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Directional crystallization of B_4C–NbB_2 and B_4C–MoB_2 eutectic compositions

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Abstract

We studied the directional crystallization of different compositions in B_4C–NbB_2 and B_4C–MoB_2 systems. The eutectic compositions for both systems are evaluated. It is shown that in the first system the rod-like eutectic structure is formed, in second, the ''Chinese hieroglyphics''. In both cases high hardness and high microplasticity are observed, which are much more than for individual component phases. These compositions may be considered as a new kind of self-strengthening composite materials.

Keywords: B_4C–NbB_2 system; B_4C–MoB_2 system; Eutectic composition; Real structure; Directionally crystallization; Microhardness

1. Introduction

Recently it was shown that it was possible to obtain self-strengthened (natural) ceramic–ceramic composites ''in-situ'' during directional co-crystallization of different refractory compounds—oxides, carbides, borides and, silicides. The special interest presents mixtures having eutectic composition, as in this case it is possible to create sufficiently uniform and perfect real structure, which in turn provides high mechanical properties of materials.

The typical examples of this kind of composites are materials consisting of rare-earth hexaborides and *d*-transition metal diborides. The regular structure is formed by hexaboride single crystal matrix and diboride single crystal whiskers uniformly distributed in this matrix [1–3]. In these composites diboride phase with hexagonal crystal structure in most cases forms elongated along *c*-axis very uniform needle-like single crystals, which reinforce the main phase.

One of interesting substances related to the group of nonmetallic refractory compounds is boron carbide B_4C. This compound presents interest both from the fundamental point of view due its unusual crystal structure and some its physical properties, and due its successful application in different technical fields, particularly due its hardness and neutron adsorption ability. But in some cases its application in individual form is limited by very high brittleness, and then the question of creating new compositions with its participation is very important.

It is known that some B_4C–MeB_2 constitutional diagrams have eutectic character with negligibly small mutual solubility [4–5]. This permits one to suppose the possibility of obtaining in such systems stability in wide temperature range real structure and, consequently, its stability during exploitation. It supposes also the possibility to use directional crystallization to obtain composite in such systems.

A fine grain structure with plates or needles of diboride phase oriented along crystallization direction was obtained by zone melting of alloys of eutectic composition in B_4C–ZrB_2 system [6]. In the B_4C–TiB_2 system by direction crystallization also rod-like diboride grains are formed [7].

It has been shown that by spontaneous crystal growth the V B group metal diborides grow in random crystallography direction and VI B group diboride grows mostly in the [001] direction [8]. But by the co-crystallization of two-phase composites it is not always realized and the crystallography correlation of both phases is determined also by several other reasons, as heat flow direction, crystal structures of both phases correlation, the volume ratio of both phases in eutectic composition, etc.

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2. Experiment

The real structures of the directionally crystallized pseudobinary eutectic compositions in B_4C–NbB_2 and B_4C–MoB_2 systems were studied.

The source materials for the first system were NbB_2 powder supplied by Donetsk Chemical Reactive Plant ($\sim$99.5% of the main substance) and B_4C powder synthesized in the Institute for Problems of Materials Science ($>$ 99.9% of the main substance, real composition $B_{4,3}C$). They were mixed in appropriate quantities, cold pressed and sintered in vacuum at 1500°C as rods having 8–10 mm diameter and 50–100 mm length for the following zone melting.

In the MoB_2–B_4C case the source materials were Mo, B ($>$99.9%) and B_4C powders. The rods were prepared by two methods. By the first one Mo, B and B_4C powders were mixed, cold pressed and sintered. By the second one Mo, B and B_4C powders were mixed, cold pressed and melted in the arc furnace. For the homogenization the obtained pieces were crushed; obtained powders were cold pressed and then sintered similarly to the first method.

Sintered rods were zone melted by induction method using high-frequency equipment in argon gas at pressure up to 0.2 MPa.The rate of zone moving was in limits 3–8 mm/min; the relative speed of rotation of liquid zone (for better homogenization) was 1.5 rev/min.

