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Modification of a SiC–Cr_5Si_3 ceramic surface by laser irradiation

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Abstract

The influence of IR-laser irradiation (1064 nm, 175 W) on a SiC–Cr_5Si_3 ceramic composite material was investigated by X-ray diffraction analysis, electron microscopy, atomic force microscopy, and X-ray microanalysis. The irradiation of specimens was carried out in air. It was established that, on the surface of the ceramics, a porous SiO_2 layer formed. The ablation products are silicon oxide nanoparticles of different shape.

Keywords: SiC ceramics; Laser irradiation; Oxidation

1. Introduction

The laser irradiation of composite ceramic materials results in the essential reorganization of their surfaces, since it is accompanied by thermophysical effects that are difficult to obtain by other methods of heating [1–6]. In view of the fact that the processes of surface modification of functional composite ceramics cause the formation of new properties of the material and, hence, the extension of the fields of their application, it is rather important to elucidate the nature and mechanisms of surface reorganization in different irradiation modes.

In [7], it was established that the laser irradiation of a ceramic surface with $\lambda = 1064$ nm and $P = 240$ mW in air is accompanied by a rise in the temperature of the surface to 2000 K. As this takes place, silicon evaporates from SiC, and the surface layer is enriched with carbon. Chromium silicide melts. As a result, the roughness decreases, and the ceramic surface is covered with the chromium silicide melt. An increase in the irradiation time leads to the oxidation of chromium silicide and the enrichment of the surface with chromium and silicon oxides.

The purpose of the present work is to investigate the modification of the surface of a ceramic SiC–Cr_5Si_3 material under the influence of high-power IR-laser radiation in air (i.e., in an oxygen-containing atmosphere).

2. Experimental procedure

The composite ceramic material was prepared by high temperature sintering at $T = 2073$ K under a pressure $P = 5$ GPa in a lens-type high-pressure apparatus for 2 min from α-SiC powder with Cr and Si additives, the amounts of which were calculated for the formation of chromium silicide (Cr_5Si_3). Specimens were 5 mm in diameter and 10 mm in length.

The specimens were irradiated with an infrared laser ($\lambda = 1064$ nm and $P = 175$ W) in air. The radius of the beam was 2 mm. The rate of movement of the beam was 2 mm/s. During irradiation, ablation products precipitated on a quartz substrate.

An X-ray analysis of the specimens was performed in a Siemens D-500 diffractometer using Cu Kα radiation. Scanning electron microscopy studies were carried out with an HU-200F unit. An X-ray microanalysis of samples was performed in a "Comebax SX50" unit. Atomic force microscopy (AFM) measurements were carried out on a Nanoscope IV of Digital Instruments in the tapping regime with a silicon nitride tip in height and phase modes. IR-spectra were obtained on a Specord M-80 spectrometer.

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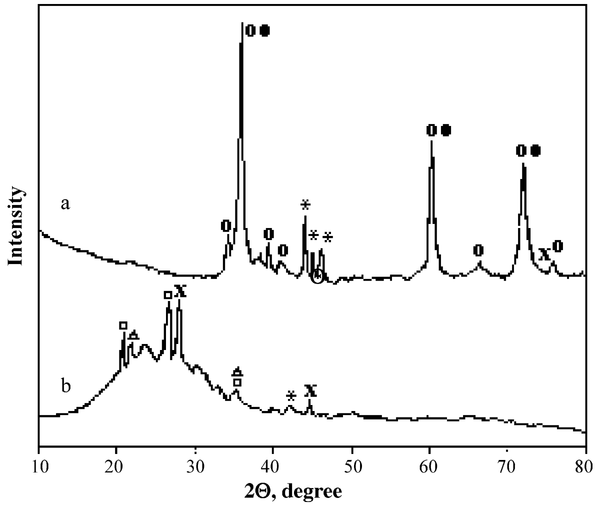

Fig. 1. A fragment of an X-ray diffraction pattern of a SiC–10% wt. Cr_5Si_3 material. (a) inicial simple; (b) ‘‘foam layer’’ (the surface after irradiation). (o) α-SiC; (●) β-SiC; (*) Cr_5Si_3; (×) Cr_3Si; (□) quartz; (△) cristobalite.

3. Results

3.1. Initial specimens

According to the X-ray phase analysis data, in the ceramics, along with α-SiC, small amounts of β-SiC and chromium silicide (Cr_5Si_3) are present (Fig. 1a).

