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Microstructure and properties of liquid-phase sintered tungsten heavy alloys by using ultra-fine tungsten powders①

YU Yang(于 洋), WANG Er-de(王尔德)
(School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China)

Abstract: The microstructure and properties of liquid-phase sintered 93W-4.9Ni-2.1Fe tungsten heavy alloys using ultra-fine tungsten powders (medium particle size of 700 nm) and original tungsten powders (medium particle size of 3 μm) were investigated respectively. Commercial tungsten powders (original tungsten powders) were mechanically milled in a high-energy attritor mill for 35 h. Ultra-fine tungsten powders and commercial Ni, Fe powders were consolidated into green compacts by using CIP method and liquid-phase sintering at 1 465 ℃ for 30 min in the dissociated ammonia atmosphere. Liquid-phase sintered tungsten heavy alloys using ultra-fine tungsten powders exhibit full densification (above 99% in relative density) and higher strength and elongation compared with conventional liquid-phase sintered alloys using original tungsten powders due to lower sintering temperature at 1 465 ℃ and short sintering time. The mechanical properties of sintered tungsten heavy alloy are found to be mainly dependent on the particles size of raw tungsten powders and liquid-phase sintering temperature.

Key words: tungsten heavy alloys; mechanical milling; liquid-phase sintering; ultra-fine tungsten powders; mechanical properties

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1 INTRODUCTION

Liquid-phase sintered tungsten heavy alloys (WHAs) show a typical microstructure where BCC tungsten particles are embedded in FCC W-Ni-Fe matrix. Generally, liquid-phase sintered WHAs are fabricated by blending raw powders of tungsten, nickel and iron and sintering at temperature above 1 460 ℃ in a hydrogen atmosphere[1]. Tungsten heavy alloys have been widely used as kinetic energy penetrators, counterweights, radiation shields, vibration damping devices and electrical contacts because of their high density, strength, ductility and low cost relative to other refractory metals[2-4]. Tungsten also does not pose the health hazard that was found with depleted uranium alloys used as long rod kinetic energy penetrators. Recently, numerous investigations have been carried out to improve the mechanical properties of tungsten heavy alloy, including adjusting Ni/Fe ratio, adding refractory elements such as Mo and Re, liquid-phase sintering, mechanical alloying (MA), and deformation strengthening[5-18], etc. The MA technique developed by Benjamin[19] is an advanced fabrication process that can produce ultra-fine and homogeneous powders. Therefore, MA technique can be used as a process to fabricate ultra-fine tungsten particles in order to improve the characteristics of raw powders, so the mechanical properties of WHA can be reinforced via liquid-phase sintering and other strengthening means.

The research of this program is to enhance the ductility of 93W-4.9Ni-2.1Fe tungsten heavy alloys through controlling the partifcle size of raw tungsten powders and microstructural parameters such as tungsten particles size, distribution of binder phase and tungsten particles. The mechanical properties of WHA are found to be related to microstructural parameters such as tungsten particle size, binder phase volume fraction and tungsten-tungsten contiguity[20]. The technical basis for this research program lies in the relationship between microstructure and extended plasticity in metals. In particular, the high plasticity in metals has been shown to be directly correlated with fine particle size in metals. In this study, the correlation between characteristics of raw tungsten powders and mechanical properties of liquid-phase sintered 93W-4.9Ni-2.1Fe heavy alloy is investigated.

2 EXPERIMENTAL

2.1 Preparation of ultra-fine tungsten powders

Commercial elemental W powders with a medium particle size of 3 μm was used as the starting milling material. Mechanical milling of W powders was performed in an argon atmosphere by using a high-energy attritor mill. Commercial elemental Ni powders and Fe powders with a medium particle size

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Correspondence: YU Yang, Candidate for PhD; Tel: +86-451-86414267; E-mail: hityuyang@263.net

of 5 μm were used as the starting materials. The characteristics of original powders are listed in Table 1. Table 2 gives the composition of sintered samples used in this investigation.

