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ARTICLE

Microstructure Evolution and Properties of Tungsten Reinforced by Additions of ZrC

Li Pengfei, Fan Jinglian, Han Yong, Zhang Man, Cheng Huichao, Tian Jiamin

State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China

Abstract: In order to prepare high performance tungsten used as plasma face material, a trace amount of ZrC was added into tungsten, and the densification behavior, properties and microstructure evolution of W-ZrC composites sintered at temperatures in the range of 1150~2000 °C in flowing hydrogen atmosphere were investigated. Results show that W-ZrC composite powders begin to form fine tungsten grains at 1300 °C. The growth rate of grains is high below 1600 °C, and then slows down. The maximum relative density and tensile strength are 99.6% and 460 MPa under the optimum sintering process, respectively. ZrC particles are uniformly dispersed at grain boundaries and in grains interior with particle size from 0.1 μm to 2 μm. Minor ZrC can effectively prevent the migration of grain boundaries and refine grain sizes from 100 μm of pure tungsten to 30 μm of W-ZrC composites. Minor ZrC can change the fracture mode and improve the strength and toughness of tungsten.

Key words: zirconium carbide; densification; microstructure evolution; grain refinement

Tungsten (W) has been considered as the most promising candidate material for the plasma facing material (PFM) in future fusion reactor due to its excellent performances, including high melting point, good thermal conductivity, low thermal expansion coefficients, high energy threshold for physical sputtering and low tritium inventory[1-3]. However, low temperature brittleness, recrystallization brittleness (recrystallization temperature 1200 °C), radiation reduced brittleness, and poor plasticity and strength have restricted the application of pure W when using as a PFM. It has been shown that compounding with a second phase or alloying with other elements is a good method to strengthen and toughen W[4,5]. Among the strengthening phases, ZrC is one of the most attractive phases owing to its high hardness, high thermal stability and high melting temperature (3540 °C). ZrC particle phases can inhibit grain growth and stabilize the microstructure when exposed to high temperature[6-8]. Moreover, the dispersed ZrC particles can increase the high temperature strength, plasticity, and recrystallization temperature of tungsten[9-12].

W-ZrC composites can be fabricated by hot pressing and spark plasma sintering[13-18]. However, those methods show a weakness in complex geometric shapes and industrial-scale production. The method of conventional forming and intermediate frequency sintering is of benefit to fabricating tungsten material in mass production and reduce the price[19]. In order for industrial-scale production of high performance tungsten, it is crucial to obtain the material microstructure evolution law. At present, the comprehensive evolution law of densification behavior and grain size of W-ZrC composites along with the sintering process is rarely reported. In this paper, W-ZrC composites were fabricated by intermediate frequency sintering, and their densification behavior, grain growth behavior and properties were studied.

1 Experiment

As starting materials, tungsten powders (average particle size of 2.5 μm, purity of 99.9%) and nanoscaled ZrC powders (50 nm, 99%, as shown in Fig.1a) were used. Then the W and ZrC powders were wetly mixed in a planetary ball-milling

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Corresponding author: Fan Jinglian, Ph. D., Professor, State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, P. R. China, Tel: 0086-731-88836652, E-mail: fjl@csu.edu.cn

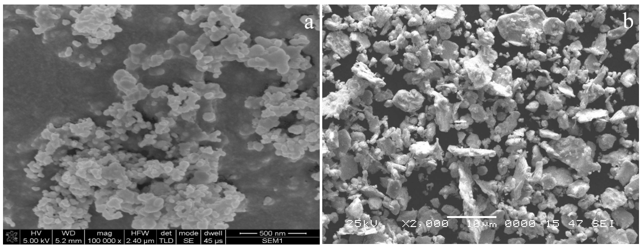

Fig. 1 SEM images of the ZrC powder (a) and W-0.5ZrC composite powders (b)

machine (QM-ISP 2CL, Nanjing Nan Da Instrument Plant, China) for 300 min using Stainless Steel jars with tungsten balls. Absolute ethanol was used as the milling media. Purified Ar (99.99%) was used as the protection atmospheres. The milled composite powders (as shown in Fig.1b) were dried in a vacuum oven at 80 °C for 1 h, and then die-pressed under 400 MPa pressure to form standard I-shaped tensile samples. The green compacts had a relative density of about 50%. Then, the green compacts were sintered in a tungsten rod furnace in flowing hydrogen atmosphere (dew point of 40 °C) in a temperature range of 1150~2000 °C. The heating rate was 5 °C /min and the cooling rate was 10 °C/min. The composite powders which contained 0.1~0.7ZrC are denoted as W-0.1ZrC, W-0.3ZrC, W-0.5ZrC and W-0.7ZrC, respectively.

