Journal of Alloys and Compounds, 191 (1993) 191–195
JALCOM 512

Synthesis and sinterability of composite powder of the TiB_2–B_4C system

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(Received July 14, 1992)

Abstract

Composite powders of composition TiB_2–xB_4C ($x = 0.3$, 0.5, 0.7 and 1.0) were synthesized by a solid state reaction between TiC_xN_{1-x} and amorphous boron. The formation of TiB_2 and B_4C occurs by a stepwise process: (1) the formation of TiB_2 by the substitution of boron for carbon or nitrogen atoms in TiC_xN_{1-x}; (2) the simultaneous or subsequent formation of B_4C by the reaction between unreacted boron and free carbon released from TiC_xN_{1-x}. The formation reaction of a well-dispersed composite powder of the TiB_2–xB_4C system was completed by heat treatment of the starting powder mixed in the mole ratio TiC_xN_{1-x}: $B = 1:(4x+2)$ under a flowing argon atmosphere at 1500 °C for 60 min. The synthesized powder, which was densified at 4 GPa and 1600 °C for 15 min, exhibited favourable sinterability. The sintered compact showed a relative density of 93.7%–97.0% and a Vickers microhardness of 35.3–37.3 GPa depending on the composition.

1. Introduction

Titanium diboride (TiB_2) and boron carbide (B_4C) have high melting points and hardnesses as well as low densities compared with those of other transition metal borides and carbides [1] as seen in Table 1. The thermal expansion coefficients of the two compounds are quite similar, but the electrical conductivity varies from metallic (TiB_2) to semiconducting (B_4C) behaviour. However, TiB_2 and B_4C are difficult to sinter [2] and several composite systems based on the two boron compounds have been investigated in order to prepare dense sintered compacts [3–10].

Sintered composites based on the TiB_2–B_4C system are expected to be useful for corrosion- and wear-resistant tools or electrode materials if a successful processing route can be developed. A fine-grained composite powder with a homogeneous distribution of TiB_2 and B_4C is required to prepare dense and tough sintered compacts in this system [11].

Recent papers describe a new procedure to synthesize fine TiB_2 powder by a controlled solid state reaction between titanium nitride (TiN) and amorphous boron [12, 13] and the subsequent preparation of sintered single-phase TiB_2 compacts by hot pressing [14]. A similar formation reaction for the synthesis of mixed TiB_2–B_4C powder would be the solid state reaction between titanium carbonitride (TiC_xN_{1-x}) powder and amorphous boron powder according to

$$TiC_xN_{1-x} + (4x+2)B \longrightarrow TiB_2 + xB_4C + [(1-x)/2]N_2 \quad (1)$$

In the present work the synthesis of TiB_2–B_4C composite powder was investigated by varying the value of x from 0.3 to 1.0. The sinterability of the synthesized powder was investigated by high pressure sintering.

2. Experimental details

2.1. Synthesis and sintering of composite powder

Commercially available TiC_xN_{1-x} powders (Nihon Sin-Kinzoku Co., grain size 1.3–1.4 μm, purity better

TABLE 1. Properties of TiB_2 and B_4C

	Density (g/cm^3)	Melting point (°C)	Hardness Hv (kg/mm^2)	Resistivity (Ω cm)	Thermal expansion coefficient (deg^{-1})
TiB_2	4.53	2790	3400	9×10^{-6}	4.6×10^{-6}
B_4C	2.51	2450	4200	1	4.5×10^{-6}

