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PREPARING SIC-TIB$_2$ COMPOSITE VIA LIQUID PHASE SINTERING

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Abstract: Silicon carbide (SiC) and titanium diboride (TiB_2) namely as super high-temperature structure materials offer the excellent property of good mechanical properties with high melting point, high thermal stability and good chemical stability towards both acids and bases. However, the use of monolithic SiC and TiB_2 is limited by poor sinter ability and low fracture toughness. Some research works showed that the composites of SiC-TiB_2 had better mechanical properties than monolithic ceramic. In this study, Silicon carbide – titanium diboride (SiC-TiB_2) composite had been prepared by hot-pressure sintering with Al_2O_3-Y_2O_3 as sintering additives under relatively lower temperature. The sintering behaviors, mechanical properties and electrical conductivity with different TiB_2 content were researched. The results showed that the density of sintered could achieve 97% theoretical in 1900℃, new phase (YAG) had been formed during sintering. With the increasing of TiB_2 content, the bending strength and fructure toghness of composites increaed, while the Electrical resistivity dreased.

Keywords: SiC-TiB_2 composite, liquid phase sintering, mechanical properties, conductivty

Introduction

Silicon carbide (SiC) and Titanium diboride（TiB_2）namely as super high-temperature structure materials offer the excellent property of good mechanical properties with high melting point, high thermal stability and good chemical stability towards both acids and bases in high temperature[1,2]. But the applications of these ceramics are limited due to the low fracture toughness. It is known that fracture toughness can be improved by incorporation of second phase particles with different thermal expansion coefficients. TiB_2 has higher thermal expansion coefficients(about $8.5*10^{-6}$) than that of SiC (about $4*10^{-6}$)[3,4]. The mismatch of the thermal expansion improve toughness by deflecting the cracks around the TiB_2 particles. [5]. SiC and TiB_2 all have high covalence bond and the low self-diffusion coefficient, which cause difficult to dense. For example, even the sintering temperature arrived 2400℃~2500℃, the sintering pressure was the 1GPa, the relative density of TiB_2 sintered sample just archived 94.5 ~99% theory [6]. The densification of SiC always uses liquid phase sintering additives such as Al_2O_3-Y_2O_3, AlN-$Y_2O_3$to decrease the sintering temperature[7,8]. Composites of SiC-TiB_2 can be fabricated by hot-pressing with the aid of C and Al or B [9,10] or pressureless sintering with *in situ* synthesis of TiB_2 through a reaction between TiC and boronto a near full density at temperatures in excess of 2000℃[11,12]. It has been also report that the composites were fabricated from β-SiC and submicron TiB_2 powders with the liquid forming additives of Al_2O_3 and Y_2O_3 by hot-pressing at 1850℃ and subsequent annealing at 1950 ℃. The annealing led to the in situ growth of elongated a-SiC grains, due to the β→α phase transformation of SiC, and the coarsening of TiB_2 grains. The fracture toughness of the SiC-50 wt% TiB_2 composites after 6 h annealing was 7.3 $MPam^{1/2}$[13]. Black SiC powder prepared by Archision method and self-propagating Synthesis (SHS) TiB_2 powder are considered as the cheapest powders of these ceramics. In this study, SiC-TiB_2 composites were prepared by submicron black SiC powder and SHS TiB_2 powder as raw materials, Al_2O_3-Y_2O_3 as

liquid phase additives. The effect of different TiB_2 content on sintering behaviors, mechanical properties and electrical conductivity had been researched.

Experimental

Black SiC (α -SiC) and TiB_2 powder was manufactured by Ningxia mechanical research institute. The chemical analysis of the powder was performed by manufacturer and the data were as showed in table 1 SiC,TiB_2 powders and sintering additives were mixed in attrition mill for about 1hr in alcohol using SiC balls as medium. The compositions of various powder mixtures prepared and the nomenclature used to describe the samples are specified in Table 2.The milled slurry was separated from the milling ball and possible wear debris by screening through 320mesh. The slurry dried in a stirring evaporator and completed dried in a drying oven at 80℃。 The dried powder was sieved through 100 meshes. The mixed powder was dried under pressure of 100Mpa. The rectangular shaped green samples of approximately 10×50×50mm were sintered in a graphite furnace (made by Noberte China). The samples were put into a graphite crucible using carbon paper as separating. The samples were hot pressed at 1900℃ for 1hr with 25Mpa applied pressure.in an argon atmosphere.

