Reactive hot-pressed LaB₆-W₂B₅ ceramics

D D Nesmelov¹, E S Novoselov¹, D D Titov², S S Ordan’yan¹ and S N Perevislov³
¹Saint-Petersburg State Institute of Technology (SPSIT), Saint-Petersburg, Russia
²Baykov Metallurgy and Materials Institute (IMET RAS), Moscow, Russia
³Grebenschikov Institute of Silicate Chemistry (ISC RAS), Saint-Petersburg, Russia

E-mail: dnesmelov@yandex.ru

Abstract. The heterogeneous LaB₆-W₂B₅ composite with LaB₆ content of 50 vol. % was fabricated by reactive hot pressing of the powder mixture of LaB₆, W and amorphous boron at 1800 °C and 30 MPa for 15 min. The structure and phase composition of the synthesis products were analyzed by SEM, EDX and XRD methods. The effect of the pressure-induced anisotropic W₂B₅ grains growth was observed. The elastic modulus of composites investigated by resonance frequency method, and the Vickers hardness via indentation method.

1. Introduction

Lanthanum hexaboride is one of the most widely used thermionic emitter material [1-3] and promising candidate for solar-heat absorption and other plasmonic resonance based applications [4-7]. High melting point of lanthanum hexaboride (2510 - 2715 °C) and strong covalent bonds B-B in the B₆ octahedron leads to the poor sinterability of polycrystalline LaB₆. An active increase in the diffusion mobility of atoms in the LaB₆ crystal lattice is observed only at temperatures above 0.8 of the melting point. So, the pressureless sintering temperature of polycrystalline LaB₆ reaches 2300 °C [8], which is quite high and leads to intensive grains growth. The most popular technics for activation of LaB₆ sintering with the use of externally applied pressure are the hot-pressing (HP) and spark-plasma sintering (SPS) [7, 9]. The densification of polycrystalline LaB₆ can be further enhanced by introducing second-phase additives, which interact with LaB₆ to form a eutectic [10-12]. The preparation of ceramic composites based on LaB₆-MeB₂ (Me = d-metals) and LaB₆-SiC eutectic systems was studied in most detail [13, 14].

Another way to decrease the sintering temperature is to provide the in-situ reactive sintering via hot pressing or SPS. Different starting mixtures were used by several researchers to obtain composites in LaB₆-based systems: La₂O₃-B₂O₃ [15], La₂O₃-ZrO₂-B₂O₃ [16], La₂O₃-ZrO₂-Zr₂B₂C [17], Al₂O₃-Ti-LaB₆-TiB₅ [18], LaH₂-GdH₂-B [19], LaB₁₂-BaH₂-B [20] etc. In most cases, the reactive hot-pressing allows decreasing of sintering temperature and leads to the formation of a dense sintered body.

The aim of this work is to investigate the possibility of in-situ synthesizing LaB₆-W₂B₅ composite ceramics by reactive hot-pressing method from the LaB₆ + W + B starting mixture at a relatively low temperature of 1800 °C, and to analyze phase and chemical composition of LaB₆-W₂B₅ ceramics, using as a reference samples furnace-synthesized LaB₆-W₂B₅ powder mixtures. Solid-state synthesis of W₂B₅ usually carries out by the reaction of elemental tungsten and boron: 2W + 5B = W₂B₅. The reaction is exothermic (ΔH = 176 kJ / mol), resulting in overheating of the mixture and rapid growth.
of large crystals. The LaB$_6$ particles role in our experiment was also to block the nucleating centers of W$_2$B$_5$ grains growth in order to reduce the rate of exothermic heat generation to inhibit crystal growth.

2. Materials and Method
Commercial powders of LaB$_6$ (99.0 wt. %) metallic tungsten (99.9 wt. %) and amorphous boron (99.0 wt. %) were used in this study. The average size of LaB$_6$, W and B$_a$ starting powders (the 50th percentile particle size, $d_{50}$) determined by laser diffraction was 12, 60 and 1.1 µm respectively. Powders were mixed and milled on vibratory ball-mill in gasoline-solvent media with tungsten balls (balls to material weight ratio B:M = 10:1) for 20 hours. Powders were mixed in ratio of 26.5 wt. % LaB$_6$ – 64.1 wt. % W – 9.4 wt. % B$_a$ for obtaining the LaB$_6$- 50 vol. % W$_2$B$_5$ composite. The addition of 7 wt. % W appeared in mixture due to the wear of W balls, which was determined by weighing the balls before and after ball-milling. This additional tungsten was taken into account when weighing the initial mixture. After the ball-milling, the average particle size decreased to $d_{50} = 2.9$ 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 1800°C and a pressure of 30 MPa for 15 min in argon gas. After hot-pressing samples were polished for microstructural and micromechanical analysis.

