Rare Metal Materials and Engineering
Volume 46, Issue 1, January 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(1): 0063-0067.

ARTICLE

Effect of Ultra-high Temperature Heat Treatment on Microstructures of W/ZrC Cermets Fabricated by Different Routes

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Abstract: W/ZrC cermets were fabricated by displacive compensation of porosity (DCP) and hot pressing (HP) separately, and then they were heat treated at 2600 ℃ for 1 h. Microstructure changes of W/ZrC cermets before and after heat treatment was investigated. Results show that both of two W/ZrC cermets have an increase in open porosity, a linear expansion and mass loss after the heat treatment. Annealed DCP-derived W/ZrC cermets are still composed of dispersive W phases and continuous ZrC phases, but residual WC, W_2C and Zr-Cu alloy are gone; instead, a large increase of pores and a sharp reduction of W phases appear. While a new phase of W_2C forms in annealed HP-derived W/ZrC cermets, W grains have a tendency to congregate together to form a big agglomerate phase.

Key words: W/ZrC cermets; microstructure change; heat treatment

W/ZrC cermets, known as a new type of ultra-high temperature candidate composites which combine refractory metal tungsten (W) and ultra-high temperature ceramic zirconium carbide (ZrC), possess extremely high melting point (ZrC up to 3540 ℃, W up to 3422 ℃)[1,2], high temperature strength[3], great hardness[4] and excellent resistance to thermal shock and ablation[5,6], etc. As a result W/ZrC cermets attract increasing attention in ultra-high temperature fields, especially in aerospace applications[7-10]. At present, there are four routes of fabricating W/ZrC cermets, including hot pressing (HP)[3,11,12], spark plasma sintering (SPS)[13], in *situ* reaction sintering (SRS)[14] and displacive compensation of porosity (DCP)[4,6], and W/ZrC cermets fabricated by different routes have different enhancement mechanisms. The first three routes are mainly based on using ZrC to reinforce high temperature strength of W, so ZrC is a reinforcing phase in W/ZrC cermets and has a relatively low content compared to W phase. Song[11] reported that ZrC phase in HP-derived W/ZrC cermets were homogeneously distributed in tungsten matrix composites, and with ZrC content increasing (from 0% to 40%, volume fraction), flexural strength of W/ZrC cermets firstly increased and then decreased. ZrC particles improved the strength of composites through load transferring and grain refinement. The last route is based on using W to enhance fracture toughness of ZrC, so W is a reinforcing phase, totally opposite to the former. Zhang[4] reported that W phase in DCP-derived W/ZrC cermets was discontinuous, and could impede the extending of crack. Consequently, W/ZrC cermets had a fracture toughness of 7.0±0.7 MPa $m^{1/2}$, nearly 7 times to pure ZrC ceramic. In a word, W/ZrC cermets fabricated by different routes have different microstructures, and different microstructures have a great influence on properties of W/ZrC cermets.

Up to now, many studies have been done about the fabrications, microstructures and properties of W/ZrC cermets. However there are few reports about microstructure changes of W/ZrC cermets at high temperature, such as the

Received date: December 25, 2015
Foundation item: Foundation of Shanghai Aerospace Science and Technology; Aid Program for Innovative Group of National University of Defense Technology; Aid Program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province
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ultra-high temperature environment of a solid-fueled rocket nozzle, which is heated to more than 2500 ℃[15]. Under these extreme conditions, microstructure changes of W/ZrC-based nozzle may develop to be a disaster for a rocket. So it is worthwhile to do some researches on microstructure changes of W/ZrC cermets at ultra-high temperature.

In the present paper, W/ZrC cermets, which were prepared by two typical routes: DCP and HP, were heat treated at 2600 ℃ for 1 h. Microstructure changes of the two W/ZrC cermets before and after ultra-high temperature heat treatment were studied.

