Method for the modification of graphite subsurface layer to a solid mixture of SiC and graphite

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Abstract. We studied the interaction of molten Si and graphite surface during annealing in different atmospheres (CO, vacuum, Ar). The studies have shown that during annealing in CO atmosphere a composite material of SiC and graphite in a thick subsurface layer of the graphite is being formed, whereas at vacuum and Ar atmosphere the modified layer is either thin or absent. The composition and structure of both the composite material itself and the interface between the composite material and the graphite matrix were investigated using the methods of scanning electron microscopy and Raman spectroscopy. Studies have shown that the composite material obtained by this method has a branched fibrous structure consisting of small tubular layers of silicon carbide interspersed with large monocrystalline grains of silicon carbide of the cubic polytype, which leads to significant strengthening of the material. Thus the proposed method can be used to form a thermal protective, chemically resistant coating on graphite surface.

1. Introduction

Composite materials are widely used in dentistry, aerospace, construction, automotive, shipbuilding and many other fields of industry. There are many methods for obtaining different composite materials. In this work, we studied the interaction of molten Si and SiC with the graphite matrix in different atmospheres (CO, vacuum, Ar) and show that during annealing in CO atmosphere a thick subsurface layer of composite material is being formed consisting of small SiC particles having nano sizes interspersed with large single-crystal SiC particles of about 10 μm in size inside the graphite basement. Large single-crystal SiC particles act as reinforcing elements that provide the necessary mechanical characteristics of the material, and the graphite matrix acts as a binder. At the same time annealing in Ar or vacuum atmosphere leads to formation of significantly thinner layers or absence of SiC coating.

The proposed technology of annealing of graphite with molten silicon in CO can be used both to increase the chemical inertness and operating temperature of graphite products, and to obtain a single-crystal SiC powder. Thus, studying the processes occurring during modification and studying the physical characteristics of the resulting mixture of SiC and graphite is a relevant task.

2. Experimental methods

The graphite modification method [1] is partially based on the technology of synthesis of epitaxial SiC films inside a silicon (Si) matrix due to the replacement of Si atoms by carbon atoms [2–4]. It should be
noted that the conversion of Si to SiC occurs uniformly over the entire area of the Si substrate. This process is realized as a result of a topochemical reaction:

$$2Si_{\text{solid}} + CO_{\text{gas}} \rightarrow SiC_{\text{solid}} + SiO_{\text{gas}},$$

(1)

The synthesis of SiC films occurs at a temperature of 1100–1300°C in an atmosphere of carbon monoxide (CO). It should be noted that the thickness of SiC films obtained by atomic substitution usually does not exceed 250 nanometers. Upon further heating to 1400–1450°C, the silicon base melts and if it is placed on a graphite surface, then graphite is being modified to a mixture of graphite and SiC crystals, and a monocrystalline silicon carbide film is formed on the surface. To study the structure obtained by this method, a graphite plate was taken, on which a piece of a silicon plate with an area of 1 cm$^2$ was put. The system was heated in a vacuum chamber to 1410°C in an atmosphere of CO 5 minutes. The pressure in the chamber during heating was constant 2 torr. The resulting structure was investigated using a scanning electron microscope (SEM). Studies of the surface and cross-section of the modified region were carried out. Also, the resulting structure was investigated by Raman spectroscopy. The Raman spectra were recorded both in the region of a graphite plate over which Si was initially put and far from this region.

In order to confirm effect of CO on the SiC formation process, within the framework of this work experiments were carried out also on the melting of Si on a graphite plate in argon (Ar) atmosphere and in vacuum. The experiment on melting in Ar was carried out at a pressure inside the chamber of 1.5–2 Torr.

3. Results and discussion

Figure 1 shows the SEM-images of surface of the modified in the presence of CO graphite plate and it’s cross-section. One can note on the image of the surface that it is covered with crystals of different sizes. The obtained crystals do not have a common crystallographic direction. Visually, the area of the graphite plate over which the modification occurred in this case has a greenish tint. From the cross-section image, one can determine the depth to which graphite was modified, that is about 1 mm. A further magnification of the cross-section shows that the entire modified region consists of individual faceted crystals within the graphite matrix.

Figure 1. SEM image of a modified region of surface (a), cross-section (b), microcrystal SiC on the cross-section (c).
Figure 2 (a,b) shows the Raman spectra taken from the surface of the graphite plate in the modified region and far from it. Far from the region in which the modifications took place, the Raman spectrum is typical for graphite [5], all its main bands are clearly visible (1351 cm\(^{-1}\), 1571 cm\(^{-1}\) and 2692 cm\(^{-1}\)). In the case of the modified region, the spectrum radically differs from the typical graphite spectrum, the main bands of the spectrum becomes the SiC band of the cubic polytype (796 cm\(^{-1}\)) [6], and graphite bands disappear at all. The obtained result suggests that mainly cubic SiC crystals lie on the surface of the modified region.

One should note that when Si was melted on a graphite plate in argon (Ar) atmosphere and in vacuum, the Si molten mass has not penetrated into the graphite effectively. In these cases, at a temperature of 1410 °C, a common interface is formed between Si and graphite, and a piece of a silicon wafer turns into a rounded droplet on top of the graphite. Raman spectra taken from the surface of the obtained droplets unambiguously show that it consists of solid Si with very thin layer of SiC (see Figure 2c).

We also note, that the method of Si melting on a graphite plate presented in this work can be used in various modifications. So, for example, in [1], variants of Si preliminarily deposited on graphite in the form of a powder or a thin film were considered. Also in [1], a technique is described which includes dipping a graphite part into liquid silicon, which is in a heat-resistant crucible inside a vacuum reactor, followed by pulling it out of the melt in CO atmosphere. Thus, the method of graphite modification by melting Si in an atmosphere of carbon oxide is a new way to obtain a promising composite material that can be used in various fields of industry.

![Figure 2](image.php)

**Figure 2.** Micro-Raman spectrum of the initial surface of a graphite plate (**a**), and the surface of the Si on graphite modified in CO atmosphere (**b**), and Si on graphite modified in argon atmosphere (**c**).
4. Conclusions
A method of graphite modification into crystalline SiC by melting Si substrates on the surface of the graphite plate in a CO atmosphere is presented. Structural studies of the modified region were carried out. It is shown that the modification occurs not only on the surface, but extends to the depths up to 1 mm. It was also found that the modified region partially consists of separate non-textured misoriented SiC crystals. Using the Raman technique, an analysis of the composition of the modified region was carried out. We also have shown, that the graphite subsurface modification by molten Si takes place actively in presence of CO, whereas in an Ar atmosphere or in the vacuum it does not occur.

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