PROPERTIES OF MATERIALS BASED ON ULTRADISPERSED NITRIDE POWDERS

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As is known, the use of ultradispersed powders (UDP) causes intensification of the sintering process. As the result of the presence of uncompensated bonds and the absence of forces holding the atoms on the surface in the "ideal" position a change in the various physicochemical and technological properties of the articles in the ultradispersed state occurs and, above all else, there is a significant increase in their activity [1, 2].

The purpose of this investigation was to study the influence of the degree of dispersion and the phase composition of the original powders and also of activating and strengthening components on certain properties (hardness and phase composition) of nitride-base hot pressed ceramic materials.

For comparison silison nitride powders of different degrees of dispersion obtained by furnace (FS) and plasma chemical synthesis (PCS) were used. Yttrium and aluminum oxides were used as the sintering activator and titanium nitride [3] obtained by plasma chemical synthesis served as the strengthening component. The TiN was added not only by mixing of all of the constituents of the charge but also in the stage of plasma chemical synthesis together with the Si_3N_4. The element composition of the original powders (Table 1) was determined by chemical and spectral analyses, and the phase composition of both the original powders and of the materials by x-ray diffraction in CuK_α-radiation.

The mixing and grinding of the charges for materials 1 and 3 (Table 2) were done in a medium of acetone in a cemented carbide drum for 100 and 72 h, respectively. As the result of grinding the tungsten content was 0.8-1.0%. The mixtures of ultradispersed powders for the remaining materials not requiring grinding were obtained in a planetary mixer. The hot pressing was done in multicavity graphite dies at 1800-1830°C with uniaxial application of a pressure of 20 MPa. The induction heating was done from a high-frequency generator. The density of the specimens was determined by hydrostatic weighing and the hardness by indentation of the surface of ground specimens with a Vickers pyramid with loads of 50-500 N.

In addition to β-Si_3N_4, the ultradispersed silicon nitride powder used contains α-modification and amorphous phase (AP). In combined synthesis of silicon and titanium nitrides with an increase in the latter the quantity of α-Si_3N_4 decreases in comparison with β-Si_3N_4 until complete disappearance of silicon nitride in compositions containing more than 54 wt.% TiN. In this case unidentified lines (UL) appear. In individual cases an amorphous phase which is apparently x-ray-amorphous silicion nitride is also recorded (Table 1, mixtures 6-11). The appearance of this phase does not have a regular character and therefore such changes in phase composition probably are related to deviations in the method of production of the original powders.

Accoridng to Fig. 1a, which shows the time relationship of the hardness with a load of 50 N of material of ultradispersed silicon nitride with addition of yttrium oxide, at 1800°C with a hot pressing time of more than 35 min the hardness drops. A study of the composition of the specimens with the minimum and maximum hardnesses showed that in addition to the basic phase of β-silicon nitride they contain Si_2ON_2 with an insignificant hold time and high hardness. In the case of low hardness the latter is absent and, according to the results of qualitative x-ray diffraction analysis, there appear intense lines of free silicon which may be related to dissociation of Si_3N_4 and Si_2ON_2 as the result of an increase in hot pressing time. Taking this into consideration the hot pressing time of all of the remaining materials must not exceed 30 min. For stabilization of the properties obtained in this manner a grain boundary phase was additionally crystallized by controlled cooling for 20-30 min or additional heat treatment.

