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The nature of the microstructure and interface boundary formation in directionally solidified ceramic boride composites

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14. ABSTRACT

The goal of the present work has been the revealing of regularities/ patterns of structure formation of self-reinforced composite materials. For this was supposed to study the eutectic morphology transformation from fiber-like to platelet-like one with the increase of reinforcing phase content under conditions of directional crystallization. $LaB_6 – (Ti_x,Cr_{1-x})B_2$ system has been chosen as the object for investigation on the assumption that of all previously studied eutectics the systems with titanium and chromium had minimal and maximal content of diboride phase, respectively. At the same time, on the initiative/suggestion of the project partner investigation of $(La_xCe_{1-x})B_6$ and $(Ti_x,Cr_{1-x})B_2$ single crystal growth has been carried out. Investigation of the directionally solidified $LaB_6 – (Ti_x,Cr_{1-x})B_2$ composites fully confirmed the current theoretical understanding of the transition of the eutectic morphology with increasing Cr content, ie with the increase of the reinforcing phase volume. New results were obtained when attempting growing $(Ti_x,Cr_{1-x})B_2$ single crystals: the existence of extreme melting temperature was discovered, which allowed to grow single crystals with x = 0, 0.2, 0.8 and 1. In order to grow single crystals with x = 0,4-0.6 it is necessary to modernize the outfit. Simultaneously, in consultation with the partner investigation of $LaB_6 – (Ti_x,Zr_{1-x})B_2$ system were continued. New studies show that even at x=0.1 there is a significant increase in crack propagation resistance compared with x = 0. Investigations carried out by means of HRTEM and EBSD showed that the rotation the growth axis occurs at x = 0.25, and the crack propagation is significantly influenced by the stress field in the matrix caused by the influence of the reinforcing phase as well as the interaction energy on the phases interface. We can assume that it is the latter that determines the conditions of nucleation of eutectic colonies crystallization.

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THE NATURE OF THE MICROSTRUCTURE AND INTERFACE BOUNDARY FORMATION IN DIRECTIONALLY SOLIDIFIED CERAMIC BORIDE COMPOSITES

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SUMMARY

This project addresses major challenges associated with structural ceramics for ultra high temperature applications. The challenges associated with ceramics include insufficient strength, low toughness, and poor creep resistance at very high temperatures. To achieve a meaningful scientific understanding, scientists require intrinsic properties of constituent phases. Further, there is need for novel approaches to enhance toughening and retain strength at temperature. Thus, this project has two broad objectives that will be pursued simultaneously. These objectives are: (i) development of technologies to produce a wide range of metal hexaborides, metal diborides and metal silicides single crystals for the investigation of intrinsic properties, and (ii) development of directionally solidified eutectic ceramics with enhanced toughness, and formulation of in-situ composite mechanics for multiphase structures.

The focus of the proposed project is to examine single crystals and polyphase material systems across a broad compositional and therefore microstructural range, which includes but is not limited to eutectic growth (i.e. off-eutectic and eutectic materials). The off-eutectic directional solidification work and cellular solidification combines two novel concepts recently advanced: the one step solidification of in-situ composite of ceramics showing high strength and creep resistance and the choice of compatible interphase material at the phase boundaries, allowing tailoring of physical properties over wide limits, specifically impacting material toughness.

INTRODUCTION

This proposal addresses two major challenges associated with structural ceramics for ultra high temperature applications. The challenges associated with ceramics are insufficient strength, low toughness and poor creep resistance at the very high temperatures of interest for aerospace applications. To achieve a meaningful scientific understanding, scientists require in-depth knowledge about intrinsic properties of constituent phases. The intrinsic properties of single crystals are of paramount importance and thus could provide a pathway to engineer new composite structures. We propose to investigate the intrinsic properties of single crystals that are relevant for ultra high temperature applications. In order to achieve a significant increase in toughening and to further retain the strength at elevated temperatures a new multifunctional approach is proposed. The multifunctionality comprises a plain combination of at least two functions or structure and functions. The multifunctionality will be achieved through directional solidification of polyphase structures comprising the load-bearing and functional phase. The three-year effort will focus on different eutectic systems that will be produced by directional solidification.

In recent years, ceramic directionally solidified eutectics (DSEs) have attracted considerable attention because of their thermodynamic compatibility and microstructural stability up to the eutectic invariant point [1]. Oxide DSEs have received the most recent attention because they have demonstrated excellent strength and creep resistance up to high temperatures (>1200˚C), which makes them attractive as high-temperature structural materials [2-4]. One limiting property of this class of materials, however, may be the low fracture toughness because the interfaces between the two phases typically adopt low-energy orientation relationships during the directional solidification process, which prevents significant interface de-bonding [5]. On the other hand, while boride DSEs have received relatively less attention, there are indications that these materials may have some advantageous mechanical properties in comparison to their oxide counterparts.