The density was measured by Archimedes' technique with deionized water as the immersing medium. Tensile strength was tested on the Instron-3369 type mechanical testing machine, and the operating parameters are: measuring strain rate 1.0 mm/min, maximum dynamic load ± 250 kN, accuracy ± 0.5%. The specimens were polished by wet-grinding with 180#, 240#, 400#, 800#, 1500#, 2000# grit silicon carbide abrasive paper. The samples were characterized for their microstructure features by metallographic microscope (MeF3, Leica, Germany). Microstructure characterization and the elemental composition were examined by field emission scanning electron microscopy (NOVA TM NanoSEM230, Czech) and energy dispersive spectroscopy (EDS) analysis.

2 Results and Discussion

2.1 Microstructure evolution

Fig. 2 shows the relationship between relative density and sintering temperature of W-0.5ZrC composites. With the sintering temperature increasing from 1150 °C to 1600 °C, the relative density increases rapidly. And then the growth rate slows down, and the maximum density is obtained at 1900 °C. Fig. 3 displays the metallographic microstructure of W-0.5ZrC composites sintered at 1150, 1300, 1400, 1500, 1600 and 1700 °C. As shown in Fig.3, the grain of W-0.5ZrC composites sintered at 1150 °C cannot be observed while very fine grains appear after sintering at 1300 °C. Fig.4 shows the fracture surfaces of W-0.5ZrC composites sintered at 1150 and 1300 °C. As can be seen, sintering neck is formed between adjacent powders and there are no obvious grain growth at 1150 °C. The SEM images are consistent with the observation of metallographic images. Compared with samples sintered at 1300 °C (Fig.4b), the grain of W-0.5ZrC composites grows obviously with the sintering temperature increasing.

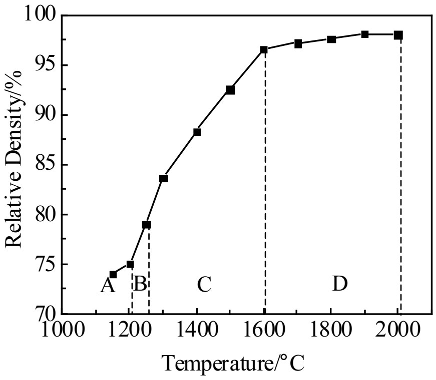

Fig. 2 Relative density of W-0.5ZrC composites at different sintering temperatures

According to the densification curve and microstructure evolution discussed above, the densification behavior of the W-0.5ZrC composites can be divided into four stages marked as A, B, C and D. The first stage is before 1200 °C (process A): the relative density increases slowly. The composite powders recover and sintering neck forms. The second stage is from 1200 °C to 1300 °C (process B): recrystallization process. The relative density of the compact increases significantly. The third stage is 1300~1600 °C (process C): the relative density of the compact continues to increase, and the grain grow up and interior pores further disappears. The fourth stage is 1600~2000 °C (process D): the relative density of the powder compact has reached 95.5% or above, the pores are spherical and closed. As the shrinking and disappearing of pores mainly depend on the grain boundary diffusion and volume diffusion, the final densification process is slow.

2.2 Properties of W-ZrC composites

As is discussed above, W-ZrC composites have fine grains when sintered at 1300 °C. So the sintering process is to be further optimized: heating up to 1300 °C and holding for 2 h and subsequently sintering at the higher temperature (1860, 1890, 1920, 1950, 1980 °C) in flowing hydrogen atmosphere in order to prepare tungsten composites with low oxygen content. The relative density and tensile strength of tungsten composites with different ZrC contents and different sintering temperatures from 1860 °C to 1980 °C are shown in Fig. 5 and Fig.6. With the increase of sintering temperature, the relative density and tensile strength increase at first and then decrease. At the same time, as the content of ZrC increases from 0.1 wt% to 0.7 wt%, the relative density and tensile strength increase and reach the maximum of 99.6% and 460 MPa

