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Phase Formation during Anneal of Supersaturated TiB_2–CrB_2–WB_2 Solid Solutions

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Numerous transition metal diborides of AlB_2 structure type reveal large mutual solid solubility. Temperature-depending homogeneity ranges bordering immiscibility gaps within the system TiB_2–CrB_2–WB_2 provide the opportunity to tailor an *in situ* grown typical platelet-shaped phase emerging from a supersaturated host matrix. Results are presented where variations in composition, manufacturing parameters, and heat treatment lead to precipitates of a "W_2B_5" structure accompanied by the formation of another tungsten boride less rich in boron in a (Ti, W, Cr)B_2 matrix. All phases are characterized by high melting points and hardness. The enhanced formation of the matrix as well as the precipitation mechanism were activated by the addition of 6 to 20 mole% CrB_2 to the system TiB_2–WB_2. Within the ternary solid solution, a particular composition range exists exhibiting a thermal expansion behavior similar to boron carbide. Attempts are made to toughen boron and silicon carbide ceramics by processing this *in situ* growth of platelets out of dispersed transition metal diboride particles within a carbide matrix. © 1997 Academic Press

EXPERIMENTAL

Powder blends of TiB_2, "W_2B_5," and CrB_2, supplied by H. C. Starck, total impurities less then 1 wt.% within the range of 20–70 mole% TiB_2, 10–70 mole% W_2B_5, and 6–20 mole% CrB_2 were prepared by high-energy milling.

The reaction sintering was carried out in a hot press under a pressure of 50–60 MPa for 30 min in hexagonal boron nitride-coated crucibles. The sintering conditions in the graphite resistance furnace, argon atmosphere, remained constant throughout the experiments. All specimens have been equilibrated at 2000°C for 8 h and subsequently annealed at 1600°C for 2–8 h in order to observe phase partitioning and precipitation. This additional heat treatment was carried out without pressure under argon. Quenching occurred in all cases by free cooling of the system, i.e., with an average rate of 10 K/min approximately to 1200°C, and with a lower rate finally to room temperature.

All samples were examined by X-ray diffraction to determine the phases and to calculate lattice parameters. The microstructure was investigated by SEM and EDX, and partially also by TEM. The final composition of the particular W-containing TiB_2-type and W_2B_5-type solid solutions was calculated from the quantitative analyses according to the stoichiometry WB_2.

The samples equilibrated at 2000°C were used for investigation of thermal expansion. The standard ANTON PAARHTK 10 high-temperature attachment of a Philips powder X-ray diffractometer was improved technically to reach high temperature in inert atmosphere and vacuum (1). The measurements were carried out in a vacuum of 10^{-3} Pa from room temperature up to 1500°C.

The lattice parameters were calculated with a program based on least-squares refinement. By scanning pure silicon as a standard, the room temperature results were corrected with errors of ± 0.001 Å. The correction applied to the measurements of the high-temperature unit resulted in an error of ± 0.003 Å regarding the high-temperature lattice parameters.

Results of high-temperature X-ray measurements are used to calculate the linear thermal expansion coefficients for the *a* and *c* directions, respectively, and the mean coefficient of thermal expansion.

RESULTS

TiB_2–WB_2–CrB_2 Solid Solubility

The borders of the (Ti, W)B_2 homogeneity range were studied between 1500°C and 2000°C and around the quasi-binary eutectic with approximately 63 mole% WB_2 solved in TiB_2 at 2230°C (2). The system TiB_2–CrB_2 shows a continuous solid solution which is limited by the solidus line at approximately 2200 ± 50°C and an immiscibility gap in the TiB_2-rich corner, reaching its critical point at approximately 2000°C and 20 mole% CrB_2 (2). The system CrB_2–WB_2 is of eutectic type ($T_e = 2030 \pm 50$°C) with a solid solubility of 10 mole% CrB_2 in WB_2 and 37% WB_2 in CrB_2 at the eutectic temperature (2).