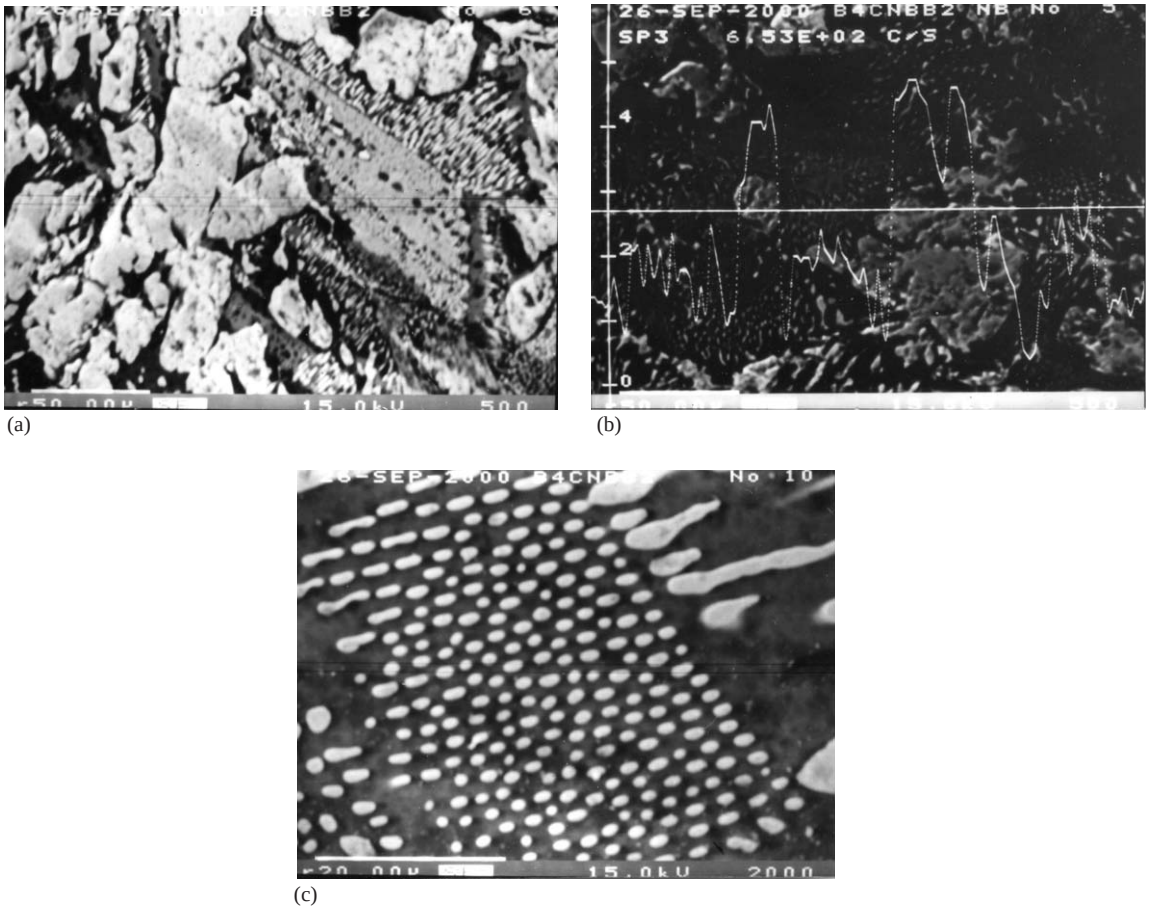
The structure study was made by means of X-ray diffractometer HZG-4A, scanning electron microscope Stereoscan S4-10 and Electron Probe Analyzer CX-50.

The presence of only two source phases in the NbB_2–B_4C system was confirmed by X-ray analyses and the electron probe analyses had shown negligible small or absence of their mutual solubility in solid state.

In the samples of the MoB_2–B_4C system prepared from previously sintered powders the MoB_2 and B_4C phases and very small trace of Mo_2B_5 phase were seen. In the samples prepared from previously arc melted materials the amount of the Mo_2B_5 phase was somewhat more. Further, in this case the electron probe analyses had shown the presence of a small amount of carbon in molybdenum boride phase.