0925-8388/93/$6.00

than 96 wt.%) and amorphous boron (Rare Metallic Co., grain size 0.5–3 μm, purity better than 96.6 wt.%) were used as starting materials. The compositions of the as-received TiC_xN_{1-x} powders ($x=0.3$, 0.5, 0.7 and 1.0) were confirmed by X-ray measurements of the lattice constants. The initial powders were heat treated separately at 600 °C for 60 min in vacuum and subsequently mixed in an agate mortar in the mole ratio TiC_xN_{1-x}:B = 1:(4x+2), the net contents of TiC_xN_{1-x} and boron in the as-received powders being used for the calculation of the mole ratio. The mixed powder was again pretreated under vacuum (1×10^{-5} Torr) at 600 °C for 60 min and subsequently heated in an argon stream (flow rate 60 ml min^{-1}) for 40 min to a given temperature in the range between 900 and 1500 °C. The soaking time was varied between 0 and 360 min. Finally, the synthesized powder was densified at 4 GPa and 1600 °C for 15 min in a girdle-type high pressure apparatus [15].

2.2. *Analysis and evaluation of synthesized powder and sintered compact*

The synthesized powder and sintered compact were characterized by X-ray diffraction. The relative amount formed and the crystallinity of each crystalline phase were evaluated by the relative intensities of the specified diffraction lines, 101 for TiB_2, 021 for B_4C and 200 for TiC_xN_{1-x}, using the 220 line for silicon as an internal standard. Commercial well-crystallized powders of TiB_2 and B_4C were used for comparison of the crystallinity of the synthesized powder. The contents of Ti and B in the synthesized powders were measured by inductively coupled plasma (ICP) emission analysis. The synthesized powders and the fractured or polished surfaces of the sintered compacts were examined by scanning electron microscopy (SEM) and X-ray microanalysis (XMA). The bulk density of the sintered compact was measured by Archimedes' method and the Vickers microhardness was measured with a load of 0.5 kgf.

3. Results and discussion

3.1. *Effects of treatment temperature on the formation of TiB_2–B_4C powder*

The influence of treatment temperature on the formation of TiB_2 and B_4C was examined in the temperature range 900–1500 °C with a constant holding time of 60 min. Figure 1 shows the relation between relative X-ray intensity (I/I_{Si}) of each phase and treatment temperature for $x=1$, *i.e.* starting powder composition TiC+6B. The X-ray diffraction patterns of the products obtained at 1000, 1200 and 1500 °C are shown in Fig. 2. A small amount of TiB_2 is already detectable at 900 °C and this amount increases progressively with

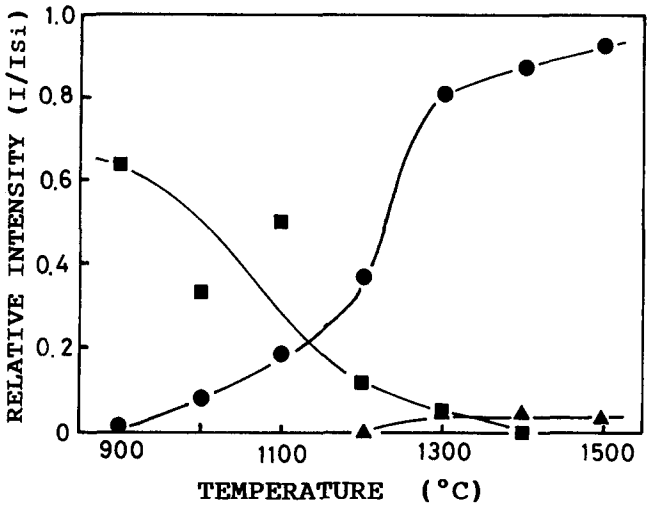

Fig. 1. Relative X-ray intensity plotted against treatment temperature; holding time 60 min; starting powder composition TiC+6B; ●, TiB_2; ▲, B_4C; ■, TiC.