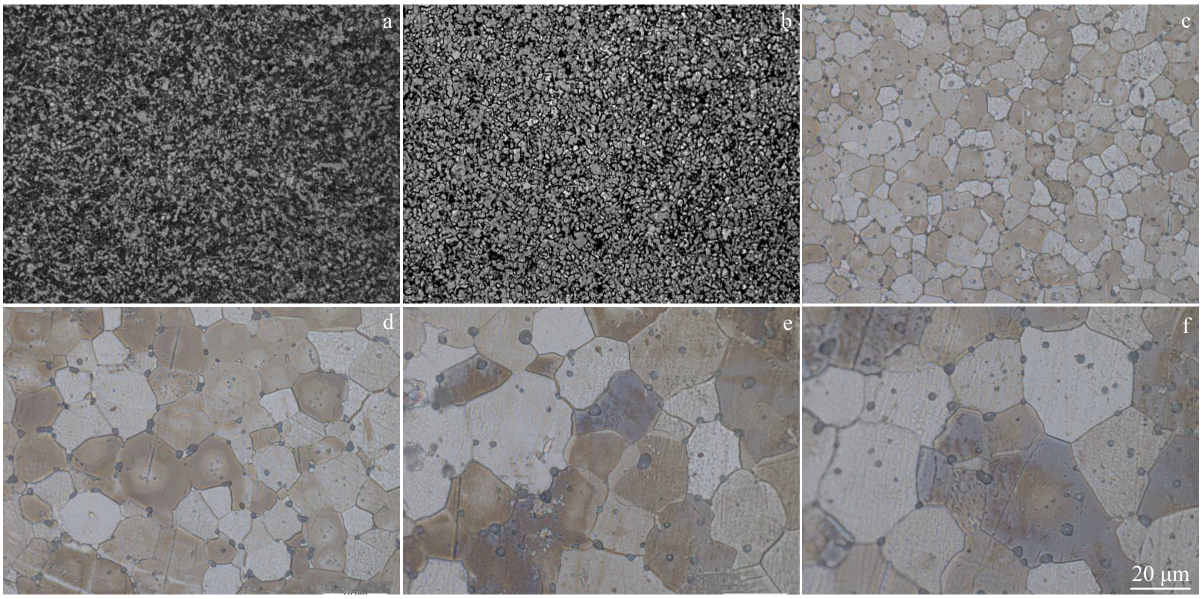

Fig.3 Microstructures of the etched surfaces of W-0.5ZrC composites sintered at 1150 °C (a), 1300 °C (b), 1400 °C (c), 1500 °C (d), 1600 °C (e), and 1700 °C (f)

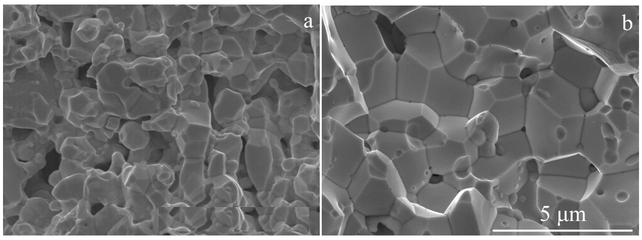

Fig.4 Fracture morphologies of W-0.5ZrC composites sintered at (a) 1150 °C and (b) 1300 °C

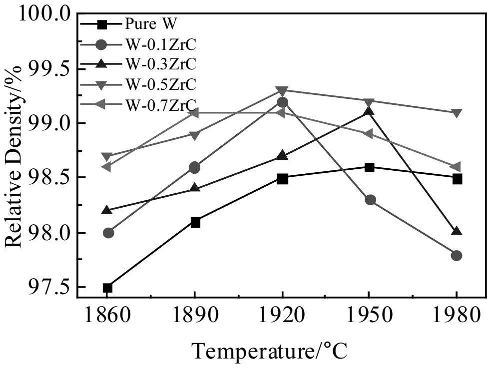

Fig.5 Relative density of W-ZrC composites with different ZrC contents sintered at 1860~1980 °C

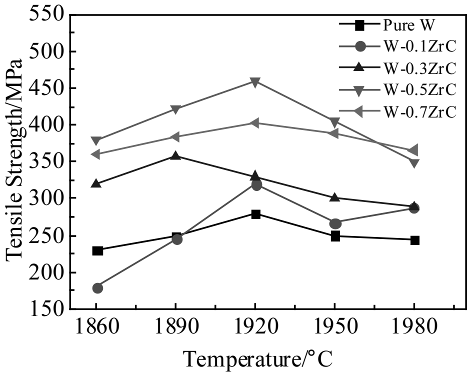

Fig.6 Tensile strength of W-ZrC composites with different ZrC contents sintered at 1860~1980 °C

for W-0.5ZrC composites sintered at 1920 °C, respectively. According to solid phase sintering densification theory, with the sintering temperature increasing, the diffusion ability of atoms and interior pore is enhanced, which is good for densification. However, with the temperatures further rising, the migration rate of grain boundary is bigger than that of pore, which produces closed pores in the grain[20]. The closed porosity is difficult to eliminate. So with the sintering temperature rising up, there is a maximum value for the relative density and tensile strength of the W-ZrC material. It is worth noting that the materials have a higher relative density under the optimized sintering process.

