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ON THE TRANSITION OF SILICON CARBIDE FROM THE HEXAGONAL MODIFICATION TO THE CUBIC ONE UNDER THE ACTION OF HIGH PRESSURES AND HIGH TEMPERATURES

(Presented by Academician N. V. Belov on 4 VI 1966)

The principle of obtaining synthetic diamond and cubic boron nitride is based on the transformation of the starting substance with the hexagonal crystal lattice of the α-modification (graphite, hexagonal boron nitride) into the cubic β-modification. The $\alpha \to \beta$ modification transition is effected under the action of high pressures and high temperatures (^{1}–^{3}). It was of interest to trace an analogous modification transition from a hexagonal structure to a cubic one (of the diamond or sphalerite type) in some other material.

Silicon carbide was chosen as the material for investigation; its α-modification, as is known (^{4}), crystallizes in the hexagonal system and may have, owing to growth faults and dislocation defects, an innumerable number of polytypes (^{5}, ^{6}). The most widespread polytype of α-SiC has a 6-layer hexagonal packing (6H–SiC). The β-SiC modification has a cubic structure of the sphalerite type.

Experiments on the modification transformation $\alpha \to \beta$ SiC were carried out on a high-temperature high-pressure apparatus designed at the Institute of High Pressure Physics of the Academy of Sciences of the USSR by a group under the direction of L. F. Vereshchagin (^{7}). The pressure calibration was made from the jumps in electrical resistance of bismuth, thallium, and barium (^{8}). The temperature was calibrated with the aid of a chromel–alumel thermocouple introduced into the high-pressure chamber through an electrode. The material under investigation was placed in the graphite capsule of the compression chamber and subjected, for a short time (of the order of minutes), to high pressures of about 30–70 kbar at temperatures of about 1200–1400°. For comparison, experiments were made on compression of the same material in the same apparatus, but at room temperature. As a result of the experiments, the material was pressed into specimens of cylindrical form. The structure of silicon carbide in the initial state and after the experiments was investigated by X-ray diffraction in a

Fig. 1. Microphotograms of Debyegrams of green silicon-carbide powder: a—in the initial state; b—after compression under a pressure of 67 kbar at a temperature of ~1200–1400°C

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Debye-type powder camera.

The first experiments were performed on two representatives of hexagonal silicon carbide of industrial purity: green KZ M-14 (SiC 98.28%; Si + SiO_2 0.93%; Fe_2O_3 0.56%; C_free 0.23%) and black KCh 4 (SiC 93.22%; Si + SiO_2 3.30%; Fe_2O_3 1.83%; Al_2O_3 1.25%; C_free 0.40%). In the initial state, the indicated powders were a well-crystallized α-modification of silicon carbide of the following structural composition: KZ 75% 6H + 20% 15R + 5% 4H; KCh 70% 6H + 20% 4H + 7% 15R. (In KCh, in addition to silicon carbide, about 3% silicon was detected.)

Then the experiments on high-temperature compression were repeated on two more representatives of silicon carbide. One of them was a material of increased chemical purity: KZ 3 (SiC 99.84%;

Fe_2O_3 0.02%; Al_2O_3 0.06%; CaO 0.03%; MgO 0.02%; TiO_2 0.03%) and in its initial state was a hexagonal modification of silicon carbide with structural composition 85% 6H + 15% 15R. Another representative of silicon carbide, K3 16, was structurally single-phase, containing in the initial state only one polytype, 6H—SiC. Its chemical composition was: SiC 98.85%; Si + SiO_2 0.40%, Fe_2O_3 0.71%; C_{free} 0.04%.

On the Debyegrams of all specimens subjected to high-temperature compression, the transition of silicon carbide from the hexagonal modification to the cubic one is clearly observed: the intensity sharply decreases and the sharpness of the lines characteristic of the α-modification deteriorates (which is especially well seen on reflections corresponding to the indices $10^3/2n_c$ and $21^3/2n_c$ in the hexagonal aspect*); the principal lines of silicon carbide, common to all its structural varieties and together constituting the X-ray pattern of β-SiC, remain intense and sufficiently sharp (Fig. 1). In comparison with the Debyegram of a standard β-SiC, the lines of cubic silicon carbide on the X-ray patterns of specimens subjected to high-temperature compression are only slightly broadened and weakened, which indicates the fine-crystalline character and insufficient perfection of the lattice of the cubic modification that has formed.