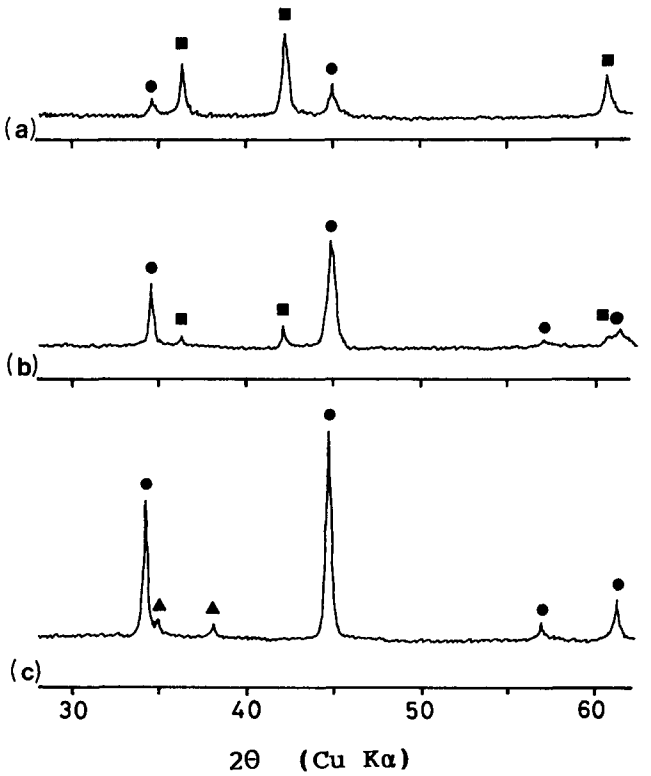

Fig. 2. X-ray diffraction patterns of specimens heat treated at (a) 1000, (b) 1200 and (c) 1500 °C for 60 min; starting powder composition TiC+6B; ●, TiB_2; ▲, B_4C; ■, TiC.

increasing temperature up to 1200 °C, while the amount of TiC decreases (see Figs. 2(a) and 2(b)). Amorphous boron cannot be detected by X-ray diffraction. The following substitution reaction would proceed in the low temperature range, resulting in the formation of crystalline TiB_2 and amorphous carbon:

$$TiC + 2B \longrightarrow TiB_2 + C \qquad (2)$$

A trace of B_4C was detected at 1300 °C, as shown in Fig. 1. In the temperature range 1200–1300 °C a steep increase in the relative intensity of TiB_2 was observed owing to the accelerated formation reaction of TiB_2. The crystallinity of TiB_2 was found to be comparable with that of commercial well-crystallized TiB_2. In the intermediate temperature range the solid state reaction between unreacted boron and free carbon would take place in addition to reaction (2):

$$4B + C \longrightarrow B_4C \quad (3)$$

The following direct formation reaction of TiB_2 and B_4C between TiC and amorphous boron would also proceed simultaneously with the stepwise reactions (2) and (3):

$$TiC + 6B \longrightarrow TiB_2 + B_4C \quad (4)$$

Above 1300 °C a gradual increase in the relative intensity of TiB_2 is observed. However, the relative intensity of B_4C did not increase even at this elevated temperature (see Fig. 2(c)), where the crystallinity was estimated to be low compared with that of commercial well-crystallized B_4C.

Figure 3 shows the relation between relative X-ray intensity and treatment temperature for $x = 0.3$, *i.e.* the starting powder composition $TiC_{0.3}N_{0.7} + 3.2B$. Analogous formation of TiB_2 and B_4C was observed, except that a steep increase in the relative intensity was not seen in the temperature range 1200–1300 °C. According to reaction (1), nitrogen gas would be generated and removed from the reaction system [12]. For both $x = 0.5$ and 0.7 a similar temperature dependence of the relative intensity as shown in Fig. 3 was observed, although the formation of TiB_2 was slightly depressed with decreasing value of x. This could be attributed to the different stabilities of each TiC_xN_{1-x} composition.

