MODERN METHODS FOR OBTAINING SILICON NITRIDE POWDERS

M. A. Juraeva
Almalyk Branch of Tashkent State Technical University, Uzbekistan

Sh. A. Karimov
Tashkent State Technical University, Tashkent, Uzbekistan

Sh. M. Shakirov
Tashkent State Technical University, Tashkent, Uzbekistan

ABSTRACT

The article presents the prospect of using materials based on silicon nitride in various fields of technology and a comparative analysis of the cost of raw materials for the production of tungsten hard alloys, tool materials based on silicon nitride, as well as a literature review of modern methods for producing silicon nitride powders and their properties. It is shown that at present the main methods of obtaining silicon nitride powders are self-propagating high-temperature synthesis (SHS).

Keywords: Material, technology, method, synthesis, ceramics, self-propagating high-temperature synthesis of synthesis oxides, carbides, silicon nitride, tungsten carbide, method, synthesis, powder, grinding, adiabatic temperature, azite technologies, combustion wave front, Carbothermal reduction, gas-phase synthesis, imide.

INTRODUCTION

The cost of tools for cutting or grinding all kinds of materials is mainly determined by the cost of the tool material and the technology of its production. Currently, the most common tool material is tungsten carbide-based hard alloys with a number of valuable properties, the main of which is high hardness (HRA 82-89), combined with high wear resistance. The cost of 1 kg of tungsten carbide powder on the world market is from 70 to 100 US dollars, depending on the particle size and purity of the powder, and the cost of 1 kg of cobalt powder is from 40 to 50 US dollars. Attempts to replace tungsten or cobalt in the tool material with other metals in order to reduce its cost have not yet yielded significant results, since the technology of manufacturing the tool material becomes more complicated or the cost of the tool remains the same [1].

Therefore, new research is aimed at developing materials that, on the one hand, have higher hardness and wear resistance than hard alloys, and on the other, do not require the use of expensive equipment and technology. These conditions are most satisfied by some high-strength ceramic materials, specially developed in relation to the requirements [2, 3].

Most of the ceramic materials are created on the basis of chemical compounds that combine high hardness and chemical stability, which remains in a wide range of temperatures and external loads. The number of substances that satisfy these requirements, first of all, should include aluminum oxide (Al_2O_3), silicon nitride (Si_3N_4), as well as oxynitride phases (sialons) formed in Si-Me-ON systems, where as a metal replacing silicon atoms can be Al, Mg, Be, Y, Ti, Zr, rare earth elements [1]. Since the addition of metallic elements to nitride ceramics is insignificant, and oxide ceramics consists mainly of corundum ($A1_2O_3$), it can be argued that the basis of instrumental materials is the four most widespread chemical elements in the earth's crust and atmosphere - nitrogen, oxygen, aluminum, silicon, which also determines the significant advantage of tool ceramics over hard alloys containing such rare and scarce metals as tungsten, molybdenum, cobalt, nickel, etc.

Among nonmetallic refractory compounds, the most widely used are silicon carbide SiC, boron carbide B_4C, silicon nitride Si_3N_4, and boron nitride BN. Due to their extremely high hardness and a number of other specific properties, these compounds are now widely used, primarily in the tool and manufacturing industries, and are also part of wear-resistant and chemically resistant materials.

At the end of the 20th century, silicon nitride took the leading place among the nonmetallic refractory compounds listed above in terms of the number of publications, seminars, conferences. For example, in the fall of 1993, when a symposium on silicon ceramics was held in Tokyo in September, the conference "Silicon Nitride 93" was held in October in Stuttgart, and in November the Hawaiian Islands hosted a symposium on structural silicon ceramics. And this is after the representative symposia of the Society for Materials Research and the Ceramic Society, devoted to the scientific and technological aspects of silicon nitride materials, were held in the United States in December 1992 and April 1993.

METHODS OF OBTAINING POWDER SI_3N_4

Powders Si_3N_4 is obtained by methods: direct synthesis in various versions, carbothermal reduction, gas phase reactions of synthesis and decomposition, as well as mechanical grinding as an additional type of processing. The main methods of synthesis of silicon nitride powders in recent years have been supplemented, perhaps, only by mechanical synthesis, which has become widespread in the synthesis of powders of many refractory compounds and intermetallides [4-6].

It is shown in the work that the use of ammonia in grinding silicon is much more efficient than nitrogen. The hydrogen formed during the dissociation of ammonia binds oxygen impurities in the atmosphere and reduces the likelihood of the formation of an oxynitride film on the surface of the particles, which prevents the nitriding of silicon. Intensive grinding of silicon in ammonia for 150 h, followed by vacuum annealing at 800 ° C (τ = 8 h) leads to the formation of α- Si_3N_4, containing, however, 14.22 at.% Oxygen, 1.28 at .% iron and 1.99 at.% titanium.

