Rare Metal Materials and Engineering
Volume 48, Issue 3, March 2019
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2019, 48(3): 0751-0757.

ARTICLE

Toughening Mechanisms and Interfacial Bonding of W-ZrC Composites

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

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

Abstract: W-ZrC composites are promising materials for plasma face components. In this paper, the W-ZrC composites were prepared by the method of "sol gel–heterogeneous precipitation–spray drying–hydrogen reduction–ordinary consolidation sintering". The toughening mechanisms and interfacial bonding of the W-ZrC composites were studied. The results show that ZrC particles can improve the strength and toughness of tungsten. The relative density and tensile strength of W-0.5wt%ZrC were 99.2% and 460 MPa, respectively after sintering at 1920 °C. Preliminary transient high-heat flux test shows that the W-ZrC composites can endure high-heat flux of 200 MW/m^2 (5 ms). ZrC particles have a process of growing up and rounding, and translate into nearly spherical particles when sintering at 1600 °C for 1 h. At the interfacial bonding zone of ZrC particles and tungsten, W, Zr, and C elements exhibit a smooth transition. The hardness of W，ZrC and interfacial bonging zone are 12, 22, and 18 GPa, respectively. SEM-EDS element line scanning and nanoindentation results indicate that the W and ZrC particles form (W, Zr)C compound.

Key words: Tungsten; ZrC particles; toughening mechanisms; rounding phenomenon; interfacial bonding

Tungsten (W) is a promising material for plasma face components owing to the characteristics of high melting point, good thermal conductivity, excellent thermal stability, and moderate thermal expansion[1-3]. However, shortages such as low temperature brittleness, recrystallization brittleness (recrystallization temperature 1200 °C), radiation reduced brittleness, and poor strength have restricted the possible applications of pure tungsten[4-6]. Zirconium carbide (ZrC) has been introduced into tungsten to increase the mechanical properties of tungsten for its high hardness (~20 GPa), high melting temperature (~3445 °C), and good ablation[7,8]. To date, several sintering methods have been developed to prepare W-ZrC composites, such as (1) ordinary consolidation sintering[9-11], (2) hot pressing[12,13], (3) in-situ reactive sintering[14,15], (4) spark plasma sintering[16,17], and (5) displacive compensation of porosity (DCP)[18-20]. ZrC particles can inhibit grain growth and stabilize the microstructure when exposed to high temperatures[9,13]. Moreover, the dispersed ZrC particles can increase the high temperature strength, plasticity, and recrystallization temperature of tungsten[12].

However, as a predominant preparing method of W-ZrC powders, mechanical alloying is easy to introduce other low melting point phases[18-20] and so it is difficult to uniformly distribute ZrC powder. Therefore, in this paper, W-ZrC composite powder was prepared by the method of "sol gel–heterogeneous precipitation–spray drying–hydrogen reduction," and subsequently ordinary consolidation sintering was introduced to produce fine-grain tungsten materials[9]. Then, the toughening mechanisms and interfacial bonding of W-ZrC composites were investigated

1 Experiment

Ammonium metatungstate (AMT) and nanoscaled ZrC powders (50 nm, as shown in Fig.1a) were used as the raw materials. According to the stoichiometric ratios, sol-gel was prepared by adding the solid metal salts (AMT) and nanoscaled carbide powder into the deionized water with constant stirring, and a

Received date: March 15, 2018
Foundation item: National Magnetic Confinement Fusion Program (2014GB115000); National Natural Science Foundation of China (51474242, 51404308)
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

proper amount of organic polyethylene glycol (PEG) was used to control the concentration of the sol-gel. Then, W-ZrC composite powder was produced by a multi-step process, which induced a sol-spray drying process of the precursor solution at 250~350 °C with a feed rate of 40~50 mL/min, and a subsequent reducing by two-step hydrogen reduction process (at 450 °C for 1.5 h, and then 750 °C for 1.5 h) in flowing hydrogen atmosphere (dew point of -40 °C). The composite powders (as shown in Fig.1b) were die-pressed under 400 MPa pressure to form standard I-shaped tensile samples. The green compacts were heated to 1000 °C in a flowing hydrogen atmosphere at a rate of 5 °C/min and sintered at 1000 °C for 2 h, and finally heated up to 1860~1980 °C at a heating rate of 3 °C/min for holding 3 h. The W-ZrC composites with 0.1wt%, 0.3wt%, 0.5wt%, and 0.7wt% ZrC powder content were abbreviated as W-0.1ZrC, W-0.3ZrC, W-0.5ZrC, and W-0.7ZrC.