3.2. *Effects of holding time on the formation of TiB_2–B_4C powder*

Figures 4(a) and 4(b) show the relation between relative X-ray intensity and holding time for a starting powder composition $x = 1$ and treatment temperatures of 1200 and 1500 °C respectively. TiB_2 formed at 1200 °C according to reaction (2) up to 60 min, after which B_4C began to form, but TiC remained in coexistence up to 240 min. A holding time of over 240 min was required in order to complete the formation reaction of the composite powder comprising crystalline TiB_2 and low crystalline B_4C. However, at 1500 °C it is found in Fig. 4(b) that the TiB_2–B_4C composite powder can be synthesized even without soaking by the direct formation reaction of both powders according to reaction (4).

Figure 5 shows the relationship between relative X-ray intensity and holding time for a starting powder

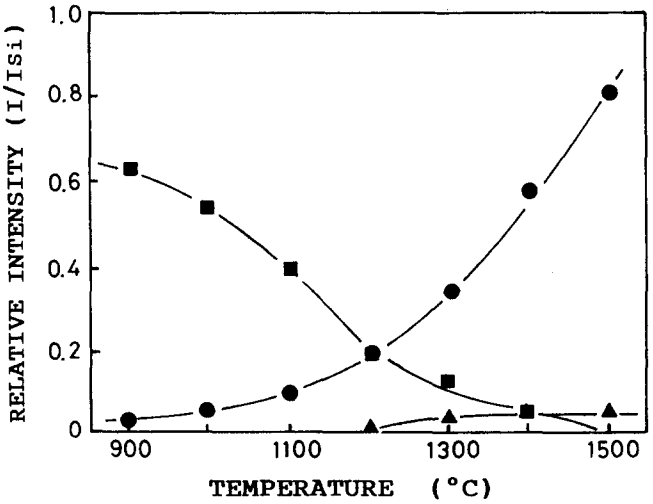

Fig. 3. Relative X-ray intensity plotted against treatment temperature; holding time 60 min; starting powder composition $TiC_{0.3}N_{0.7} + 3.2B$ ($x = 0.3$); ●, TiB_2; ▲, B_4C; ■, $TiC_{0.3}N_{0.7}$.

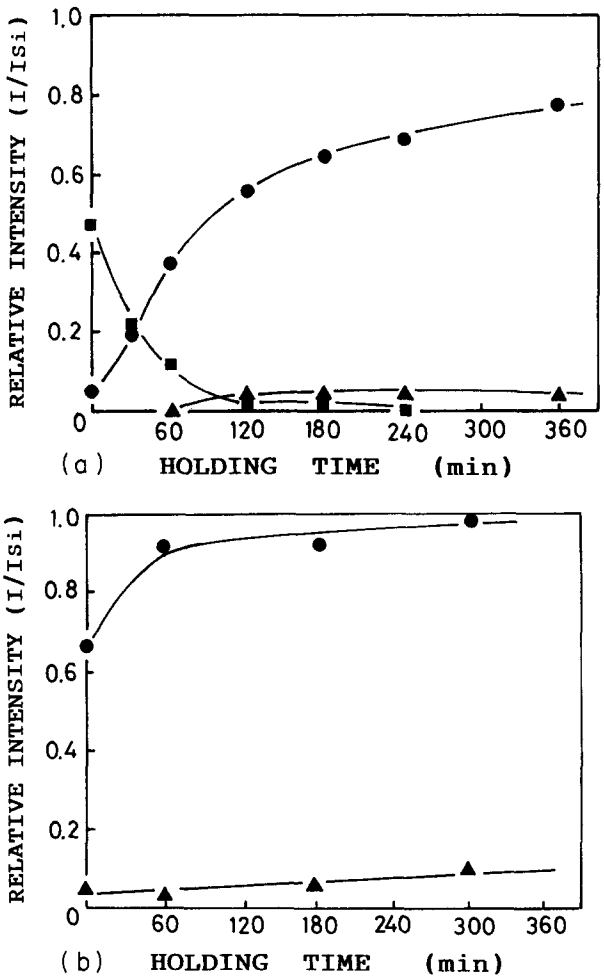

Fig. 4. Relative X-ray intensity as a function of holding time; treatment temperatures (a) 1200 and (b) 1500 °C; starting powder composition TiC + 6B; ●, TiB_2; ▲, B_4C; ■, TiC.

