

## Effects of the Sintering Atmosphere and Ni Content on the Liquid-phase Sintering of TiB<sub>2</sub>-Ni

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(Received September 25, 2000, Accepted February 7, 2001)

### ABSTRACT

The effects of the sintering atmosphere and Ni content on the densification of TiB<sub>2</sub>-Ni have been investigated. TiB<sub>2</sub> powder compacts containing 10, 20, and 30 wt% Ni were liquid-phase sintered at 1500–1700°C in vacuum or in flowing Ar. The densification was enhanced as Ni content increased. For a given Ni content, the densification was faster in compacts with larger grain size. These densification behaviors agree well with the prediction of the recently developed pore-filling theory. For samples containing high Ni contents, 80TiB<sub>2</sub>-20Ni and 70TiB<sub>2</sub>-30Ni, the densification was faster in vacuum than in Ar. In particular, 70TiB<sub>2</sub>-30Ni was fully densified at 1700°C for 60 min in vacuum. The suppressed densification in Ar was due to the entrapped Ar in the isolated pores. On the other hand, for 90TiB<sub>2</sub>-10Ni, the Ar-sintering resulted in higher densification than did the vacuum-sintering. This result was attributed to the suppression of Ni volatilization by the Ar in the furnace and a retarded isolation of pores due to the limited amount of liquid in the sample. Therefore, vacuum sintering is recommended for the preparation of TiB<sub>2</sub>-Ni with a high Ni content while Ar sintering is recommended for the preparation of TiB<sub>2</sub>-Ni with a low Ni content.

**Key words:** TiB<sub>2</sub>-Ni cermet, Liquid phase sintering, Sintering atmosphere, Densification, Densification mechanism

## 1. Introduction

Titanium diboride (TiB<sub>2</sub>) is a good structural material with a high melting point (2980°C), hardness, abrasion resistance, corrosion resistance, and electrical conductivity.<sup>1-4</sup> Because of these properties, the material is used for crucibles of molten metals, rocket nozzles, electrodes for aluminum refining, and cutting tool bits of the next generation. In addition, TiB<sub>2</sub> has high impact resistance and strength to weight ratio, which allow it to be used as a ceramic armor material.<sup>3,4</sup>

In order to use TiB<sub>2</sub> as the material for the above applications, it is essential to prepare a dense compact. However, the sinterability of TiB<sub>2</sub> is very low because of its covalent bond nature, high melting point, and high anisotropy in a thermal expansion coefficient. Various attempts have been made to prepare dense TiB<sub>2</sub> sintered bodies: 1) addition of active metals for a liquid-phase sintering,<sup>1,5-7</sup> and 2) use of ultrafine powder.<sup>8-11</sup> The commonly used active metals were Ni, Fe and Co, which enhanced the sinterability and improved the fracture toughness. Nevertheless, the densifi-

cation was limited because of the volatilization of the active liquid metal in vacuum or the entrapped gas in an inert atmosphere.<sup>12</sup> On the other hand, the use of ultrafine powder has a limitation because of low productivity and the high cost of the powder.

In the present study, the densification of TiB<sub>2</sub> during liquid phase sintering has been investigated using a relatively low cost TiB<sub>2</sub> powder with the addition of Ni powder. Particular attention has been paid to the effect of the Ni content, TiB<sub>2</sub> particle size, and sintering atmosphere. The experimental results have been discussed based on the recently developed pore-filling theory of liquid-phase sintering.<sup>13</sup>

## 2. Experimental

Various TiB<sub>2</sub> samples containing 10, 20 and 30 wt% Ni were prepared from commercial TiB<sub>2</sub> (3.3, 2.5 or 0.9 μm in size, H. C. Starck, Berlin, FRG), Ni (2.5 μm, Aldrich, Milwaukee, WI, USA) and WC (0.9 μm, Taegutech, Taegu, Korea) powders. Proportioned powders were vibratory ball-milled for 20 min in ethanol using a polyethylene bottle and Si<sub>3</sub>N<sub>4</sub> balls. The ball-milled powders were dried at 80°C and granulated using a 500 mesh sieve. The granulated powders

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were uniaxially pressed in a die at  $\sim 1$  MPa into disks  $\sim 9$  mm in diameter and  $\sim 4$  mm in height, and then isostatically pressed at 200 MPa. The compact density was  $\sim 55\%$  of the theoretical value.

