Laser Irradiation of SiC-MoSi$_2$ Composite Ceramics

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Abstract:
The influence of continuous IR laser irradiation ($\lambda = 1064$ nm, $P = 240$ mW) on SiC—MoSi$_2$ composite ceramics was investigated by X-ray diffraction, electron microscopy, atomic force microscopy, and X-ray microanalysis. The irradiation of specimens was carried out in air. It was established that, due to heating of the surface under laser irradiation, oxidation of SiC and MoSi$_2$ and sublimation of SiO (SiO$_2$) and MoO$_3$ take place. Depending on the content of the components in the ceramics and the irradiation time, SiO$_2$ or MoO$_3$ layers form on the surface or disappear from it. For a long irradiation time, the oxidation and cleaning of the surface (sublimation of oxides) are cyclic in character.

Keywords: SiC, MoSi$_2$, Laser irradiation, Oxidation, Sublimation.

1. Introduction

Composite ceramic materials are successfully used as structural materials operating under conditions of high temperatures, speeds, and aggressive environments. Composites on the base of silicon carbide and molybdenum disilicide can be classified with these materials [1-5]. Since properties of ceramic composites substantially depend on their manufacturing methods, different variants of the synthesis of binary and more complex systems on the base of SiC—MoSi$_2$ are actively developed [6—13]. A new method of control of properties of composite SiC-based ceramics consists in modifying properties of its surface by laser irradiation in different regimes and different gas atmospheres [14]. Irradiation in air initiates a number of oxidizing processes [15, 16] that proceed in corrosion of ceramics [17—20].

The aim of the work is to investigate the modification of the surface of SiC—MoSi$_2$ ceramics under long radiation in a continuous regime. A low-power radiation source was chosen for reasons of creating conditions favoring evaporation and preventing the formation of plasma and a significant amount of a liquid phase. Thus, the modification process of the surface of the composite ceramics caused by oxidation and evaporation can be observed in a “slow” regime. High-power continuous and pulse irradiation, accompanied by fast heating of the surface and plasma formation, hardly enable one to determine the role of individual components in the irradiation-induced modification of the surface.

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2. Experimental Procedure

Composite ceramic specimens 5 mm in diameter and 10 mm in length were made from \( \beta \)-SiC and MoSi\(_2\) powders with a mean particle size \( d_{\text{mean}} \sim 30—60 \) nm and from their powders mixtures prepared in a ball mill (balls and the drum walls of the mill were hard faced) for 1 h with the compositions 50 wt.% \( \beta \)-SiC—50 wt.% MoSi\(_2\), (specimens I), 80 wt.% \( \beta \)-SiC—20 wt.% MoSi\(_2\), (specimens II), and 80 wt.% MoSi\(_2\)—20 wt.% \( \beta \)-SiC (specimens III) in a lens-type high-pressure apparatus under a pressure \( P = 4 \) GPa in the temperature range 1500—1800 \(^\circ\)C. The rate of increase of temperature was 35 \(^\circ\)C/s. The exposure time at each set temperature was 60 s.

The specimens were irradiated with an infrared laser (\( \lambda = 1064 \) nm, \( P = 240 \) mW) in air. The radius of the laser beam was 0.45 mm. The power density was \( \sim 38 \) W/cm\(^2\). The irradiation time was varied from 30 to 300 min.

An X-ray analysis of the specimens was performed using a Siemens D-500 diffractometer in Cu \( K_\alpha \) radiation. Scanning electron microscopy studies were carried out with an HU-200F unit. An X-ray microanalysis of specimens was performed in a Comebax SX50 unit. Atomic force microscopy measurements were carried out on a Nanoscope IV of Digital Instruments in the tapping regime with a silicon nitride tip using the height (topography) regime with a cross-sectional profile and the phase regime.

3. Results
3.1. SiC and MoSi\(_2\) Ceramics

The initial molybdenum silicide ceramics consists of \( \alpha \)-MoSi\(_2\) (Fig. 1a). The initial silicon carbide ceramics primarily consists of \( \beta \)-SiC and contains traces of \( \alpha \)-SiC, Si, and C. The presence of traces of Si and C is due to the features of the synthesis of SiC nanopowders under sintering conditions of the ceramics (Fig. 1b).