Tab.1 Characteristic of raw materials

powder	D_{50}/ μ m	purity/%	O.wt/%	C/wt%	Fe/%
SiC	0.8	97.5	1.0	1.2	<50ppm
TiB_2	6	98.5	0.4	0.15	0.15

Tab. 2 composition of samlpes

sample	SiC /wt%	TiB_2 /wt%	SiC:TiB_2	Al_2O_3 /wt%	Y_2O_3 /wt%	ρ_{theore} /gcm^{-3}
1#	72	18	80:20	7	3	3.54
2#	58.5	31.5	65:15	7	3	3.67
3#	45	45	50:50	7	3	3.82

The phase of composition was determined by X-ray diffraction using Cu-K radiation (XRD-6000 Shimadzu Japan) , a step width of 0.2 with an exposure time of 2 degree/min per position. Bulk densities were measured by Archimedes's principle by a water displacement method. The theoretical densities were calculated according to the rule of mixtures. The hardness was determined by using a load of 49N in a micro-hardness test fitted with a Vicker's square indenter (Wolpert U.S.A). The specimens were cut to 3×4×36mm pellets to test three point bending strength using universal testing machine (DXS-1 xinsansi China) . The tensile edges were beveled to remove stress concentrations and edge flaws caused by sectioning. The fracture toughness was tested by single edge notched beam(SENB) method Specimen size is 4x2x40 mm. On the orientation of height it was cut out a edge notch with depth 2.0 mm and width <0.2 mm. The test was conducted in universal testing machine by using the span length 16 mm and the velocity of pressure head 0.5 $mm \cdot min^{-1}$s. The maxima loading in fracture was test and the fracture toughness was calculated as following:

$$K_{IC} = \frac{3P_c L}{2BW^2} \cdot \sqrt{a} \cdot Y(\frac{a}{w}) \quad . \qquad (1)$$

The electrical resistivity was measured with the four linear point method using 3×4×36mm pellets.

Observation of the microstructure has been performed by SEM (ssx-550 Shimadzu Japan) on fracture surfaces and also on finished surface polished by 1 μ m diamond paste.

Results and discussion

Fig 1 shows the results of sintered densities and theoretical densities of hot-pressed samples. The relative densities of all samples were higher than 96%, but lower than 98%, with the increasing of TiB_2 content, the relative densities decreasing. This indicated that SiC-TiB_2 can be densified at a temperature lower 150-200℃ than solid state sintering in early works[12].

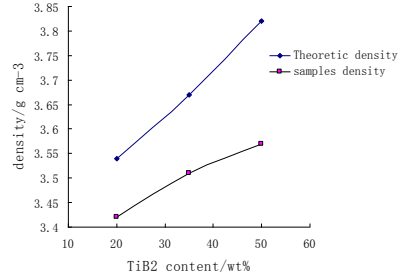

Fig 1. Samples density with different TiB_2 content

In this work, the TiB_2 particles was prepared by self-propagating Synthesis (SHS) method which is a very cheap one but have drawback of relatively large, particle size above 6 μ m. That is the main reason of difficult to dense. Al_2O_3 and Y_2O_3 additives in the sintering SiC are known to form liquid phase with SiO_2 in the surface of SiC and to promote densification through liquid phase sintering. In this study, the oxygen content of TiB_2 is about 0.4%, much less than SiC which is about 1.0%. More TiB_2 content According to Al_2O_3-Y_2O_3 diagram, In the sintering, additives react. To form compound YAG ($5Al_2O_3$: 3 Y_2O_3) which had been confirmed by XRD analysis (Fig 2). The new phase formation makes the theoretical density changes.

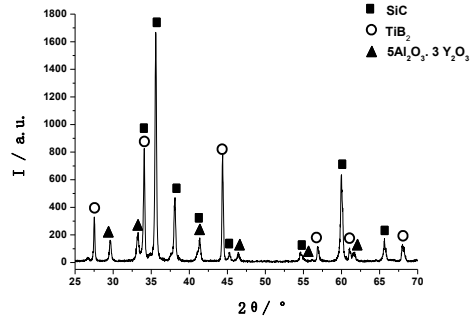

Fig 2 XRD pattern of sintered sample

Mechanical properties of the composite are shown in table 2. The overall values for strength of sintered composites are higher than that for monolithic SiC which is about 350~500Mpa. It is also noted that the bending strength of composites increased with increasing TiB_2 content. The increasing of bending strength is considered to be the addition of high strength component TiB_2

which monolithic strength is 600~700Mpa[14]. The improvement of matrix material strength cause the bending strength of sintered samples increases with TiB_2 content.

