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THE ACTION OF HIGH STATIC AND DYNAMIC PRESSURES ON ALUMINUM NITRIDE

The application of high pressures to substances promotes their transition into denser modifications; as a rule, this is associated with an increase in the coordination numbers of the atoms forming the given substance (^{1}). On the other hand, an increase in density and in the coordination numbers of atoms causes an increase in the hardness of the substance (^{2}). From this point of view, it is of particular interest to investigate the action of high pressures on those substances which, already in their ordinary form, possess sufficiently high hardness, in the hope of obtaining new superhard materials.

The hardness of aluminum nitride, like many of its other properties, depends substantially on the methods of obtaining this compound and reaches 9 on the Mohs scale. Aluminum nitride crystallizes in a hexagonal wurtzite-type lattice with lattice constants $a = 3.104$ Å and $c = 4.965$ Å (^{3}). According to other authors, $a = 3.112$ and $c = 4.982$ Å. The space group is C_{6v}^4—$c6mc$ (^{4}). The coordination numbers of both aluminum and nitrogen are equal to 4. The x-ray density is 3.25 g/cm^3. There are data on the preparation of cubic aluminum nitride with $a = 4.104$ Å (^{5}) by nitriding steel containing aluminum.

Hexagonal aluminum nitride is an isoelectronic analogue of carbon (^{6}), with an electronegativity difference of $\Delta X = 2$. High pressure can reduce and equalize the electronegativities of atoms and, consequently, promote the formation of covalent bonds.

It was natural to assume that high static and dynamic pressures are capable of causing the formation of a denser form of aluminum nitride.

For the investigation, wurtzite-like aluminum nitride of high purity, grade OSU-93, obtained by the electric-arc method and containing 67.3% Al and 32.6% N, was used. The impurity content did not exceed 0.1%. Dynamic pressures and, independently of them, static pressures combined with the action of high temperatures or large plastic deformations were applied to the sample. It is known that shear stresses produced in a sample in one way or another promote the course of chemical reactions and substantially alter the kinetics of phase transitions.

Under shock compression, plastic flow appears in the substance under investigation, ensuring rapid growth of the nucleus of the new phase behind the front of the shock wave, apparently by displacement of the mass of the initial phase near crystallization centers and by selective attachment of the corresponding atoms to the growing particles of the new phase. Therefore the study of aluminum nitride was carried out in parallel by several independent methods.

The dynamic action on aluminum nitride was carried out by the method of preserving cylindrical ampoules described earlier (^{7}). Charges with different amplitudes of the shock wave were used. The bulk dens—

···the porosity of aluminum nitride varied from 1.14 to 0.41 g/cm^3. The initial aluminum nitride was a light-gray powder of high dispersity (0.0005 mm), and therefore was isotropic. After shock compression, veins of various colors were observed in all zones of the ampoule: glossy black, bluish, and light brown. The main mass was glassy and almost transparent. X-ray diffraction showed that particles colored in different colors were identical. Optical anisotropy appeared in some of the crystals; the refractive index of these crystals did not exceed 2.05. The pycnometric density of the shock-compressed aluminum nitride (3.17 g/cm^3) was slightly greater than the initial density (3.04 g/cm^3). It should be noted, however, that in this case no relationship is observed between the density of the shock-compressed substance and the amplitude of the shock wave.

The behavior of aluminum nitride under conditions of static compression and plastic deformation was investigated using the apparatus described earlier (^{8}). The method of investigation used was the determination of the change in shear stress as a function of pressure. The specimen under test was subjected simultaneously to the action of high normal pressure and large shear stresses. The pressure apparatus was calibrated by polymorphic transitions in bismuth, thallium, barium, and lead. The starting substance was the same wurtzite-like aluminum nitride that was used in the shock-compression experiments. The pressure was varied from 50 to 400 kbar, with a maximum shear stress of up to 100,000 kg/cm^2. In some experiments the specimen was held under pressure for 25 h. The use of such a long holding time in the experiment did not make it possible to achieve a complete transition of aluminum nitride into a new phase, just as in the shock experiments.

After the experiment the substance acquired a black color and scratched glass. On the mirror surfaces of the punches between which the specimen was compressed, rather large dents appeared.