In general, borides of rare-earth and d-transitional metals have outstanding refractory properties with high hardness, high chemical stability and ultra-high melting points that usually range between 2300-3200°C. LaB_6-ZrB_2 DSEs, which have a eutectic temperature of 2470°C, exhibit high bend strength (1000~1320 MPa [6]) and excellent thermal shock resistance (500 K/min) [7]. Fracture toughness has been investigated in LaB_6-ZrB_2 DSEs using conventional, macroscopic 3-point bend and Vickers micro-indentation methods. In the conventional tests, LaB_6-ZrB_2 DSEs showed exceptionally high fracture toughness (16.3~27.8 $MPam^{1/2}$ [6] or 17.8 $MPam^{1/2}$

[7]) when the initial notches were cut perpendicular to the rod axis. The Vickers indentation method was also utilized by Chen et al. [7], who performed tests on planes parallel and perpendicular to the rod axis, and quantified the fracture toughness as 8.2 $MPam^{1/2}$ and 8.7 $MPam^{1/2}$, respectively.

This project aims to thoroughly characterize the microstructure, crystallography and interface structure of RB_6-MeB_2 (where R – Sm, La, Eu and Me – Ti, Zr, Hf or their solid solution) DSEs and to establish the interrelation between the phase interface condition, lattice mismatch of their crystal lattices, crystallographic orientation of the matrix phase relative to the direction of crystallization, thermal expansion coefficient mismatch between constituent phases of the composite, and structure formation processes together with the stress condition in directionally crystallized eutectic composites based on refractory boride compounds.

METHODS, ASSUMPTIONS AND PROCEDURES

Composite materials based on lanthanum hexaboride and samarium hexaboride (MeB_6) with both individual titanium or zirconium diborides ($Me^{II}B_2$) and their solid solutions ($Ti_xZr_{1-x}B_2$) with varying component ratio as a reinforcing phase were chosen for the realization of the present project.

Directional crystallization of alloys that permits to grow the necessary composites directly from the melt was chosen as the processing method for the project objective realization. Under such conditions two phases are simultaneously grown from the melt with a certain mutual crystallographic orientation, which provides the possibility of *in situ* sample formation.

Synthesis and growth of eutectic composite materials by means of directional crystallization was carried out on the “Crystall-111” setup (modernized by the authors) by means of vertical inductive crucible-free zone melting process.

On the first stage of the present investigation starting materials, hexaborides and diborides, were synthesized from high-purity oxides and boron and metal iodides and boron, respectively. Considering the literature data on the interrelation of crystallization parameters of the chosen class of materials and of their mechanical properties with mutual orientation of the matrix phase and eutectic growth direction a considerable amount of time and effort were spent on lanthanum and samarium hexaborides perfect single crystals growth. The latter were used as inoculants for composite materials crystallization with constant orientation. Still another important task was high-precision eutectic composition determination for each material. In particular, a considerable nonlinearity of the diboride volume content in the eutectic composite material based on samarium hexaboride LaB_6-$Ti_xCr_{1-x}B_2$ depending on the Ti/Cr ratio in the system was established.

Rod-like samples (4.5-5mm in diameter) of RE-hexaboride based materials reinforced by individual diborides or solid solutions on their base were prepared by the above described method. After certain tooling in order to obtain highly polished surface, samples were investigated by XRD and metallography, and were also passed to the American counterpart (NASA Glenn Centre, Cleveland, USA) for complex analysis according to the project agreements.

RESULTS AND DISCUSSION

1 Investigation of highly heterogeneous structural material systems with a composite media (eutectic structure)

1.1 Fabrication of the samples of solid solutions (Ti,Cr)B_2 by directional crystallization, investigation of their crystal structure and properties

Since a number of compounds is formed in the Ti-Cr system a sequence of $(Ti_x,Cr_{1-x})B_2$ (x=0; 0,2; 0,4; 0,6; 0,8; 1,0) solid solutions has been synthesized and investigated.

Ultrapure starting materials with a total content of impurities not higher than 20 ppm were used for materials synthesis.

Metal shavings and pure boron (fused) were mixed in a proper proportion, compacted by cold pressing and subsequently subjected to arc melting.

All samples were investigated with high precision for chemical composition, lattice parameters and microhardness.

In order to ensure a stable zone melting process all billets (blanks) must have uniform density, heat conductivity and dimensions. For this purpose all samples after arc melting were disintegrated in the Abech mortar, pressed into a transverse mold and sintered in vacuum at 1600 C.

The results of our investigations showed that the lattice parameters and microhardness for all samples are linearly dependent on the chemical composition.

The existence of a singularity in the melting temperature of $(Ti_x,Cr_{1-x})B_2$ solid solutions has been established. As a result, TiB_2 and $Ti_{0.2}Cr_{0.8}B_2$ single crystals, and a CrB_2 polycrystal were grown by our method. However, the singularity of the melting temperature did not allow to accomplish zone melting for the rest of the samples (for the remaining samples). Since the homogeneous/uniform samples of certain dimensions were not available (the material after arc melting had high internal strain) it was impossible to conduct the melting temperature measurements. The melting temperature can be estimated by the power needed for the molten zone formation and its luminosity.

