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Laser Ablation Behavior of W/ZrC Cermet Fabricated by Displacive Compensation of Porosity (DCP) Method

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Abstract: W/ZrC cermet was successfully fabricated by a Displacive Compensation of Porosity method, and then laser ablation behaviors of W/ZrC cermet under different laser energy and ablation time were studied. Results showed that a small ablation pit was produced on the W/ZrC cermet during the laser ablation, and depth of the ablation pit increased with increasing laser power and prolonging ablation time. Besides, several homocentric loops which had different kinds and microstructures of oxides were formed around the ablation pit. The volatilization of residual Cu and formation of ZrO_2 layer played significant roles in protecting W/ZrC cermet from being further oxidized during the laser ablation.

Key words: W/ZrC cermet; laser ablation; microstructure

Refractory metal tungsten (W) is widely used in high temperature applications, owing to its high melting point (3410℃), superior high temperature strength, excellent resistance to thermal shock and low coefficient of thermal expansion, *etc*[1-2]. However, W can be easily oxidized in oxygen containing environment at elevated temperature, which restricts its application in many high temperature fields like rocket nozzle[1,3]. In order to improve the antioxidant ability of W, an ultra-high temperature ceramic (UHTC) zirconium carbide (ZrC) is introduced into W since its high compatibility of chemical, thermal and mechanical properties with W, especially its outstanding ablation resistance[4-6]. Researchers found that a dense Zirconium oxide (ZrO_2) lamella produced on surface of W/ZrC cermet could protect materials from being further oxidized, and with increasing of ZrC content, oxidation resistance of W/ZrC cermet would be stronger[7-8]. What's more, ZrC has a relatively low density (ρ[ZrC]=6.63 g/cm^3, one third of ρ[W]) and can greatly improve high temperature strength of W. As a result, W/ZrC cermet possesses a great application prospect in aerospace, aircraft, defense, and many other industries[9-11].

Up to now, four routes have been developed to fabricate W/ZrC cermet, including Hot Pressing (HP)[7,10], Spark Plasma Sintering (SPS)[12], *in Situ* Reaction Sintering (SRS)[13-14] and Displacive Compensation of Porosity (DCP)[4,15]. In recent years, the DCP method has attracted much more attentions than other three methods because of its relatively low preparation temperature, simple process, low cost and near net shape for complex components and so on. Fabrication of W/ZrC cermet by DCP method mainly involves two steps: (i) Preparation of a rigid, porous and shaped WC perform; (ii) Infiltration of a molten Zr-Cu alloy into the holes of WC preform. Eventually, Zr-Cu alloy will react with WC according to reaction as follows:

$$\{Zr\}(l)+x WC(s) \rightarrow ZrC_x(s)+x W(s) \tag{1}$$

Where {Zr} refers to zirconium present in molten Zr-Cu alloy, and residual Cu-enriched liquid will be extruded back out during the reaction[4]. After that, a dense, shaped body which contains desired ceramic ZrC phase and metal W phase is produced.

In our previous works, W/ZrC cermet was successfully fabricated by Displacive Compensation of Porosity (DCP) method, and results showed that the W/ZrC cermet had many eminent properties, including high strength, great hardness and good resistance to thermal shock, *etc*, as shown in papers[5,15]. However, ablation resistance of W/ZrC cermet in ultra-high temperature is still unknown. Recently, many researchers used laser to test ablation resistance of high temperature materials. The laser which has a high energy density can heat materials up to an extremely high temperature in a few sec-

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onds. Liu, *et al* reported that temperature of the laser ablation center of SiC-ZrC coated carbon/carbon composites was about 2900℃[16]. In this work, W/ZrC cermet fabricated by DCP method was ablated by a pulse laser. Laser ablation behaviors of W/ZrC cermet under different laser energy and ablation time were studied, and ablation mechanisms of W/ZrC cermet were analyzed.