As a reference sample, the furnace-synthesized LaB$_6$-W$_2$B$_5$ powder mixture was prepared from the same starting powders. The vacuum-dried powder mixture was compacted via cold pressing at 50 MPa to the 50 %-porosity green-body, which were placed into the graphite crucible and sintered at 1800°C at 10$^{-2}$ Pa for 1 hour in a SSHVA vacuum-furnace.

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

The elastic (Young’s) modulus of ceramics was measured using the Zvuk-130 meter of natural oscillation frequencies implements the method of forced oscillations (resonance method) [21], based on the relationship of the propagation rate of acoustic waves, $C_l$, with the density, $\rho$, and Young’s modulus, $E$:

$$C_l = \sqrt{E/\rho}, \quad (1),$$

Indentation tests were carried out with the use of Vickers hardness tester PMT-3 under the load of 44 N. For calculation of $H_v$ (Vickers hardness, GPa) we use equation (2):

$$H_v = 1854 \cdot \frac{P}{D^2}, \quad (2),$$

where $P$ – load, N; $D$ – measured diagonal of the indentation, µm.

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

3. Results and discussion
Dense ceramics were obtained by hot-pressing, while about 25%-porosity samples were obtained after synthesis in a vacuum furnace at the same temperature. The relative density of hot-pressed LaB$_6$-W$_2$B$_5$ samples, measured by the hydrostaltical method, was 92 % of the theoretical value. Taking into account the density of samples, obtained by both methods, the XRD measurements of hot-pressed ceramics were provided on the cross-sections, while the furnace-synthesized samples were crushed in a mortar and then analyzed by powder XRD method.

The XRD-spectra of initial powder mixture (blue curve), vacuum-furnace synthesized mixture (red curve) and hot-pressed LaB$_6$-W$_2$B$_5$ ceramics (green curve) presented in Figure 1.
The initial powder mixture spectra contain diffraction peaks of W metallic and LaB₆. The presence of boron is not detected because of its amorphous structure. Weak reflections of tungsten oxides are present above the background, but their intensity is so small that the scale of the illustration does not allow them to be distinguished. After the synthesis, there are distinct diffraction peaks of well-crystallized two main phases – cubic LaB₆ and hexagonal W₂B₅. The reflexes of impurity WB-phase are clearly defined only at the red curve – vacuum-furnace synthesized LaB₆-W₂B₅ spectra. There are no WB peaks in the spectra of hot-pressed LaB₆-W₂B₅. This fact is due to a relatively long holding time (1h) at a high temperature under vacuum, which leads to partial loss by vaporization and sublimation of reactants and results in chemical composition fluctuation. In contrast, during hot-pressing, the holding time is shorter and the evaporation of the components is prevented by the pressure of the argon atmosphere.

![Figure 1. XRD patterns of LaB₆-W₂B₅ initial reaction mixture and synthesized composites](image)

A disproportionately high diffraction peak of W₂B₅ at the 2θ = 25.6° evidence a predominant reflection from (101) lattice planes. This indicates anisotropic W₂B₅ grain growth.

SEM-micrographs of hot-pressed samples (Figure 2A, B) demonstrates an uneven phase distribution in the structure of composites. Large-area white fields in Fig. 1A and B are a result of anisotropic W₂B₅ grains growth in a (101) plane, which is in a good agreement with XRD-spectra data.

![Figure 2. A, B – SEM images of reactive hot-pressed LaB₆-W₂B₅ ceramics; C - optical image of Vickers indentation](image)

As can be seen from Fig. 1B, W₂B₅ grains have a plate-like morphology and different orientation, but predominantly orientation of the largest W₂B₅ grains is perpendicular to the pressure direction. The average size of the largest W₂B₅ particles along (101) plane is of several tens of µm, while the
thickness of the plates is 1-5 μm. There were no plate-like grains observed in the reference samples of a vacuum-furnace synthesized mixture, so we can conclude anisotropic growth of W₂B₅ grains is caused by the external pressure effect (Figure 3).

![Diagram of W₂B₅ grains growth under pressure](image)

**Figure 3.** Scheme of W₂B₅ anisotropic grains growth under the load during the hot-pressing: W₂B₅ plate-like grains are distributed in a LaB₆ matrix

LaB₆ grains have a conventional morphology without any signs of anisotropic growth. The average LaB₆ grain size does not exceed 5 μm, but it is observed some agglomerates with a size of about 10-20 μm, caused by local inhomogeneity of initial powder mixture.