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 had a measuring strain rate of 1.0 mm/min. The samples were polished and subjected to Vickers micro-hardness testing at room temperature with a load of 50 g and a dwell time of 15 s. The samples were then subjected to nano-hardness testing at room temperature (UNHT+ MCT, CSM, Switzerland, the max load: 0.50 mN, the loading rate: 1.00 mN/min, the unloading rate: 1.00 mN/min, pause: 15.0 s). Microstructure characterization and the elemental composition were examined by field-emission scanning electron microscopy (FEG-SEM, JSM-6360LV, JEOL, Japan) and energy dispersive spectroscopy (EDS) analysis.

The optimized W-ZrC composites were used to conduct a preliminary transient high heat flux test. First, the material was cut into rectangle modules with dimensions of 15 mm×11 mm×3.5 mm, after polishing treatment, and they were then subjected to a single shot with power density of 100, 200, 300, and 400 MW/m^2, for 5 ms at room temperature on EMS60 electron beam facility. The high heat flux density D was measured by the following equation:

$$D = IU / S \quad (1)$$

Where, I is current, U is voltage, and S is area.

2 Results and Discussion

2.1 Toughening mechanisms

The relative density and tensile strength of W-ZrC composites with different ZrC contents sintered at 1860~1980 °C are shown in Fig.2 and Fig.3, respectively. W-0.5ZrC composites obtained the highest relative density and tensile strength of 99.2% and 460 MPa, respectively, when sintering at 1920 °C. Compared with pure tungsten tensile strength of 270 MPa, W-ZrC composites are evidently strengthened. Based on relative density and tensile strength of the composites

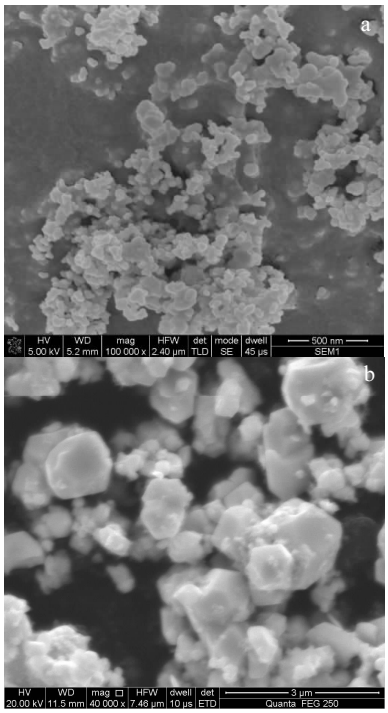

Fig.1 SEM images of the powders: (a) ZrC powder and (b) W-0.5ZrC composite powders

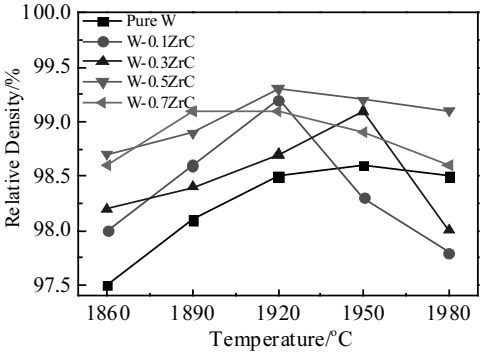

Fig.2 Relative density of W-ZrC composites sintered at 1860~1980 °C with different ZrC contents

sintered at different temperatures, the optimum sintering temperature is 1920 °C.

