Rapid Synthesis of Ternary Carbide Ti$_3$SiC$_2$ through Pulse-Discharge Sintering Technique from Ti/Si/TiC Powders

Z.F. ZHANG, Z.M. SUN, and H. HASHIMOTO

Ti/Si/TiC powders with molar ratios of 1:1:2 (M1) and 2:2:3 (M2) were prepared for the synthesis of a ternary carbide Ti$_3$SiC$_2$ by using the mixture method for 24 hours in an Ar atmosphere. The synthesis process was conducted at 1200 °C to 1400 °C under a pressure of 50 MPa, using the pulse-discharge sintering (PDS) technique. After sintering, the phase constituents and microstructures of the samples were analyzed by X-ray diffraction (XRD) technique and observed by optical microscopy and scanning electron microscopy. The results showed that the phases in all the samples consisted of Ti$_3$SiC$_2$ and small amounts of TiC, and the optimum sintering temperature was found to be in the relatively low range of 1250 °C to 1300 °C. By the standard additive method, the relative content of Ti$_3$SiC$_2$ was calculated. For the M1 samples, the lowest TiC content can be only decreased to about 3 to 4 wt pct, whereas the content of Ti$_3$SiC$_2$ in the M2 samples is always lower than that in the M1 samples. When the M2 powder was sintered at 1300 °C for 8 to 240 minutes, the TiC peaks were found to show a very low intensity, and the corresponding content of Ti$_3$SiC$_2$ was calculated to be higher than 99 wt pct. The grain size of Ti$_3$SiC$_2$ increased from 5 to 10 μm to 80 to 100 μm in the entire applied sintering temperature range. The relative density of the M2 samples was measured to be higher than 99 pct at sintering temperatures above 1275 °C. It indicates that the PDS technique can rapidly synthesize high-content Ti$_3$SiC$_2$ from the Ti/Si/TiC powders in a relatively low temperature range.

I. INTRODUCTION

TO improve the properties of products or structures, especially for those employed at high temperatures, many efforts have been made to fabricate high-performance materials, including metals and ceramics. Recently, ternary carbide Ti$_3$SiC$_2$ was found to be a novel material which combines many of the best attributes of both metals and ceramics, such as a low density (4.53 g/cm^3) and high melting point (~3000 °C). Besides, this ternary compound is elastically stiff, electrically and thermally conductive, machinable, relatively soft, and resistant to thermal shock.[1] Also, it can deform by a combination of delamination and kink-band formation in individual grains, as well as by the formation of shear bands.[2,3] Therefore, this material is very damage tolerant of different deformation modes before fracture. The combination of strength, ductility at elevated temperatures, nonsusceptibility to thermal shock, and good machinability is seldom observed in other materials.[4] Therefore, it is desirable to fabricate high-content Ti$_3$SiC$_2$ samples and to develop new synthesis techniques for a broad application of this novel material.

Ti$_3$SiC$_2$ was first synthesized by Jeitschko and Nowotny[5] *via* chemical reaction in 1967, followed by Goto and Hirai,[6] using the CVD (chemical vapor deposition) method, in 1987. In the past decade, various processes, including (1) arc melting,[7] (2) chemical reaction,[6] (3) hot isothermal pressing (HIP) or self-propagating high-temperature synthesis (SHS)–HIP,[8–14] and (4) reactive sintering[15–20] were employed and developed to synthesize Ti$_3$SiC$_2$ samples. Among these synthesis methods, the sintering process is a common way to fabricate bulk Ti$_3$SiC$_2$ samples mainly by the following three reactions: (1) 3Ti + Si + 2C → Ti$_3$SiC$_2$, (2) 3Ti + SiC + C → Ti$_3$SiC$_2$, and (3) Ti + Si + 2TiC → Ti$_3$SiC$_2$. Among the three reactions, the first reaction was frequently employed for the synthesis of Ti$_3$SiC$_2$ by many researchers, such as Pampuch *et al.*,[8] Lis *et al.*,[9] Gao *et al.*,[10] Li and co-workers,[11,12] Racault *et al.*,[15] Radhakrishnan *et al.*,[16,17] and Zhou and co-workers.[18,19] However, Barsoum and El-Raghy[13,14] successfully synthesized high-content Ti$_3$SiC$_2$ samples through the second reaction in the temperature range from 1450 °C to 1600 °C. Li and Miyamoto[20] synthesized Ti$_3$SiC$_2$ samples through cold isostatic pressing and reactive sintering a Ti/Si/TiC mixture at temperatures near 1400 °C. Recently, we developed two new reactions to synthesize Ti$_3$SiC$_2$ samples through mixtures of Ti/SiC/TiC and Ti/TiSi$_2$/TiC powders by using a pulse-discharge sintering (PDS) technique.[21,22] The result showed that the sintering processes could be rapidly completed at the relatively low temperature of 1300 °C. The PDS technique is a recently developed densification method which consists of a pulse electrical discharge process when plasma is generated between powder particles, followed by resistance heating while a uniaxial pressure is applied. It is assumed that densification is achieved by the contribution of three factors: plasma generation, resistance sintering, and pressure application.[23,24,25] Therefore, the metals and ceramics can be sintered rapidly under relatively low temperatures, with fine grains and high performances due to the application of the PDS technique. In the present research, we further synthesized Ti$_3$SiC$_2$ samples from Ti/Si/TiC powder through the PDS technique at a relatively low temperature range.

Z.F. ZHANG, formerly STA Fellow, AIST Tohoku, National Institute of Advanced Industrial Science and Technology, is AvH Fellow with IFW-Dresden, Institute for Metallic Materials, D-01171, Dresden, Germany. Contact Z.F. Zhang@ifw-dresden.de and z.m.sun@aist.go.jp Z.M. SUN and H. HASHIMOTO, Senior Research Scientists, are with AIST Tohoku, National Institute of Advanced Industrial Science and Technology, Sendai, 983-8551, Japan.
Manuscript submitted February 19, 2002.