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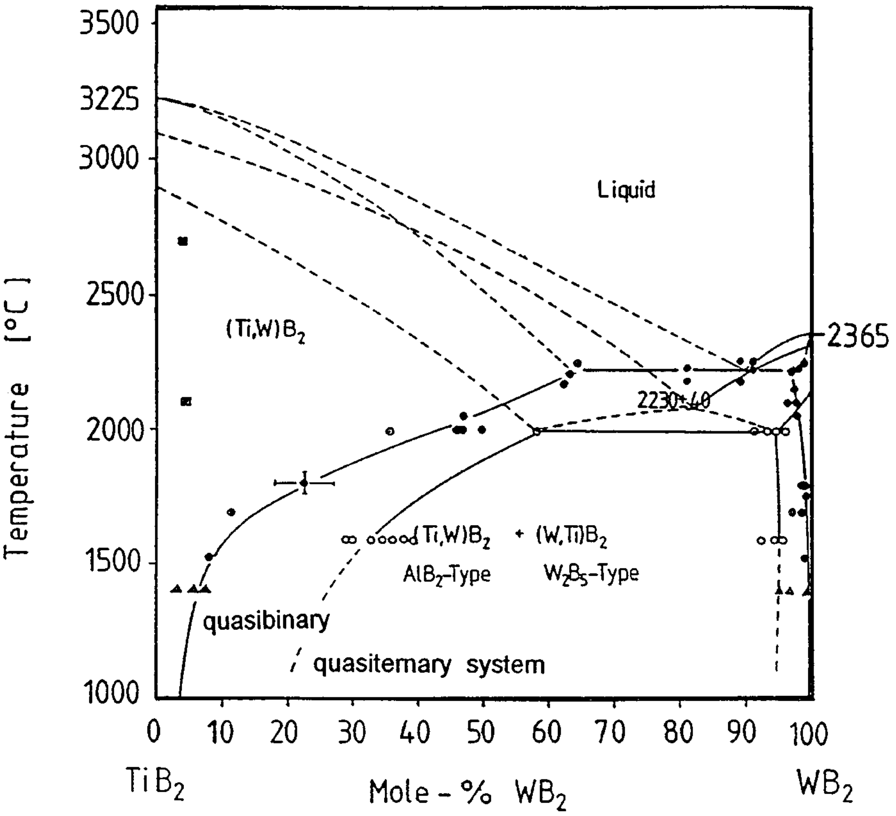

FIG. 1. Quasi-binary phase diagram TiB_2–WB_2 with 10 mole% CrB_2.

The broad solid solubility range of the diborides TiB_2 and WB_2 was reason for investigations of ternary solid solutions. The range of 6–20 mole% CrB_2 was examined with emphasis on phase stability and decomposition effects. Ternary solid solutions were obtained at 2000°C and furthermore annealed to achieve platelet precipitation. These experiments resulted in an "extended" phase diagram (Fig. 1) (3).

The stability range of the ternary mixed crystal with AlB_2 structure type is enlarged in comparison to the binary (Ti, W)B_2 solid solution; i.e., the maximum WB_2 content at 1600°C is 10 mole% while it reaches up to 30 mole% (with 10% CrB_2) and 35% within (Ti, W, Cr)B_2. More important is to focus on a supersaturated host matrix, the solubility of WB_2 at about 2000°C is increased from 30 to 40% (with 10% CrB_2) and 45% in ternary crystals with 15 mole% CrB_2.

Regarding the W_2B_5 structure platelets, dissolving up to 6 mole% CrB_2 at 1600°C, the solubility for TiB_2 is slightly enlarged to $\sim$4 mole% in contrast to $\sim$1% in binary (W, Ti)B_2.

Annealing of ternary host crystals at lower temperature results in a phase separation, consisting of a W- and Cr-enriched TiB_2 matrix phase and tungsten boride phases. This process is based on two procedures: Small particles of residual WB_2 not having been dissolved completely initiate the growth of platelets close to the grain boundary of the host crystals. These platelets are able to grow across the grain boundary into a neighboring grain. Inside the host crystal, an epitaxial precipitation of very fine platelets of W_2B_5-type crystals with $(0001)_{W_2B_5}$ parallel to $(0001)_{TiB_2}$ of the host crystal is well known (2). These precipitates of 0.05–0.2 μm in thickness and 0.5–5 μm in diameter can be coarsened by prolonged heat treatment.

The presence of CrB_2 activates the nucleation of platelets tremendously. A binary composition with a fixed TiB_2/WB_2 ratio requires an incubation period of several hours while a phase separation within ternary solutions is initiated during the first two hours (see Fig. 2) (3).