At high pressures and high temperatures the experiment was carried out as follows. The initial aluminum nitride was placed in a cylindrical graphite heater, which in turn was installed in a pyrophyllite container serving as the pressure-transmitting medium. The high-pressure chamber was placed in a hydraulic press. When the necessary pressure was reached in the chamber, heating was switched on. The pressure in the chamber was measured with a piston manometer ([9]). The temperature was determined from the power of the current flowing through the heater, using the curve of the dependence of the temperature in the chamber on the current power. The maximum pressure was 55 kbar, and the temperature 1000°. The specimen was held at this pressure and temperature for 10 min. After holding, the temperature and pressure were gradually reduced. The final product had a bluish-blue tint.

The products of shock and static compression were studied by X-ray diffraction (RKD and RKU cameras), IR spectroscopy, pycnometry (toluene and CCl_4 were used as working liquids), and microcrystalloscopy using the immersion method. The calculation of the X-ray patterns of the initial and final products is given in Table 1.

In almost all cases, the X-ray patterns of various shock-compressed specimens, as well as of specimens subjected simultaneously to the action of high nonhydrostatic pressures and shear stresses or to high pressures and high temperatures, contained new reflections whose intensities depended on the conditions and multiplicity of shock compression, as well as on the magnitude of the pressure, shear stress, and temperature. The maximum intensity of these new reflections was observed for aluminum nitride subjected twice to the action of a charge of saturated hexogen. However, the density of specimens in which the intensity of the new reflections was maximal differed little from the density of those specimens for which the intensities of the new reflections were insignificant. Evidently, the density of the new···

Table 1

Aluminum nitride

Initial: I	Initial: $1/d^2$	Twice compressed with a hexogen charge: I	Twice compressed with a hexogen charge: $1/d^2$	Subjected to a pressure of 300 kbar with shear: I	Subjected to a pressure of 300 kbar with shear: $1/d^2$	Subjected to a pressure of 55 kbar and a temperature of 1000°: I	Subjected to a pressure of 55 kbar and a temperature of 1000°: $1/d^2$
10	0,1378	2	0,0566	1	0,0567	1	0,0560
7	0,1612	10	0,0918	3	0,0918	8	0,0915
8	0,1782	10	0,1372	10	0,1372	10	0,1372
6	0,2993	5	0,1626	10	0,1613	10	0,1613
9	0,4136	6	0,1795	10	0,1811	10	0,1811
7	0,5002	5	0,2225	–	0,2225	–	0,2220

Initial: I	Initial: $1/d^2$	Twice compressed with a hexogen charge: I	Twice compressed with a hexogen charge: $1/d^2$	Subjected to a pressure of 300 kbar with shear: I	Subjected to a pressure of 300 kbar with shear: $1/d^2$	Subjected to a pressure of 55 kbar and a temperature of 1000°: I	Subjected to a pressure of 55 kbar and a temperature of 1000°: $1/d^2$
2	0,5511	5	0,3052	1	0,302	8	0,2973
6	0,5739	1	0,3380	–	0,279	10	0,4160
4	0,5908	8	0,4162	6	0,344	7	0,5040
1	0,6441	5	0,5030	8	0,416	1	0,5310
2	0,7121	1	0,5305	7	0,504	2	0,5570
4	0,9122	4	0,5731	–	0,531	6	0,577
2	0,9650	–	0,6664	–	0,557	2	0,596
1	1,0056	–	0,7243	7	0,577	–	0,653
		–	0,7535	–	0,596	1	0,716
		–	0,8542	–	0,653		
		1	0,9175	1	0,716		
		–	0,9707	–	0,787		
		–	1,0062	3	0,892		
				1	0,975		
				1	1,006		
				1	1,056		

of the modification of aluminum nitride differs hardly at all from the density of the initial material. This might have been expected for a sphalerite-like modification; however, detailed processing of the X-ray diffraction pattern did not confirm the formation of this modification.

At present, the study of this transformation is continuing, in order to isolate the new modification, fully identify it, and determine the pressure parameters under which it is formed.

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Note: Figure translations are in progress. See original paper for figures.