

Sintering of boron carbide under high pressures and temperatures

S K Singhal & B P Singh*

Division of Engineering Materials, National Physical Laboratory
Dr K S Krishnan Road, New Delhi 110 012, India

Received 10 January 2005; accepted 25 January 2006

Sintered compacts of boron carbide were prepared by subjecting fine powder of boron carbide to high pressures and temperatures (5-6 GPa, 1000-1500°C) in the presence of a suitable binding material, namely TiC (5wt.%) or Co (5wt.%). The composites prepared by this method showed a microhardness of about 2800 kg/mm², which is very close to the microhardness of pure boron carbide. The compacts were characterized using scanning electron microscopy, and X-ray diffraction techniques. SEM study showed that the grains of boron carbide were uniformly distributed throughout the binding material and no grain growth was observed in the composites. Although composites of diameter 6.0 mm and 2-3 mm thickness are synthesized in this method, the process can be up-scaled for producing large size (12 mm diameter) composites required in various cutting tools and other applications.

IPC Code: C04B 35/563

Boron carbide (B₄C) is a superhard abrasive material with a microhardness of about 3000 kg/mm² which is next only to diamond (9000 kg/mm²) and cubic boron nitride (4400 kg/mm²). Its hot hardness is even better than diamond and cubic boron nitride. Because of high hardness it is extensively used as a lapping agent in place of diamond. It is also used for polishing high speed steel and carbide tip tools although its reaction with many metals under high-temperature conditions prohibits its use as a die material for wire drawing. It is reported that the development of hard metal cutting tools and high speed steels could not have been possible without the availability of boron carbide as a grinding medium. Boron carbide is brittle and not especially impact resistant. It is, therefore, often used after shrink finishing parts into metal sleeves to maintain forces on the parts. Apart from machining operations sintered B₄C finds wide applications as sand blasting nozzles and hard ceramic bearings. In aerospace industry boron carbide due to its capability to generate tremendous amount of heat (12400 kcal/kg) in combination with oxygen is finding use as a rocket propellant. In nuclear industry it is well accepted as a control and shielding material for neutrons due to its favourable absorption characteristics. The presence of strong directed covalent bonds in the compound lattice determines its physico-mechanical properties and extraordinary

chemical stability. Commercially, it is produced by reacting and fusing boric oxide and carbon in an electric arc furnace. However, not much information is available for producing the dense polycrystalline sintered boron carbide because of the proprietary nature of this material. One method of making the dense polycrystalline boron carbide is by hot pressing (including hot isostatic pressing)¹. In some cases densification is conducted by hot pressing (1900-2200°C at 0.02-0.04 GPa for 15-45 min) in graphite dies under vacuum or argon atmosphere. To prevent reaction with the mold, which can result in damaged parts and dies, a BN coating is used on the inner mold surfaces. However, this process is expensive and limited to providing simple shapes. B₄C can also be sintered to about 93% of theoretical density by combining fine powder of boron carbide with the addition of small amount of carbon. In this case powders of extremely small particle size are required to obtain high density. Sintering can be done in induction or resistance heating furnaces in an inert atmosphere. Sintering aids, e.g., SiC have been found to enhance sintered densities. However, hot pressing limits the size and complexity of shapes, which can be produced, and to shape these diamonds grinding is used. In this method the pressure-less sintering is normally achieved by sintering the material at about 2000-2500°C either directly or with the aid of some suitable binders selected from the carbides of group IV-VI (Ti, V, W, Cr)²⁻¹⁷, but in most of cases the

*For correspondence (E-mail: bpsingh@mail.nplindia.ernet.in)

relative densities of the as-sintered materials do not exceed 93% of theoretical density (2.51 g/cm^3). It is well known that the use of high-pressure powders of hard materials (diamond, cubic boron nitride and silicon nitride) can be effectively and efficiently sintered into a large size hard and tough mass at relatively lower temperatures either directly or with the use of suitable binders. The binding materials generally used in case of diamond or cBN are the carbides, nitride and silicides of Ti, V, W and Cr. All these binding materials have a high hardness, melting temperature, and thermal conductivity and impart almost the desired properties in the sintered compacts as required in cutting tools and other applications. Usually, a small amount of some metals such as Al, Co and Ni is added to these binders in order to impart sufficient toughness in the composites. Therefore, we have undertaken this work of producing the sintered composites of B_4C under high pressure and temperature with the aid of titanium carbide and cobalt as the binding materials.

