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Two-step sintering of a TiB_2–Ni cermet

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The effect of atmosphere control on the sintering behaviour of TiB_2–20 wt % Ni ceramics was investigated. Sintering was performed at 1700 °C for 1 h with commercial TiB_2 powders produced by the carbothermic reaction. Under a fixed single atmosphere such as vacuum or Ar, densification was limited and large pores remained. However, a sintered density above 99% of theoretical could be achieved by a two-step sintering procedure in which the atmosphere was changed from vacuum to Ar at 1600 °C during the heat-up with subsequent isothermal sintering being performed at 1700 °C for 1 h. Qualitative considerations about these phenomena are discussed.

1. Introduction

Titanium diboride has a high hardness, a high melting point, and a high electrical conductivity. In addition, it shows good resistance to corrosion and wear [1]. Because of these physico-chemical properties, TiB_2 has been considered as a candidate material for cutting tools, metal melting crucibles, ceramic armours, etc. [2, 3]. However, its strongly covalent nature and significant thermal expansion anisotropy have made the fabrication of highly dense bodies difficult [3]. Thus, until recently hot pressing technology has been the major fabrication method for dense TiB_2 bodies [3–6]. This method, however, has limited applications to the production of complex shapes and is also relatively expensive.

Baumgartner and Steiger [7] were the first to succeed in densifing TiB_2 ceramics up to 98% of theoretical density by pressureless sintering. Finch *et al.* [8] and Kang *et al.* [9] have also reported that they obtained dense bodies without pressure assistance. They should, however, have used active submicrometre powders but this powder preparation process seems to be costly. Furthermore, extreme care must be taken in the handling of such powders, since very small amounts of impurities such as oxygen are reported to seriously inhibit the densification process [10]. Thus there is still a need to develop a more convenient method to fabricate dense TiB_2 ceramics using commercially available powders which have relatively large particle sizes.

An alternative way to obtain a dense TiB_2 body is the use of a relatively large amount of an additive that forms a liquid phase at the sintering temperature. Such an approach has been reported for the production of dense TiB_2 bodies in the form of ceramic–metal composites using binder phases of Fe [11, 12] or Ni alloys [13].

In this present paper, liquid phase sintering of TiB_2 ceramics with the addition of Ni as a binder phase is attempted. The effect of the sintering atmosphere on the densification of this ceramic is investigated.

2. Experimental procedure

Specimens were prepared from a mixture of 80 wt % TiB_2 powder (Grade A, Hermann C. Starck, Berlin, Germany) and 20 wt % (about 11 vol %) Ni powder (Teledyne Wah Chang, Albany, OR, USA) with average particle sizes of 1.9 μm and 5 μm, respectively. The powders were wet-mixed in a polypropylene bottle using acetone as a liquid medium. After drying, the mixtures were granulated and compacted into a cylindrical shape of 10 mm diameter and about 5 mm height. These were then isostatically pressed at 150 MPa and the resulting green compacts had densities of approximately 55% of theoretical.

The green compacts were dried at 50 °C for a day, soaked at 1000 °C for 1 h in vacuum (10^{-2}–10^{-3} Pa) in order to burn out the organic binders and other volatile species, and then sintered at 1700 °C and 1800 °C for various times in a tungsten-mesh furnace (Centorr Associates, Inc., Suncook, NH, USA). The temperature was measured by an optical pyrometer (IR-630, Minolta Camera Co., Ltd., Tokyo, Japan) within an accuracy of ± 5 °C through a quartz window. The heating and cooling rates were 15 °C per min and 30 °C per min, respectively. The sintering atmosphere was vacuum in the range of 10^{-2}–10^{-3} Pa or flowing Ar maintaining a slight over pressure above 0.1 MPa. In two-step sintering the atmosphere was

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changed from vacuum to Ar at various temperatures during heating and the specimens were subsequently sintered at 1700 °C in a flowing Ar atmosphere.