The theoretical hardness of monolithic SiC is about 2300Mpa, the hardness of TiB_2 is about 3000Mpa, in this study, SiC-35%wt TiB_2 composite owned the best hardness value. In the ideal case, the hardness of composites should increase with the increasing of TiB_2 content, the experimental results show that, when the TiB_2 content reached 50%, the hardness decreased. The reason of hardness decreasing should be the porosity of composite. In that case, the relatively density of sintered sample was only up to 93.5% of theoretical density, porosity was about 4.5%.

The hardness as a function of the elastic module with liner relation has a quantitative relation formula E = 20Hv. The porosity of composite effect the elastic modulus greatly, the elastic modulus (E) and volume fraction of porosity (p) stands relationship as following [15]:

$$E=E_0（1-f_1p+f_2p^2） \quad (2)$$

The higher porosity make the elastic module decreasing and decreasing the hardness of composite.

Table 3 mechanicle properities of composites

TiB_2 Contents/%	Bending strength/ Mpa	Hardness Hv/Mpa	Fracture toughnessKic/ $Mpam^{1/2}$
20	359	2601	5.88
35	445	2896	6.26
50	460	1910	6.39
50*	210	2220	2.5

50* SiC-TiB_2 composite prepared by solid state sintering at 2180℃[12]

All composite have higher fracture toughness than monolithic ceramics and composite which prepared by solid state sintering. The mismatch of thermal expansion coefficients between SiC and TiB_2 is considered as one reason of high fracture toughness. During cooling processing of fabrication, the large shrinkage of second phase particles compared to SiC matrix is expect to create compressive residue stress around the particle which lead to increasing the fracture toughness of composites[3] Secondly, the change of fracture mode caused by liquid phase sintering is other reason of toughness increase. Microstructure observe of break surface show that there are intergranular fracture instead of transgranular fracture comparing with solid state sintered composite (Figure 3), due to the presence of liquid phase.

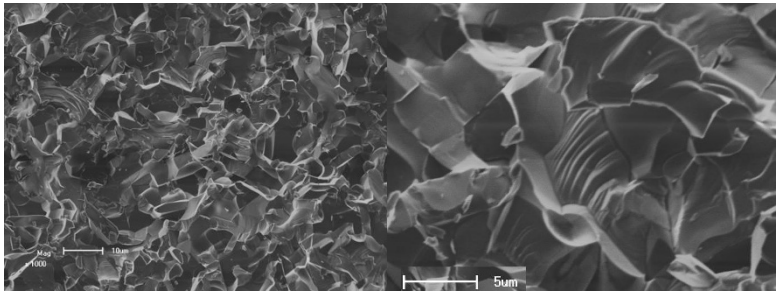

Fig3 SEM pictures of different break surface(left: liquid phase sintered by this work, right: solid state sintered)

Fig 4 show the Change of composites conductivity with different TiB_2 contents. The conductivity decreases with the increase of TiB_2 content in exponential function decline. Monolithic TiB_2 ceramics has good electrical conductivity and thermal conductivity, but monolithic SiC ceramics is a semiconductor or poor conductor, so there is a direct relationship between the content of TiB_2 and conductivity of SiC-TiB_2 composites. The conductivity of SiC-35%TiB_2 composite can meet the need of the electric spark machining (EDM) therefore, given another low cost post processing for high hardness ceramics.

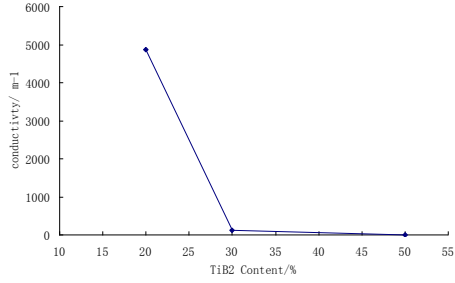

Fig 4.composites conductivity with different TiB_2 contents

Conclusion

1) Using cheaper raw materials,(black SiC and SHS TiB_2), SiC-TiB_2 composites were prepared by hot pressing at 1900 ℃ via liquid phase sintering. The relative density of composites achieved to 94%-97% theoretical density, and the relative density decreased with the TiB_2 content increasing.

2) All composites sowed the better flexural strength and fracture toughness than monolithic material. The flexural strength increased with the TiB_2 content increased. The increasing of fracture toughness is due to the mismatch thermal expansion coefficients and liquid phase sintering which changed the fracture mode from transgranular fracture to intergranular fracture.

3) The resistivity of composites decreased exponentially trend with increasing TiB_2 content. The electrical properties of SiC-35%TiB_2 composites can meet the need of EDM.

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