



Ceramic materials of the quasi-binary LaB_6 – MoB_2 system

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Abstract

Alloys of the quasi-binary LaB_6 - MoB_2 system synthesized by melting in an atmosphere of helium have been studied. It has been established that the phase diagram of the system is eutectic and the phases do not interact. The eutectic colony crystallizes in form of the platelike eutectic on the basis of the LaB_6 crystal of a cubic structure. It has been also shown that the crystallization from melt under conditions of crucibleless zone melting is accompanied by the MoB_2 phase decomposes during cooling with precipitation of the submicron Mo_2B_5 and α - MoB crystallites. This results in an increase of hardness. According to the Mo – B phase diagram, the decomposition temperature of the MoB_2 increases with increasing the boron content. In addition, the degree of the decomposition is higher if the melting point of alloy is higher, since the intensity of diffusion process increases at high temperatures.

Keywords: ceramics, eutectic alloy, crucibleless zone melting, metal boride

I. Introduction

Boride-based ceramics are widely used in engineering as wear resistant materials for sputtering and melting of machinery surfaces or fabrication of nozzles for sand blasters. Materials on the basis of lanthanum hexaboride are ideal for cathodes, which provide a strong base for the development of modern electron-beam technologies for sputtering, welding and dimensional processing of metals and alloys.

The principal shortcoming of boride-based materials as materials for cathodes is low impact toughness, 2–5 $\text{MPa}\cdot\text{m}^{1/2}$. This can be improved at the expense of reinforcement with fibers or through synthesis of materials with eutectic composition, which, in general, are considered as natural composites. Since, in working conditions cathode is heated with a rate of 1000–1500°C/min, it is necessary to increase the heat conductivity, strength, and fracture toughness of cathode materials. Strengthening with the fibers as well as rods formed in eutectic alloys under conditions of directed crystallization provides the best results [1–3]. However, strength and fracture toughness of such composite materials are influenced by the nature of matrix and fibers of composite materials. Therefore the search of quasi-binary

systems with an eutectic character of the phase diagram and a rodlike form of one of the eutectic phase components is an urgent problem. Seven quasi-binary systems LaB_6 - MeB_2 where Me – Ti, Zr, Hf, V, Nb, Ta, Cr have been studied by many researchers and reviewed in ref. 4.

In the present work the phase diagram, the process of structure formation and properties of the eutectic alloy of the LaB_6 - MoB_2 system have been studied for the first time.

II. Experimental

According to the Mo – B phase diagram [5,6], at high temperatures molybdenum diboride exists as a phase of variable composition, namely $\text{MoB}_{1.9-2.49}$ (66.6 at% B – 71.4 at% B). In this work, a diboride of intermediate composition in the homogeneity region namely $\text{MoB}_{2.2}$ with a melting point of 2230°C was used, since insignificant changes in its chemical composition cannot affect its properties and process of crystallization of the LaB_6 - MoB_2 alloys.

$\text{MoB}_{2.2}$ was synthesized from mixture of elements: 19.9 mass% (68.8 at%) boron and the rest was molybdenum. Polyvinyl alcohol as a plasticizer was added to the mixture. The prepared mixture was pressed under a pressure of 50 MPa and dried at about 100°C for 5 h. The water evaporated, and polymerization of the

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polyvinyl alcohol occurred, which led to an increase in the strength of samples. This procedure was also used in the preparation of samples for melting of the LaB_6 - $\text{MoB}_{2.2}$ alloys. The samples were heated in a vacuum furnace up to 1600–1700°C and held for 1 h. Then they were milled to fractions under 40 μm . The X-ray analysis showed that the product is $\text{MoB}_{2.2}$ with the following lattice parameters: $a = 0.3032$ nm, $c = 0.3096$ nm and $c/a = 1.021$ (for comparison, the parameters of the stoichiometric molybdenum diboride are: $a = 0.3026$ nm, $c = 0.3060$ nm and $c/a = 1.014$).