Table 1 Properties of original powders

Original powder	Purity/ %	Average size/ μm	Impurity/ %		
			C	O	P
W	99.9	3.0	< 0.01	< 0.08	—
Ni	99.5	5.0	< 0.10	< 0.10	< 0.000 5
Fe	99.5	5.0	< 0.02	< 0.20	—

Table 2 Composition of liquid-phase sintered samples(93W-4.9Ni-2.1Fe)

Sample	Composition	Medium size of W particles/ μm
I	Ultra-fine W powders+ binder(Ni, Fe)	0.7
II	Original W powders+ binder(Ni, Fe)	3.0

2.2 Preparation of tungsten heavy alloy specimens

The evolution of W powders milled for different time was evaluated by X-ray diffraction (XRD) analysis. The crystallite size and microstrain of the as-milled powders were calculated on the basis of the half-width of the most intensive diffraction peaks of the XRD patterns. The morphologies and particles size of the as-milled W powders were analyzed by scanning electron microscopy (SEM). The mixed ultra-fine W powders and Ni-30% Fe powders (binder phase) were blended in a tumbler ball mill for 25 h. Then the mixed powders were consolidated into green compacts by cold isostatic pressing (CIP). The sintering process was carried out in a molybdenum tube furnace in dissociated ammonia atmosphere at 1 445 ℃, 1 465 ℃ and 1 480 ℃ for 30 min. The sintering process of WHA sample by using ultra-fine tungsten powders is shown in Fig. 1. The particle size distribution of two kinds of tungsten powders used in this study is shown in Fig. 2. The same binder phase for two samples was used.

All sintered specimens were annealed at 1 200 ℃ for 2 h in vacuum and then water quenched to degas hydrogen. The density of the sintered specimens was measured by the Archimedes water immersion method. The size of tungsten particles and distribution of binder phase of sintered WHAs were characterized by using scanning electron microscope. Room temperature tensile tests were performed at a strain rate of $2.0\times10^{-3}\ s^{-1}$.

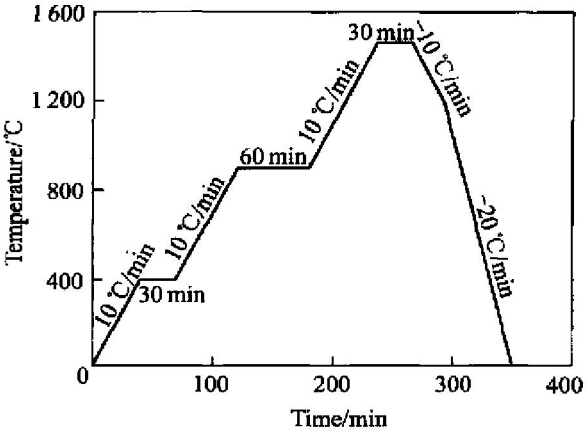

Fig. 1 Sintering temperature, sintering time and heating rate of sample by using ultra-fine tungsten powders
(Sintering at 1 445 - 1 480 ℃ for 30 min)