1 Experiment

DCP-derived W/ZrC cermets (abbreviated to D-W/ZrC in this paper) were fabricated in our previous works, and details were shown in Ref. [4], while HP-derived W/ZrC cermets (abbreviated to H-W/ZrC in this paper) were fabricated as Ref. [3]. After sampling by wire cutting, W/ZrC cermets were polished with diamond pastes. At last, they were put into a graphite furnace and heat treated at a rate of 10 ℃/min to 2600 ℃ in argon atmosphere for 1 h.

Densities (ρ_0, apparent density) and open porosities (P_0) of specimens were examined using Archimedes water immersion technique. Firstly, mass of a dried specimen was tested as m_1. Secondly, the dried specimen was immerged into non-ion water under vacuum environment for 30 min, and then the mass of a wet specimen was detected in air (m_2) and water (m_3). Lastly, ρ_0 and P_0 were calculated as follows:

$$\rho_0 = \frac{m_1\rho_1}{m_1 + m_3 - m_2} \quad (1)$$

$$P_0 = \frac{m_2 - m_1}{m_3} \quad (2)$$

where ρ_1 refers to the density of non-ion water.

Phase identification of specimens before and after heat treatment was performed by a Siemens D-500 X-Ray Diffractometer (XRD), and the scanning rate was chosen at 2 °/min, 2θ=20 °~80 °. Microstructures were examined by a Quanta-200 scanning electron microscope with accessorial energy-dispersive spectroscopy (EDS), which can obtain backscattered electron (BSE) images to distinguish different phases, and to determine chemical composition. What's more, an ImageJ software was used to calculate phase content.

2 Results and Discussion

2.1 Microstructure of original W/ZrC cermets

XRD patterns of W/ZrC cermets fabricated by DCP and HP methods are shown in Fig.1. Distinct diffraction peaks of W and ZrC are observed in both the two diffractions. However, compared to the diffractions of H-W/ZrC, D-W/ZrC cermets have some other peaks of WC, W_2C and a weak diffraction peak of Zr-Cu alloys, which indicate that W/ZrC cermets fabricated by the DCP method contain more impurities. Besides, the diffraction intensity ratio of W peaks to ZrC peaks in H-W/ZrC is also bigger than that of D-W/ZrC. This difference to some extent reveals that the contents of W and ZrC in the two W/ZrC cermets are different, and W has a bigger percentage in H-W/ZrC than D-W/ZrC.

Backscattered electron images of the two W/ZrC cermets are shown in Fig.2. It is clear that microstructures of D-W/ZrC and H-W/ZrC are both mainly composed of bright W phases, dark ZrC phases and pores as shown in Fig.2a and Fig.2c. However, there are also 10.7% (volume fraction) residual Zr-Cu alloys in D-W/ZrC, and part of W phases is actually a core-shell construction, which contains a grey W_2C core and a relatively bright W coating as shown in Fig.2b, identical to the results reported by Dickerson[16] and Zhang[4]. Besides, W phases and ZrC phases in D-W/ZrC are dispersive and continuous, respectively, while they are totally opposite in H-W/ZrC. Moreover, phase contents are different in the two W/ZrC cermets. For example, the volume fraction of W phases in D-W/ZrC is 44.7%, smaller than 69.5% of H-W/ZrC, and the volume fractions of ZrC phases are 43.3% and 29.4%, respectively.

2.2 Physical changes of annealed W/ZrC cermets

Physical measurements of the two W/ZrC cermets before and after heat treatment are listed in Table 1. Compared to the original state, annealed D-W/ZrC has a linear expansion of 5.3%, and also its open porosity increases to 9.29%, nearly 5 times of the initial value. Contrarily, density of annealed D-W/ZrC alters to 8.08 g·cm^{-3}, decreasing by 22.8%. The large decrease of density may be caused by not only thermal expansion, but also formation of closed pores as described in Section 2.3. The same changes also occur in H-W/ZrC, but there is a much more visible increase of open porosity which is nearly 12 times of the initial value and more than 2 times of that of the annealed D-W/ZrC. This sharp increase of porosity is mainly caused by formation of a tympania on the surface of H-W/ZrC as shown in Fig.3. However, the mass loss of D-W/ZrC is bigger than that of H-W/ZrC, needless to say

