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Preparation of a TiB_2 composite with a nickel matrix by pulse plasma sintering with combustion synthesis

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Abstract

Ti/B/Ni powders were sintered in a pulsed plasma with the participation of the SHS reaction. The material obtained after 10 min of this combined process was a composite that contained TiB_2 and Ni phases. Microscopic examinations have shown that nickel occurs at the boundaries of the TiB_2 grains, where it forms a thin film, and also appears in the form of small agglomerates. The density of the composites is 99.8%, and their hardness is 2500 HV1.

Keywords: Sintering; Composites; Borides; Hardness; Pulse plasma sintering; TiB_2

1. Introduction

The pulse plasma sintering (PPS) method is an attractive method of consolidating powders that are difficult to sinter, such as intermetallic composites and ceramic materials. This method has many advantages, for example in that the process lasts for a short time, the consumed energy is low, and the powder particles are in an activated state.[1–3]

The self-propagation high-temperature synthesis (SHS) yields various compounds in an easy way.[4] Generally, however, the product contains numerous pores, formed by the gases that evolve from the contaminations present in the powder during the SHS reaction.

The present study was concerned with producing a TiB_2 composite from titanium, boron and nickel powders using the PPS technique with participation the SHS reaction. The specific conditions prevailing during the PPS process enable the reaction to be initiated simultaneously in the entire powder volume. The products of the SHS reaction are consolidated and sintered using high-current electric pulses of energy of several kJ delivered during a time of several hundreds microseconds. The composites thus obtained were examined microscopically and their mechanical properties were determined.

2. Materials and methods

2.1. Materials

High purity powders of titanium (ABCR GmbH&Co., 99.7%), amorphous boron (amorphous 96%) and nickel (ABCR GmbH&Co., 99.9%) were manually mixed in a mortar. The composition of the mixture was selected so as to suit the reaction:

$$Ti + 2B + 5\,vol\%\,Ni \rightarrow TiB_2 + 5\,vol\%\,Ni$$

Three grams of the thus prepared mixture were poured directly into a graphite die (with an internal diameter of 11 mm) intended for carrying out the sintering process.

Nickel was chosen to form the metallic matrix because of its relatively low melting temperature (1450 °C), and also with the intention to take advantage of the investigations of Hoke and Meyers[5] who, when examining several metallic

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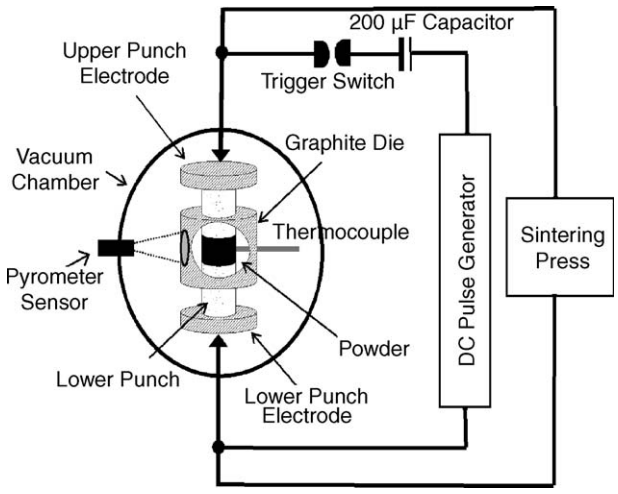

Fig. 1. Schematic representation of the apparatus for pulse plasma sintering.

elements (Cr, Ni, Hf, Mo, Ta) suitable for use as the matrix of TiB_2/metal composites, found that a nickel matrix ensured the highest density. They also found that a 5–10% addition of Ni changes the mechanism of consolidation from breakup of the skeletal structure to some type of easier consolidation mechanism, perhaps via grain boundary sliding.

2.2. Pulse plasma sintering

In the PPS apparatus, the material is placed in a graphite die between two graphite punches. Fig. 1 shows a schematic diagram of the apparatus used for the high-current pulse sintering accompanied by the SHS reaction. The energy source, which delivers the high-current electric pulses that heat up the powder to be sintered, is a capacitor battery (200 μF). An energy source of this kind supplies current pulses, periodically repeated, whose duration is about several hundreds of microseconds and the electric current amplitude is tens of kilo-amperes (Fig. 2).

Thanks to the short duration of the electric pulses (500 μs) compared to the interval between them (1 s) the average temperature (measured) of the sintered material is lower than the instantaneous temperature that is achieved during the current flow periods. Fig. 3 shows schematically the temperature variation during the PPS process.

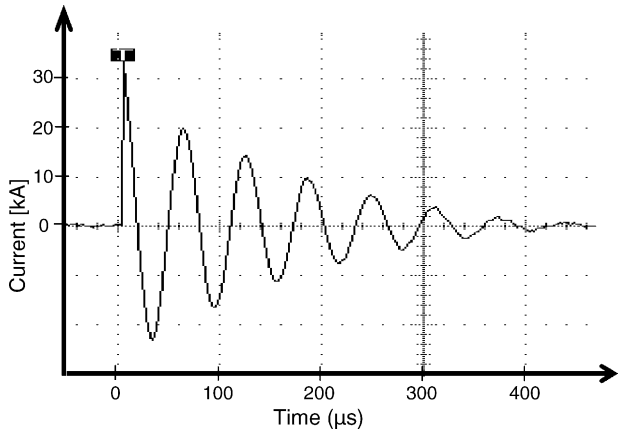

Fig. 2. Oscilloscopic image of waveforms during a capacitor discharge.