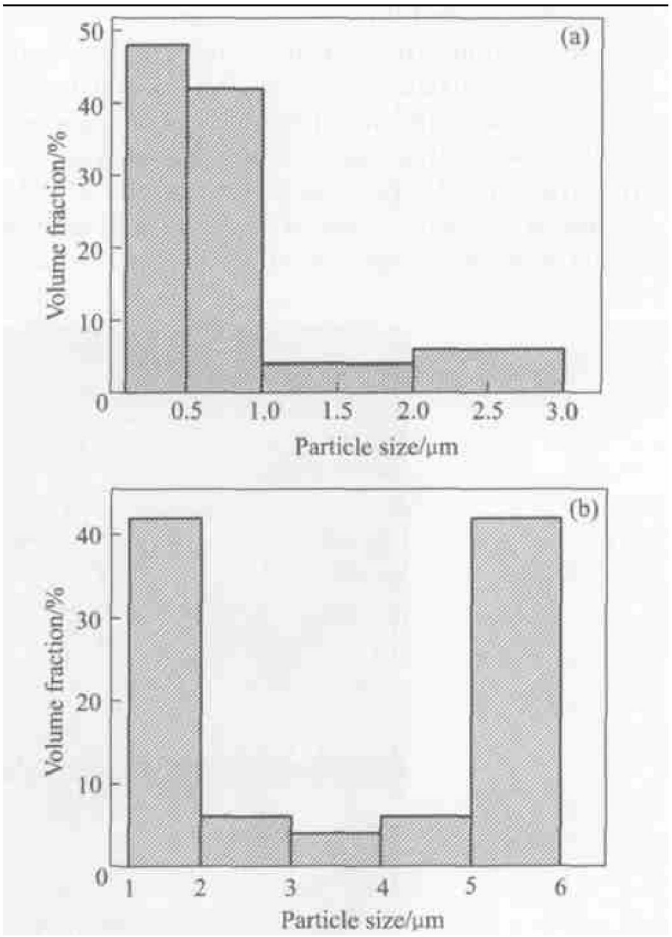

Fig. 2 Particle size distribution of tungsten powders
(a) —Ultra-fine tungsten powders obtained by mechanical milling for 35 h;
(b) —Original tungsten powders

3 RESULTS AND DISCUSSION

3.1 Microstructure of ultra-fine tungsten powders

Fig. 3 and Fig. 4 show the X-ray diffraction spectra and the changes in lattice parameter of W grains with increasing milling time measured by

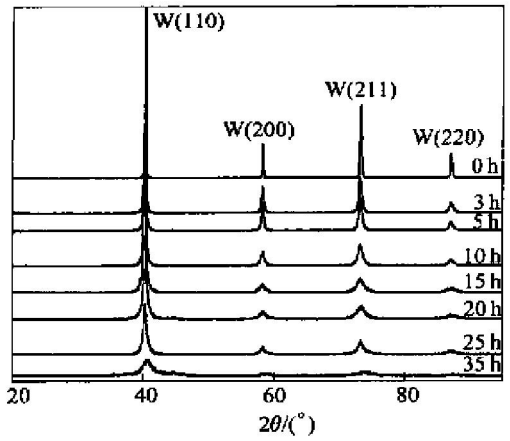

Fig. 3 XRD spectra of W powders milled for various milling time

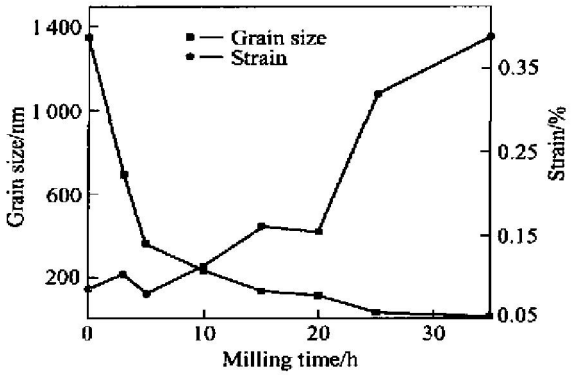

Fig. 4 Effect of milling time on grain size and microstrain of W

XRD. Broadening of the XRD peaks and reduction in intensity are associated with the refinement of crystalline size and internal elastic strain. The average crystalline size is about 14 nm and the accumulated microstrain is 0.41% after milling for 35 h. The W particles morphologies and microstructure for the starting sample and 35h-milled sample are shown in Fig. 5(a) and (d) respectively. The original W powder is characterized by well-formed crystal with an average size of 3 μm. The mechanical milling process has significantly decreased the W particle size and also changed its shape. It can be clearly seen that the original polyhedron W particles change into irregular particles after being milled for 35 h. At the same time, the medium particles size of tungsten powders decreases to ultra-fine size, about 700 nm.