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TABLE 1. Composition and Specific Surface of the Original Powders

Mixture	Original powders	Chemical analysis, wt. %						Phase composition
		Si_{tot}	N	Ti	Si_{fr}	O	Sum of impurities* (Fe, Al, Ca, Mg, Mn, Cu, etc.)	
1	Si_3N_4(FS)	55,4	35,8	0,02	0,1	1,6	2,00	β-Si_3N_4
2	Si_3N_4 (PCS)	59,0	30,2	1,4	6,3	3,6	1,00	AP; α-, β-Si_3N_4; Si_{fr}
3	TiN (PCS)	0,01	19,3	—	—	2,4	0,10	TiN
4	Y_2O_3 (FS)	—	—	—	—	—	0,01	Y_2O_3
5	Al_2O_3 (PCS)	—	—	—	—	—	0,10	α-Al_2O_3
6	Si_3N_4+TiN (PCS)	52,8	31,1	9,5	4,1	4,6	0,10	α-, β-Si_3N_4; AP; TiN; Si_{fr}
7	" "	44,3	29,7	20,1	6,1	4,3	0,10	β-, α-Si_3N_4; TiN, Si_{fr}
8	» »	36,6	27,3	32,3	6,7	3,5	0,10	β-, α-Si_3N_4; TiN, Si_{fr}
9	» »	27,8	27,0	41,0	3,8	9,8	0,10	β-Si_3N_4; TiN; Si_{fr}
10	» »	17,8	25,0	55,0	2,1	10,7	0,10	AP; TiN; Si_{fr}; UL
11	» »	8,1	23,0	67,5	0,8	8,6	0,10	TiN

*Semiquantitative spectral analysis.

TABLE 2. Properties of the Hot Pressed Materials

Material No.	Weight % of the components				Porosity, %	Hardness HV, GPa, with load		Phase composition
	Si_3N_4	Y_2O_3	Al_2O_3	TiN		50 N	200 N	
1*	95	5	—	—	1,8	12,2	—	β-Si_3N_4
2	100	—	—	—	7,8	12,7	14,3	β-Si_3N_4; Si_2ON_2; Si_{fr}
3	95	5	—	—	0	19,9	16,5	β-Si_3N_4; Si_2ON_2, Y_2SiO_5; Si_{fr}
4	99	1	—	—	4,0	18,8	16,7	—
5	90	5	5	—	2,3	17,9	16,5	β-Si_3N_4; Si_2ON_2; UL
6	95	3	2	—	3,8	19,6	15,9	—
7	75	3	2	20	2,2	18,4	16,1	β-Si_3N_4; TiN; Si_2ON_2
8	83	5	—	12	0,9	20,3	16,5	—
9	70	5	—	25	0,4	19,6	16,0	β-Si_3N_4; TiN; Si_2ON_2, Y_2SiO_5; Si_{fr}
10**	65	5	—	30	2,6	19,9	16,2	β-Si_3N_4; TiN; Y_2SiO_5; Si_{fr}
11	55	5	—	40	0,8	20,0	16,5	β-Si_3N_4; TiN; Si_2ON_2; Y_2SiO_5; Si_{fr}
12	44	5	—	51	1,6	19,5	16,5	β-Si_3N_4; TiN; Si_2ON_2; β-$Y_2Si_2O_7$; Si_{fr}
13	27	5	—	68	5,5	17,6	15,6	Si_2ON; Si_2ON_2; TiN; β-$Y_2Si_2O_7$; Si_{fr}
14	12	5	—	83	6,8	15,7	13,1	Si_2ON_2; TiN

*Si_3N_4 was obtained by furnace synthesis. **TiN is added by mixing.

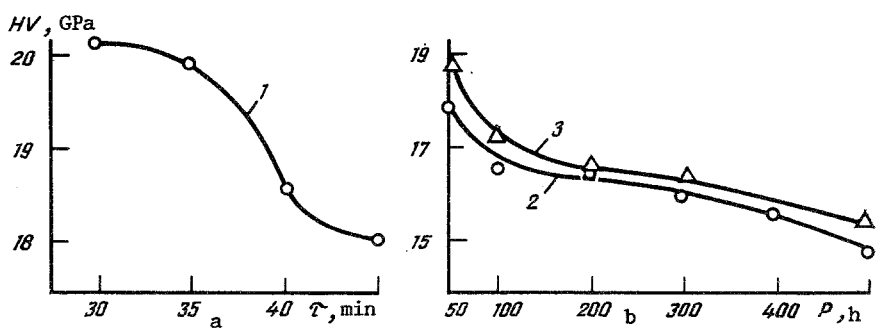

Fig. 1. Relationship of hardness to hot pressing time (a) and load (b): a: 1) material 3; b: 2) material 5; 3) 11.

