Laser sintering of Si-SiC composite layers

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Abstract. The results of studies on the production of single-layer and two-layer samples of silicon carbide composite (Si-SiC) from initial powder materials using laser radiation are presented. The efficiency of the sintering process was determined by the results of X-ray structural analysis and studies with an electron microscope.

1. Introduction

Silicon carbide is one of the unique materials for modern industrial applications. Possessing high thermal, strength and weight characteristics, it finds application in its various fields (armor plates, refractories, pipes for aggressive media, cutting tools) [1]. At the same time, the unique characteristics of silicon carbide coexist with a number of serious problems arising in the manufacture and operation of products from this material, the main of which is the absence of a melting process in it [2].

Existing methods for the production of products from crystalline and comparable in density to polycrystalline SiC often do not allow obtaining products of a given geometric shape from these materials [3, 4]. As a rule, subsequent rather laborious and expensive mechanical processing is required. Therefore, for several decades, the industrial production of various composites based on silicon carbide has been established, which in their physical and chemical properties are somewhat inferior to crystalline SiC, but, nevertheless, are finding more and more directions for use [5].

To give products made of SiC composites of a given geometric shape, various methods are used: slip casting [6], hot pressing [7], preliminary machining of compressed carbon [8, 9], printing 3D models based on liquid polymer [10-13] or melting at a high temperature of the binder [14], sintering of powder SiO2 and its subsequent transformation into silicon carbide [15]. But all these methods require mandatory heating of the formed workpiece to high temperatures in specialized furnaces of various types to ensure the conditions necessary for the corresponding chemical reaction to proceed.

In this work, we present the results of a study of the necessary conditions for the production of silicon carbide products using only laser heating and in the absence of external high pressure. The use of laser radiation for sintering silicon carbide seems to be a promising approach to solving the problem of forming products of complex shape from this material, since the laser allows control of the heating temperature at each point of action. It should be noted that the use of laser radiation in additive technologies based on sintering refractory powders of various materials is widely used, however, these technologies are poorly developed in relation to silicon carbide [16].

2. Materials and methods

Having studied various methods of obtaining materials from SiC composites, and taking into account the absence of high external pressures to compact the charge components, as well as the absence of additional furnace heating, the method of reaction sintering was chosen [17]. From the point of view
of manufacturability, this method is very difficult due to its multistage nature. The essence of the reaction sintering process consists in the formation of secondary SiC, which is a binder for particles of the original silicon carbide (primary), which is a component of the charge together with carbon and a special binder. In this case, in addition to SiC, the composite may contain both free silicon and carbon.

The process of obtaining a finished product includes several stages:
- Batch preparation (cleaning, dosage, mixing of components);
- Curing or drying (removal of solvent and polymerisation of the binder);
- Carbonization (heating in an inert atmosphere to decompose the organic binder);
- Silicon firing (vapor and liquid silicon impregnation through existing pores in the workpiece);

It was assumed that:
- Reproduce all technological cycles of reaction sintering of Si-SiC only using laser heating;
- To work out for each cycle the optimal temperature and time regimes for the implementation of the repeatability of the process;
- Investigate various combinations of charge components in order to obtain the minimum content of free carbon and silicon in the final sample;
- Carry out the growth of several layers, and investigate the boundary between them for the presence of secondary SiC bridges between the primary carbide particles;

Since, after mixing the charge, all other technological processes necessary for the reaction sintering of silicon carbide require the creation of different temperature regimes, it was decided to reproduce each of them using laser heating: first, to accelerate the solidification of the charge, then to carbonize the workpiece, and finally , for siliconizing the sample.

In this case, the thermal and time modes of exposure to laser radiation were investigated for various combinations of charge components.

The samples were prepared and then sintered following the standard procedure for the preparation of silicon carbide by the reaction method [18]. The charge for the samples was composed of a composition of silicon carbide powder with a grain size of 25-40 μm and carbon powder with a maximum length of less than 1 μm, mixed in specified ratios for several hours in a ball mill. To carry out the planned experiments, a special working chamber with entrance and observation windows was made and a test bench with the necessary measuring equipment was assembled, the diagram of which is shown in Figure 1.

The beam of a YLR-700-MM-CW fiber laser (λ = 1.07 μm) with an adjustable radiation power of up to 700 W was directed to a target located in a sealed chamber using an optical system of mirrors and lenses. The target was a tungsten cell with the composition under study and was mounted on a molybdenum plate, which could be heated by electric current to a temperature of about 1000 ° C to remove free oxygen from the powder materials used in the work.

**Figure 1** Installation diagram.
To control the heating process, a W-Re thermocouple (Type 2) was used, touching the walls of the heating cuvette with the sample. A vacuum of about 10^{-3} atm was provided by a VALUE oil vacuum pump. The wide window of the chamber made it possible to visually observe and register the course of the processes under study.

The target was irradiated with a laser when the chamber was filled with a gas (argon or nitrogen) at normal pressure and in a vacuum.