The metallographs of W-ZrC materials with various ZrC contents (Fig.4) show that the W grain size decreases with an increase of ZrC content. The average grain size (μm) and Vickers micro-hardness of W-ZrC composites sintered at 1920 °C are exhibited in Table 1. The grain size of pure tungsten is about 140 μm. The grain of tungsten material is refined to 60 μm after adding nano-sized ZrC powder. ZrC particles are uniformly distributed in the grain interior and

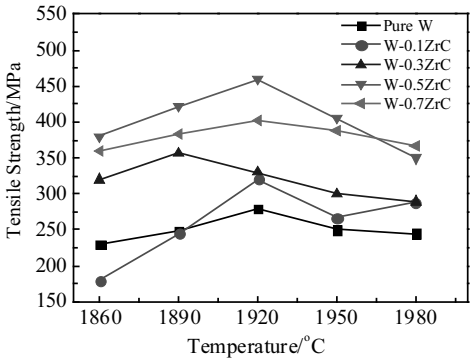

Fig.3 Tensile strength of W-ZrC composites sintered at 1860~1980 °C with different ZrC contents

grain boundaries of tungsten (as shown in Fig.4d, 4e). The result reveals that ZrC can hinder grain boundary migration and play an important role in refining tungsten grain during the high temperature sintering process. The relation of Hall-Petch is as follows:

$$\sigma_y = \sigma_i + K_y d^{-1/2} \quad (2)$$

In the formula, σ_y is the eternal stress, σ_i and K_y are the constants related to the material, and d is the grain diameter. Simultaneously, attributed to the grain refinement and high hardness of ZrC particles, the microhardness of the material is improved. The hardness (HV) of W-0.7ZrC is 4390 MPa.

2.2 High heat flux test

The surface microstructure of W-0.5ZrC samples after high heat flux test is shown in Fig.5. It reveals that no cracks

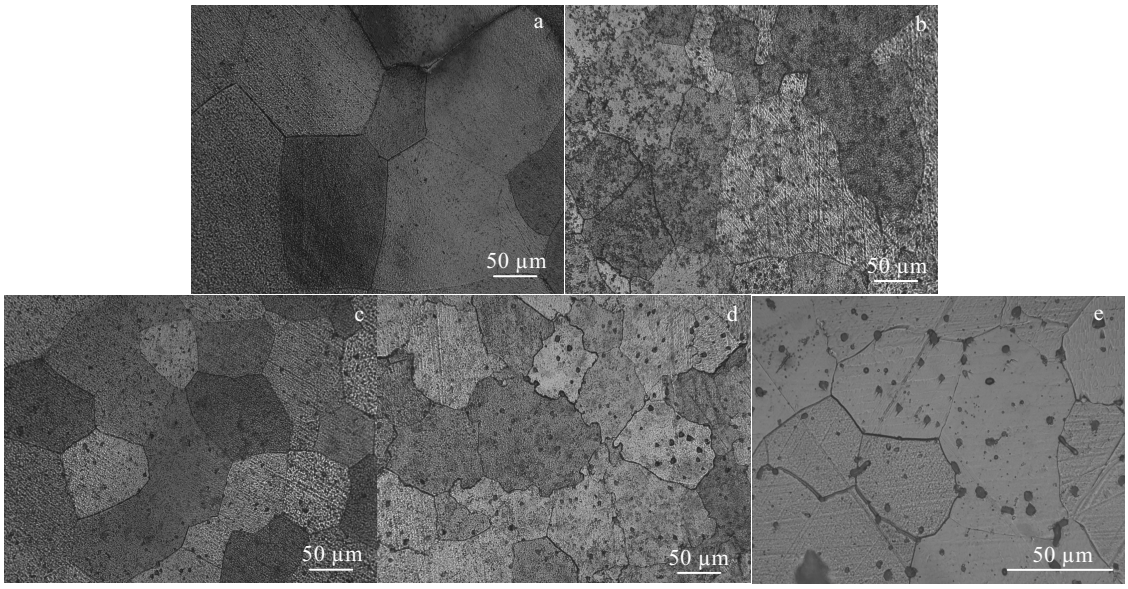

Fig.4 Optical micrographs of W-ZrC composites sintered at 1920℃: (a) pure W, (b) W-0.1ZrC, (c) W-0.3ZrC, (d) W-0.5ZrC, and (e) W-0.7ZrC