3.2 Microstructure and mechanical properties of liquid-phase sintered samples

Fig. 6 shows SEM micrographs of sample I

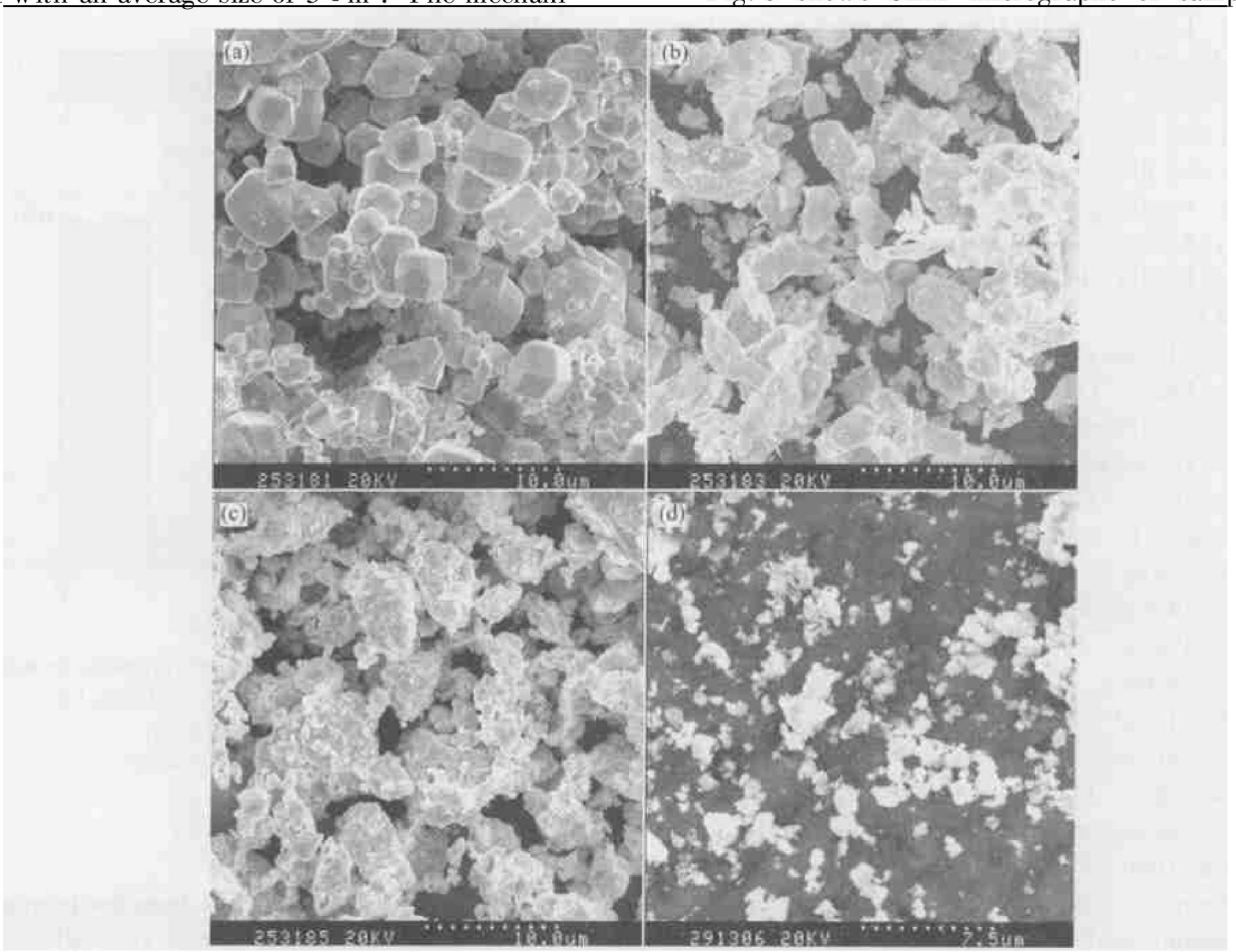

Fig. 5 Morphologies of as-milled W powders
(a) —0 h; (b) —5 h; (c) —15 h; (d) —35 h

