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Hot pressing of SiC–TiC composites

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Sintering behaviour during hot pressing of SiC–TiC composite ceramics has been investigated with special emphasis on the effect of various processing parameters on the density and mechanical properties of the sintered body. At hot pressing temperatures greater than 2000° C, significant densification occurred in SiC–50 wt %TiC (–0.5 wt % B–1 wt % C) composites. The room temperature flexural strength of the sintered body increased with the hot pressing temperature up to 2000° C and reached a highest value of 710 MPa in accordance to the variation of density with temperature. In sintering of composites without additives, densification was enhanced with the addition of up to 25 wt %TiC, with relative densities higher than 98% observed when hot pressing at 2150° C for 2 h.

1. Introduction

Applications of ceramics for structural uses have been realized in various industrial fields where the applications were confined so far due to the limited performance of existing engineering materials such as metals, alloys, and/or organic polymers. Ceramic materials have excellent refractoriness with high specific strength as well as wear resistant properties based on their inherent hardness, and they also exhibit superior anti-corrosion properties against various chemicals.

Although silicon carbide based ceramics have been known to be hardly densified during sintering without using additives, due mainly to the strong covalent bond of SiC, Alliegro *et al.* [1] and Lange [2] have succeeded in obtaining fully densified SiC based ceramics through hot pressing during which liquid phase sintering occurs when aluminium compounds are used as sintering aids.

In the approach of solid phase sintering, Prochazka [3] established a pressureless sintering technique of the SiC using boron and carbon as the sintering aids. Since that time much attention has been focused onto SiC based ceramics, followed by much research concerning the effect of sintering aids on densification. As to the role of boron and carbon during the sintering of the SiC, Prochazka [3] has proposed that the boron forms amorphous B_4C on the surface of the SiC which lowers the grain boundary energy, and the carbon reduces the SiO_x on the surface of the SiC. Through these mechanisms the surface of the SiC is activated which results in substantial enhancement of densification during sintering.

On the other hand, titanium carbide, a material with non-stoichiometric composition usually represented by $TiC_x(x: 0.52–0.98)$ has quite high hardness (Hv: 3200) and refractoriness (melting point > 3000° C) [4]. These characteristics allow the material to be used as cutting tools and etc. TiC as one of the transition metal carbides, exhibits metal-like properties such as metallic luster, electrical conductivity and plasticity with operation of 12 independent slip systems at high temperatures. Deformation behaviour and mechanisms have been investigated for both single crystal [5] and polycrystalline TiC [6] at a range of temperatures.

Nevertheless, both SiC and TiC exhibit extremely poor reliability based upon their low toughness in the monolithic state. Furthermore, there are difficulties in machining SiC due to chipping which arises from its inherent brittleness and high hardness, this contributes to the high cost of such ceramics.

Recently, incorporation of some other non-oxide material with the SiC based ceramics has been widely investigated to solve the above mentioned problems. As examples of such incorporations, the composites $SiC–Si_3N_4$ [7, 8], SiC–AlN solid solution [9, 10], SiC–TiC–(Al–C) [11] and $SiC–TiB_2–(B–C)$ [12, 13] were investigated from the aspect of improving the mechanical properties, where aluminium, boron and carbon are the sintering aids. The composites, $SiC–ZrB_2–(Al_2O_3)$ [14] and SiC–carbides, nitrides and borides of transition metals [15] have also been studied with the aim of increasing the conductivity of the SiC based materials.

In the present work, the sintering behaviour during hot pressing of SiC–TiC particle dispersion type composites has been investigated with the aim of clarifying the effect of hot pressing condition, sintering aid and crystalline form of SiC on the sinterability and mechanical properties of sintered bodies.

2. Experimental procedure

The starting powders used are listed in Table I along with their particle size, purity and manufacturers. Powders of either α or β types of SiC were mixed with TiC together with one of the sintering aids such as (a) B_4C powder and carbon black, (b) Al_2O_3 and (c) no addition. The amount of TiC addition to the SiC was in the range from 0 (monolithic SiC) to 100 wt % (monolithic TiC). Well-mixed powders were obtained by ball-milling in *n*-hexane for 24 h using polyamide media. After drying the powders were loaded into a graphite die with an inner diameter of 90 mm, and hot

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pressed at temperatures between 1800 and 2150° C for 2 h under a pressure of 40 MPa in an argon gas atmosphere. Hot pressed discs of SiC–TiC composites were machined into bars (3 mm × 4 mm × 38 mm) for flexural tests and the densities of each bar were measured by the water displacement (Archimedes) method.