Ceramic materials of the LaB_6 - MoB_2 system were produced using a method of crucibleless melting of pressed compacts— LaB_6 , $\text{MoB}_{2.2}$ and their mixtures (with 20, 40, 60, and 80 mass% $\text{MoB}_{2.2}$ and in the eutectic region 62, 63, and 64 mass% $\text{MoB}_{2.2}$). Before melting all samples were pressed under a pressure of 100 MPa. Temperature was measured by an optic pyrometer with an accuracy of $\pm 50^\circ\text{C}$ on three samples of each composition.

Upon melting, samples were cut and prepared for metallographic examination. The structure of alloys was studied on an optic microscope Neophot–21. Microhardness and crack resistance were determined using a microhardnessmeter PMT–3 with a Vickers pyramid (load on indenter 1.5 N). X-ray diffraction spectra were obtained on a DRON–3M unit with a graphite monochromator in $\text{Cu}_{K\alpha}$ radiation.

III. Results and Discussion

Lanthanum hexaboride has a cubic structure of the space group $\text{O}^1\text{h-Pm}3\text{m}$ of the structure type CaB_6 , and molybdenum diboride has a hexagonal structure of the space group $\text{D}^16\text{h-C6/mmm}$ of the structure type AlB_2 . The distances between boron atoms in these compounds differ insignificantly.

The peculiarities of changes in the melting point and microstructure of the LaB_6 - MoB_2 alloys of different compositions evidence to an eutectic character of the alloys crystallization (Fig. 1). The starting temperature of

melting was evaluated as an average of the corresponding values for three samples.

In the eutectic the content of $\text{MoB}_{2.2}$ is 63 mass%. The temperature of the eutectic transformation is 2130°C . The phases do not interact. The structure of the alloys is shown in Fig. 2. In the under-eutectic alloys the molybdenum diboride phase crystallizes along the boundaries of lanthanum hexaboride crystals, whereas in the over-eutectic alloys it precipitates in the form of cubic crystals and the eutectic has a fine-grained structure composed of hexaboride lanthanum and diboride molybdenum layers.

The structure of the alloys can be easily seen from the thin sections of eutectic colonies (Fig. 3). Firstly, one can conclude that the principal part in the formation of eutectic colony is played by the LaB_6 phase, which initiates eutectic crystallization. As seen, eutectic colonies are crystallized on primary single crystals, i.e. LaB_6 cubes. This is natural as this phase has relatively high entropy of melting (468.16 kJ/mol compared to 96.14 kJ/mol for MoB_2).

Secondly, in order to imagine the process of the eutectic colony crystallization, let us examine the structure shown in Fig. 3, where cross sections of the colonies formed on the basic cubic LaB_6 crystal are presented. It can be seen that there is (Fig. 3a) a square of purple colour, which is a LaB_6 plate. From its corners dark (cherry colour) diagonals originate, which are sections of the eutectic pyramids faces. This indicates that pyramids are separated from each other by LaB_6 plates. So, in the section there are four trapeziums, small bases of which are located on the square sides. The trapeziums have a lamellar structure composed of LaB_6 and MoB_2 plates parallel to the LaB_6 cube faces. The partition of this colony is made by the cube (001) plane. In Fig. 3b another colony can be seen, namely a three-beam star. It is cut by the octahedron (111) plane and, naturally, has the structure of LaB_6 or MoB_2 plates inclined to the pyramid faces with an angle of 45° . In the first case, four trapeziums with a small base on the basic cube crystal plane (001) are dissected, in the second case—three on the (111) plane.

Thus on the basis of examination of the colony structure layers, one can draw a conclusion that the colony is composed of six four-face pyramids on the basic cubic LaB_6 crystal. Herein, the eutectic pyramids are cut by plates of lanthanum hexaboride, which are formed owing to growth of the basic LaB_6 cube edges and at the intersects of the pyramids faces the eutectic of a platelike structure grows. As seen, as a whole, the eutectic colony consists of a two-phased cube and has a structure of the basic crystal with high melting entropy.