Experimental Procedure

The high pressure sintering of boron carbide samples was carried out in a 200-ton cubic press of H.Tracy Hall's design. This press is capable of generating pressures up to about 6 GPa in a pyrophyllite cubic capsule of 16 mm edge. A schematic diagram of the cube in a 200-ton cubic press is shown in Fig. 1. A through-hole of 8 mm was drilled in the pyrophyllite cube to contain the experimental materials. The sample was heated indirectly by passing a heavy current drawn from a low-voltage a.c. source through a graphite sleeve surrounding the sample. A high-current step-down transformer provided the low-voltage a.c. source. The pressure calibration was carried out using standard fixed points of phase transitions of Bi (I-II) at 2.54

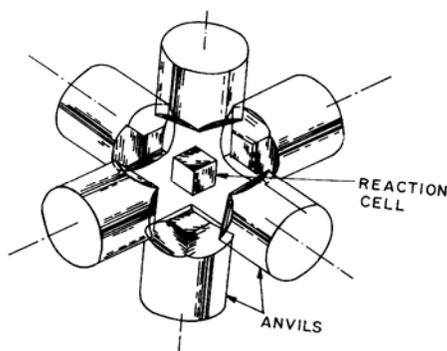
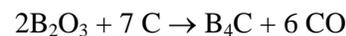


Fig. 1—Schematic diagram of the cube in a 200 ton cubic press.

GPa, Yb (fcc-bcc) at 3.9 GPa and Ba (I-II) at 5.5 GPa. The temperature was calibrated in terms of electric power input in watts using a Pt-Pt/Rh10 % thermocouple placed at the center of the reaction cell. Commercially available B_4C powder (5-10 μm , NRD corporation, Japan) was homogeneously mixed with either 5 wt.% of TiC powder (2-5 μm , NRD corporation, Japan) or 5 wt.% of Co powder (< 2 μm , Aldrich Chemical Company, USA). The mixture was facilitated by the addition of a small quantity of methanol, which was later removed by heating the powder to 200°C . The powder mixture was pressed into a disc of 6 mm in a carver press using a steel die and punch at a pressure of about 0.3 GPa and packed in a reaction cell as shown in Fig. 2.

It has been found that generally a thin layer of boric oxide is formed on the surface of boron carbide fine powder, which limits its densification. Therefore, it is necessary to suppress the detrimental role of boric oxide, which could be done⁷ either by heating it at temperatures higher than 1300°C in presence of amorphous carbon so that any small amount of boric oxide can be eliminated as indicated in the following reaction:



There are a number of ways of introducing carbon into boron carbide powders. One method uses the pyrolysis of phenol formaldehyde resin at temperatures higher than 600°C which on decomposition gives amorphous carbon and removes B_2O_3 as indicated in the abovementioned reaction. In the other method MC type carbides was added to the reaction charge (M denotes a transition metal of groups IV-VI).

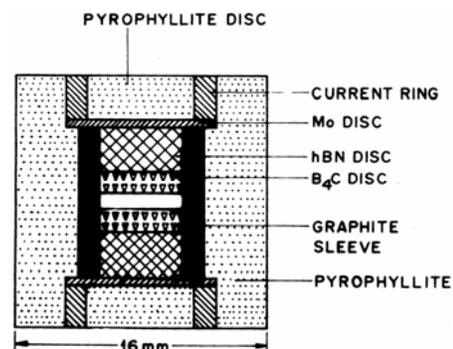
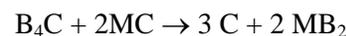


Fig.2—Reaction cell assembly used to sinter boron carbide.

From the experimental results as observed by XRD analysis it appears that this is a temperature dependent reaction and the minimum temperature required is about 1000°C or higher. This was confirmed by the very low peak intensity of carbon as observed in the B₄C compacts sintered at 5.5 GPa and 1000°C. The peak intensity of carbon was relatively high as observed in the B₄C composites sintered at 5.5 GPa and 1300°C. The X-ray diffraction pattern of the starting boron carbide powder used in the present study is shown in Fig. 3. It can be seen from this XRD pattern that most of the peaks corresponding to B₄C are present. Two series of experiments on high pressure sintering of boron carbide were carried out. In the first series titanium carbide was used as the main binding material and in the second series of experiments cobalt powder was used as the binder. B₄C composites synthesized with the use of TiC are labelled as Type A and those sintered using cobalt binder are labelled as Type B. Different weight ratios of the binders (5-10 wt.%) was used in the compaction of B₄C. In both cases it was found that optimum value of hardness is obtained if B₄C and TiC/Co was used in a ratio of 95 : 5 wt.%. In the following the results of characterization of these compacts using X-ray diffraction technique, scanning electron microscopy, microhardness measurement are described.