1　Experimental procedure

WC powders (D_{50}=6 μm, purity: 99.9%, Xiamen Golden Egret Special Alloy Co., Ltd., China) were mixed with 3wt% polycarbosilane (average molecular weight: 1300) in xylene and ball milled for 2 h, and then the mixed materials were dried at room temperature. The dried mixture were die-pressed at 10 MPa for 10 min to produce a porous rigid preform, and then heat treated at 1600℃ for 1 h in vacuum. The open porosities of sintered preforms, measured by Archimedes' principle, varied from 49% to 52%, which were coincided to the theoretical porosity of DCP method. Lastly, the WC porous preforms were infiltrated with molten Zr_2Cu alloy at 1300℃ for 1 h to fabricate W/ZrC cermet.

W/ZrC cermet was statically ablated by a pulse laser (Pulse width: 210 nm, YLP-1-120-50-50 HC Fiber Laser, produced by IPG company) with a diameter of irradiated area of 132 μm in natural environment. Laser ablation behaviors of W/ZrC cermet under different laser energy and irradiation time were investigated.

A Siemens D-500 X-Ray Diffractometer (XRD) was used to identify phase compositions of W/ZrC cermet. Backscattered electron images and Secondary electron images were obtained by a Quanta-200 with accessorial energy-dispersive spectroscopy (EDS). The ablation depth of W/ZrC cermet was examined also by Quanta-200 as following process: (i) Distance of lens to the un-ablated surface of specimen was measured as d_1; (ii) Distance of lens to the bottom of ablation pit was measured as d_2. So the ablation depth $d = d_2 - d_1$.

2　Results and discussion

Backscattered electron image and XRD patterns of W/ZrC cermet fabricated by DCP method are shown in Fig. 1. Fig. 1(a) showed that W/ZrC cermet had a dense microstructure which was composed of three phases: dispersive white grains, continuous dark matrix and grey parts as red arrow indicated. According to previous works[15] and XRD patterns, these three phases were tungsten, zirconium carbide and copper, respectively. Though residual copper was not the target product, it might intensify ablation resistance of W/ZrC cermet through self transpiration cooling in high temperature[15,17].

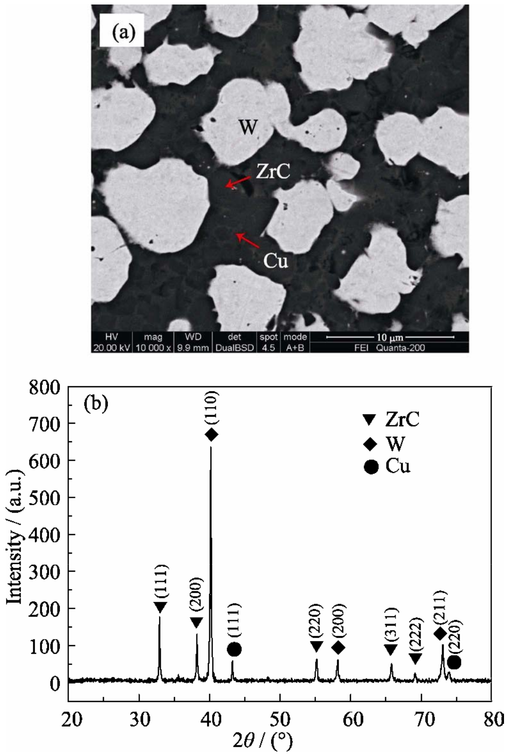

Fig. 1　Backscattered electron image (a) and XRD pattern (b) of W/ZrC cermet fabricated by DCP method

Morphologies of the ablation surface of W/ZrC cermet under different laser energy and ablation time are shown in Fig. 2. A small ablation pit was produced on W/ZrC cermet after being ablated by laser, and many oxides were accumulated around the ablation pit. Besides, the ablation pit had a visible diameter increase with increasing laser energy as shown as Fig. 2(a) to Fig. 2(c), but it eventually retained about 130 μm which was approximate to the diameter of irradiated area. The reason which led to the ablation pit be smaller than irradiated area at low laser energy was that lots of oxides were jammed in the ablation pit as shown in Fig. 2(a). When laser energy increased, temperature of the ablation pit rose to a high level, making the oxides volatilize directly rather than stay in the ablation pit. What's more, prolonging ablation time could also heat the irradiated area and its surroundings to an ultra-high temperature, resulted in not only an increase of ablation depth, but also a more serious microstructure changes of the ablation pit surroundings as shown in Fig. 2(d) to Fig. 2(f).