Based on the data of electron microscopy, AFM, and X-ray microanalysis, it is possible to conclude that chromium silicide is inhomogeneously distributed between SiC grains (Fig. 2).

3.2. Irradiation on air

During irradiation in air, on the surface of the specimen, a strong white porous layer of thickness 3 μm forms. The surface is similar to foam glass, on which accumulations of fine particles are present (Fig. 3). In AFM studies in the topography regime, similar results were obtained (Fig. 4a). The pore size ranges from 40 μm to 15 nm. On a micrograph taken in the phase mode, white nanosized particles lying on a surface with another phase composition are seen (Fig. 4b).

The X-ray microanalysis data show that, on glassy surfaces, the basic elements are silicon (64.94 wt.%) and oxygen (~30.36 wt.%). The carbon content is ~4 wt.%, and the chromium content is ~0.7 wt.%. At places of accumulation of nanosized particles, oxygen and an increased chromium content (~5.17 wt.%) are recorded.

In the analysis of distributions of elements from the surface of the formed porous layer to the ceramic surface, it was established that the oxygen content decreases, whereas the chromium content and the silicon content increase.

The X-ray phase analysis data shows (Fig. 1b) that the ‘‘foam layer’’ mainly consists of an amorphous phase (an intensive halo with a maximal intensity at $2\theta \sim 24^\circ$, which is

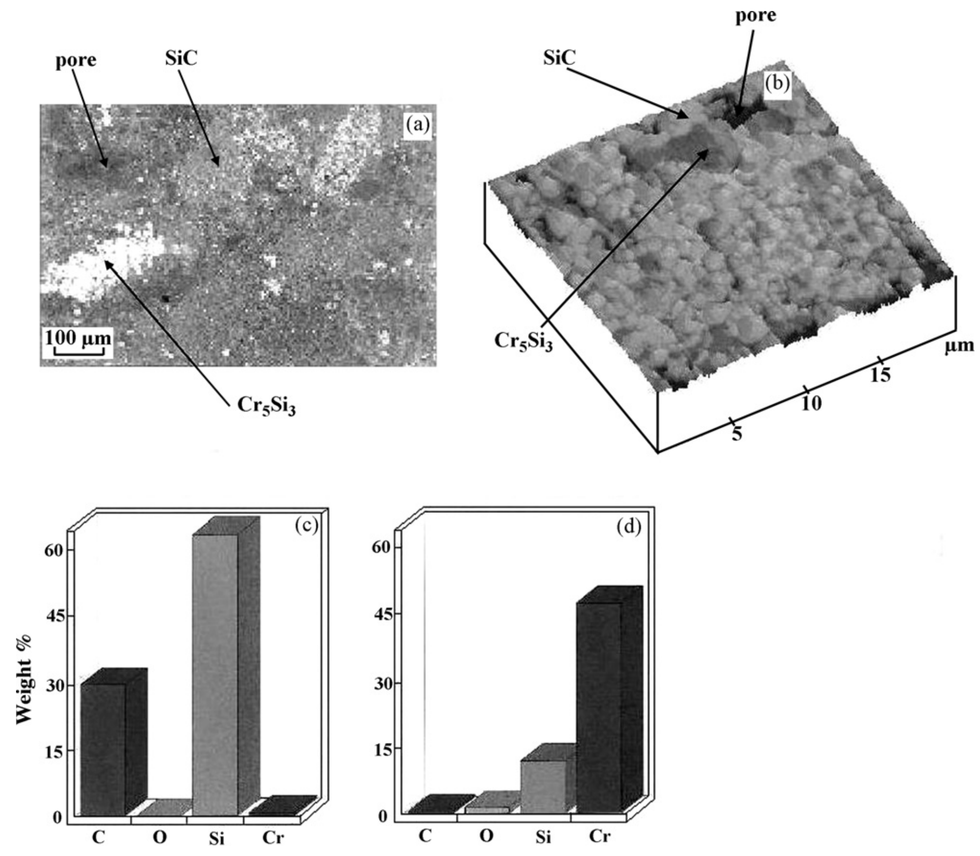

Fig. 2. Micrographs of SiC–10% wt. Cr_5Si_3 ceramics obtained with (a) scanning electron microscopy (SEM), (b) atomic force microscopy, and X-ray microanalysis (c, d); (c) corresponds to SiC; (d) corresponds to Cr_5Si_3.

