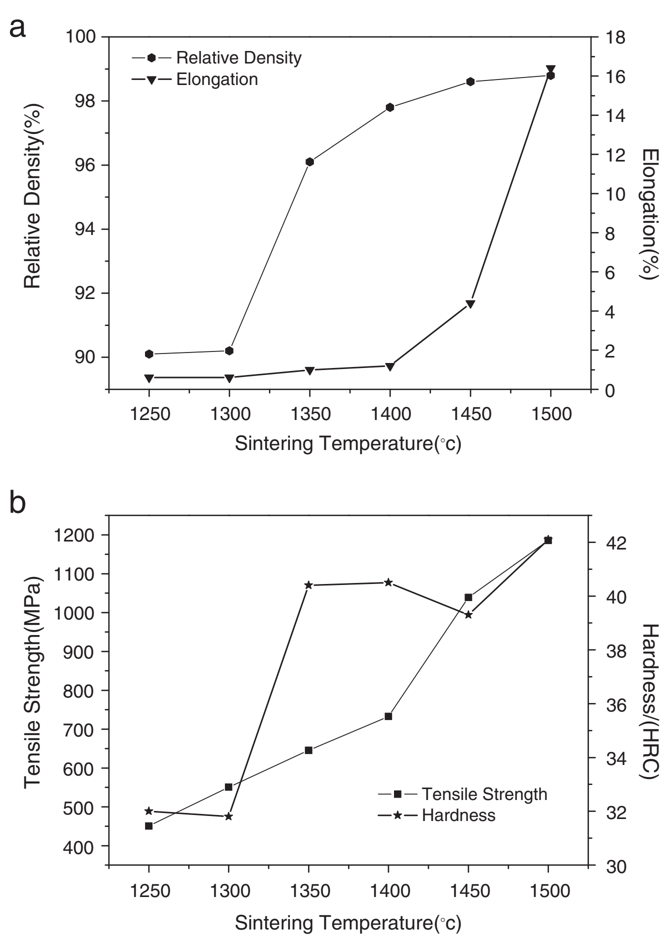

Fig. 2. The variation of: (a) relative density and elongation and (b) tensile strength and hardness of 93W-4.9Ni-2.1Fe alloys sintered via microwave with sintering temperature from 1250 to 1500 °C for 5 min.

Existence and inhomogeneous distribution of pores greatly weaken the bonding strength of W–W and W–matrix interface, which produced cracks and resulted in low mechanical properties. With the increasing of sintering temperature, pores in the samples were reduced and gradually eliminated. It can be seen from Fig. 3(c) and (d) that the polygonal tungsten grains formed significantly and (Ni,Fe) matrix phase emerged between tungsten grains. W–W intergranular failure and matrix failure were the primary fracture mode, resulting in improved mechanical proprieties. Tungsten grains in Fig. 3(d) was larger than those in Fig. 3(c), which suggested that dissolution–precipitation process occurred during solid state sintering [14]. Fig. 3(e) shows the fracture of sample sintered via microwave at 1450 °C for 5 min. Due to the higher sintering temperature, pores in Fig. 3(e) are gradually eliminated. Compared with Fig. 3(d), it is found that most tungsten grains transform from polygonal to spherical, suggesting that microwave sintering at 1450 °C is liquid-phase sintering process. These results reflect the advantage of lower sintering temperature of microwave sintering. It can also be seen from Fig. 3(e) that the fracture mode was primarily W-matrix interfacial separation with a few cleavage fracture of tungsten grains.

The fracture mode of tungsten-based alloys had direct effect on the mechanical properties. It is well known that there exist four kinds of fracture modes: matrix failure, W cleavage, W–W intergranular failure and W–matrix interfacial separation, and W cleavage had the maximum fracture strength. A certain amount of W cleavage was visible in Fig. 3(f), thus, the highest tensile strength was obtained by the sample sintered at 1500 °C, which indicated that this alloy was sintered by more full liquid-phase sintering process. During the process of more full liquid-phase sintering, the dissolution–precipitation appear obviously, the tungsten grains are spherical and uniformly surround by matrix phase, capillary force and viscous flow will tremendously contribute to the densification of alloys, resulting in mechanical properties improvement.

