Laser Synthesis of Al$_2$TiO$_5$ and Y$_3$Al$_5$O$_{12}$ Ceramics from Powder Mixtures Al$_2$O$_3$-TiO$_2$ and Al$_2$O$_3$-Y$_2$O$_3$

M. Vlasova$^1$, M. Kakazey$^1$, B. Sosa Coeto$^1$, P. A. Marquez Aguilar$^1$, I. Rosales$^1$, A. Escobar Martinez$^1$, V. Stetsenko$^2$, A. Bykov$^2$, A. Ragulya$^2$

$^1$Center of Investigation in Engineering and Applied Sciences of the Autonomous University of the State of Morelos (CIICAp-UAEMor), Av. Universidad, 1001, Cuernavaca, Mexico.

$^2$Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3, Krzhizhanovsky St., Kiev, 252680, Ukraine

Abstract:
The phase formation process in the zone of laser irradiation of 60 wt.% Al$_2$O$_3$–40 wt.% TiO$_2$ and 60 wt.% Al$_2$O$_3$–40 wt.% Y$_2$O$_3$ compacts has been investigated by the XRD, electron microscopy, and atomic force microscopy methods. In the laser irradiation zone the ceramic track is formed. Due to no uniformity of heating of the powder mixture Al$_2$O$_3$–TiO$_2$ the ceramic track consists of a surface layer of the $\alpha$-Al$_2$TiO$_5$ and the bulk layer from the $\beta$-Al$_2$TiO$_5$. Ceramic track formed during irradiation of Al$_2$O$_3$–Y$_2$O$_3$ mixture consists of a surface amorphous layer of Y$_3$Al$_5$O$_{12}$ with inclusions of $\alpha$-Al$_2$O$_3$ domains and the bulk layer consisting of a mixture of dendrites $\alpha$-Al$_2$O$_3$ and Y$_3$Al$_5$O$_{12}$.

Keywords: Al$_2$O$_3$, TiO$_2$, Y$_2$O$_3$, Laser treatment, $\alpha$, $\beta$-Al$_2$TiO$_5$, $\alpha$-Al$_2$O$_3$, Y$_3$Al$_5$O$_{12}$

1. Introduction

The binary systems Al$_2$O$_3$ - TiO$_2$ and Al$_2$O$_3$ – Y$_2$O$_3$ are eutectic systems [1-6]. Investigation of phase formation and properties of ceramic materials derived from these mixtures devoted considerable number of works [7-14]. A distinguishing feature of such ceramic materials is the ability to obtain outstanding mechanical properties, the thermal and micro structural stability in the implementation of the conditions of directionally solidified eutectic (DSE) [15, 16]. One method of obtaining DSE is a laser processing of ceramic materials obtained from binary eutectic compositions [15-18]. Of no less interest is the investigation of the phase formation in such binary powder mixtures in a moving zone of high temperature heating. These conditions correspond to laser heating. Undoubtedly, regimes of irradiation (capacity, speed of movement of the beam and other parameters) as in the case of surface treatment of ceramics should be fundamental factors of phase formation. The specificity of the temperature distribution in a porous powder mixture in the vertical and horizontal directions [19, 20] suggests that the resulting ceramic material must have complex
phase composition. This means that its application could significantly expand.

The purpose of this paper is to study the features of phase formation in the powder mixtures Al₂O₃ - TiO₂ and Al₂O₃ – Y₂O₃ while moving of laser beam along the surface of compacted mixtures.

2. Experimental Procedure

In the present work, specimens were prepared from analytically pure Al₂O₃, TiO₂ and Y₂O₃ powders (produced by REASOL).

A powder mixtures a 60 wt. % Al₂O₃–40 wt. % TiO₂ (type 1) and a 60 wt. % Al₂O₃–40 wt. % Y₂O₃ (type 2) were compacted in pellets with a diameter of 18 mm and a thickness of 2–3 mm under a pressure of 7 MPa.

Laser treatment was performed in an LTN-103 unit (continuous-action laser with \( \lambda = 1064 \text{ nm} \)). The power of radiation \( (P) \) was 120 W, the diameter of the beam \( (d) \) was 1.5 mm, and the linear traversing speed of the beam was \( v = 0.15 \text{ mm/s} \).

3. Results

3.1. Type 1 Specimens

After laser irradiation of compacts from a 60 wt. % Al₂O₃–40 wt. % TiO₂ powder mixture, according to XRD analysis data, the channel material of the specimens contained the \( \beta \)-Al₂TiO₅ and \( \alpha \)-Al₂TiO₅ crystalline phases, a little of Al₂O₃ and traces of TiO₂ (Tab. I and

![Electron micrographs of cross section of channels formed after laser irradiation of compacted mixtures. (a) 60 wt. % Al₂O₃–40 wt. % TiO₂, (b) 60 wt. % Al₂O₃–40 wt. % Y₂O₃.](image-url)
Fig. 2 a). The $\beta$-Al$_2$TiO$_5$ is the main phase. An analysis of the intensities of diffraction lines of Al$_2$TiO$_5$ and Al$_2$O$_3$ revealed the distortion of the ratio of intensities (Tab. II), which is characteristic of textured materials.

