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Fabrication of TiB_2/TiC composites by the directional reaction of titanium with boron carbide

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Dense TiB_2/TiC composites were fabricated by the directional reaction of molten titanium with boron carbide preform. The reaction between pure molten titanium and boron carbide preform could not progress due to reaction choking. However, when a few weight per cent of nickel were added in the titanium, the reaction progressed continuously and resulted in TiB_2/TiC composites. A gradient of grain sizes was observed in the reaction products. The processing temperature affected the microstructure of the reaction products rather than the reaction rate. The degree of grain-size gradient in the reaction product increased with the processing temperature.

1. Introduction

Recently, work has been reported on the fabrication of ceramic–metal composites by the directional reaction of a molten metal with boron carbide preform [1, 2]. This process can be regarded as being similar to the reaction of a molten silicon with porous carbon preform [3], and even though there are many differences, it can also be compared with Lanxide technology of the directional reaction of molten metal by a gaseous oxidant [4–6]. The advantage of this process is that the temperatures required for fabrication are much lower than in the conventional consolidation methods (pressureless sintering, hot pressing), because the processing is usually done near the melting point of the reactant metal. In addition, the process has the potential to make very large bodies and complex parts with a minimum dimensional change from the original preform.

Most recently, ZrB_2/ZrC composite based on the reaction of molten zirconium with boron carbide preform was reported (Lanxide NX-3400^{TM}) [1, 2]. The reaction was carried out at temperatures (1850–2000 °C) above the melting point of zirconium. The reported properties of this material were excellent and included values for room-temperature flexural strength of 800–900 MPa and for fracture toughness of 16–18 MPa $m^{1/2}$.

This paper presents the results of study on the fabrication of a new ceramic composite, TiB_2/TiC, by the directional reaction of molten titanium with boron carbide preform. TiB_2/TiC composite has great potential as lightweight armour materials and cutting tools [7], but it has been difficult to obtain fully dense bodies by the conventional sintering methods. (Hot pressing and pressureless sintering of TiB_2 generally require temperatures in excess of 1800 and 2000 °C, respectively [8].) Through the reaction process, however, dense TiB_2/TiC bodies can be obtained at near the melting point of titanium (about 1700 °C).

Preliminary experiments showed that the reaction between pure molten titanium and boron carbide preform occurred only on initial contact and could not progress further. However, when nickel was added in the titanium, the reaction could continuously progress and the reaction product grew into the boron carbide preform. The objective of this study was a microstructural evaluation of TiB_2/TiC composites made by the directional reaction process. The effect of nickel added to the titanium on the reaction of molten titanium with boron carbide is discussed; the effect of processing temperature on the microstructure of the reaction products was also investigated.

2. Experimental procedure

B_4C (Tetrabor F1200, ESK Gmbh, Munchen, Germany), Ti (Aremco Products Inc., Ossing, NY), and Ni (Aremco Products Inc., Ossing, NY) powder used in this experiment had average grain size of 3, 44 and 5 μm, respectively. They had specified purities of 99.9%. B_4C preform was prepared by uniaxial pressing at 30 MPa into the graphite crucible (25 mm inside diameter). These green compacts were about 10 mm thick and had densities between 45% and 50% theoretical density of B_4C. Titanium and nickel were mixed in a polypropylene bottle using a vibratory mill (Model 8000, Spex Industry Inc., Edison, NJ). This mixture was uniaxially pressed at 200 MPa in a steel die.

Reaction was performed at the temperature range 1600–1800 °C under an argon atmosphere using a tungsten resistance furnace (Centorr Associate, Inc.,

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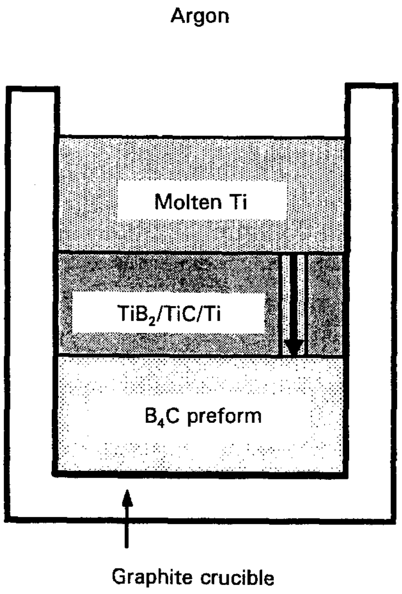

Figure 1 Schematic illustration of the directional reaction process for the production of TiB_2/TiC composites.