![Fig. 1. Fragments of X-ray diffraction patterns of MoSi\(_2\) (a), \( \beta \)-SiC (b), and composite 50 wt.%\( \beta \)-SiC—50 wt.%MoSi\(_2\) ceramic (specimen I) (c, d): (a), (b), and (d), \( T_w = 1800 \) \(^\circ\)C; (c) \( T_w = 1500 \) \(^\circ\)C. \( t_w = 60 \) min. (\( \bullet \)) \( \beta \)-SiC; (\( \circ \)) \( \alpha \)-MoSi\(_2\); (\( \blacksquare \)) \( \beta \)-MoSi\(_2\); (\( \bigcirc \)) Si; (\( \triangle \)) C.](image-url)
3.2. Composite SiC—MoSi₂ Ceramics

3.2.1. X-ray phase analysis

In composite ceramics, as the molybdenum disilicide content in the initial mixtures increases, the content of α-MoSi₂ increases, and the content of β-SiC decreases (Fig. 2 a). In the high-temperature synthesis region, β-MoSi₂ forms. Its content rises with the increasing of α-MoSi₂ content in the initial powder mixtures and an increasing of temperature of treatment (sintering) (Fig. 2 a, b and Fig. 1c, d).

![Graph](image)

**Fig. 2.** Change of diffraction line intensity in ceramics depending on the content of components in initial mixtures β-SiC + MoSi₂ (a) and temperature treatment (b). For a: \( T_r = 1800 ^\circ C \); \( t_r = 60 \) min. For b: mixture 50 wt.% β-SiC + 50 wt.% MoSi₂. (1) β-SiC; (2) α-MoSi₂; (3) Si; (4) β-MoSi₂.

3.2.2. Electron microscopy, AFM, and X-ray microanalysis

In the electron micrographs of the initial composite ceramics (Fig. 3), dark-grey and light-grey grains are seen. According to X-ray microanalysis, dark-grey grains correspond to SiC, and light-gray grains are MoSi₂. On MoSi₂ grains, darker regions are observed. They can be assigned to regions of Mo₃Si₃ localization (Table 1). Pores (black) and zones of formation of oxides (white) are also present.
Tab. I. Distribution of elements in different regions of the 50 wt.% SiC: 50 wt.% MoSi$_2$ sample obtained at 1800 °C.

<table>
<thead>
<tr>
<th>Colour of particle surface</th>
<th>Elements, wt.%</th>
<th>Type of compound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>C</td>
</tr>
<tr>
<td>Dark-grey</td>
<td>69.78</td>
<td>30.22</td>
</tr>
<tr>
<td>Light-grey</td>
<td>65.97</td>
<td>not</td>
</tr>
<tr>
<td>Dark-grey</td>
<td>86.04</td>
<td>1.81</td>
</tr>
<tr>
<td>White</td>
<td>48.3</td>
<td>-</td>
</tr>
</tbody>
</table>

The AFM data indicate that the surface of the ceramics has different morphology (see Fig. 4-7). The surface of the specimen II (Fig. 4a, 5a) is more loose (friable) than the surface of the specimen III (Fig. 6a, 7a).

Fig. 3. Electron micro photo of ceramics with 80 wt.% β-SiC + 20 wt.% MoSi$_2$ (a) and 20 wt.% β-SiC + 80 wt.% MoSi$_2$ (b). $T_\text{r} = 1800 ^\circ \text{C}; t_\text{r} = 60 \text{ min.}$

Using data of electronic microscopy and the microanalysis, it has appeared possible to attribute dark areas to grains of SiC or MoSi$_2$. Light loose areas belong to congestions of oxides.
3.3. Irradiated Composite SiC—MoSi$_2$ Ceramics

During irradiation of composite ceramic specimens II, in the first 60 min, a significant change in the state of the surface is observed. The surface becomes smoother. The silicon and oxygen disappear from it, whereas the molybdenum content increases (Fig. 4a, b, Tab. 2). As the irradiation time increases (60 min $\leq t \leq 120$ min), oxygen is again recorded on the surface, and its roughness increases. At the same time, the surface changes its color from dark to light (see Fig. 4b, c, Tab. II).