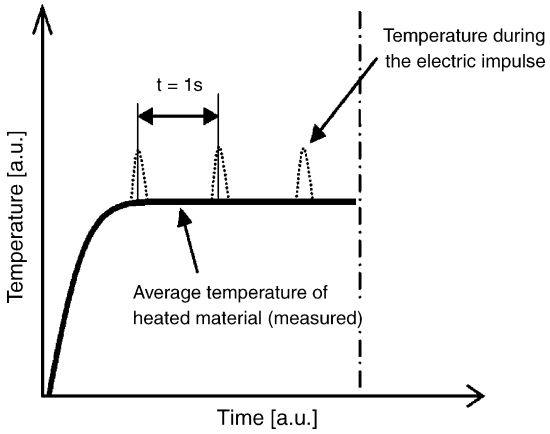

Fig. 3. Variation of the temperature during the pulse plasma sintering process.

During the flow of the high-current electric pulses, the heating proceeds according to the Joule law where the powder particles are in contact, and through spark discharges between the particles where they are separated by pores.[1]

2.3. Experimental

The samples were first heated in a pulsed way at 600 °C for 3 min and then sintered at three different temperatures: 1300, 1250 and 1150 °C, under a load of 60 MPa for 10 min. The electric pulses, dissipating the energy $E = 8.1$ kJ in each cycle were applied at every second during the whole PPS process.

The temperature was measured with an Ahlborn pyrometer, which collected the radiation signal from the die surface. The temperature inside the die, measured with a thermocouple, was higher than that indicated by the pyrometer by about 10%. The heating rate was about 10 °C/s.

The phase composition of the sintered materials was determined with a PHILIPS PW 1140 X-ray diffractometer equipped with a PW 1050 goniometer using Co Kα radiation. The microstructure and the chemical composition were examined in a HITACHI S 3500N scanning electron microscope equipped with a Noran Vantage EDS-Thermo system designed for chemical analyses. The hardness was measured using a ZWICK hardness-meter under a load of 1 kG (HV1) applied for 15 s, whereas the density was measured by the Archimedes method using a Gilbertini E154 balance.

3. Results and discussion

The BSE image (Fig. 4) shows micrograph of the fracture surface of the TiB_2/Ni sinter consolidated by the PPS method. Fig. 5 reveals that nickel occurs on the grain boundaries,

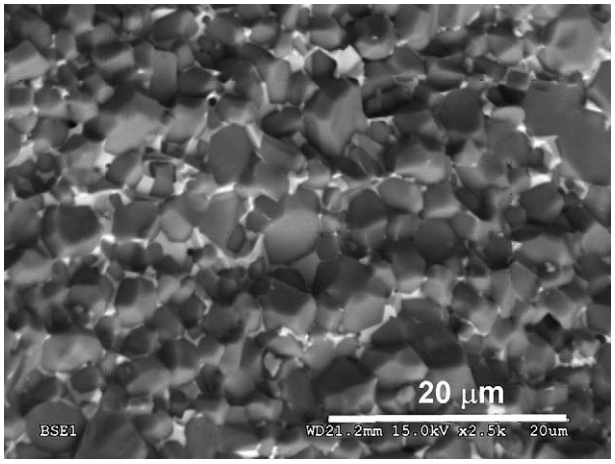

Fig. 4. Backscattered electron micrograph of the fracture surface of the TiB_2/Ni composites.

where it forms a thin film (A) which links the TiB_2 grains, but it is also present in the form of larger agglomerates (B).

The aim of the present study was to use Ti, B and Ni powders for producing a composite that would contain the hard high-melting TiB_2 phase and the matrix of free nickel using the PPS method. The composites produced by reactive sintering may contain additional compounds, such as TiB, Ni_3Ti or Ni_3B.[6] In our experiments with the PPS method, we however succeeded to produce a composite that contains the TiB_2 and Ni phases alone (Fig. 6), with no other phases discoverable by the diffraction method. This is particularly important in view of the exceptional process conditions (e.g., the short process duration, the relatively low temperature, and the high nickel content (ca. 10 wt.%) favourable for the formation of such phases.

