

The primary phase part in microstructure formation of *in-situ* eutectic composite of $\text{LaB}_6\text{-ZrB}_2$

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The crystal orientation relationships (COR) of $\text{LaB}_6\text{-ZrB}_2$ eutectic phase produced by directional solidification (DS) correspond to non-optimum coherency conditions of phase boundaries. Another peculiar feature of this eutectic is the dominant role of primary low temperature phase (LaB_6) in the cooperative eutectic growth. As a rule, it is just the high-temperature phase that plays a leading role in the crystallization and promotes heterogeneous nucleation of the second phase. In contrast, in $\text{LaB}_6\text{-ZrB}_2$ eutectic system, the high-temperature ZrB_2 whiskers start to grow on (100) faces of low-temperature LaB_6 phase. A possibility of discrete changes in growth direction of the composite regular structure up to 90° has been revealed. It is suggested that all above mentioned features are defined mainly by the nucleation processes during the eutectic co-crystallization process, rather than by the ordinary fundamental criteria of interface surface energy minimization that occurs due to the semi-coherent habit facets formation.

Установлено, что кристаллические ориентационные соотношения фаз эвтектики $\text{LaB}_6\text{-ZrB}_2$, полученной методом направленной кристаллизации, соответствуют не самым выгодным условиям когерентности межфазных границ. Особенностью этой эвтектики является также превалирующая роль матричной, низкотемпературной фазы в процессе кооперативного эвтектического роста. В отличие от обычного случая, когда высокотемпературная фаза играет ведущую роль при эвтектической кристаллизации и является зародышеобразующей для второй фазы, в эвтектической системе $\text{LaB}_6\text{-ZrB}_2$ кооперативный эвтектический рост волокон высокотемпературной фазы ZrB_2 начинается на фасетах (100) низкотемпературной фазы LaB_6 . Обнаружена способность дискретного изменения направления роста регулярной структуры композита вплоть до 90° . Предполагается, что все упомянутые особенности определяются в основном процессами зародышеобразования во время кооперативной эвтектической сокристаллизации, а не привычными фундаментальными критериями минимизации энергии поверхности межфазных границ за счет формирования их полукогерентных габитусных поверхностей.

Heterogeneous interface is a source of new properties of modern composite materials. *In-situ* composites based on binary eutectics can be considered as the most outstanding family of such materials. The extreme technical properties of such materials are provided by means of directional solidification (DS) treatment and are defined by crystal orientation relationships (COR) and the composite microstructure topology. The latter characteristics depend on interaction peculiarities on the phase interface. More-

over, for the case of well-pronounced habit facets of the interface, the COR is defined as a rule by the interface surface energy minimization. Therefore, understanding of phase lattices conjugation along the interface, micro- and macro-characteristics of interface interaction, and the microstructure dependence from the solidification conditions is needed for technology optimization.

The DS eutectic (DSE) of $\text{LaB}_6\text{-ZrB}_2$ system possesses all above-mentioned features and peculiarities of the *in-situ* composites

that makes it quite useful as a model DSE. This compound is characterized by outstanding combination of properties such as excellent thermal shock resistance, high thermal emission capability, and chemical stability [1]. In this work, the material sample was shaped as a rod of about 8 mm in diameter. Its composition can be described as the LaB_6 single crystal matrix into which a "bunch" of hexagonal ZrB_2 single crystal fibers is incorporated [1]. The fibers of 0.4 to 0.6 μm in diameter and at least 100 μm length are oriented parallel to each other. The eutectic components have no mutual solid solubility and, as a result, the phase interface is very sharp (Fig. 1). The common feature of these composites is a limited number of fixed COR. The LaB_6 - ZrB_2 DSE shows one unique natural COR. This is $(100) \text{LaB}_6 \parallel (0001) \text{ZrB}_2$, $[01\bar{1}] \text{LaB}_6 \parallel [1\bar{1}00] \text{ZrB}_2$. Another possible COR $(111) \text{LaB}_6 \parallel (0001) \text{ZrB}_2$, $[110] \text{LaB}_6 \parallel [1\bar{1}00] \text{ZrB}_2$ is realizable only if a single crystal seed of the LaB_6 matrix phase oriented along the (111) normal is used for the growing. That COR has been already practically realized but it is not investigated to date [3, 4].