The sintered specimens were polished to # 1200 SiC paper and etched in a mixed solution of hydrochloric and nitric acid at room temperature. A reflected optical microscope and also a scanning electron microscope (SEM) were used for microstructural observations. The sintered specimens were subjected to X-ray diffraction (XRD) with CuK_α radiation to identify the phases present. The porosities of the sintered specimens were determined by the point count method with grid lines of 2 mm spacing on five photomicrographs for each specimen. Relative densities were calculated by subtracting the porosities, since the evaporation loss of the liquid phase precluded the calculation of theoretical densities of the specimens. The average pore size was determined from the average intercept length obtained by the linear analysis on the photomicrographs. The apparent porosities (the ratio of open pore volume to total volume) were measured using the Archimedes principle.

3. Results and discussion

3.1. Sintering under Ar atmosphere and in vacuum

In the sintering of TiB_2–20 wt % Ni ceramics, the sintering atmosphere greatly affected the densification process. Under a fixed single atmosphere such as vacuum or flowing Ar, the densification was restricted and the full density could not be obtained as is shown in Fig. 1. Under an Ar atmosphere, the sintered densities reached a maximum value of 94.2% when sintered at 1700 °C for 15 min and continuously decreased for extended sintering times. The sintered densities were also limited to, in this case, 95.6% in the vacuum conditions investigated.

The restricted densification under the Ar atmosphere can be explained by the entrapped gas effect. It has already been reported by many researchers that densification is restricted for both solid state and liquid phase sintering when pores contain a slowly diffusing or non-diffusing gas such as Ar [14–19]. According to the work of Kwon and Yoon [20], at the melting temperature of a component having a relatively lower melting point in a two or multi-component system, initially the melted phase is sucked into the capillaries between solid particles. Then the pores are re-filled due to the flow of the liquid phase with the increase of solid grain size [21]. This pore-filling process can easily take place when the pores are either in a vacuum or contain gases which can rapidly diffuse through the liquid matrix. If this is not the case then, the internal pore pressure exerted by an inert or slowly diffusing gas can inhibit the pore-filling process. Since the capillary force inducing the pore filling is relatively small, the pore-filling process can be inhibited even in cases where the entrapped gas pressure is low [17, 18].

Accompanying the inhibition of pore filling by the entrapped gas, a simultaneous pore growth and density decrease has often been observed during liquid phase sintering. This phenomenon is called over-firing or de-densification and is known to occur by pore coalescence and/or Ostwald ripening of pores [16, 19, 22, 23]. If the pore-filling process is inhibited by the internal pore pressure exerted by the entrapped gases then the pores will start to grow in order to lower their total surface energy. If the pore size increases then the surface tension force of the pore will weaken and thus the total pore volume will tend to expand. A decrease of the relative density will result from the expansion of the pore volume.

A density decrease with the simultaneous pore growth was also observed in our specimens. In Fig. 2 the variations of the sintered density and the average pore size with the sintering time at 1800 °C under an Ar atmosphere are shown. The pore size increased with extended sintering time which resulted in a continuous decrease of the relative density. So, it could be concluded that under the Ar atmosphere the densification process was inhibited due to the entrapped Ar gas effect.

Whilst the limited densification in the case of an Ar atmosphere resulted from the entrapped gas effect, the large porosity remaining after vacuum sintering was

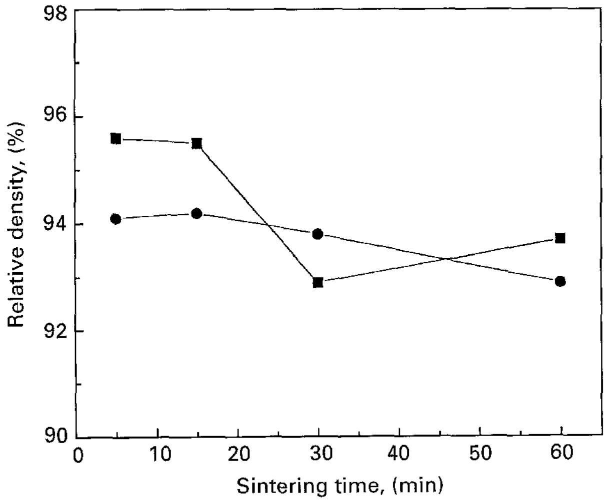

Figure 1 Relative density versus sintering time for the specimens sintered at 1700 °C under (●) a flowing Ar atmosphere and (■) in vacuum.