The structure of the eutectic LaB_6 - MoB_2 colony exactly corresponds to the structure of the classic eutectic Bi-Sn colony, in which eutectic grows in the form of rodlike-structured pyramids on the basic bismuth rhombohedron crystal [7].

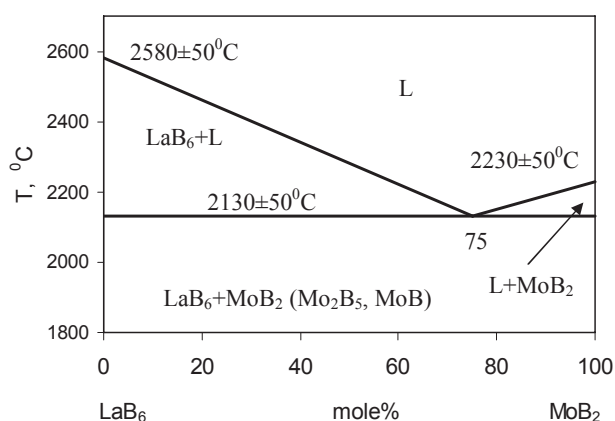


Figure 1. Melting diagram for the LaB_6 - $\text{MoB}_{2.2}$ system

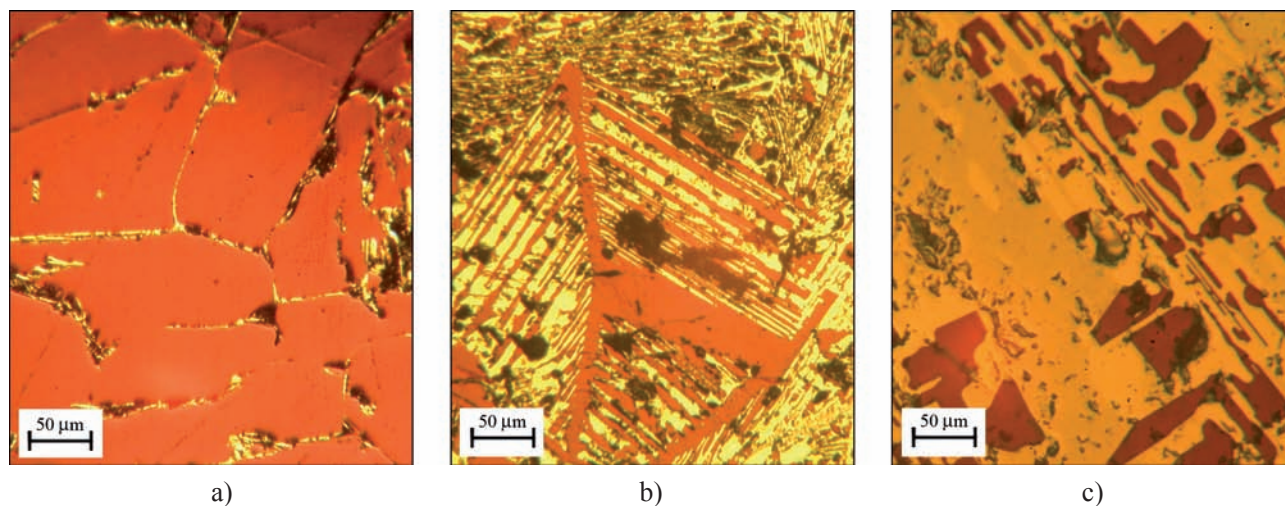


Figure 2. Microstructure of (a) undereutectic, (b) eutectic, and (c) overeutectic $\text{LaB}_6\text{-MoB}_{2.2}$ alloys