1.2 Investigation of eutectic compositions in the LaB_6-(Ti,Cr)B_2

Investigation of eutectic relation in the LaB_6-$(Ti_x,Cr_{1-x})B_2$ (for x=0; 0,2; 0,4; 0,6; 0,8; 1,0) have been started.

Eutectic relation in the LaB_6-$(Ti_x,Cr_{1-x})B_2$ (for x=0,4 and 0,6) were determined.

Eutectic relations in the LaB_6-$(Ti_x,Cr_{1-x})B_2$ (for x=0.2, 0.4, 0.6 and 0,8)were determined.

Eutectic relations in the LaB_6-$(Ti_x,Cr_{1-x})B_2$ (for x=0.2, 0.4, 0.6 and 0,8)were determined.

Taking into account that the volume content of the diboride phase in its eutectic with LaB_6 for the LaB_6 - TiB_2 and LaB_6 - CrB_2 alloys has a nonlinear character we have accomplished a high-precision investigation of the exact eutectic composition on the LaB_6 – $(Ti_xCr_{1-x})B_2$ system versus x. Their main characteristics and sample compositions are given in Table 1.

Table 4. – Initial powder characteristics and sample compositions in the LaB_6 – $(Ti_xCr_{1-x})B_2$ system

Sample #	I	II	III	IV	V	VI	VII
Ti (ат %)	100	80	60	40	80	0	0
Cr (ат %)	0	20	40	60	20	100	100
$Ti_xCr_{1-x}B_2$ (об %)	10,71	14,14	18,66	25,27	32	54,86	62,26
LaB_6 (об %)	89,29	85,86	81,34	74,73	68	45,14	37,74

Microstructure of the produced samples was studied by optical and electron microscopy.

It has been shown that if the chromium content in the diboride does not exceed 60 at.% the volume of the diboride phase remains less than 30 vol.% which results in a fiber-like structure formation. The samples with 80 at.% chromium a hieroglyph-like structure was formed. For the composition LaB_6-CrB_2 formation of two eutectics with different values of the LaB_6/CrB_2 ratio has been determined, which В образцах с 80 ат% Cr формировалась иероглифоподобная эвтектика, а для состава LaB_6-CrB_2 были зафиксированы эвтектики с двумя соотношениями LaB_6/CrB_2, that suggests the existence in the system of an area of limited solubility in the liquid state (Fig.1). It should be specifically noted that under identical crystallization conditions the chromium diboride based eutectic was more coarse-grained.