Results and Discussion

X-ray characterization

Figs 4a and 4b show typical X-ray diffraction patterns of the sample of Type A synthesized at 5.5 GPa and temperatures of 1000°C and 1300°C respectively using TiC as the binding material. It can

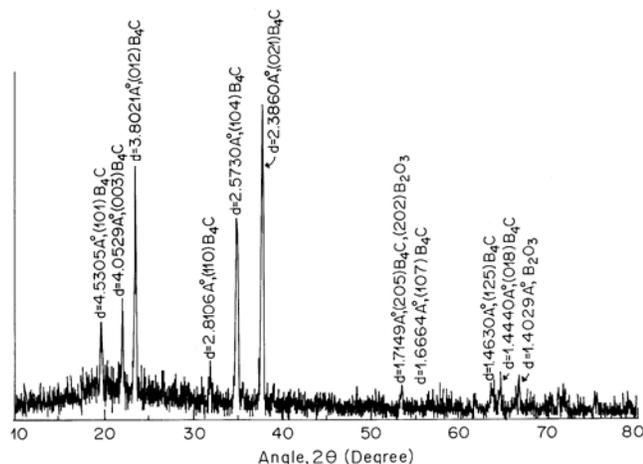
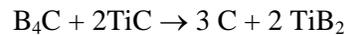


Fig. 3—X-ray diffraction pattern of pure boron carbide powder.

be seen that the observed XRD patterns demonstrate the presence of B₄C and TiC crystalline phases. However, a closer look at the XRD pattern suggests that in the B₄C compacts synthesized at higher temperatures (1300°C, Fig. 4b) a minor phase of TiB₂ is also formed as a result of solid state reaction during high pressure - high temperature sintering. This minor phase (TiB₂) is not present in B₄C compacts synthesized at lower temperatures (1000°C, Fig. 4a). In the case of composite synthesized at 1300°C presence of some peaks of C_g (002) and (101) were observed with 'd' values of 3.362 and 2.039 Å respectively presumably due to the reaction of the sample and graphite heater used to heat the specimen at higher temperatures. The formation of TiB₂ at higher temperatures could be understood on the basis of following chemical reaction:



Formation of TiB₂ in B₄C composites is not deleterious in its mechanical properties. Its presence is expected to improve the mechanical properties as it is also used as the binding material in the compaction of hard ceramics.

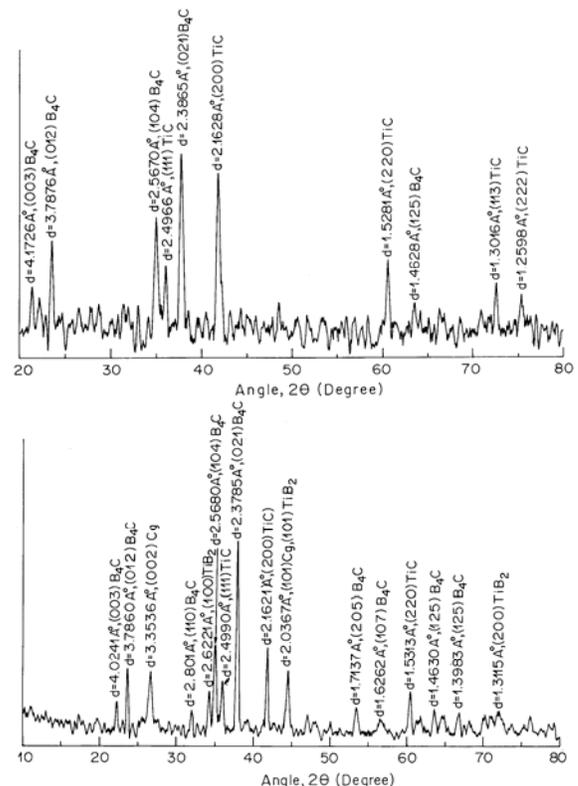


Fig. 4—XRD pattern of a B₄C composite sintered at 5.5 GPa using TiC as the binding material (a) 1000°C and (b) 1300°C