![Fig. 4. AFM images of 80 wt.% SiC + 20 wt.% MoSi$_2$ ceramic obtained in the regime of phase. (a) initial samples; (b) after 60 min. of irradiation; (c) after 120 min.; (d) after 180 min.; (e) after 300 min. of irradiation.](image)

However, in the time interval 120 min $\leq t \leq 180$ min, the surface changes again, and the molybdenum and oxygen contents in it decrease, whereas the silicon and carbon contents increase (Fig. 4c and 4d, Tab. II). As the irradiation is further continued, the modification
cycle of the surface is repeated (see Fig. 4d and 4e, Tab. II).

During irradiation of composite ceramic specimens III, the oxidation of molybdenum occurs first. As the irradiation time is increased to 60 min, on the surface of the specimen, a layer containing Mo, Si, and O forms (Tab. II). The formation of a loose light layer can be observed (see Fig. 6a - 6c). In the time interval $120 \text{ min} \leq t \leq 180 \text{ min}$, the oxygen-containing layer disappears from the surface, and MoSi$_2$ and SiC are recorded on it (see Fig. 6d and Tab. II).

![AFM cross section analysis of profiles of 80 wt.% SiC + 20 wt.% MoSi$_2$ ceramic](image)

**Fig. 5.** AFM cross section analysis of profiles of 80 wt.% SiC + 20 wt.% MoSi$_2$ ceramic (a) initial samples; (b) after 30 min. of irradiation; (c) after 60 min.; (d) after 120 min., (e) after 180 min.; (f) after 240 min.; (g) after 300 min of irradiation.

As the irradiation is continued for more than 180 min, the formation of an oxygen-containing layer is again observed (Fig. 6e and Tab. II). Accordingly the relief of a surface changes (Fig. 5, 7).
Tab.II. Change of element content on the surface of irradiated samples

<table>
<thead>
<tr>
<th>Time of irradiation, min.</th>
<th>Content of elements, wt.%</th>
<th>80 wt.% SiC + 20 wt.% MoSi₂</th>
<th>20 wt.% SiC + 80 wt.% MoSi₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>C</td>
<td>Mo</td>
</tr>
<tr>
<td>Initial</td>
<td>66.03</td>
<td>23.18</td>
<td>4.34</td>
</tr>
<tr>
<td>30</td>
<td>66.53</td>
<td>20.75</td>
<td>9.99</td>
</tr>
<tr>
<td>60</td>
<td>68.18</td>
<td>4.71</td>
<td>25.97</td>
</tr>
<tr>
<td>120</td>
<td>65.60</td>
<td>8.39</td>
<td>7.12</td>
</tr>
<tr>
<td>180</td>
<td>67.91</td>
<td>28.68</td>
<td>2.17</td>
</tr>
<tr>
<td>240</td>
<td>68.76</td>
<td>25.27</td>
<td>1.76</td>
</tr>
<tr>
<td>300</td>
<td>65.85</td>
<td>22.62</td>
<td>1.22</td>
</tr>
</tbody>
</table>

The investigation of the cross-sectional profile in the topography regime made it possible to evaluate changes in the height of the relief $\Delta h$ during long irradiation (Fig. 8). It is described by the formula $\Delta h = h_{\text{max}} - h_{\text{min}}$, where $h_{\text{max}}$ and $h_{\text{min}}$ are, respectively, the maximum value and minimum value of the height of the relief. From Fig. 8 it can be seen that these changes are cyclic in character.

4. Discussion

The obtained results show that, during long laser irradiation of the investigated composite ceramics, the complex oxidation (corrosion) process proceeds. Depending on the SiC and MoSi₂ contents in the ceramics and the irradiation time, the oxidation of SiC or the oxidation of MoSi₂ plays the determining role in the modification of the surface during long irradiation.

In the case of composite ceramics II, in the initial stage of irradiation, the removal of the initial oxidation product of SiC, basically SiO₂, occurs. Then the oxidation of “cleared” SiC proceeds by the reactions

$$\text{SiC} + \text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2,$$

$$\text{SiO}_2 + \text{SiC} \rightarrow \text{SiO} + \text{CO}_2.$$

These reactions occur at $T \geq 1600 \, ^{\circ} \text{C}$ [21]. As a result, the relief becomes smoother, and, on the surface, SiC and MoSi₂ appear (see Fig. 4b).

