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The peculiarities of the structure formation in directionally crystallized eutectics EuB_6–MeB_2

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Abstract

The possibility of producing fiber-strengthened eutectic composites in situ in the quasibinary EuB_6–MeB_2 (Me–Zr, Hf, Sc) alloys is shown. By directional crystallization of the eutectic composition perfect real structures on the base of uniformly distributed MeB_2 fibers in the EuB_6 matrix may be formed.

Keywords: Boride eutectics; Direction crystallization; Europium hexaboride

1. Introduction

Europium hexaboride has attracted the attention of many scientists due to its interesting properties. Its nuclear properties present a special interest due to the very high neutron absorption of both boron and europium atoms for the thermal and especially for the fast neutrons [1–3].

Unlike other isomorphous rare earth hexaborides europium hexaboride dissolves a small amount of carbon [4] which reduces the possibility of the formation of unstable europium carboborides in moisture media which in turn makes this compound more stable under operational conditions. Furthermore it was shown that the EuB_6 neutron absorbing characteristics exceed the similar properties of other boron and europium-containing materials (B_4C, Eu_2O_3) [3].

The compact pieces of europium hexaboride are usually produced by sintering, hot pressing or melting of source powders. The sintering process results in a high porosity of pellets, while the hot pressing due to strong contamination of EuB_6 with carbon and formation of europium carboborides results in the destruction of pellets on exposure to a moisture media. The melting processes (a crucibleless induction heating or the arc melting in a cooled cup) make it possible to obtain the EuB_6 pieces both in polycrystal and single crystal forms without the essential contamination with carbon. However, the decomposition of europium hexaboride owing to the europium high vapor pressure at its melting temperature (≥2580°C) may take place [5].

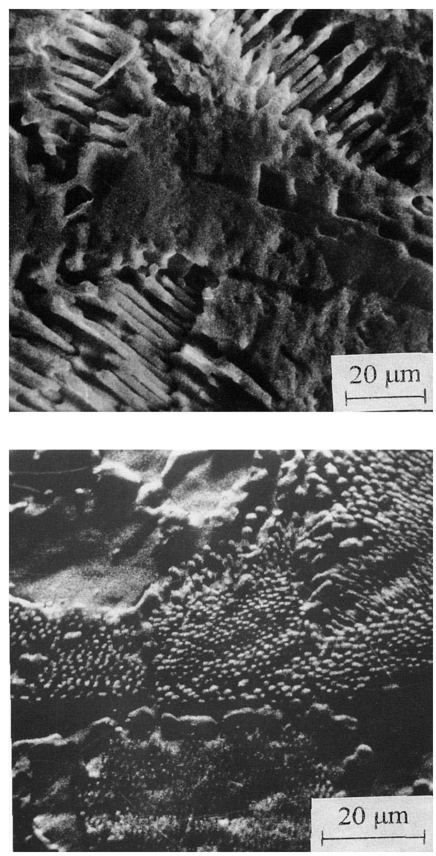

Fig. 1. Structure of the EuB_6–ZrB_2 alloy (32 mol% ZrB_2) after arc melting (a) and after drop quenching (b) (etched).

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Apart from this, a very important drawback to the use of europium hexaboride items, especially as possible functional elements of different devices, is their high brittleness [6]. Attempts to strengthen them by using powder metallurgy technology methods, including different composites based on EuB_6 have been unsuccessful [7,8].

This work presents the results of the investigations of the possibility of creating fiber-strengthened europium hexaboride composites, as was done for isomorphous lanthanum hexaboride [9–13].

2. Materials and methods

By analogy with the systems based on lanthanum hexaboride the possibility of eutectic formation in the EuB_6–MeB_2 systems was supposed and ZrB_2, HfB_2 and ScB_2 were selected as d-transition metal diborides.

Zirconium diboride was chosen, as it is known that this diboride forms perfect single crystal whiskers in the eutectic LaB_6–ZrB_2 mixture. We also used mixtures with hafnium diboride in order to find possible additions, which should increase the neutron absorption ability and with scandium diboride, which may reduce the density of a composite material.

The reducing of europium oxide with boron produced the source EuB_6 powder. The arc melting of the scandium and boron mixtures produced ScB_2. The ZrB_2 and HfB_2 powders were furnished from Chemreaktiv (Donetsk, Ukraine).