Table 1 Room-temperature properties of W-ZrC composites sintered at 1920 ºC

Sample	Average grain size/μm	Tensile strain/%	Hardness, HV(50 g)/MPa
Pure W	140	1.8	4050±50
W-0.1ZrC	100	1.9	4200±50
W-0.3ZrC	80	2.1	4250±50
W-0.5ZrC	70	3.1	4320±50
W-0.7ZrC	60	2.9	4390±50

appear at the power density of 100～200 MW/m^2, but when the power density increases to 300 MW/m^2, small cracks appear (Fig.5c). The magnified image shows that the crack includes closed main crack (～300 μm, as shown in C, D of Fig.5e) and microcrack (～60 μm, as shown in E, F of Fig.5f). The crack is caused by thermal stress and formed along the grain boundaries, which is the weakest spot of tungsten bulk.

SEM images of W-0.5ZrC cross section after high heat flux test are shown in Fig.6. There is no obvious defect in the cross section at the power density of 100～200 MW/m^2. However, when the power density increases to 300 MW/m^2, longitudinal cracks are produced and expanded. The magnified image shows that there is interaction between cracks and ZrC particles. When the second phase particles are encountered with the crack propagation, some cracks cut the second phase particles and changed the direction of expansion, whole some crack propagation terminated in second phase particles. The above results demonstrate that the second phase particles of high modulus can consume the energy of crack propagation.

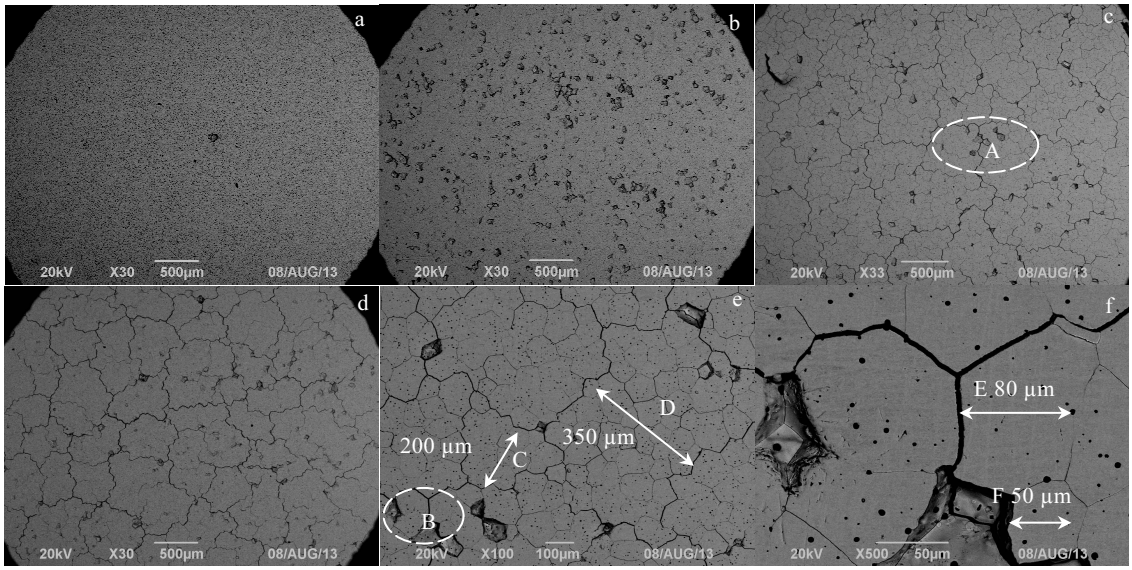

Fig.5 Surface SEM images of the W-0.5ZrC after high heat flux test: (a) 100 MW/m^2; (b) 200 MW/m^2; (c) 300 MW/m^2; (d) 400 MW/m^2; (e) magnified image of the area A in Fig.5c; and (f) magnified image of the area B in Fig.5e