Beside this random distribution of platelets, some compositions yield parallel orientated, lamellar precipitates during the temperature treatment (Fig. 3). This structure appears like the characteristic feature of a eutectically solidified melt.

During the investigation of a particular composition range, a new type of epitaxial precipitation of tungsten boride occurred. Stabilized by a certain amout of titanium and chromium atoms, the (001) plane of a high-temperature

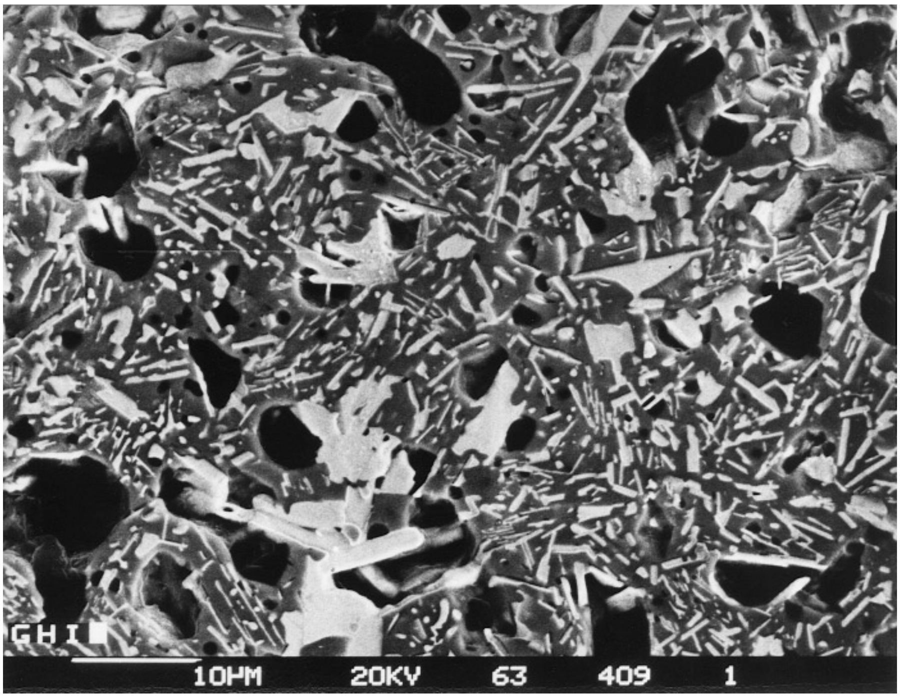

FIG. 2. W_2B_5 platelets in $(Ti, W, Cr)B_2$.

monoboride phase is grown perpendicular to the prism plane of the TiB_2-structured host crystal (Fig. 4).

The effect of incorporation of different transition metal atoms into the TiB_2 (space group *P6/mmm*) and the WB structures (space group *Cmcm*) results in a coincidence of lattice parameters (Table 1).

This epitaxial fit remains restricted to a particular composition range:

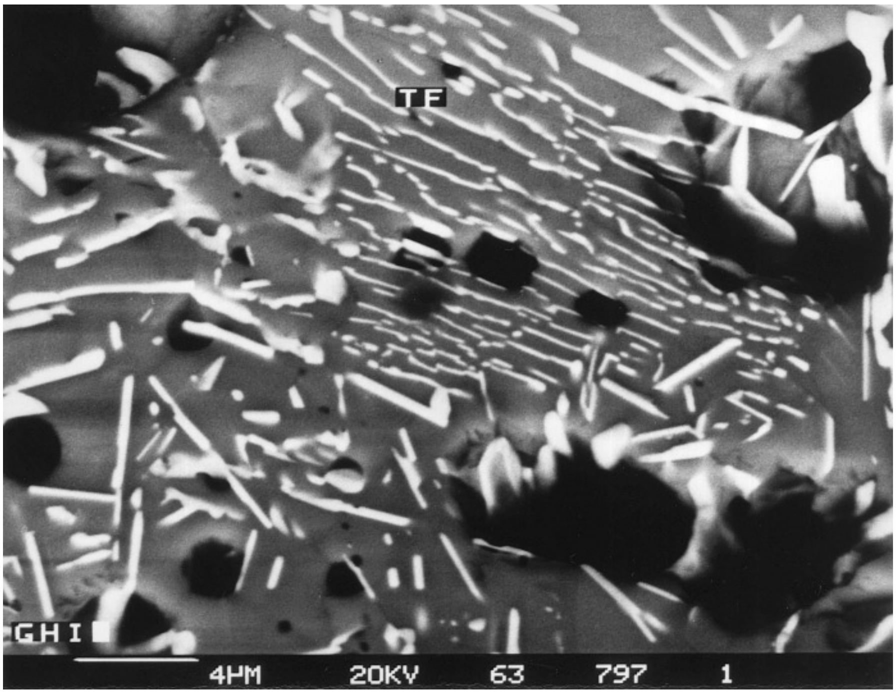

FIG. 3. Lamellar precipitates in $(Ti, W, Cr)B_2$.

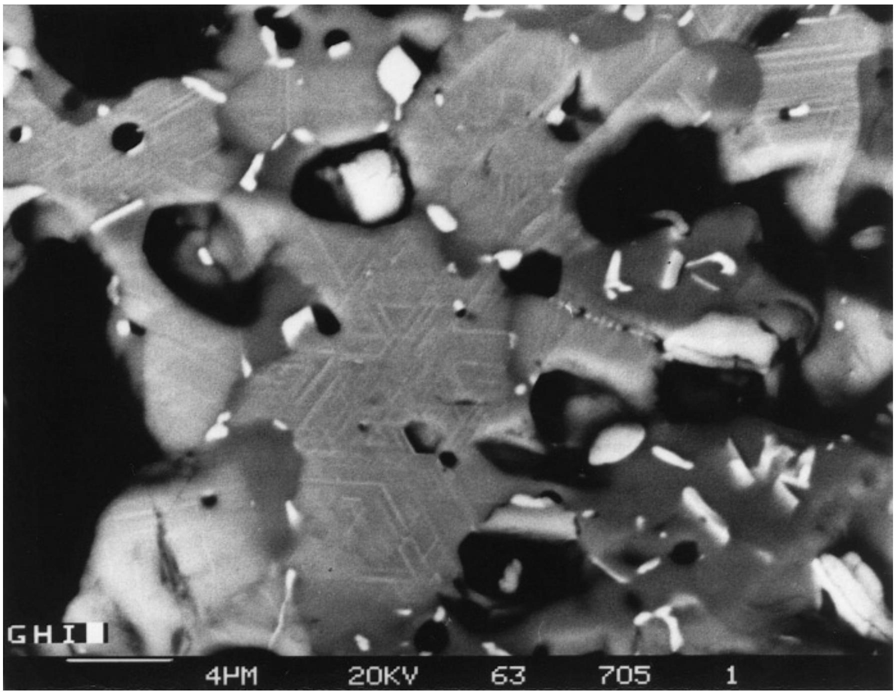

FIG. 4. β-WB growing epitaxially on TiB_2.

$$40\text{–}55\ \text{mole\%}\ TiB_2,\ 35\text{–}40\ \text{mole\%}\ WB_2,\ \text{and}\ 10\text{–}15\ \text{mole\%}\ CrB_2.$$

Within the errors of calculation, a linear dependence of the β-(W, Cr, Ti)B lattice parameters on the molar amount of chromium atoms x_{Cr} solved in the orthorhombic WB structure could be established

$$k_{(W,Cr)B} = k_{WB} - (0.123 \pm 0.005)^* \, k_{WB} {}^* \, x_{Cr},$$

with k = lattice parameters a, b, c.

According to the small amount of 1–6 mole% titanium detected in the β-WB phase, no significant influence on the WB lattice could yet be found.

The growth of stabilized β-WB on prism planes of matrix crystals resembles the hexagonal symmetry of TiB_2 crystals, which is recognized in SEM pictures. The SEM observations suggest WB precipitates of nearly 100 nm thickness (see Fig. 4). TEM analysis provides evidence of a more complicated substructure. The β-WB is composed of a number of single WB monolayers of less than 10 Å in thickness (confer the calculated b spacing of 8.28 Å), being separated from each other by residual matrix material (see Figs. 5, 6).

