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Processes Connected With Local Laser Heating of TiB₂ Armor Ceramics

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Abstract:

The process of high-temperature heating of TiB₂ armor ceramics in air in a continuous and pulsed mode of laser irradiation has been studied by the X-ray diffraction and SEM methods. It has been established that, in the irradiation zone, the temperature increases up to 3000 °C and over, resulting in the decomposition of TiB₂ and appearance of ablation products, which, in passage of air, oxidize and form dense films (in the pulsed mode) or “reticulated” films (in the CW mode) consisting of boron and titanium oxides. The mechanism of laser-induced breakdown of TiB₂ ceramics is similar to the mechanism of ballistic destruction.

Keywords: TiB₂ ceramics; Local laser heating; Ablation.

1. Introduction

Titanium diboride (TiB₂) is known as a ceramic material with a relatively high strength. It is characterized by a high melting point (~2970 °C), high hardness (35 GPa), and low density (4.52 g/cm³) [1, 2]. Titanium diboride ceramics is extensively used for cathodes and thermocouple sheaths in electrolyzers for aluminum smelting by the Hall-Héroult process, crucibles for molten metal’s, metal evaporation boats for thermal vacuum deposition, and wear-resistant coatings for cutting tools [3-6]. TiB₂ is usually sintered by hot pressing [7-11]. In view of the necessity to reduce its sintering temperature ($T_{sint} \sim 2/3 T_{melt}$), increase the fracture toughness, and provide the noncatastrophic fracture mode, additives of different types are introduced into TiB₂ powders [12-22]. Among the most thoroughly investigated composites are ceramics obtained from TiB₂–NiCl₂ mixtures [23-30].

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Laser machining is a promising method of treatment of refractory ceramics [31-37]. Note that, in [38], the laser treatment of TiB₂ ceramics of this type was carried out in a pulsed irradiation mode (\(\lambda = 1064\) nm) for 10 h. The pulse energy was 31 J, and the pulse duration was 15 ms. As result of such treatment, on the surface of the ceramics, a crater with a depth of 500 μm and a diameter of the upper part of the hole of \(~800\) μm was formed. However, breakdown of specimens was not observed. Since the composites based on TiB₂ are used as light ballistic armor [39-42], it was interesting to perform “laser ballistic bombardment” of the composite structural ceramics based on TiB₂ in the mode of intensive laser irradiation. The main aim of the present work is not only to establish the fact of breakdown of ceramics, but also to investigate the products of decomposition of the ceramics of this type.

2. Materials and Experimental Procedures

Titanium diboride ceramics were prepared from a 95 wt.% TiB₂–5 wt.% NiCl₂ mixture by hot pressing in vacuum (\(10^{-4} - 10^{-5}\) mmHg) at \(1800\) °C for 45 min [38]. The obtained cylindrical specimens had a diameter \(d = 5\) mm and a length \(l = 10\) mm.

The laser treatment was performed with a single-mode ytterbium fiber laser model YLS-1000-SM (IPG Photonics) that operates at 1070 nm and 1-kW average power in two modes, namely, a continuous-wave (CW) and quasi-continuous-wave (QCW) (pulsed) mode. In the QCW mode, a 2-ms pulse width and 250-Hz repetition rate were obtained by a direct pump switch. It was assumed that the first irradiation mode would make it possible to heat a specimen to a large depth. The pulsed irradiation mode of large power must promote intensification of the ablation process. The distance from the irradiation source to the specimens was 1.2 cm. In both modes, specimens were treated for 5 s. The ablation products were deposited on a glass ceramic substrate located parallel to the surface of the specimen.

Treated specimens and deposited ablation products were investigated by the X-ray diffraction method (D2 PHASER diffractometer, Bruker) and scanning electron microscopy (Hitachi SU 5000 scanning electron microscope).

3. Results and Discussion

3.1. Characterization of ceramics

According to our data and data presented in [38], the main phase of the ceramics obtained from the 95 wt.% TiB₂–5 wt.% NiCl₂ mixture at \(T_{\text{sint.}} = 1800\) °C is TiB₂ (Fig. 1, I a). The ceramics consists of TiB₂ grains (Fig. 2, a, a’), on the boundaries of which inclusions (white) containing nickel atoms are located.