Table I. Collected Molar Ratio of Ti:Si:C in Ti_3SiC_2 Monolithic Phase Region from Isothermal Sections at 1200 °C and 1400 °C of Ti-Si-C Ternary Phase Diagrams Provided by Different Authors

	Ratliff et al.[26]		Carim et al.[7]		Naka et al.[27]	
	T = 1200 °C		T = 1200 °C		T = 1400 °C	
	Low	High	Low	High	Low	High
Ti (at. pct)	49.3	51.4	45.8	52.8	47.3	50
Si (at. pct)	18.8	20.8	16.7	21.5	17.1	20
C (at. pct)	29.2	31.3	29.2	38.8	32.4	33.8

II. EXPERIMENTAL PROCEDURE

Commercially available Ti, Si, and TiC powders with sizes and purities of 10 μm and 99.9 pct (Ti), 10 μm and 99.9 pct (Si), and 2 to 5 μm and 99 pct (TiC), respectively, were employed. First, several isothermal sections of the Ti-Si-C ternary-phase diagram at 1200 °C and 1400 °C, obtained from different investigators, were compared.[7,26,27] The atomic percentages of Ti, Si, and C in the Ti_3SiC_2 monolithic-phase region were calculated from three ternary-phase diagrams of Ti-Si-C, and the quantitative results are listed in Table I. It is found that the monolithic-phase region of Ti_3SiC_2 has a relatively wide composition range. For instance, the atomic percentage of Ti ranges from 45 to 52 pct, and the atomic percentages of Si and C are in the range of 16.7 to 22 pct and 29 to 38 pct, respectively. In the present sintering process, the stoichiometric ratio (Ti:Si:TiC = 1:1:2) of the Ti/Si/TiC powder (M1) was selected. Another molar ratio of Ti:Si:TiC was selected as 2:2:3 and referred to as M2. Whereas the atomic percentages of Ti, Si, and C in the stoichiometric M1 powder are, respectively, 50, 17, and 33 pct, the percentages in M2 powder will be equal to 50, 20, and 30 pct in the monolithic-phase region of Ti_3SiC_2 from the Ti-Si-C ternary-phase diagrams. In addition, another Ti/Si/TiC powder (M3) with a molar ratio of 2:3:4 was prepared for comparing the effect of excess Si. Before sintering, the M1, M2, and M3 powders were mixed in a Turbular shaker mixer in an Ar atmosphere for 24 hours. During mixing, some zirconia balls, measuring 3 mm in diameter, were put into the container to ensure better mixing. The powder mixtures were filled in a cylindrical graphite mold with an i.d. of 20 mm, o.d. of 50 mm, and height of 40 mm, with two graphite punches of 20 mm in diameter and 25 mm in length pressed at two ends. The graphite dies and powder-mixture set were fixed in a PDS apparatus, with two water-cooled copper electrodes, which serve also as the pressing plates, compressed from the upper and lower ends, respectively. Before initiating the sintering, the chamber was evacuated to a pressure of 10^{-3} Pa.

During sintering, the heating rate was controlled in the range from 50 °C to 60 °C/min, and the applied pressure was maintained at 50 MPa. The sintering process was controlled at 1200 °C to 1400 °C for 8 to 240 minutes. After sintering, each side of the sample surface was ground to remove the graphite layer and the affected zone of carbon (more than 0.3 mm in depth). The phase analysis of the samples was conducted by X-ray diffraction (XRD) with Cu K_α radiation at 30 kV and 40 mA. The samples were mechanically polished and etched by a solution of
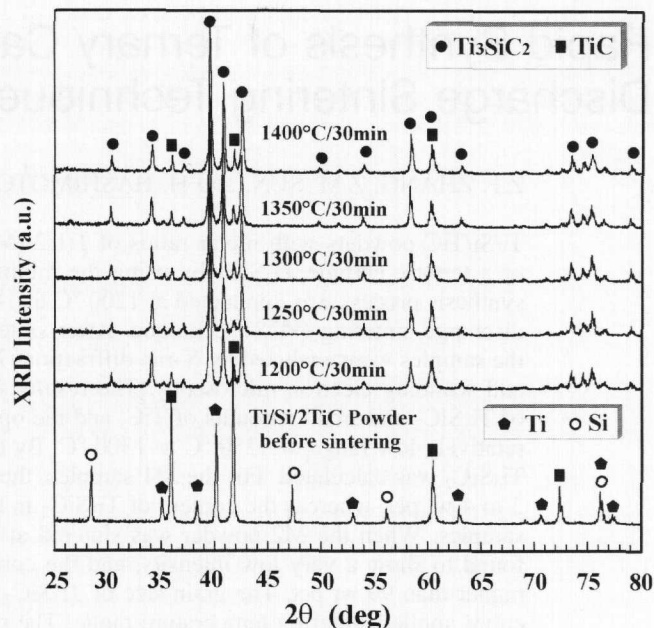

Fig. 1—XRD patterns of mixed Ti/Si/2TiC powder and the M1 samples sintered at 1200 °C to 1400 °C for 30 min.

$H_2O:HNO_3:HF$ (2:1:1) to expose the Ti_3SiC_2 grains. The microstructures of the samples were observed by scanning electron microscopy (SEM) and optical microscopy (OM). The density of the synthesized samples was measured by means of the Archimedes method.

III. RESULTS AND DISCUSSION

A. *The XRD Analysis of the Synthesized Samples*

Figure 1 shows the XRD patterns of the mixed Ti/Si/2TiC powder prior to sintering and of the M1 samples sintered at 1200 °C to 1400 °C for 30 minutes. For the powder, Ti, Si, and TiC peaks can be clearly seen in its XRD pattern. When the M1 powder was sintered at different temperatures, all the Ti and Si peaks disappeared, and Ti_3SiC_2 peaks with high intensities appeared in the XRD patterns. Meanwhile, the TiC peak intensities were substantially decreased at all the sintering temperatures. This indicates that the M1 samples mainly consist of Ti_3SiC_2 phase and a small amount of TiC. When the M1 powder was sintered for 15 minutes in this temperature range, their XRD patterns nearly showed the same features as those sintered for 30 minutes.