TABLE 1
Lattice Parameters of TiB_2 and β-WB Solid Solution

	Lattice parameters (Å)		
TiB_2	a, 3.030		c, 3.229
$(Ti, W, Cr)B_2$	a, 3.028		c, 3.179
β-(W, Cr, Ti)B	c, 3.026	b, 8.276	a, 3.142
β-WB	c, 3.07	b, 8.40	a, 3.19

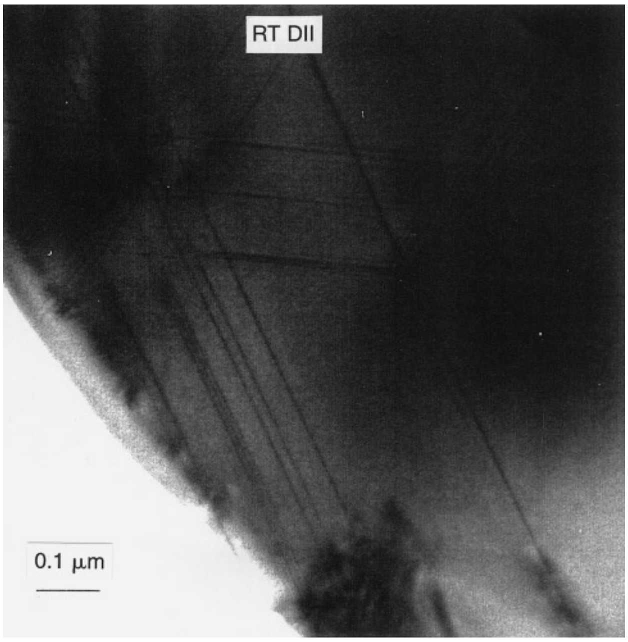

FIG. 5. β-WB layers in $(Ti, W, Cr)B_2$.

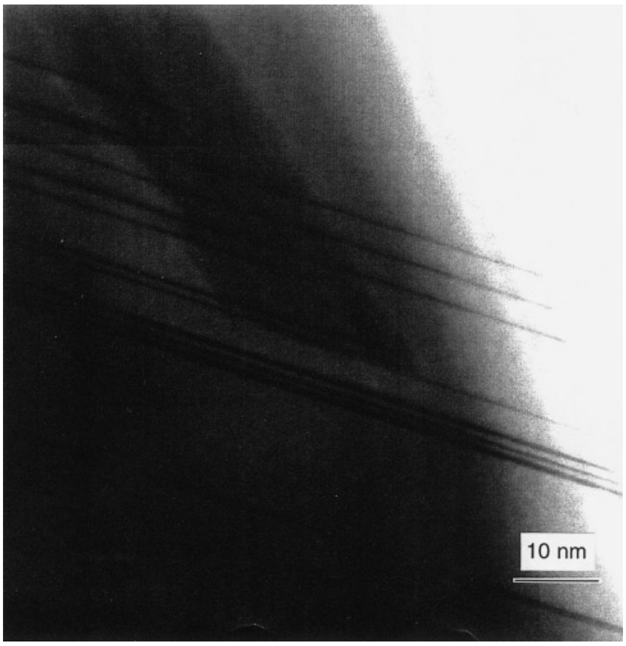

FIG. 6. β-WB layers in (Ti, W, Cr)B_2.

Thermal Expansion

The structure of transition metal diborides is generally described as a sequence of alternating metal and boron layers (e.g., (4)). In contrast to the common AlB_2 structure, the "W_2B_5" structure contains an additional layer of puckered boron and thus an enlarged stacking sequence (5, 6).

In general, the expansion in the *a* direction is governed by the strong covalent bond in the boron layer which is only slightly influenced by the surrounding transition metal atoms. In contrast, an exchange within the metal sublattice with tungsten and chromium atoms occupying the titanium position leads to a remarkable variation of the *c* spacing (e.g., Table 1).

The lattice expansion with increasing temperature reveals the main difference between binary (TiB_2–WB_2) and ternary compounds. Due to it's small atomic radii, the addition of CrB_2 causes a contraction of the matrix lattice with a significant decrease of the *c* axis parameter. Consequently, the mean thermal expansion and the anisotropic misfit stresses are reduced.

A ternary solution with 10 mole% CrB_2 and 45 mole% of TiB_2 and WB_2, respectively, reveals a mean coefficient of thermal expansion close to boron carbide (see Fig. 7).

