Journal of Alloys and Compounds 729 (2017) 749–757

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Influence of annealing on crucible-free float zone melted LaB_6-TiB_2 composites

T.O. Soloviova [a, *], O.P. Karasevska [a], J. Vleugels [b], P.I. Loboda [a]

[a] National Technical University of Ukraine "KPI", Peremohy Av. 37, 03680 Kyiv, Ukraine
[b] KU Leuven, Department of Materials Engineering, KasteelparkArenberg 44, B-3001 Heverlee, Belgium

ARTICLE INFO

Article history:
Received 12 February 2017
Received in revised form
19 September 2017
Accepted 20 September 2017
Available online 21 September 2017

Keywords:
Boride composite
Directional solidification
Non-equilibrium phase
Residual stresses
Annealing
Fracture resistance

ABSTRACT

Polycrystalline and textured eutectics LaB_6-TiB_2 were obtained by the floating zone melting (FZM) method for powders using polycrystalline (PC) and (111) single crystalline (MC) seeds. The phase composition, microstructure, crystallographic orientation, residual stresses and mechanical characteristics in PC and MC composites after FZM process and their changes during annealing were studied. It is shown that the annealing temperature and the exposure time necessary to achieve the equilibrium eutectic phase and optimum mechanical properties in PC composites are lower than in the MC ones. Crack resistance and hardness in PC and MC composites after FZM process are smaller than the values in the equilibrium state and this difference is due in part to the residual stresses in both phases. It is established that under optimal annealing conditions, it is possible to substantially increase the mechanical characteristics of PC and MC eutectics. Fracture resistance rises in 1.5–1.6 times and hardness from 14 to 15 GPa to 25 and 27 GPa in MC and PC composites, respectively.

1. Introduction

Monolithic and composite borides are of growing industrial interest for a wide range of applications such as cathodes, cathode assemblies, heat resistant materials, protective coatings, catalysts, abrasives, polishing paste, cutting tools, etc. [1–6]. Boride composites are obtained by many different methods like directional solidification [7–11], solid-state sintering [12], liquid phase sintering [13], arc-melting [14], high-temperature reactive sintering [15], pulsed electrical current sintering [16], hot pressing [17], etc.

Among the common methods that allow obtaining ceramic matrix composites with well-connected discrete reinforcing fibers and low energy interfaces in one single technological operation is directional solidification [17]. The process conditions like temperature and crystallization rate allow to realize eutectic structures with aligned discrete matrix fibers [18,19]. The high process temperatures however require the use of powerful equipment which might contribute to contamination of the melt. By conventional powder metallurgy on the other hand, the material matrix and reinforcing fibers are consolidated in a sequence of manufacturing operations comprising powder mixing, component shaping and sintering, hot pressing or impregnation. These methods are often quite expensive and do not provide a high purity, density, and uniform reinforcing phase alignment. The method of directional solidification is therefore becoming increasingly used because of the ability to remove unwanted impurities by repeated passages of zone melting, the possibility to obtain relatively large size composites, and different reinforcing fiber dispersions. The main advantage of the method is to control the contamination and the amount of reinforcing compound during composite fabrication. The use of crucible-free float zone melting (FZM) increases the adaptability of the method in which the phase morphology, diameter and number of fibers is regulated by the nucleation and growth rate ratio, which is defined by the thermal conditions and the saturation composition of the components at the crystallization front [20]. Crucible-free FZM of composites however can result in considerable thermal stresses, due to the high cooling rates and thermal gradients ($\geq$1000 °C/cm) and difference in thermal expansion/shrinkage of the constituent phases [21,22]. This leads to non-equilibrium phase compositions and large thermal residual stresses.