The DSE atomic structure of interface boundary (ASIB) was investigated in order to understanding better its structure and to determine the regulation possibilities of its formation and properties by varying the crystallization rate.

The analysis of high-resolution transmission electron (HRTEM) micrographs of the interface (Fig. 1a) allows suggest that LaB_6 - ZrB_2 is a new eutectic structural type of *in situ* eutectic composite. However, to reach some final conclusions, a full-scale investigation of the interface along the fiber is necessary. The comparison of the LaB_6 - ZrB_2 composite structure with other *in situ* DSE composites described in the literature reveals a number of differences. The HRTEM (Fig. 1a) shows that the habit atomic planes along the interface are not semi-coherent. Consideration of the data on other DSE shows that even if the interface is macroscopically smooth (not faceted), nevertheless, on the microscopic scale the interface is formed by "habit" crystal low index planes with semi-coherent conjugation interrupted by steps. The spatial frequency of steps regulates macroscopic curvature of the interface. The semi-coherency is a way to minimize the interface surface energy, and the problem of COR deduction from optimal interface semi-coherency becomes a non-trivial task. As it is clearly seen from

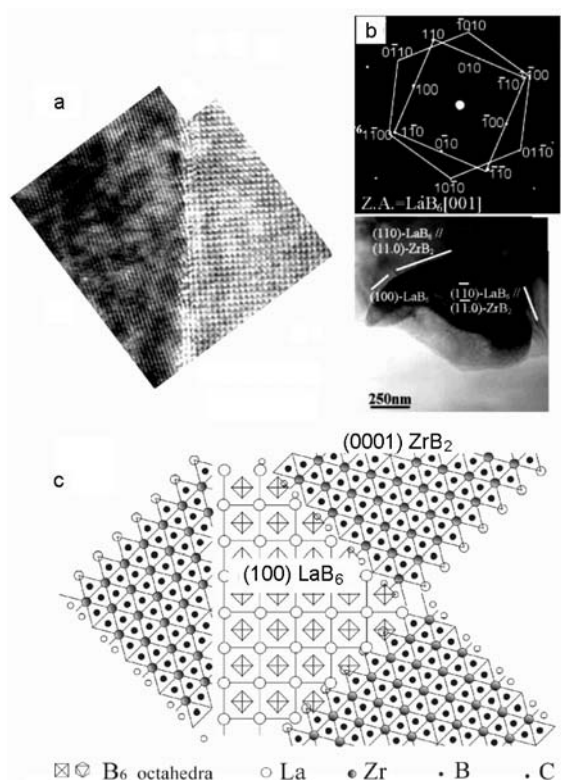


Fig. 1. a) HRTEM photograph of interface of transversal section of DSE. b) Electron diffraction pattern for COR of DSE. c) Scheme of atomic structures for possible facets.

the HRTEM presented in Fig. 1a, there exist fragments of real interface without any coherency at all. Furthermore, the naturally formed COR cannot be considered as an optimal one.

The coherency parameters are presented in Table. The COR characterized in the row 4 shows the best possible parameters, i.e., minimal misfits ($\Delta d/d$). As it has been mentioned above, such COR is realizable only under special conditions. Moreover, HRTEM investigation of interface atomic structure for a real fiber (Fig. 1a) reveals that the habit plane $\{100\}$ in LaB_6 does not have any corresponding low index plane in ZrB_2 . Consequently, this part of the interface is not coherent. However, according to a schematic representation of the possible interface atomic configuration (Fig. 1c), at least two other variants of the habit plane orientation can satisfy the semi-coherent condition. The semi-coherency criteria were chosen by the generalization of 17 most thoroughly investigated *in situ* composites among all ones referred to in Chemical Abstracts since 1967. All 17 composites have both well defined COR and interface facets,