The formation of a fiber eutectic structure in the above mentioned boride mixtures was checked using samples prepared by arc melting in an argon atmosphere, with quenched drops obtained by throwing the melt onto a cooled copper cup and with the directionally crystallized rods.

The directional crystallization was achieved by means of an induction zone melting process using Crystal-111 equipment. With the high evaporation rate of europium in mind, the argon pressure in the chamber was set up at 2.5 MPa.

In previous works devoted to the lanthanum hexaboride-based eutectics it was shown that their strength properties correlate with the real structure; the more perfect the real structure is, the more strength, fracture toughness and thermal shock resistance of the materials are achieved [11]. Thus in this work, the main emphasis was on the research of the real structure of composites.

The structure of the samples was investigated using scanning electron microscopes Stereoscan 54-10 and

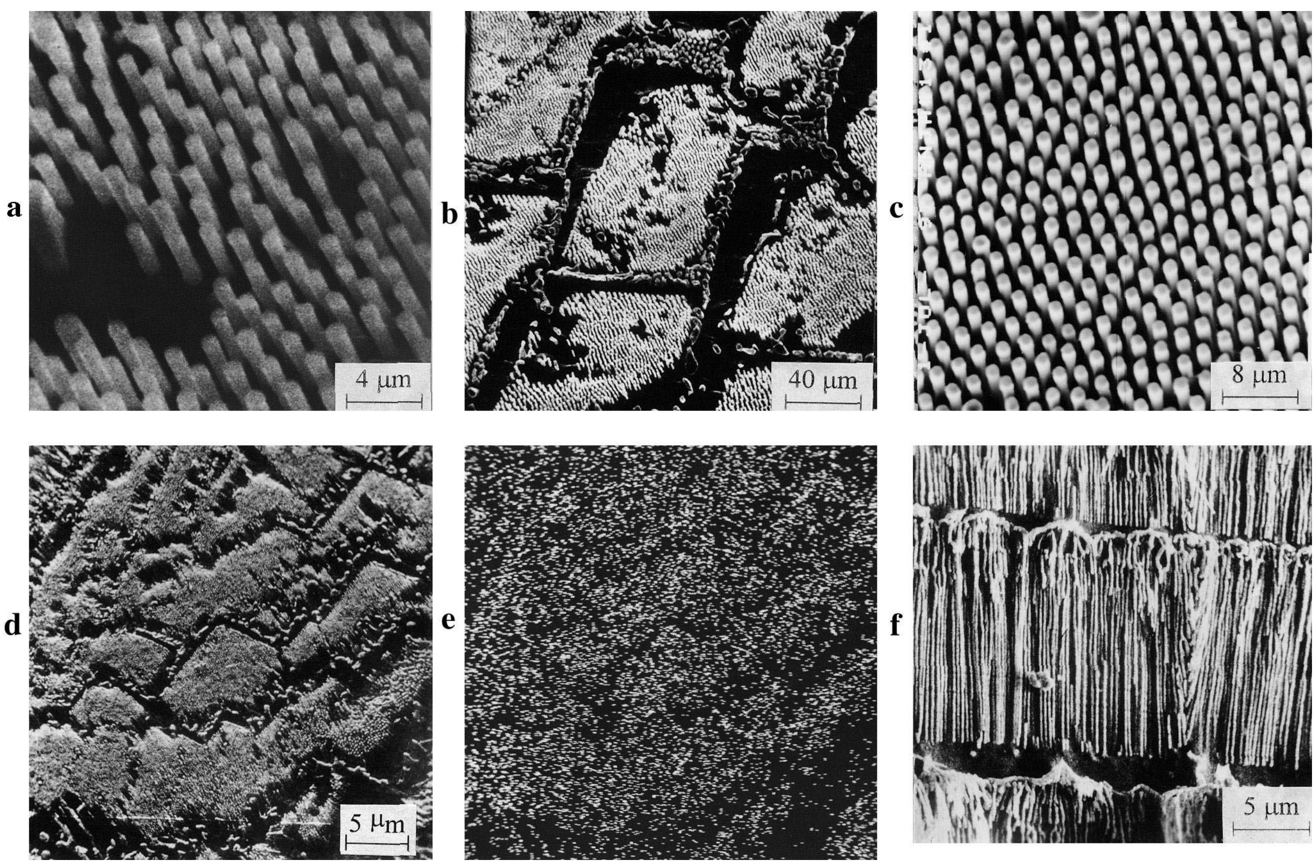

Fig. 2. Structure of the cross (a–d) and longitudinal (f) sections of the EuB_6–ZrB_2 alloy samples containing 32 mol% ZrB_2 (a, b) and 37 mol% ZrB_2 (c–f) (etched). (e) X-ray map of the microstructure, presented in (d) in X-ray ZrLα radiation.

