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Microstructure and Hardness of cBN–Zr Composite

E. Benko,[a] J. Morgiel,[b] T. Czeppe[b] and T. Barr[c]

[a]Institute of Metal Cutting, 37A Wrocktouska, 30-011 Kraków, Poland
[b]Institute of Metallurgy and Materials Science, 25 Reymonta St., 32-050 Kraków, Poland
[c]University of Wisconsin—Milwaukee, Materials Department and Laboratory for Surface Studies, Milwaukee, USA

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Abstract

This paper summarizes theoretical and experimental studies of cBN–Zr composites of cBN:Zr molar ratio equal 9:1. From theoretical calculations it follows that Zr reacts with cBN in the full range of pressure ($1{\cdot}3\times10^{-3}$–1×10^{7} *Pa) for temperatures 950 and 1750°C to form at two new phases:* ZrB_2 *and ZrN whose amount depends on the conditions of synthesis. Experimentally, composite based on cubic boron nitride (cBN) with zirconium addition used as a binding material was prepared by high pressure hot pressing. Samples before and after heat treatment were characterized using transmission electron microscope. The TEM showed that after sintering a thin zone of fine* ZrB_2 *and ZrN crystallites was formed at the cBN/Zr interface. After additional heat treatment the ZrN crystallites grew forming a layer up to 2 mm thick built from columnar grains of 0·1–0·2 mm in diameter. The* ZrB_2 *remained as a thin (0·1 to 0·2 μm) layer of very fine equiaxial crystallites between the ZrN and cBN. The hardness of such sintered material was 20 GPa/HK1, after additional heat treatment at 950°C for 1h in vacuum of* 3×10^{-3} *Pa the hardness increased up to 29 GPa/HK1. © 1998 Published by Elsevier Science Limited.*

1 Introduction

Cubic boron nitride (cBN), due to its high hardness and oxidation resistance is widely used in the metal cutting industry especially for the turning of hard steel or for different operations requiring extra high accuracy. The fabrication of these tools is achieved by sintering the BN powder with metals of the IV to VI groups of the periodic table and later by binding of the layer of such composite on to a particular working surface.[1,2] The practice proved, that of all binders used to the present, one of the toughest BN/metal composites is obtained with zirconium additions.[3–12] Chemical reactions between Zr and cBN occur resulting in the formation of some new phases. But, the location of, and the defect structure of these phases, so essential in understanding mechanical properties aspects of the material, remained unknown.

Thus, the main goal of this paper is to elucidate the nature of the interactions between Zr and cBN. In particular the results of phase equilibria calculations for Zr–B–N system are presented for a wide range of pressures and for temperatures 950 and 1750°C.

In the present study the results of investigation of the microstructure of BN sintered with Zr composite by transmission electron microscopy are presented. The influence of that microstructure on the mechanical properties of the material is also discussed.

2 Calculations of Phase Equilibrium for the 9BN–1Zr System

The calculations of phase equilibria for the BN-Zr system were carried out using the VCS (Villars, Cruise, Smith) algorithm[13] i.e. an algorithm belonging to so-called stoichiometric algorithms.

In this procedure, the Gibbs energy of the whole reaction mixture is minimized subject to side conditions of elemental abundance and not-reactivity of the mole numbers. Reaction–extent variables derived from the transformation of the mass balance equations are the unknowns of the function being minimized.

Thus, the problem can be reduced to the minimization of the unrestricted function and in each iteration the mass–balance equations are fulfilled. The details of the procedure can be found elsewhere.[13] In the calculation of chemical equilibria of the system investigated and related ones it is not known *a priori* which phases and components will appear in the equilibrium state (for given Tp and initial feed composition). The advantage of the VCS algorithm relies on the fact that only species which may, but do not need to appear at equilibrium must be specified. Therefore, the program written on the basis of the VCS algorithm requires only the knowledge of the species which can occur at equilibrium together with their standard Gibbs energies of formation. In addition, the calculations require the knowledge of the exact number of moles of elements introduced to the system and the values of p and T as well as the initial estimate. It should be noted here that the user of the program does not need to specify the number and form of independent reactions possibly occurring in the system under consideration. The VCS algorithm is one of the most powerful tools for the calculation of chemical equilibria, especially for systems with a large number of condensed phases.