Three-point flexural tests were conducted at room and elevated (at 1200 and 1500° C under a dynamic flow of argon gas) temperatures, according to the method specified as JIS R-1601 and R-1604, respectively. The fracture toughness, K_{IC} was determined by using a SEPB method [16].

3. Results and discussion

3.1. Hot pressing conditions

Figure 1a shows the variations of the attainable density with hot pressing temperature under similar conditions, 40 MPa with a 2 h soak time for β-SiC (-1 wt % B–1 wt % C), β-SiC–50 wt % TiC (-0.5 wt % B–1 wt % C) composites and TiC. For monolithic TiC sufficient densification in excess of 99% theoretical density (TD) was achieved at temperatures over 1800° C. However, in the case of monolithic SiC, densification corresponding to 98% TD did not occur even at 2000° C. According to the results of linear shrinkage measurement, the densification seems to start at 1250° C for TiC and at 1500° C for SiC, respectively. In the case of SiC–50 wt % TiC composite, the densification curve approximately followed that of SiC as shown in the figure. Although bulk diffusion of TiC may initially occur in the composite even at 1300° C, SiC particles prevent substantial densification. Between 1900 ~ 2000° C, densification of the SiC is the major factor influencing strength component, and at temperatures exceeding 2000° C, the density of all samples becomes approximately the same.

The flexural strength at room temperature increased with the hot pressing temperature in accordance with the increase in the density for SiC and SiC–50 wt % TiC, the highest strengths recorded were 620 and 710 MPa, respectively (see Fig. 1b). On the other hand, TiC which was hot-pressed at 1800° C, exhibited a high strength (680 MPa), but the strength decreased monotonically to 420 MPa with increasing hot-pressing temperature. The reason why the strength decreased is thought to be due to grain growth of TiC to sizes around $2 \sim 5\,\mu$m.

Next, using a fixed hot pressing condition of 2150° C for 2 h under 40 MPa, composition was varied. As shown in Table II, relative densities in excess of 98% TD were attained in all the composites sintered.

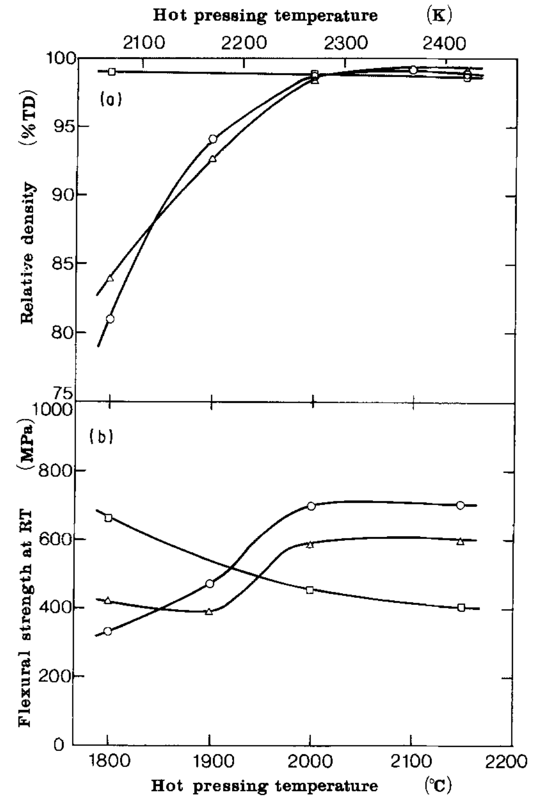

Figure 1 Effect of hot-pressing temperature on (a) densification and (b) flexural strength of sintered bodies for (○) SiC–50 wt % TiC, (△) SiC and (□) TiC. 40 MPa for 2 h.

3.2. Sintering additives

Figure 2a shows the variation of relative density with TiC content for β-SiC–TiC composites system without sintering aids when hot pressing at 2150° C for 2 h. Sufficient densification in excess of 98% TD was achieved in the composites with TiC content higher than 25 wt %. However, the composite with less than 25 wt % TiC was hardly densified due to the inherent low sinterability of SiC. As a matter of fact the minimum amount of TiC addition into SiC for which the composites have sufficiently high density was influenced by the hot pressing conditions, such as temperature, pressure and soaking time, and characteristics, especially particle size, of the starting powders. Flexural strength of SiC–TiC composites without sintering aids at both room temperature and 1500° C (in an argon atmosphere) is also shown in Fig. 2b as a function of the TiC content. In the composition with greater than 25 wt % TiC, the room temperature flexural strengths were almost equivalent to those of the composites with boron and carbon additions [17]. However, both the room and elevated temperature strengths decreased much drastically for those com-