Suncook, NH). A schematic illustration of the reaction is shown in Fig. 1. Titanium (+ x nickel) compact was placed on top of the B_4C preform in the graphite crucible. The weight of the titanium compact was five times the weight of B_4C. The titanium compact melted into a liquid phase at the reaction temperature.

The degree of reaction was determined by weighing the amount of unreacted B_4C. The reaction products were cross-sectioned, polished, and chemically etched by in an HNO_3 solution. Microstructures were examined using an optical (ICP 405, Carl Zeiss, Oberkochen, Germany) and scanning electron microscope (SEM). Phase analysis for the reaction products was performed by an X-ray diffractometer (XRD) and an energy dispersive spectroscopy (EDS) in SEM.

3. Results and discussion

3.1. Phase analysis and microstructure

The reaction of titanium with boron carbide is exothermic [9].

$$3Ti + B_4C \rightarrow 2TiB_2 + TiC$$

$$\Delta G = -395\ \mathrm{kJ/mol^{-1}},\ 1700\,^{\circ}\mathrm{C} \qquad (1)$$

The reaction of pure titanium with B_4C preform was conducted at a temperature near the melting point of titanium. The reaction occurred only on initial contact and could not be made to progress further. However, when a few weight per cent of nickel were added to the titanium, the reaction progressed continuously and resulted in TiB_2/TiC composite. The effect of nickel on the reaction will be discussed in detail in the next section.

Phase and microstructural analysis were performed on specimens formed by the reaction of Ti(+ 10 wt % nickel) with B_4C preform. X-ray diffraction patterns of the reacted specimens (Fig. 2) showed the presence of TiB_2, TiC, and a minor unidentified metal phase which may be Ti–Ni–B–C. Unreacted B_4C was not detected in the reaction products.

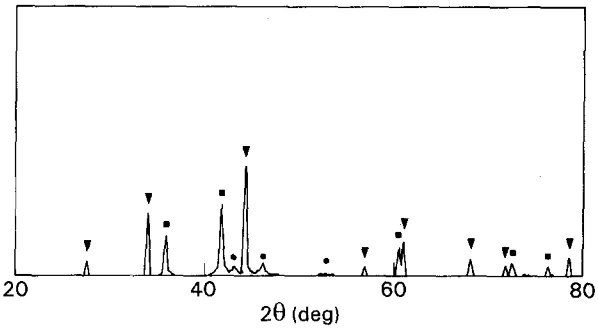

Figure 2 XRD pattern of the reaction product formed by the directional reaction of B_4C with Ti(+ 10 wt % Ni) for 60 min at 1700 °C. (▼) TiB_2, (■) TiC, (●) Ti–Ni phase.