The powder compacts were placed in a graphite crucible and sintered in a graphite furnace in a  $10^{-2}$  torr vacuum or in a flowing Ar atmosphere. The sintering temperature was varied from 1500 to 1700°C. The samples were heated to their sintering temperature at  $\sim 20^\circ\text{C}/\text{min}$  and furnace-cooled after the sintering.

The sintered samples were cut and polished to a 1  $\mu\text{m}$  finish. The microstructure of the samples was observed on polished sections under a scanning electron microscope. The average grain size and the pore size distribution in 2-dim. were determined via the areal analysis method using the Matrox Inspector 2.1 program (Matrox Electronic Systems Ltd., Dorval, QC, Canada). The sintered density was measured following the ASTM C373 method which utilizes the Archimedes principle. The relative densities of the samples were metallographically measured on their polished section.

### 3. Results and Discussion

#### 3.1. Sintering in Vacuum

When the  $\text{TiB}_2$ -Ni powder compacts were sintered in a  $10^{-2}$  torr vacuum, the sintered density increased as sintering temperature and time increased, but the weight decreased because of the volatilization of Ni during the liquid-phase sintering. For example, approximately 12% of weight loss resulted when sintering a 70 $\text{TiB}_2$ -30Ni (wt%) sample at 1700°C for 60 min.

Figure 1 plots the sintered densities of 90 $\text{TiB}_2$ -10Ni (hereinafter called as N10), 80 $\text{TiB}_2$ -20Ni (N20), and 70 $\text{TiB}_2$ -30Ni (N30) samples sintered at 1500, 1600, and 1700°C for 10 min and also at 1700°C for 60 min. For all of the samples, the sintered density increases as the sintering temperature and sintering time increase. Under the same sintering condition, the sintered density increases as the Ni content (liquid fraction) increases. In the case of a high Ni content of 30 wt%, the sample is fully densified within 60 min at 1700°C.

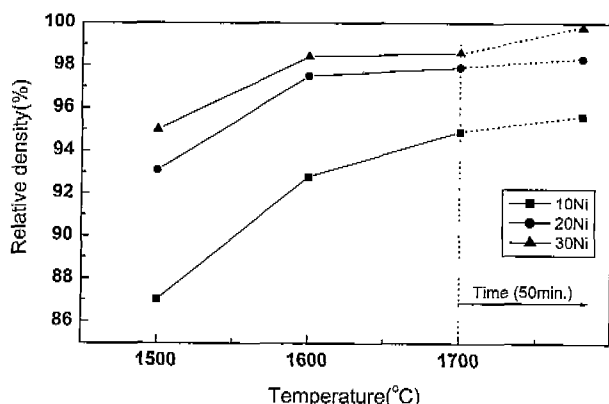


Fig. 1. The effect of Ni content on the relative density of  $\text{TiB}_2$ -Ni sintered at 1500, 1600 and 1700°C for 10 min and also at 1700°C for 60 min in vacuum.

These results are similar to those observed during the conventional liquid-phase sintering of other materials.

Figure 2 shows the microstructures of N10, N20 and N30 samples sintered at 1700°C for 60 min. The N30 sample is fully densified while the N10 sample contains a considerable volume of pores. The shape of  $\text{TiB}_2$  grains in all of the samples is a round-edged polyhedron, indicating that the anisotropy in interfacial energy is not very high. According to a recent investigation,<sup>14)</sup> the growth of round-edged grains in a liquid matrix is controlled by the diffusion of atoms in the liquid matrix. Therefore, the growth of the  $\text{TiB}_2$  grains is also thought to occur via diffusion control.