The calculations were performed for the temperature 950°C and 1750°C, for the pressure $1{\cdot}3\times10^{-3}$–1×10^{7} Pa and for samples 9:1 BN :Zr molar ratio. It was assumed that the following species can be present in the equilibrium state: B(g), B_2(g), N_2(g), BN(g), Zr(g), H_2(g), ZrB_2(s), ZrN(s), B(l), Zr(l), ZrN(l), ZrB_2(l), Zr(s), Zr(s), cBN(s), hBN(s), B(s) (g, l and s denote gas, liquid and solid respectively). Thermodynamic data necessary for calculation were taken from Ref. 14. The complete list of results of the calculations can be obtained from the author.

According to the calculations of chemical equilibria in the system cBN–Zr at temperatures 950°C and 1750°C for the pressure range of $1{\cdot}3\times10^{-3}$–1×10^{7} Pa, Zr can react with boron nitride in very wide range of pressure.

Two new phases are formed namely titanium boride (ZrB_2) and titanium nitride (ZrN), whose content is strictly dependent on the parameters of the process (Tp). In 950°C at pressure $1{\cdot}3\times10^{-3}$ Pa ZrB_2 is the only solid phase present in equilibrium state. In 1750°C the pressure range in which only this solid phase is stable decreases to 3×10^{3} Pa. Gaseous N_2 appears in 950°C at low pressure. In 1750°C at low pressure in equilibrium state coexist gaseous N_2, B, BN.

3 Experimental Procedure

Cubic boron nitride (ABN-300, De Beers, 3–5 mm grain size) and zirconium (HC Starck, 3–5 mm grain size) were mechanically mixed in ethyl alcohol and then pressed into pellets of f = 6 mm under a pressure of $10\times^{7}$ Pa at a temperature of 1750°C for 3 min. The molar ratio of cBN:Zr around 9:1 was kept constant. Then the sintered material was thermally treated at 950°C for 1 h in vacuum 3×10^{-3} Pa.

4 Microstructure of cBN-Zr Composites

Thin foils for transmission electron microscopy were prepared by mechanical dimpling and final ion milling under 5 kV/1 mA. Microstructural observations and chemical microanalysis were performed in a Philips CM 20 TWIN (200 kV) transmission electron microscope equipped with a Link Ex11 X-ray energy dispersive spectroscopy (EPX)-system. The X-ray spectra utilized a lithium drifted silicon detector covered with a ultra thin window (UTW) enabling the analysis of light elements except the boron.

5 Determination of Hardness

Hardness tests are commonly used for the study of plasticity as well as cracking phenomena in extra hard materials. Various tests have been devised for material hardness determination.

Most of them are based on the following formula:[14,15]

$$H_V = 0{\cdot}189F/d^2 = \text{const}$$

where F—loading; d—diameter or diagonal of indentation.

In extra hard materials testing, the shape of indenter significantly influences the measured hardness i.e. measured values strongly depend on this shape.[16] It was found that in the case of such materials the Diamond Pyramid Hardness testers (Vicker's, Knoop's and Berkowicz's type) should be used. On the other hand the results are not the same when indenters of different shape are used even with the same indentation load. This may occur because different energy is needed for material deformation around the indentation when various indenter are used. This deformation is much greater in case of pyramids i.e. Vicker's or Berkowicz's than with Knoop's indenter.[17] It was stated also that the greater material deformation around the indentation is related to the higher hardness.

In extra hard materials tests the indenter which gives the minimum deformation around indentation is required. Furthermore, the indentation diameter should be much greater than grain size in the investigated material. The Knoop's indenter fulfils the above requirements and also has a longer life as compared with the other types. Before hardness measurements the samples were polished with a diamond paste with diminishing granulation until

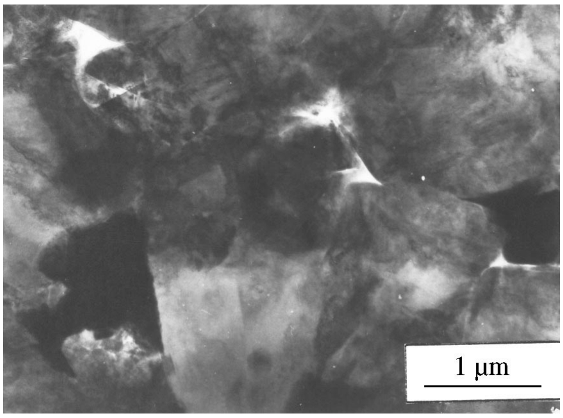

Fig. 1. Boron nitride grains sintered with zirconium.