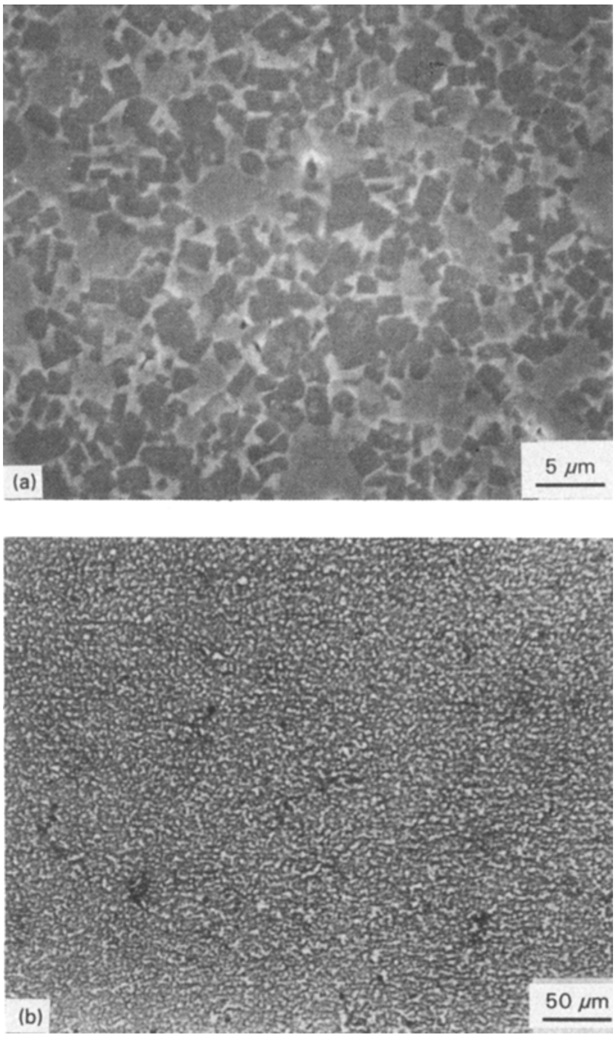

Figure 3 (a) Scanning electron and (b) optical micrographs of the TiB_2/TiC specimens formed by the directional reaction of B_4C with Ti (+ 10 wt % Ni) for 60 min at 1700 °C. The dark, grey, and white phases are TiB_2, TiC, and Ti–Ni metal, respectively.

Fig. 3 shows the polished and etched surface of a reaction product, in which the dark, grey, and white phases are TiB_2, TiC, and Ti–Ni metal, respectively. Each phase was shown to be relatively well-dispersed. The microstructure typically contained no pores. The composition of the liquid phase was confirmed as 70 wt % Ti and 30 wt % Ni by the EDS analysis.

3.2. Effect of nickel on the reaction of titanium with boron carbide

Fig. 4 shows the degree of reaction with holding time for the specimens formed by the reaction of B_4C with titanium containing various amounts of nickel. The reaction between pure titanium and B_4C occurred only on contact and resulted in a dense TiB_2/TiC surface layer, as shown in Fig. 5a. The reaction could not progress further, because this layer acted as a protective layer to prevent molten titanium from being supplied to the B_4C preform. As a result, growth of the product was stopped. However, the reaction between B_4C and titanium containing nickel was progressed continuously. In specimens formed by the reaction of B_4C with titanium containing 5 and 10 wt% nickel (Fig. 5b and c), metal phase was observed at the grain boundaries, phase boundaries, and triple junctions, unlike in Fig. 5a, indicating that molten titanium could be continuously supplied to the B_4C preform along the channels (grain boundaries and phase boundaries) in TiB_2/TiC product. It is thought that nickel added to the titanium led to the thermodynamic condition (γ_{gb}, γ_{pb} $> 2\gamma_{sl}$) under which molten titanium could penetrate into grain boundaries and phase boundaries of TiB_2/TiC. Thus, the reaction could progress continuously towards B_4C preform without reaction checking.

The infiltration rate through the product layer (TiB_2/TiC) was observed to be slower than the rate of reaction between titanium and B_4C when the B_4C preform consisted of fine particles (< 3 μm). Therefore, the overall reaction rate was determined by the infiltration rate through the product layer. The overall reaction rate increased with the nickel content in the titanium and this resulted from the increase of the infiltration rate. It is known that the parabolic infiltration rate constant is proportional to the cosine of the wetting angle and inversely proportional to the viscosity of the molten metal [10]. Therefore, it could be deduced that nickel added to the titanium decreased the viscosity and/or increased the wettability of molten titanium to promote the infiltration rate.

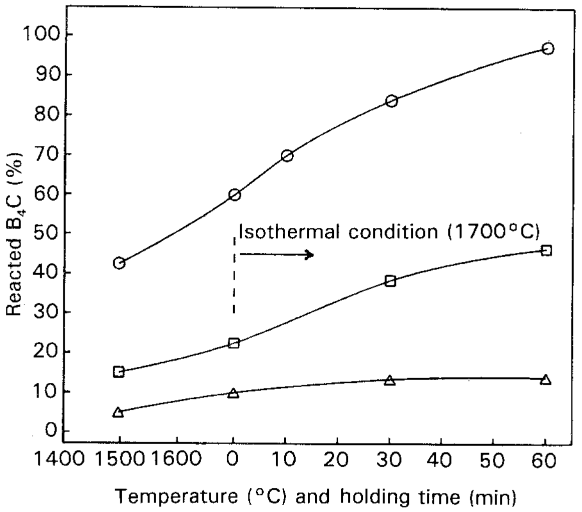

Figure 4 The degree of reaction versus holding time at 1700 °C for various nickel contents in molten titanium. (○) Ti–10% Ni, (□) Ti–5% Ni, (△) Ti–0% Ni.

