Structure and thermal diffusivity of SiC-NbC ceramics

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Abstract. The structure and thermal diffusivity of SiC-NbC ceramic materials are investigated. It is shown that with a change in the composition in sintered ceramics, the lattice parameter changes, and also in the near-contact region there is a mutual diffusion of silicon and niobium. This indicates the formation of solid solutions. As the niobium carbide content and temperature increase, the thermal diffusivity of SiC-NbC ceramic materials decreases.

1. Introduction

Ceramic based on silicon carbide has high mechanical strength, thermal conductivity, heat resistance and a low coefficient of thermal expansion. Due to the combination of these properties, SiC ceramics is already widely used in many branches of mechanical engineering, microelectronics and structures where there are high temperatures.

The addition of transition metal carbides to silicon carbide allows one to improve the mechanical properties and obtain ceramic materials based on silicon carbide with different electrical conductivities in the range from metal to semiconductor [1,2]. In particular, in the SiC–NbC system, the addition of niobium carbide to silicon carbide leads to an increase in fracture toughness up to 5.4 MPa m¹/² and Vickers hardness of 17.8 GPa.

2. Experimental Methods

Ceramic SiC-NbC was obtained by sintering at a temperature of 2373 K in an atmosphere of Ar for 1 hour. Powder SiC (green) polytype 6H was used. 5 μm SiC and NbC powders were mixed in a ball mill. The amount of SiC and NbC powder was: SiC (10%wt.)–NbC (90%wt.), SiC(30%wt.) – NbC (70%wt.), SiC (50%wt.) – NbC (50%wt.), SiC (70%wt.) – NbC (30%wt.), SiC (90%wt.) – NbC (10%wt.). The density and porosity of the obtained SiC-NbC ceramic samples were determined by the method of filling and hydrostatic weighing. The density and porosity data for SiC-NbC ceramics are presented in Table 1. It can be seen that the density of the samples increases from 1.68·10³ to 5.23·10³ kg/m³ with an increase in the NbC content from 10 to 90% by weight, and the porosity decreases.

The structure of the obtained ceramic materials SiC-NbC studied by the integrated intensity of the X-ray powder diffractometer model Empyrean series 2 company PANalytical (X-ray tube voltage in the mode U=40kV, I=30mA), and scanning electron microscope «ASPEX» PSEM eXpress TM. Nickel filter, copper tube (Cu), 2θ -geometry. The elemental
composition and distribution profile of the components in a thin layer near the boundary of the SiC - NbC systems was studied by Auger electron spectroscopy on an Auger - JAMP microanalyzer.

The thermal diffusivity was measured by a laser flash method (LFA 457 MicroFlach). Samples for measuring thermal diffusivity had dimensions: diameter – 12.7 mm, height – (2-3) mm.

| Temperature, K | NbC, %wt. | Density, 10³ kg/m³ | Porosity, % |
|---------------|-----------|-------------------|-------------|
| 2373          | 10        | 1.68              | 53.7        |
| 2373          | 30        | 1.82              | 53.4        |
| 2373          | 50        | 2.29              | 52.4        |
| 2473          | 70        | 3.39              | 38          |
| 2373          | 90        | 5.23              | 17          |

Table 1. Density and porosity of SiC-NbC ceramics.

3. Results and Discussion
Survey roentgenograms were taken in the range of Bragg angles 2Θ = 15⁰±40⁰, with sample rotation, at maximum X-ray tube operating conditions and in the most sensitive range of reflection intensity measurements.

On the X-ray diffraction patterns, all lines corresponding to the X-ray spectra of both SiC and NbC are observed (comparison with tabular data on the ASTM file cabinet). No other lines corresponding to the formation of a new phase were found. To estimate the interplanar distances d (3,00) and d (00,18), a survey was performed in the range of angles 2Θ = 59⁰ ± 60⁰ and 2Θ = 66⁰ ± 68⁰. Interplanar distance calculated by the position of the line for wavelengths λ₁ and λ₂ separately. The error in the measurement d (3,00) and d (00,18) was ± 0.00004 Å and ± 0.00003 Å respectively. The results and measurements are shown in table 2.

In addition, in the X-ray diffraction patterns, individual weak reflexes are observed that are not repeated for samples of various compositions. When analyzing the angular positions of these lines, they cannot be identified as lines belonging to any compound of the type NbC, SiC₄, NbₓSi₄, NbₓSi₂, SiₓNb₄. It is seen from the X-ray diffraction patterns that, with a change in the NbC content, the intensity of lines corresponding to SiC decreases, and the intensity of lines corresponding to NbC increases.

| NbC, % | 1 shoot | II shooting |
|-------|---------|-------------|
|       | d(3,00) | d(00,18)    | d(3,00) | d(00,18)    |
| 0     | d₁=0.8887 | d₁=0.8379  | d₁=0.8887 | d₁=0.8399  |
|       | d₂=0.8883 | d₂=0.8378  | d₂=0.8884 | d₂=0.8392  |
| 10    | d₁=0.8881 | d₁=0.8386  | d₁=0.8881 | d₁=0.8389  |
|       | d₂=0.8893 | d₂=0.8386  | d₂=0.8390 | d₂=0.8388  |
| 30    | d₁=0.8832 | d₁=0.8383  | d₁=0.8891 | d₁=0.8383  |
|       | d₂=0.8895 | d₂=0.8387  | d₂=0.8890 | d₂=0.8387  |
| 50    | d₁=0.8897 | d₁=0.8385  | d₁=0.8853 | d₁=0.8385  |
|       | d₂=0.8895 | d₂=0.8381  | d₂=0.8851 | d₂=0.8385  |
| 70    | d₁=0.8885 | d₁=0.8381  | d₁=0.8889 | d₁=0.8389  |
|       | d₂=0.8892 | d₂=0.8380  | d₂=0.8890 | d₂=0.8384  |
| 90    | d₁=0.8887 | d₁=0.8384  | d₁=0.8880 | d₁=0.8388  |
|       | d₂=0.8893 | d₂=0.8382  | d₂=0.8891 | d₂=0.8382  |
The identified lines from sample to sample are not reproduced. Since no additional lines indicating the formation of a new phase were found, it can be concluded from the analysis of X-ray diffraction patterns of SiC - NbC ceramics of various compositions that no phase transitions occur during sintering at a temperature of 2373 K and new compounds are not formed.