Fig. 4 shows the optical microscopy images of 93W-4.9Ni-2.1Fe alloys sintered at different temperatures for 5 min via microwave sintering. Because of the low sintering temperature, the samples sintered via microwave at 1400 °C or much lower were fabricated by solid-phase sintering, consequently, the small quantities of tungsten fibers used for improving the degreasing efficiency and reducing deformation of the defatted samples are visible in Fig. 4(a), (b) and (c), whose microstructure distributes inhomogeneously. Meanwhile, as can be seen from Fig. 3(a), (b) and (c), numerous pores exist in the alloys sintered via microwave at 1250, 1300 and 1350 °C. It suggested that it were the pores and the inhomogeneous microstructure that led to tremendous changes of hardness on various parts of the samples. Fig. 4(b) and (c) show sintering necks between the tungsten grains (marked by arrows), which would promote the diffusion between tungsten grains and contribute to the densification of the alloy [14]. As the sintering temperature was increased, diffusion was enhanced and densification was accelerated, which resulted in the improvement of tensile strength. In Figs. 3(d) and 4(d), most of tungsten grains are polygonal. During solid-phase sintering, densification increased with tungsten grains growth and pores reduction and elimination. Fig. 4(e) shows that the near spherical tungsten grains are surrounded by a certain amount of matrix phase, which further implies that the alloys sintered via microwave at 1450 °C are liquid-phase sintering process. When the temperature is higher than 1460 °C, the samples will be sintered at the liquid-phase sintering process [5]. However, the microwave sintering is a kind of activated sintering, because microwave field can reduce the tungsten diffusion barrier and promote a lower sintering temperature. Consequently, when microwave sintering temperature is at 1450 °C, a certain amount of liquid phase occur in the alloys and tungsten grains coarsen obviously. Liquid phase spread in the surface of grains and filled the pores between tungsten grains, leading to a greater densification with the relative density of 98.6% in Fig. 2(a). However, due to the short sintering time, the liquid-phase sintering process had not been fully completed, consequently, the tungsten grains were not

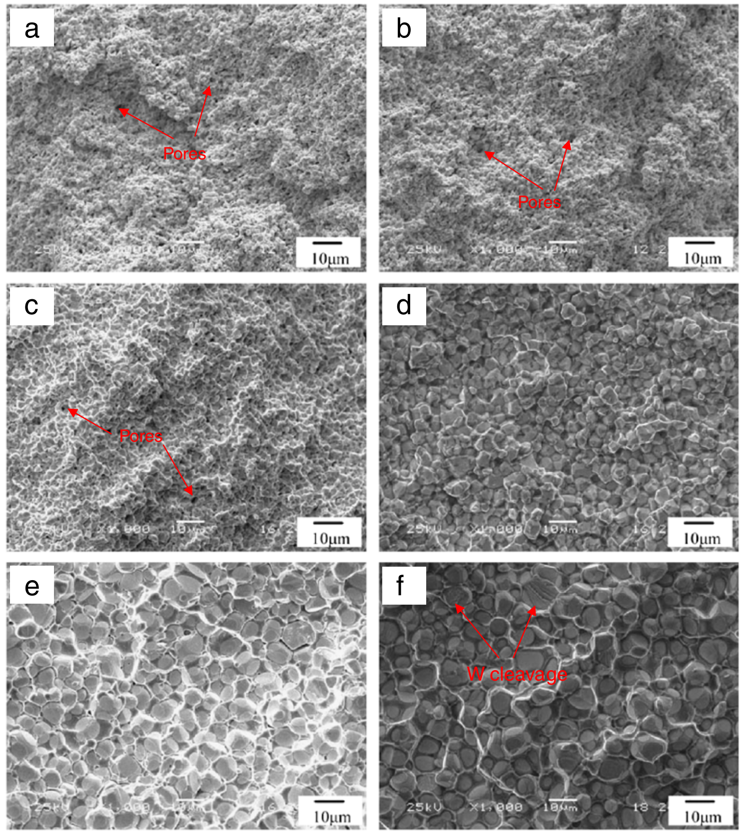

Fig. 3. Fractures of 93W-Ni-Fe alloys sintered at different temperatures for 5 min via microwave sintering:(a) 1250 °C; (b)1300 °C; (c)1350 °C; (d) 1400 °C; (e)1450 °C; and (f) 1500 °C.