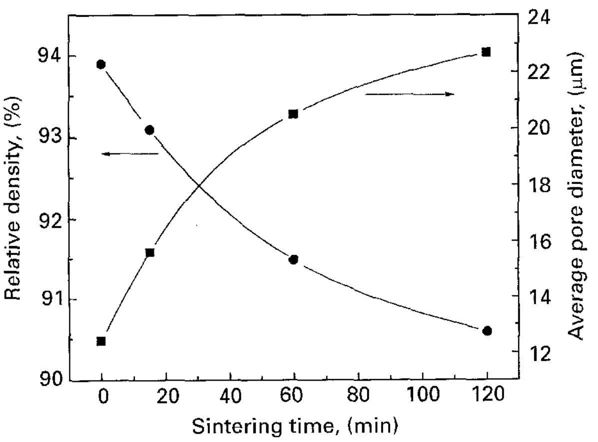

Figure 2 Variation of the sintered density and pore size with sintering time. The specimens were sintered at 1800 °C under an Ar atmosphere.

believed to be due to a significant evaporation loss of the liquid phase during the heating and soaking periods. The variations of relative density and weight loss of the specimens sintered at 1700 °C in vacuum are shown in Fig. 3. The increase in weight loss with sintering time shown in Fig. 3 closely follows the trend in the decrease of the relative density. The XRD pattern (Fig. 4) of the sample sintered at 1700 °C for 15 min in a vacuum shows that the liquid phase had crystallized into a Ni_3B phase. This eutectic liquid phase, however, may contain some Ti and other impurities in the used TiB_2 powder [24].

Shaw [25] has examined the effect of the liquid volume fraction and shrinkage on the pore-filling process. He argued that the pore filling would occur sequentially from the smaller pores to the larger ones as the shrinkage occurs or as the volume fraction of liquid increases. This means that assuming no shrinkage and a constant initial microstructure of the powder compact, the critical pore size below which the pores can be filled with liquid will decrease as the volume fraction of liquid decreases. Thus it is thought that the densification in the vacuum atmosphere was restricted by the evaporation loss of the liquid phase which caused a decrease in the amount of liquid phase and thus prevented the large pores from being filled with the liquid.

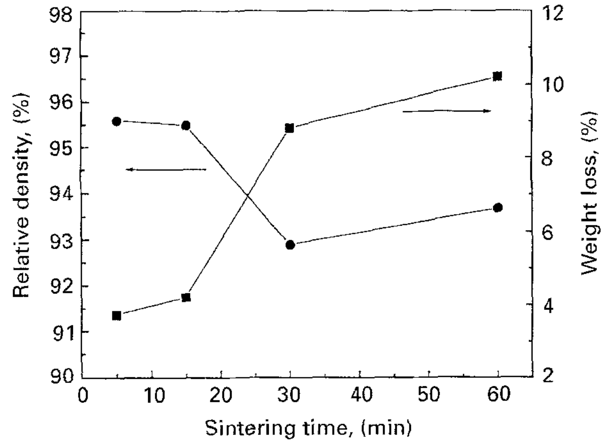

Figure 3 Relative density and weight loss with sintering time for the specimens sintered at 1700 °C in vacuum.