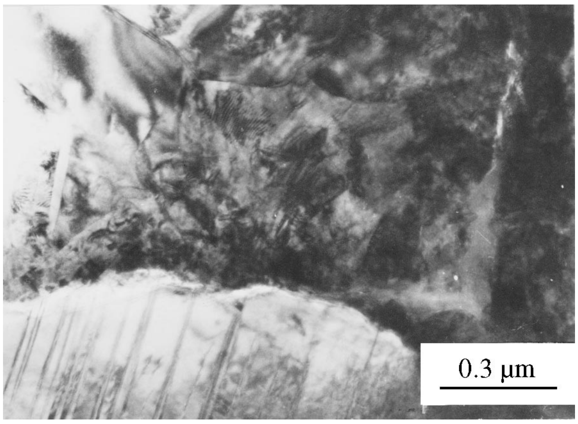

Fig. 3. Polycrystalline zirconium rich island within BN matrix with borides and nitrides formed after additional heat treatment at 950°C for 1hr.

11—12 class of surface quality was obtained. The polishing was performed by means of Struers automatic grinding–polishing machine. In the hardness measurements by Knoop's method the indentation load of 9·81 N was used.

6 Results

The observations of the thin foils of the investigated composites just after sintering showed that the material was built of cBN grains of 3 mm mean size (Fig. 1). They seem to fit well even though voids of up to 0·5 mm at the grains triple points were frequent. Some of these voids are sources of web of cracks along the cBN grain boundaries as seen in the central part of Fig. 1. Zirconium added as binding material was broken in to small jagged grains and oriented in 2.2 mm clumps a few microns apart. It shows only limited penetration of this composite visible as singular short tapered whiskers extending from metallic islands in and between the cBN grains. The higher magnifications showed that the external Zr grains were covered by very small randomly oriented crystallites [Fig. 2(a)]. The selected area diffraction from such area taken with the smallest aperture (*f*–10 μm, demagnification four times) gave patterns with diffractions spots arranged in broken rings [Fig. 2(b)]. The splitting of the second ring as marked with arrows definitely indicate the presence of not only ZrN, but also ZrB_2 can not be excluded. The EDX analysis of the local composition in the thinnest parts of the fine crystalline areas confirmed the presence of zirconium but not of nitrogen.

Unfortunately boron was out of range of the EDX detector/window installed on the microscope used in this investigation. Both ZrN and ZrB_2 were therefore possibly present after sintering.

The additional heat treatment at 950°C for 1 h changed only the structure of the Zr rich clumps (Fig. 3). Their central parts was built of zirconium, as was confirmed by EDS the selected area diffraction pattern [Fig. 4(b)], but with enlarged and frequently twinned grains [Fig. 4(a)]. These zirconium cores were fringed by columnar grains; f = 0·01–0·02 mm [Fig. 5(a)], which were identified through electron diffraction as that of ZrN [Fig. 5(b)]. The last layer at the interface with cBN grains was again formed of very small randomly