A study of the structural parameters “a” and “c” of the SiC unit cell was carried out by two-time shooting of each sample and when determining the parameters $k_{\alpha 1}$ and $k_{\alpha 2}$ separately, followed by averaging.

For SiC - NbC ceramics sintered at 2373 K, the parameter c decreases with an increase in the NbC content. The value of parameter “a” remains the same. A change in the parameter “c” implies a partial replacement of silicon atoms by Nb atoms in tetrahedrons.

In addition to the shift of the diffraction lines associated with a change in the unit cell parameters, an anomalous intensity distribution is observed in a series of reflections (00.18) from samples sintered at 2373 K, which manifests itself in ratios $J_{\alpha 1}$ and $J_{\alpha 2}$.

The line intensities $k_{\alpha 1}$ and $k_{\alpha 2}$ in the $k_{\alpha}$ doublet (theoretical and experimental) are referred to as 2:1. This ratio is associated with energy transitions that occur during the formation of characteristic x-ray radiation.

The ratio $J_{\alpha 1}/J_{\alpha 2}$ for ceramic samples with 10% weight. NbC is 2:1. As SiC is replaced by NbC, the line intensity $J_{\alpha 1}$ gradually decreases, while it $J_{\alpha 2}$ increases.

It should be noted that the study of the distribution of the intensity profile reveals a very diverse distortion of the crystal lattice. Moreover, depending on the type of violation in the lattice, diffraction effects can manifest themselves on reflections of different types in different ways. In this case, such a change in intensity is presumably associated with one-dimensional disordered SiC. Since the SiC structure has a polytypism, it can be assumed that the disordering of densely packed SiC layers occurs. In this case, a violation of the order inside the layer does not occur.

With the change in the percentage of SiC and NbC to ceramics sintered at 2 to 373 K, there is a one-dimensional disordering packed layers SiC along the axis "c".

In Figures 1-4 shows the experimental data on the temperature dependence of the thermal diffusivity of SiC - NbC ceramics of various compositions (10-90% wt.) NbC.

With increasing temperature and niobium content, thermal diffusivity decreases. This may be due to the microstructure of SiC - NbC ceramic materials.

In Figure 5 shows the microstructure of a ceramic sample with SiC composition (70%) - NbC (30%) and composition spectra at points 1, 2 and 3, respectively. Point 1 corresponds to a grain of silicon carbide, point 2 corresponds to niobium carbide, and point 3 is an intermediate phase, in which silicon and niobium are located. This indicates that solid-phase diffusion occurs in the contact zone.

**Figure 1.** The dependence of thermal diffusivity of ceramics SiC(90%)-NbC(10%).  
**Figure 2.** The dependence of thermal diffusivity of ceramics SiC(70%)-NbC(30%).
Figure 3. The dependence of thermal diffusivity of ceramics SiC(50%)-NbC(50%).

Figure 4. The dependence of thermal diffusivity of ceramics SiC(10%)-NbC(90%).

Figure 5. Microstructure of SiC - NbC ceramics (30%) and spectra at points 1, 2, and 3, respectively.

In Figure 6 shows the Auger spectra of a single crystal of NbC (a), a single crystal of SiC (b). Along with the peaks of silicon and carbon, a Nb peak is observed in the SiC single
crystal (Figure 6 (c)), which confirms the presence of active mutual diffusion in the SiC - NbC system during solid phase sintering.

In Figure 7 shows Auger profiles of atomic concentrations of $C_{\text{Nb}}$ in SiC and $C_{\text{Si}}$ in NbC at $T = 2420$ K and $P = 40$ MPa.

According to the concentration profiles of Nb, in SiC and Si in NbC, it can be seen that they are similar and concentrated near the interface, and a continuous increase in the partial atomic concentrations of $C_{\text{Nb}}$ leads to a decrease in $C_{\text{Si}}$ and vice versa (Figure 7). The observed behavior of the partial atomic concentrations of $C_{\text{Nb}}$ in the SiC and $C_{\text{Si}}$ in NbC, indicating the formation of a continuous series of solid solutions in the contact area of SiC to NbC. It is seen that the solubility of Nb in SiC is higher than the solubility of Si in an NbC single crystal. A detailed analysis of the interface showed the absence of second-phase inclusions and chemical compounds that occur in the SiC-NbC system.

![Figure 6. Auger spectra of single crystals of NbC (a), SiC (b) and in solid SiC - NbC solution at a point spaced 1 μm from the boundary (c)](image)

![Figure 7. Concentration profiles of Nb in SiC and Si in NbC at $T = 2373$ K (Auger analysis)](image)
4. Conclusion
X-ray diffraction analysis of SiC - NbC ceramic materials of various compositions showed that phase transitions do not occur during sintering at a temperature of 2373 K and new compounds are not formed. For SiC - NbC ceramics sintered at 2373 K, the parameter c decreases with an increase in the NbC content, which indicates the formation of solid solutions. With the toast of temperature and NbC content in SiC - NbC ceramic materials sintered at a temperature of 2373 K, the thermal diffusivity decreases. In the near-contact region, solid-phase diffusion occurs between the SiC and NbC grains.

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References
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