Table. COR parameters of DSE and phase lattices conjugation at the interface

No.	Phases		Lattice type	Interface type. Comments.	COR ("H" — habit surface, "DS" — direction of solidification)	Interplane spacing $d(hkl)$ (Å)		Ref.
	α	β				$d(hkl) \alpha$	$\frac{\Delta d}{d}$, (%)	
						$d(hkl) \beta$		
1.	LaB ₆	CaB ₆	Surface of DSE fibers	[100] LaB ₆ [0001] ZrB ₂ — DS, [01 $\bar{1}$] LaB ₆ [1 $\bar{1}$ 00] ZrB ₂	$d(100) = 4.156$	14	[2-4]	
	ZrB ₂	AlB ₂			$d(0001) = 3.528$			
					$d(01\bar{1}) = 5.876$	7		
					$d(1\bar{1}00) = 5.487$			
					$d(011) = 5.876$	7		
				$2d(11\bar{2}0) = 6.336$				
2.	TiC	NaCl	Surface of DSE lamellas	(111) TiC (0001) TiB ₂ — H, [011] TiC [01 $\bar{1}$ 0] TiB ₂ — DS	$d(011) = 3.06$	1	[7]	
	TiB ₂	AlB ₂			$d(01\bar{1}0) = 3.03$			
3.	ZrC	NaCl	Surface of DSE lamellas	(111) ZrC (0001) ZrB ₂ — H, [011] ZrC [01 $\bar{1}$ 0] ZrB ₂ — DS	$d(011) = 3.32$	5		
	ZrB ₂	AlB ₂			$d(01\bar{1}0) = 3.168$			
4.	LaB ₆	CaB ₆	COR for minimum misfit.	(111) LaB ₆ (0001) ZrB ₂ , [01 $\bar{1}$] LaB ₆ [1 $\bar{1}$ 00] ZrB ₂	$d(111) = 7.198$	2	[3,4]	
	ZrB ₂	AlB ₂			$2d(0001) = 7.056$			
					$d(01\bar{1}) = 5.876$	7		
					$d(1\bar{1}00) = 5.487$			
					$d(011) = 5.876$	7		
				$2d(11\bar{2}0) = 6.336$				

and precisely defined crystal orientation parameters. Based on this data, we can claim that semi-coherent interface is realized when the lattice misfit does not exceed 15 %, independently of the composite type: metal-metal, metal-ceramic, or ceramic-ceramic.

For LaB₆-ZrB₂, the most preferable habit combination is (110) LaB₆ || (1 $\bar{1}$ 00) ZrB₂ (see Fig. 1c, right lower corner). Such atomic structure allows that one boron pair may be a common part of the boron sublattices of both phases. The idea of "joining boron pair" [3, 4] explains the natural COR. Moreover, this hypothetical suggestion proved to be in good agreement with the experimental data on mechanical strengthening of DSE composites [5, 6]. The simplest explanation is that COR is determined by two details of interface. First, the joining of boron pairs is possible in that interface area where its surface is parallel to (110) LaB₆ || (1 $\bar{1}$ 00) ZrB₂ planes (Fig. 1c, right lower corner of the scheme). Second, it is possible at picks of steps of other crystal habit plans, such fragment is shown in Fig. 1a. A fundamental question is the cause or way of energy minimization of non-coherent interface surface. This leads to the only possible suggestion based on the previous investigations:

those peculiarities of phase lattices conjugation along interface are determined by directional covalent character of bonds in boron sublattices.