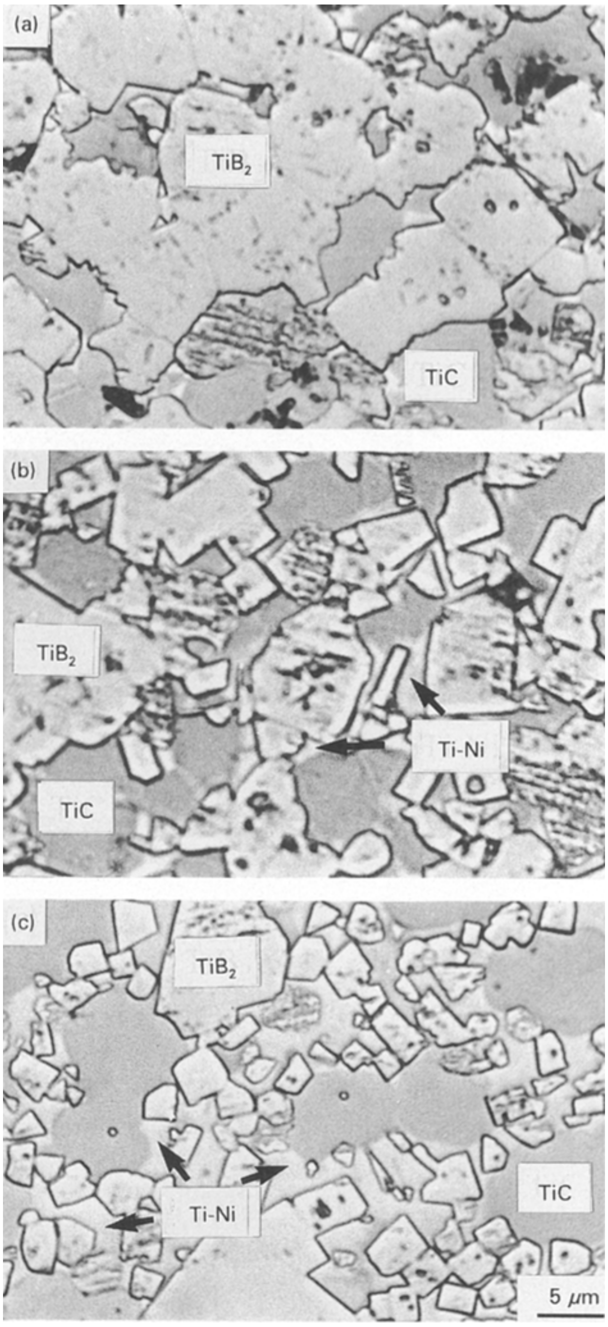

Figure 5 Optical micrographs of TiB_2/TiC specimens formed by the directional reaction of B_4C with (a) Ti(+ 0 wt % Ni), (b) Ti(+ 5 wt % Ni) and (c) Ti(+ 10 wt % Ni) for 60 min at 1800 °C.

On the other hand, when the B_4C preform consisted of coarse particles (> 10 μm), the infiltration rate was observed to be faster than the reaction rate. This phenomenon is similar to the result observed in the reactive infiltration of molten silicon for the fabrication of reaction-bonded silicon carbide [3]. The reaction of titanium with B_4C consisting of coarse particles (> 10 μm), is under study at present.