While MoSi₂ appears on the surface, the oxidation process begins to develop. One of the reactions proceeding in the high-temperature region is the following [13]:

$$2\text{MoSi}_3 + 7\text{O}_2 = 2\text{MoO}_3 + 4\text{SiO}_2.$$

Both SiO₂ and MoO₃ disappear (sublimate) from the surface, whereas mainly grains of SiC again appear on it (Fig. 4 c, d). Then the cycle is repeated (see Fig. 4 e). It should be noted that the boiling (evaporation) temperature of SiC is 2980 $^{\circ} \text{C}$ [22]. Consequently, under irradiation, the temperature of the surface is not lower.

Oxidation of a surface is accompanied by increase in its roughness. Removal of an oxide layer from a surface leads to smoothing of a relief (Fig. 5, 8).
On the surface of the composite ceramic specimen III, the oxidation of MoSi$_2$ (basically) and the sublimation of molybdenum oxide from the surface (see Fig. 6 c, d) are more clearly seen. Then the oxidation cycle of the surface (see Fig. 6 e) is repeated. Accordingly the relief of a surface changes (Fig. 7, 8). The evaporation temperature of MoO$_3$ is 1257 °C [22]. Therefore it is possible to assume, that process oxidation-evaporation proceeds with greater speed, than for ceramics II.

The thickness of the oxide layer can be estimated roughly as $\Delta h = h_{\text{max}} - h_{\text{min}}$, where $h_{\text{max}}$ is the maximal height of a relief, and $h_{\text{min}}$ is the minimal height of a relief under the given
conditions of an irradiation. From Fig. 8 it is visible that the change of $\Delta h$ has a cyclic character.

According to [13] at oxidation of MoSi$_2$ under a layer of SiO$_2$ and MoO$_3$, Mo$_5$Si$_3$ is formed:

$$5\text{MoSi}_2 + 7\text{O}_2 = \text{Mo}_5\text{Si}_3 + 7\text{SiO}_2$$

and by the decomposition reaction of the higher silicide into the lower silicide at high temperatures ($T > 1900^\circ\text{C}$)

$$5\text{MoSi}_2 = \text{Mo}_5\text{Si}_3 + 7\text{Si}.$$
Fig. 8. Change of thickness of the oxide layer depending on the time of irradiation. (1) for 80 wt.% SiC + 20 wt.% MoSi$_2$; (2) for 20 wt.% SiC + 80 wt.% MoSi$_2$ ceramics.

Thus, by varying the irradiation time, it is possible to modify the surface of the composite ceramics. The formation of the oxygen-containing layer can be considered as the formation of a protective corrosion-resistant coating. The removal of the oxygen-containing layer and the appearance of molybdenum silicides can be considered as the metallization of the surfaces since MoSi$_2$ is characterized by metallic conductivity. In this case, silicides can play the role of high-temperature solders in welding of refractory metals [13]. Moreover, the sublimation products can be the base of the formation of composite films and coatings that can be used in catalysis processes [23].

5. Conclusions

1. For the used irradiation regime, the temperature of the surface of the SiC–MoSi$_2$ ceramics is not lower that 3000 ºC.
2. Long irradiation of SiC–MoSi$_2$ specimens in air causes cyclically repeated processes on the surface, namely, oxidation of the components of the composite ceramics and evaporation (sublimation) of formed oxides from the surface. In this case, it is possible to arrest the process at different stages of modification of the ceramic surface.

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Садржај: Проучен је утицај континуалне ласерске инфрацрвене радијације (λ = 1064
nm, P = 240 mW) на SiC—MoSi2 композитну керамику коришћењем рентгенске
dифракције, електронске микроскопије и атомске микроскопије и рентгенске
микроанализе. Зрачење узорака извршено је у ваздуху. Одређено је да се дешава
оксидација SiC и MoSi2 и сублимација SiO (SiO2) и MoO3 услед грејања површине
изложене зрачењу. У зависности од садржаја компоненти у керамици и времена
зрачења формирају се слојеви SiO2 или MoO3 на површини ли нестаје са ње. За дужа
времена зрачења оксидација и чишење површине (сублимација оксида) су циклично
карактера.
Кључне речи: SiC, MoSi2, ласерско зрачење, оксидација, сублимација.