Hardness and fracture-toughness of hot-pressed LaB$_6$-TiB$_2$ ceramics

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Abstract. Microstructural analysis and investigations of mechanical properties via indentation-techniques have been performed on a LaB$_6$ - 15 vol. % TiB$_2$ ceramics, obtained by the hot-pressing at $T = 1900$ °C and $P = 30$ MPa in argon gas. The relative density of hot-pressed material was up to 97% of theoretical. XRD, SEM and EDX analysis of ceramics were performed. The Vickers hardness (18.5 GPa) and fracture-toughness (3.9 MPa·m$^{1/2}$) were compared with the values, measured on a single-crystalline LaB$_6$ ($H_v = 21$ GPa, $K_I = 2.4$ MPa·m$^{1/2}$) and arc-melted eutectic composite LaB$_6$-TiB$_2$ ($H_v = 23$ GPa, $K_I = 6.7$ MPa·m$^{1/2}$).

1. Introduction
Traditionally LaB$_6$ is widely used as a thermionic emitter because of its low work function, high thermionic current density, and good stability at high temperatures [1-3]. During last decade LaB$_6$-based solid solutions became the object of interest because of their promising optical properties [4-7]. Another use of lanthanum hexaboride is to use it as a second phase to activate the sintering of ultrahigh-temperature ceramics based on refractory zirconium and hafnium diborides [7]. As a structural material lanthanum hexaboride exhibits relatively high strength, hardness and Young's modulus, which is due to strong covalent bonds within the B$_6$ octahedron. But insufficient fracture-toughness of single-crystalline LaB$_6$ (about 1.5-2.5 MPa·m$^{1/2}$) can be a critical factor in conditions of high mechanical loads. Near-full density polycrystalline LaB$_6$ demonstrates the same values of fracture-toughness. However, mechanical properties of LaB$_6$ can be enhanced by the strengthening with second phase, for example, MeB$_2$ (where Me = Ti, Zr, Hf, Cr, V, Nb etc.) [8-17]. All of the quasibinary systems LaB$_6$-MeB$_2$ are eutectic-type [18-23], which allows obtaining dense ceramic materials via solid-state sintering at temperatures below 0.87$_{\text{eut}}$ $\approx$ 2100-2200 °C. As shown in [24, 25], the creation of composite ceramic materials based on LaB$_6$-MeB$_2$ systems makes it possible to increase the fracture-toughness up to 3.7-4.5 MPa·m$^{1/2}$. This effect is associated with a crack deflection mechanism in hetero-phase structure. A significant decrease in sintering temperature of composite ceramics based on LaB$_6$-MeB$_2$ systems leads to the formation of more fine-grained structure in comparison with single-phase polycrystalline LaB$_6$. This effect is due to a two main factors: decreasing the sintering temperature caused by eutectic-type of interactions and lengthening of diffusion paths in the hetero-phase structure, which inhibits grain growth during sintering.

In the present study we investigated the microstructure, phase composition, hardness and fracture-toughness of LaB$_6$-TiB$_2$ ceramic composite, obtained by hot-pressing of submicron LaB$_6$ and TiB$_2$ powders. It was of considerable interest to investigate the Vickers hardness and fracture-toughness of
LaB₆‧TiB₂ hot-pressed ceramic composite and to compare these results with similar characteristics of single-crystalline LaB₆ and arc-melted eutectic composite LaB₆‧TiB₂, which were not quite correctly measured by us earlier in work [27].

2. Materials and Method

Commercial powders of LaB₆ (99.0 wt. %) and TiB₂ (99.0 wt. %) were used in this study. The average size of starting powders (the 50th percentile particle size, d₅₀) determined by laser diffraction was 12 and 15 µm respectively. Powders were mixed and milled on vibratory ball-mill in gasoline-solvent media with SiC balls (balls to material weight ratio B:M = 10:1) during 80 hours. Powders were mixed in ratio 85 vol. % LaB₆ – 15 vol. % TiB₂. The additional 2.3 mass. % SiC appeared in mixture due to the wear of SiC balls, which was determined by weighing the balls before and after grinding. After ball-milling, the average particle size decreased to d₅₀ = 0.75 µm.

The vacuum-dried powder mixture was placed into graphite press-form with an internal diameter of 25 mm and sintered on a Thermal Technology HP20-3560-20 hot press at an isothermal holding temperature of 1900°C and a pressure of 30 MPa for 15 min in argon gas. After hot-pressing samples were polished for microstructural and micromechanical analysis.

Reference samples were obtained by the floating zone method (single-crystalline LaB₆) [27] and electric-arc melting (eutectic alloy LaB₆‧TiB₂) [26].

The phase composition of ceramics was determined using the X-ray diffraction (XRD) analysis (Rigaku SmartLab 3, Cu Kα radiation, λ = 1.5406 Å) in the 2θ range of 10–90° with 0.01° step. The microstructure of samples was investigated using an optical microscope Meiji Techno 7200 and SEM Tescan Vega 3SBH. Analysis of elements concentration was carried out using Aztec X-Act analyzer (Oxford Instruments). The volume fractions of phases were calculated via the Thixomet-Lite system for image analysis using the fraction areas measuring from SEM-micrographs.

Indentation tests were carried out with the use of Vickers hardness tester PMT-3 under the load of 7.2 N. For calculation of Hv (Vickers hardness, GPa) we use equation (1):

\[ Hv = 1854 \cdot \frac{P}{D^2}, \]

where \( P \) – load, N; \( D \) – measured diagonal of the indentation, µm.