3.3. Effect of temperature on the microstructure

The microstructures of the reaction products are significantly affected by the reaction temperature, however the reaction temperature had no effect on the reaction rate. Fig. 6 shows the microstructure in the planes

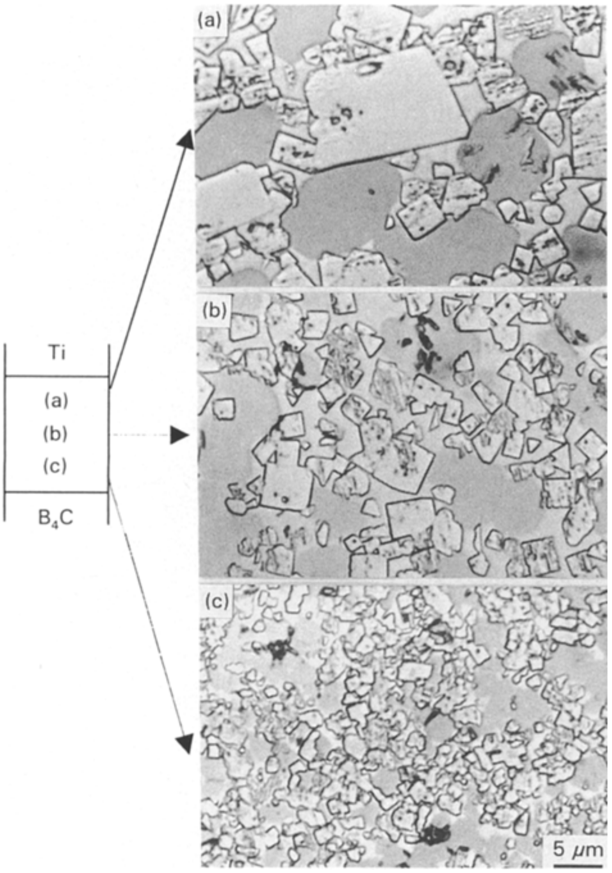

Figure 6 Optical micrographs showing the grain-size gradient of TiB_2/TiC specimens formed by the directional reaction of B_4C with Ti(+ 10 wt % Ni) for 60 min at 1800 °C.

perpendicular to the growth direction of the reaction product for the specimen formed by the reaction of B_4C with titanium containing 10 wt % nickel at 1800 °C for 60 min. The reacted specimens were about 10 mm thick. In this and following figures, a, b and c denotes the top (nearest to the molten titanium), middle, and bottom (nearest to the boron carbide preform) region of a specimen, respectively. In Fig. 6 it can be seen that there is a gradient of grain size, namely, the average grain size in the top region, a, is larger than that of bottom region, c.

This grain-size gradient can be attributed to the different time period for grain growth in the reaction process. This is schematically shown in Fig. 7. In the first stage, the reaction begins on contact between molten titanium and B_4C, and TiB_2 and TiC grains are nucleated in that region. As the reaction progresses with the continuous supplying of molten titanium through the reaction product, the reaction front moves downwards and new TiB_2 and TiC grains are nucleated at the lower region. At the same time, the already nucleated TiB_2/TiC grains in the upper region will start to grow in order to lower the interface energy (Stage II).

This process continues to the end of the reaction. The reaction front continuously moves downwards and produces new nuclei of TiB_2 and TiC grains, and grains in the upper region also continuously grow (Stage III). Therefore, a difference in the time period for grain growth between the upper region and the lower region in a specimen should arise. Because the reaction proceeded quite slowly in this experiment (about 10 mm h^{-1} at 1600–1800 °C), there should have been an equal time difference for the growth of grains between the upper region and the lower region. In other words, the grains in the top region have grown for about 60 min, but the grains in the bottom region have only just formed. This process will finally lead to a gradient in grain size in a specimen fabricated by the directional reaction as shown in Fig. 6.

Figs 8 and 9 show the microstructures for the specimens produced at 1700 and 1600 °C, respectively. They also show gradients in grain size similar to the specimen produced at 1800 °C. However the degree of the gradient in grain size and the average grain size are relatively small. This difference can be attributed to the difference in grain growth rate with temperature. Because the grain growth rate is higher at higher temperature, the grains in the upper region in a specimen produced by the directional reaction grow faster at the higher temperature than at the lower temperature and the grain-size gradient will also be larger at the higher temperature. Thus, at the lower temperature, not only the average grain size but also the degree of the grain-size gradient was smaller than at the higher temperature, as shown in Figs 8 and 9.