3. Results and discussion

The information about the eutectic compositions in the NbB_2–B_4C and MoB_2–B_4C systems is very limited. According to [4] the eutectic composition for NbB_2–B_4C



(a) (b) (c)

Fig. 1. The structure of Nb–B–C composition (46 mol% NbB_2): (a) general view, (b) the distribution of niobium, (c) eutectic colony.

system contains near 35–37 mol% of NbB_2. For MoB_2–B_4C system such data are absent. Some elements of these both constitutional diagrams near liquidus surface were studied in [9].

Then for each system several compositions were chosen.

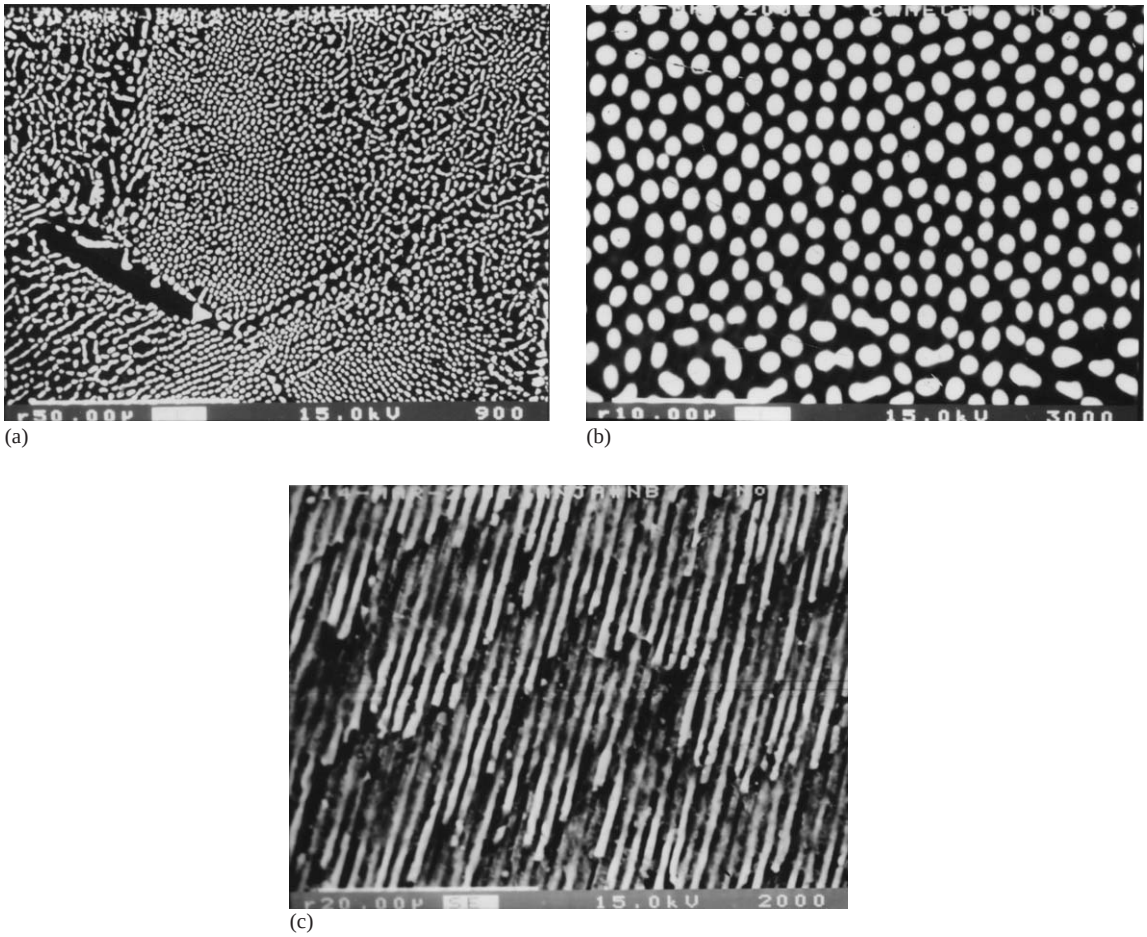
In the B_4C–NbB_2 system two compositions were studied: $Nb_{11}B_{76}C_{13}$ (~ 46 mol% NbB_2) and $Nb_{7,5}B_{77}C_{15,5}$ (~ 33 mol% NbB_2). The structure of the first composition had shown a significant excess of the diboride phase (Fig. 1a) that is confirmed by X-ray analysis in niobium characteristic radiation (Fig. 1b). Discrete parts of rod-like eutectic areas observed also are (Fig. 1c).