Fig.7 is the stress-strain curve of tungsten composites with different ZrC contents sintered at 1920 °C. There is very little plastic deformation during the tensile deformation process, but the tensile strength and strain stress are significantly increased by adding minor ZrC. Compared with pure tungsten, the tensile strength and strain stress of W-0.5ZrC composites increase by 84% and 105%, respectively. Generally, the fracture mode of tungsten is brittle cleavage fracture at room temperature because there are few slip systems for centered cubic crystal structure during deformation. With the addition of carbide, the shape and length of dislocations will be changed once it meets the second phase particles, and the new fracture surface will consume deformation energy; thereby the strength and toughness are improved.

Fig.8 is tensile fracture morphologies of W-(0~0.7)ZrC composites sintered at 1920 °C. The grain sizes of pure tungsten is about 100 μm (Fig. 8a). As the ZrC addition increases, the size of W grain decreases. The average grain size of W-0.5ZrC is just one-third of pure W, which implies that the minor ZrC particles can effectively prevent the migration of grain boundary during sintering process. Further observation of the fracture surfaces indicates that the pure W shows a transgranular cleavage fracture surface (Fig. 8a), while there are some intergranular fracture in W-ZrC composites. This indicates that ZrC can effectively enhance the strength of the grain boundary of W. Fine W grains are useful to improve the strength and toughness of the W-ZrC composites[19]. The fracture surfaces of W-ZrC composites are rougher than those of the pure W, indicating that the crack travels a longer path. The fracture characteristics are consistent with the stress-strain curve of W-ZrC composites.

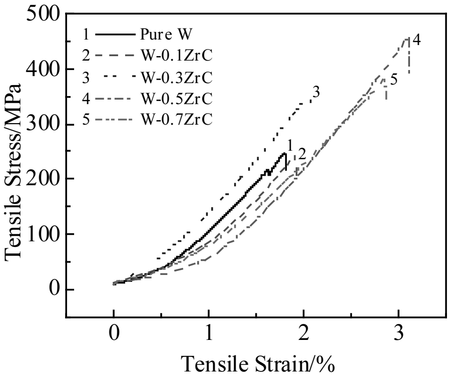

Fig.7 Stress-strain curves of W-ZrC composites with different ZrC contents sintered at 1920 °C

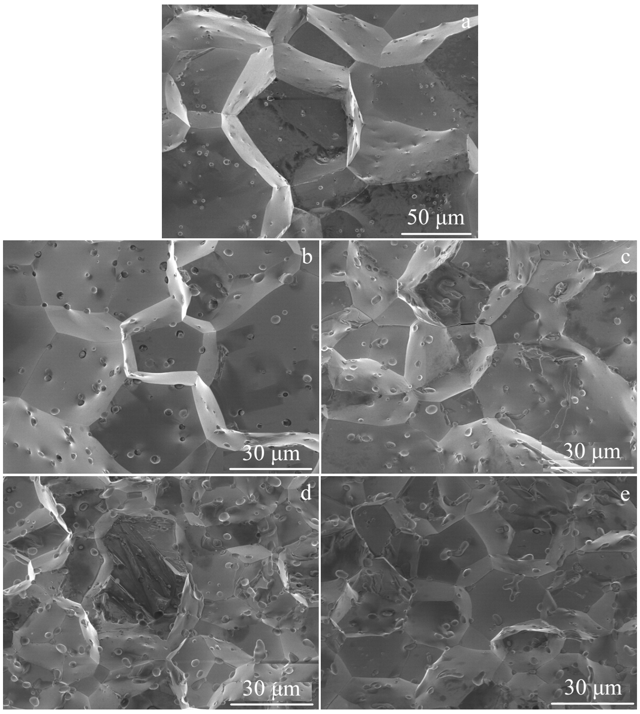

Fig.8 Tensile fracture morphologies of W-ZrC composites sintered at 1920 °C: (a) pure W, (b) W-0.1ZrC, (c) W-0.3ZrC, (d) W-0.5ZrC, and (e) W-0.7ZrC

