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TiC-Fe cermets fabricated by SHS①

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Abstract: The dense TiC-Fe cermets were produced by self-propagating high temperature synthesis and pseudo-hot isostatic pressing(SHS/PHIP). The influence of Fe content on the combustion temperature, combustion velocity, density and microstructure of products was studied. The composition and microstructure of the product were analyzed. The results showed that the cermet consists of quasi-spherical TiC particles and Fe-binder phases. A thin diffusion layer was found between Fe binder phase and TiC particle. In the range of 10 % ~ 20 % Fe content, the combustion temperature and velocity decrease more slowly than the other contributions.

Key words: SHS/PHIP; TiC-Fe cermet; microstructure; Fe-binder phase **Document code:** A

1 INTRODUCTION

Recently, the self-propagating high temperature synthesis (SHS)[1] has been rapidly improved and drawn much attention because of its high energy efficiency, high productivity, high-purity product and simple equipment since it was proposed by Merzhanov in 1967. This process can be used not only for fabricating more than 500 compounds such as carbide, boride, silicide, nitride and intermetallic but also for cermet composites[2~5].

The cermets consisted of TiC and metal (usually Ni, Co, Mo) have many commercial uses[6]. Since metal binders greatly affect the properties of cermet, it is necessary and possible to employ metals or alloys with high properties instead of the rare and expensive metals[7]. Though Saidi *et al*[8] studied the reaction mechanism of Ti-C-Fe system, little effort on substituting Fe binder for Ni, Co strategic materials has been made to produce dense TiC-Fe cermet.

In this paper, several dense TiC-xFe (short form TFx, x is the mass fraction of Fe in percent) cermets were produced by self-propagating high temperature synthesis and pseudo-hot isostatic pressing (SHS/PHIP). The influence of Fe content on the combustion temperature, combustion velocity, density and microstructure of products was studied. The composition and microstructure of the products were analyzed.

2 EXPERIMENTAL

The reactants of Ti (99.5 % purity, an average particle size of 50 μm) and C (98.5 % purity, an average particle size of 1 μm) were used to synthesize TiC ceramic with an atomic ratio 1 ∶1. The reactant of Fe (98.5 % purity, an average particle size of 45 μm) was added in the light of mass ratio. The homogeneous mixtures with the desired composition were prepared by milling the reactants in stainless pot for 24 h. The powder was dried for 24 h in drier with circulating water.

Green compacts for measuring the combustion temperature and velocity were cylinder, 20 mm in diameter and approximate 40 mm in height, which were formed at pressure of 120 MPa in a stainless steel die. The green densities of the compacts were 60 % theoretically. The dried pellets were placed in a vacuum reaction chamber. Tungsten filaments were positioned behind the bottom surface of the pellets for igni-

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tion. The combustion temperature and velocity were measured by tungsten-rhenium thermocouple linked to computer.

Dense samples were produced by self-propagating high temperature synthesis and pseudo-hot isostatic pressing(SHS/PHIP). Fig.1 is the schematic of SHS/PHIP equipment. Square compacts, 70 mm in length and width and approximate 20 mm in height, were made at pressure of 16 MPa in a stainless steel die. The green densities of the compacts were theoretically 50%. The samples were covered with commercial casting sand (a particle size of 0.2 ~ 0.8 mm) and ignited by tungsten filaments. The compaction was performed within 20s by quickly pressing the sand containing the sample just after the SHS reaction. The pseudo isostatic-HIP using sand as the pressure medium is well known to cause pseudo isostatic pressing. The combustion products were quickly covered with sand and then cooled slowly.

The microstructure and chemical composition of reaction products were investigated using EPMA, TEM and EDS. The densities of products were measured by Archimedes method.

3 RESULTS AND DISCUSSION

Fig.2 shows the influence of Fe content on the combustion temperature and velocity. It was found that the combustion temperature and velocity decrease rapidly, when Fe content is less than 10%; while in the range of 10% ~ 20% Fe content, the combustion temperature and velocity decrease slowly; and then, they decrease rapidly again with increasing Fe content. The combustion temperature is always above the melting point of Fe when Fe content is no more than 40%. The variation characteristic of the combustion temperature and velocity with Fe content is possibly affected by the second combustion mode[9]. During the reaction, the molten Fe wrapping the Ti particles can produce $FeTi_2$ which is an eutectic compound with a melting point of 1 085 ℃, it is favorable for the diffusion of elements. With increasing the temperature, the $FeTi_2$ compound decomposes, and then Ti and C react to from TiC[8]. The rapid diffusion due to the low melting point eutectic compound causing the diffusion layer thin and the more energy for the melting of Fe result in the combustion temperature and velocity with 10% ~ 20% Fe content decreasing more slowly than the other contribution. With increasing Fe content, the combustion temperature and velocity decrease rapidly again because too much energy is needed for the melting of Fe.