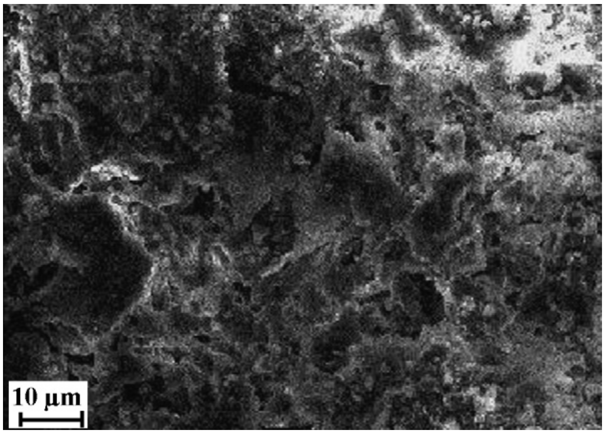

Fig. 3. Micrograph (SEM) of a ceramic surface after irradiation.

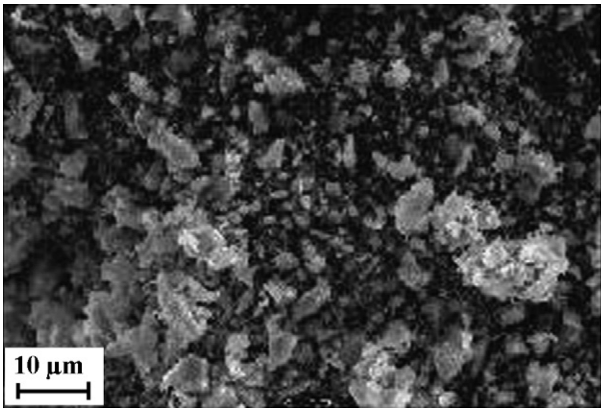

Fig. 5. Micrograph of ablation products obtained by laser irradiation in air.

assigned to SiO_2 glass). Quartz, cristobalite, Cr_3Si, and traces of Cr_5Si_3 are also present.

Thus, the neogenic surface is mainly composed of porous silica glass with inclusions of nanosized particles of chromium silicides and chromium oxide, whose contents are insignificant.

In the electron micrograph presented in Fig. 5, one can see that the ablation products consist of particles of different shape.

The AFM method made it possible to reveal most clearly the formation of two types of particles differing in morphology, namely grains with a size 60–10 nm and solidified flattened petal-shaped drops of the melt (Fig. 6). In Fig. 6, it is seen that the solidified drops form a complex tubular porous structure. Grains, in turn, form aggregates with pores between them.

In an IR-spectrum of the ablation product, in the frequency range 400–2000 cm^{-1}, absorption bands characteristic of cristobalite, fused quartz, and silicon oxide films are observed (Table 1 and Fig. 7a).

According to the X-ray microanalysis data, in grains, oxygen and silicon are present. In petal-shaped formations, besides these two elements, chromium (no more than 0.5 wt.%) is registered.

4. Discussion

The obtained data on the formation of the porous thick silica glass layer and chromium oxide nanosized particles on the ceramic surface indicate that the surface intensively oxidizes. The source of the formation of SiO_2 can be both silicon carbide and the chromium silicide, whereas chromium oxide can be formed only from chromium silicide as a result of its oxidation.

The presence of cristobalite, quartz, and fused quartz indicates that the temperature on the ceramic surface attains ~2000 K. At this temperature, silicon carbide evaporates by the reaction [8,9]:

$$\mathrm{SiC} = \mathrm{Si_g} + \mathrm{C_s},$$

where the subscripts g and s designate the gaseous and the solid state, respectively.

The evolution of Si vapors in passing through the oxygen-containing atmosphere is the source of the formation of silica precipitating in the form of particles.

The melting point of Cr_5Si_3 is 1973 K. The diffusion of oxygen in the melt must be accompanied by the formation of the surface layer consisting of silicon and chromium oxides.