3.2. Laser treatment of ceramics

3.2.1. Target

In the CW and pulsed modes, already in the initial stage of irradiation, in the ceramic specimens, craters with micro- and macrocracks form. Then rapid breakdown of specimens into large and small fragments occurs (Fig. 2 b, b’, b’’). The breakdown into small fragments is typical of regions adjacent to the crater, whereas the other parts of cylindrical specimens break down into large debris. The breakdown process of the ceramics is accompanied by the formation of ablation products, which deposit on ceramic fragments and on the substrate (Fig. 2 b’’’).

From the XRD data it can be concluded that, in CW-mode treatment, on the surface of the target, phase transformations that coincide with those typical of the TiB₂ ceramics
sintered at 2000 °C, proceed [36] (see Fig. 1, b, I target). Along with the presence of TiB₂, the appearance of TiB, NiB, and Ni₃B, which are products of high-temperature decomposition of titanium diboride and intergranular NiₓBᵧ and NiₓBᵧTⁱₓ interlayers, is registered [38]. Therefore, it can be concluded that, in the CW irradiation mode, the temperature on the surface of the ceramics is ≥ 2000 °C. Since laser treatment was carried out in air, the retardation of the oxidation process of decomposition products can be explained by the hindered penetration of oxygen into the crater (especially, into its lower part) because of the counter flow of out flowing ablation products.

In the QCW (pulsed) irradiation mode, along with the presence of TiB₂, the formation and active oxidation of new titanium borides are registered (see Fig. 1, c, I target), and, in XRD patterns, peaks of anatase and rutile are identified. The oxidation process can be described by the following equation [43, 44]:

\[ TiB_n + \frac{1}{2} \left( m + \frac{3}{2} n \right) O_2 = TiO_m + \frac{n}{2} B_2O_3 \]

The simultaneous presence of the high-temperature and low-temperature modifications of TiO₂ indicates that different places of the target surface and the surface layer of the target have different temperatures of heating, which is characteristic of local pulse laser treatment of refractory ceramics [45]. It can be supposed that rutile forms in the high-temperature zone of decomposition of TiBₙ, whereas anatase forms at a substantial distance from the crater. Note that the anatase → rutile transition occurs gradually in the temperature range (400–1000) °C [46]. This means that, in the irradiation zone, in the process of decomposition of boron titanates, at first, amorphous titanium oxide forms, and as it flies apart, rutile and anatase form depending on the temperature of the gaseous medium.

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**Fig. 1.** X-ray diffraction patterns of a TiB₂ specimen, laser irradiated surface (I), and ablation products on the substrate (II). In I: (a) initial ceramics; (b) surface of a fragment formed from the bottom of the ceramic specimen after irradiation in the continuous mode; (c) surface of fragments formed from the different parts of ceramics after irradiation in the pulse mode. In
II: (a, a’) ablation products obtained after irradiation in the continuous mode; (b, b’) ablation products obtained after irradiation in the pulse mode.

Fig. 2. SEM micrographs of a TiB2 ceramic surface before (a, a’) and after pulsed laser treatment at different places (b-b’’’). Secondary electron images (a, a’).

The absence of peaks of boron anhydride on the surface of the target is explained by two factors: the high volatility of B2O3 at relatively low temperatures and by the formation of titanium polyborates in the temperature range 1000–1300 °C [44]. The disappearance of the peaks of nickel borides and the appearance of weak broadened superposition peaks at 2θ ~ 33°, 43°, and 56° can be associated with the formation of nickel titanates [47-50] and, possibly, nickel polyborates [42, 50-54].

3.2.2. Products of ablation on substrate

In the CW irradiation mode, ablation products at place 1 (on the edge of the substrate) are an amorphized material (Fig. 1, a II substrate), which is represented by a halo at 2θ ~ 20°. According to [55], this broad peak is assigned to weakly ordered anatase. Peaks of H3BO3 are also present [56, 57]. This confirms the decomposition of TiB2, followed by the formation of TiO2 and B2O3. During storage in air, boron anhydride, in turn, absorbs moisture and transforms into H3BO3. At place 2, which is close to the crater of the target (at the center of
the substrate), peaks of Ni$_2$B$_2$O$_5$ and vitreous B$_2$O$_3$ and traces of rutile and H$_3$BO$_3$ (Fig.2, a’, II substrate) are registered.