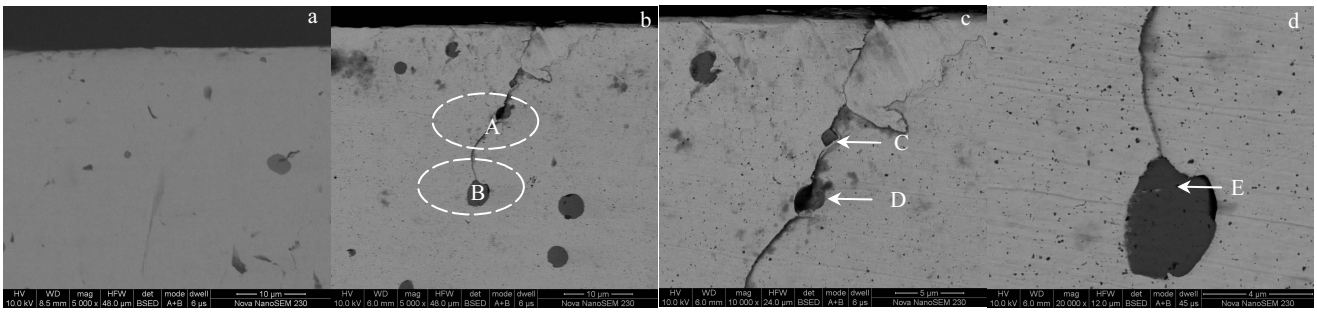

Fig.6 SEM images of W-0.5ZrC cross section after high heat flux test: (a) 100 MW/m^2, (b) 300 MW/m^2, (c) magnified image of the area A in Fig.6b, and (d) magnified image of the area B in Fig.6b

2.3 Interfacial bonding between tungsten and ZrC particles

To further research the strengthening and toughening mechanism of ZrC particles, the distribution of ZrC and the interdiffusion of interface atoms between ZrC and W in sintering progress were investigated. Fig.7 shows SEM-BSE micrographs of polished surfaces of W-0.5ZrC composites sintered at 1150, 1300, 1400, 1500, 1600, and 1700 °C. There are many small black dots in the SEM-BSE micrographs. EDS analysis was carried out on the samples (see Fig.7c). Results illustrate that the main component of black point is Zr and C element, so the black point is the added ZrC particles. With the temperature increasing, the number of ZrC particles decreases, while the diameter of ZrC particles gradually increases. It is noteworthy that the ZrC particles have many edges and are in irregular shape when sintering at 1150~1500 °C (Fig.7a~7d), though the second phase particles are clearly rounded (Fig.7e, 7f) when the sintering temperature exceeds 1500 °C.

SEM images and element line scanning of ZrC particles sintered at 1400 and 1700 °C are shown in Fig.8. W, Zr and C elements show a smooth transition, indicating that W and ZrC particles form (W, Zr)C compound. With the increase of sintering temperature, the thickness of interfacial region between the particles and the tungsten matrix basically remains unchanged. However, compared with the sample sintered at 1400 °C, the region of high Zr, C elements content significantly increase when the sintering temperature is 1700 °C. This phenomenon indicates that diffusion and growing occur in the ZrC particles during the sintering process. The process of ZrC particles gradually growing and rounding can be explained by the lowest energy principle. There is interfacial energy between the ZrC particles and the tungsten matrix. When the volume fraction of the second phase parti-