Fig. 1. Microphotograms of Debyegrams of green silicon-carbide powder: *a* —in the initial state; *b*—after compression under a pressure of 67 kbar at a temperature of ~1200–1400°C.

In contrast to high-temperature compression, compression of silicon carbide at

Fig. 2

Figure 2: Fig. 2

room temperature did not lead to any substantial changes in its structure: on the Debyegrams of the material after cold compression, all the lines present on the photographs of the initial, hexagonal silicon carbide specimens are observed. The difference from the initial Debyegrams in this case consists only in a very slight broadening of all lines, monotonically increasing with increasing diffraction angle θ, and indicating the formation in the lattice of hexagonal silicon carbide of slight residual internal stresses. No changes in interplanar spacings were found.

The phenomenon of the modification transition $\alpha \to \beta$ SiC under the action of high-temperature compression is traced equally distinctly both on specimens of technical silicon carbide and on silicon carbide of increased purity, and on the structurally single-phase polytype 6H—SiC.

As a characteristic of the amount of residual α-modification in the sample after testing, the ratio of the intensities $I_{\text{hex}}/I_{\text{tot}}$ of two neighboring lines of one X-ray pattern may serve. Microphotometrically, I_{hex} and I_{tot} were determined and their ratio was found for two pairs of lines: $10^3/2n_c$ and 110; $21^3/2n_c$ and 300. Determinations were carried out for 12 high-temperature-compression experiments, 2 cold-compression experiments, and 4 investigated representatives of silicon carbide in the initial state (Fig. 2)**. The difference in the initial the data for the different silicon carbide specimens is due to differences in their structural composition. From Fig. 2 a qualitative analogy is evident among the results obtained on 4 different silicon carbide specimens. A tendency is found for the completeness of the modification transition $\alpha \to \beta$ to depend on the particle size of the starting material: the finer the particles, the more complete the transition. However, with increasing pressure the effect of particle size on the completeness of the transition weakens.

Fig. 2. Ratio of the intensities of pairs of lines $I_{\text{hex}}/I_{\text{gen}}$ on Debye patterns of silicon carbide as a function of the applied pressure. A—$I_{\text{hex}}/I_{\text{gen}} = I_{109}/I_{110}$; B—$I_{\text{hex}}/I_{\text{gen}} = I_{219}/I_{300}$. Symbols: a—green silicon carbide of increased purity KZ 3; b—structural silicon carbide 6N—SiC KZ 16; v—green silicon carbide of industrial purity KZ M-14; g—black silicon carbide of industrial purity KCh 4. Black symbols—compression with heating; white symbols—compression at room temperature.

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[*] n_c is the packing repeat of the polytype in the direction of the c axis of the hexagonal lattice. For 6H—SiC $n_c = 6$; for 4H—SiC $n_c = 4$.

[**] Operator: T. V. Sofronov.

After hot compression at $\sim$ 30 kbar, the structural composition of the silicon carbide powders studied lies within the range from 60% α + 40% β to 15% α + 85% β, depending on the initial particle size. After hot compression under a pressure of 60–70 kbar, the content of the cubic modification in the samples was 70–85%. In fine silicon carbide powder the completeness of the $\alpha \to \beta$ transition is equally high over the entire pressure interval studied: after hot compression of the KZ M-14 micropowder under pressures of $\sim$ 30, 60, and 70 kbar, the content of the cubic modification in it was $\sim$ 85%.

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CITED LITERATURE

1. F. P. Bundy, H. T. Hall et al., Nature, **176**, 4471 (1955).
2. H. Liander, ASEA J., **28**, No. 5-6 (1955).
3. R. H. Wentorf, J. Chem. Phys., **26**, No. 4, 956 (1957); **34**, No. 1 (1961).
4. G. S. Zhdanov, Z. V. Minervina, ZhETF, **15**, issue 11 (1945).
5. G. S. Zhdanov, Z. V. Minervina, DAN, **48**, issue 3 (1945).
6. R. S. Mitchell, Zs. Kristallogr., **109**, No. 1, 1 (1957).
7. L. F. Vereshchagin et al., DAN, **145**, No. 1 (1962).
8. G. C. Kennedy, P. N. La Mori, *Progress in Very High Pressure Research*, N. Y.—London, 1961, p. 304.

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