TABLE I Particle size, purity and manufacturers of the starting powders

Starting powder	Average particle size (μm)	Purity (%)	Manufacturer and grade
β-SiC	0.3	> 98	Ibiden Co., Ltd., (Ultrafine)
α-SiC	0.4	> 98	Showa Denko K.K., (DU A-1)
TiC	1.2	> 99	Kojundo Chem. Lab. Co. Ltd.
B_4C	1.0	> 99	Denki Kagaku Kogyo KK, (1500 A)
C	0.02	> 99	Mitsubishi Chem. Ind., (600 MA)
Al_2O_3	0.2	> 99.995	Sumitomo Chem. Ind., (AKP-50)

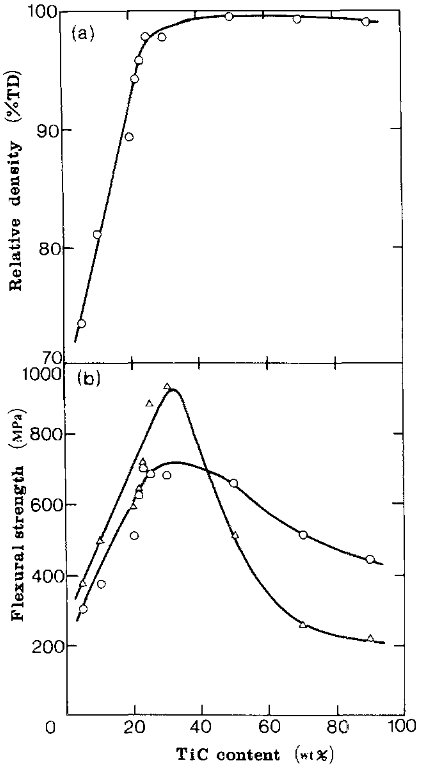

Figure 2 Effect of TiC content on densification (a) and flexural strength of sintered bodies at both (○) RT and (△) 1500° C (b) for SiC–TiC ceramics hot pressed at 2150° C for 2 h under a pressure of 40 MPa.

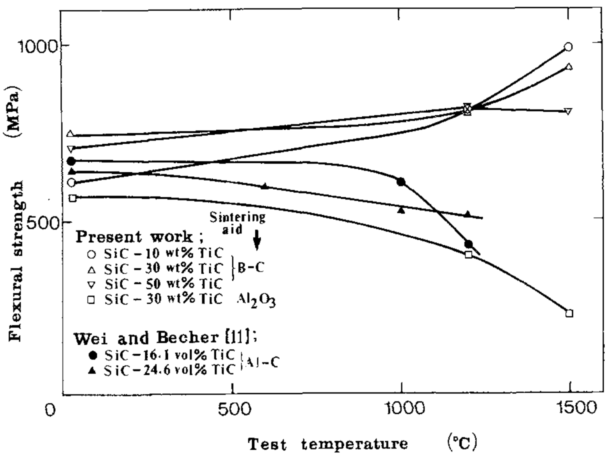

Figure 3 The temperature dependence of flexural strength for various SiC–TiC composites, showing the effect of sintering aids on the high temperature strength.

posites with less than 25 wt % TiC content, compared with those of composites containing boron and carbon. This is partly due to the lower densities of the composites without sintering aids. On the other hand, the high temperature strengths were lower than those of SiC–TiC composites with boron and carbon. Therefore, it may be suggested that additions of boron and carbon will affect the fracture behaviour of the composites at elevated temperature. Carbon will be especially effective at removing oxide phases at grain boundaries in the sintered body by reducing SiO_2 and TiO_2 on the surface of starting SiC and TiC powders.

Aluminium and its compounds such as Al_2O_3, are known to be effective as additives for sintering SiC based ceramics. In Table III relative densities and flexural strength (at both room and elevated temperatures) of β-SiC–TiC composites with 2 wt % Al_2O_3 additions were compared to those of composites with boron and carbon as sintering aid under the fixed hot pressing condition of 2150° C for 2 h. In the case of Al_2O_3 additions sintered bodies with densities higher than 99% TD could be attained. However, the flexural strength was lower than for those composites with boron and carbon, in particular the high temperature strength decreased drastically as shown in Fig. 3 together with the results obtained by Wei and Becher [11]. This reduction in strength may be caused by the formation of a glassy phase (Al_2O_3–SiO_2 system) at the grain boundaries introduced during liquid phase sintering of the SiC [2]. In fact, contrary to the SiC–TiC–B–C system, intergranular type fracture was dominant in SiC–TiC–Al_2O_3 system at elevated temperature.