The second composition was much close to the eutectic one. In this case sufficiently uniform needle-like eutectic structure was formed. Only very small inclusions of boron carbide phase are seen (Fig. 2a). The structure of the most volume of the samples for both transversal and longitudinal cross-sections shows the boron carbide matrix and rods or whiskers of niobium diboride phase (Fig. 2b,c). This structure reminds us what is known before for MeB_6–MeB_2 eutectic systems. But in this case the whiskers diameter is more (1–2 μm in compared with 0.5–0.8 μm for MeB_6–MeB_2 systems).

In the B_4C–MoB_2 system several compositions were studied: $Mo_{11}B_{76}C_{13}$ (~46 mol% MoB_2), $Mo_{12,5}B_{7,5}C_{12,5}$ (~50 mol% MoB_2), $Mo_{14}B_{75}C_{11}$ (~56 mol% MoB_2), $Mo_{15,8}B_{73,7}C_{10,5}$ (~60 mol% MoB_2), $Mo_{17,5}B_{73}C_{9,5}$ (~65 mol% MoB_2) and $Mo_{19,5}B_{72,2}C_{8,3}$ (~70 mol% MoB_2).

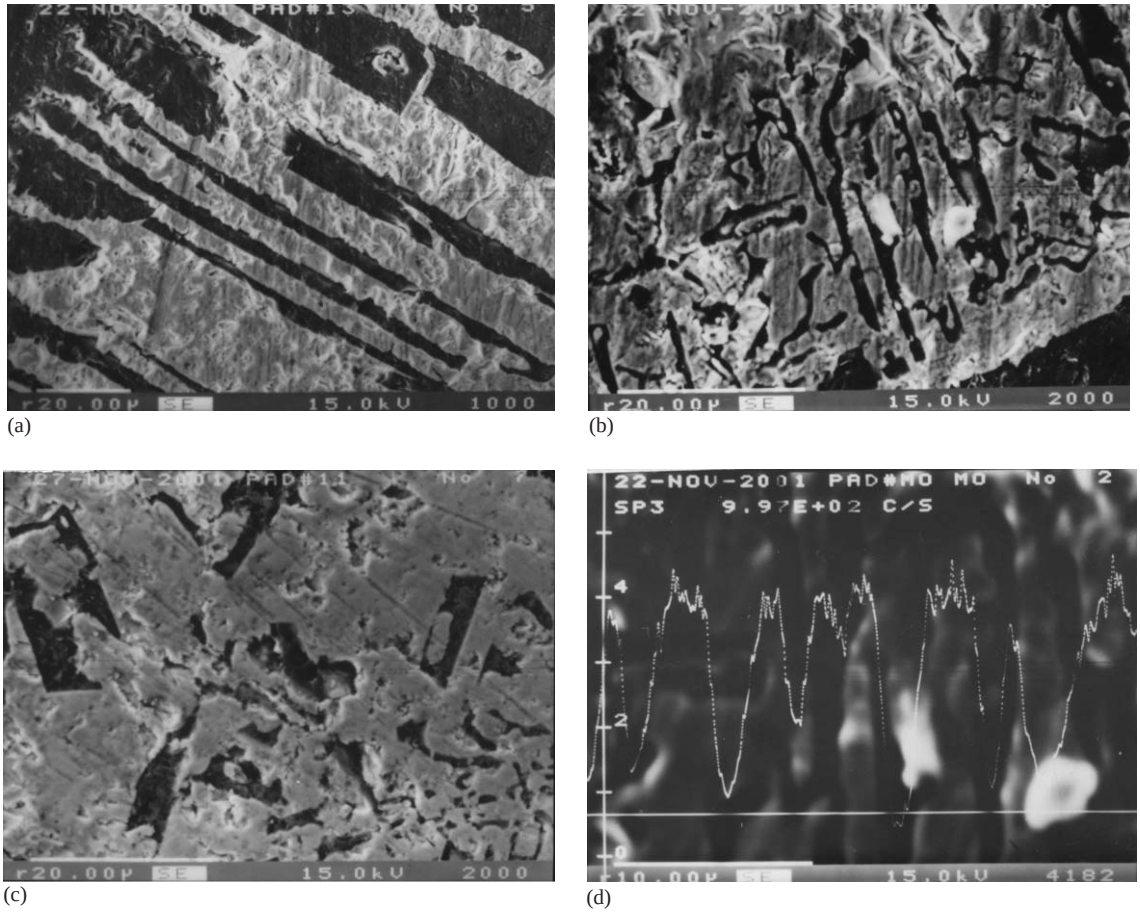
The typical structures of obtained composites prepared from the previously arc remelted powders (46, 50 and 56 mol% of MoB_2) are shown in Fig. 3. In each case large excess of boron carbide phase is seen. The samples prepared from sintered powders with higher molybdenum boride content and those which contained only traces of Mo_2B_5 phase, gave more uniform structure (Fig. 4). It shows that the composition having 70 mol% MoB_2 is more close to eutectics (Fig. 4c).