Camebax SX-50. The phase composition and the single crystal perfection were studied using X-ray diffractometer HZG-4A.

3. Results and discussion

For the investigation of alloys in the EuB_6–ZrB_2 system, compositions in the limits of 32–42 mol% of ZrB_2 were chosen. The lower limit of the ZrB_2 content was taken as similar to the eutectic composition in the LaB_6–ZrB_2 system [9]. The samples were produced by all the above mentioned methods, i.e. arc melting, quenched drops and directional crystallization.

The arc melting method showed the existence of eutectic blended plate-like and fibrous structures (Fig. 1a). The quenched drop method confirmed the formation of a eutectic whisker structure (Fig. 1b), similar to that observed in the LaB_6–ZrB_2 system [10].

The directional crystallization of alloys having 32 mol% of ZrB_2 results in the formation of a regular fibrous (whiskers) eutectic structure (Fig. 2a). Some excess of the matrix EuB_6 phase distributed in interlayers between eutectic columns has been observed (Fig. 2b).

The increasing of the content of the ZrB_2 phase up to 37 mol% causes a considerable lowering of the amount and size of such interlayers (Fig. 2d and f). The amount and size of such interlayers in this case is negligible, which testifies to their proximity to the eutectic composition. The composite eutectic structure having a single crystal matrix of EuB_6 and, uniformly distributed in it, the practically equithickness single crystal whiskers of the ZrB_2 phase with a diameter near 1.0 μm and length up to 900 μm is formed (Fig. 2c and f). According to the X-ray map of the microstructure of this sample in X-ray ZrLα radiation (Fig. 2e) the surplus phase that is separated on boundaries of eutectic columns is the europium-based phase.

A further addition of the diboride phase up to 42 mol% proves to be in excess. The X-ray map analyses of the non-etched surface of such samples in X-ray ZrLα and EuLα radiation confirmed this conclusion (Fig. 3a–c).

The results which we obtained, permitted us to conclude that the eutectic composition for the EuB_6–ZrB_2 system exists in the range of 37–40 mol% ZrB_2. The determination of the eutectic composition in the systems on the base of the europium boride is complicated owing to the uncontrolled shift of the melted zone composition, in comparison with the source mixture due to the volatility of europium.

Earlier it was shown that the quasibinary LaB_6–TiB_2 [14], LaB_6–ZrB_2 [15], LaB_6–HfB_2 [16] and LaB_6 –CrB_2 [17] systems have a eutectic temperature lower in limits 100–200° compared with that for individual LaB_6. Similarly the lower melting temperature of the eutectic mixtures on the EuB_6 base causes a reduction of the evaporation rate of the europium from the melt in comparison with that for the individual EuB_6. Moreover, for compositions that are close to the eutectic point the melting process is the most stable.

Fig. 3. Microstructure (a) and X-ray maps of the not etched surface of the EuB_6–ZrB_2 alloy with 42 mol% ZrB_2 in ZrLα (b) and in EuLα (c) radiation.

The fracture surface of such materials presents a wood-like character (Fig. 4a). We can also observe some areas where the whiskers are drawn off from the matrix channel and ruptured near the crack surface (Fig. 4b). Such a branching fracture surface, characterized by cleaving and