The ablation depth of W/ZrC cermet versus different laser energy and ablation time are shown in Fig. 3. Fig. 3(a) showed that the ablation depth increased with increasing laser energy, and reached to a maximum of (477.9±34.1) μm with a 40 J/s laser. The bigger laser energy is, the higher temperature attained during ablation process, which accelerates the speed of oxidation and volatilization of substances, and so results in an increase of ablation depth. The ablation time also had a same influence on ablation depth of W/ZrC cermet as shown in

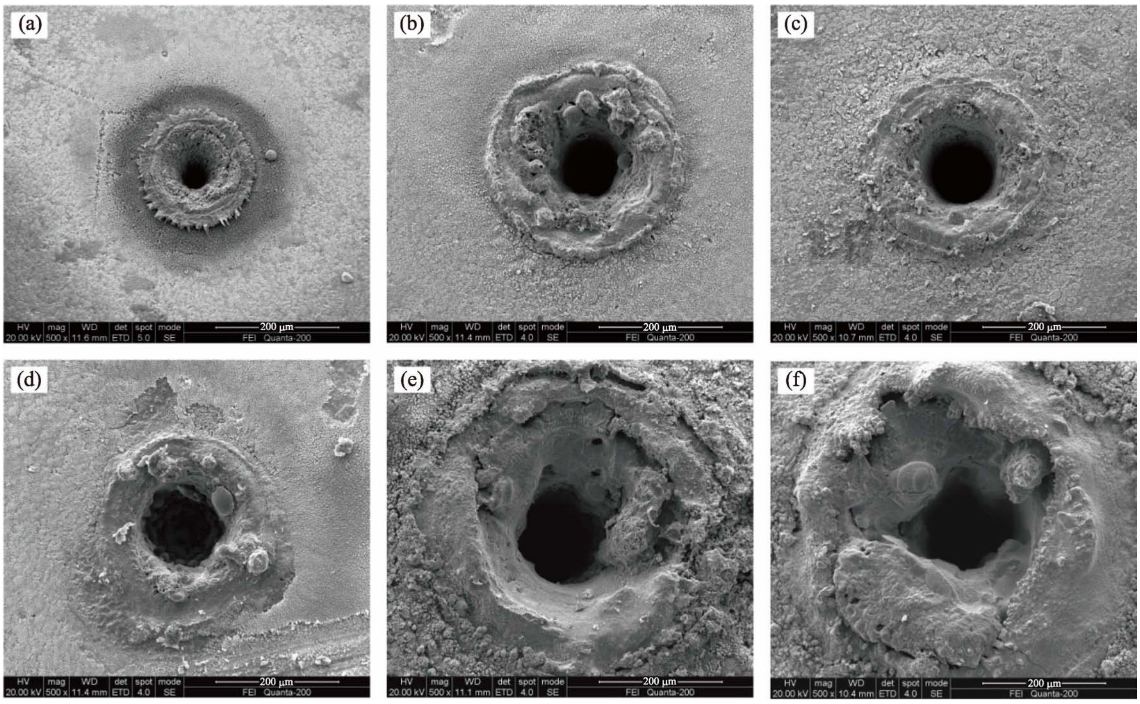

Fig. 2 Morphologies of the laser ablation surface of W/ZrC cermet
Under different laser energy for 30 s: (a) 10 J/s; (b) 20 J/s; (c) 30 J/s
Under different ablation time with a 30 J/s laser: (d) 5 s; (e) 60 s; (f) 120 s