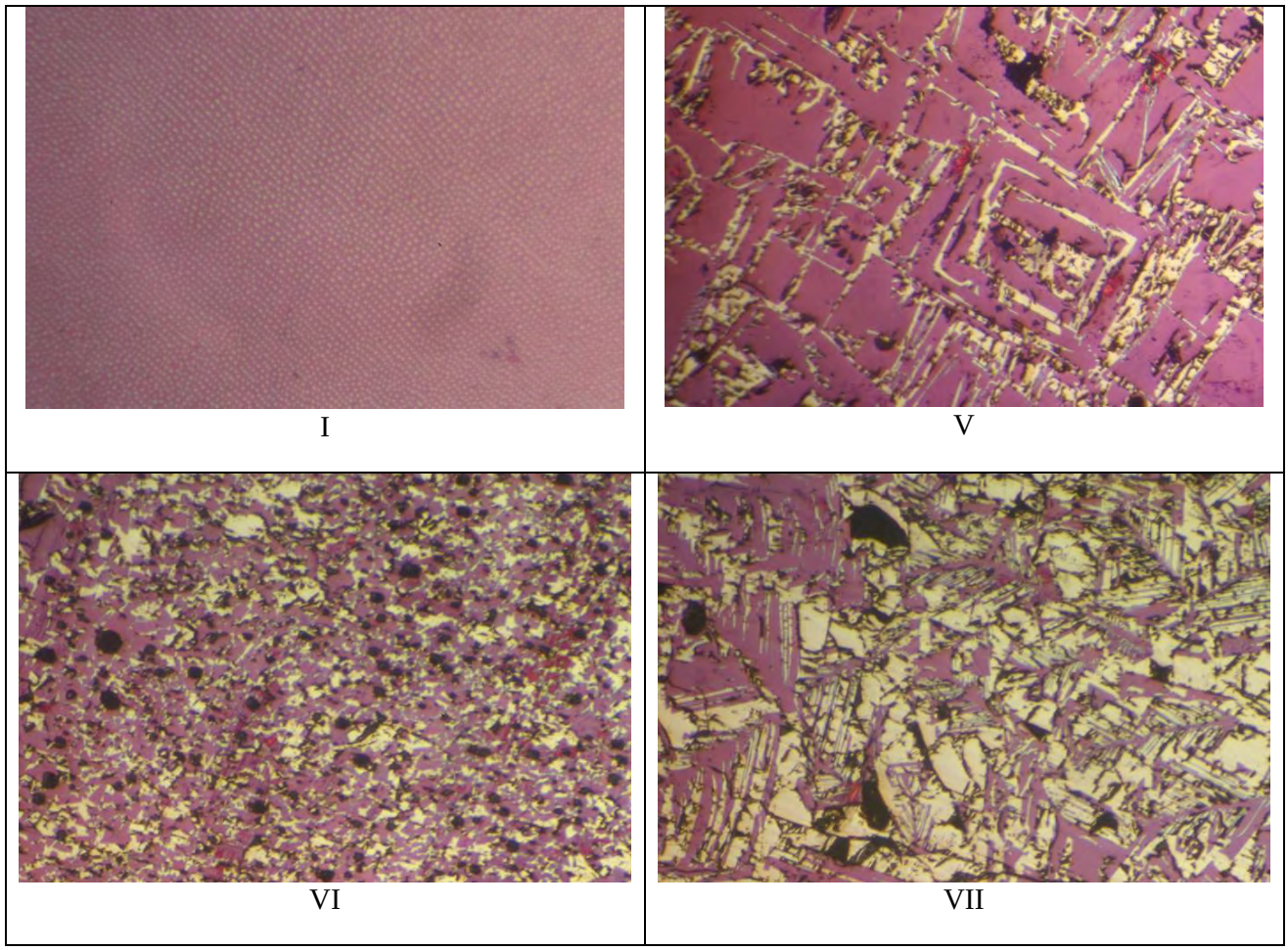

Fig.1 – Microstructure of LaB_6-$(Ti_xCr_{1-x})B_2$: multi-component samples (Roman numerals correspond to the compositions shown in Table 1)

This is very clearly seen in the sample with 59 vol% CrB_2 where one can observe the boundary eutectic colonies with different ratios of LaB_6/CrB_2.

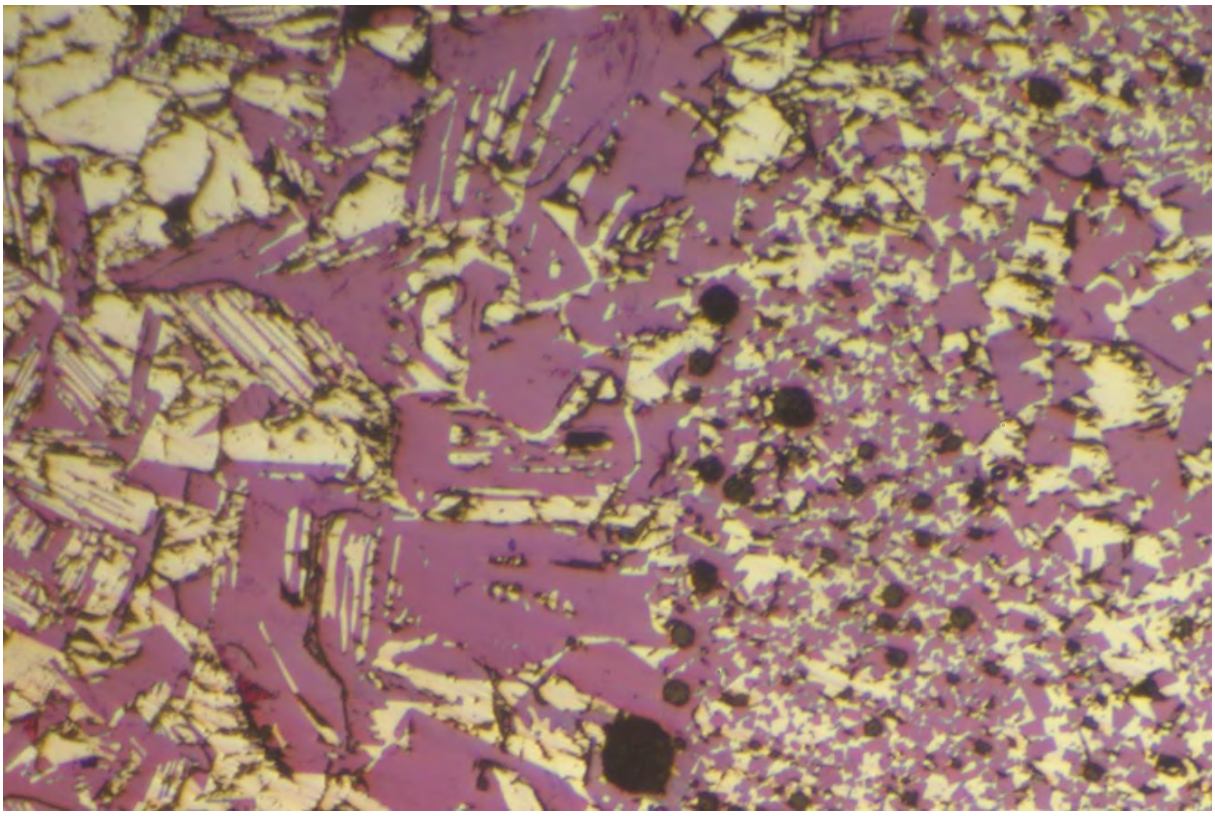

Fig.2 – Microstructure of LaB_6-CrB_2 with 59 vol% CrB_2

Thereby was confirmed the basic idea of the present work that when there is no substantial contribution of interaction energy anisotropy on the phase interface the morphology of the reinforcing phasse is determined by its volume concentration. The question of anisotropy influence, which was recorded in the previous project (P 261), has been partially taken up in the second section of the paper.