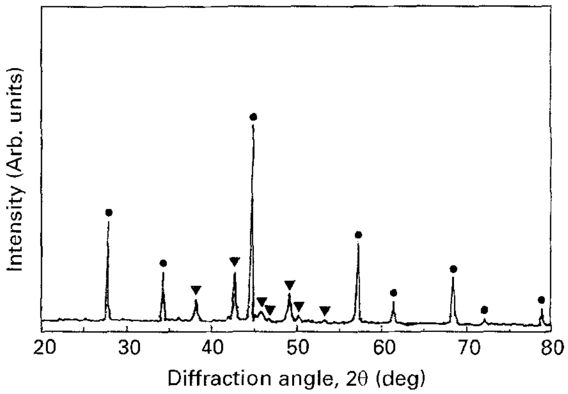

Figure 4 XRD patterns of the specimens sintered at 1700 °C for 15 min in vacuum. The diffraction peaks marked as (●) belong to TiB_2 whilst those marked (▼) belong to Ni_3B.

A slight increase in the sintered density between the sintering times of 30–60 min can be seen in Fig. 3. This could be attributed to a dimunition of the evaporation rate of the liquid phase and also to grain growth with the longer sintering time. Grain shape accommodation which is mainly induced by grain growth can lead to denser packing of grains [26, 27]. Fig. 5 (a–c) shows the microstructures of specimens sintered in vacuum at 1700 °C for various soaking periods. The large grain growth as shown in Fig. 5(c) resulted in a change of the TiB_2 grain shape, which seemed to enable the elimination of some pores.

3.2. Sintering with controlled atmosphere (Two-step sintering)

In two-step sintering, the atmosphere was changed from vacuum to Ar at various temperatures during

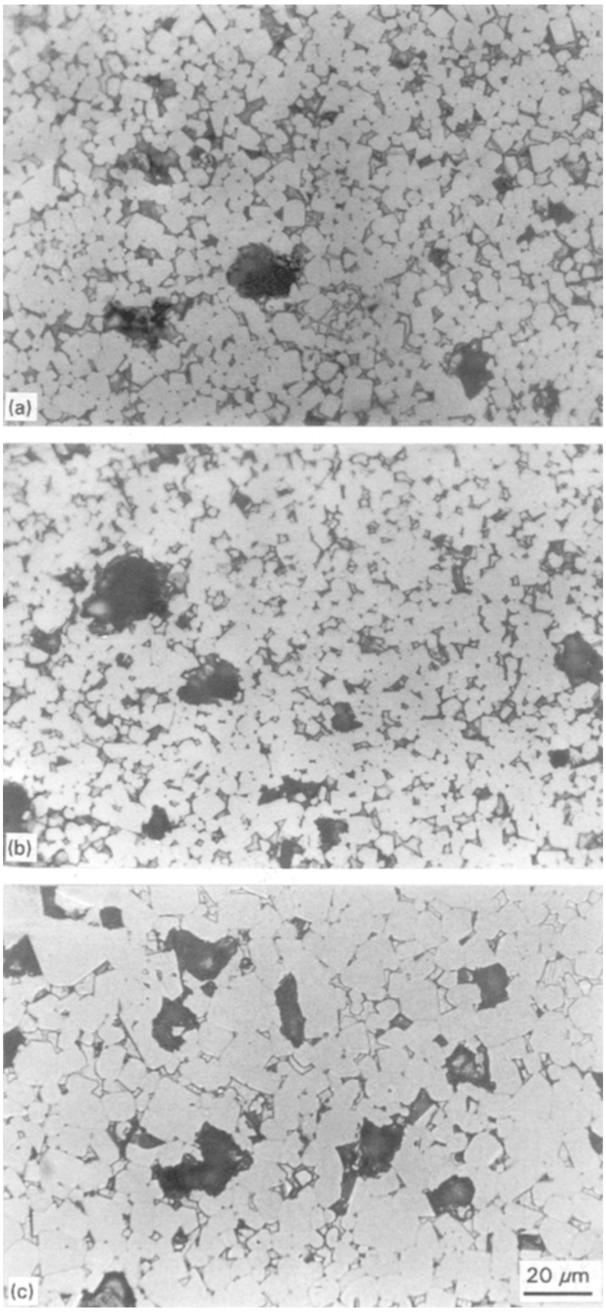

Figure 5 Microstructures of the specimens sintered at; 1700 °C for (a) 15 min (b), 30 min, and (c) 60 min in vacuum.