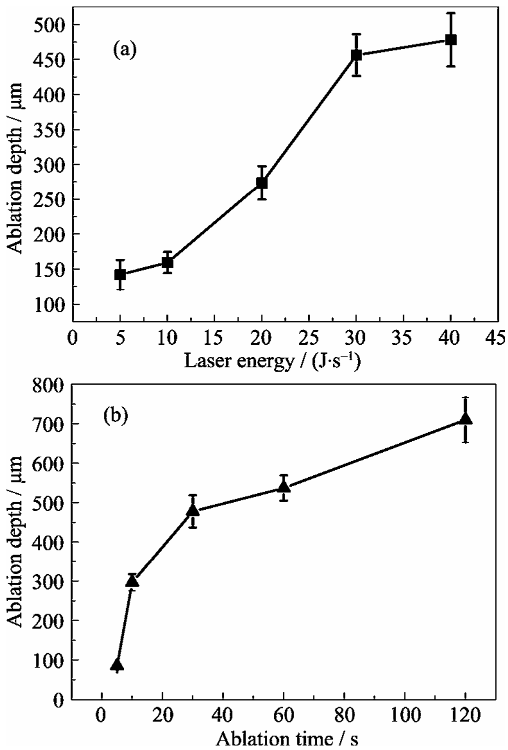

Fig. 3 The laser ablation depth of W/ZrC cermet
(a) Under different laser energy for 30 s; (b) Under different ablation time with a 30 J/s laser

Fig. 3(b). However, it was worthwhile observing that the growth rate of ablation depth slowed down when the ablation time over 30 s. This may be ascribed to oxides which were produced at the earlier stage of laser ablation protecting inside materials from being oxidized and volatilized.

To study laser ablation behaviors of W/ZrC cermet, Fig. 2(a) was further analyzed since it had a typical structure of homocentric loops and a reservation of oxides, as shown in Fig. 4. Fig. 4(a) revealed that four loops could be distinguished around the ablation pit. Loop I had a porous structure which was composed of a large amount of grains as shown in Fig. 4(b), and EDS analysis indicated that most of them were zirconium and oxygen elements, which were conjectured to be ZrO_2. However, as can be seen from Fig. 4(c), loop II which was a compact and spurting layer was mainly composed of tungsten, copper and oxygen elements, and was conjectured to be a mixture of WO_3 and CuO or Cu. The formation of a spurting shape was caused by splashing of melted WO_3 and CuO or Cu from the ablation pit to its surroundings during the laser ablation process. However, ZrO_2, which has a high melting point, was hardly melted, so it kept stable in the ablation pit as Loop I. With laser power increasing, the melted WO_3 and CuO or Cu were volatilized directly in the ablation pits, and no spurting shapes were produced as shown in Fig. 2(b) and Fig. 2(c). Fig. 4(d) and Fig. 4(e) showed that Loop III and Loop IV were composed of loose particles, and the more distant from the ablation center, the smaller of the particles. According to the EDS analysis, these particles were mainly made up of WO_3. What's more, due to W grains were dispersive in W/ZrC cermet as shown in Fig. 1, the continuous distribution of WO_3 particles on loop III and loop IV indicated that these oxides were blasted from the ablation center by hot airflow. At last, EDS analyses in Fig. 4(c) to Fig. 4(e) also indicated that there was a gradual decrease of copper