Table 1 lists the measured grain sizes of N10, N20 and N30 samples sintered at 1700°C for various periods of time. At the initial stage of sintering (1 min), the grain size is almost the same, 2.5–2.6  $\mu\text{m}$ , irrespective of the Ni content.

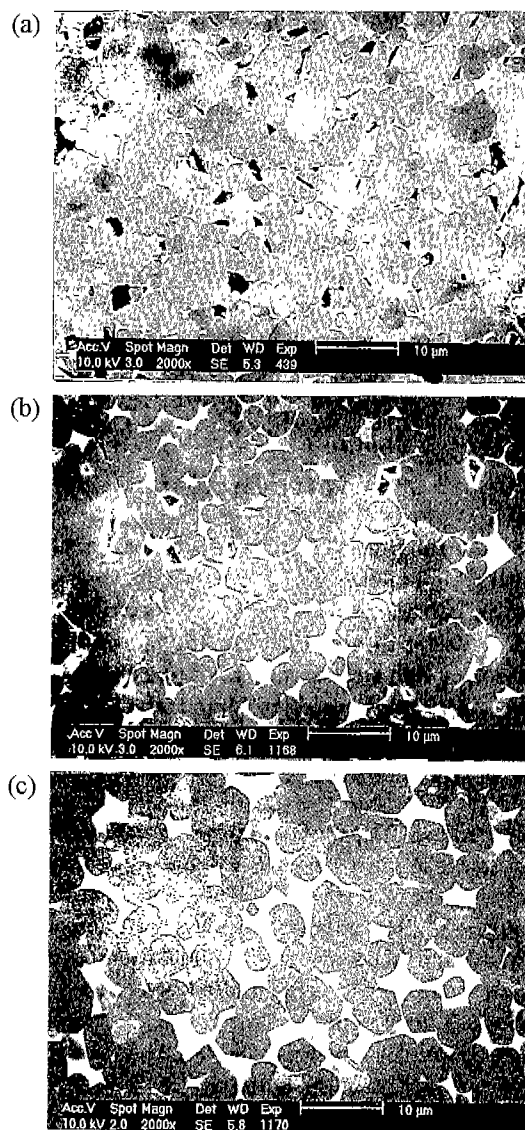


Fig. 2. SEM micrographs of  $\text{TiB}_2$ -Ni samples with (a) 10, (b) 20, and (c) 30 wt% Ni sintered at 1700°C for 60 min in vacuum.

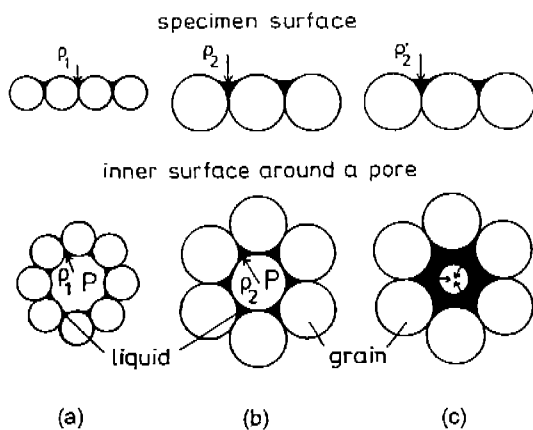
**Table 1.** Average Grain Size (μm) of various TiB<sub>2</sub>-Ni Samples Sintered at 1700°C for various Times in Vacuum

Sintering Time (min) \ Samples	90TiB <sub>2</sub> -10Ni	80TiB <sub>2</sub> -20Ni	70TiB <sub>2</sub> -30Ni
1	2.5	2.6	2.6
10	2.7	3.2	3.1
30	2.8	3.6	3.5
60	2.9	4.0	3.9