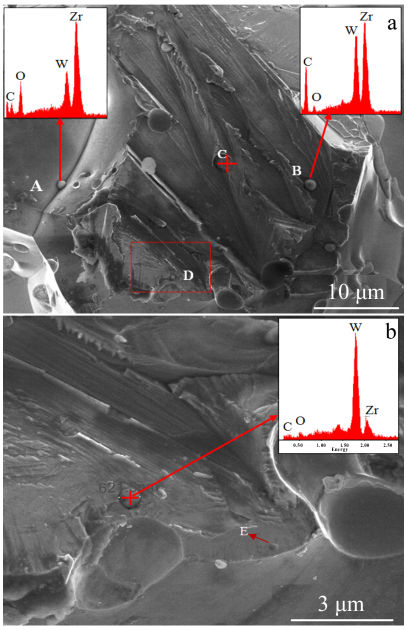

Fig.9 Tensile fracture morphologies and EDX analysis of W-0.5ZrC composites (a) and magnified image of the area D (b)

Fig.9 is the high magnification SEM image of the fracture surface of W-0.5ZrC composites and EDX analysis of the second phase particles. Fig.9b is further enlargement of region D. The fracture morphologies show significant river-like dissociation step, and ZrC particles are uniformly dispersed at grain boundaries (Fig.9a-A) and grain interior (Fig.9a-B, C, Fig.9b-E) with particle size of 0.1~2 μm. Some ZrC particles fracture (Fig.9a-C) during the process of tensile deformation. Compared with tungsten (310 GPa)[13], ZrC has higher elastic modulus (470 GPa)[21]. According to the model of equal strain, the stress born by ZrC particles is higher than that of matrix W when the material is deformed. So the second phase particles will increase the resistance of moving dislocation when the dislocation encounters with the second phase particles. Then the EDX analysis shows that the second phase particles are composed of W, Zr, C, O elements, which proves that the second particles are ZrC. The O element indicates that part of ZrC transforms into ZrO_2 when sintered at high temperature. It is beneficial to reduce the excess O in the materials. So tensile strength and roughness of W-0.5ZrC composites are almost twofold of those of pure W.

3 Conclusions

1) W-ZrC composite powders begin to form fine tungsten grain at 1300 °C. The grain sizes and relative density of W-ZrC composites increase rapidly with the increase of sintering temperature from 1150 °C to 1600 °C, and then the growth rate slows down after 1600 °C.

2) The performance of tungsten is greatly increases by addition of minor ZrC particles. As ZrC content increases, the grain size of W decreases obviously, and the relative density increases gradually. Particularly, the tensile strength and strain stress of W-0.5ZrC reach the maximum of 99.6% and 460 MPa, compared with pure tungsten, increased by 84% and 105%, respectively.

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添加微量 ZrC 对钨材料组织演变和性能的影响

李鹏飞，范景莲，韩　勇，章　曼，成会朝，田家敏

(中南大学 粉末冶金国家重点实验室，湖南 长沙 410083)

摘　要：为了批量化制备面向等离子体用高性能钨材料，在钨中添加少量 ZrC 第二相粒子提高钨的性能，系统的研究了 W-ZrC 材料在 1150~2000 ℃常压氢气气氛烧结下的致密化行为、晶粒和第二相颗粒的长大行为，并在优化工艺下研究了 ZrC 含量对材料性能和组织的影响。 结果表明，W-ZrC 复合粉末在 1300 ℃开始形成非常细小钨晶粒， 晶粒在 1600 ℃之前增长速率很大，在 1600 ℃之后速率变缓。在优化的烧结工艺下，W-ZrC 材料的相对密度和抗拉伸强度最高分别可达到 99.6%和 460 MPa。ZrC 以为 0.1~2 μm 粒子均匀分散在 W 基体的晶界和晶粒内部。ZrC 可以有效地阻碍 W 晶界的迁移，有效的将钨的晶粒由 100 μm 细化至 30 μm 左右。ZrC 改变了钨材料的断裂模式，并提高其强度和韧性。

关键词：碳化锆；致密化；微观结构演化；晶粒细化

作者简介：李鹏飞，男，1986 年生，博士，中南大学粉末冶金国家重点实验室，湖南 长沙 410083，电话：0731-88836652，E-mail: lipf166@163.com