heating. In the previous section the final density was restricted in a flowing Ar atmosphere because of the entrapped gas effect and in vacuum by the evaporation of the liquid phase. If the atmosphere is changed from vacuum to Ar when the pores are isolated then the entrapped gas effect can be avoided because the insides of the pores will be in a state of vacuum. In order to determine the optimum condition at which the atmosphere should be changed, the apparent porosity and weight loss were plotted as a function of temperature (Fig. 6). The data were obtained after heating the specimens to each temperature and then cooling down immediately to room temperature. As can be seen in Fig. 6, the compromise temperature, at which the apparent porosity is a minimum and the weight loss is moderate, is 1600 °C.

Fig. 7 shows the relative densities for the specimens finally sintered at 1700 °C for 1 h after changing the atmosphere at the temperatures depicted in Fig. 6. In the cases when the Ar gas was used whilst the fraction of open pore volume was large (e.g., 1300 °C or 1400 °C), the densification was restricted similarly to the case of solely using Ar gas during all intervals of sintering. The Ar gas probably flowed into the pores when they were connected to the specimen surface and then become entrapped when the pores were closed during subsequent heating. This entrapped Ar gas could exert an internal pressure thereby limiting the densification. The resultant microstructure is shown in Fig. 8(a). Large pores remain which might be caused by the interruption of the pore-filling process by the entrapped gas effect.

In the cases that Ar was used when the open pore volume was relatively small (above 1500 °C), the entrapped gas effect was minimized and a high density could be obtained. However in the case of changing

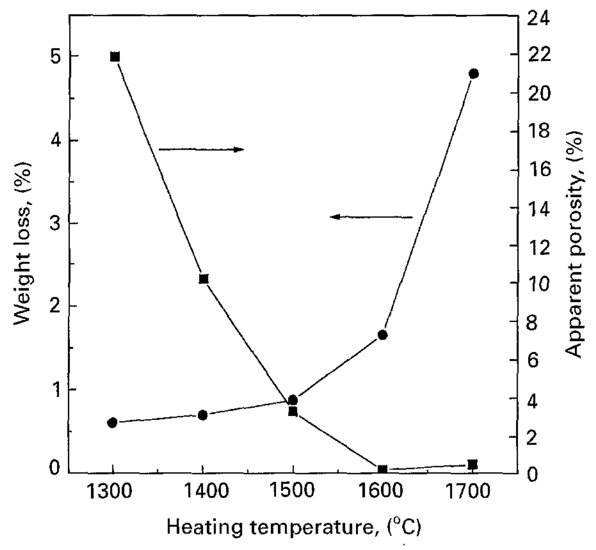

Figure 6 Variation of the apparent porosity and weight loss with temperature. The data were obtained from the specimens heated to each temperature and then immediately quenched.

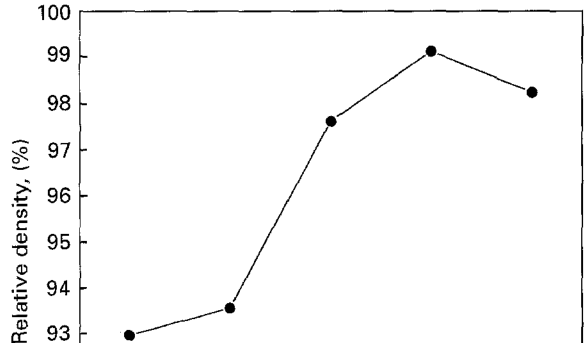

Figure 7 Relative density as a function of the Ar flow temperatures for the specimens finally sintered at 1700 °C for 1 h.