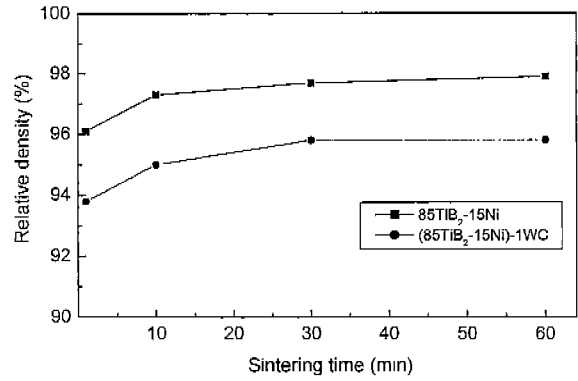
The grain size of the N10 sample increases slightly as sintering time increases while the grain sizes of the N20 and the N30 samples increase considerably. This result is not in agreement with the grain growth behavior predicted by the diffusion-controlled grain growth theory.<sup>15,16</sup> In our samples, however, considerable volumes of pores are included in the samples at the beginning, and they must impede the grain growth. The measured grain sizes in Table 1 include such a pore effect on grain growth. We think that the suppression of grain growth in the N10 sample is due to a higher porosity in the sample than in the other samples.

According to the pore-filling theory,<sup>13</sup> the densification during liquid-phase sintering is determined by the grain growth. Figure 3 illustrates the pore filling process.<sup>17</sup> Since the radius of the liquid meniscus increases linearly with the size of grains (Figs 3(a) and 3(b)), a pore is completely wet when the liquid meniscus radius becomes equal to the pore radius during the grain growth, the critical moment for liquid filling (Fig. 3(b)). Then a pressure imbalance in the liquid arises between the sample surface and the pore surface with further grain growth, and induces the pore filling (Fig. 3(c)). Therefore, the densification during liquid phase sintering occurs with the grain growth.<sup>14,18</sup>

The densification behavior presented in Fig. 1 may be



**Fig. 3.** Schematic showing the liquid filling of a pore during grain growth: (a) before pore filling, (b) critical moment for filling, and (c) liquid flow just after the critical moment. P is the pore and ρ is the radius of curvature of the liquid meniscus ( $\rho_1 < \rho_2, \rho_2 < \rho_2'$ ).<sup>17</sup>



**Fig. 4.** Densification of 85TiB<sub>2</sub>-15Ni (wt%) samples with and without 1 wt% WC sintered at 1700°C in vacuum.

**Table 2.** Average Grain Size (μm) of 85TiB<sub>2</sub>-15Ni Samples with or Without 1 wt% WC Sintered at 1700°C for various Times in Vacuum

Sintering Time (min) \ Samples	85TiB <sub>2</sub> -15Ni	(85TiB <sub>2</sub> -15Ni)-1WC
1	2.5	1.6
10	2.8	1.8
30	3.2	2.0
60	3.4	2.1

explained either by the conventional contact-flattening theory<sup>19</sup> or by the pore-filling theory.<sup>13</sup> To test the theories, we prepared two kinds of samples with different grain sizes. To vary the grain size, 1 wt% WC was added to 85TiB<sub>2</sub>-15Ni (hereinafter called as N15). The N15 samples with and without 1 wt% WC were sintered at 1700°C for various periods of time up to 60 min. WC is known to suppress the growth of TiB<sub>2</sub> grains.<sup>20</sup> The grain size data in Table 2 clearly demonstrate this suppression effect. Figure 4 shows the densification curves of the N15 samples with and without WC at 1700°C. It is clear that, although the liquid content is the same, the densification occurs much faster in the sample without WC than in the sample with WC. Since the diffusion of solute atoms in a liquid matrix is not greatly affected by the presence of a small amount of a third phase, it is not probable that the result is due to the change in solute diffusivity in the liquid. The classical liquid-phase sintering theory, the contact flattening theory, predicts that the densification is faster as grain size decreases, if all other conditions are the same, contrary to the present experimental observation. On the contrary, the pore-filling theory predicts faster densification as the grain size increases; this is in good agreement with our observation. In particular, the density and the grain size of the N15 sample without WC sintered for 1min are slightly higher and larger than those of the sample with 1wt% WC sintered for 60 min. This result supports again the prediction of the pore-filling theory that the densification of TiB<sub>2</sub>-Ni compacts occurs with grain growth.