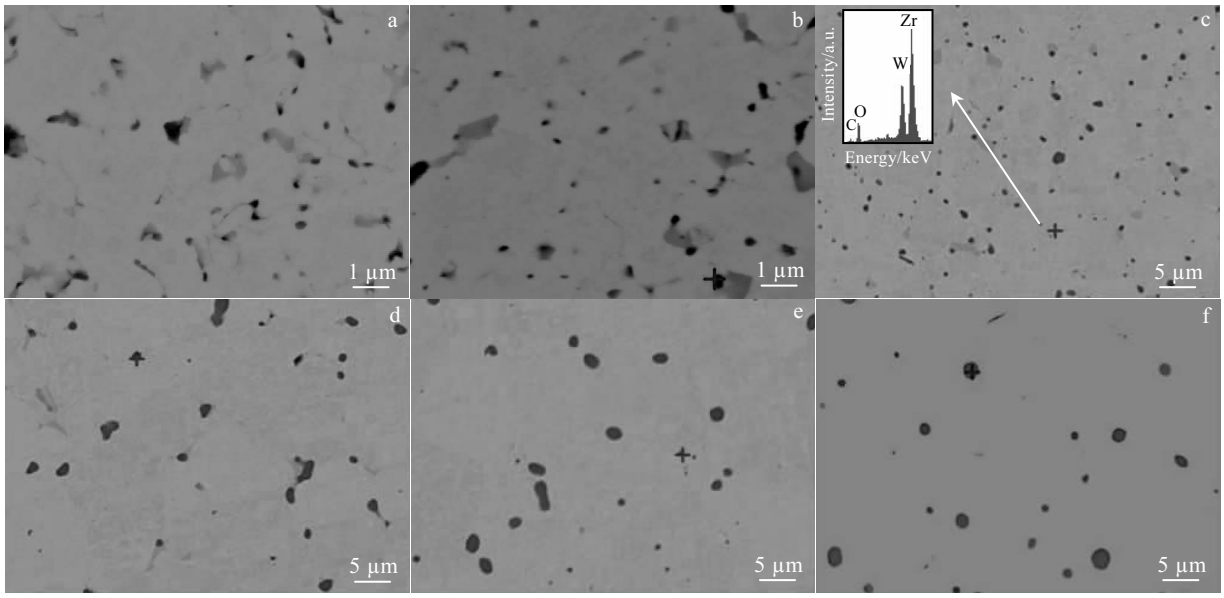

Fig.7 SEM-BSE images of polished surface of W-0.5ZrC composites sintered at different temperatures: (a) 1150 °C, (b) 1300 °C, (c) 1400 °C, (d) 1500 °C, (e) 1600 °C, and (f) 1700 °C

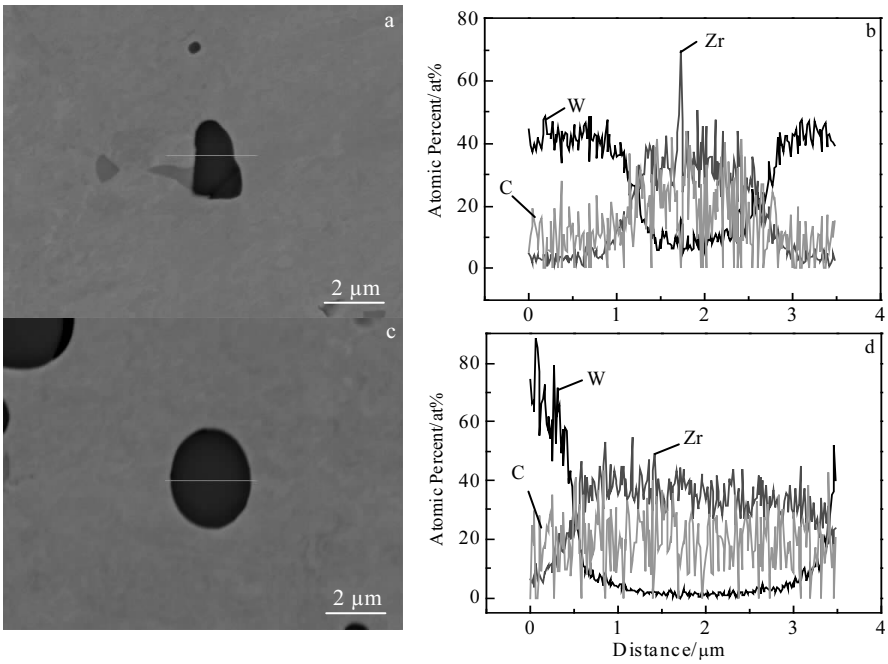

Fig.8 SEM-BSE images (a, c) and EDS element line scanning (b, d) of ZrC particles sintered at 1400 °C (a, b) and 1700 °C (c, d)

cles is fixed, the larger and more regular the second phase particles are, the smaller the interfacial energy within the W-0.5ZrC system is. This principle causes the disappearance of small particles and the rounding of large particles. The ability of atomic diffusion increases with the increase in temperature, and the rounding phenomenon of ZrC particles is more obvious.