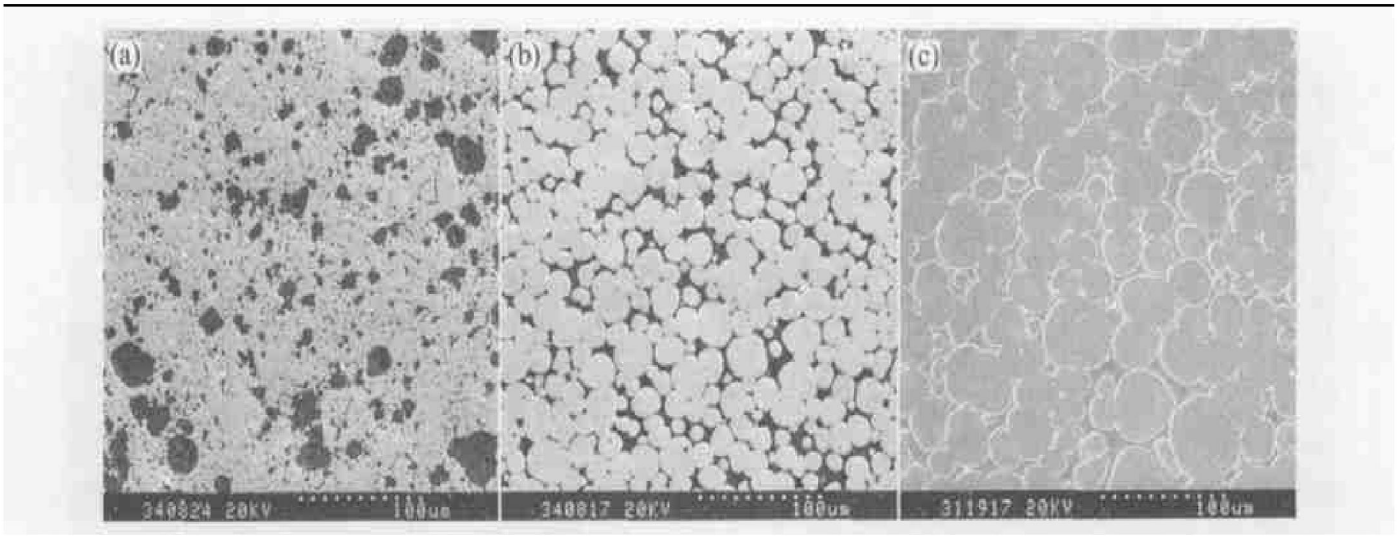

Fig. 6 SEM micrographs of sintered 93W-4. 9Ni-2. 1Fe tungsten heavy alloys (sample Ⅰ) sintered at 1 445 ℃(a), 1 465 ℃(b), 1 480 ℃(c) for 30 min

sintered at temperature ranging from 1 400 ℃ to 1 480 ℃ for 30 min. When sintered at 1 445 ℃, the tungsten particles remain high contiguity, as shown in Fig. 6(a). However, the tungsten particles are quasi-spherical in shape when sintered at 1 465 ℃. At the same time, the matrix volume fraction increases and the tungsten-tungsten contiguity decreases. For sample Ⅰ, the average size of tungsten particles increases from 20 μm to 50 μm, as shown in Fig. 6 (b) and (c). It indicates that the growth of fine tungsten particle is very sensitive to temperature. The stored energy and defects of W particles by severe cold working during MA enhance the diffusion capabilities between different atoms during sintering process and result in a high density. When sintered at temperature below 1 465 ℃, sample Ⅰ shows lower density than samples sintered at 1 465 ℃(the relative density is above 99%), as shown in Fig. 7. Particularly, the density of sample Ⅰ sintered above 1 480 ℃ decreases because of the increase of liquid phase volume, which results in porosities. Sample Ⅰ could obtain higher density than sample Ⅱ at the same sintering temperature, that is to say, 93W-4. 9Ni-2. 1Fe alloy used ultra-fine tungsten powders could be densified easily compared with conventionally sintered 93W-4. 9Ni-2. 1Fe alloy during LPS, as shown in Fig. 7 (sintering time: 60min). Fig. 8 shows the effect of sintering time on relative density. It is also indicated that sample Ⅰ can acquire higher density at the same sintering temperature than that of sample Ⅱ, it need short sintering time.