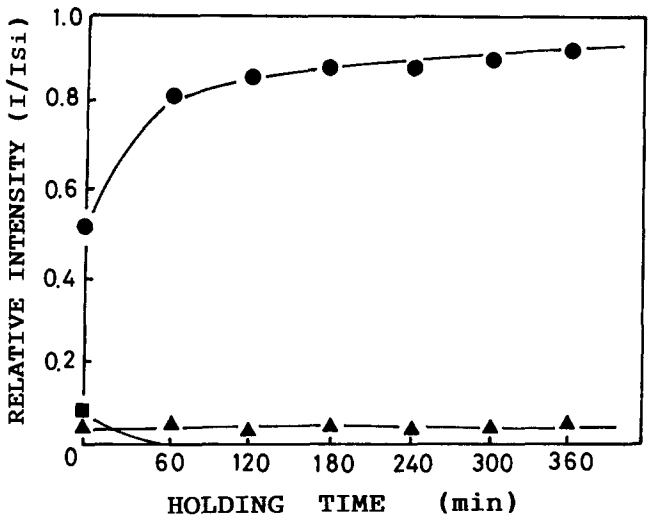

Fig. 5. Relative X-ray intensity as a function of holding time; treatment temperature 1500 °C; starting powder composition $Ti_{0.3}N_{0.7}+3.2B$ ($x=0.3$); ●, TiB_2; ▲, B_4C; ■, $TiC_{0.3}N_{0.7}$.

composition $x=0.3$ and a treatment temperature of 1500 °C. A composite powder of composition TiB_2–$0.3B_4C$ was synthesized after a holding time of 60 min. At the treatment temperature of 1200 °C, however, the solid state reaction (4) did not complete even after 360 min, with a residual $TiC_{0.3}N_{0.7}$ detected.

3.3. Surface appearance of synthesized composite powder

Figure 6 shows scanning electron micrographs of the surface appearance of the composite powders synthesized under the treatment conditions of 1500 °C for 60 min using the starting powder compositions $x=0.3$, 0.7 and 1.0. It was confirmed by ICP emission analysis that the atomic ratios Ti:B of the synthesized powders correspond to those of the starting powder compositions (1:(4x+2)). In the specimen with $x=0.3$ a homogeneously mixed powder of TiB_2 and B_4C can be seen, where the white-coloured grains are TiB_2 and the grey-coloured grains are B_4C. The grain size of TiB_2 is 1.5–2.0 μm, which is a little larger than that of the starting TiC_xN_{1-x} powder. This suggests that the formation of the composite powder would occur by the substitution of boron for carbon or nitrogen atoms and the crystallization of TiB_2 within the TiC_xN_{1-x} particles. Neither coagulation nor partial sintering of the powder was observed. The formation of B_4C around the TiB_2 particles would lead to the good dispersibility of the synthesized powder. The amount of B_4C is found to increase with increasing x, as seen by the fine-grained B_4C powder covering the TiB_2 grains in Figs. 6(b) and 6(c). Some coagulation of the synthesized powder was observed, however, in the case of a longer treatment time of 360 min, with increasing crystallinity of the TiB_2 grains.

3.4. Sinterability of synthesized composite powder

Table 2 shows the bulk density and microhardness of the sintered compacts which were prepared at 4 GPa and 1600 °C for 15 min from the synthesized composite powder of various compositions ($x=0.3$, 0.5, 0.7 and 1.0). The density increased as the x value decreased and a sintered compact with a relative density of 97.0% was obtained at $x=0.3$ (*i.e.* $TiB_2+0.3B_4C$). The density of the specimen with $x=0.7$ increased from 93.7% to 95.6% with increasing heat treatment time from 60 to 300 min. The microhardness of the composite sintered compact is found to increase linearly with composition x, which verifies that the hardness depends on the composition ratio B_4C:TiB_2.

