The research of improvement on microstructure and properties of TiC-TiB_2 composite ceramic prepared by SHS centrifugal casting

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Abstract. By changing the mass fraction of Ni in the ($Ti+B_4C$) reaction system, TiC-TiB_2 composite ceramics with different Ni mass fraction were prepared by SHS centrifugal casting. TiC-TiB_2 composite ceramics are composed of a lot of TiB_2 platelets, irregular TiC grains and a few of intermittent net Ni alloy by XRD、FESEM and EDS. The results indicate that appropriate Ni addition promotes diffusion between groups and air flow in melting ceramics. The appropriate Ni addition results in the grain refinement and densification of the ceramics. When the mass fraction of Ni addition is 15%, the relative density of the ceramics is 96% and the fracture toughness is $13.6MPa\cdot m^{0.5}$.

Introduction

TiC-TiB_2 ceramic possess good mechanical property, electrical properties and excellent corrosion resistance and oxidation resistance. Especially compared with the TiC and TiB_2 single-phase ceramic, its chemical stability and high temperature mechanical performance is so excellent that it is widely applied in machinery, metallurgy, aerospace, nuclear industry and military industry[1]. However, it's difficult to achieve densification by conventional sintering process because of the low self-diffusion coefficient, high melting point and covalent coordination ratio. What's more, due to the lack of effective toughening mechanism, the fracture toughness of TiC-TiB_2 composite ceramics is still at a low level. Therefore, the main direction and research focus of TiC-TiB_2 ceramics is to improve the obdurability and densification[2-5].

The research shows that the sintering character of ceramic can be improved by adding metal sintering additives like Fe, Ni, Cr, Mo and so on[6]. Liu Shengming[7] who used in-situ method prepared Al_2O_3-Ti(C,N)-Fe composite material. The result shows the additive of Mo can fine the grain and improve the wettability between Ti (C, N) and Al_2O_3. Zhang Jinling[8] explored the effect of Fe on the microstructure and properties of TiB_2-Al_2O_3 composite ceramics. The results show that the addition of Fe can improve the density of the composites. In summary, the suitable metal additives can not only improve the mechanical properties of ceramics, but also promote the densification of ceramics.

By changing the mass fraction of Ni in the ($Ti+B_4C$) reaction system, TiC-TiB_2 composite ceramics with different Ni mass fraction were prepared by SHS centrifugal casting. By comparing the effect of different content of Ni additive on the phase composition, microstructure and mechanical properties of ceramic, confirming the optimum additive mass fraction.

Experiment

Sample Preparation. Raw materials were prepared from high purity (>97%) B4C powder with particle size less than 3μm, high purity (>99%) Ti powder with particle size less than 34 μm as well as high purity (>99.7%) Ni powders with particle size range of 30-63μm. The molar ratio (Ti to B_4C) of 3:1 was chosen as the starting composition and the addition of Ni powder was 0, 5%, 10%, 15%, and 20% respectively. The above powder blends were mechanically homogenized by ball milling for 2h. Then the mixed reaction material is filled into the graphite crucible to compact under uniaxially cold-press about 200 MPa. After that, the prepared graphite crucibles were fixed on the centrifugal machine.The combustion reaction was triggered with the electrical heat W wire (diameter of 0.5 mm) while the centrifugal machine provided a high-gravity acceleration of 2000g (g=9.8 m/s^2, where g means the gravitational constant). When the combustion reaction was over, the centrifugal machine continued to run for 30 seconds. The samples with different mass fraction of Ni were prepared.

Analysis detection. The hardness of ceramic was tested by HVS-50 digital display Vivtorinox hardness tester. The fracture toughness was measured by an electronic universal testing machine with CMT5105 model. The phase composition was identified by Rigaku RINT X-ray diffraction (XRD) with a step of 0.02^o and a scanning rate of 2^o/min. The microstructure of the composite and fracture morphology were examined by Sirion-200 field emission scanning electron microscopy (FESEM). Electron probe microanalysis (EPMA) was conducted by Link ISIS-300 energy dispersive spectrometry (EDS).

