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Some Peculiarities of Eutectic Crystallization of LaB_6–(Ti, Zr)B_2 Alloys

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The structures of eutectic LaB_6–(Ti, Zr)B_2 alloys are studied after directional crystallization. The eutectic compositions and monovariant equilibrium between two quasibinary eutectics in this system were determined. Varying the TiB_2/ZrB_2 borides ratio permits us to control in their solid solutions the corresponding cell dimensions and, consequently, the boron–boron distances in the resulting quasibinary borides. Our previous assumptions that the perfectness of the real structure is determined by differences in the distances between boron atoms in boron sublattices of hexa- and diboride phases were confirmed. It is shown that forming the regular whiskers structure is much easier for complex (Ti, Zr)B_2 boride than for individual TiB_2 or ZrB_2 borides. © 2000 Academic Press

Key Words: **boride; eutectic; direction crystallization.**

INTRODUCTION

Recently during investigation of direction crystallization of quasibinary boride alloys in the LaB_6–MeB_2 (where *Me* is any *d*-transition metal) system the existence of a specific crystallographic correlation between both boride phases was observed which determined the regularity of obtained fiberlike eutectic structure (1, 2).

It was assumed that the structure of the composite should be more perfect when the boron–boron distances in the boron sublattices of both borides coincide (3). It was assumed also that the fiber diameter and their volume content may correlate with differences in the boron–boron distances.

EXPERIMENTAL

In this work, in order to check assumption of a correlation between the boron–boron distances and the real structure of eutectic alloys, solid solutions in the TiB_2–ZrB_2 system were chosen as the diboride component of the eutectic boride system.

It is known that in this system a continuous solid solution exists (4–6). According to (4) the parameter *a* of its hexagonal structure, which determines the boron–boron distance in the boron sublattice, is changed in this system close to linear dependence, and then it is possible to evaluate this values for different TiB_2–ZrB_2 compositions. The corresponding values of boron–boron distances in the studied borides are presented in Table 1.

By directional crystallization from the melt the thermodynamic equilibrium structure is formed at the crystallization temperature. Due to the difference in the thermal expansion coefficients of boride phases we should compare only the boron–boron distances at the same temperature. Unfortunately experimental data for the cell parameters of the studied borides close to the crystallization temperature (~ 2800 K) are absent, and thus we evaluated the values of boron–boron distances for such conditions using known data for thermal expansion coefficients (7, 8). The obtained data are also given in Table 1. It is seen that boron–boron distances in LaB_6 hold an intermediate position among TiB_2 and ZrB_2 and it is obvious that in any mixed (Ti, Zr)B_2 boride this distance should coincide.

The directional crystallization of the boride eutectic composition was performed using the induction zone melting method described in (9, 10). As source materials powders of LaB_6, TiB_2, and ZrB_2 borides mixed in corresponding proportions were used. The eutectic composition was evaluated on the basis of the regularity and perfectness of the composite crystal structure, as it was shown (11) that regular structure in such alloys usually exists only when its composition coincides with the eutectic.

RESULTS AND DISCUSSION

Figure 1 shows the differences in structure pictures for LaB_6–$(Ti_{0.5}Zr_{0.5})B_2$ composition for molar contents of LaB_6 of 66% and 63%. It is seen that in these cases the composition is shifted from the eutectic point to hypoeutectic and hypereutectic. In the first case (Fig. 1a) the visible inclusion according to X-ray diffraction analyses results from the LaB_6 boride phase and in the second (Fig. 1b)