The kinetics of the interaction of silicon with nitrogen is significantly influenced by the degree of defectiveness of the initial powders, which is confirmed by the methods of X-ray diffraction analysis, EPR and IR spectroscopy in the study of silicon grinding. [7] The mechanism of the reaction of silicon with nitrogen was analyzed in detail earlier in [8, 9].

In recent years, the features of the interaction of silicon with nitrogen have been intensively studied in relation to the processes of self-propagating high-temperature synthesis (SHS) [10, 11]. In fig. 1 shows the change in the calculated adiabatic combustion temperature of silicon and the degree of reaction depending on the nitrogen pressure. It also shows the effect of the degree of dilution of the initial silicon with silicon nitride, which affects the decrease in the nitrogen pressure and combustion temperature. The authors of [11] distinguish three reaction zones: in the first (I) combustion is limited by nitrogen filtration, in the second (II), the reaction is controlled by high-temperature dissociation of silicon nitride, and, finally, in the third zone (III), combustion is limited by reaction kinetics. In this zone, at the front of the combustion wave, there is a complete transformation of silicon into nitride (n * = 1).

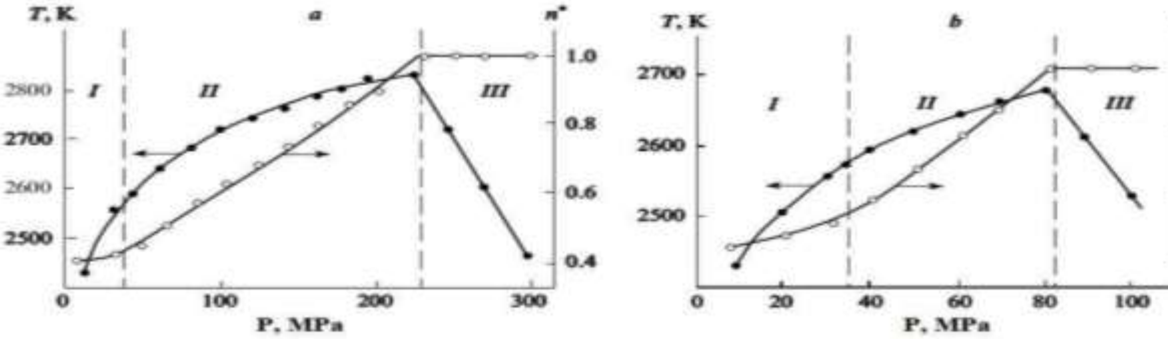

Fig 1. Influence of nitrogen pressure on the adiabatic combustion temperature and the degree of silicon reaction (n *): a - Si; b - Si: Si3N4 = 50:50. The calculations were performed for a porosity of 65%.

In fig. 2 shows one of the thermo grams obtained during the combustion of a mixture of Si (50 wt%) + Si_3N_4 (50 wt%) in nitrogen under a pressure of 50 MPa. The maximum combustion temperature (~ 2500K) recorded in these experiments differs by about 100 - 150 K. from the calculated values.

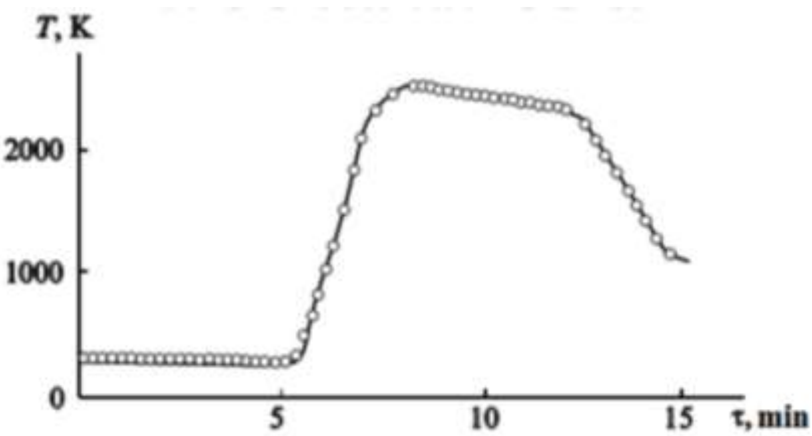

Fig 2 Typical thermo gram of combustion of a Si: Si_3N_4 = 50:50 mixture in nitrogen under a pressure of 50 MPa (porosity 65%) [11]

One of the advantages of silicon nitride powders obtained by the SHS method is their relatively low oxygen content (0.4 - 0.6%) [12]. This is achieved through the use of pure raw materials. Ordinary powders obtained by the SHS method are characterized by a significantly higher content of impurities (for example, the amount of oxygen in them is 1.5 - 2%); works [13-15] are devoted to the study of their technological and other properties.