Figure 2 summarizes the XRD patterns of the 2Ti/2Si/3TiC powder and the M2 samples sintered at 1225 °C to 1325 °C for 15 minutes. The XRD pattern of the 2Ti/2Si/3TiC powder is similar to that of the Ti/Si/2TiC powder in Figure 1. It is interesting that the two TiC peaks at $2\theta = 36$ and 41.8 deg TiC(111) and TiC(200, respectively) were decreased to very low intensity in the M2 samples sintered at 1275 °C to 1325 °C. In particular, the TiC peaks became too weak to be identified in the XRD patterns when the M2 sample was sintered at 1300 °C, and the primary diffraction peaks corresponded to Ti_3SiC_2 phase. To further compare the effect of sintering time on the content of Ti_3SiC_2, the M2 powder was sintered at 1300 °C for different times, and their XRD patterns are shown in Figure 3. For careful
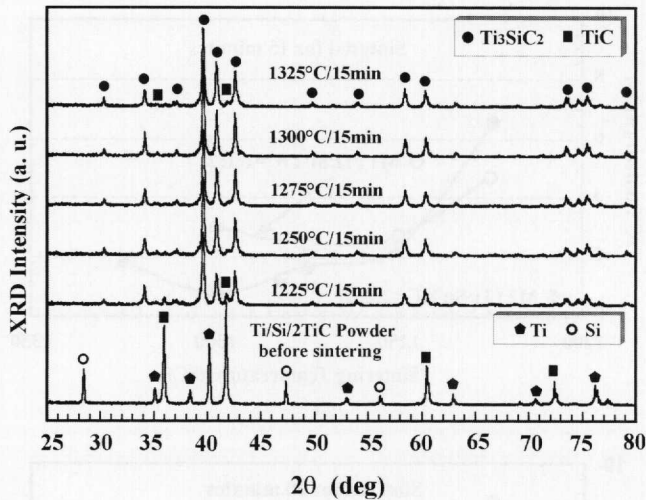
Fig. 2—XRD patterns of 2Ti/2Si/3TiC powder and the M2 samples sintered at 1225 °C to 1325 °C for 15 min.
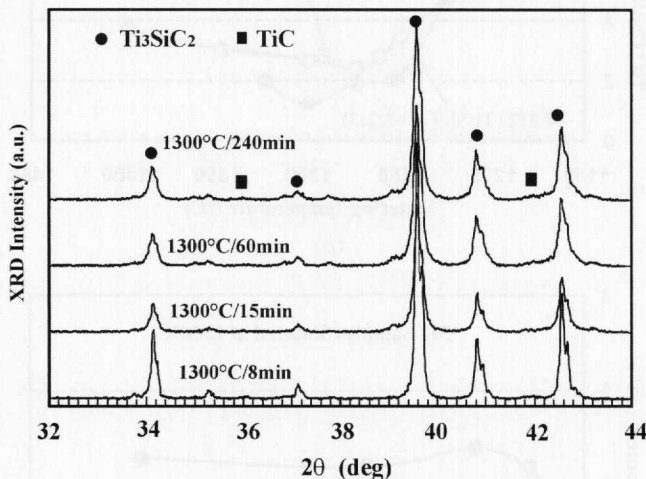

Fig. 3—XRD patterns of the M2 samples sintered at 1300 °C for 8 to 240 min.

observation, the scanning range for the XRD patterns were performed in $2\theta = 32$ to 44 deg at a slow scanning rate of 0.02 deg/s. It can be clearly seen that, over the sintering-time range of 8 to 240 minutes, all the TiC peaks are very low or negligible, indicating that the TiC content has been decreased to a substantially low value in all the M2 samples sintered at 1300 °C.

B. Calibration of the Standard Additive Method

To determine the quantitative relationship between TiC content and the intensity ratio of TiC to Ti_3SiC_2 peaks, one bulk sample was sintered at 1300 °C for 15 minutes. Then, the sample was drilled (using a steel drill) to collect Ti_3SiC_2 powder. The collected Ti_3SiC_2 powder was incorporated into pure TiC powder of 2 to 5 μm in size to make different mixtures of (Ti_3SiC_2 + TiC) with weight ratios of 90:10, 80:20, 70:30, 60:40, and 50:50, respectively. These mixed powders were examined by X-ray diffractometry in the range of $2\theta = 32$ to 44 deg with a slow scanning rate of 0.02 deg/s to determine the difference in the peak intensities of TiC and
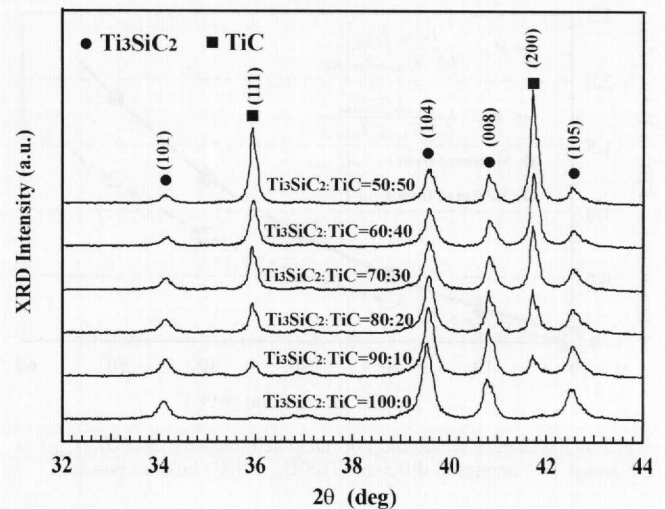

Fig. 4—XRD patterns of the Ti_3SiC_2 powders and the (Ti_3SiC_2 + TiC) mixtures with weight ratios of 90:10, 80:20, 70:30, 60:40, and 50:50.

Ti_3SiC_2. This procedure is often referred to as the standard additive method.[20] Figure 4 shows the XRD patterns of the five groups of mixture powders, along with the collected Ti_3SiC_2 powder. It can be seen that the intensity of TiC peaks (I_{TC}) monotonically increases with the added TiC amount. Meanwhile, the intensity of Ti_3SiC_2 peaks (I_{TSC}) decreased gradually with the addition of TiC. Besides, it is noted that the lower content of TiC can result in a higher peak intensity in comparison with the Ti_3SiC_2. It indicates that the diffraction intensity is quite different for the two phases of Ti_3SiC_2 and TiC. For a two-phase material, for example, Ti_3SiC_2 and TiC, their diffraction peak intensities can be expressed as follows:

$$I_{TSC} = \frac{K_{TSC}W_{TSC}}{2\rho_{TSC}(W_{TSC}(\mu_m)_{TSC} + W_{TC}(\mu_m)_{TC})} \quad [1]$$

$$I_{TC} = \frac{K_{TC}W_{TC}}{2\rho_{TC}(W_{TSC}(\mu_m)_{TSC} + W_{TC}(\mu_m)_{TC})} \quad [2]$$

where ρ_{TC} and ρ_{TSC} are the densities of the TiC and Ti_3SiC_2 phases, respectively; W_{TC} and W_{TSC} are the weight percentages of TiC and Ti_3SiC_2 phases, respectively; K_{TC} and K_{TSC} are the diffraction constants of the TiC and Ti_3SiC_2 phases, respectively; and $(\mu_m)_{TC}$ and $(\mu_m)_{TSC}$ are the absorption coefficients of the TiC and Ti_3SiC_2 phases. Therefore, the relative intensity of the TiC to Ti_3SiC_2 peaks (I_{TC}/I_{TSC}) will be

$$\frac{I_{TC}}{I_{TSC}} = \frac{\rho_{TC}K_{TC}W_{TC}}{\rho_{TSC}K_{TSC}W_{TSC}} = K\frac{W_{TC}}{(1 - W_{TC})} \quad [3]$$