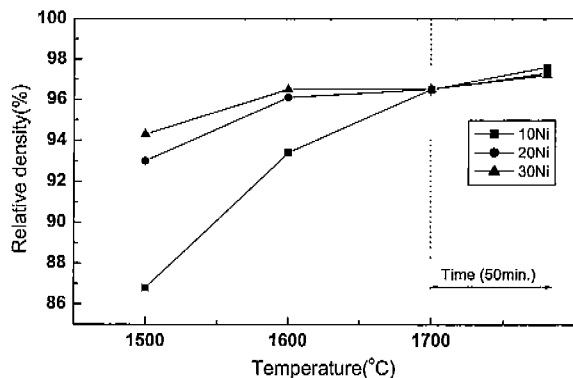


Fig. 5. The effect of Ni content on the relative density of  $\text{TiB}_2\text{-Ni}$  sintered at 1500, 1600 and 1700°C for 10 min and also at 1700°C for 60 min in Ar.

### 3.2. Sintering in Ar

Figure 5 plots the measured densities of N10, N20 and N30 samples sintered at 1500, 1600 and 1700°C for 10 min in Ar and also at 1700°C for 60 min in Ar. As in the case of the vacuum sintering, the sintered density tends to increase as the sintering temperature and the sintering time increase. However, as the sintering proceeds, the densification behavior becomes different from that in vacuum. After sintering at 1500°C for 10 min, the sintered density is similar to that in vacuum, irrespective of the sample. However, for the samples containing large amounts of liquid (N20 and N30) sintered at 1600 and 1700°C, the sintered densities are lower than those obtained in vacuum. This result must be due to the entrapped Ar gas in the isolated pores, which impedes the densification.<sup>21,23</sup> In contrast, the densification of the N10 sample is higher than that in vacuum as the sintering proceeds. This result might be attributed to a considerable suppression of Ni volatilization by the Ar in the furnace. The suppression of Ni volatilization results in larger amount of liquid Ni in the sample than that in the same sample with high Ni volatilization in vacuum. For the N10 sample, this positive effect on densification would exceed a negative effect of entrapped Ar gas in the isolated pores.

The effect of entrapped Ar gas in isolated pores can be estimated assuming that the pores are isolated at 92% relative density. Then, the sintering conditions for pore isolation of the N10, N20 and N30 samples were 1600°C 10 min, 1500°C 10 min, and 1470°C 10 min, respectively. Figure 6 shows that the pore size distribution is almost the same for the three different samples. Assuming that the Ar pressure in the furnace is 1atm and the Ar gas entrapped in the pores behaves like an ideal gas, the Ar pressure in the isolated pores at 1700°C is estimated to be 1.05 atm for N10 and 1.13 atm for N30. This estimation confirms that the entrapped gas pressure is higher in the sample with a larger amount of Ni.

In addition to the effect of gas pressure increase in the pores at the sintering temperature of 1700°C, the effect of pore coalescence during sintering must be introduced. As the grain growth occurs, the pores containing insoluble gases coalesce<sup>23</sup> and the pore coalescence results in a dedensification. Since the grain growth is much faster in the N30