In order to confirm there was a transition region between W and ZrC, the hardness test was carried out by nanoindentation from the second phase particles to the W matrix. Eight-point hardness test is shown in Fig.9a, and the hardness (HV) value is shown in Fig.9c. The results reveal that the hardness gradually decreases and then becomes stable. According to the reported hardness of W-ZrC composites[21,22],

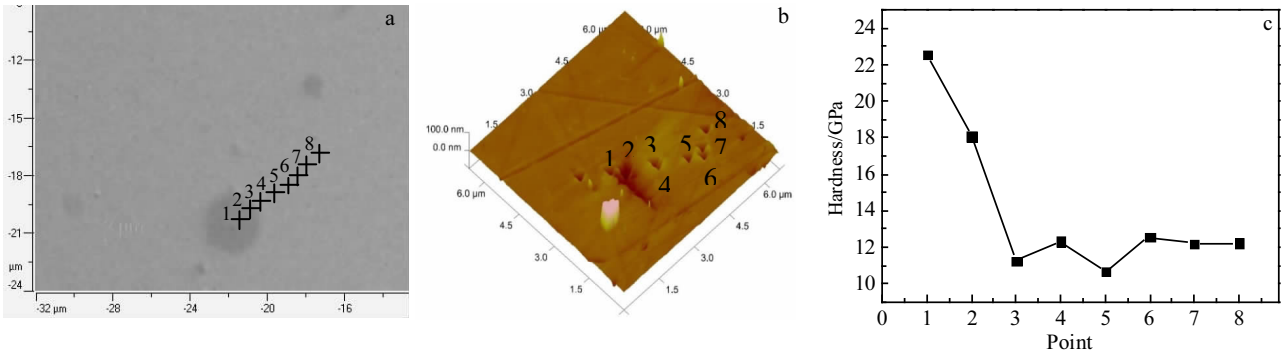

Fig.9 Nano-indentation hardness of W-0.5ZrC composites sintering at 1920 ºC: (a) test point of nano-indentation; (b) atomic force microscope images after testing; (c) hardness value of different test points

among the (W, Zr)C, W and ZrC phases, ZrC have the highest hardness value. Consequently, the region hardnesses of 12, 22, and 18 GPa belong to W matrix, ZrC, and interfacial, respectively. The transition region is the composite phase (W, Zr)C which forms through the diffusion of ZrC and W[23].

3 Conclusions

1) The W-ZrC composites are prepared by micro/nano composite technology by a process of "sol gel-heterogeneous precipitation-spray drying-hydrogen reduction-ordinary consolidation sintering."

2) With the increase of sintering temperature, the relative density increases rapidly, and the relative density and tensile strength reached the maximum value of 99.2% and 460 MPa at 1920 °C, respectively. ZrC particles can refine tungsten grains and increase the strength.

3) Preliminary transient high-heat flux test was performed to evaluate the thermal response. W-0.5ZrC composites can endure high-heat flux of 200 MW/m^2 (5 ms).

4) ZrC particles have a process of growing up and rounding, and almost translate into spherical particles at 1600 °C. At the interface of ZrC particles and tungsten, W, Zr, and C elements show a smooth transition. The hardness of W matrix, ZrC, and interfacial region are 12, 22, and 18 GPa, respectively. The above research indicates that the W and ZrC particles form (W, Zr)C compound.