Results and discussion

Effect of Ni content on combustion process. The centrifugal casting technology will release a large number of heat instantly so that promote the deflagration mode generating[9], leading the thermal environment near the vacuum that avoid the reaction with oxygen and nitrogen. Therefore, the following reactions may occur in the Ti-B4C-Ni combustion system:

$$2Ti+Ni=NiTi_2 \qquad (1)$$

$$Ti+Ni=NiTi \qquad (2)$$

$$Ti+3Ni=Ni_3Ti \qquad (3)$$

$$B_4C+16Ni=4Ni_4B_3+3C \qquad (4)$$

$$B_4C+5Ti=4TiB+TiC \qquad (5)$$

$$B_4C+3Ti=2TiB_2+TiC \qquad (6)$$

After calculation, we can get the standard Gibbs free energy-temperature curve, as shown in Figure 1. As can be seen from Figure 1, the standard Gibbs free energy of the above reactions is less than 0, which belongs to the exothermic reaction. Therefore, the above reactions can be carried out spontaneously in thermodynamics. The reaction (6) has the lowest standard Gibbs free energy change, which indicates that the reaction will take precedence. Assuming all of the heat released by the combustion was absorbed by the reactants and Ni additive, it can be calculated that the adiabatic temperature was 3193K. So the calculation results of the adiabatic temperature of the combustion process with different mass fraction were shown in Figure 2[10]. According to the experience about the combustion reaction adiabatic temperature ventured by Merzhanov[11], when the adiabatic temperature is higher than 1800K, the combustion synthesis reaction can proceed spontaneously.

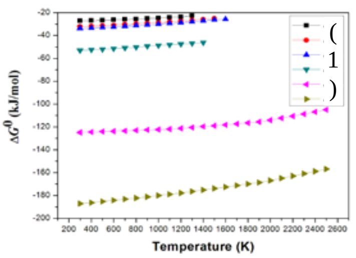

Fig. 1 Standard Gibbs free energy-temperature curve of formula(1)-(6)

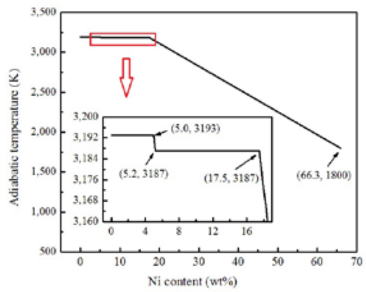

Fig. 2[10] The variation curves of adiabatic temperature of combustion system with different mass fraction of Ni additive

Table 1 shows reaction rate of combustion with different mass fraction of Ni.It can be seen from the table that the reaction combustion rate increase with the increase of Ni content. In the process of combustion, the Ni was non-reactive. Along with the increase of Ni content, the proportion of Ni metal liquid phase reaction system gradually increased, resulting in liquid phase of reaction front gradually increased. Therefore, the combustion rate of the reaction system is accelerated.

Table 1 combustion rate corresponding to different Ni content

Ni content/%	0	5	10	15	20
combustion rate/(mm/s^{-1})	819	1215	1413	1617	1712

Effect of Ni content on Microstructure of ceramics. Figure 3 shows the XRD spectra of TiC-TiB_2 multiphase ceramics with different content of Ni. The experimental samples are composed of TiB_2 ceramic matrix and TiC second phase, and the intensity of Ni diffraction peak increases with the increase of the content. There are no other impurities in the reaction product, which is consistent with the pre design and the thermodynamic calculation results.

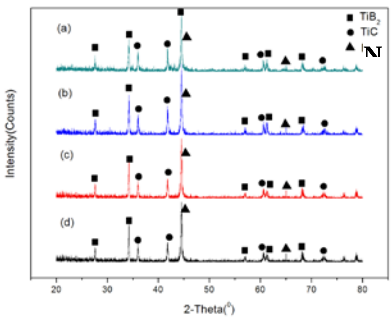

Fig. 3 XRD spectra of TiC-TiB_2 powders with different Ni content(a)5%(b)10%(c)15%(d)20%

Figure 4 shows the microstructure of TiC-TiB_2 composite ceramics with different Ni mass fraction. It can be seen from the figure that the TiC-TiB_2 multiphase ceramics are composed of dark gray crystal, gray irregular crystal and white structure. The proportion of each phase, grain size and pore density changed along with the change of Ni content.