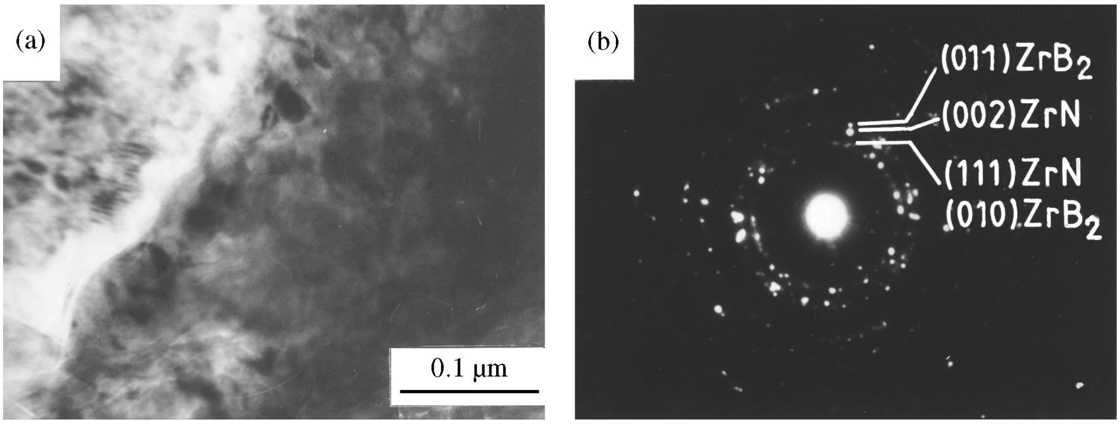

Fig. 2. (a) Polycrystalline zirconium islands within cBN matrix with ZrB_2 layer and (b) accompanying electron diffraction pattern from ZrB_2.

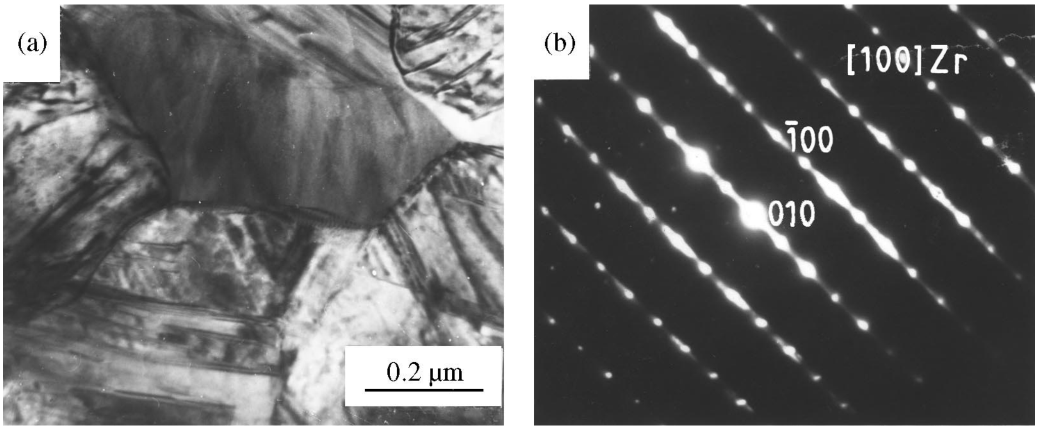

Fig. 4. (a) Zirconium grains from central part of zirconium rich islands and (b) accompanying electron diffraction pattern.

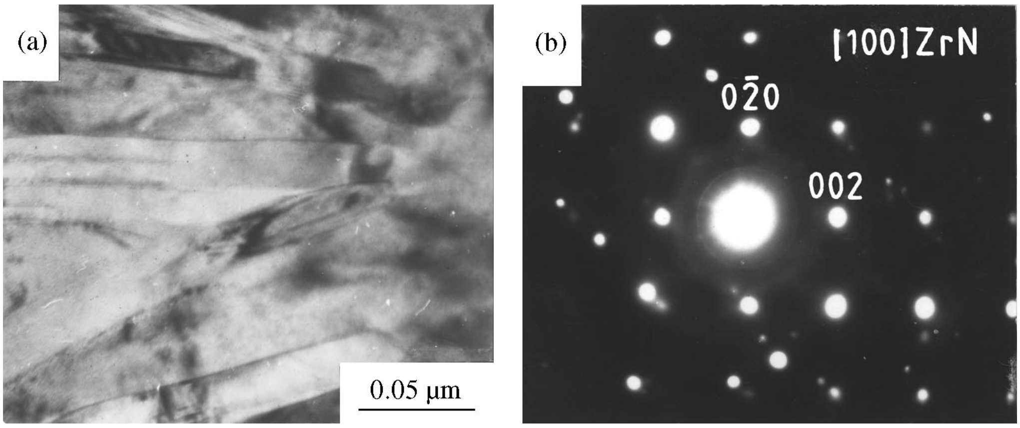

Fig. 5. (a) Columnar ZrN grains in a layer next to zirconium grains and (b) accompanying electron diffraction pattern.