Here, K is the ratio of $\rho_{TC}K_{TC}$ to $\rho_{TSC}K_{TSC}$ as a constant. From the XRD results in Figure 4, the integrated intensity ratios of the TiC(200) and TiC(111) peaks to Ti_3SiC_2(104) were calculated, and the quantitative relationship between I_{TC}/I_{TSC} and the added TiC amount is shown in Figure 5. From the figure, a noticeable feature is that the intensity ratios do not show linear relations with the added TiC amount, which is consistent with Eq. [3]. However, in a similar method,[20] the intensity ratio I_{TC}/I_{TSC} clearly showed a linear relation with the added TiC amount. As we know, when adding TiC into the (Ti_3SiC_2 + TiC) mixture, the content ratio of TiC to Ti_3SiC_2 in the mixture will not be
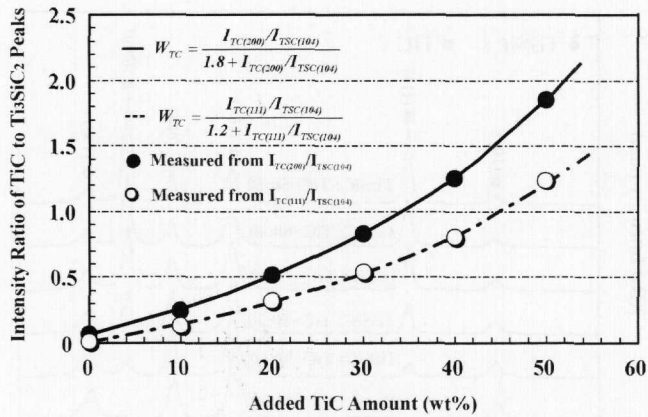
Fig. 5—Quantitative relationship of integrated intensity ratio (I_{TC}/I_{TSC}) *vs* the added TiC amount in different (Ti_3SiC_2 + TiC) mixture powders.

proportional to the added TiC amount. Since the intensity ratio I_{TC}/I_{TSC} represents the content ratio of TiC to Ti_3SiC_2, it is natural that there should not be a linear relation between the intensity ratio and added TiC amount. From the present results, the constant K was calculated to be 1.80 and 1.20, respectively, when calculated from $TiC(200)/Ti_3SiC_2(104)$ and $TiC(111)/Ti_3SiC_2(104)$, as shown in Figure 5. When knowing the integrated intensity ratio of a two-phase mixture of (Ti_3SiC_2 + TiC), by rearranging Eq. [3], the relative weight percentages of Ti_3SiC_2 and TiC can be expressed as follows:

$$W_{TSC} = \frac{K}{K + I_{TC}/I_{TSC}} \quad [4]$$

$$W_{TC} = \frac{I_{TC}/I_{TSC}}{K + I_{TC}/I_{TSC}} \quad [5]$$

If the volume fractions of Ti_3SiC_2 and TiC are used, the constant K will be equal to 1.95 and 1.30, calculated from the TiC main and second peaks of (200) and (111), respectively.

C. The TiC Content of the Synthesized Samples

By using the calibrated Eqs. [4] and [5], the relative weight percentages of Ti_3SiC_2 and TiC in all the M1 and M2 samples were calculated from the XRD patterns of Figures 1 through 3. For the M1 samples, the TiC content was calculated from its main and secondary peak intensities of TiC(200) and TiC(111) at $2\theta = 41.8$ and 36 deg, respectively. It is found that the TiC contents calculated by the two peak intensities are identical. For the M2 samples, the TiC content was only calculated from its main peak intensity of TiC(200) at $2\theta = 41.8$ deg, because the XRD intensity at the secondary peak (TiC(111)) at $2\theta = 36$ deg is very low or negligible. Figure 6(a) shows the TiC content in the M1 and M2 samples sintered at 1225 °C to 1325 °C for 15 minutes. It can be seen that the TiC content in the M1 samples is approximately constant (about 3 to 4 pct) at 1250 °C to 1300 °C. However, the TiC content in the M2 samples is less than that in the M1 samples sintered in this temperature range. At 1300 °C, the TiC content in the M2 sample is reduced to a very low value of 0.8 wt pct. When the sintering process was conducted for 30 minutes, as shown in Figure 6(b), the M2 samples also had a lower TiC content than the M1 samples
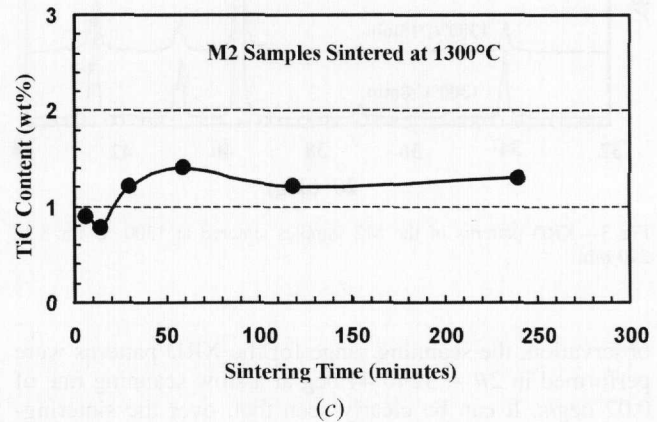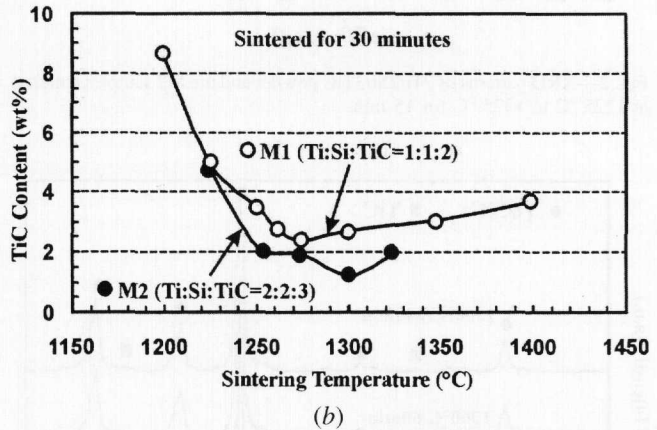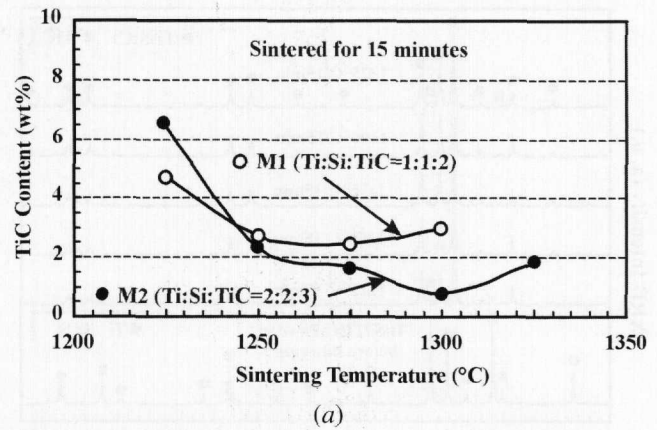