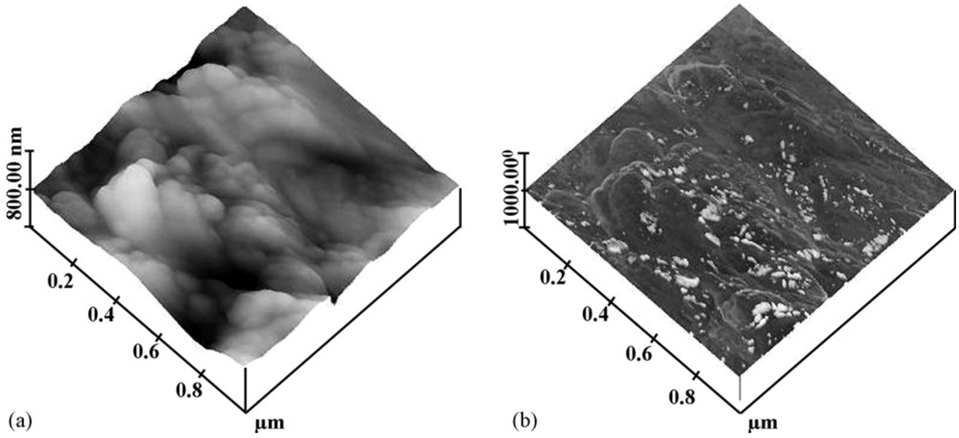

Fig. 4. Micrograph (AFM) of a ceramic surface after irradiation: (a) exposition in the topography mode, (b) exposition in the phase mode.

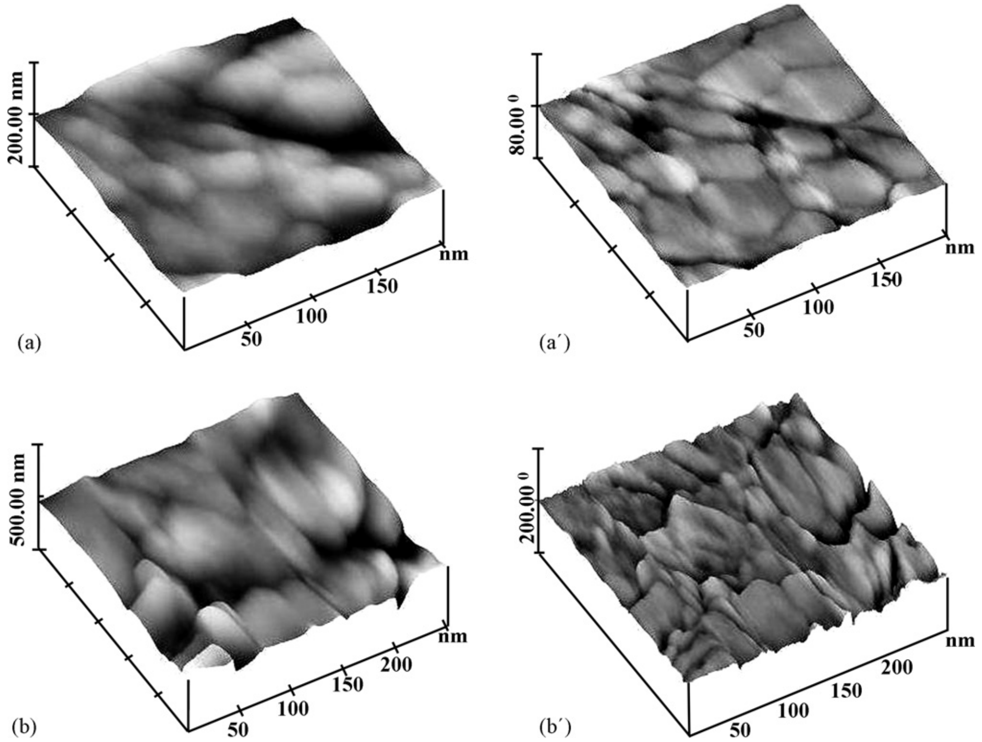

Fig. 6. AFM data of ablation products precipitated in air: (a, b) exposition in the height mode. (a′, b′) exposition in the phase mode. (a, b) and (a′, b′) are different regions of ablative product deposition on quartz substrate.

Table 1
IR absorption bands observed in the frequency range 400–2000 cm^{-1} in SiO_2 and films

Material	IR-frequency (ν), cm^{-1}				Ref.
Cristobalite	487m	654w	800m	1100s	[13]
Quartz	465–470m		798 780m	1084s	[13]
Fused quartz	476s		802m	1114s	[13]
Silicon oxide films	46–449m	560w	783–826w	1026–1055s 1163–1179sh	[14]
Ablation product	475m	630w	800w	1125s	This work

Note: s—strong, m—middle, w—weak intensity of adsorption band, sh—shoulder on the main band.