Fig. 5 depicts typical X-ray diffractogram of B₄C composite of Type B synthesized at: (a) 5.5 GPa, 1000°C; (b) 5.5 GPa, 1200°C using cobalt as the binding material. In this case also the major crystalline phases present correspond to that of the starting mixture namely B₄C and cobalt carbides such as Co₃C and Co₂C which were formed during the high pressure-high temperature sintering reaction. Formation of carbides of cobalt also improves the toughness of synthesized B₄C composites.

Microstructure evaluation

Fig. 6a shows a typical SEM micrograph of B₄C compact of Type A recorded in secondary electron emission mode with 0° tilt using 5% TiC as the binding material and sintered at 5.5 GPa, 1300°C. The black contrast represents B₄C grains and the white contrast represents the binder (TiC). It can be seen that the binder grains are uniformly distributed within the B₄C matrix lying within the interspaces of B₄C grains, which facilitate the binding of B₄C grains. No appreciable grain growth was observed in these compacts as revealed from the recorded SEM

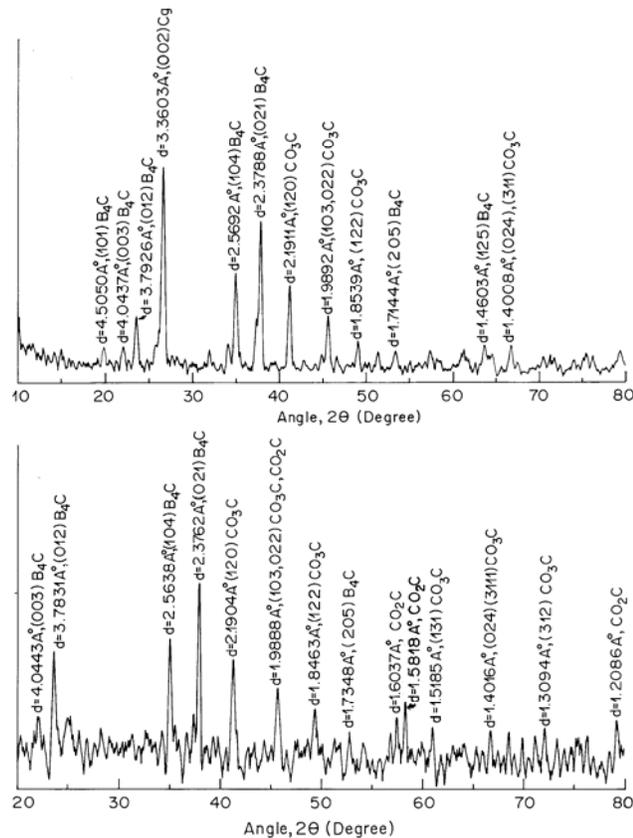


Fig. 5—XRD pattern of a B₄C composite sintered at 5.5 GPa using Co as the binding material (a) 1000°C and (b) 1200°C

micrographs. No major cracks or micro-pores were observed in the investigated composites. However, some micro cracks were observed occasionally in few specimens. Similar features were also observed for Type B B₄C compacts which were synthesized using cobalt as the binder as can be seen in the SEM micrograph shown in Fig. 6b and sintered at 5.5 GPa, 1200°C.

Microhardness measurements and sintering mechanism

The Knoop microhardness of the sintered B₄C compacts was measured under a load of 500 g on a Zwick 3212 microhardness tester. Prior to such hardness measurements the B₄C samples were lapped and polished by fine diamond paste to obtain a mirror-like finish on the surface so that the indentation could be measured accurately.