oriented crystallites [Fig. 6(a)]. The electron diffraction patterns from that area gave broken ring patterns similar to ZrB_2 as in the material before additional heat treatment [compare Fig. 2(b) and 6(b)]. The detailed examination of ZrB_2/cBN interface showed that both phases were usually separated from each other by a several nanometer trench formed either by thermally induced stresses or by growth voids (Fig. 7). The slightly more rounded edges at the cBN side, than at the ZrB_2 indicate that at least its nucleation was of diffusional character. The microanalysis showed that each of the above zone contained Zr but nitrogen was found only within the columnar grains.

The hardness measurements performed on the investigated material are presented in Table 1. They indicate, that the very high starting hardness of about 20 GPa/HK1 of cBN sintered with Zr can be further increased up to 29 GPa/HK1 by further high temperature treatment.

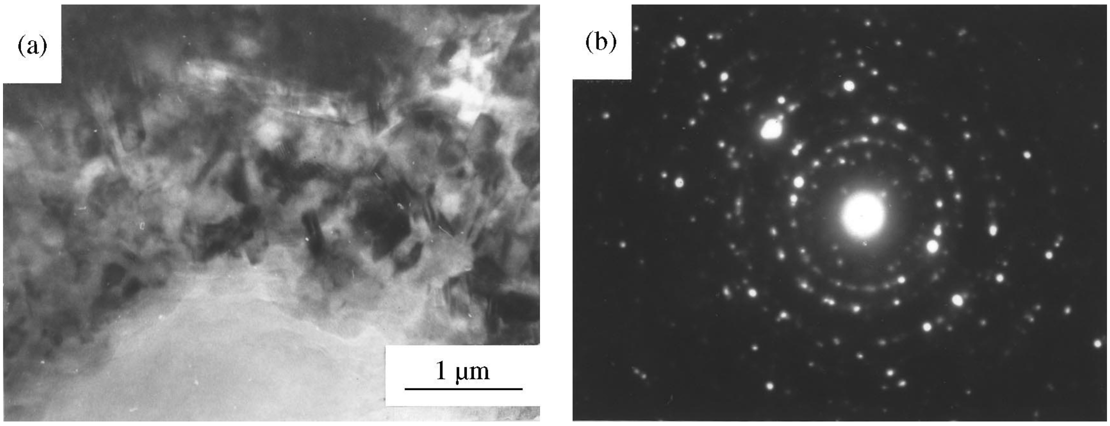

Fig. 6. (a) Equiaxed ZrB_2 crystallites zone between ZrN and BN and (b) accompanying electron diffraction pattern.

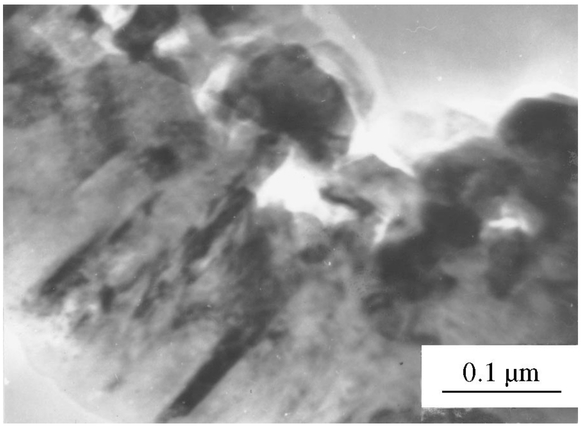

Fig. 7. Voids at the ZrB_2/BN interface.

7 Conclusions

The performed investigations confirmed formation of both ZrB_2 and ZrN within the cBN/Zr sintered composite as predicted by thermodynamic calculations by VCS algorithm.Both ZrB_2 and ZrN were found to be present just after sintering. After additional heat treatment their layers or zones in reference to the location of cBN grains were identified in the sequence; cBN/ZrB_2/ZrN/Zr. As the volume of zirconium is replaced during post-sintering heat treatment by the borides and nitrides, the hardness of the cBN/Zr composite increases. The formation of voids at the ZrB_2/cBN interface with at least partial diffusional character indicates that only the optimization of both of these tendencies might give better material for practical applications.

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