Figure 7 shows the X-ray diffraction pattern of the surface of a sintered compact of the TiB_2–$0.3B_4C$ system. The existence of highly crystallized TiB_2 and low crystalline B_4C was confirmed by comparison with the crystallinity of commercial TiB_2 and B_4C. Figure 8

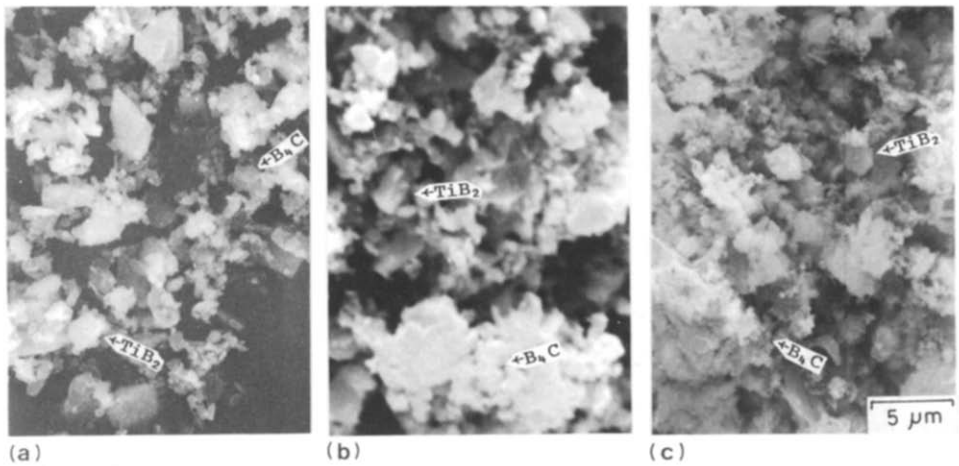

Fig. 6. Scanning electron micrographs of composite powder TiB_2+xB_4C; treatment temperature 1500 °C; holding time 60 min; $x=$ (a) 0.3, (b) 0.7 and (c) 1.0.

TABLE 2. Bulk density and microhardness of the composite sintered compact prepared at 4 GPa and 1600 °C for 15 min

Composition (x)	Bulk density (g/cm^3)	Relative density (%)	Microhardness (kg/mm^2)
0.3	3.78	97.0	3630
0.5	3.56	96.7	3680
0.7	3.31	93.7	3760
1.0	3.04	91.0	3860

Synthetic conditions of composite powder: 1500 °C, 60 min.

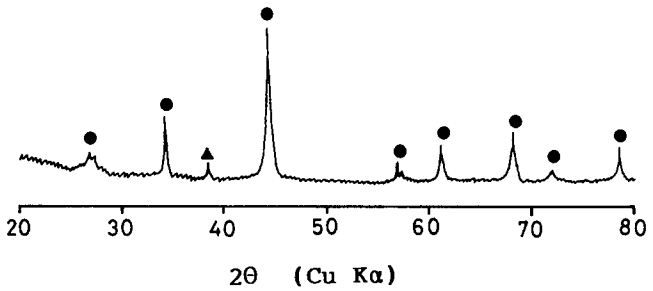

Fig. 7. X-ray diffraction pattern of surface of sintered compact of TiB_2–$0.3B_4C$; ●, TiB_2; ▲, B_4C.