This microstructural gradient in the specimens produced by the directional reaction may lead to gradients in mechanical and electrical properties. In fact, TiB_2/TiC composite fabricated in this experiment at

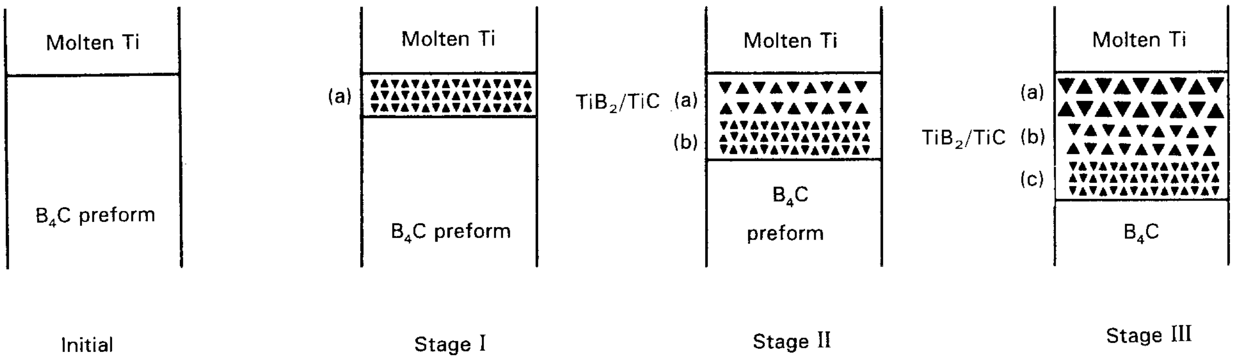

Figure 7 Schematic illustration of the reaction procedure and grain growth in the directional reaction of molten Ti(+ Ni) with B_4C. (The size of the triangles represents the grain size.)

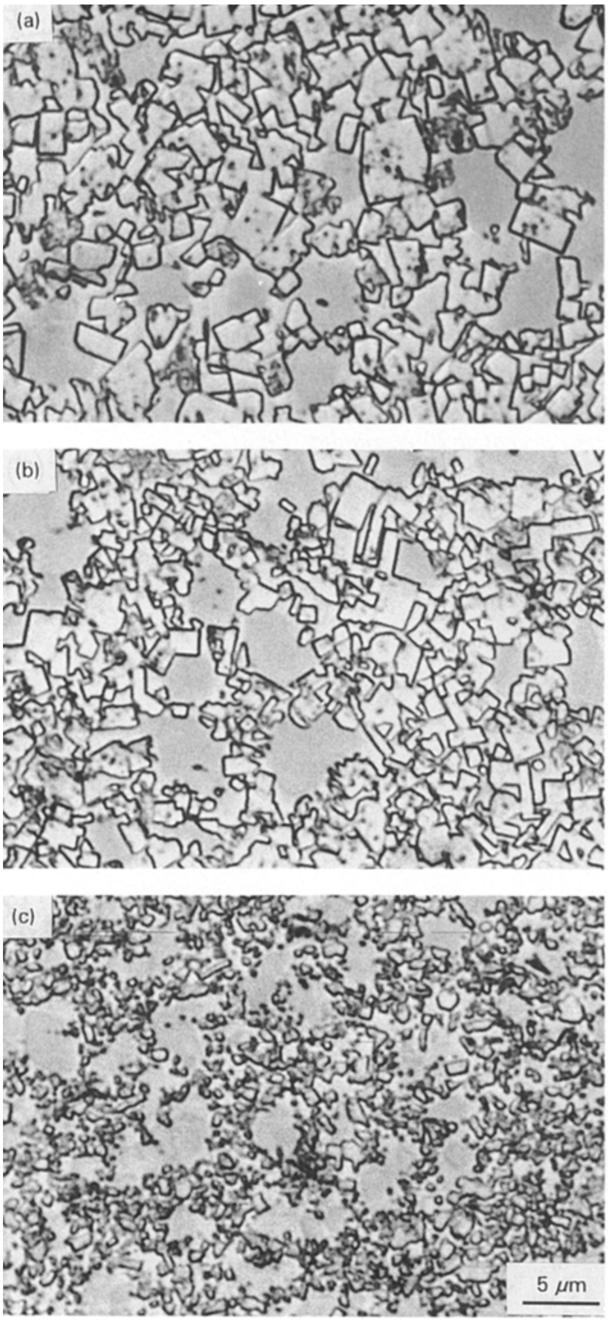

Figure 8 Optical micrographs showing the grain-size gradient of TiB_2/TiC specimens formed by the directional reaction of B_4C with Ti(+ 10 wt % Ni) for 60 min at 1700 °C.