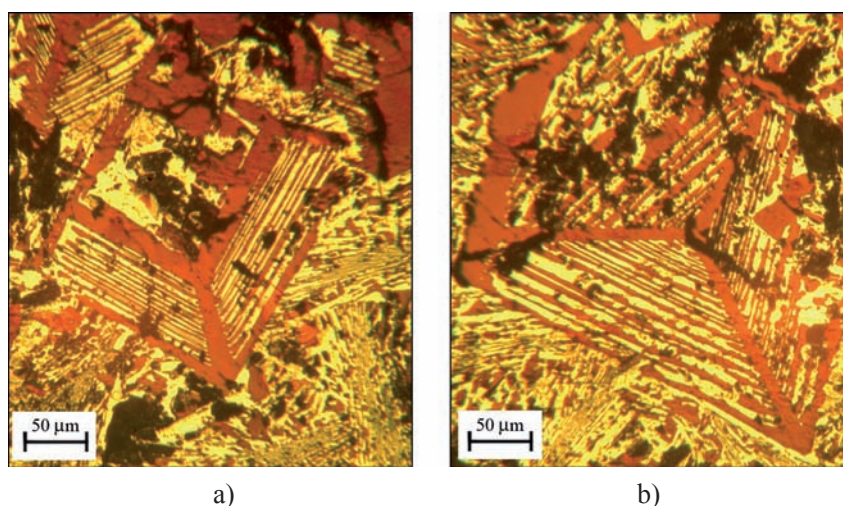


Figure 3. Cross section of colonies of the $\text{LaB}_6\text{-MoB}_{2.2}$ eutectic by the cube (001) (a) and octahedron (111) (b) planes

Table 1. Properties of the $\text{LaB}_6\text{-MoB}_{2.2}$ alloys

Portion of MoB_2		Melting temperature T_m [°C]	Hardness [GPa]	
[mass %]	[mol %]		LaB_6 phase	MoB_2 phase
0	0	2580	19,8	—
40	53,5	2250	19,8	26
63*	75	2130	—	32
80	87,4	2180	19,8	25
100	100	2230	—	28

* Eutectic

Properties of the $\text{LaB}_6\text{-MoB}_{2.2}$ alloys are consistent with those of eutectic systems with no phase-phase interaction (Table 1).

As follows from these data, the microhardness of lanthanum hexaboride remains the same in all of the alloys while that of molybdenum diboride changes in under- and overeutectic alloys: the higher the melting point of alloy, the higher its microhardness. Such dependence can be interpreted in the only way: according to the phase diagram Mo-B. Upon melting the $\text{MoB}_{2.2}$

phase decomposes into MoB_2 and Mo_2B_5 in the temperature range 2130–1500°C and below 1500°C the eutectic decomposition of the diboride into MoB and Mo_2B_5 is occurred. The amount of the formed Mo_2B_5 increases with increasing the melting point of alloy, so in such a case the hardness of the phase (which actually is non-equilibrium since under rapid cooling diffusion processes does not have enough time to be realized) increases as well. This is confirmed by X-ray diffraction analysis (Fig. 4), which identifies the phase as a mixture of three