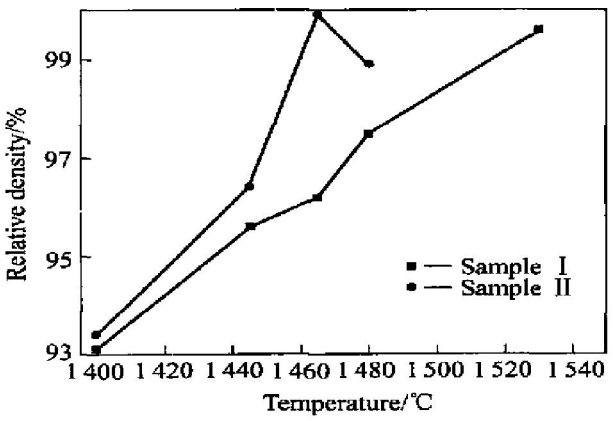

Fig. 7 Effect of sintering temperature on relative density

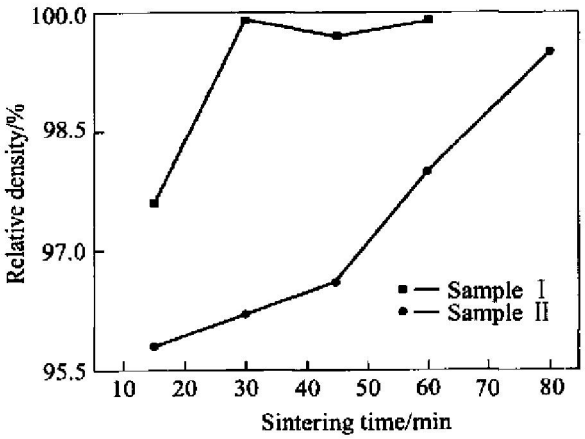

Fig. 8 Effect of sintering time on relative density (Sample Ⅰ sintered at 1 465 ℃ and sample Ⅱ sintered at 1 530 ℃)

All sintered specimens were annealed at 1 200 ℃ for 2 h in vacuum condition and then water-quenched. Fig. 9 shows the SEM micrographs of annealed 93W-4. 9Ni-2. 1Fe samples. The distribution of binder phase for sample Ⅰ is more homogeneous than that of sample Ⅱ. Then the correlation between microstructure factors and mechanical properties are obtained from tensile tests of sintered 93W-4. 9Ni-2. 1Fe alloys at 1 465 ℃ for 30 min. The fracture surfaces of specimens show that the different fracture modes operate for different conditions including com-

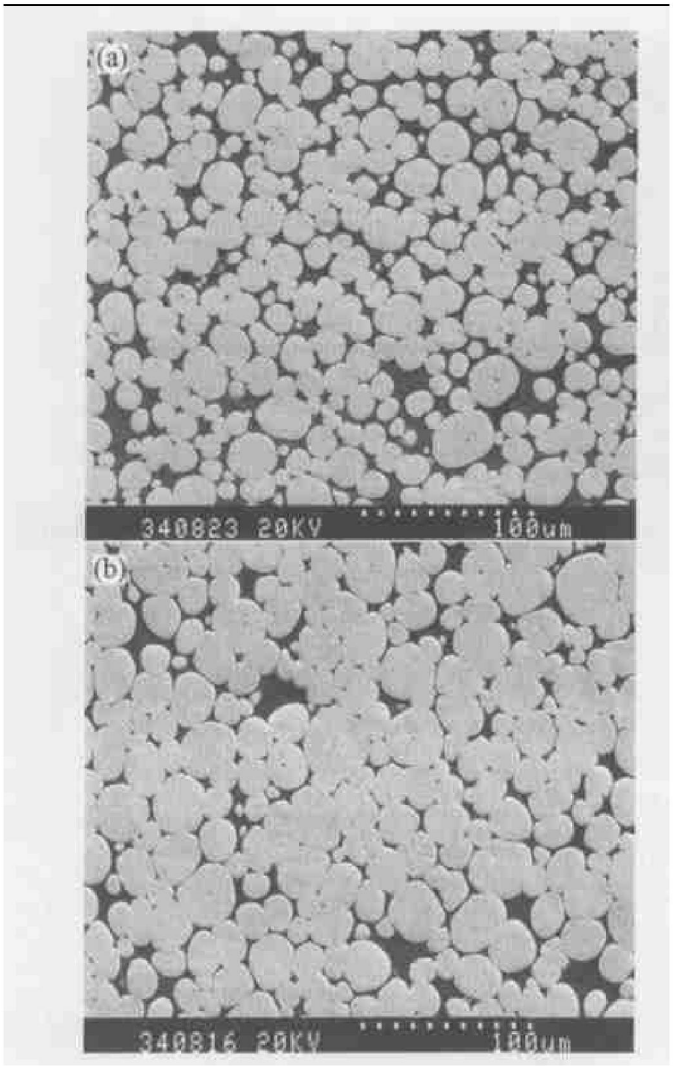

Fig. 9 SEM micrographs of sintered samples after heat treatment at 1 200 ℃ for 2 h in vacuum
(a) —Sample I (sintering at 1 465 ℃);
(b) —Sample II (sintering at 1 530 ℃)

