Research on self-propagating high temperature synthesis prepared ZrC-ZrB₂ composite ceramic

Cheng Yong¹, Su Xunjia¹, Hou Genliang¹, Xing YaKun²
The Second Artillery Engineering College, Xi’an 710025, China; Chong Qing Communication Constitution

E-mail: wenzibinbin2009@126.com

Abstract: ZrC-ZrB₂ composite ceramic material is prepared by self-propagating high temperature synthesis, using Zr powders, CrO₂ powders and Al powders as raw materials. Samples are studied by XRD and SEM, the results show that: ZrC-ZrB₂ composite ceramic is attained after self-propagating high-temperature reaction, with Zr⁺ B₄C as the main reactive system, and which is added respectively different content (CrO₃ + Al) system. The study finds that the ceramic composite products are mainly composed of ZrC and ZrB₂ phase, and other subphase. Compared to the main reactive system composite ceramic, composite ceramic grains grow up obviously, after introduction of the highly exothermic system (CrO₃ + Al) in the main reactive system, and with the gradual increase of the content (CrO₃ + Al).

Key words: SHS; ZrC-ZrB₂; composite ceramic.

Self-propagating high-temperature synthesis (SHS), also known as combustion synthesis, is a way to use reactant own adiabatic reaction heat released by situ synthesis of new materials. It has the outstanding advantages with simple process, fast synthesis, less energy consumption [1-3]. In recent years, the self-propagating high-temperature synthesis technology has been widely applied in material preparation with high temperature, refractory and wear resistant, such as intermetallics, ceramic and composite materials [4-6]. At present, most researches focus on carbide, boride such as Ti, W, Si, Mo, but the research on ZrC and ZrB₂ ceramic is relatively less.

ZrC possess a very high melting point (3530°C), a good ultra-temperature performance, therefore, ZrC can be used as high temperature structural material which has been applied in the aerospace field. Because of the high melting point of ZrB₂ (as high as3050°C), especially its outstanding resistance to high temperature oxidation, it is often used for the resistance of ablative materials in the environment of high temperature oxidation [7]. Carbide has the highest melting point, but its fracture toughness is very low, and it is easy to be oxidized. Boride has a good comprehensive performance, its thermal shock resistance in high temperature, low fracture toughness and creep resistance are very good [8]. In this report, Zr
Powders and B₄C powders are used as raw materials, ZrC-ZrB₂ composite ceramic with high melting point, excellent ablation resistance and good thermal shock performance is prepared by self-propagating high temperature synthesis.

1、The experimental process

The test put to use B₄C powders with particle size of 3.5 μm, purity of greater than 98%, Zr powders with particle size less than 43μm, purity more than 99%, and chemical pure Al powders and CrO₃ powders with particle size of between 43~61μm. Zr and B₄C as the main reactive system, ingredients are respectively added to the mass fraction of the highly exothermic system 0, 12.3%, 15.5%, 19.3%, (CrO₃+Al) of which is for reaction to provide heat, and its combustion synthesis is ZrC-ZrB₂ composite ceramic. Thereinto, (Zr+B₄C) and (CrO₃+Al) system is prepared at a molar ratio, see below.

\[
3\text{Zr} + \text{B}_4\text{C} \rightarrow \text{ZrC} + 2\text{ZrB}_2 (1) \\
\text{CrO}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Cr} + 1094 \text{kJ} (2)
\]

Ceramic phase which based on Rigaku D/Max 2250 PC type X-ray diffraction analysis use Cu target, operating voltage 40 kV, operating current of 200 ma, and scanning speed of 10°/min. Observation of ceramic fracture is carried out by the characterized Sirion - 200 type field emission scanning electron microscopy (FESEM) microscopic.