After siliconizing firing, the samples were placed in a mixture of two concentrated acids (HF + HNO₃, in a 1:1 ratio) for 12 hours to remove residual free silicon. After the procedure of washing and drying the samples, they were investigated by various methods (weighing, determination of density, phase X-ray structural analysis (X-ray diffractometer Panalytical X’Pert Pro MRD, Netherlands), electron microscope JSM-7001F (JEOL, Japan)).

Figure 2 on the left, shows a diagram of the phase composition of a sample industrially synthesized in an induction furnace for about 40 hours, and on the right (Figure 3) for comparison is a diagram of a sample obtained using laser heating in less than a minute.

The hexagonal polytype SiC-6H is shown in green, the cubic polytype SiC-3C is in blue, and the polytypes with a large lattice period are shown in gray. Initially, both types of charge contained only the hexagonal polytype SiC-6H, but in different amounts. The appearance of these diagrams confirms the appearance of secondary SiC in the form of a cubic SiC-3C polytype and polytypes with a large lattice period, and this is typical both for the traditional synthesis carried out in an induction heating furnace and for the synthesis of silicon carbide using laser heating.

There is no silicon in the diagrams because to remove it, all the samples we obtained were necessarily etched with a mixture of acids prior to research. The slight difference in the ratios of the final constituent components for the two sintering methods can be explained by the different concentration of hexagonal SiC-6H in the initial mixtures for each charge.

In addition, the samples were examined by scanning electron microscopy. Figure 4 and Figure 5 shows photographs of the microstructure of a fracture and surface in a single-layer sample synthesized by a laser.

On the Figure 4 presented the sample fracture section. One can see the areas of synthesis of secondary silicon carbide along the faces of the initial SiC crystals, as well as "bridges" - the areas between the particles of the primary carbide, from the newly formed secondary silicon carbide (some of them are shown by arrows).

The presence of free Si and C in the final product worsens the properties of the Si-SiC composite compared to crystalline or polycrystalline SiC, free carbon reduces the mechanical strength, and the presence of free silicon lowers the thermal stability, but these disadvantages can be mitigated by obtaining a high-quality bond between the particles of primary SiC. The larger the number of particles
of the initial SiC during the synthesis reaction formed bridges with each other from secondary SiC, the more durable and integral framework is formed from them. The presence of such a frame significantly improves the mechanical, chemical and radiation resistance at high temperatures, since all the main types of loads fall on it. That is why we paid great attention to the issue of bridges between particles in our studies.

Figure 4 View of the sample fracture section at a magnification of 3500 times.

Figure 5 View of the surface in composite at a magnification of 800 times.

Figure 5 shows the microstructure of the surface of a single-layer sample synthesized by a laser. In the selected area, one can clearly see the growth and coalescence of secondary SiC crystals in the form of flat parallel plates, which is very typical for hexagonal polytypic silicon carbide structures [19].

The presented research results indicate the presence of a SiC synthesis reaction in laser-treated samples, and the observed presence of secondary silicon carbide bridges between primary SiC particles and the growth of plates on the surface of SiC particles allowed us to start a series of experiments on growing another layer.

The second layer was applied to the sample after cleaning one of its surfaces from silicon residues. All other operations (drying, carbonization, and siliconization) were carried out similarly to the above scheme.

Figure 6 shows a photograph of the view of two layers in an optical microscope. The size of the fracture section of this sample is not more than 2.5x1.5 mm. The composition of the charge had a slightly different combination of components, because of this they differ in color, but the boundary between the layers is clearly visible.

Figure 6 Two layers at an magnification of 20 times.

Figure 7 View of the fracture of two layers of SiC at an magnification of 170 times.
For two-layer samples, studies were also carried out using an electron microscope. Figure 7 shows the microstructure of a fracture in a two-layer sample synthesized by a laser. This angle was chosen deliberately, since the insufficient adhesion of particles on the left edge of the upper layer (highlighted area 1) and more than satisfactory filling of the space between the particles of the first and second layers (highlighted area 2) with secondary SiC are clearly visible. This situation can be explained by nonuniform heating of the sample by laser radiation. Both of the photos are made after etching free Si.

Conclusions.
The possibility of carrying out each of the necessary cycles of reaction sintering of the Si-SiC composite from the initial powder components using laser heating was confirmed, and in different media.

The results of laboratory studies show the formation of secondary silicon carbide in the form of bridges between particles of primary SiC and represent the cubic SiC-3C polytype and polytypes with a long lattice period.

In a two-layer sample, regions were found in which the boundary between the layers is not visible, which may indicate the possibility of creating conditions for the formation of a continuous SiC framework between the layers using laser heating. Полученные результаты позволяют надеяться на continuation of experiments on the implementation of such works as the elimination of cracks or holes in finished products, welding, reduction of the roughness of materials from the Si-SiC composite, as well as, in the future, the beginning of research on the possibility of creating a 3D printing technology.

The use of a laser in the Si-SiC composite synthesis technology allows solving these problems locally without heating the rest of the product, which can be extremely important when working with containers filled with hazardous or harmful substances.

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