3.3. Crystalline form of SiC

For the composition containing 50 wt % TiC, the effect of crystal form on the sinterability and mechanical properties of the composite was investigated. The relative density and mechanical properties of the sintered composites are compared among β-SiC–50 wt % TiC, (25 wt % α-SiC + 25 wt % β-SiC)–50 wt % TiC and α-SiC–50 wt % TiC. As shown in Table IV although the sinterability of these composites were almost equivalent from the densification point of view, the β-SiC–TiC composite exhibited a superior flexural strength and fracture toughness. The superiority of the β-SiC was mainly due to a larger thermal expansion coefficient mismatch between it and TiC compared to α-SiC crystals and partly because of a lower impurity (metallic element) level compared to that of the α-SiC powders used. Because the thermal expansion coefficient of β-SiC

TABLE II Composition of SiC–TiC (–B–C) composites and their density attained by hot pressing at 2150° C for 2 h

Composition (wt %)				Relative density (% TD)
SiC*	TiC	B†	C	
98.0	–	1.0	1.0	99.2
88.1	10.0	0.9	1.0	98.0
68.3	30.0	0.7	1.0	98.9
48.5	50.0	0.5	1.0	98.8
28.7	70.0	0.3	1.0	98.7
8.9	90.0	0.1	1.0	98.5
–	100	–	–	98.6

*β-SiC
†Converted from B_4C

TABLE III Effect of sintering aids on the density and mechanical properties of SiC–TiC composites, hot pressed at 2150° C for 2 h

TiC content (wt %)	Sintering aids	Density (% TD)	Flexural strength (MPa)			Fracture toughness K_{IC} (MPa m$^{1/2}$)
			RT	1200° C	1500° C	
10	No addition	81.1	380	400	500	–
30		97.8	690	800	930	–
50		99.6	660	580	510	–
10	B and C	98.0	610	830	970	2.65
30		98.9	750	800	930	5.05
50		98.8	710	830	800	6.00
10	Al_2O_3 (2 wt %)	99.9	580	350	180	–
30		99.6	570	390	230	–
50		99.2	550	360	220	6.10

($4.4 \times 10^{-6} deg^{-1}$) is slightly lower than that of α-SiC ($4.8 \times 10^{-6} deg^{-1}$), the residual stress generated by the difference in thermal expansion coefficient in both SiC and TiC ($7.9 \times 10^{-6} deg^{-1}$) phases must be higher in the former. This reflects the difference in the fracture toughness for both composites. It is also well known that α-SiC powders usually contains more metallic impurities than β, which may result in lower strength of the sintered bodies due to segregation of metallic elements at the grain boundaries. Consequently β-SiC is more favourable for the fabrication of SiC–TiC composites.

4. Conclusions

Sintering and densification behaviour of SiC–TiC composite ceramics were investigated by hot pressing. In the case of the SiC–50 wt % TiC (–0.5 wt % B–1 wt % C) composite, significant densification occurred at hot pressing temperatures greater than 2000° C. The room temperature flexural strength of sintered bodies increased with temperature up to 2000° C, and exhibited the highest value (710 MPa) that was related to the variation in density with temperature. For SiC–TiC composites with no addition of sintering aids, the density of the sintered body increased abruptly with up to 25 wt % TiC additions, and then relative densities greater than 98% were achieved when hot-pressing at 2150° C for 2 h. On the other hand, by using sintering aids of boron and carbon for SiC, dense sintered bodies were obtained for all the TiC contents in the SiC–TiC system. The flexural strength both at room (RT) and elevated temperatures exhibited maximum values at around 30 wt % TiC, they are 710 MPa at RT and 920 MPa at 1500° C, respectively. The effectiveness of boron and carbon as sintering aids is shown by the increases in strength at temperature in excess of 1000° C, compared with strength reductions when using aluminium compounds as sintering aids. The β-type of SiC as a raw material was favourable for fabrication of the present SiC–TiC composites from the view point of mechanical properties of the sintered body.

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TABLE IV Effect of the crystal form of SiC on the mechanical properties of SiC–50 wt % TiC (–0.5 wt % B–1.0 wt % C), hot pressed at 2150° C for 2 h

Crystal form of SiC	Relative density (% TD)	Fracture toughness (MPa m$^{1/2}$)	Flexural strength (MPa)	
			RT	1500° C
β	98.8	6.0	710	800
α + β*	98.4	5.5	660	330
α	98.5	5.2	560	280

*α:β = 1:1