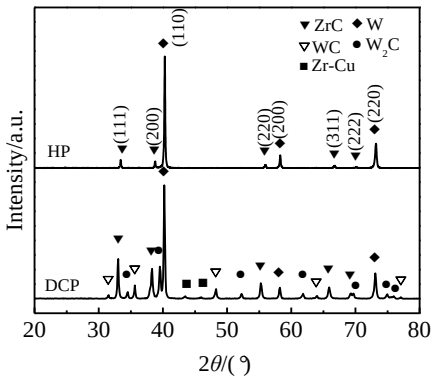

Fig.1 XRD patterns of W/ZrC cermets fabricated by different routes

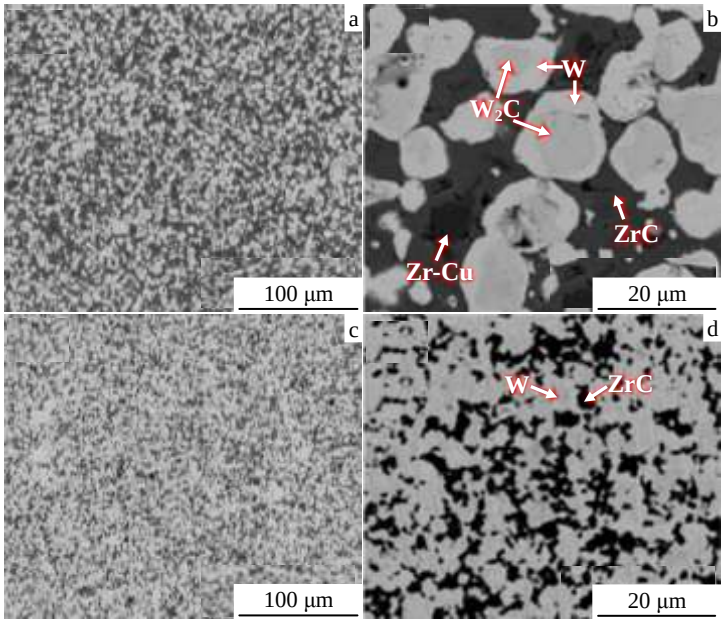

Fig.2 Backscattered electron images of W/ZrC cermets fabricated by different routes: (a, b) D-W/ZrC and (c, d) H-W/ZrC

Table 1 Physical measurements of the two W/ZrC cermets before and after heat treatment

Specimen		Density/g cm^{-3}	Open porosity, volume fraction/%	Linear expansion ratio/%	Mass loss/wt%
D-W/ZrC	Original	10.46	1.62	—	—
	Annealed	8.08	9.29	5.3	1.12
H-W/ZrC	Original	15.38	1.50	—	—
	Annealed	11.21	19.18	4.0	0.58

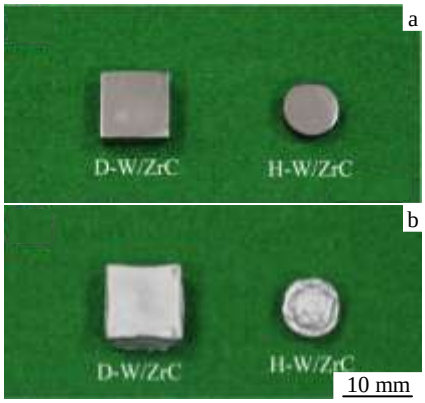

Fig.3 Optical images of W/ZrC cermets before (a) and after (b) heat treatment at 2600 ℃

residual low melting point Zr-Cu alloys in D-W/ZrC has a great influence.