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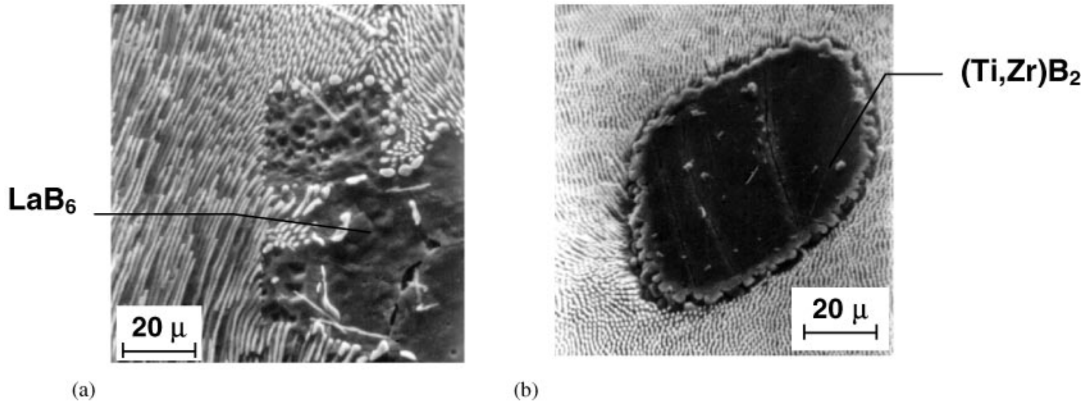

FIG. 1. Structure of LaB_6–$(Ti_{0.5}Zr_{0.5})B_2$ composition for molar content of LaB_6 66% (a) and 63% (b).

$(Ti, Zr)B_2$ solid solution. It is worth mentioning that in the case of a diborides solid solution the quantity of the single phase inclusions and their dimensions are much less than in the case of individual diborides, which agrees with broadening of the eutectic structure region in many component systems.

Figure 2 represents the structures of the eutectic composition in the LaB_6–$(Ti_xZr_{1-x})B_2$ system for different Ti/Zr ratios. The evaluation of the boron-boron distance at 2800 K for the TiB_2–ZrB_2 solid solution according to Vegard's rule shows that it coincides with the distance in the LaB_6 phase a composition near 22 mol% of Zr in the $(Ti, Zr)B_2$

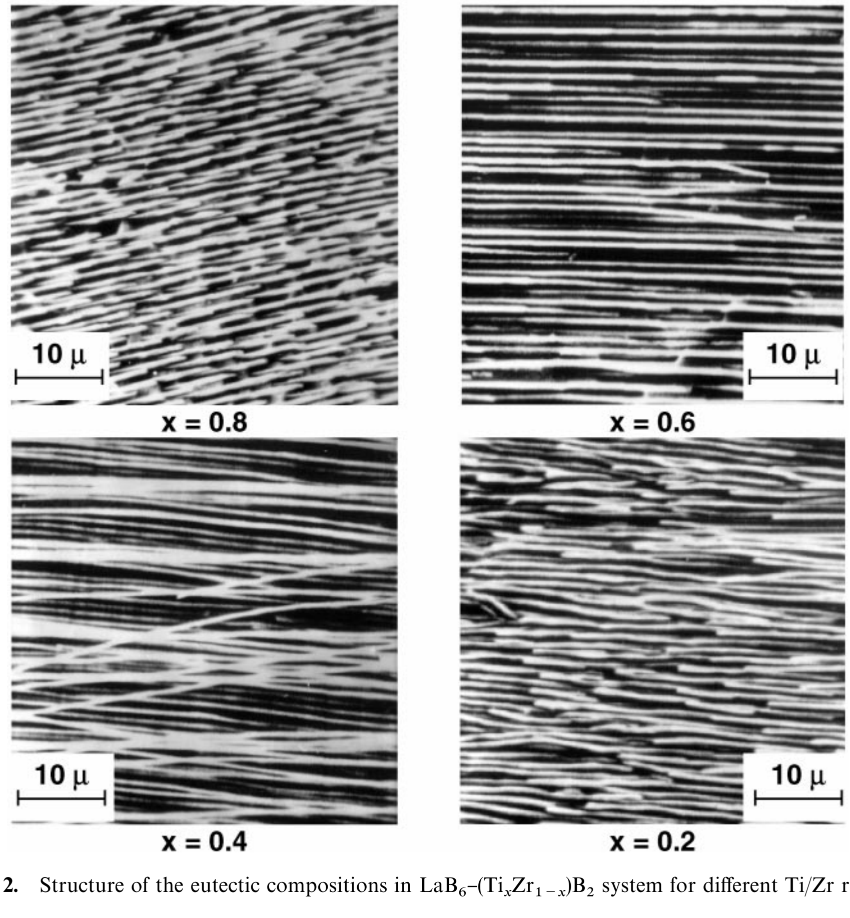

FIG. 2. Structure of the eutectic compositions in LaB_6–$(Ti_xZr_{1-x})B_2$ system for different Ti/Zr ratios.