(a)

(b)

(c)

Fig. 6—TiC content in the samples sintered at various temperatures for different times: (a) M1 and M2 samples sintered at 1225 °C to 1325 °C for 15 min, (b) M1 and M2 samples sintered at 1200 °C to 1400 °C for 30 min, and (c) M2 samples sintered at 1300 °C for 8 to 240 min.

at the sintering temperature range. Figure 6(c) shows the effect of sintering time on the TiC content in the M2 samples sintered at 1300 °C. It is apparent that the TiC content in the M2 samples is approximately constant (<1.5 wt pct over a wide sintering-time range of 8 to 240 minutes), which would be favorable for controlling the microstructure and optimizing the performance of Ti_3SiC_2 samples or products. This indicates that the present optimum sintering temperature (1300 °C) through the PDS technique is about 200 °C to 300 °C lower than that of the synthesized samples from Ti/Si/C and Ti/SiC/C powders by the HIP technique.[11–15,17–19] In addition, the relative content of Ti_3SiC_2 can be further
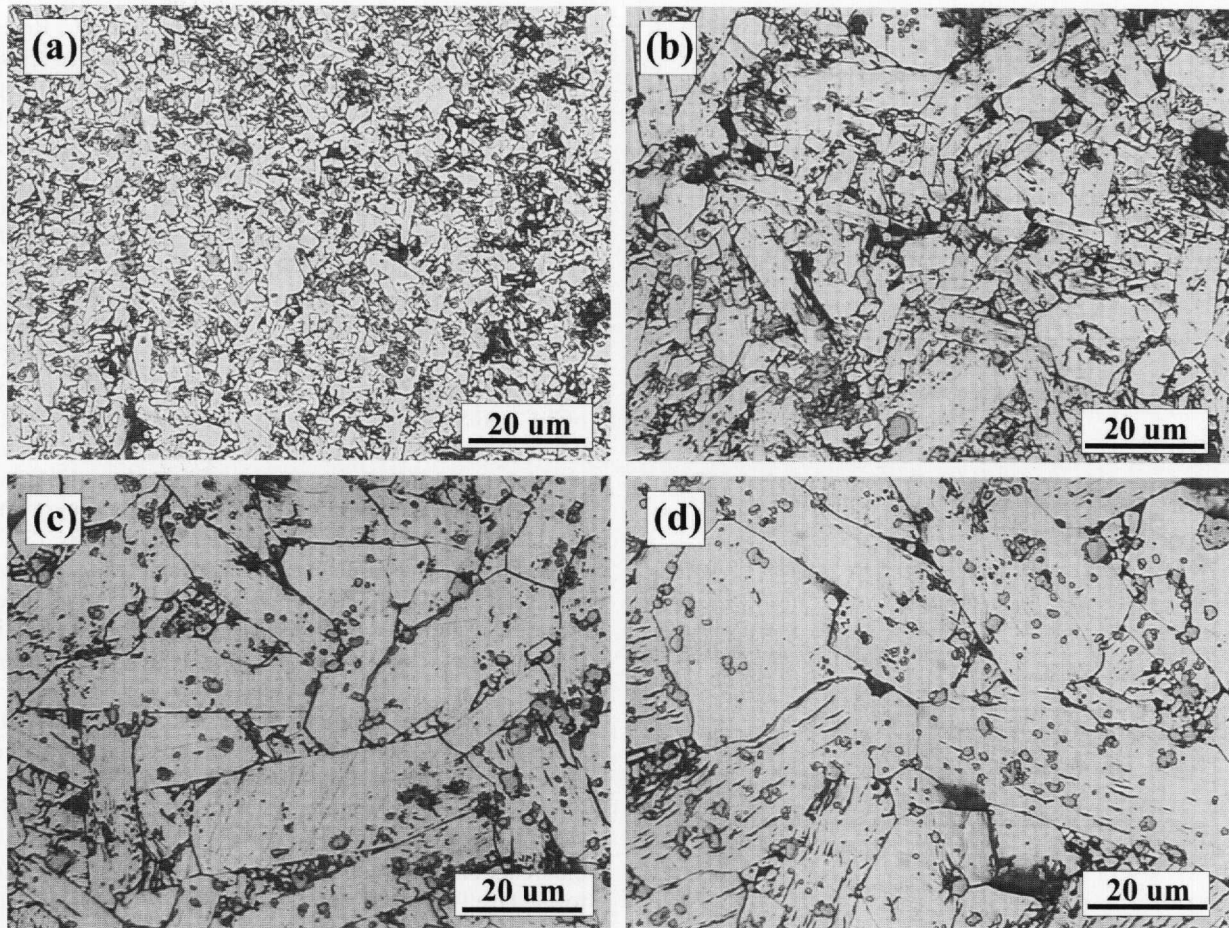
Fig. 7—Microstructure of the M2 samples sintered from 2Ti/2Si/3TiC powders at different temperatures: (*a*) microstructure of the fine grains (T = 1250 °C, t = 30 min); (*b*) microstructure of the fine and platelike grains (T = 1300 °C, t = 30 min); (*c*) microstructure of the platelike grains (T = 1300 °C, t = 120 min); and (*d*) microstructure of the coarse grains (T = 1400 °C, t = 30 min).

improved by adjusting the molar ratio of the Ti/Si/TiC powder mixture from 1:1:2 to 2:2:3.