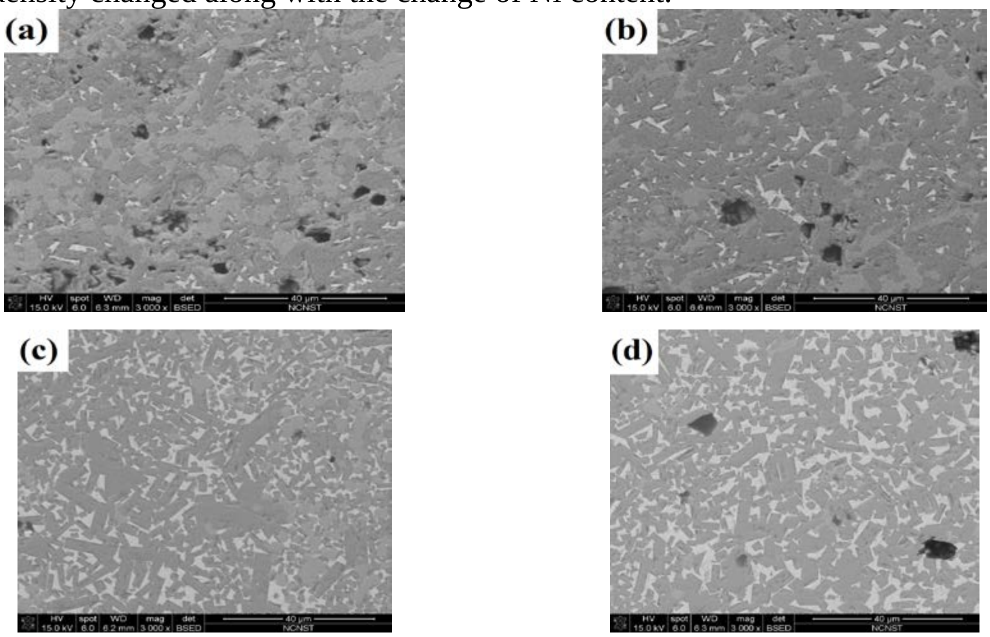

Fig. 4 Microstructure of TiC-TiB_2 ceramics with different Ni mass fraction FESEM (a)5% (b) 10% (c)15% (d) 20%

It can be observed from the figure (a) that when the content of Ni is low, the growth of some TiB_2 lamellae is abnormal, and the grain size distribution is wider. Due to the influence of the primary phase of TiB_2, the growth space of TiC is compressed in the vicinity of the TiB_2 film. There are a lot of hole defects in the ceramic matrix, and some of the holes can even reach 10 μ m.

With the increase of Ni content, the grain size of TiB_2 on ceramic substrate is gradually refined and the grain size distribution tends to be uniform, as shown in Figure 4 (b) and 4 (c). The growth space of TiC increases gradually, the grains are spherical and the grain size decreases gradually. The number and size of the holes on the ceramic substrate are reduced and the density of the material is improved. As is shown in figure (d) when the Ni content further increased up to 20%, The homogeneity of the ceramic structure began to deteriorate and the ceramic density decreased.

Effect of Ni content on mechanical properties of ceramics. Table 2 shows the mechanical properties of TiC-TiB_2 multiphase ceramics with different mass fraction of Ni. With the increase of Ni content, the relative density, fracture toughness and bending strength of the ceramic firstly increased and then decreased, and the above indexes reached the maximum when the Ni mass fraction was 15%. On the one hand, there are the smallest wetting angle between Ni and TiB_2, TiC. On the other hand, the melting point of Ni is much lower than that of TiB_2 and TiC. In the late stage of solidification, Ni will be in the form of metal liquid phase in the system that promote the compactness of ceramic. At the same time, the introduction of Ni increases the reaction rate, shortens the reaction time, refines the ceramic grains and improves the microstructure. What's more, in the process of crack propagation, the small size of the TiB_2 grains can be strengthened by crack pinning, crack deflection, crack bridging, or crystal pulling out. However, with the increase of Ni content, the hardness of ceramics will decrease. In summary, when the mass fraction of Ni was 15%, the mechanical properties of TiC-TiB_2 composite ceramics were optimized, the relative density was 96%, and the fracture toughness was 13.6MPa·$m^{0.5}$.

Table 2 Properties of TiC-TiB_2 ceramics with different Ni addition

Ni content/%	density/g·cm^{-3}	relative density/%	fracture toughness/MPa·$m^{0.5}$	bending strength/MPa
5	4.49	92.2	11.8	790
10	4.80	94.5	13.5	870
15	5.08	96.0	13.6	950
20	5.21	94.7	13.3	805

Summary

1.By changing the mass fraction of Ni in the ($Ti+B_4C$) reaction system, TiC-TiB_2 composite ceramics with different Ni mass fraction were prepared by SHS centrifugal casting.

2.By XRD, EDS, FESEM analysis, TiC-TiB_2 multiphase ceramics consists of a large number of small TiB_2 lamellae, irregular TiC grains and the distribution of the discontinuous Ni bonding phase between the crystals.

3.The introduction of Ni is beneficial to the diffusion of the components that promote the discharge of gas and the homogenization of the components, and finally to improve the density and microstructure of the ceramics.

4.when the mass fraction of Ni was 15%, the mechanical properties of TiC-TiB_2 composite ceramics were optimized, the relative density was 96%, and the fracture toughness was 13.6MPa·$m^{0.5}$.

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