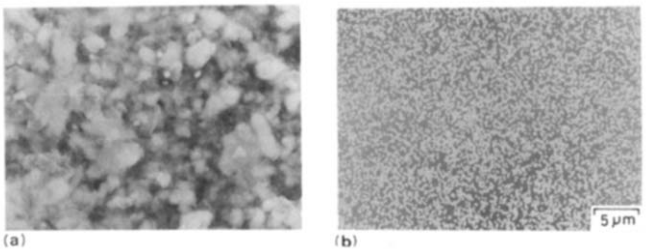

Fig. 8. XMA images of sintered compact of TiB_2–$0.3B_4C$; (a) reflected electron image; (b) Ti Kα image.

shows (a) the electron reflection image of the polished surface of the same sintered compact and (b) the XMA image of Ti Kα. The homogeneous distribution of TiB_2 and B_4C grains is confirmed. Therefore the sintered composite is considered to be composed of fine-grained and well-crystallized TiB_2 grains dispersed in a low crystalline B_4C matrix.

4. Conclusions

Composite powders of the TiB_2–B_4C system were synthesized by a solid state reaction between TiC_xN_{1-x} and amorphous boron and the sinterability of the synthesized powder was evaluated by high pressure sintering. The results can be summarized as follows.

(1) Fine-grained composite powders of composition TiB_2+xB_4C ($x=0.3$, 0.5, 0.7 and 1.0) were synthesized by heat treatment of the TiC_xN_{1-x} and B starting powders mixed in the ratio of $1:(4x+2)$ in an argon stream at 1500 °C for 60 min. The substitution of boron for carbon or nitrogen atoms and the simultaneous or subsequent reaction between unreacted boron and free carbon released from TiC_xN_{1-x} occur to form a well-dispersed TiB_2–B_4C composite powder.

(2) The synthesized powder was sintered at 4 GPa and 1600 °C for 15 min. The relative density of the sintered composite increased to 97.0% at $x=0.3$. The sintered compact was composed of fine-grained and well-crystallized TiB_2 grains dispersed in a low crystalline B_4C matrix. The microhardness increased with increasing B_4C content.

Details of the microstructure and the mechanical, electrical and oxidation resistance properties of the sintered composite will be reported in another paper.

References

1 G. V. Samsonov and I. M. Vinitskii, *Handbook of Refractory Compounds*, IFI/Plenum, New York, 1980, p. 1.
2 S. L. Dole, S. Prochazka and R. H. Doremus, *J. Am. Ceram. Soc., 72* (1989) 958.
3 T. Watanabe and S. Kouno, *Ceram. Bull., 61* (1982) 970.
4 D. C. Halverson, A. J. Pyzik, I. A. Aksay and W. E. Snowden, *J. Am. Ceram. Soc., 72* (1989) 775.
5 T. Watanabe, *Funtai-oyobi-Funmatsu-Yakin, 36* (1989) 365.
6 J. D. Whittenberger, R. K. Viswanadham, S. K. Mannan and B. Sprissler, *J. Mater. Sci., 25* (1990) 35.
7 T. Tani and S. Wada, *J. Mater. Sci., 25* (1990) 157.
8 T. Tani and S. Wada, *J. Mater. Sci. Lett., 9* (1990) 22.
9 W. A. Zdaniewski, *Am. Ceram. Soc. Bull., 65* (1986) 1408.
10 C. H. MacMurthy, W. D. G. Boecker, S. G. Seshadri, J. S. Zanghi and J. E. Garnier, *Am. Ceram. Soc. Bull., 66* (1987) 325.
11 E. S. Kang, C. W. Jang, C. H. Lee and C. H. Kim, *J. Am. Ceram. Soc., 72* (1989) 1868.
12 T. Matsudaira, H. Itoh, S. Naka, H. Hamamoto and M. Obayashi, *J. Mater. Sci., 23* (1988) 288.
13 H. Itoh, T. Matsudaira, S. Naka and H. Hamamoto, *J. Mater. Sci., 24* (1989) 420.
14 H. Itoh, S. Naka, T. Matsudaira and H. Hamamoto, *J. Mater. Sci., 25* (1990) 533.
15 H. Itoh, S. Tajima, M. Tamaki and S. Naka, *J. Mater. Sci., 23* (1988) 2877.