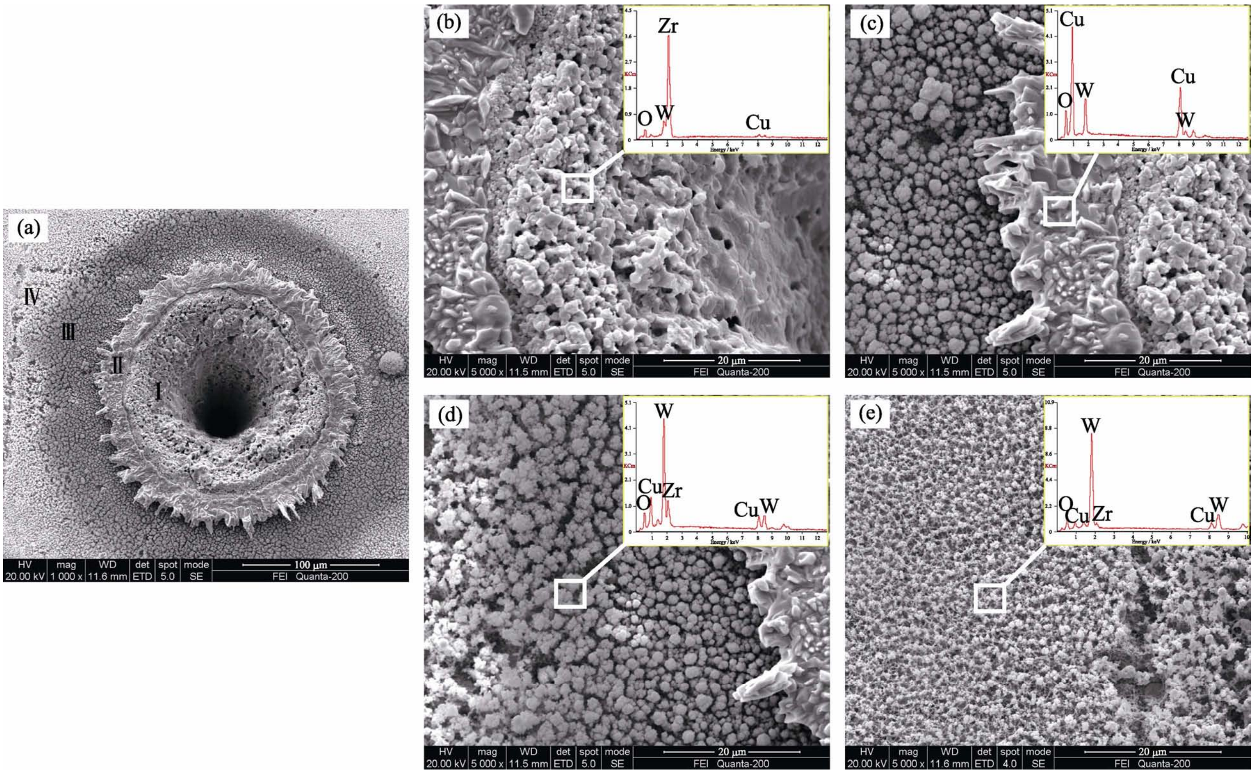

Fig. 4　Morphologies and EDS analysis of the laser ablation surface of W/ZrC cermet
(a) Macro morphology; (b-e) Micro morphologies relative to part I -IV, respectively

element from loop II to loop IV, revealed that a volatilization of residual Cu in W/ZrC cermet did occur and had a function of transpiration cooling during the ablation process.

Secondary electron image and backscattered electron image of the polished surface of ablated pit of Fig. 4(a) are shown in Fig. 5. It could be seen that the ablation pit was surrounded by a vivid two-layer structure. EDS analysis indicated that the submarginal layer was mostly composed of ZrO_2, which was the same as Loop I of unpolished pit as shown in Fig. 4(b), but it had a much more dense structure, favorable to protecting materials from being oxidized. However, another layer which was thinner than the submarginal layer was composed of WO_3 and CuO or Cu except ZrO_2, as shown in Fig. 5(b). The reason for formation of a vivid two-layer structure might be that, WO_3 and CuO or Cu which had low melting point melted and flowed from the submarginal layer to its surroundings which had a low temperature during the ablation process, only ZrO_2 remained here for having a relatively high melting point, and this ZrO_2 layer played a significant role in protecting materials from being further ablated.

From all the above-mentioned discussion, two processes were surely happened during the laser ablation. One was oxidization of W, ZrC and Cu. Because the laser ablation was conducted in natural environment which had sufficient oxygen, W, ZrC and Cu were supposed to be oxidized to WO_3, ZrO_2 and CuO as shown in reaction (2) to (4), respectively. The other was fusion and volatilization of