D. *Microstructure and Density of Ti$_3$SiC$_2$ Samples*

It was found that the microstructure of Ti$_3$SiC$_2$ samples was not influenced by the molar ratio of Ti/Si/TiC in the M1 and M2 samples. Figure 7 shows a typical microstructure of the M1 and M2 samples sintered at different temperatures and times. When the sintering temperature was 1200 °C, the microstructure consists of homogeneous fine grains of 5 to 10 μm in length and 2 to 5 μm in width. When the sintering temperature was increased to 1250 °C, some grains began to grow and appeared in a platelike shape of more than 10 μm in length, as shown in Figure 7(a). At an increased sintering temperature of 1300 °C, the platelike grains could continue to grow with increased sintering time. As shown in Figures 7(b) and (c), the grain size can reach about 30 to 40 μm (t = 30 minutes) and 40 to 50 μm (t = 120 minutes), respectively. Meanwhile, the volume fraction of the platelike grains increased with sintering time. At higher sintering temperatures of 1350 °C and 1400 °C, the size of the platelike grains can grow to more than 80 to 100 μm in length and 30 to 50 μm in width, as shown in Figure 7(d). From the previous micrography results, it can be concluded that the grain size and volume fraction of the coarse

grains strongly depend on the sintering temperature. In the optimum sintering temperature of 1300 °C, the typical microstructure consists of fine grains (5 to 10 μm) and platelike grains (30 to 50 μm), which was defined as a duplex microstructure.

Figure 8 shows the dependence of density in the M2 samples on the sintering temperature and time. It can be seen that when the sintering temperature is below 1250 °C, the measured density (ρ_M) is less than 4.50 g/cm^3. When the sintering temperature increased to above 1275 °C, the measured density was increased to 4.50 to 4.52 g/cm^3, which is quite close to the theoretical density of pure Ti$_3$SiC$_2$ (4.53 g/cm^3). Since the theoretical density of TiC is equal to 4.90 g/cm^3, the theoretical density (ρ_T) of the synthesized M2 samples was calculated by taking the relative content of Ti$_3$SiC$_2$ in Figure 6 into account, and the results are also shown in Figure 8(a). Therefore, the relative density of the M2 samples can be obtained from the ratio ρ_M/ρ_T of the measured density to the theoretical density. It is apparent that the relative density of the M2 samples is quite high (97.7 to 99.4 pct) at all the sintering temperatures. At sintering temperatures above 1275 °C, the relative density of the M2 samples is greater than 99 pct. For the M2 samples sintered at 1300 °C for different times, the relative densities are quite high even after short-time sintering (Figure 8(b)). Recently, high-temperature compressive tests were conducted on the
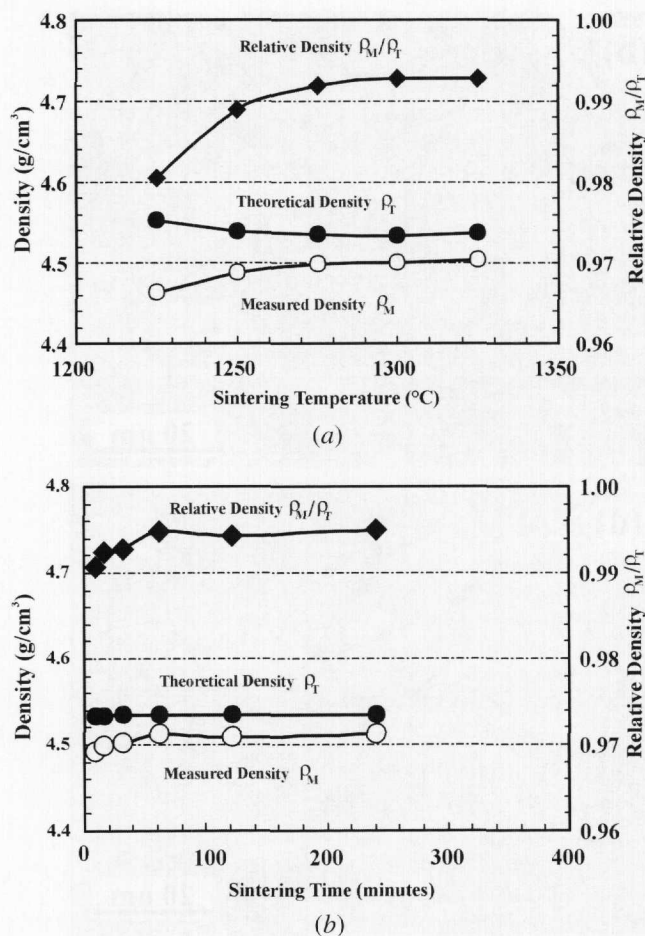
Fig. 8—Variation of the measured density, theoretical density, and relative density of the M2 samples with sintering temperature (at T = 15 min) (a) and sintering time (at T = 1300 °C) (b).

Ti_3SiC_2 samples sintered at the temperature of 1300 °C for 15 minutes. It was found that the Ti_3SiC_2 samples began to display plastic deformation behavior in compression at the temperature of 900 °C,[28] which is about 200 °C to 300 °C less than the samples made from Ti/SiC/C powder by the HIP technique.[29] Meanwhile, when the same samples were subjected to four-point bending, the Ti_3SiC_2 samples displayed large plastic deformation at temperatures higher than 1200 °C.[30] From the aforementioned results, it can be concluded that high-performance Ti_3SiC_2 samples can be synthesized from the 2Ti/2Si/3TiC powder in the relatively low sintering temperature range of 1250 °C to 1300 °C.

E. *Synthesis Processes of Ti_3SiC_2*

During the past decade, Ti_3SiC_2-rich samples were synthesized by many investigators through various powder mixtures and sintering processes, as listed in Table II. It can be seen that, in general, the sintering temperature is higher than 1350 °C for most synthesis processes, and a long sintering time was necessary regardless of the starting powders (*i.e.,* Ti/Si/C, Ti/SiC/C, or Ti/Si/TiC). To explain the synthesis processes of Ti_3SiC_2, several reaction mechanisms were proposed. Zhou *et al.*[18] synthesized Ti_3SiC_2 from Ti/Si/C powder through a hot-pressing process in the range of 1450 °C to 1600 °C. They proposed a solid-liquid reaction mechanism