2 Investigation of the potential role of dopant element(s) in the modification of structure and properties of MeB6 single crystal, and family of MeB2 (where Me =Zr, Hf, Ti, Cr and other combinations) single crystals.

2.1 Fabrication by directional crystallization of some borides and silicides in coordination with the Employer

2.1.1 (La_x,Ce_{1-x})B_6 (for x=0; 0,2; 0,4; 0,6; 0,8; 1,0)

According to the research plan (La_x,Ce_{1-x})B_6 solid solutions (x=0; 0,2; 0,4; 0,6; 0,8; 1,0) were synthesized from high-purity materials and subsequently their single crystals were grown.

The starting material was obtained by synthesis from the high-purity metal oxide and boron (all components had impurities not exceeding 40 ppm). Due to the fact that studies of these solid solutions with a concentration of 10 at.% of lanthanum have been conducted in conjunction/together with scientists from Moscow at this period were found singularities in the transport properties, this compound was added to the list requested by the Customer.

2.1.1 The influence of Ti addition on fracture toughness and failure of directionally solidified LaB_6–ZrB_2 eutectic composite with single crystal matrix.

In accordance with the results obtained in the previous partnership project (P261) and in accordance with AFOSR representative Dr. Ali Sayir preliminary work (was carried out for investigation of the influence of Ti additives to the LaB_6-$(Ti_x,Zr_{1-x})B_2$ eutectics on its mechanical properties.

With the destruction of natural fiber reinforced composites three directions of crack propagation relative to the direction of crystallization (fiber growth) are possible (Figure 3).

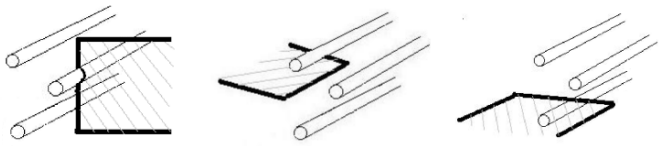

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Fig. 3. Possible directions of crack introduction for toughness measurement

Previously, it was shown that the maximum crack propagation resistance is observed in the first case. But in this paper, a tasked has been set to detect a change of the interaction energy at the interface by replacing some of the atoms of zirconium diboride for titanium atoms. In this case, one could expect that the maximum effect will be manifested in the second case of crack propagation (fig.3). However, the actual samples obtained by directional solidification, have the shape of a large sized rod specifically along the fibers. Therefore, a special scheme of fracture toughness test was used. The method of Brazilian test was chosen for this purpose (fig. 4). This method implies diametric compression of the disks with a central crack and allows to test the specimens of small dimensions, which is essential, because the diameter of eutectic rods is ~ 5 mm. The central crack was introduced in the plane, parallel to the axis of the eutectic rod, in direction, perpendicular to the axis. Such a location of crack gives possibility to investigate the interaction of crack with fiber-matrix interface and insures that fracture toughness value depends only on the interface properties. The introduction of the crack to the central part of the sample ensures that the value of fracture toughness is not dependent on the properties of the outer layer of eutectic rod, which can contain chemical contaminations or irregularities of structure. The method has advantages of higher fracture stress, and lower dispersion of results for the same materials. Failure mode is pure mode I for vertical crack position (fig. 4) due to the tensile stresses that appear near the edge of the crack after loading [8, 9]. Fracture toughness can be calculated by the next formula [10]:

$$K_{1C} = \frac{1{,}01227 \cdot P_f}{\mathrm{h}\sqrt{\lambda \mathrm{R}}} \cdot \sqrt{\frac{\lambda}{1-\lambda}} \cdot (1 - 0{,}60387\lambda + 1{,}67239\lambda^2 - 1{,}16988\lambda^3),$$

where

$$\lambda = \frac{2a}{D},$$

2a is the length of crack, D is the specimen diameter, P_f, h and R are respectively the fracture stress, the specimen height and radius.

The fracture test was conducted on the setup for testing of ceramics "CeramTest". The loading rate was 0,2 mm/min.

For each composite samples with two types of cracks were prepared. Cracks were introduced by electro-spark cutting in <100> and <110> crystallographic directions of matrix with a different angles to <100> axis, determined by X-ray experiment in back-reflection geometry.

The fracture surface of specimens after the fracture toughness test was examined by the means of scanning electron microscopy. Only surfaces that formed as a result of main crack propagation were studied.

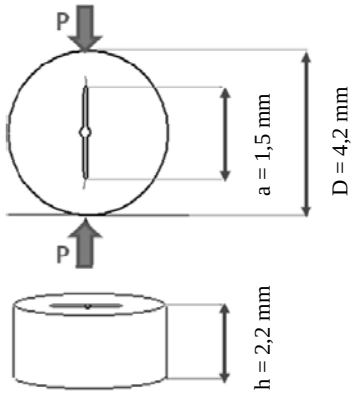


Fig. 4. Scheme of specimens that were used for fracture toughness test

It should be noted that the given method of the fracture toughness measuring is not universally accepted by researchers, but it enabled us the best way possible to capture the effect of partial replacing of zirconium atoms for titanium ones on the interaction energy at the phase interface.