Tab. I. Phase composition in zone of channel.

<table>
<thead>
<tr>
<th>N</th>
<th>Composition of compact</th>
<th>Phase composition in zone of channel after laser irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60 wt.% Al$_2$O$_3$ - 40 wt.% TiO$_2$</td>
<td>$\beta$-Al$_2$TiO$_5$, $\alpha$-Al$_2$TiO$_5$, little $\alpha$-Al$_2$O$_3$ and traces TiO$_2$</td>
</tr>
<tr>
<td>2</td>
<td>60 wt.% Al$_2$O$_3$ - 40 wt.% Y$_2$O$_3$</td>
<td>Y$_3$Al$_5$O$_12$, $\alpha$-Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

Tab. II. The ratio of intensities of X-ray diffraction lines for the phases $\alpha$-Al$_2$O$_3$, $\alpha$-Al$_2$TiO$_5$ and Y$_3$Al$_5$O$_12$

<table>
<thead>
<tr>
<th>Type of specimen</th>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$I_1/I_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standart $\alpha$-Al$_2$TiO$_5$</td>
<td>$d_1 = 0.2601$ nm</td>
<td>$d_2 = 0.1466$ nm</td>
<td>5</td>
</tr>
<tr>
<td>N 1</td>
<td>$\sim$</td>
<td>$\sim$</td>
<td>0.63</td>
</tr>
<tr>
<td>Standart $\beta$-Al$_2$TiO$_5$</td>
<td>$d_1 = 0.3351$ nm</td>
<td>$d_2 = 0.16839$ nm</td>
<td>125</td>
</tr>
<tr>
<td>N 1</td>
<td>$\sim$</td>
<td>$\sim$</td>
<td>1.41</td>
</tr>
<tr>
<td>Standart Y$_3$Al$_5$O$_12$</td>
<td>$d_1 = 0.2886$ nm</td>
<td>$d_2 = 0.13119$ nm</td>
<td>7.99</td>
</tr>
<tr>
<td>N 2</td>
<td>$\sim$</td>
<td>$\sim$</td>
<td>1.79</td>
</tr>
<tr>
<td>Standart $\alpha$-Al$_2$O$_3$</td>
<td>$d_1 = 0.2552$ nm</td>
<td>$d_2 = 0.1602$ nm</td>
<td>1.10</td>
</tr>
<tr>
<td>N 1</td>
<td>$\sim$</td>
<td>$\sim$</td>
<td>0.08</td>
</tr>
<tr>
<td>N 2</td>
<td>$\sim$</td>
<td>$\sim$</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Note: As standards were used data [30].
The surfaces of channels are represented by Al₂TiO₅ grains, textured along the direction of traversing of the laser beam (Fig. 3 a). On a cross-section of a channel (Fig. 3 b) it is seen that between the crystallites are present pores and cracks. The electron-probe microanalysis showed the presence of Al, Ti, and O in the channel material (Fig. 3 c).

Fig. 3 Electron micrographs of channel formed after laser irradiation of compacted powder mixture from a 60 wt.% Al₂O₃ - 40 wt.% TiO₂ (a, b) and microanalysis in point 1 (c). (a) top view, (b) cross section the channel

Fig. 4 AFM images of the surface of a track at different magnification. Amplitude regime.

The AFM data indicate that Al₂TiO₅ grains consist of nanoparticles with a size of ~7 nm, which form chains of different length and orientation (Fig. 4). Between particles and chains of particles is the amorphized material.
3.2. Type 2 specimens

Laser processing of a mixture 60 wt. % Al₂O₃ – 40 wt. % Y₂O₃ is accompanied by formation of yttrium aluminium garnet (YAG) and surplus of Al₂O₃ (see Tab. I and Fig. 2 b). The YAG and Al₂O₃ are textured (see Tab. II).

![Fig. 5](image1)

**Fig. 5** Electron micrographs of channel formed after laser irradiation of compacted powder mixture from a 60 wt.% Al₂O₃ - 40 wt.% Y₂O₃ (a, b) and microanalysis in points 1 and 2 (c). (a) fracture, (b) cross section the channel.

![Fig. 6](image2)

**Fig. 6.** AFM images of the surface of a track at different magnification. Amplitude regime.

On micro photo of fracture and cross section of specimen (Figs. 4 a, b) is seen that between large crystallites are included another type of crystallites. According to microanalysis
they contain such elements as the Al, Y and O (Fig. 5 c, place 1). In grains with facet are present the Al and O (Fig. 5 a, place 2 and Fig. 5 b). The Fig. 5 b shows the typical microstructure of solidified Al$_2$O$_3$-YAG eutectic with large content of Al$_2$O$_3$ dendrites [16, 21]. The black phase corresponds to alumina and grey phase is YAG. This is typical faceted-faceted eutectic structure.

The AFM image (Fig. 6) shows that the solidified eutectic YAG-Al$_2$O$_3$ has a complex morphology. Chains of different form, length and orientation are intertwined. These chains consist from nanoparticles with a size of ~5-7 nm. Between them is present the glass-like solidified material. The most part of chains also is covered by such glass-like layer.