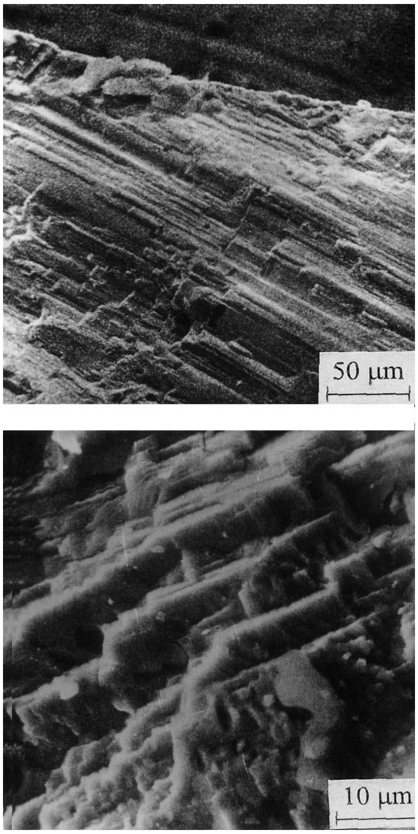

Fig. 4. Fracture surface of the eutectic EuB_6–ZrB_2 alloy: (a) the general view, (b) the regions with drawn-off whiskers.

shearing off, favor the rising of the mechanical properties of the material [18].

The alloys in the EuB_6–HfB_2 system were produced using the arc melting and the directional crystallization methods. Compositions having 16, 21 and 32 mol% of HfB_2 were studied and similarly to the EuB_6–ZrB_2 system three kinds of structures, hipoeutectic, eutectic and hipereutectic were obtained.

The composition closest to the eutectic point was obtained at 21 mol% of HfB_2. In this case the directional crystallization also resulted in the formation of regular whiskers structure (Fig. 5), similar to those obtained in the EuB_6–ZrB_2 system.

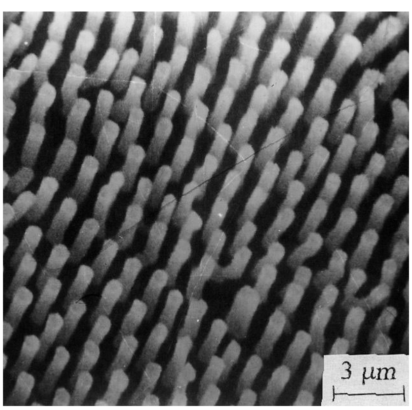

Fig. 5. Structure of the cross section of EuB_6–HfB_2 eutectic alloy (etched).

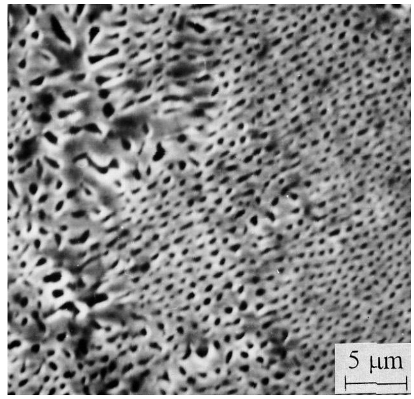

Fig. 6. Structure of the cross section of EuB_6–ScB_2 eutectic alloy (etched). (Contrary to the ZrB_2 and HfB_2 systems the ScB_2 phase due to much less chemical stability is pitted from the EuB_6 matrix).

EPMA analyses have not shown remarkable (or any) mutual solubility of both borides. Similar results were obtained earlier for the studied LaB_6–MeB_2 (Me: Ti, Zr, Hf) systems [14–16] and for the EuB_6– Hf system [19].

The alloys of the EuB_6–ScB_2 system were only produced by the arc melting method, as in this case it was possible to employ small amounts of scandium. For this reason the results obtained only have a preliminary character.

Compositions containing 22, 33 and 45 mol% of ScB_2 were studied and in all cases structures presenting eutectic columns and an excess of the matrix EuB_6 phase were formed. The eutectic areas showed a mixed plate and fiber character. A minor quantity of excess matrix phase and a more regular fiber eutectic structure (Fig. 6) was obtained in the composite having 45 mol% of ScB_2.

4. Conclusion

It is shown that EuB_6, similarly to LaB_6, in some compositions with typical d-metals borides can form a fiber-strengthened structure, consisting of the diboride single crystal whiskers distributed in a single crystal matrix of hexaboride.

The regular structures may be obtained in situ by directional crystallization of the eutectic compositions of the studied systems. Such a structure should ensure mechanical properties higher those obtained for the individual EuB_6 pieces, as was shown for LaB_6–MeB_2 directionally crystallized eutectic systems [9].

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