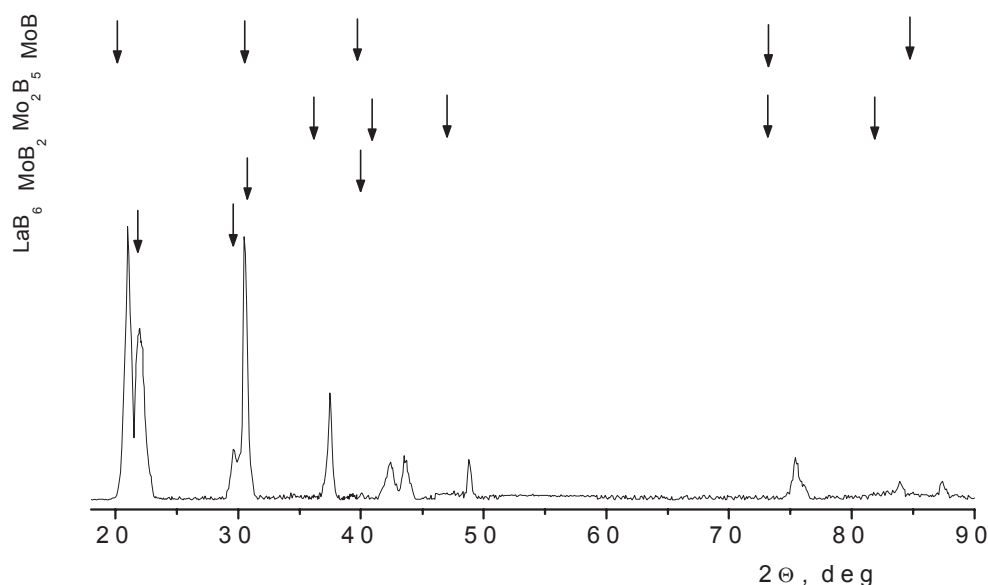


Figure 4. XRD pattern of the eutectic $\text{LaB}_6\text{-MoB}_{2.2}$ alloy. The arrows indicate the positions of the reflection maxima of the MoB , Mo_2B_5 , MoB_2 and LaB_6 phases

phases MoB_2 , Mo_2B_5 , and MoB , in which the interplane distances practically correspond to the reference ones. None of these phases in a pure state has such a high microhardness (microhardness of the Mo_2B_5 phase is the highest and equal to 23.5 GPa).

IV. Conclusions

The results obtained indicate that the phase diagram of the $\text{LaB}_6\text{-MoB}_{2.2}$ alloys has an eutectic character with coordinates of the eutectic point $T_m \text{ eut. K} - 2130^\circ\text{C}$, 75 mol % $\text{MoB}_{2.2}$. In the ternary La-Mo-B system this is a quasi-binary eutectic form.

The data of metallographic and X-ray analyses evidence to the absence of components dissolution.

The eutectic has a platelike structure. The eutectic colonies grow in the form of four-face pyramids on the (001) planes of the basic LaB_6 crystal.

The microhardness of the LaB_6 phase in the alloys studied does not change, whereas that of the $\text{MoB}_{2.2}$ phase increases with rising the melting point of the alloys due to its decomposition into submicron Mo_2B_5 and $\alpha\text{-MoB}$ crystallites during rapid cooling under conditions of crucibleless zone melting. According to the Mo – B phase diagram, the decomposition temperature of MoB_2 increases with increasing the content of boron. The higher the melting point of alloy, the higher the de-

gree of decomposition since the intensity of diffusion processes increases at high temperatures.

The microhardness of the alloy of eutectic composition is higher than that of pure phases (similar to uppermost eutectic alloys).

References

1. K.I. Portnoi, B.N. Babich., I.L. Svetlov, *Composite nickel-based materials*, Metalurgiya, Moscow 1979.
2. P.I. Loboda, Yu.I. Bogomol. "The thermal stability of the directionally reinforced boride ceramics microstructure", *Ceramics*, **69** (2002) 117–124.
3. P.I. Loboda, G.P. Kysla, Yu.I. Bogomol, M.A. Sysoev, "Effect of crystalline orientation of matrix and rod diameters on properties of directionally crystallized eutectic alloys", *Metallofizika, Novejshye Tehnologii*, **28**, (2006) 147–155.
4. S. Ordanyan, "On regularities of interaction in the $\text{LaB}_6\text{-MoB}_2$ systems", *Neorganicheskie Materialy*, **24** [2] (1988) 235–238.
5. Yu.B. Kuzma, N.F. Chaban, *Binary and ternary systems containing boron*, Metalurgiya, Moscow 1990.
6. Yu.B. Kuzma, *Crystal chemistry*, Vyshcha shkola, Lviv 1983.
7. Yu.N. Taran, V.I. Mazur, *Structure of eutectic alloys*. Metalurgiya, Moscow 1978.