2.3 Microstructure changes of annealed W/ZrC cermets

XRD patterns of the two W/ZrC cermets obtained before and after heat treatment are shown in Fig.4. Fig.4a shows that many diffraction peaks of original D-W/ZrC disappear after heat treatment, excepted W and ZrC peaks. Moreover, ZrC peaks are found to shift to high angle, while W peaks shift contrarily, and some of the two phase diffraction peaks even get an overlap eventually, such as peaks around at 40 ° and 57 °. The peaks shifting of ZrC are caused by diffusion of W atoms into ZrC grains to form a (W, Zr)C solid solution phase[17]. Meanwhile, there are also some Zr and C atoms diffusing into W grains, which make W peaks shift to low angle[13]. Slight shifting of ZrC peaks are also observed in the diffraction patterns of H-W/ZrC as shown in Fig.4b. But more noticeable phenomenon is that some new peaks of W_2C appear. According to Zhang's reports, the new W_2C phase is made up of W and C atoms which are both precipitated from (W, Zr)C solid solution[17]. Because W_2C is a kind of brittle phase, its formation may be bad for the properties of H-W/ZrC.

Backscattered electron images and EDS analyses of the two W/ZrC cermets after heat treatment are shown in Fig.5. Fig.5a reveals that microstructures of annealed D-W/ZrC are still composed of dispersive W phases and continuous ZrC phases, but residual Zr-Cu alloys are gone, resulting in a large amount of pores[18,19], and the volume fraction of pores which was calculated by ImageJ software reaches up to 25.4%, much bigger than the open porosity as shown in Table 1. This phenomenon indicates that some closed pores are produced in the annealed D-W/ZrC. The vanishment of Zr-Cu phase can be ascribed to two aspects. One is the melting and volatilization

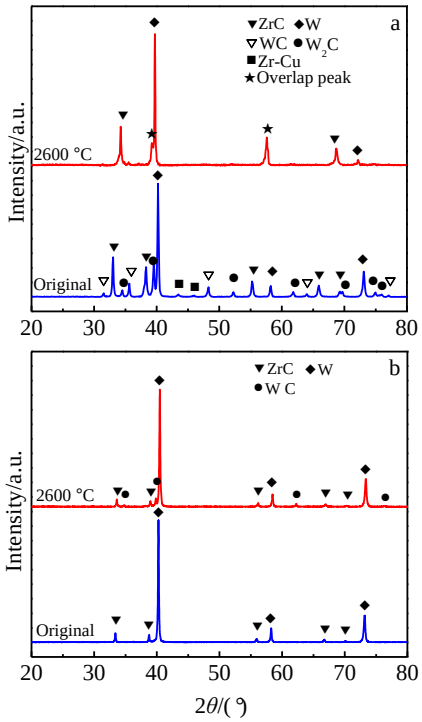

Fig.4 XRD patterns of D-W/ZrC (a) and H-W/ZrC (b) cermets obtained before and after heat treatment at 2600 ℃

loss of Zr-Cu alloys[6,19]. The other is Zr atoms in Zr-Cu alloys continue to participate in the substitution reaction, while Cu is volatilized during the heat treatment[19]. Synchronously, the quantity increasing and sintering of ZrC crystals may conduce to formation of closed pores in the original position of residual Zr-Cu alloys. What's more, EDS analyses indicate that lots of W atoms have diffused into ZrC phases to form a (W, Zr)C solid solution phase, which in turn, cause a sharp reduction of both quantity and size of W grains. Besides, the core-shell construction of W grains also disappears, indicating that substitution reaction of DCP method could continue during the heat treatment.

Compared to annealed D-W/ZrC, different microstructure changes occur in annealed H-W/ZrC. Firstly, the annealed H-W/ZrC has a dense microstructure as shown in Fig.5c, which further proves that its large open porosity as shown in Table 1 is caused by formation of a tympania. What's more, few tiny pores remain in ZrC phase, indicates that ZrC particles are sintered together during the heat treatment. Secondly, it could be easily observed that W phase has a tendency to congregate together, resulting in producing a big agglomerate phase. Meanwhile, Fig.5d reveals that W phases in annealed H-W/ZrC has an orbicular shape, and also they are bigger than that of original W/ZrC cermets. All these may be caused by the ultra-high temperature making the W particles be sintered and grow up. Furthermore, EDS analyses indicate that many W atoms also diffuse into ZrC phases in annealed H-W/ZrC. Last but not least, since W_2C phase detected by XRD in annealed H-W/ZrC is formed through dissolution and precipitation, it is too small to be distinguished in Fig.5c and Fig.5d. A further study is needed in the future.