In the pulsed mode of irradiation of the ceramics, the XRD pattern of ablation products is typical of the mixture of weakly ordered anatase and nickel borate phases (Fig. 2, II, b, b’), which, in rough approximation, can be considered as low-temperature TiO$_2$:B, Ni [58-60].

![Fig. 3. SEM micrographs of ablated products obtained in the CW mode at different magnifications.](image)

Ablation products formed in the CW mode and deposited on the substrate organize chain structures (Fig. 3 a, b). In the case where they overlap, compacted areas form on the substrate. A similar aggregation process occurs also in the gas phase. In this case, porous spherical particles form from chain formations (Figs. 3 c, d).

![Fig. 4. SEM micrographs of ablation products obtained in the pulsed irradiation mode.](image)
In the pulsed irradiation mode, ablation products form dense layers on the substrate (Fig. 4 a). At the same time, in the gas phase, spherical particles, which consist of ablation products integrated in dense fragments, form (Fig. 4 b).

Note that differences in the morphology of deposition products on the substrate agree with the notions of the more intensive course of the ablation process in the pulse mode. This means that, in the pulsed mode, the temperature in the irradiation zone attains or exceeds 3000 °C.

![Fig. 5. Simplified scheme of breakdown of a TiB₂ ceramic specimen under laser irradiation (a, a’) and bullet firing (d). In (b) and (c): decomposition and ablation products of ceramics inside the crater and on the substrate in passage through air.](image)

The obtained data enable us to represent a simplified scheme of high-temperature decomposition of TiB₂ ceramics under the conditions of oxidizer (O₂) deficiency in the crater zone (CW mode of laser treatment) and pulsed inflow of O₂ into the crater zone (pulsed mode of laser treatment). In this case, it should be taken into account that the breakdown process of a ceramic specimen (process I) occurs practically coincidentally with the process of release of vaporous ablation products from the crater zone (process II) (Figs. 5 a–c). The causes of the breakdown of specimens under high-power laser treatment are high stress gradients and temperature gradients between the ceramic body and the crater walls. The first factor is determined by the development of pressures of ablation products in the crater, compression of the material adjacent to the crater walls, and its fragmentation. In regions more remote from the crater, the ceramics has different temperatures and, therefore, different tensile stresses and
different shear stresses (the second factor). This leads to the breakdown of the ceramics into larger fragments. In principle, the presented model of laser-induced breakdown of TiB$_2$ ceramics is similar to the ballistic model of destruction (Fig. 5 d) [40, 61-63].

4. Conclusion

The performed investigations enabled us to reveal the common and distinctive features of the breakdown of TiB$_2$ ceramics in CW and pulse modes of laser bombardment in air. In both cases, “laser bombardment” from a small distance is accompanied by the formation of a crater in the ceramic body, breakdown of the ceramics into small and large fragments, the appearance of ablation products and their subsequent oxidation. Depending on the irradiation mode of the TiB$_2$ ceramics, it is possible to obtain dense (in the pulse mode) and “reticular” (in the CW mode) films, consisting of titanium oxides and boron oxides, in particular, vitreous B$_2$O$_3$. The difference in the type of films is determined by the intensity of irradiation (in the pulse mode, it is larger) and the pulsed character of oxygen inflow into the crater zone. In the CW irradiation mode, the access for oxygen to the crater is hindered due to the release of ablation products from the crater. The mechanism of laser-induced breakdown of TiB$_2$ ceramics is similar to ballistic model of destruction.

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Садржај: Процес високо-теппературског загревања TiB₂ керамике у ваздуху у континуалном и пулсном моду лазерског загревања праћен је рендгенском дифракцијом и скенирајућом електронском микроскопијом. Утврђено је да у зони загревања температура рaste до преко 3000 °C, долази до распадања TiB₂ и појаве абляционих продуката, који у струји ваздуха оксидирају и формирају густе филмове (у пулсном моду) или “ретикуларне” филмове (у континуалном моду) који се састоje од оксида TiO₂.
бора и титаніуму. Механізм лазерського пробою TiB₂ керамики є схожим
ором у балістичному пробою.
Ключне речи: TiB₂ керамика, локаль лазерно засуване, абляція.

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