position and sintering temperature, as shown in Fig. 10. Tungsten heavy alloy can exhibit four fracture modes such as tungsten-tungsten interfacial debonding, tungsten-binder phase interfacial debonding, binder phase rupture and tungsten cleavage. Compared with conventional liquid-phase sintered 93W-4.9Ni-2.1Fe alloy (Sample II), tungsten cleavage and matrix rupture are mainly observed in sample I which uses ultra-fine tungsten powders. The mechanical properties can be explained in terms of microstructural factors such as tungsten grain size, distribution of binder phase. The high strength of a WHA is obtained by decreasing tungsten particle size and homogeneous distribution of binder phase. As the strength of pure tungsten is very high, more cleavage of tungsten particles indicates that tungsten heavy alloy has higher strength. The macro-fractograph of tensile fracture surfaces and mechanical properties can be seen from Fig. 10 and Table 3.

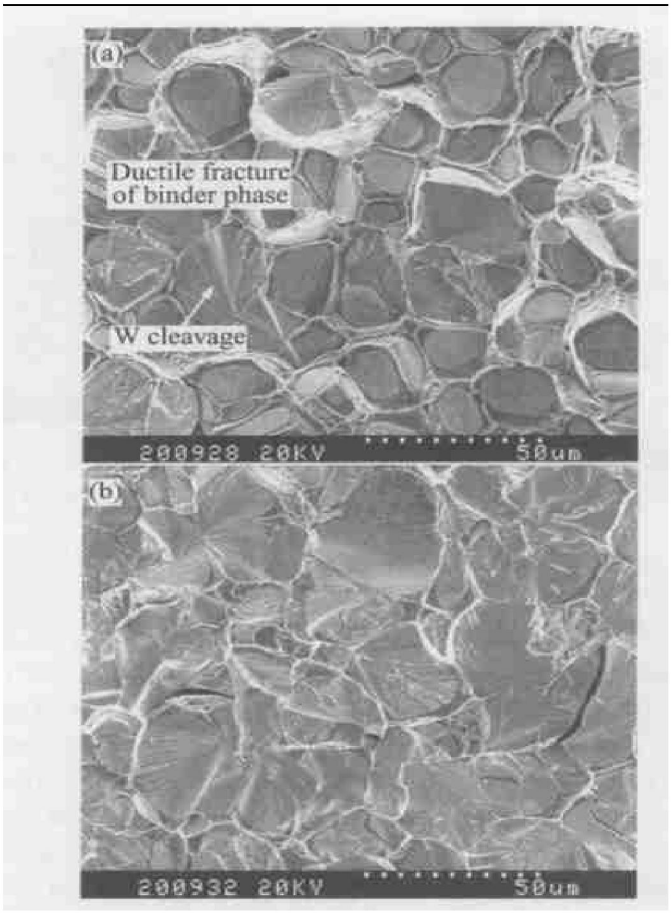

Fig. 10 Fractographs of tensile fracture surfaces for sintered samples after heat-treatment in vacuum
(a) —Sample I; (b) —Sample II

Table 3 Mechanical properties of liquid-phase sintered samples (room temperature)

Sample	σ_b/MPa	δ/%
I	1 024	23.4
II	960	23.0

3.3 Effect of W particles size on mechanical properties of liquid-phase sintered samples

Ultra-fine tungsten powders can be produced by mechanical milling and the size distribution is more homogeneous than the starting tungsten powders, as shown in Fig. 2. Moreover, 93W-4.9Ni-2.1Fe WHA used ultra-fine tungsten powders exhibits higher strength, elongation and fine microstructure after liquid-phase sintering at 1465 ℃ for 30 min.

4 CONCLUSIONS

Ultra-fine tungsten powders (medium particle size of about 700 nm) can be obtained by mechanical milling. After liquid-phase sintered at 1 465 ℃, 93W-4.9Ni-2.1Fe WHA using ultra-fine tungsten powders shows fine microstructure, in which quasi-sphere tungsten particles are about 20 μm in diameter and the binder distribution is homogeneous. Liquid-

phase sintered WHA exhibits high relative density (above 99%) and high mechanical properties due to fine tungsten particle and binder phase of homogeneous distribution. The mechanical properties of liquid-phase sintered WHA are found to be mainly related to microstructural parameters such as original tungsten particle size and sintering temperature.

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