After preparation of samples for fracture toughness test special attention was paid to the examination of the edge of the crack that was introduced to the specimen by electro-spark cutting. As it can be seen from fig. 4, the sharp thin microcracks form on the edge of the crack. The presence of such microcracks is very important, as it insures that the fracture toughness measurement is performed correctly.

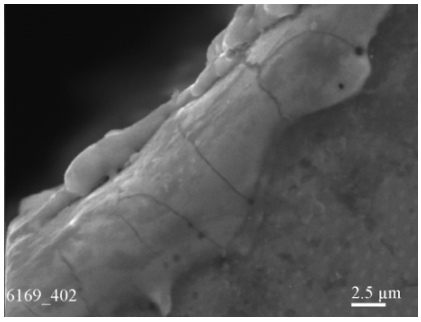
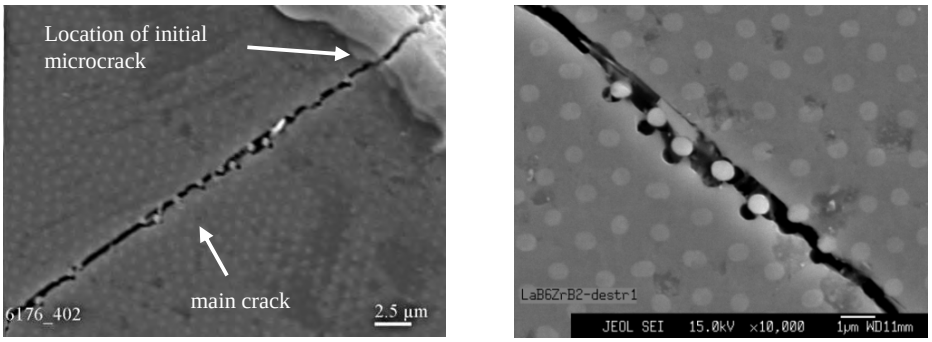


Fig. 5. The appearance of the crack edge in the LaB_6–ZrB_2 composite

During the fracture test, the specimens of both composites exhibit brittle failure. The main crack develops from one of the sharp microcracks that are introduced during electro-spark cutting (fig. 5a) and then propagates in the direction of introduced central crack independently from its type (<100> or <110>). For all the specimens the crack does not penetrate inside the fibers, but is deflected by them while propagation through the matrix (fig 6 b).



a) b)

Fig. 6. The main crack path in the <100> direction of LaB_6 matrix, visible on the face of the sample (LaB_6–ZrB_2 composite). a) development of main crack from one of microcracks; b) appearance of main crack at high magnification.

The results of fracture toughness test are shown in Table 2. It can be seen that the average value of fracture toughness for each type of cracks is more than 25% higher for LaB_6– $(Ti_{0.1}Zr_{0.9})B_2$ composites than for initial composites (LaB_6–ZrB_2). The results also show the presence of anisotropy in fracture toughness for different crystallographic orientations of introduced crack. The values of fracture toughness are higher in <100> direction of matrix than in <110> direction for both composites.

Table 2.
Fracture toughness values for samples of different composites with different crack orientations

Samples of composites with different crack orientations	$<K_{1C}>$, MPa*$m^{1/2}$
LaB_6–ZrB_2 <110>	6.05 ± 1.03
LaB_6–ZrB_2 <100>	7.03 ± 1.07
LaB_6–$(Ti_{0.1}Zr_{0.9})B_2$ <110>	8.19 ± 1.11
LaB_6–$(Ti_{0.1}Zr_{0.9})B_2$ <100>	8.97 ± 1.22

The difference in the peculiarities of failure mechanism can be seen from fig. 7. For cracks introduced in 100 direction, the higher amount of cleaved microplates of the material is observed on the fracture surface in comparison with the case of <110> cracks (fig. 7a, b). The fracture surface of the matrix phase tends to be flat and smooth for <100> cracks (fig. 7a, c). The clearly observed mechanism of crack interaction with the fibers is interfacial debonding.

The slight difference can be noticed between the appearance of the fracture surface in the previous case and in the case of the cracks that propagate in <110> direction. These cracks tend to be deflected nearby to the phase interface of certain part of fibers, but without interfacial debonding (fig. 7e). The mentioned trend becomes clearly distinct in the composites with Ti addition (fig. 7f). For both composites with <110> crack the matrix fracture surface does not lie in one plane.

The changes after addition of Ti can also be observed for the crack which is introduced in <100> direction (fig. 7c and d). Namely, the surface becomes less smooth close to the fiber-matrix interface. Such changes can be attributed to the increase of resistance to crack propagation due to formation of higher stresses nearby to fiber-matrix interface, and are in good agreement with increase of fracture toughness.

The differences in values of fracture toughness, as well as different appearance of the fracture surface for composites with Ti addition can be explained by the joint effect of the increase of interface cohesion strength and changes of fiber characteristics, such as Young's modulus, shear modulus, and coefficient of thermal expansion.

