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Grain growth behavior and mechanical properties of zirconium micro-alloyed and nano-size zirconium carbide dispersion strengthened tungsten alloys

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ABSTRACT

Dense fine-grained pure W, W–1.0 wt.%Zr (WZ), W–1.0 wt.%ZrC (WZC) and W–1.0 wt.%Zr–1.0 wt.%ZrC (WZZC) alloys were fabricated by spark plasma sintering. The grains in WZ and WZZC alloys are stable at annealing temperatures below 1400 °C (1 h), while the grains in pure W grow significantly above 1100 °C annealing. The tensile tests indicate that WZ is ductile already at 400 °C, which is about 200 °C lower than that for pure W. WZC exhibits higher hardness at room temperature than pure W. The ultimate tensile strength of WZC at 600 °C is 798 MPa, about 2.6 times that of pure W. Based on microstructural analysis, the good thermal stability of tungsten grains in WZ and WZZC samples is suggested to be originated from the W–Zr–O and/or Zr–C–O particles which are dispersed on or near the grain boundaries of tungsten and inhibit their migration. The improved tensile properties of the WZ, WZC and WZZC alloys originate (i) from the enhanced GB cohesion by Zr micro-alloying and (ii) from dispersion strengthening by nano-sized ZrC particles.

1. Introduction

Tungsten is a promising candidate as plasma facing material (PFM) in fusion reactors and target material in spallation neutron sources, because of its excellent properties such as high melting point, low sputtering ratio, high thermal conductivity and neutron yield [1–3]. However, tungsten exhibits a low temperature embrittlement due to its high ductile to brittle transition temperature (DBTT), recrystallization embrittlement, as well as radiation embrittlement. These problems affect its use in nuclear fusion applications. Although it is usually not used for structural purposes due to its brittleness at low temperatures, W based alloy must retain structural integrity over the lifetime. In this sense, improving the mechanical properties of W based materials is particularly important for their application in nuclear fusion environment.

It is known that polycrystalline W has a high DBTT of about 800 °C. This is mainly attributed to the sensitivity of polycrystalline W to impurities such as O, N and P, which aggregate on the grain boundaries (GBs) and decrease the GB cohesion [4–6]. Therefore, reducing the aggregation of impurities on the GBs of W and refining grain are crucial for fabricating high performance W based materials.

Refining the grains to obtain nano-structure or ultra-fine grained (UFG) W may solve this problem to some extent by increasing GBs area and decreasing the average concentration of impurities at GBs, and thus improves the toughness of W [7]. Moreover, the large amount of GBs could serve as effective sinks for irradiation induced point defects and thus may improve the irradiation-resistance [8–10]. Nevertheless, the large density of GBs also leads to an inherent instability especially under high temperature [11]. Meanwhile, it remains one difficult issue that pure W has low high-temperature strength, undergoes recrystallization at relatively low temperature (~1200 °C) and its grains grow rapidly at higher temperatures which further reduces the fracture toughness [12]. Favorable properties, such as low-temperature ductility and good machining capabilities, have been achieved for tungsten–rhenium alloys. These advantages are, however, counter balanced by a higher radiation-induced embrittlement rate and higher cost because of the expensive Re.

It was reported that micro-alloying could strengthen GBs of refractory materials by adding minor active elements such as titanium (Ti), zirconium (Zr) and hafnium (Hf). These micro-alloying elements can react with impurities such as O and C to form compounds with high melting temperature [13,14]. Meanwhile, first-principle calculations also indicate that the cohesion effect of transition metals, such as Zr, Hf, and Re, on W GBs could significantly strengthen the GBs [12]. In our previous work [15], W–Zr alloy showed considerable enhancement in the room-temperature fracture strength and toughness due to the Zr capturing oxygen in tungsten, forming nano-scale zirconia particles,

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alleviating the detrimental effect of oxygen and hence effectively strengthening the GBs of W.

On the other hand, dispersing minor carbide or oxide fine particles with high thermodynamic stability, such as TiC, ZrC, La_2O_3 and Y_2O_3, into tungsten is very effective in refining the grains, inhibiting the movement of dislocations and stabilizing the microstructure at high temperature, and thus increase the high-temperature strength, recrystallization temperature and decrease the grain growth rate of tungsten [11,16–20]. For example, UFG W–TiC compacts showed high fracture strength of 2 GPa at room-temperature, super-plasticity at 1400–1700 °C, and superior resistance to neutron irradiation [16]. Among the strengthening phases, ZrC has a very high hardness, and its melting temperature is as high as 3540 °C, which is much higher than TiC (3160 °C), La_2O_3 (2215 °C) and Y_2O_3 (2690 °C). These superior performances make ZrC very attractive in the strengthening of tungsten.

Most tungsten products are fabricated by powder metallurgy (PM) methods, because of the difficulties associated with the high melting point of the material at 3410 °C. Among various PM techniques, spark plasma sintering (SPS) is a pressure-assisted sintering that utilizes a large pulsed DC current (1000–5000 A) to heat the compacts and molds. The SPS process provides fast heating rate (up to 1000 °C/min) and short sintering time, and allows the consolidation of powder materials into dense fine-grained products at lower sintering temperature.

The aim of this work is to combine the micro-alloying, dispersion strengthening and SPS technique to obtain high performance W alloys. Dense fine-grained pure W, W–1.0 wt.%Zr, W–1.0 wt.%ZrC and W–1.0 wt.%Zr–1.0 wt.%ZrC alloys were fabricated through SPS method. The consolidation behavior, thermal stability, microstructure, tensile behavior and hardness were comparatively investigated.