References

1 Piazza G, Matthews G F, Pamela J *et al*. *Journal of Nuclear Materials*[J], 2007, 367-370: 1438

2 Ezato K, Suzuki S, Seki Y *et al*. *Fusion Engineering and Design*[J], 2015, 98-99: 1281

3 Roosta M, Baharvandi H. *International Journal of Refractory Metals and Hard Materials*[J], 2010, 28: 587

4 Kim J H, Park C, Lim J *et al*. *Journal of Alloys and Compounds*[J], 2015, 623: 282

5 Zhang L H, Jiang Y, Fang Q F *et al*. *Materials Science and Engineering A*[J], 2016, 659: 29

6 Han Y, Fan J L, Liu T *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2011, 29: 743

7 Zhao Y W, Wang Y J, Jin X Y *et al*. *Materials Chemistry and Physics*[J], 2015, 153: 17

8 Chakrabarti T, Rangaraj L, Jayaram V *et al*. *Materials Today: Proceedings*[J], 2016, 3(9): 3077

9 Fan J L, Han Y, Li P F *et al*. *Journal of Nuclear Materials*[J], 2014, 455: 717

10 Li P F, Fan J L, Cheng H C *et al*. *Rare Metal Materials and Engineering*[J], 2016, 45(11): 2970

11 Li P F, Fan J L, Zhang M *et al*. *The Chinese Journal of Nonferrous Metals*[J], 2016, 26(9): 1952 (in Chinese)

12 Wang Y J, Peng H X, Zhou Y *et al*. *Materials Science and Engineering A*[J], 2011, 528: 1805

13 Zhang T Q, Wang Y J, Zhou Y *et al*. *Materials Science and Engineering A*[J], 2010, 527: 4021

14 Roosta M, Baharvandi H, Abdizade H *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2011, 29: 710

15 Kim J H, Zhe G, Lim J *et al*. *Journal of Alloys and Compounds*[J], 2015, 647: 1048

16 Kim J H, Seo M, Kang S *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2012, 35: 49

17 Xie Z M, Zhang T, Liu R *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2015, 51: 180

18 Khoee A A N, Habibolahzadeh A, Qods F *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2014, 46: 30

19 Zhang S M, Wang S, Li W J *et al*. *Journal of Alloys and Compounds*[J], 2011, 509: 8327

20 Lipke D W, Zhang Y S, Liu Y J *et al*. *Journal of the European Ceramic Society*[J], 2010, 30: 2265

21 Xie Z M, Liu R, Zhang T *et al*. *Materials & Design*[J], 2016,

107: 144
22 Kim J H, Park C, Ha D J *et al*. *Journal of Alloys and Compounds* [J], 2015, 637: 183
23 Zhou P, Peng Y B, Du Y *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2015, 50: 274

W-ZrC 材料的强韧化机理和界面结合的研究

李鹏飞，范景莲，韩 勇，章 曼，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：W-ZrC 材料是核聚变面向等离子体部件用很具发展潜力的材料之一。采用“溶胶-非均相沉淀-喷雾干燥-热还原-常压氢气烧结”方法制备了 W-ZrC 材料，研究了 ZrC 添加对材料的强韧化作用机理以及 W 与 ZrC 的界面结合情况。结果表明：ZrC 粒子能够提高钨的强度和韧性，其中 W-0.5%ZrC（质量分数）在 1920 ℃烧结时其相对密度和抗拉强度分别达到了 99.2%和 460 MPa。瞬态高热负荷冲击显示: W-ZrC 材料在承受 200 MW/m^2 (5 ms)的高热流冲击时材料表面没有裂纹，ZrC 粒子能够消耗裂纹扩展中的能量并且阻碍裂纹扩展。通过 W 和 ZrC 的界面结合研究发现，ZrC 在烧结过程中存在长大和球化的过程，并且在 1600 ℃烧结 1 h 时转变为近球形粒子。ZrC 和 W 界面结合区域中的 W、Zr、C 含量呈现光滑过渡，并且显微硬度显示 W、ZrC 和界面结合区域的硬度分别为 12、22 和 18 GPa。EDS 线扫描和纳米压痕结果表明: 在 W 和 ZrC 粒子界面处形成了(W, Zr)C 固溶相。

关键词：钨；ZrC粒子；强韧化机理；球化现象；界面结合

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