The purpose of this work was to determine the influence of thermal annealing on the phase composition, residual stresses and mechanical properties of textured and polycrystalline eutectic

* Corresponding author. Tel.: +380958481756.
E-mail address: tsolov@iff.kpi.ua (T.O. Soloviova).

https://doi.org/10.1016/j.jallcom.2017.09.223
0925-8388/

LaB_6-TiB_2 ceramic composites, with a eutectic temperature of 2370/2408 °C [23,24], obtained by crucible-free FZM.

2. Materials and methods

LaB_6 and TiB_2 powders (purity 98 wt%, average grain size 1 μm, Reaktiv Co Donetsk, Ukraine) were mixed in the eutectic LaB_6 + 15,7 vol.% TiB_2, composition [24]. In order to assist the purification of the starting powder mixture during crucible-free FZM, 2 vol.% amorphous boron (purity 99.8 wt%, particle size 0.5 μm, Reaktiv Co Donetsk, Ukraine) powder was admixed. 15 ml of a 2.5 wt% polyvinyl alcohol aqueous solution was used as binder per 100 g of powder mixture. After mixing by 10 times manual wet sieving through a 100 μm mesh sieve, the dried powder mixture was sieve granulated (1000 μm mesh) and uniaxial pressed in a hydraulic press at 100 MPa in a steel cylindrical mold with a working cavity diameter of 10 mm and length of 145 mm. Directionally reinforced LaB_6–TiB_2 composites were obtained by the original floating zone method, developed at the National Technical University of Ukraine (NTUU "Igor Sikorsky Kiev Polytechnic Institute"). FZM was performed at a speed of 3 mm/min in the "Crystal 206" (Russia) induction equipment in a 0.1 MPa helium environment using a LaB_6 single crystal (direction {111}, prepared by FZ melting, diameter 10 mm and height 10 mm) substrate for the single crystalline composites (MC) and for the polycrystalline composites (PC). Annealing of the composites was carried out in vacuum (10^{-3} mbar) with a heating rate of 20–25 °C/min up to 1200 °C, 1400 °C or 1600 °C in a graphite crucible for 1–2 h. Natural furnace cooling was used after the dwell time.

The crystals were axially sliced into discs (ϕ = 8 mm, h = 6–8 mm) by electrical discharge machining. The cross-sectioned surfaces, i.e. perpendicular to the FZM direction, were polished using diamond suspensions of 15 and 3 μm. Microstructure investigation of the composites was performed by scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands). Concentration profiles of lanthanum and titanium were preformed on PEM 106I (Selmi, Ukraine) with E.P.M.A. The density of the ceramics was measured by the Archimedes method in distilled water (10 times for each sample). X-ray studies were performed on a XRD diffractometer (Ultima IV, Rigaku, Japan) using $Cu_{K\alpha}$ radiation. Phase analysis of composites and macrostresses in its components was carried out using "θ–2θ" diffraction patterns (size of «2θ», θ steps was 0.02°, measuring time of 4s/step) with software (Rietveld analysis, RIR and etc.) and according to the Stokes-Wilson method, microstresses and size of coherently scattering regions (CSR) were estimated. The crystallographic orientation of the phase components of the MC and PC composites was analyzed on the pole figures obtained with stepwise rotation (2°) and inclination (2°) of the samples. The data of X-ray analysis were considered as functions of the annealing treatment in the PC and MC composites. The error in the measurement of macrostresses depends on the accuracy of the determination of the angles of reflexes on the diffractometer Ultima IV (≤0.001°), that according to Hooke's law [25] lies within 0.3–0.5 GPa for the LaB_6 and TiB_2.

The microhardness was measured by Vickers pyramidal indentation (Model FV-700, Future-Tech Corp., Tokyo, Japan) with time exposure of 15 s, and averaging 10 measurements under a load of 30 N. The indentation fracture resistance, K_{1c}, was calculated by the empirical formula [26]:

$$K_{1C} \sim 0.16 \cdot Hv \cdot \alpha^{1/2} \cdot (c/\alpha)^{-3/2}, \quad (1)$$

With α, half the diagonal of the indentation (m); Hv, the microhardness of the material (GPa) and c, the length of the radial crack (m). Accuracy microhardness measurement (ΔHv,%) largely depends on the length of the crack spread values and varies depending on the uniformity of the stress state of the material.