Fracture-toughness \( K_{IC} \) was calculated according to the equation (2):

\[ K_{IC} = 0.0889 \cdot \frac{Hv \cdot P}{\sqrt{4l}}, \]

where \( P \) – load, N; \( l \) – measured length of the indentation-induced crack from corner of indentation, µm.

At least 10 indentations were made, from which the mean values of the lengths of the diagonals and cracks were calculated.

3. Results and discussion

The relative density of hot-pressed LaB₆‧TiB₂ samples, measured by the hydrostatical method, was up to 97% of the theoretical value. Such a high density, compared to polycrystalline LaB₆, obtained at the same conditions, is due to a eutectic-type of phase interactions in the LaB₆‧TiB₂ system. The significant decrease in melting point is associated not only with liquid-phase sintering mechanism above the eutectic temperature but with activation of solid-state diffusion at the hetero-phase grain boundaries, which leads to a decrease in sintering temperature. As can be seen in the optical and SEM images of polished samples (Figure 1A and 1B) the structure of ceramics is two-phase: TiB₂ grains are distributed in LaB₆ matrix.
Analyzing the morphology of the grains, we can note, that the main part of them has a complex shape, formed by association of several smaller particles during the hot-pressing. The median size of TiB$_2$ grains, calculated using statistical analysis of SEM micrographs, is about 1.8 μm, which is 2.5 times larger than the initial particle size. The phases area fractions calculation from SEM micrographs, as well as EDX-analysis, showed that the composition of ceramics, in addition to LaB$_6$ (84 mol %) and TiB$_2$ (14 mol %) includes 2 mol % of SiC. This result is in a good agreement with the value of SiC-balls wearing during the ball-milling, established by weighing the balls before and after milling.

The XRD-spectra of hot-pressed LaB$_6$-TiB$_2$ ceramics presented in Fig.2. There are distinct diffraction peaks of well-crystallized two main phases – cubic LaB$_6$ and hexagonal TiB$_2$. Also, the most intensive reflexes of hexagonal SiC-phase are clearly defined. The spectrum contains weak diffraction peaks of impurity phases; their intensity is close to the background intensity. They can be recognized as peaks of boron nitride and lanthanum nitride, which appeared due to the use of a protective coating of BN on a graphite mold.
Figure 2. XRD patterns of hot-pressed LaB₆-TiB₂ ceramics

The average hardness of LaB₆-TiB₂ ceramic composite (HV = 18.5 GPa at the load of 7.2 N) was significantly lower than the theoretical value calculated by the rule of mixtures (28.2 GPa, based on data from [28] and 25.9 GPa, based on data from [13]). This may be due not only to the effect of porosity in ceramics but also to the previously noted effect of microplastic deformation in heterophase composite ceramics [29]. The hardness of single-crystalline LaB₆ and LaB₆-TiB₂ arc-melted alloy was 21 GPa and 23 GPa, respectively.

The fracture toughness of LaB₆-TiB₂ ceramic composite was 3.9 MPa-m¹/², which is higher than the fracture toughness of LaB₆ single crystal (3.1 MPa-m¹/²) and quite lower than the fracture-toughness of arc-melted LaB₆-TiB₂ alloy (6.7 MPa-m¹/²).

All the experimental values of Vickers hardness and fracture-toughness of hot-pressed LaB₆-TiB₂, single-crystalline LaB₆ and arc-melted alloy LaB₆-TiB₂ presented at the Ashby plot on Fig. 3, as closed dots 1, 2 and 3, respectively. Open dots are the literature data from [8, 9, 13, 15]. Thus, three areas corresponding to: 1) polycrystalline materials obtained by hot pressing or spark-plasma sintering, 2) single crystals, and 3) directionally crystallized eutectics can be distinguished on the Ashby plot.

Figure 3. Ashby plot of LaB₆-MeB₂-based materials (Me = Ti, Zr).

The main mechanism for increasing the fracture-toughness of hot-pressed and arc-melted samples is caused by an increase in the length of the crack propagation path due to its deflection by TiB₂ grains (Figure 1B) or fibers (Figure 1D). In the case of hot-pressed LaB₆-TiB₂ ceramics, the crack propagation is mainly intergranular, but some TiB₂ grains cracked by the transgranular mechanism.
Also, we can see the TiB₂ grain spalling (Fig. 1D) when the reinforcing grains debonded from the matrix.

4. Conclusion
The LaB₆ - 15 vol. % TiB₂ ceramics with 97% density was obtained by the hot-pressing at T = 1900 °C and P = 30 MPa in argon gas. XRD, SEM and EDX analysis of ceramics were performed. The Vickers hardness (18.5 GPa) and fracture-toughness (3.9 MPa·m¹/²) of hot-pressed ceramics were compared with the values, measured on a single-crystalline LaB₆ (Hv = 21 GPa, Kᵢc = 2.4 MPa·m¹/²) and arc-melted eutectic composite LaB₆-TiB₂ (Hv = 23 GPa, Kᵢc = 6.7 MPa·m¹/²). The reinforcement effect caused by the mechanism of crack deflection is most pronounced in the case of arc-melted LaB₆-TiB₂ alloy, and to a lesser extent observed in hot-pressed LaB₆-TiB₂ ceramics.

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