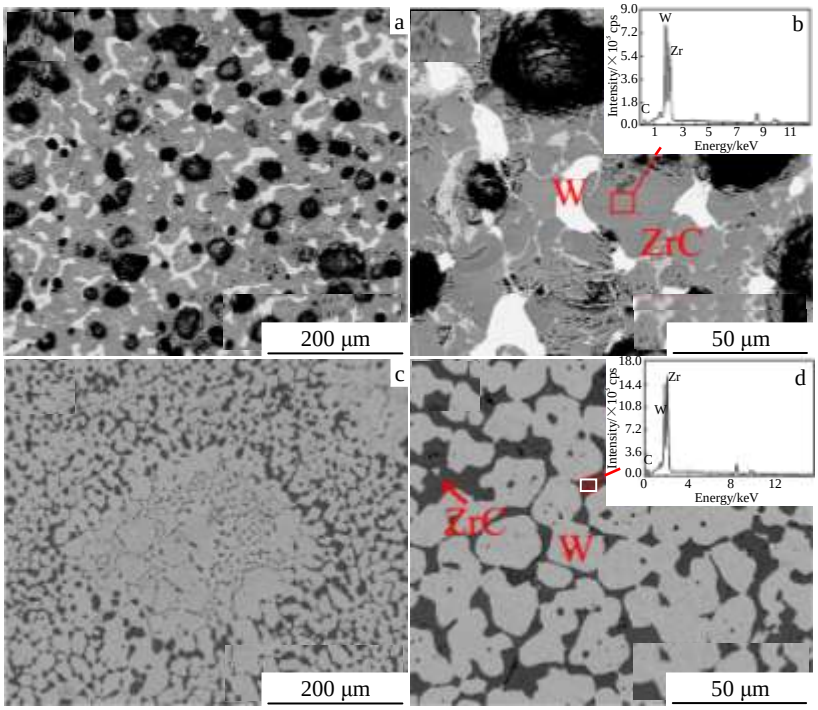

Fig.5 Backscattered electron images and EDS spectra of the two W/ZrC cermets after heat treatment at 2600 ℃: (a, b) D-W/ZrC and (c, d) H-W/ZrC

3 Conclusions

1) W/ZrC cermets may be fabricated by DCP and HP methods, and then they are heat treated at 2600 ℃ for 1 h.

2) The melting loss of residual Zr-Cu alloys and formation of tympania respectively leads to a mass loss, a density decrease and an open porosity increase in D-W/ZrC and H-W/ZrC.

3) Compared to the raw samples, both of the two annealed W/ZrC cermets are still composed of W phases and ZrC phases, but annealed D-W/ZrC has a large increase of pores and a sharp reduction of W phases, and also a disappearance of residual WC, W_2C and Zr-Cu alloys. While annealed H-W/ZrC has a new phase of W_2C, and its W grains congregate together to form a big agglomerate phase.

4) The changes of W phase and ZrC phases in both two W/ZrC cermets are related to the diffusion of W atoms into ZrC phases.

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超高温热处理对不同工艺制备的 W/ZrC 金属陶瓷微观结构的影响

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摘　要：分别采用置换填充工艺（DCP）和热压烧结工艺（HP）制备了 W/ZrC 金属陶瓷，然后在 2600 ℃下对其进行热处理 1 h。研究了热处理前后 2 种 W/ZrC 金属陶瓷的组织结构变化。研究表明，热处理后 2 种材料都出现开孔率增大、线膨胀及质量损失。其中 DCP 法 W/ZrC 金属陶瓷在热处理后仍由分散分布的 W 颗粒相和连续的 ZrC 相组成，但原始材料中残留的 WC、W_2C 及 Zr-Cu 合金相都消失，取而代之的是大量的孔隙，同时 W 相含量也急剧减小。而 HP 法 W/ZrC 金属陶瓷在热处理后则有新相 W_2C 生成，同时其 W 颗粒相有聚集的趋势，形成了大块团状相。

关键词：钨/碳化锆金属陶瓷；微观结构变化；热处理

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