TABLE 1
Boron–Boron Distances in Studied Borides at Room Temperature and Near 2800 K

Boride	B–B distance, nm at room temperature	 ~ 2800 K
LaB_6	0.1755	0.1791
TiB_2	0.1750	0.1772
ZrB_2	0.1830	0.1859

phase. Keeping in mind the negative deviation from Vegard's rule of the cell parameters in the TiB_2–ZrB_2 system (4), the coincidence may be achieved for composition shifted to the ZrB_2 direction. Really it is seen that the perfection of whiskers is better for a Ti/Zr ratio of ~ 3/2 than for other compositions. From Fig. 2 it is seen also that the thickness of fibers increases for mixed (Ti, Zr)B_2 boride in comparison with the individual borides, as evidenced by the lower misfit of boron–boron distances in the LaB_6 and MeB_2 phases.

Using the fact that the regularity of the eutectic structure is more perfect at the eutectic composition, the evaluation of such compositions for the studied system was made. The obtained picture of monovariant equilibrium between two quasibinary eutectic compositions in the quasiternary LaB_6–TiB_2–ZrB_2 system is shown in Fig. 3.

It is known that the strength properties of whiskers (fibers) strengthened compositions increase with the volume constitution of whiskers phase (12). In our case such growth is observed in the case of solid (TiB_2–ZrB_2) solutions in comparison with individual diborides. Due to differences in the density of the TiB_2 and ZrB_2 borides (4.52 and 6.09, respectively) the volume part of the mixed diboride phase also is increased (Fig. 4). According to what is known for fiber composite peculiarities this should result in strengthening of the material.

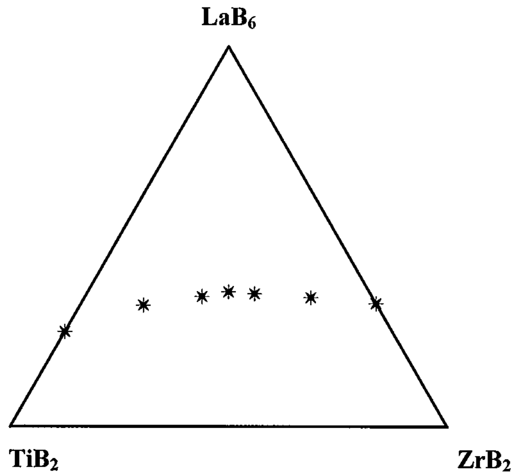

FIG. 3. Monovariant equilibrium in the quasiternary LaB_6–TiB_2–ZrB_2 system.

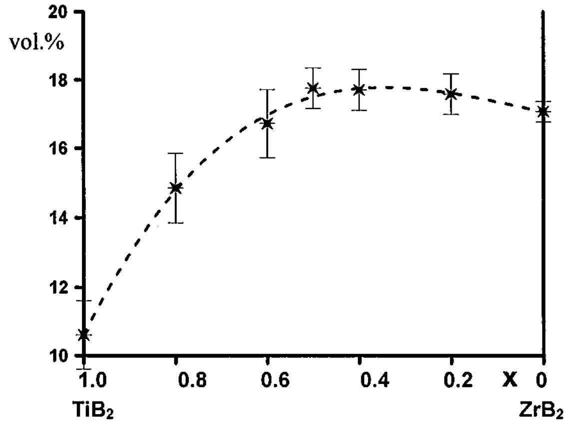

FIG. 4. Volume content of the diboride phase whiskers in the eutectic LaB_6–$(Ti_xZr_{1-x})B_2$ composite.

CONCLUSION

Varying the boron–boron distance in continuous solid solutions of boride phases makes it possible to increase the perfectness and regularities of the real structure of directionally crystallized MeB_6–MeB_2 eutectic composites.

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