2、Results and discussion

Figure1 is the XRD patterns of the composite ceramic, due to the main reactive system (Zr+ B₄C) and the added different (CrO₃+Al) content. Figure1 (a) is the main reactive system composite ceramic XRD spectrum, and it is known that the composite ceramic is mainly composed of ZrC and ZrB₂. Figure1 (b, c, d) is the added different (CrO₃+Al) content of the composite ceramic XRD spectrum, and it is found that after the added different (CrO₃+Al) content, the composite ceramic is mainly composed of ZrC, ZrB₂, α-Al₂O₃ and (Zr,Cr)₃B₂. The composite ceramic compared to the main reactive system doesn’t change, still ZrC and ZrB₂, but introduction of the new-product phase α-Al₂O₃ and (Zr,Cr)₃B₂. α-Al₂O₃ is Al restore CrO₃ to generate its product.
Figure 2 shows the fracture microstructure of the combustion synthesis product. The gray tissue is the reaction synthesis of ZrC-ZrB$_2$ matrix, the white particles are Al$_2$O$_3$ particles. The black holes appear in Figure 2, is caused by the loosen raw powders and the volatilized trace impurities as well as the volatilized gases of the raw powders in the combustion process. In the raw reaction process, if imposed pressure from the external (i.e. the SHS / Qip process), the relatively dense ZrC- ZrB$_2$ composites can attain . (Figure 2 (a) - (d)) can be seen, when excluding (CrO$_3$ + Al), ZrC-ZrB$_2$ grain is refinement, and shows variety of irregular sphericities. When adding a certain amount (CrO$_3$ + Al), ZrC-ZrB$_2$ particles are significantly large, while the holes aperture accordingly also becomes small. The trend of ZrC- ZrB$_2$ particles growing up is strengthened, when (CrO$_3$ + Al) content increase to 19.3% from 12.3%, which is closely related to the combustion synthesis reaction temperature within the range of the content. The formation and growth of a new phase is not only with the thermodynamic factors, but also with kinetic factors. Due to the grain growth is exponential relationship with the combustion temperature [9-10], the (CrO$_3$ + Al) is a highly exothermic system, increase of (CrO$_3$ + Al) content raises the combustion temperature of the reaction, and thus with the (CrO$_3$ + Al) content increases, it gradually raises the combustion temperature of the reaction, and promotes the growth of ZrC-ZrB$_2$, so that the grains appear more obviously. While grain growth, due to the high-calorie, cooling time accordingly becomes long, the gas generated by the reaction can be fully released, so that the holes aperture corresponding becomes smaller.

(Figure 2 (a)-(d)) can be seen, as ( CrO$_3$+Al ) content gradually increase, the composite ceramic grain is increasingly large, the holes aperture becomes small, while corresponding introduction of the more Al$_2$O$_3$ and Cr$_2$C impurity phases. Al$_2$O$_3$ possess the melting point (2303°C),which is lower than the ZrB$_2$ (3050°C),and thus the more impurity phases content will greatly affect the performance of the ZrC-ZrB$_2$ composite ceramic, so (CrO$_3$ + Al) synthesizes ZrC-ZrB$_2$ composite ceramic in high exothermic system at the same time try to reduce the impurity phase.
Fig. 2 SEM of fracture of the self-reactive spray formed preforms with different (CrO$_3$+Al) content

3. Conclusion

- Zr and B$_4$C powders as raw materials, according to Zr/B$_4$C for 3/1 (mole ratio) ingredients, it is known that ZrC-ZrB$_2$ composite ceramic with a high performance is attained.

- When excluding (CrO$_3$ + Al), ZrC-ZrB$_2$ grain is refinement, and it shows variety of irregular sphericities. When adding a certain amount (CrO$_3$ + Al), particles are significantly large, while the holes aperture accordingly also becomes small.

- As (CrO$_3$+Al) content gradually increase, the corresponding introduction of the more impurity phases, (CrO$_3$ + Al) synthesize ZrC-ZrB$_2$ composite ceramic in high exothermic system at the same time try to reduce the impurity phase.

References:

[1] Khanra A K, Godkhindi M M, Pathak L C. [J]. Materials Science and Engineering A,
[2] Shen Ping, Zou Binglin. [J]. Material Science and Engineering A, 2007: 300-309
[3] Lu Dajun, Quan Wanglin, An Zhanjun. [J]. Journal of Functional Materials, 2006, 37(3): 456-458.
[4] Mossino P. [J]. Ceramics International, 2004, 30(3): 311-332.
[5] Yeh C L, Yeh C C. [J]. Journal of Alloys and Compounds, 2005, 388(2): 241-249.
[6] Nassaj E T, Mirhosseini S H. [J]. Journal of Materials Processing Technology, 2003, 142(2): 422-426.
[7] Jiang Danyu. [J]. Rare Metals Letters, 2006, 28(2): 22-26.
[8] Wang Yanbing. [D]. The Second Artillery Engineering College, 2007: 1-3.
[9] Wu Shengqin. [J]. Journal of Materials Science and Engineering, 2004: 45
[10] Lu Dajun. [J]. Journal of Functional Materials, 2006: 32-33.