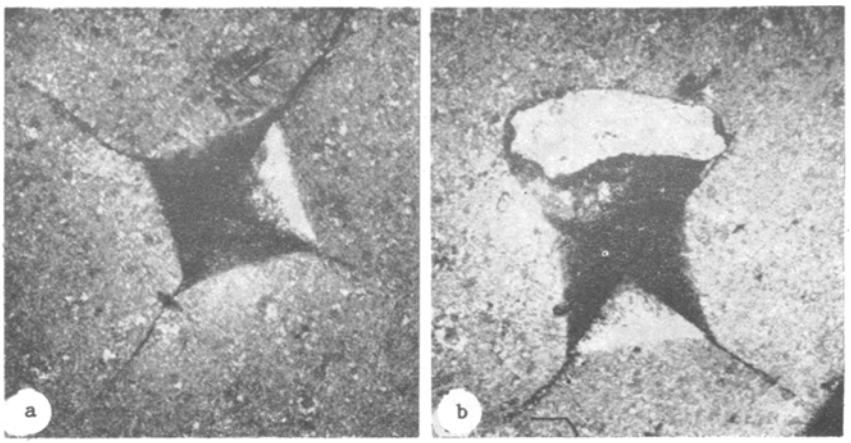

Fig. 2. Form of impression with a change in Vickers hardness: a) radial cracks; b) surface spall.

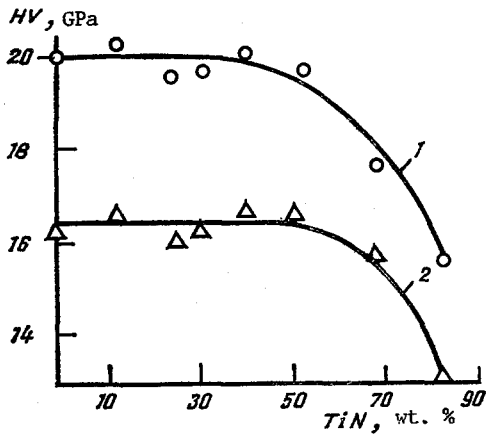

Fig. 3. Relationship of hardness to titanium nitride content with loads of 50 (1) and 200 N (2).

The influence of load on the hardness of ultradispersed silicon nitride powder-base materials was investigated with the use of additions of yttrium and aluminum oxides and also of titanium nitride. As may be seen from Fig. 1b, in the whole range of loads used the hardness drops with an increase in them. The HV(P) relationship has a nonlinear character and in the general case is characteristic of materials the indentation of tips into which is accompanied by fracture in the zone of indentation. In addition, as shown in [4], the amount of the measured hardness is determined by the resistance of the material to brittle fracture and not to plastic deformation. Therefore the hardness characterizes the strength properties of the material and may correlate with its crack resistance. The degree of influence of the fracture process on hardness varies with load and depends upon the character and type of cracks formed and upon the scale of the fracture zone. Therefore in this article the hardnesses of the different specimens were compared not only with P = 50 N but also with P = 200 N, with which were formed in the area of indentation radial cracks (Fig. 2a) or surface lobed cracks and spalls (Fig. 2b), respectively.