Microhardness measurements on B₄C compacts of Type A and B showed a point to point variation of

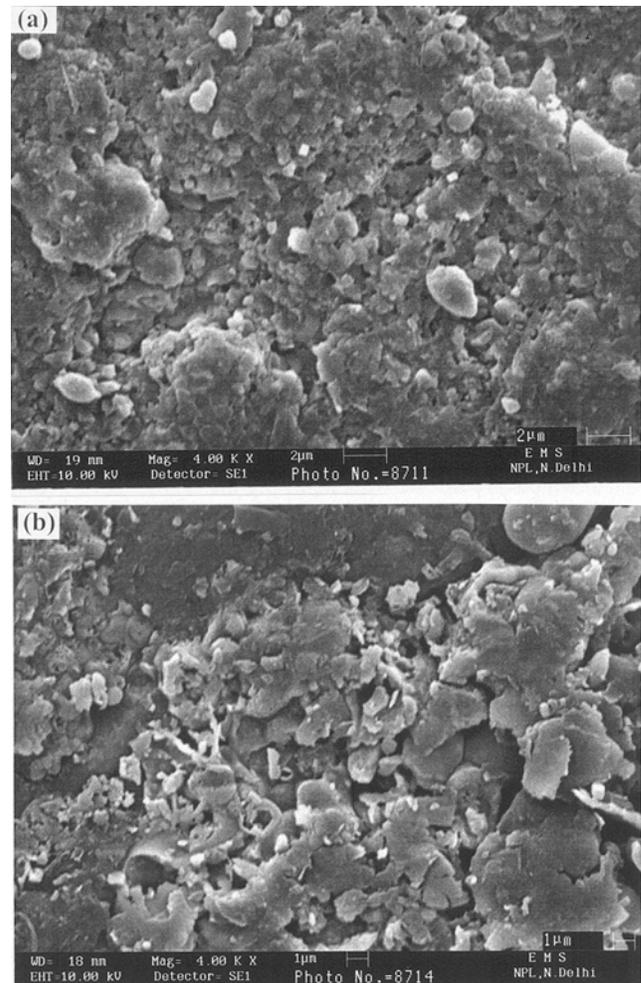


Fig. 6—SEM micrograph of a B₄C compact sintered at 5.5 GPa (a) using TiC, 1300°C and (b) using Co, 1200°C

Knoop hardness on the specimens surface, although the variation was not large. The samples synthesized at lower temperatures (1000°C) were found to be relatively soft in their hardness values (1100-1400 kg/mm²) as compared to those sintered at higher temperatures (1200-1300°C). The best B₄C compacts of both the types showed a Knoop hardness value of around 2800 kg/mm² which is quite close to the hardness of pure boron carbide (3000 kg/mm²). In order to further assess the extent of sintering achieved in B₄C composites synthesized by using TiC and Co as the binders under high P-T conditions density measurements were carried out on these specimens. Table 1 shows the results of these measurements. This table includes the density of same specimens whose microhardness values are reported here. It is observed that in case of Type A specimens synthesized with 5% TiC binder at 5.5 GPa and 1300°C about 99 % densification (density = 2.57 g/cc) was achieved with a microhardness value of about 2800 kg/mm². As expected there exists a good co-relationship between the degree of compaction and microhardness. In case of specimens synthesized at lower temperatures the measured density values were found to be lower (2.49 g/cc) resulting in samples with less densification of B₄C powders. This result is corroborated with the observation of lower values of microhardness (about 1400 kg/mm²). Similar observations were observed in case of B₄C composites of Type B with 5% Co as the binding material with a maximum microhardness value of about 2500 kg/mm² at 5.5 GPa and 1200°C.

A co-relationship between the microstructure and the hardness values was observed in synthesized B₄C composites. Lower values of microhardness were related to the segregation of binders leading to localized clustering. The small variation of microhardness on the specimen surface of well-synthesized compacts is apparently related to microstructural fluctuations.

The sintering mechanism of B₄C composites is more or less similar to that observed for other super