of Ti_3SiC_2 among the liquid Si and solid Ti and C. Recently, Li *et al.*[11] and Sato *et al.*[12] proposed another possible reaction path for the synthesis of Ti_3SiC_2 from Ti/Si/C powders. They concluded that (1) Ti first reacted with C to form TiC particles; (2) Ti and Si reacted to form a liquid phase of Ti-Si; and (3) the final formation of Ti_3SiC_2 was from the solid-liquid reaction between the TiC particles and the Ti-Si liquid phase. For the synthesis reaction from Ti/SiC/C powder, Barsoum and El-Raghy[13,14] proposed that C and Si diffuse into Ti particles to form TiC_x and $Ti_5Si_3C_x$, then those phases, in turn, react to form Ti_3SiC_2. Radhakrishnan *et al.*[16] employed the reaction $3TiC + 2Si \Rightarrow Ti_3SiC_2 + SiC$ to form a composite of Ti_3SiC_2 and SiC from a mixture of TiC and Si. From the aforementioned synthesis processes, it is apparent that Ti_3SiC_2 can be formed by different starting powders and sintering processes. But, when the powders were sintered by the PDS technique, the sintering temperature could be decreased to a lower range (below 1350 °C) for a short time, regardless of the starting powders used (*i.e.,* Ti/SiC/TiC, Ti/TiSi$_2$/TiC, or Ti/Si/TiC),[21,22,31] as listed in Table II. It indicates that the PDS technique can effectively improve the reaction process of Ti_3SiC_2 from different powders.

For the present synthesis processes, we considered that there might be three possible reaction paths to synthesize Ti_3SiC_2 from the starting powders of Ti/Si/TiC. One is the liquid-solid reaction among Ti, TiC particles, and liquid Si, as proposed by Zhou and co-workers.[18,19] In addition, from the reaction by Radhakrishnan *et al.*[16] Ti_3SiC_2 can be formed by TiC and Si particles in the first step. Then, another reaction between SiC and Ti can result in the formation of Ti_3SiC_2, as reported in a diffusion couple of SiC/Ti by Iseki *et al.*[32] Therefore, the Ti powder will react with the released SiC to form Ti_3SiC_2. This process can be understood to mean that all the Ti/Si/TiC powders will alternately react to be synthesized Ti_3SiC_2, which can be regarded as the second possible reaction path from Ti/Si/TiC powders. The third possible reaction path to form Ti_3SiC_2 might result from the Ti-Si liquid phase and TiC particles. For the Ti-Si system, there are two eutectic reactions for the Si-TiSi$_2$ and Ti-Ti$_5$Si$_3$ compositions, both at a temperature of 1333 °C.[11,12,20] When the sintering processes were controlled at the eutectic temperature, the eutectic liquid phase may begin to appear between Ti and Si particles. Finally, Ti_3SiC_2 will be easily formed at the interfaces between the Ti-Si liquid and TiC particles, *i.e.,*

$$2TiC + Ti\text{-}Si \text{ (liquid)} \Rightarrow Ti_3SiC_2 \qquad [6]$$
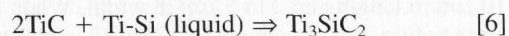
To confirm the formation of the Ti-Si liquid phase, a 2Ti/3Si/4TiC powder (M3) with more excess Si was sintered at 1250 °C and 1300 °C for 15 minutes through the PDS technique. The XRD patterns of the M3 samples are shown in Figure 9. It can be seen that, except for the Ti_3SiC_2 and TiC phases, there were other kinds of diffraction peaks at 2θ = 39 and 43.2 deg, respectively. They were identified to correspond to $TiSi_2$ phase, which is close to the formation of the Ti-Si eutectic phase. This indicates that the eutectic phase of the Si-TiSi$_2$ had formed during sintering at 1250 °C to 1300 °C, which would provide direct evidence for the proposed synthesis process of Ti_3SiC_2 by Reaction [6].

| Investigators	Molar Ratio	Synthesis Methods	Sintering Conditions	Content
Lis et al.[9]	Ti:Si:C = 3:1:2	SHS-HIP	1400 °C/3 h	82 vol pct
Zhou and Sun[18,19]	Ti:Si:C = 6:3.3:5	hot pressing	1550 °C/1 h	93 wt pct
Gao et al.[10]	Ti:SiC:C = 3:1:1	HIP	1500 °C/30 min	97 vol pct
Radhakrishnan et al.[15,16]	Ti:Si:C = 3:1.1:2	hot pressing	1350 °C/5 h	96 vol pct
	Ti:Si:C = 3:1.2:2	hot pressing	1350 °C/5 h	98.7 vol pct
Li et al.[11]	Ti:Si:C = 3:1.1:2	HIP	1500 °C/1 h	97 vol pct
Sato et al.[12]	Ti:Si:C = 3:1:2	HIP	1400 °C/1 h	96 vol pct
Barsoum et al.[13,14]	Ti:SiC:C = 3:1:1	HIP	1600 °C/1 to 4 h	98 vol pct
Zhang et al.[22,23,31]	Ti:Si:C = 5:2:3	PDS	1300 °C/15 min	93.6 wt pct
	Ti:SiC:TiC = 4:2:1	PDS	1350 °C/15 min	92 wt pct
	Ti:TiSi₂:TiC = 1:1:3	PDS	1300 °C/15 min	95 wt pct
Present work	Ti:Si:TiC = 2:2:3	PDS	1300 °C/15 min	99 wt pct
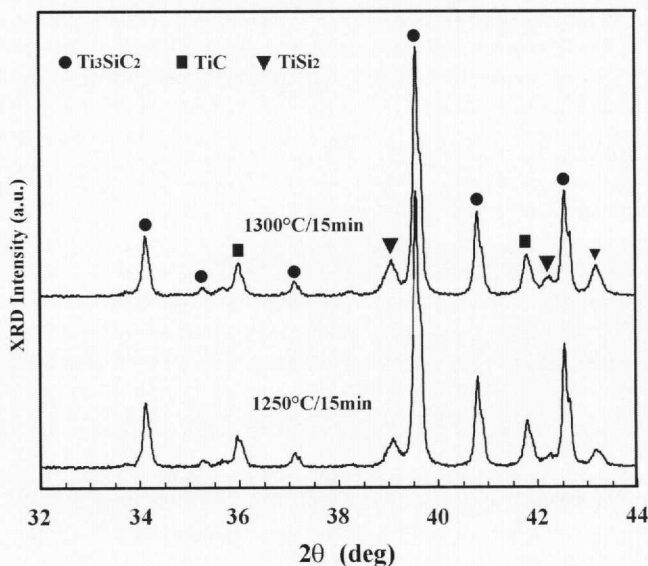
Fig. 9—XRD patterns of the M3 samples sintered from Ti/1.5Si/2TiC powder at 1250 °C and 1300 °C for 15 min.