The density of the sintered composites slightly decreases with increasing process temperature (Fig. 7). In the sample sintered at the highest temperature, i.e., 1300 °C (on the die surface), the binding phase was observed to flow out and gather on the sample peripheries. At this temperature of the

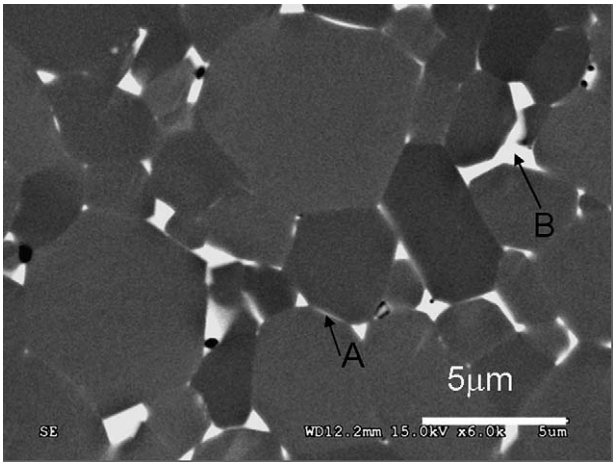

Fig. 5. SEM micrograph of TiB_2/Ni composites.

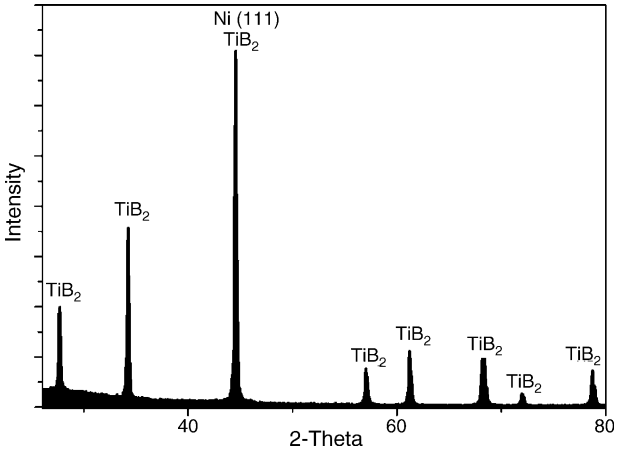

Fig. 6. XRD patterns of the TiB_2/Ni composites.

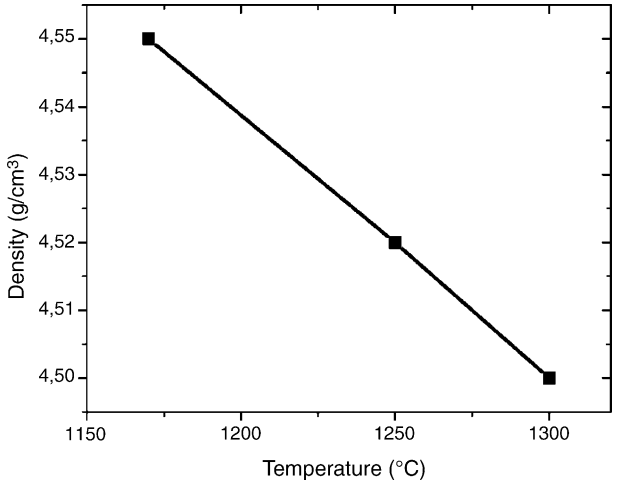

Fig. 7. Density vs. temperature for the PPS TiB_2/Ni composites.

die surface, the temperature within the sample is 1430 °C (10% higher, as mentioned earlier), which is close to the melting point of nickel. Since the content of nickel in the material is high and it becomes molten during the process,

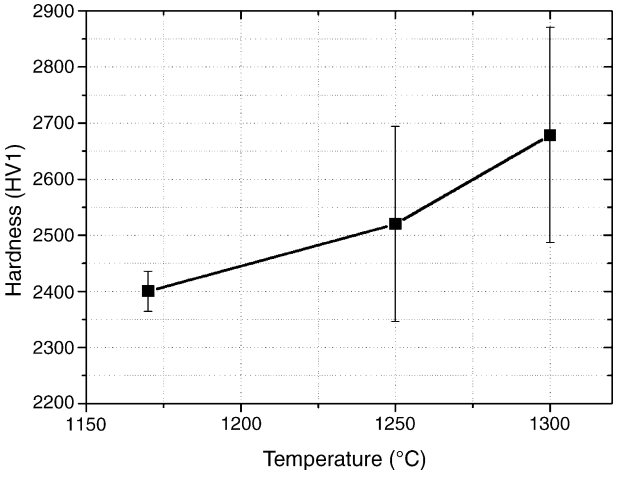

Fig. 8. Hardness vs. temperature for the PPS TiB_2/Ni composites.

the porous product of the SHS reaction is infiltrated by nickel and the nickel excess flows out on the surface of the sample being sintered.

The hardness of the composites increases as the PPS process temperature is increased (Fig. 8), and this is accompanied by an increased deviation of the hardness values from their average value. This effect is due to the loss of the soft nickel matrix material, which at the same time contributes to the decreased homogeneity of the sintered sample.

4. Conclusion

By subjecting titanium, boron and nickel powders to a PPS process with the participation of the SHS reaction, we produced a TiB_2/Ni composite with a density of 99.8% of the theoretical value. Nickel was observed not only to collect in the form of a thin film on the boundaries of the TiB_2 grains, but also to form larger agglomerates. We have proved that by using the PPS process accompanied by the SHS reaction, it is possible to produce a sintered TiB_2/Ni composite at a low temperature of 1150 °C during a short time of 10 min.

Acknowledgements

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