hard materials namely diamond or cubic boron nitride. By sintering one means bonding together a mass of small particles into a large, coherent piece. During this process the contact patches between particles grow and the total volume of the mass shrinks leading to a sufficiently dense and strong mass even though some voids may remain. Sintering of pure B₄C is extremely difficult. Due to the high fraction of covalent bonding (>90 %) pore eliminating mass transport mechanisms such as grain boundary and volume diffusion become effective at temperatures of the order of 2000°C. Generally for pure materials the sintering temperature is about 60-70 % that of the melting temperature. As the melting temperature of B₄C is about 2450°C, a suitable sintering temperature will be about 1600°C or higher. Therefore, in case of pressure-less sintering a temperature of the order of about 2000-2300°C is required and in case of hot pressing a sintering temperature of about 1900-2000°C is required at a pressure of about 0.02 - 0.04 GPa under vacuum or Ar atmosphere. Vacuum or inert atmosphere is necessary as above 500-600°C it starts converting from diamond structure into the graphite structure. Application of high pressure and temperature help in densification and composite formation by particle rearrangement followed by considerable plastic deformation. However, as in case of diamond or cubic boron nitride the sintering of pure B₄C is very difficult because of its high microhardness (3000 kg/mm²). If the sintering is performed directly without using any binding material, then the pressure gradient inside the vessel is expected to be very high. The pressure at the points where B₄C grains are in direct contact with each other is believed to be very high and in other places (most places) the local pressure is that of the voids. Thus, because of the presence of these voids the microhardness of the resultant B₄C is expected to be low unless the synthesis pressure is very high (> 10 GPa). Therefore, the practical problem to this solution is to use some binders as the sintering aids which not only make it possible to sinter at lower pressures but also promote densification and bonding at temperatures much lower than those required in pressure less or hot press sintering of B₄C powder. Further, the presence of small quantity of sintering aids not only help in filling the voids between B₄C grains but also form a strong bond with B₄C particles thereby resulting in a hard, tough and wear resistance composite. Also presence of small quantity of binder in B₄C compact takes care of the sudden shock

Table 1—The values of density of specimens

B ₄ C Composite	Theoretical density	Practical density	% Diff.	Degree of compaction
<i>Type A</i> (using 5 % TiC)				
P = 5.5 GPa, T = 1000°C	2.59	2.49	3.8	96.2
P = 5.5 GPa, T = 1300°C	2.59	2.57	0.77	99.2
<i>Type B</i> (using 5 % Co)				
P = 5.5 GPa, T = 1000°C	2.82	2.77	5	95
P = 5.5 GPa, T = 1200°C	2.82	2.79	1.06	98.9

produced at the tool tip when it comes in contact with the work piece during the machining conditions, thereby increasing the life of B₄C tool.

Conclusions

Although the composites of boron carbide are obtained using hot isostatic pressings, the high pressure sintering is also very effective for producing these composites as in case of diamond and cubic boron nitride. Moreover, the microhardness of the composites produced using high pressure sintering is very close to the microhardness of pure boron carbide and the process, therefore, can be used for producing composites upto about 12 mm diameter required in various applications. These sizes of composites are generally used for making various cutting tools.

Acknowledgements

The authors are grateful to the Director, National Physical Laboratory, New Delhi, for his encouragement. Sincere thanks are due to Mr K N Sood and Dr R P Pant and Dr Rajeev Chopra for assistance in recording the SEM micrographs, XRD

patterns and microhardness of the B₄C composites reported in this study.

References

- 1 Johnson W C, *Am Ceram Soc Bull*, (1999) 71.
- 2 Sigl L S, *Euro Ceram Soc*, 18 (1998) 1521.
- 3 Radev D D and Zakhariyev Z, *J Solid State Chem*, 137 (1998) 1.
- 4 Skorokhod V, Vlajic M D & Krstic V D, *Adv Mater Process*, 282 (1998) 219.
- 5 Radev D D, *Metallurgica*, 51 (1997) 630.
- 6 Tuffe S, Dubois J, Fantozzi G & Barbier G, *Int J Ref Metals & Hard Mater*, 14 (1996) 305.
- 7 Johnson W C, *Advanced materials & powders handbook*, 1999, 71-73.
- 8 Skorokhod V & Krstic V D, *J Mater Sci Letts*, 19 (2000) 237.
- 9 Halverson D C, Pyzik A J, Aksay I A & Snowden W E, *J Am Cer Soc* 72 (1989) 775.
- 10 Radev D D, *J Alloy Compd*, 196 (1993) 93.
- 11 Radev D D, *J Alloy Compd*, 197 (1993) 87.
- 12 Zakhariyev Z, *J Mater Sci Lett*, 7 (1988) 695.
- 13 Sigl L S, *J Am Ceram Soc*, 78 (1995) 2374.
- 14 Itoh H, *J Mater Sci*, 24 (1989) 420.
- 15 Piquero T, *Carbon*, 33 (1995) 455.
- 16 Viala J C, *J Mater Sci*, 28 (1993) 5301.
- 17 Viala J C, *Mater Res Bull*, 25 (1990) 457.