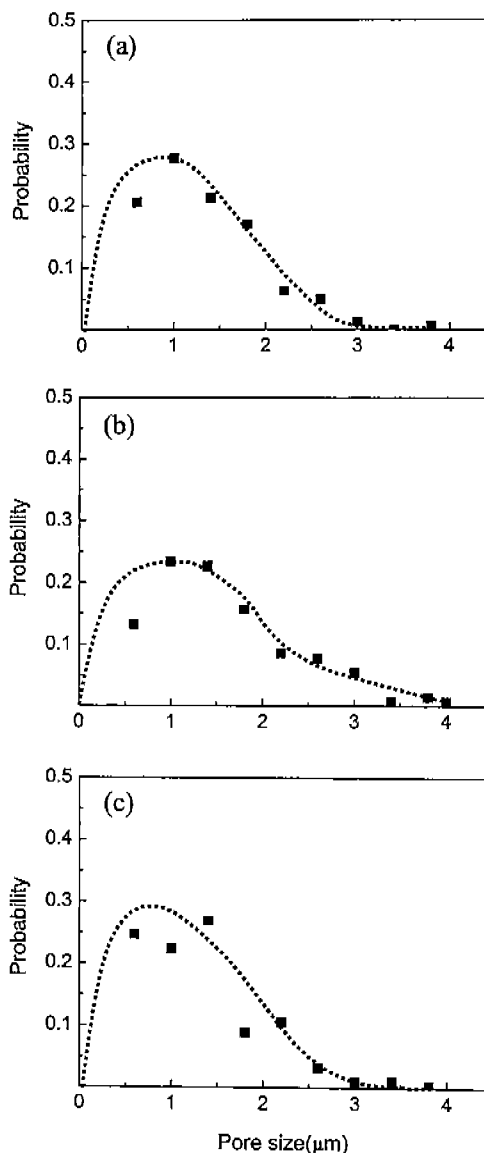


Fig. 6. The pore size distribution of various Ar-sintered  $\text{TiB}_2\text{-Ni}$  samples with ~92% relative density: (a)  $90\text{TiB}_2\text{-10Ni}$ , (b)  $80\text{TiB}_2\text{-20Ni}$  and (c)  $70\text{TiB}_2\text{-30Ni}$ .

sample than is in the N10 sample (Table 1), more dedensification is expected to occur in the N30 sample. This effect must appear together with the effect of gas pressure increase at the sintering temperature of 1700°C. The suppression of densification by entrapped Ar should then be much greater in the N30 sample than in the N10 sample, as shown in Fig. 5. Therefore, an increase in the liquid volume fraction is not always beneficial in Ar sintering, contrary to the case of vacuum sintering. On the other hand, for the sintering of a compact with a low liquid volume fraction, Ar sintering can be beneficial because of the suppression of Ni loss by Ar which may surpass the entrapped Ar effect.

## 4. Conclusions

The densification during liquid phase sintering of  $\text{TiB}_2\text{-Ni}$

has been investigated with particular emphasis on the effect of the sintering atmosphere and Ni content. In the case of vacuum sintering, Ni volatilized considerably. Nevertheless, the sample containing a large amount of Ni (30 wt%) was fully densified. In contrast, the densification and grain growth were highly suppressed in the sample containing a small amount of Ni (10 wt%). When the grain growth was suppressed by the addition of 1 wt% WC, the densification rate was much reduced. The recently developed pore-filling theory explained the experimental results while the classical contact flattening theory could not.

The densification behavior in Ar was quite different from that in vacuum. The densification of a compact with a small amount of Ni (10 wt%) was faster in Ar than in vacuum, while the densification of a compact with a large amount of Ni (20 or 30 wt%) was slower in Ar compared with that in vacuum. This result was attributed to two opposite effects of Ar: suppression of Ni volatilization from the compact and internal Ar gas pressure in the isolated pores. For the compact with a small amount of liquid, the suppression effect of Ni volatilization appeared to dominate the entrapped gas effect because of retarded pore isolation and inconsiderable coalescence of isolated pores compared with the case of the compact with a large amount of liquid. In contrast, for the compact with a large amount of Ni, the entrapped gas effect appeared to dominate because of early pore isolation and considerable pore coalescence. Therefore, a vacuum-sintering is recommended for a TiB<sub>2</sub> compact with a small amount of Ni while an Ar-sintering is recommended for a compact with a large amount of Ni.

### Acknowledgements

This work was partially supported by the Agency for Defense Development. One of the authors (Dr. Yeon-Gyu Choi) thanks the Korea Research Foundation for his post-doctoral research at KAIST.

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