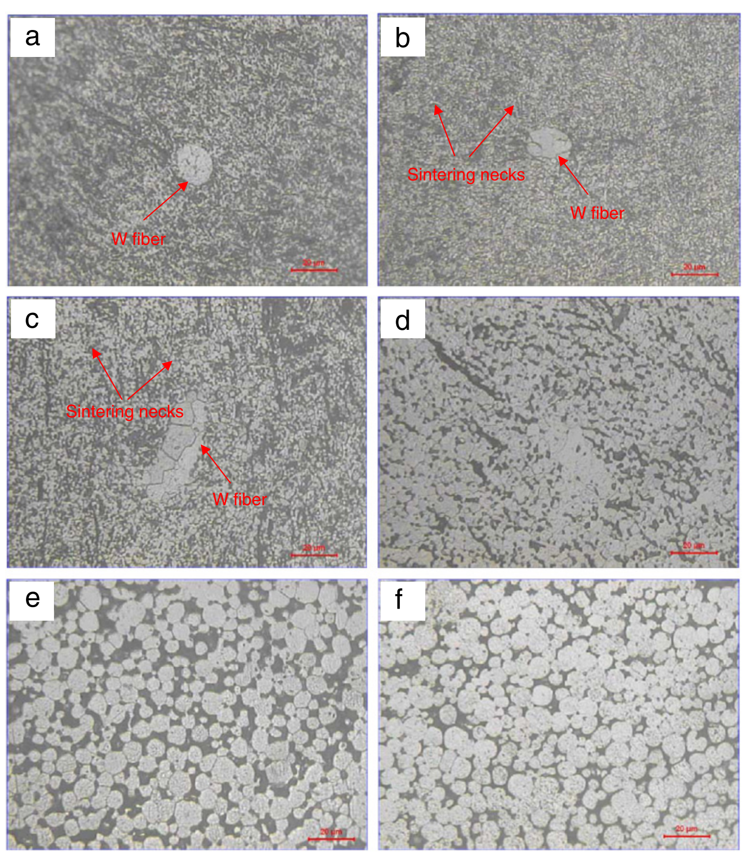

Fig. 4. Optical microscopy images of 93W-Ni-Fe alloys sintered at different temperatures for 5 min via microwave sintering: (a) 1250 °C; (b) 1300 °C; (c) 1350 °C; (d) 1400 °C; (e) 1450 °C; and (f) 1500 °C.

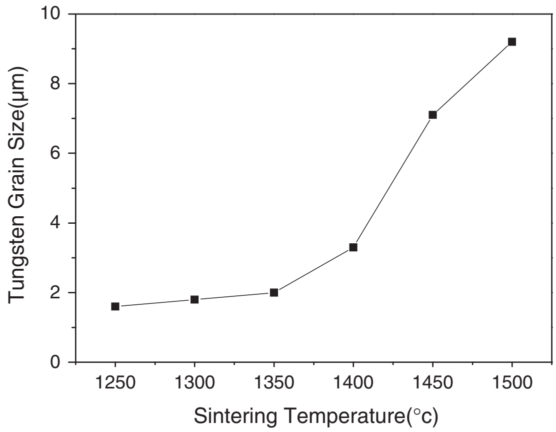

Fig. 5. The variation of average tungsten grain size of 93W-4.9Ni-2.1Fe alloys sintered via microwave with sintering temperature from 1250 to 1500 °C for 5 min.

entirely spherical, and as can be seen from Fig. 4(e), the tungsten grains and matrix phase were in an inhomegeneous distribution. The formation of a certain amount of liquid phase and the inhomegenous distribution of microstructure were the reason of the abnormal hardness. The sample of Fig. 4(f) was fabricated by liquid-phase sintering at a higher sintering temperature, in which tungsten grains grew obviously during the dissolution–precipitation process. The tungsten grains were spherical, and uniformly surrounded by matrix phase. The mechanical properties were greatly improved due to the homogeneous distribution of the microstructure of tungsten grains and matrix phase.

The average tungsten grain size of alloys sintered by microwave from 1250 °C to 1500 °C is shown in Fig. 5, it can be seen that the average tungsten grain size of alloys is gradually coarsened. However, with the increasing of sintering temperature, the pores are reduced, and the relative density is increased, these results illustrate that tungsten grains growing, pores reducing and density increasing are a simultaneously process. The maximum average tungsten grain size of alloys in Fig. 5 is 9.2 μm, which attributes to the refined crystalline strengthening and reflects the advantage of rapid sintering and refining grains of microwave sintering.

Table 1
Mass contents of dot scanning spectrum of W, Ni and Fe elements (wt.%).