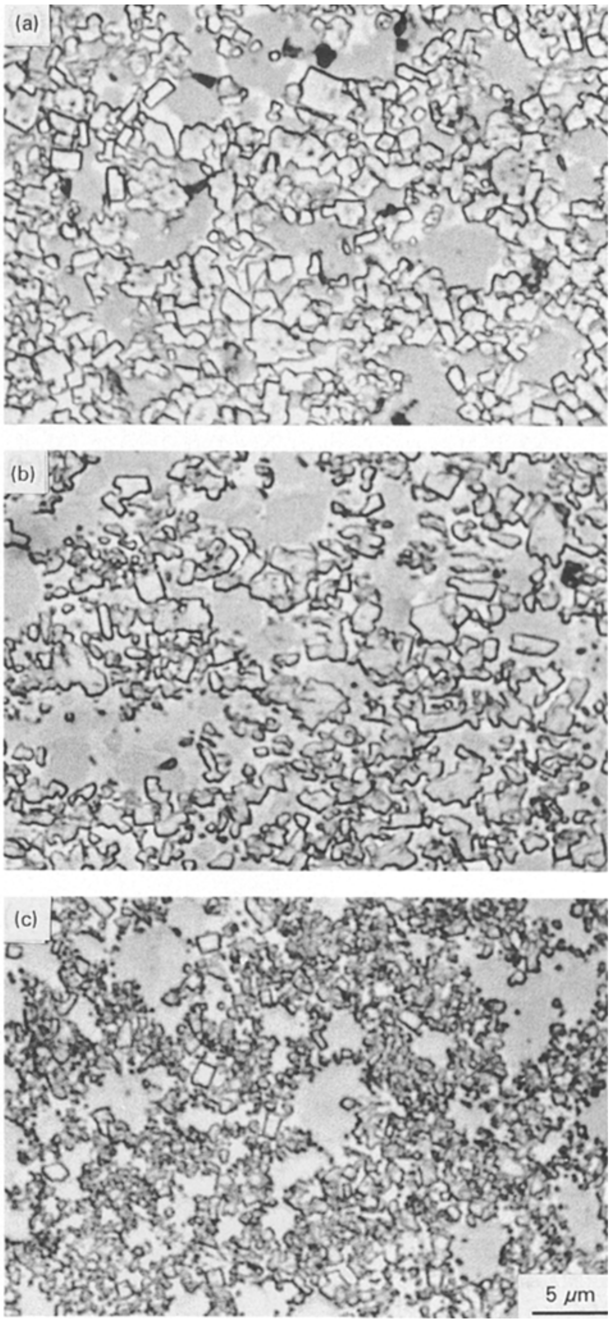

Figure 9 Optical micrographs showing the grain-size gradient of TiB_2/TiC specimens formed by the directional reaction of B_4C with Ti(+ 10 wt % Ni) for 60 min at 1600 °C.

1800 °C for 60 min showed a large difference in the flexural strength with the measuring directions. When the specimen was located with the upper region (Fig. 6a) on the tensile surface, the measured flexural strength was about 450 MPa, but when the tensile stress was loaded at the bottom region in the specimen (Fig. 6c), the measured flexural strength was about 700 MPa. This property gradient is now under study, and details will be published later. TiB_2/TiC composites made by the directional reaction have potential as functionally-gradient materials with varying mechanical properties (fracture strength, fracture toughness, and hardness) in each region of the specimen [11].

4. Conclusions

Dense TiB_2/TiC composites could be fabricated by the directional reaction of molten titanium with boron carbide preform. The reaction rate increased with the nickel content in the molten titanium, probably due to the change of the interfacial energy between grains and the molten metal and/or the lowered viscosity of the molten alloy. A grain size gradient was observed in the reaction products, which was attributed to the difference in the time period for grain growth between each region in the specimen produced by the directional reaction. Not only the average grain size but also the degree of the grain size gradient increased with increasing of reaction temperature.

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