DISCUSSION

The unexpected appearence of β-WB can be explained by a reaction process based on the high mobility of boron atoms. EXAFS studies on (Ti, W)B_2 composites (8) indicated that a high amout of boron atoms is transferred from the near titanium environment to a tungsten

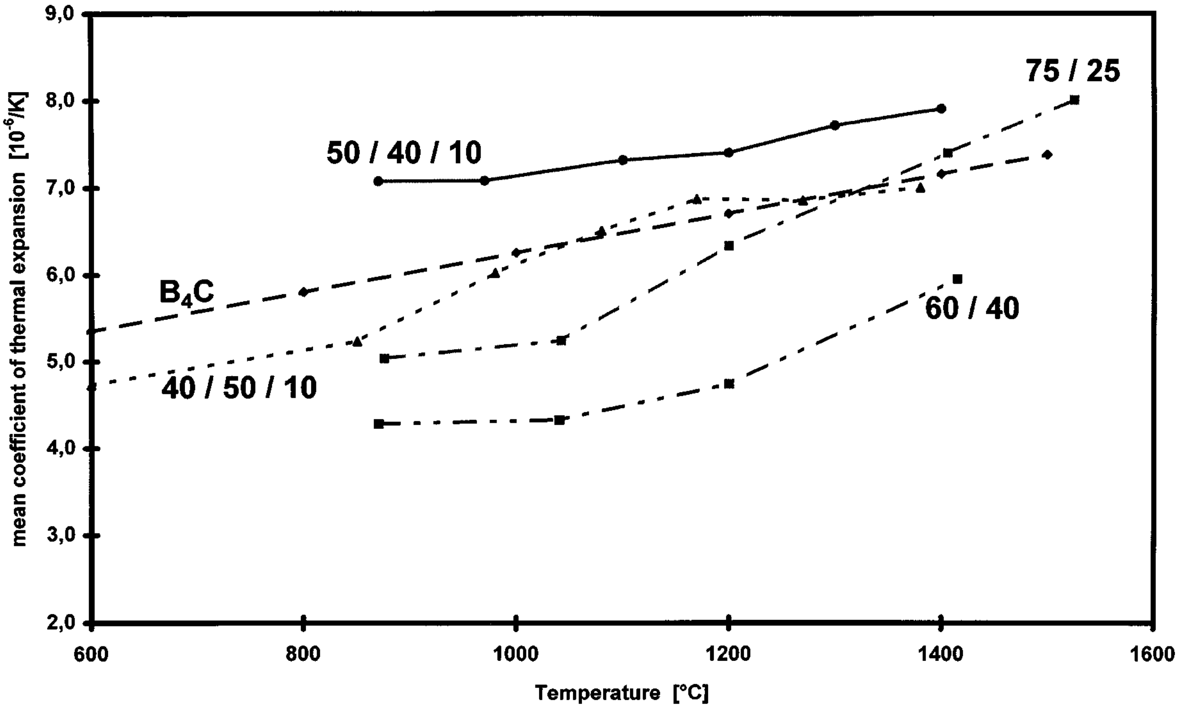

FIG. 7. Thermal expansion of (Ti, W, Cr)B_2.

neighborhood during high-temperature treatment. In a first reaction, boron and tungsten atoms may react to WB in the grain boundary region. As already pointed out above, this WB can only be stabilized within a distinguished quasiternary composition range. In general the incorporation of chromium atoms within the β-WB structure has already been shown in literature for 1400–1500°C (9), predicting the same effect for the high-temperature region.

In case the β-WB is not stabilized the following process occurs: Free boron reacts with WB to form W_2B_5, also well known from literature (10), providing in our case a fine microstructure in the appearence of W_2B_5 platelets.

Within the composition range investigated, a high amount of W_2B_5 platelets randomly oriented and homogeneously distributed in the matrix is realized (Fig. 2). These are preconditions for a successful toughening of ceramic matrices by dispersion of transition metal diboride composites due to a maximum exploitation of this *in situ* growth of platelets.

At the same time, the enhanced solid solubility in the investigated TiB_2–WB_2–CrB_2 system resulted in composites with a thermal expansion behavior similar to that of boron carbide.

Prelimary results of boron and silicon carbide reinforced by dispersed transition metal diborides give evidence of an effective crack deflection as a toughening mechanism.

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