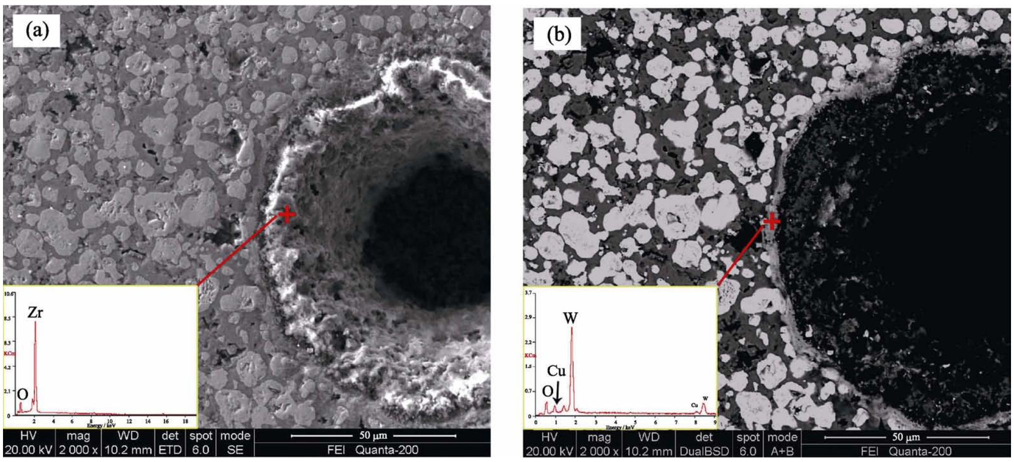

Fig. 5　Secondary electron image and backscattered electron image of the polished surface of ablation pit of W/ZrC cermet

Cu and WO_3 as shown in reaction (5) and (6), respectively. Whereas ZrO_2 kept a solid state on the ablation zone since it has a high melting point of 2715℃. What's more, according to the report of plasma ablation behavior of W/ZrC cermet fabricated by HP method[8], the main ablation mechanism of the composite in ultra-high temperature was melting ablation, which included melting loss of ZrC and W, and also decomposition of ZrC as shown in reaction (7). Due to an ultra-high temperature which can also be produced by laser ablation, the laser ablation behaviors of W/ZrC cermet fabricated by DCP method may also include decomposition of ZrC, but more researches need to to be done in future.

$$W (s) + O_2 (g) \rightarrow WO_3 (s) \tag{2}$$

$$ZrC (s) + O_2 (g) \rightarrow ZrO_2 (s) + CO (g) \tag{3}$$

$$Cu (s) + O_2 (g) \rightarrow CuO (s) \tag{4}$$

$$WO_3 (s) \rightarrow WO_3 (l) \rightarrow WO_3 (g) \tag{5}$$

$$Cu (s) \rightarrow Cu (l) \rightarrow Cu (g) \tag{6}$$

$$ZrC (s) \rightarrow Zr (g) + C (s) \tag{7}$$

3 Conclusion

W/ZrC cermet was fabricated by Displacive Compensation of Porosity method. Laser ablation behaviors of W/ZrC cermet were studied. Three conclusions can be drawn from the present studies: (i) Depth of ablation pits increased with increasing laser energy and prolonging ablation time. (ii) The laser ablation behaviors of W/ZrC cermet included oxidization of W, ZrC and Cu, fusion and volatilization of Cu and WO_3. (iii) Volatilization of Cu and formation of ZrO_2 layer played significant roles in protecting W/ZrC cermet from being ablated. However, many works need to be done about the laser ablation mechanisms of W/ZrC cermet in future.

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DCP 法 W/ZrC 金属陶瓷的激光烧蚀行为研究

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摘 要: 采用 DCP 法制备了 W/ZrC 金属陶瓷，然后研究了在不同激光能量和烧蚀时间下 W/ZrC 金属陶瓷的激光烧蚀行为。研究表明: W/ZrC 金属陶瓷在激光烧蚀过程中产生了一个较小的烧蚀坑，烧蚀坑的深度随着激光能量的增加和烧蚀时间的延长而增大。在烧蚀坑的周围，许多不同种类和结构的氧化物堆积组成了几个同心环。铜的挥发和氧化锆层的形成对防止 W/ZrC 金属陶瓷进一步氧化有着重要作用。

关 键 词: W/ZrC 金属陶瓷；激光烧蚀；微观结构

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