The phases area fractions calculation from SEM micrographs, as well as EDX-analysis, showed that the composition of ceramics is near the equivolume. The presence of a large number of plate-like W₂B₅ grains allows us to determine the structure of the equivolume composite as self-reinforced.

The average hardness of LaB₆-W₂B₅ ceramic composite was measured as $H_v = 16$ GPa at the load of 44 N. Such a low hardness, compared to the theoretical value calculated by the rule of mixtures (26.9 GPa), may be caused not only by the effect of porosity in ceramics but also by the previously noted effect of microplastic deformation in heterophase composite ceramics [22].

The average Young’s modulus (610 GPa) also was decreased in comparison with theoretical value (632 GPa). This predictable decrease is due to the imperfection of the composite structure, primarily, the presence of porosity.

### 4. Conclusion

The heterophase LaB₆-W₂B₅ composite with LaB₆ content of 50 vol. % was fabricated by reactive hot pressing of the powder mixture of LaB₆, W and amorphous boron at 1800 °C and 30 MPa for 15 min and compared to the furnace-synthesized LaB₆-W₂B₅ powder mixture, prepared from the same starting powders at the same holding temperature. The structure and phase composition of the synthesis products were analyzed by SEM, EDX and XRD methods. The 92% relative density hot-pressed ceramics contained only two main phases – cubic LaB₆ and hexagonal W₂B₅. The impurity of WB₅-phase was detected in the vacuum-furnace synthesized LaB₆-W₂B₅.

The effect of the pressure-induced anisotropic W₂B₅ grains growth was observed. The elastic modulus of the hot-pressed LaB₆-W₂B₅ composite was 610 GPa, and the Vickers hardness via indentation method 16 GPa.

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References

[1] Lafferty J M 1951 Journal of Applied Physics 3 299
[2] Taran A, Voronovich D, Oranskaya D, Filipov V, Podshyvalova O 2013 Functional materials 4 485
[3] Paderno Y B, Taran A A, Voronovich D A, Paderno V N, Filipov V B 2008 Functional materials 1 63
[4] Kowalczyk J M, Hadmack M R, Szarmes E B, Madey J M 2014 International Journal of Thermophysics 8 1538
[5] Mattox T M, Coffman D K, Roh I, Sims C, Urban J J 2018 Materials 2 226
[6] Mattox T, Urban J 2018 Materials 12 2473
[7] Sani E, Mercatelli L, Meucci M, Zoli L, Sciti D 2017 Scientific Reports 1 718
[8] Kauer E 1963 Physics Letters 3 171
[9] Li-Hong B, Jiu-Xing Z, Shen-Lin Z, Yong-Feng W 2010 Chinese Physics Letters 10 107901
[10] Ordan’yan S S, Paderno Y, Khoroshilova I K 1983 Soviet powder metallurgy and metal ceramics 251 946.
[11] Loboda P I, Kisla G P, Bogomol I I, Sysoev M A, Karasevskaya O P 2009 Inorganic Materials 3 246.
[12] Ordan’yan S S, Nesmelov D D, Vikhman S V 2009 Inorganic Materials 7 754.
[13] Yang X, Wang X, Wang P, Hu K, Li Z, Zhang J 2017 Journal of Alloys and Compounds 704 329
[14] Wang X, Zhang J X, Yang X Y, Hu K, Zhang J W 2017 Advances in Applied Ceramics 3 132
[15] Sonber J K, Sairam K, Murthy T C, Nagaraj A, Subramanian C, Hubli R C 2014 Journal of the European Ceramic Society 5 1155
[16] Min G H, Gao R, Yu H S, Han J 2005 Key Engineering Materials 297 1630
[17] Gao R, Min G, Yu H, Zheng S Q, Lu Q, Han J, Wang W 2005 Ceramics International 1 15
[18] Popov O, Loboda P, Klepko O, Solovjova T 2019 Advances in Applied Ceramics 4 217
[19] Bao L H, Zhang J X, Zhang N, Li X N, Zhou S L 2012 Physica Scripta 3 035710
[20] Zhou S L, Zhang J X, Bao L H, Yu X G, Hu Q L, Hu D Q 2014 Journal of Alloys and Compounds 611 130
[21] Buravov A D, Vikhman S V, Kovarskaya E Z, Moskovenko I B, Nekrasova O K, Smirnova M A 2012 Refractories and Industrial Ceramics 6 436
[22] Ordanyan S S, Unrod V I 2005 Refractories and Industrial Ceramics 4 276.