The phase composition of plasma chemical synthesis silicon nitride-base materials is characterized by the presence of silicon oxynitrides (Si_2ON_2, sometimes Si_2ON) and an insignificant quantity of free silicon (Table 2, materials 2-14). In the materials of combined synthesized nitride powders oxynitrides are formed even in the absence of Si_3N_4 lines in the x-ray spectra of the original powders (Table 1, mixtures 10 and 11; Table 2, materials 13-14). Obviously the x-ray amorphous phase with Si—N-bonds and oxygen participate in the formation of these compounds. With the addition of yttrium oxide to Si_3N_4-base materials with from 0 to 40 wt.% titanium nitride under conditions of long cooling or annealing

yttrium silicate Y_2SiO_5 is formed while in the case of rapid cooling the silicate is not observed (Table 2, materials 3, 9-11). An increase in titanium nitride content to 68% leads to formation of yttrium silicate with a composition of β-$Y_2Si_2O_7$ (Table 2, materials 12-13) and in the case of rapid cooling of α-$Y_2Si_2O_7$. At the maximum TiN content silicates are not found for any of the conditions (Table 2, material 14).

In hot pressing of furnace synthesized silicon nitride powders with yttrium oxide as an activator and of plasma chemical synthesized Si_3N_4 powders without an activator materials with the same hardness were obtained despite the higher porosity of the latter (Table 2, materials 1 and 2). With the addition of activator to plasma chemical synthesized Si_3N_4 the hardness of the material increases by 1.5 times (Table 2, material 3), which is related to more active compaction.

A change in the content of the activating additions Al_2O_3 and Y_2O_3 (Table 2, materials 3-7) within the limits given has an insignificant influence on the hardness of the hot pressed materials despite the difference in phase composition. The hardness of the materials of the combined synthesized nitride powders drops with more than 51 wt.% titanium nitride (Table 2, materials 13 and 14) and the character of the curve of change in hardness in relation to material composition is not related to load (Fig. 3).

Therefore the use of ultradispersed silicon nitride powder is promising for obtaining materials with a high level of hardness, which is related not only to the high degree of dispersion but also to the presence in the original powders of α-Si_3N_4, amorphous phase (and to the positive influence of their transformation into β-Si_3N_4), and also of silicates promoting liquid-phase compaction [5].

The relationship of hardness to load in the 50-500 N range is characteristic of brittle materials. The hardness of ultradispersed silicon nitride powder-base hot pressed materials does not depend upon the maximum content of oxide activating additions within limits of 1-10%. In connection with appearance in the structure of an increased quantity of free silicon as the result of dissociation of silicon nitride and oxynitride an increase in hot pressing time leads to a drop in hardness.

Depending upon the increase in TiN content combined synthesis of Si_3N_4 and TiN powders causes a change in the ratio of the α- and β-phases of silicon nitride and in the composition of the yttrium silicates and also a drop in hardness with a titanium nitride content of more than 51 wt.%.

LITERATURE CITED

1. G. M. Kheidemane, Ya. P. Grabis, T. N. Miller, and E. A. Palchevskis, "The formation of silicion nitride in a high-temperature flow of nitrogen," Fiz. Khim. Obrab. Mater., No. 3, 30-34 (1980).
2. T. N. Miller, "The plasma chemical synthesis and properties of refractory compounds," Izv. Akad. Nauk SSSR, Neorgan. Mater., 15, No. 4, 557-562 (1979).
3. O. N. Grigor'ev, I. I. Osipova, V. P. Yaroshenko, and A. M. Shatokhin, "The influence of the composition of silicon nitride ceramic materials on structure formation processes and physicomechanical properties," in: Nitrides: Methods of Production, Properties, and Areas of Use: Summaries of Papers for the Fifth All-Union Seminar (Riga, 15-17 Feb. 1984) [in Russian], Zinatne, Riga (1984), p. 98.
4. V. I. Trefilov, O. N. Grigor'ev, and A. M. Shatokhin, "The influence of the structural condition of brittle materials on the relationship of hardness to load," Dokl. Akad. Nauk SSSR, 259, No. 4, 836-839 (1981).
5. I. I. Osipova, D. A. Pogorelova, V. N. Paderno, et al., "The recrystallization of silicion nitride powders in hot pressing," Poroshk. Metall., No. 10, 43-47 (1982).