Elements	Dot 1	Dot 2
W	96.57	35.79
Fe	1.40	19.46
Ni	2.03	44.74

Fig. 6 shows the dot scanning spectrum of the samples sintered at 1500 °C. Table 1 shows the mass fraction of the elements of W, Ni and Fe. The element contents of Ni and Fe were 2.03 wt.% and 1.40 wt.% in the tungsten grains because of the low solubility in W. Whereas, the mass fraction of tungsten in (Ni,Fe) matrix phase raised to 35.79% by comparing with 23 wt.% of usual tungsten-based alloys[15], which was because microwave field accelerated the diffusion and dissolution of the tungsten atoms in (Ni,Fe) matrix phase and resulted in increasing of the solubility of tungsten element in (Ni,Fe) matrix phase. A higher content of tungsten element in (Ni,Fe) matrix phase would lead to the formation of brittle phase [8], but due to the rapid microwave sintering and quick cooling effect, the formation of brittle phase was inhibited and sample maintained a higher elongation.

4. Conclusion

With the increase of sintering temperature from 1250 °C to 1500 °C, the relative density and mechanical properties of 93W-4.9Ni-2.1Fe alloy were improved. The relative density, elongation, tensile strength and hardness (HRC) of the alloy sintered at 1500 °C were 98.8%, 16.4%, 1185.6 MPa and 42.1 (HRC), respectively.

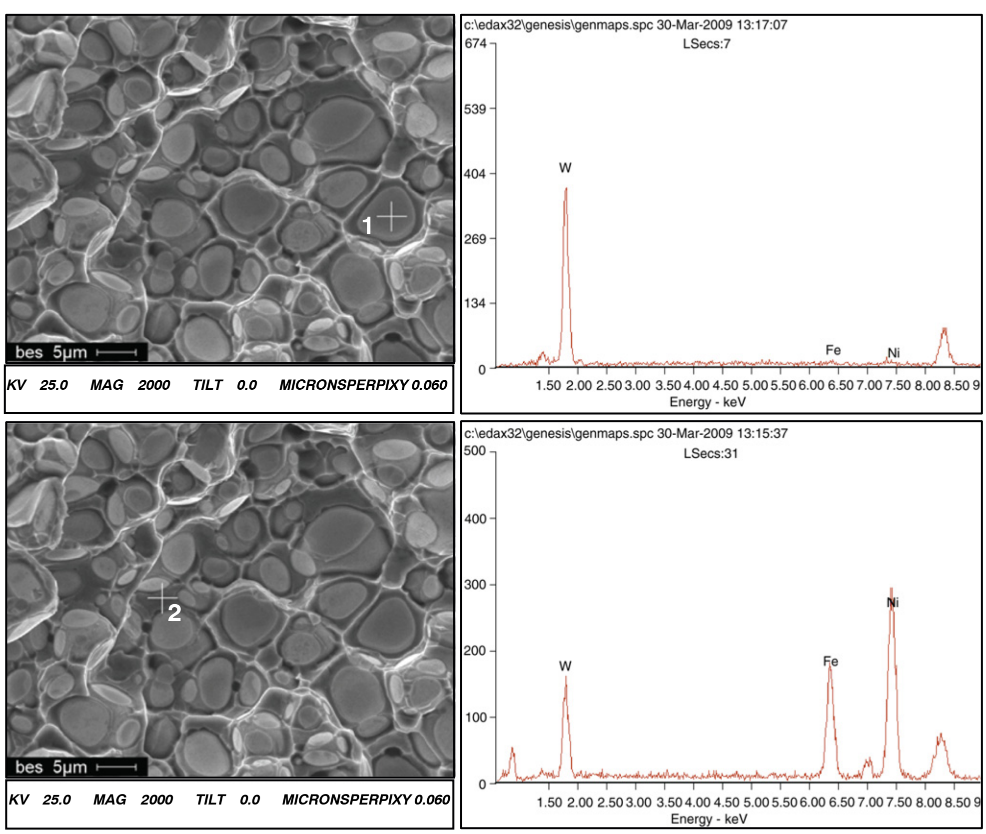

Fig. 6. Dot scanning spectrum of specimen (specimen sintered at 1500 °C for 5 min).

With the increase of sintering temperature, pores in the alloy were reduced and gradually eliminated, tungsten grains coarsened, distribution of tungsten grains and matrix phase became more homogeneous. The fracture mode of the samples was most of W–W intergranular fracture sintered at the temperature various from 1250 °C to 1450 °C.

Microwave sintering promoted the dissolution and diffusion of tungsten atoms in the matrix phase. The mass fraction of tungsten in matrix phase was up to 35.79% when sintered at 1500 °C for 5 min.

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