It is seen that if in the case of NbB_2–B_4C system NbB_2 phase has mostly needle-like (whiskers) configuration, in MoB_2–B_4C system the eutectic has another character and is close to, as it is called, a ''Chinese hieroglyphics'' structure.



(a) (b) (c)

Fig. 2. The structure of Nb–B–C composition (33 mol% NbB_2): (a) general view, transversal section. It is seen a small excess of boron carbide phase, (b) transversal section, (c) longitudinal section.



(a) (b) (c) (d)

Fig. 3. The structure of Mo–B–C compositions, prepared using previously melted powder: (a) 46 mol% of MoB_2, (b) 50 mol% of MoB_2, (c) 56 mol% of MoB_2, (d) distribution of molybdenum in sample.

These results correlate with a model that connects volume parts of participating phases and the eutectic structure configuration [10]. There was shown that the regular rod-like eutectic structure usually can be formed under directional crystallization of compositions, which contain no more than 30–35% of minor (not matrix) phase. From Table 1 it is seen that for the studied B_4C–MeB_2 systems the volume MeB_2 content in B_4C–MeB_2 eutectic is more than 35% only for B_4C–CrB_2 and B_4C–MoB_2 systems and that their eutectic structures are not rod-like.

The microhardness of several studied samples with compositions close to eutectic using the 150 g load was measured. The average value of the indentation diagonal was in the range 6.5–8μm which is much more than the dimensions of eutectic components.