3. Results and discussion

3.1. Microstructure and phase evolution after thermal annealing

3.1.1. Microstructure, X-ray analysis and density MC and PC composites after FZM

The microstructure of the cross-sectioned MC and PC composites are presented in Fig. 1.

In both samples concentration profiles of lanthanum have shown areas with different intensities La, that mean presence not only equilibrium eutectic phase LaB_6, but also nonequilibrium $LaB_{6\pm x}$. The phases can be distinguished by color: a red LaB_6 matrix with dispersed white TiB_2 phase and a small amount of dispersed beige color LaB_4 and by matching interplanar spacing measured by X-ray method [27–29]. On the microstructure of the cross-sectioned samples borides three phases can be differentiated, i.e., a red LaB_6 matrix with dispersed bright TiB_2 phase and a small amount of dispersed LaB_4 (Fig. 1 a, b). The MC composites were grown on a single crystalline LaB_6 seed with {111} direction. The (111) facet covered with pyramidal protrusions formed (001) faces (Fig. 1 a). In the PC composites, heterogeneous nucleation from the polycrystalline seed leads to a random set of spatial orientations of the crystallizing phases (Fig. 1 b). The TiB_2 rods or fibers in the MC and PC ceramics have diameters of 0.2–0.3 μm and 0.2–1.2 μm respectively, as illustrated by the backscattered scanning electron micrographs in Fig. 1 (c, d). The crystal melt around the TiB_2 enriched with lanthanum, resulting in a surrounding layer of LaB_6 after crystallization [7].

The X-ray diffraction patterns of the LaB_6-TiB_2 PC and MC composites are compared in Fig. 2 (a, b). Besides the TiB_2 (ICDD's PDF-2 01-085-2083), LaB_6 (ICDD's PDF-2 01-074-8053), LaB_4 (ICDD DB card number 01-071-0459) and $LaB_{6\pm x}$ [29] phases, an additional unknown phase was observed with d-values (interplanar spacing) of 2.7519 Å, 2.5799 Å, 2.1882 Å and 2.0864 Å. Deviations from the stoichiometry content LaB_6 and TiB_2 in crystal (uneven mixing and physical process during crystallization) lead to the allocation of transition metal, which reduces the content of eutectic component. Therefore, in both cases, the eutectic phase is interrupted by larger TiB_2 rods surrounded by a LaB_6 matrix phase implying some local microstructure coarsening.

Fig. 3 a, b, e, f represents the pole figures for the LaB_6 matrix phase and TiB_2 fibers of MC and PC composites after FZM. According to the crystalline orientation of the seeds in the MC composite, the strongest reflexes for matrix phase are arranged in such a way that they reproduce 3 orders of symmetry (Fig. 3 a), and for matrix phase PC composite the distribution of reflexes is chaotic (Fig. 3 e). However, on the pole figure matrix phase of MC composite there are reflexes that deviate from the preferred orientation and correspond to the formation of the polycrystalline part of the ceramics. Reflexes of TiB_2 fibers in MC and PC composites indicate absence of their preferential orientation after FZM crystallization (Fig. 3 b, f).

Densities MC and PC composites after FZM were 4.59 g/cm^3 and 4.82 g/m^3, respectively (Table 1). The theoretical density of the LaB_6-TiB_2 eutectic is 4.67 g/cm^3, calculated from the theoretical densities of LaB_6 (4.7 g/cm^3) and TiB_2 (4.52 g/cm^3) [30]. PC composites have a density higher and MC composites lower than theoretical. The change in density in MC and PC composites is associated with several factors, the main ones of which are the porosity and the density of the phases additional to equilibrium. After FZM green compacts the porosity always is present. In MC