The kinetic characteristics of solidification can also effect COR of DSE. The most possible candidates among such factors are thermal conductivity anisotropy of crystalline phases and different growth rates along different crystal orientations. The more complicated factor is directional anisotropy of heterogeneous nucleation. It defines the grain habits at homogeneous solidification. The heterogeneous nucleation during cooperative eutectic solidification effects the final interface properties and the composite structure. The character of the latter for LaB₆-ZrB₂ system does not correspond with any of the known eutectic structures types investigated to date [8]. It would be useful to recall the basic model details of cooperative eutectic solidification process [9]. It includes a number of features different in nature, among them, the semi-coherency. The phases of an eutectic composition can be subdivided into the "leading" and "driven", nucleating and non-nucleating, and primary and minor. Leading is, as a rule, the high temperature component. Its precipitates

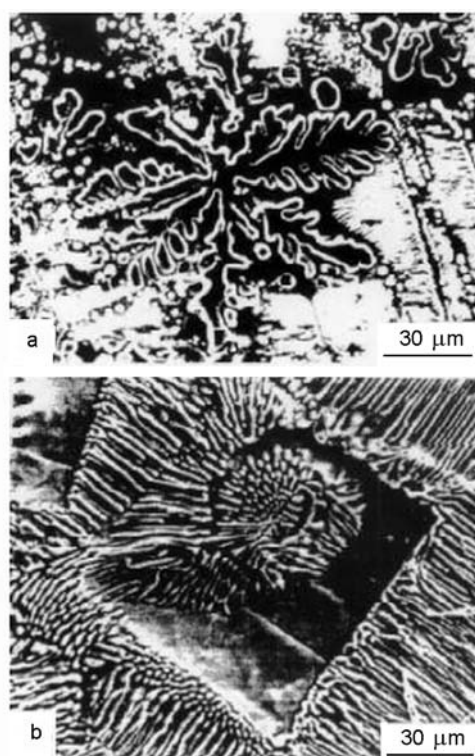


Fig. 2. Microstructure of $\text{LaB}_6\text{-ZrB}_2$ alloys: hyper-eutectic (a) and hypo-eutectic (b) composition [10].

crystallize slightly ahead of the averaged, common solidification front. It is just that component that is supposed to nucleate the cooperative eutectic growth, however, not in our case. This property is difficult to predict because it is related with the ratio of surface energies of eutectic components.

The investigation of $\text{LaB}_6\text{-ZrB}_2$ eutectic shows that it is just low temperature phase LaB_6 that nucleates the cooperative eutectic growth. This can be clearly seen from the microstructure of hyper- and hypo-eutectic in Fig. 2. The ZrB_2 seed is surrounded by the continuous layer of LaB_6 phase after which the eutectic structure starts, while the cubic LaB_6 grain in the hypo-eutectic composition just generates the growth of eutectic ZrB_2 fibers. The latter micrograph illustrates another outstanding property of this composition: ZrB_2 fibers grow preferably in alignment along $\{100\}$ of a LaB_6 grain. Thus, the matrix component is definitely nucleating one [9]. The microstructure observed at the early stages of regular DSE growth (Fig. 3) also shows the tendency of ZrB_2 fibers to nucleate along $\{100\}$ LaB_6 termination plate surface. The local growth direction must be normal to average temperature gradient which coincides with

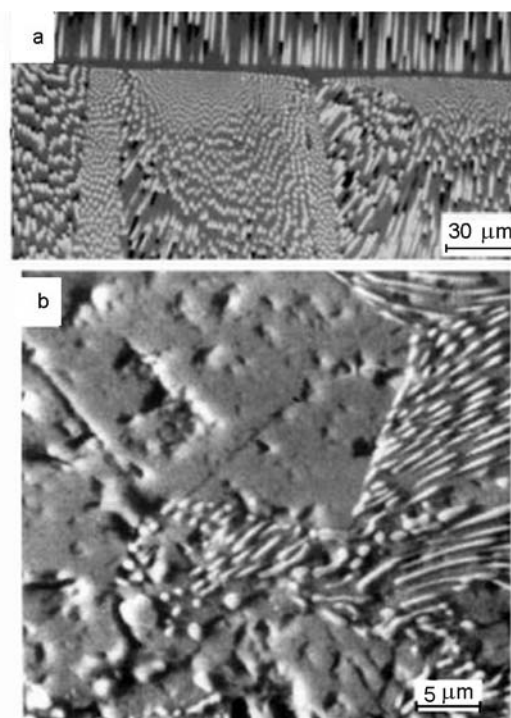


Fig. 3. Microstructure of $\text{LaB}_6\text{-ZrB}_2$ DSE: a) termination plate [2], b) starting DSE formation at the surface of re-crystallized LaB_6 grain.