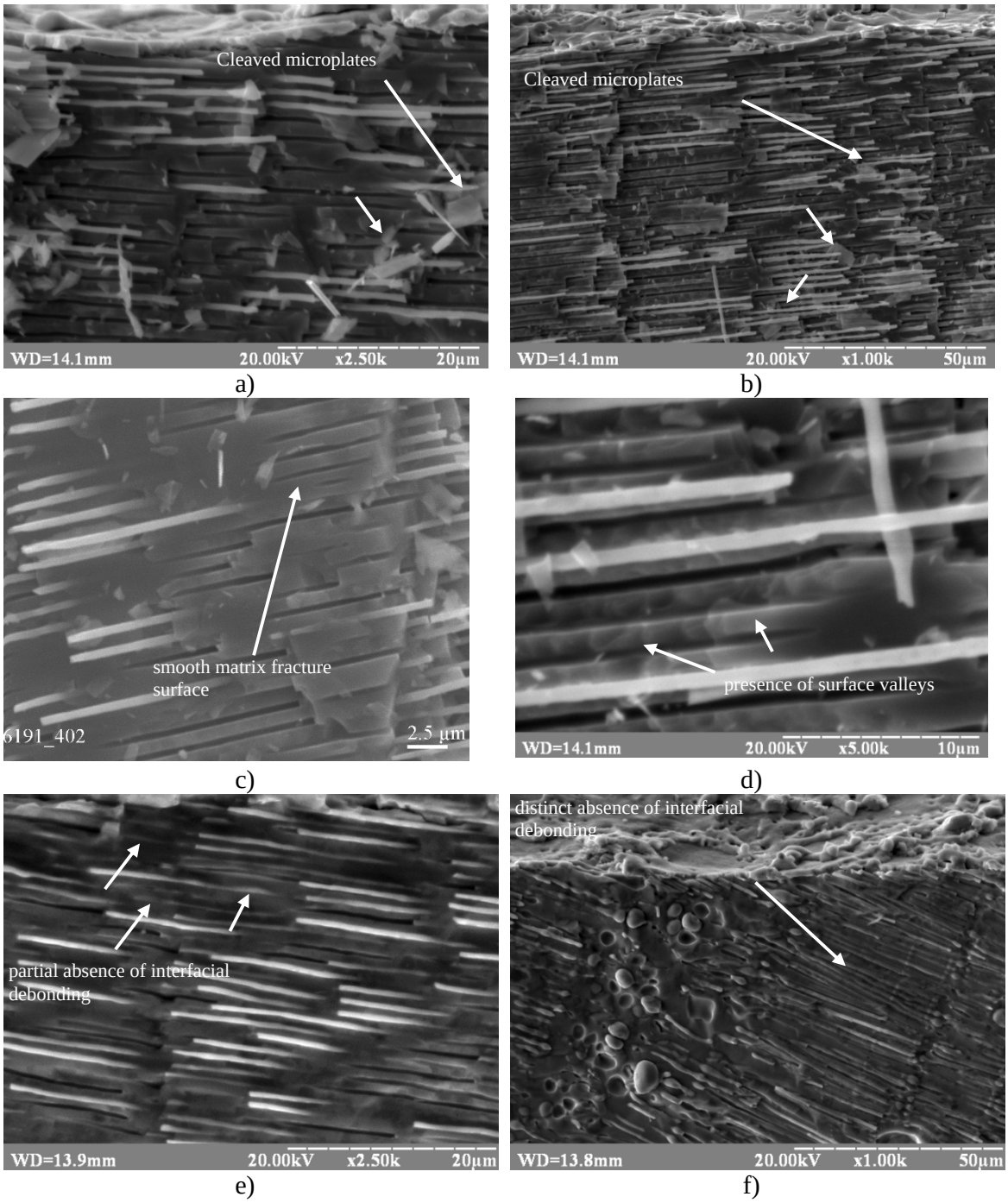


Fig. 7. Scanning microscopy photographs of fracture surface of the next composites, with the cracks introduced in the indicated directions of the matrix: a,c) LaB_6–ZrB_2, <100>; b,d) LaB_6–$(Ti_{0.1}Zr_{0.9})B_2$, <100>; c) LaB_6–ZrB_2, <110>; f) LaB_6–$(Ti_{0.1}Zr_{0.9})B_2$, <110>.