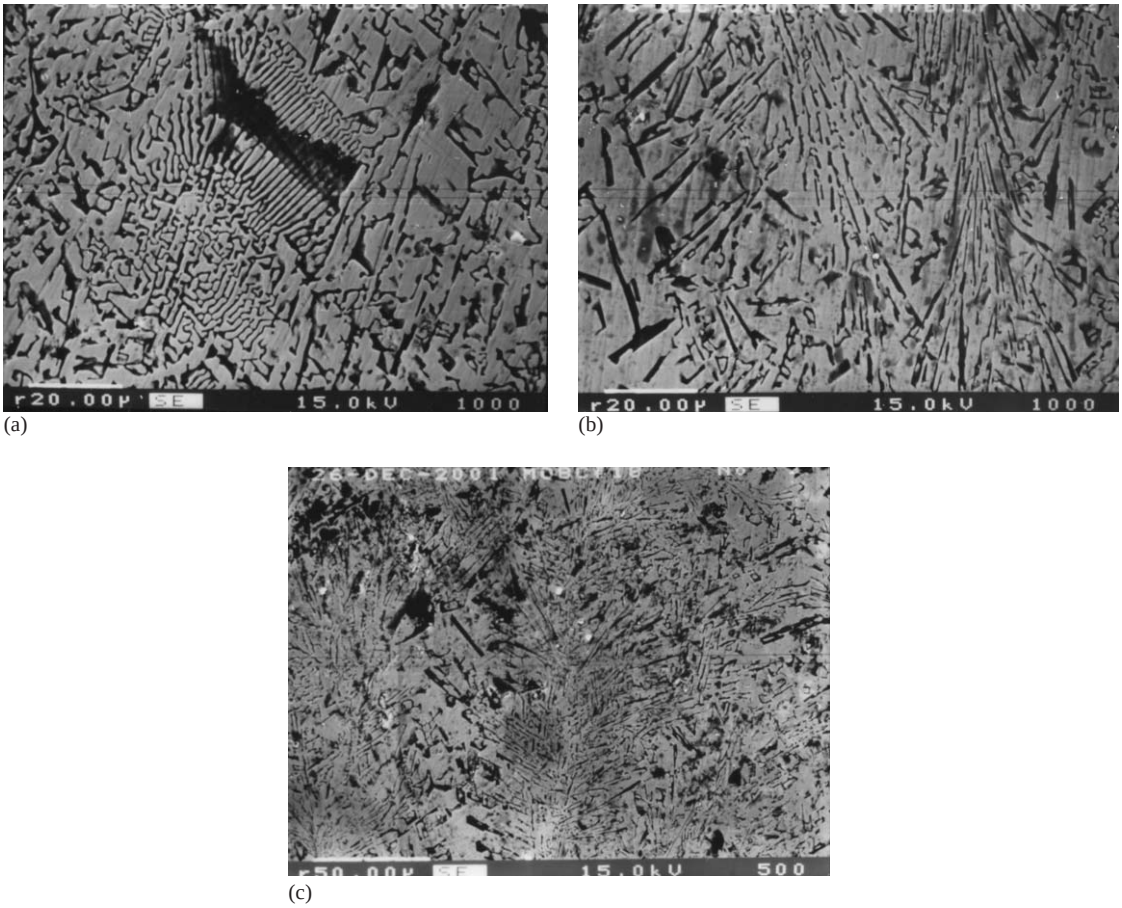
A spread in data in relation to the rod-like diboride phase dimensions was observed for the B_4C–NbB_2 system. The samples obtained at lower crystallization rate have more rough structure and, correspondently, higher hardness, ~46 GPa, apparently due to larger surface of boron carbide phase. The fine structure samples have microhardness ~41 GPa.

For the B_4C–MoB_2 system in samples with B_4C excess the microhardness of boron carbide phase (~60 GPa) is higher than for individual boron carbide (~50 GPa). Eutectic composition has microhardness ~ 35 GPa.

It should be mentioned that all indentations have no traces of cracks that suggest sufficiently high fracture toughness of studied composites.

4. Conclusion

The directional crystallization of compositions in B_4C–NbB_2 and B_4C–MoB_2 systems had shown that in the first system the rod-like is formed and in second one kind of "Chinese hieroglyphics" eutectic structure is formed. The directional crystallization of compositions in B_4C–MoB_2 system was done for the first. In the both cases the compositions combine high hardness and high microplasticity, much more than



(a) (b) (c)

Fig. 4. The structure of Mo–B–C compositions, prepared using previously sintered powders: (a) 60 mol% of MoB_2, (b) 65 mol% of MoB_2, (c) 70 mol% of MoB_2.

Table 1
The correlation between the volume part of MeB_2 phase and structure of B_4C–MeB_2 eutectics [4,5,11–14]

Pseudobinary system	Volume part of MeB_2 (%)	Eutectic structure
B_4C–TiB_2	20	Rod-like
B_4C–ZrB_2	20	Rod-like
B_4C–HfB_2	23	Rod-like
B_4C–VB_2	35	Rod-like
B_4C–NbB_2	33–35[a]	Rod-like
B_4C–TaB_2	27	Rod-like
B_4C–CrB_2	63	Disordered
B_4C–MoB_2	61–63[a]	Disordered, not regular phases distribution, ''Chinese hieroglyphics''

[a] This work.

for individual component phases. They may be considered as a new kind of self-strengthening composite materials.

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