2. Experimental details

2.1. Starting materials, ball milling method and fabrication

Pure tungsten samples, W–1.0 wt.%Zr (designated as WZ), W–1.0 wt.%ZrC (designated as WZC) and W–1.0 wt.%Zr–1.0 wt.%ZrC (designated as WZZC) alloys were fabricated from pure W (particle size 400–600 nm, purity > 99.9% trace metals basis, purchased from Xiamen Tungsten reagent Co., LTD., chemical content listed in Table 1), ZrH_2 (particle sizes 10–20 μm, purity > 99.9%, purchased from Aladdin reagent Co., LTD.) and nano-size ZrC powders (average particle size 50 nm, purity > 99%, purchased from Aladdin reagent Co., LTD.), the scanning electronic microscopy (SEM) images of which were shown in Fig. 1a, b and c, respectively. Powders were ball milled for 4 h in argon atmosphere in a planetary ball mill with ball-to-powder weight ratio of 8:1 and a rotation speed of 240 rpm. After ball milling, the aggregation of raw W powders was partially eliminated and the mixture of powders is homogeneous, as shown in Fig. 1d.

The consolidation was carried out by SPS (furnace SE-607, FCT Group, Germany) technique. The as-prepared powders were loaded in a graphite mold (as shown in Fig. 2a), heated to 1800 °C and held for 2 min under 50.9 MPa. The detailed temperature and pressure profile of the sintering program was illustrated in Fig. 2b. For each component, four samples were prepared by SPS following the same sintering program which was described in more detail elsewhere [15]. The size of the sintered samples was about 20 mm in diameter and 2.5 mm in thickness. The full densities of W, Zr and ZrC were taken as 19.25 g/cm^3, 6.49 g/cm^3 and 5.01 g/cm^3, respectively.

Table 1
Chemical composition of the as-received tungsten powders (wt.%).

	Cr	Ti	Fe	O	C	P	S	N	W
W powder	0.0005	0.0005	0.001	0.24	0.0029	0.0005	0.0005	–	Bal

2.2. Heat treatment and Vickers micro-hardness

For each alloy, four SPSed samples were cut into 4 × 4 × 1 mm^3, mechanically polished and then annealed at four temperatures (1100 °C, 1200 °C, 1300 °C and 1400 °C) for 1 h in vacuum, respectively. The heating and cooling rate were all 10 °C/min during the heat treatment process. Then the annealed samples were subjected to Vickers micro-hardness testing at room temperature (RT) with a load of 100 g and a dwell time of 15 s. Each examined sample was indented for at least 8 times in different areas.

2.3. Tensile test

For tensile testing, all of the SPSed samples were cut into dog-bone-shaped samples with a cross-section of 1.5 × 0.75 mm^2 and a working length of 5 mm as shown in Fig. 2c, and then mechanically polished to remove the cutting-induced scratches and other defects. The tensile sample was placed on the pull rod (as shown in Fig. 2d) and heated to various temperatures from 400 °C to 700 °C in a resistance-heated furnace. Then the tensile tests were carried out using an Instron-5967 machine at a constant speed of 0.06 mm/min. For each condition, five samples were tensile tested and the mechanical properties were averaged.

2.4. Microstructure characterization

The fracture surfaces of samples after destructive tensile testing were characterized by field-emission scanning electron microscope (FESEM Sirion 200, FEI). The metallography of the samples was obtained after polishing and etching (10% potassium ferricyanide with 10% sodium hydroxide aqueous solution). The average grain size of W was measured based on over 300 grains in different micrographs taken in an optical microscope (ZEISS-AX10) and the grain growth behavior of tungsten grain was investigated by combining micro-hardness testing and optical micrographs of each samples. Transmission electron microscope (JEM-2000FX) was used to study the microstructure of samples, and energy-dispersive X-ray spectroscopy (EDS, INCA) analytical system installed on TEM was used for elemental analysis.

3. Results and discussion

3.1. Characterization of milled powders and SPSed samples

The SEM or TEM micrographs of as-received W, ZrH_2, ZrC and ball-milled WZZC powders are presented in Fig. 1. The SEM micrograph of the as-received tungsten powders shown in Fig. 1a indicates that the powder particles are spherical with an average particle size of 400–600 nm and exhibit some degree of aggregation. In Fig. 1b, the zirconium hydride raw powders are flat with an average particle size of 10–20 μm. The particle size of ZrC shown in Fig. 1c is about 20–50 nm. After ball-milling, the ZrC and ZrH_2 particles were disintegrated into smaller ones and dispersed in the W powders. The ball-milled powders are less aggregated, as shown in Fig. 1d.

Relative density of the spark plasma sintered pure W, WZ, WZC and WZZC materials was listed in Table 2, which indicates that all samples were well consolidated with the relative density of higher than 97%. Especially the WZZC alloy exhibits the highest relative density of 98.3%, suggesting that minor ZrC could improve the sinterability of the sample.

3.2. Thermal stability and Vickers micro-hardness

Thermal stability of each SPSed samples was studied by annealing for 1 h from 1100 to 1400 °C. The metallographic images of samples before and after annealing are presented in Fig. 3. Spherical equiaxed tungsten grains were observed not only in the as SPSed but also in the