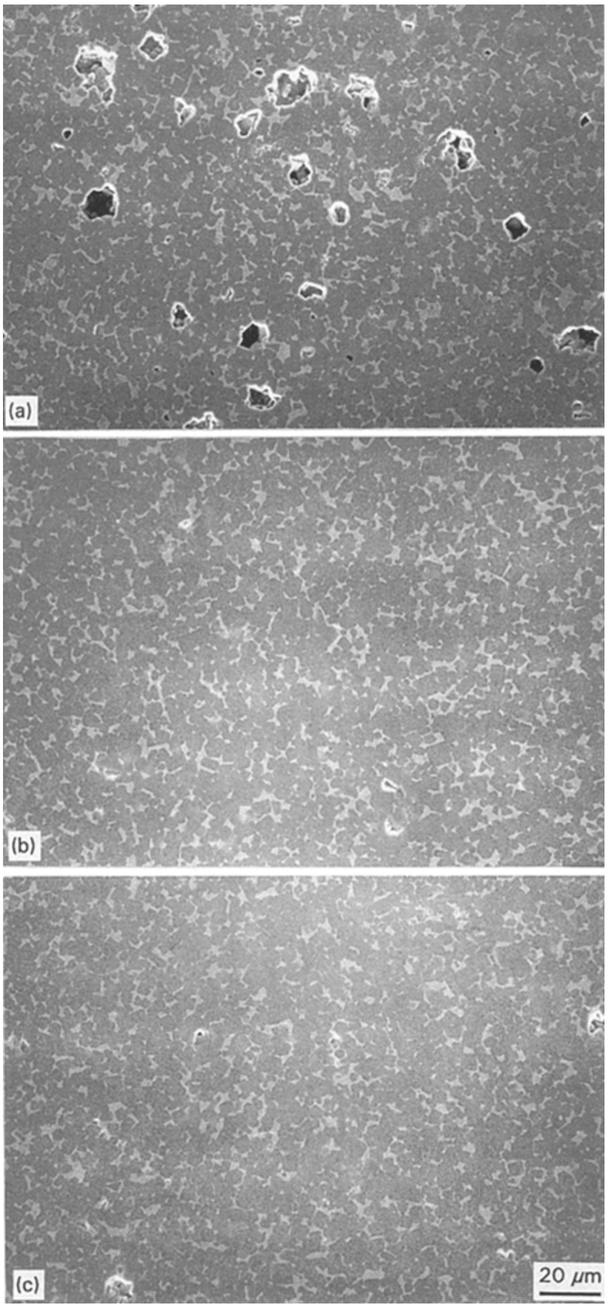

Figure 8 Scanning electron micrographs of the polished surface of the specimens finally sintered at 1700 °C for 1 h. The atmosphere was changed from vacuum to Ar at (a) 1400 °C (b) 1600 °C, and (c) 1700 °C.

the atmosphere at 1700 °C, the final sintered density was relatively low although the Ar gas was introduced after nearly all the pores were isolated. This could be attributed to the relatively large evaporation loss of the liquid phase during the heating under vacuum before the atmosphere change. In Fig. 8(c), some pores which were not filled with liquid can be seen.

Therefore, the optimum temperature at which the Ar gas should be introduced is thought to be that which combines having no open pores with a modest weight loss. This temperature was 1600 °C as is shown in Fig. 6. In this case, the weight loss was as low as 1.7% and the pores are expected not to have contained any Ar gas because the atmosphere was changed to Ar after the isolation of nearly all the pores. The pore-filling process could have readily occurred and nearly fully-dense TiB_2–Ni bodies could be obtained (Fig. 8(b)).

4. Conclusions

In the sintering of TiB_2–Ni ceramics, the sintering atmosphere greatly affected the densification process. It was shown that a significant loss of the liquid phase or the effect of entrapped Ar gas were the critical reasons for the limited densification in the case of using a fixed atmosphere of either vacuum or Ar. Sintered bodies of near-full density could be obtained by two-step sintering in which the atmosphere was changed from vacuum to Ar during heating but after the isolation of pores.

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