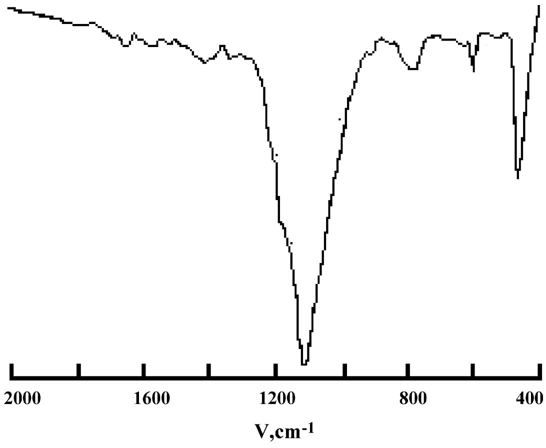

Fig. 7. IR absorption spectra of ablation products obtained in air.

The thickness of the layer increases as the irradiation time is extended until the chromium silicide melt is exhausted.

However, such simple description of the process is inconsistent with the following facts: in the surface layer, accumulations of carbon are insignificant; on the surface, a little amount of chromium oxide is detected; in the surface layer, Cr_3Si forms, whereas Cr_5Si_3 is not registered.

According to [10], SiO_2 and Cr_2O_3 do not form glassy films. Due to this, in the initial stage of oxidation, oxygen easily passes through the porous layer of oxides. The insignificant quantity of carbon can be explained by the development of the reaction: $C_s + O_2 \rightarrow CO_2(CO)_g$.

As the content of SiO_2 increases, and during its melting, the principal cause of pore formation is the passage the CO_2 through the silica melt.

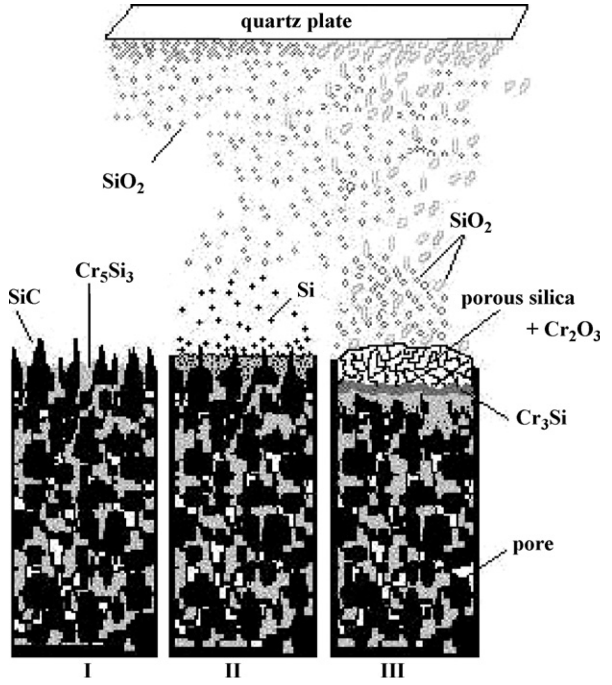

Fig. 8. Common scheme of surface modification. (I) Ceramics; (II) initial stage of laser irradiation; (III) final stage of laser irradiation.

The chromium oxide has low volatility. Therefore, it must accumulate on the surface. The absence of such effect means that reactions resulting in its disappearance proceed.

Reactions proceeding in the carbothermal reduction of oxides belong to such reactions. At such high temperature, in contact zones of oxides and carbon, the formation of gaseous Si, SiO, and Cr takes place. A part of the gaseous products volatilizes. That is why, in the precipitated ablation products, a small amount of Cr is registered. Another part of Cr goes to the Cr_5Si_3, which leads to the formation of Cr_3Si. As a result, the surface is enriched by the silica melt. Chromium silicides and unreacted carbon are under the SiO_2 melt.

At $T \sim 2000$ K silica evaporates (sublimates) [11]. This process is the basic source of the formation of nanosized particles in ablation products. However, the presence of silica petal-shaped formations testifies to another mechanism of precipitation, which is realized in parallel and consists in the ejection of silica melt drops under the action of excessive vapor pressure [12]. Common scheme of the modification of the surface is presented in Fig. 8.

5. Conclusions

1. During laser irradiation, the surface of the SiC–Cr_5Si_3 composite ceramics is heated to 2000 K.
2. The irradiation in air is accompanied by the oxidation of silicon carbide and chromium silicide and by the formation of a porous silica glass layer on the surface of the material.
3. The basic ablation product is SiO_2 nanosized particles.

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