the zone melting direction. The abnormal fiber growth rate as estimated by Jackson model [11] is about 10 times higher than the zone melting rate. It should be noted that the latter estimation describes the structure that is formed as a result of deviation or disruption of the regular eutectic growth. In such case, the Jackson model cannot be considered as correct. Nevertheless, from the above mentioned facts, we can assume the existence of a particular process of heterogenous nucleation of ZrB_2 fibers along $\{100\}$ LaB_6 . The most striking effect of this tendency may be the unique but non-optimal COR.

The capability of discrete growth direction change in the regular structure at a right angle has been revealed on the subboundary between two eutectic grains (see Fig. 4). The COR of this fragments are not investigated, but the change mentioned may result from the trend of fiber growth along cubic planes of the matrix. Note that such a capability was not observed before for this composite type [8].

The following conclusions can be formulated. The natural COR of $\text{LaB}_6\text{-ZrB}_2$ DSE is in dual contradiction with the semi-coherent principle of interface energy minimization. First, the real COR shows a non-optimal possible misfit along the interface, and the

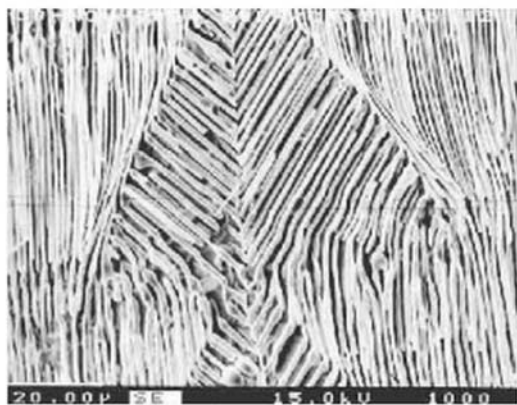


Fig. 4. Abnormal DSE growth at the sub-boundary between two eutectic grains (growth direction downwards).

structure with optimal misfit is not realized naturally. Second, for the real COR, the fragments of non-coherent interface appear. The peculiarities of interaction between components at the interface may represent a new type atomic structure of *in situ* eutectic composites which are defined by heterogeneous nucleation during solidification. The effect of discrete change of growth direction of regular DSE structure at a right angle occurs at sub-grain boundary between two eutectic bicrystals.

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Роль основної фази у формуванні мікроструктури *in-situ* евтектичного композиту $\text{LaV}_6\text{-ZrV}_2$

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Встановлено, що кристалічні орієнтаційні співвідношення фаз евтектики $\text{LaV}_6\text{-ZrV}_2$, що отримана методом спрямованої кристалізації, відповідають не найбільш вигідним умовам когерентності міжфазових меж. Особливістю цієї евтектики також є головуюча роль матричної, низькотемпературної фази у процесі кооперативного евтектичного росту. На відміну від звичайного випадку, коли високотемпературна фаза є ведучою евтектичну кристалізацію і зародкоутворюючою для другої фази, в евтектичній системі $\text{LaV}_6\text{-ZrV}_2$ кооперативний евтектичний ріст волокнин високотемпературної фази ZrV_2 починається на (100) фасетах низькотемпературної фази LaV_6 . Виявлено здатність дискретної зміни напрямку росту регулярної структури композиту на кути до 90° . Припускається, що усі згадані особливості визначаються в загальному зародкоутворюючими процесами кооперативної евтектичної кристалізації, а не звичними, фундаментальними критеріями мінімізації енергії поверхні міжфазових меж за рахунок формування їх напівкогерентних габітусних фасет.