4. Discussion

In results of irradiation of a powder mixture of Al$_2$O$_3$–TiO$_2$ attention is drawn to two facts: a) the appearance of $\alpha$-Al$_2$O$_3$ and TiO$_2$, although the ratio of components corresponds to the formation of Al$_2$TiO$_5$ (Fig. 7 a); b) the simultaneous formation of $\beta$-Al$_2$TiO$_5$ and $\alpha$-Al$_2$TiO$_5$. The explanation of these effects is the following. The formation of aluminum titanate should be viewed in different temperature zones. In low-temperature heating zone has crystallized $\beta$-Al$_2$TiO$_5$ according to the phase diagram [2]. In the high-heating zone from the eutectic melt should crystallize $\alpha$-Al$_2$TiO$_5$. The Al$_2$TiO$_5$ is sTab. only in region 1280 °C - 1860 °C and decomposes into Al$_2$O$_3$ and TiO$_2$ [22, 23]. In this case of rapid cooling of the eutectic melt the formation of a sTab. $\alpha$-Al$_2$TiO$_5$ can be attributed to the Ti$^{4+}$ cationic substitution and formation of charge compensating defects in the alpha-phased alumina lattice [24-27].

Thus, the material of track can be represented as a composite. The surface layer consists from $\alpha$-Al$_2$TiO$_5$ and Al$_2$O$_3$. At the bottom of the truck is formed $\beta$- Al$_2$TiO$_5$.

Results of laser processing of a mixture Al$_2$O$_3$ –Y$_2$O$_3$ correspond to the phase formation in region of constitution diagram of enriched by Al$_2$O$_3$ (Fig. 7 b). The $\alpha$-Al$_2$O$_3$ crystallization from the liquid eutectic under conditions of the directional rapid cooling is characterized by formation of specific "grain" structure consisting of nano-cristallites. Layers between them (see Fig. 6 b) must be characterized by high concentrations of vacancies and impurities [28, 29]. The Y$_3$Al$_5$O$_12$ - Al$_2$O$_3$ is a eutectic melt with $T_{\text{met}} = 1820$ °C [2, 4]. In a superficial thin layer of track in conditions of fast directional melting and subsequent rapid cooling of melt complete crystallization of Y$_3$Al$_5$O$_12$ is not occurring, unlike underlying layers. Therefore, the surface is amorphous and has a glassy appearance. The emergence of a complex surface topography can be explained by several factors: the directional movement of the cooling of the melt under the action of hydrodynamic forces and the formation of crystallites of corundum. In result of collision of the flow (Y$_3$Al$_5$O$_12$) with obstacles (Al$_2$O$_3$ domains) occurs as a fork of a moving stream, and the curvature of the domains of corundum.

Thus, the material can be represented as a truck composite. In the surface layer domains of Al$_2$O$_3$ are in amorphous layer of Y$_3$Al$_5$O$_12$. In the bulk layers the dendritic structure from Al$_2$O$_3$ and Y$_3$Al$_5$O$_12$ is formed.

5. Conclusions

The performed investigations showed the following:
- the laser treatment of compacted Al$_2$O$_3$–TiO$_2$ and Al$_2$O$_3$ - Y$_2$O$_3$ powder mixtures with a large Al$_2$O$_3$ content is accompanied by the formation of the same crystalline phases as those present in the constitution diagrams;
- the nonuniformity of heating of the material in the irradiation zone leads to a difference of phase composition in the axial and horizontal directions;
- the ceramic material formed upon irradiation Al₂O₃–TiO₂ mixture consists of a surface layer of the α-Al₂TiO₅ and the bulk layer of β-Al₂TiO₅;
- the ceramic material formed upon irradiation Al₂O₃–Y₂O₃ mixture consists of a surface amorphous layer of Y₃Al₅O₁₂ with inclusions of α-Al₂O₃ domains and bulk layer consisting of dendrites of α-Al₂O₃ and Y₃Al₅O₁₂.

Acknowledgement

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References


Садржај: Методама рендгенске дифракције, електронске микроскопије и АФМ-ом испитивано је формирање фаза у зони лазерске ирадијације код узорака састава 60 wt.% Al₂O₃–40 wt.% TiO₂ и 60 wt.% Al₂O₃–40 wt.% Y₂O₃. У зони лазерске ирадијационе зоне формирана је керамичка трака. Због неравномерне расподеле топлоте приликом зграња смеси Al₂O₃–TiO₂ керамичка трака на површини има слој α-Al₂TiO₅ а у унутрашњности β-Al₂TiO₅. Керамичка трака формирана током процера лазерске ирадијације смеше Al₂O₃–Y₂O₃ састоји се из површинског аморфног слоја Y₃Al₅O₁₂ са инклузијом α-Al₂O₃ домена и унутрашње смеше која се састоји из дендритана α-Al₂O₃ и Y₃Al₅O₁₂.

Кључне речи: Al₂O₃, TiO₂, Y₂O₃, лазерски третман, α-, β-Al₂TiO₅, α-Al₂O₃, Y₃Al₅O₁₂