Fig.3 is the X-ray diffraction spectrum of TF30. The X-ray diffraction spectrums of other TF*x* cermets are omitted since they are analogous. The result shows that the combustion products contain TiC and Fe. $FeTi_2$ compound

Fig.1 Schematic of SHS/PHIP equipment
1 —Mould; 2 —Sand; 3 —SHS reaction mixture; 4 —Uncompacted Ti + C; 5 —Mould; 6 —Igniting

Fig.2 Influence of Fe content on combustion temperature and velocity decomposed completely since no $FeTi_2$ was found. Though it is reported that Fe_3C compound is likely to be formed because the thin film of TiC will decompose as a result of action of molten Fe[10], no Fe_3C compound was found on the combustion products.

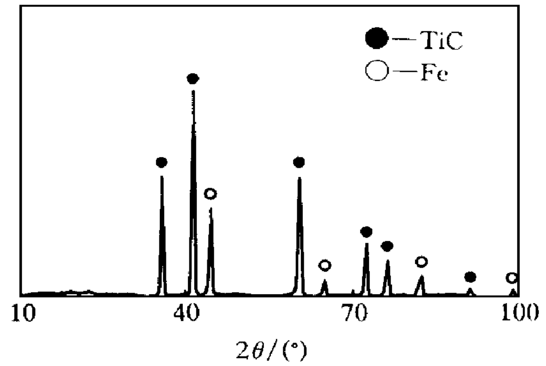

Fig.3 XRD spectrum of TF30

The EPMA photographs of TFx cermets are shown in Fig.4 according to Fe content. The TFx cermets are composed of quasi-spherical TiC particles and Fe-binder phases. The particle size gradually decreases and becomes homogenous with increasing Fe content. Since the formation of TiC particle is a process of nucleus formation and grain growth, the particle size is affected by all of the factors influencing the nucleus formation and grain growth. With increasing Fe content, the combustion temperature is lower, and then TiC particle becomes finer on account of the low grain growth for the increasing distance between atom Ti and C.

In addition, some of small pores are found between TiC particle and Fe-binder phase and on the interface of TiC particles in Fig.4. It is analyzed as follows:

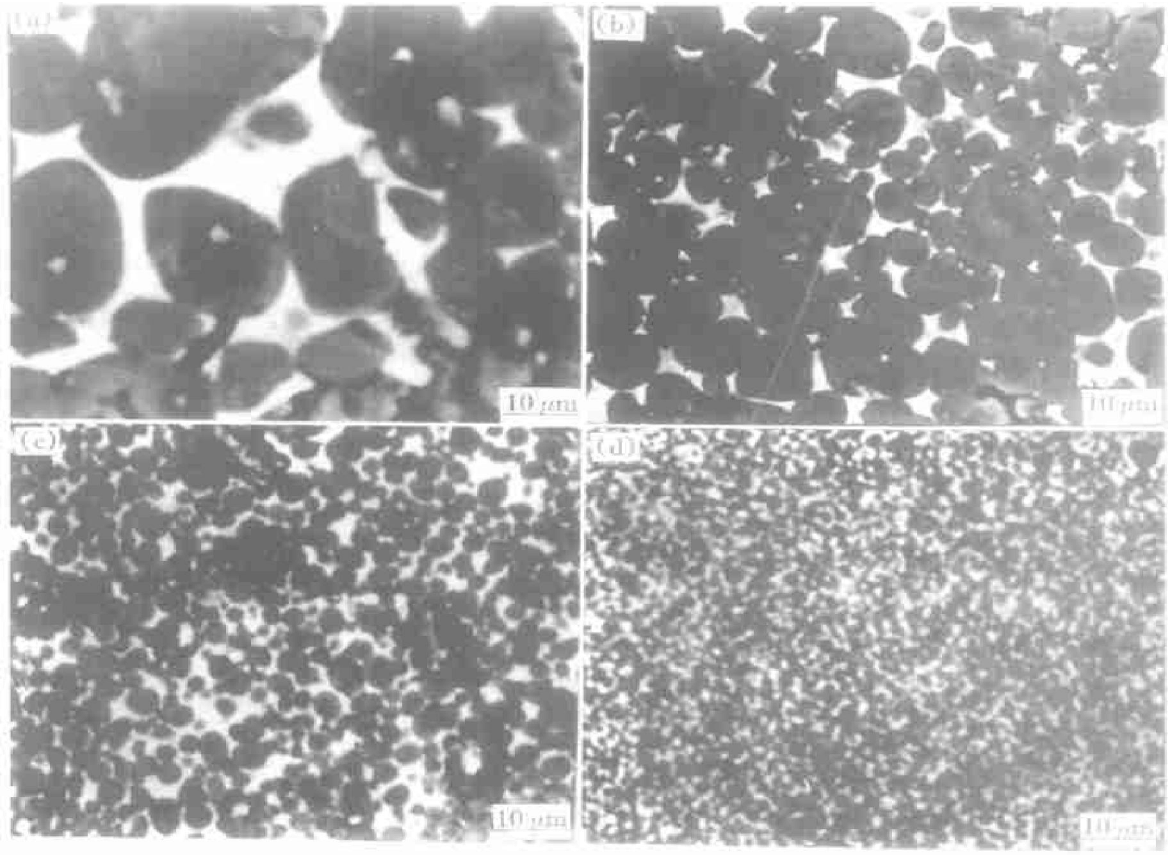

Fig.4 Microstructures of product with different Fe content
(a) —TF10; (b) —TF20; (c) —TF30; (d) —TF40

(1) Some of volatile gases such as CO are probably produced.

(2) The densification will be resisted by the negative pressure formed by the vaporization of a little of Fe in combustion materials.

(3) Some of small pores are probably formed because Fe-binders could not infiltrate all of the TiC particles due to short holding time for high temperature.

(4) It is likely to form pores between TiC particles and Fe binder phases which are not completely wetted.

Fig.5 is the influence of Fe content on the densification of combustion products. The result shows that the more the Fe content is, the higher the densification of the production is. When Fe content is 30%, the densification of the products is the highest, i.e., 96.3%. As Fe content continues increasing, the densification slightly decreases. It is beneficial for the densification that the quantity of liquid metal increases and the quantity of gases becomes little by little on account of low combustion temperature. At the same time, the consolidation of the products will hinder the processing of densification.

The TEM photographs and selected district diffraction of TF30 cermets are shown in Fig.6. A thin diffusion layer was found between Fe-binder phases and TiC particles. It is probably the result of the melting of Fe on TiC particles in combustion processing owing to the well wetting of Fe and TiC($\theta = 36°$)[11]. The thickness of the layer is determined by the holding time at high temperature and the diffusion ability of Ti and C