Additional evidence that under conditions of such a mechanism of destruction a decisive contribution to the change in energy of crack propagation in the material is provided by the interaction at the interface was given by TEM and HRTEM investigations (Fig.8)

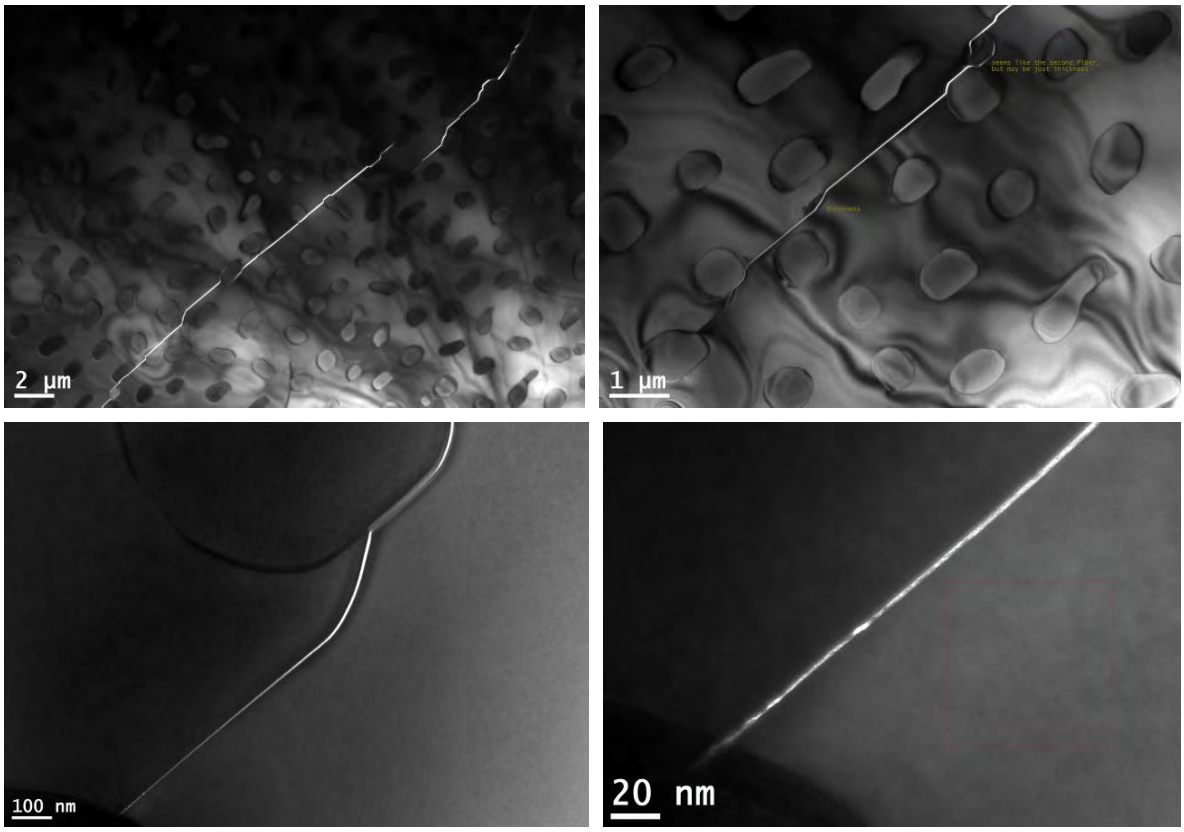


Fig. 8 TEM and HRTEM from LaB_6–$(Ti_{0,3}Zr_{0,7})B_2$ samples.

The effect of Ti addition on the fracture toughness and failure of LaB_6–ZrB_2 and LaB_6–$(Ti_{0,1}Zr_{0,9})B_2$ was studied. Investigation showed that:

1) The addition of Ti causes the 25% increase in K_{1C} in comparison to initial LaB_6–ZrB_2 composites. This increase is a result of stressed state alteration in the whole composite after the change of interaction between lattices of components on the interface.

2) The differences can be seen on the fracture surface after Ti addition both for <100> and <110> directions of crack propagation. For the first case, the fracture surface of matrix becomes less smooth due to presence of higher stresses nearby to matrix-fiber interface. For the second case, the trend of crack deflection without interfacial debonding becomes more significant.

3) For both composites K_{1C} in <100> direction is higher than in <110> one. It can be explained by the difference of crack interaction with the fibers. For the crack propagating in <100> direction, the effect of toughening by interfacial debonding is significant. The difference in crack interaction with fibers can be caused by the anisotropic distribution of stresses around fibers or anisotropic mechanical properties of matrix.

CONCLUSIONS

Complex of studies carried out in the last years (both within this project, and in collaboration with other research centers), and analysis of published data showed that high-boron compounds characterized by the presence of boron skeleton, in the pores of which the metal ions are located, is an ideal object for research that provides an opportunity to study the effect of replacement of one metal ion by the other one, that allows to design materials with desired properties.

A separate promising area of research is the study of the interaction at the phase interface in $Me^{I}B_6$ – $Me^{II}B_2$ systems, where a complete absence of mutual solubility of phases in the solid state can be achieved combined with both a change in the lattice parameters of each, and the level of interaction on the surface by using a range of metals and/or solid solutions thereof. This approach will allow to study the interaction of ions in terms of a two-dimensional spatial model.

In particular, unresolved remain the reasons for the changes of the predominant growth direction of the diboride fibers after replacing of some zirconium atoms for titanium ones, as well as the formation of lamellar/platelet-like eutectic in SmB_6-TiB_2 system.

New information about the state of the interface in the studied systems can allow to explain the change in the work function of eutectic materials when using diboride solid solutions.

Results and findings obtained in the course of the present project realization were presented as 6 talks at 6 scientific conferences, 2 articles were published in scientific journals.

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