IV. CONCLUSIONS

1. The standard additive method was calibrated to calculate to the relative content of Ti₃SiC₂ in the synthesized products. In the present investigation, the relative weight percentages of Ti₃SiC₂ and TiC can be calculated from the intensity ratio I_{TC}/I_{TSC} of the TiC(200) main peak to the Ti₃SiC₂(104) main peak by the following equations:

$$W_{TSC} = \frac{1.80}{1.80 + I_{TC}/I_{TSC}} \text{ and } W_{TC} = \frac{I_{TC}/I_{TSC}}{1.80 + I_{TC}/I_{TSC}}$$

2. When Ti/Si/2TiC (M1) and 2Ti/2Si/3TiC (M2) powders were sintered by the PDS technique, the relative weight percentages of Ti₃SiC₂ in the M1 and M2 samples can, respectively, be increased to 96 to 97 wt pct and 99 wt pct in the optimum sintering temperature of 1250 °C to 1300 °C. At 1300 °C, the TiC content in the samples made from the 2Ti/2Si/3TiC powder is approximately constant (0.8 to 1.5 wt pct) over a long sintering time range of 8 to 240 minutes. With the PDS technique, the synthesis process of Ti₃SiC₂ samples can be substantially shortened to 15 minutes, and the synthesized samples have a good densification at the sintering temperature above 1275 °C. It is suggested that the Ti/Si/TiC powder is a practical mixture for synthesizing a Ti₃SiC₂ mixture with high content through the PDS technique.

REFERENCES

1. M.W. Barsoum: *Progr. Solid State Chem.*, 2000, vol. 28, pp. 201-81.
2. M.W. Barsoum and T. El-Raghy: *Metall. Mater. Trans. A*, 1998, vol. 29A, pp. 363-69.
3. M.W. Barsoum, L. Farber, and T. El-Raghy: *Metall. Mater. Trans. A*, 1998, vol. 29, pp. 1727-38.
4. M.W. Barsoum, D. Brodkin, and T. El-Raghy: *Scripta Mater.*, 1997, vol. 36, pp. 535-41.
5. W. Jeitschko and H. Nowotny: *Monath. Chem.*, 1967, vol. 98, pp. 329-37.
6. T. Goto and T. Hirai: *Mater. Res. Bull.*, 1987, vol. 22, pp. 1195-1201.
7. S. Arunajatesan and A.H. Carim: *J. Am. Ceram. Soc.*, 1995, vol. 78, pp. 667-72.
8. R. Pampuch, J. Lis, L. Stobierski, and M. Tymkiewicz: *J. Eur. Ceram. Soc.*, 1989, vol. 5, pp. 283-87.
9. J. Lis, Y. Miyamoto, R. Pampuch, and K. Tanihata: *Mater. Lett.*, 1995, vol. 22, pp. 163-68.
10. N.F. Gao, Y. Miyamoto, and K. Tanihata: *J. Mater. Sci.*, 1999, vol. 34, pp. 4385-92.
11. J.F. Li, F. Sato, and R. Watanabe: *J. Mater. Sci. Lett.*, 1999, vol. 18, pp. 1595-97.
12. F. Sato, J.F. Li, and R. Watanabe: *Mater. Trans., JIM*, 2000, vol. 41, pp. 605-09.
13. M.W. Barsoum and T. El-Raghy: *J. Am. Ceram. Soc.*, 1996, vol. 79, pp. 1953-56.
14. T. El-Raghy and M.W. Barsoum: *J. Am. Ceram. Soc.*, 1999, vol. 82, pp. 2849-54.
15. C. Racault, F. Langlais, and R. Naslain: *J. Mater. Sci.*, 1994, vol. 29, pp. 3384-92.
16. R. Radhakrishnan, C.H. Henager, Jr., J.L. Brimhall, and S.B. Bhaduri: *Scripta Mater.*, 1996, vol. 34, pp. 1809-14.
17. R. Radhakrishnan, J.J. Williams, and M.J. Akinc: *J. Alloys Compounds*, 1999, vol. 285, pp. 85-88.
18. Y.C. Zhou, Z.M. Sun, S.Q. Chen, and Y. Zhang: *Mater. Res. Innov.*, 1998, vol. 2, pp. 142-46.
19. Z.M. Sun and Y.C. Zhou: *Scripta Mater.*, 1999, vol. 41, pp. 61-66.
20. J.T. Li and Y. Miyamoto: *J. Mater. Synth. Proc.*, 1999, vol. 7, pp. 91-96.

21. Z.F. Zhang, Z.M. Sun, H. Hashimoto, and T. Abe: *Scripta Mater.*, 2001, vol. 45, pp. 1461-67.
22. Z.F. Zhang, Z.M. Sun, H. Hashimoto, and T. Abe: *Mater. Res. Innov.*, 2002, vol. 5, pp. 185-89.
23. K. Matsugi, T. Hatayama, and O. Yanagisama: *Intermetallics*, 1999, vol. 7, pp. 1049-57.
24. R.S. Mishra, J.E. Schneider, J.F. Shackeford, and A.K. Mukheijee: *Nanostruct. Mater.*, 1995, vol. 5, pp. 525-44.
25. S.W. Wang, L.D. Chen, Y.S. Kang, M. Niino, and T. Hirai: *Mater. Res. Bull.*, 2000, vol. 35, pp. 619-28.
26. J.L. Rattliff and G.W. Powell: AFML Technical Report 70-42, National Technical Information Service, Alexander, VA (1970).
27. M. Naka, J.C. Feng, and J.C. Schuster: *Metall. Mater. Trans. A*, 1997, vol. 28, pp. 1385-90.
28. Z.M. Sun, Z.F. Zhang, H. Hashimoto, and T. Abe: *Mater. Trans.*, 2002, vol. 43, pp. 436-38.
29. T. El-Raghy, M.W. Barsoum, A. Zavaliangos, and S.R. Kalidindi: *J. Am. Ceram. Soc.*, 1999, vol. 82, pp. 2855-60.
30. Z.F. Zhang, Z.M. Sun, H. Hashimoto, and T. Abe: *Mater. Lett.*, 2002, in press.
31. Z.F. Zhang, Z.M. Sun, H. Hashimoto, and T. Abe: *J. Eur. Ceram. Soc.*, 2002, in press.
32. T. Iseki, T. Yano, and Y.-S. Chung: *J. Am. Ceram. Soc.*, 1990, vol. 97, pp. 47-51.