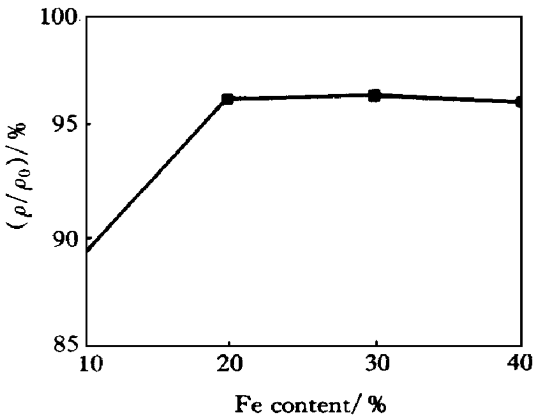

Fig.5 Influence of Fe content on densification of products

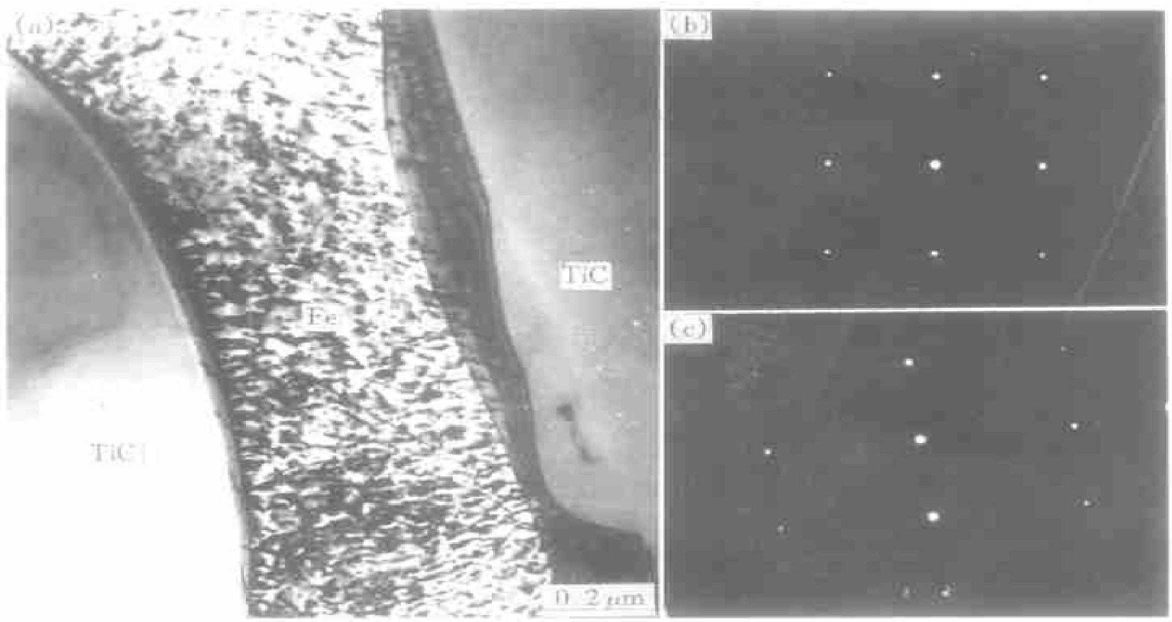

Fig.6 Microstructures of products
(a) —TEM of TF30; (b) —Fe selected area diffraction pattern;
(c) —TiC selected area diffraction pattern

atoms in the molten Fe. In the system of TiC-Fe, the chemically induced diffusion is a processing of thin liquid layer migration. When the diffusion among atoms is maintained at a dynamic equilibrium on the interface between solid and liquid, all of the contributions are gradually distributed along the thin liquid layer in which the main migration force is the diffusion of Ti and C atoms[12].

The calculating result from Fig.3 and Figs. 6(b) and (c) shows that Fe-binder phase is a body-centered lattice with a 0.2877 nm lattice constant and the lattice constant of TiC is 0.4318 nm. The lattice constant of Fe-binder phase is larger than the lattice constant of α-Fe (a = 0.2866 nm). The EDS result shows that a little of Ti was found in Fe-binder phase (the atom ratio of Fe and Ti is 9∶1). It is reported that a small amount of C can also dissolve in Fe[13]. It is considered that C atoms dissolve in the interval solid solution mode while Ti atoms in the undue-saturation solid solution mode in Fe-binder phase because of the rapidly cooling rate of the combustion products after burn. It results in not only distorting and enlarging the lattice constant but also enhancing the strength of the Fe-binder phase. As we know, the atom ratio of Ti and C is 1∶1, the atoms of C would be enrich since the quantity of Ti solution is much higher than the interval solid solution of C in Fe-binder phase (the interval solid solution of C atom is very little). However, the atom ratio of Ti and C in combustion products is basically consistent with the ratio of the reactants and no residual C is found in the products. The main cause is probably that the loss of C is unavoidable in combustion processing.

4 CONCLUSIONS

(1) Dense TiC-Fe cermets were produced by self-propagating high temperature synthesis and pseudo-hot isostatic pressing (SHS/PHIP). Addition of a small amount of Fe is beneficial to the densification of combustion product. The highest densification of products is 96.3 % when Fe content is 30 %.

(2) The combustion temperature and velocity gradually decrease with increasing Fe content. In the range of 10 % ~ 20 % Fe content, the combustion temperature and velocity decrease more slowly than the other contribution owing to the formation of $FeTi_2$ compound with low melting point.

(3) The TFx cermets consist of quasi-spherical TiC particles and Fe-binder phases. A thin diffusion layer was found between Fe-binder phases and TiC particles. The particle size of TiC becomes small with increasing Fe content.

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