The good economic performance of the SHS method in comparison with conventional silicon nitriding is reported in [16]. According to these estimates, with an annual output of 50 tons, the cost of 1 kg of Si_3N_4 powder obtained by the SHS method is ~ US $ 28, and that obtained in the usual way is ~ US $ 33.7, respectively. It is characteristic that the bulk of the costs in both cases fall on an extremely uneconomical grinding operation.

Carbothermal reduction of silicon oxide in a nitrogen atmosphere has long attracted the attention of researchers as a method that makes it possible to use not scarce raw materials, including waste (for example, rice hulls [17]). The powders obtained in this way do not differ, however, in high purity and require additional grinding. The purity can be increased by chemical cleaning by etching in acids [18]. A detailed study of the mechanism of Si_3N_4 formation under conditions of carbothermal synthesis (T = 1400-1550 ° C, PN = 0.1 h - 6 MPa), depending on the properties of soot and silica, was undertaken in [19].

It is shown, in particular, that in the range of nitrogen pressures of 2 - 6 MPa, the evaporation of silicon monoxide and the formation of nonequilibrium phases can be significantly reduced, while the content of carbon and oxygen in the reaction products is controllable. Peculiarities of carbothermal reduction of silica in nitrogen were also considered in several reports at the Stuttgart conference in 1993 [20]. It was reported, for example, that the well-known American company "Dow Chemical Company" has developed a technology for carbothermal synthesis of Si_3N_4, which provides a submicron powder with a high content of the α-phase (> 95%) and a relatively low content of oxygen (2 - 2.5%) and carbon (0 , 3 - 0.5%) [21]. The low cost of this powder and its acceptable technological characteristics are emphasized.

The method of gas-phase synthesis mainly produces ultrafine silicon nitride (UFP) powders less than 100 nm in size (mainly d <20 nm) [6]. The reactions between the vapors of silicon tetrachloride (or silane) and their derivatives with ammonia, carried out under conditions of plasma-chemical, laser, or conventional thermal heating, have been the subject of study by many researchers [22]. To the cited works, one should also add works devoted to the preparation of carbonitride powders [23].

Gas-phase synthesis under appropriate conditions, providing homogeneous nucleation, to the greatest extent guarantees the production of silicon nitride UFP. As emphasized in the review [18], the use of silicon tetrachloride and silane as starting components has certain features. On the one hand, the economical use of $SiCl_4$ is complicated by the need to take measures to remove corrosive by-products (NH_4Cl). On the other hand, a very scarce silane, which also requires appropriate handling precautions, ensures the production of high quality powders. Nonetheless, silicon tetrachloride has become widespread in the industrial synthesis of silicon imide $Si(NH)_2$. The latter decomposes at ~ 1000 ° C with the formation of amorphous Si_3N_4, which, in turn, is annealed for crystallization at 1500 ° C [24].

From the scientific results of the study of gas-phase reactions, it is possible to note the identification of features of laser synthesis of silicon nitride in the form of non-agglomerated UFPs [25], as well as calculations of thermodynamic equilibrium in the Si - H - Cl - N system in the temperature range 800 - 2600 K with the participation of SiH, SiCl, their numerous derivatives and imide [26]. The conditions of pyrolysis in various media (argon, oxygen, nitrogen, helium) of organosilicon polymers with cross-links have also been analyzed in detail [27, 28]. The use of NMR and IR spectroscopy methods helped to identify the formation of various intermediates in these experiments.

Recently, the number of works on the use of gas-phase reactions in the conditions of flow-through thermal reactors has been growing. Thus, the thermal dissociation of hexamethyldisilazane $Me_3SiNHSiMe_3$, supplied in a helium carrier gas flow (rate 8.55 10-3 mol · min^{-1}, silazane concentration - 16.5 mol.%) is described; some characteristics of the thus obtained UFP of silicon nitride are given in table [22].

Table 1. Influence of the dissociation temperature on the properties of ultrafine powder SiCxNyOz

T, ^oC	γ, $g{\cdot}см^{-3}$	S, $m^2{\cdot}g^{-1}$	Particle size d, nm		composition		
			According to BET	According to TEM	x	y	z
1100	2,614	568	4	10	1,26	0,35	0,61
1200	2,737	555	4	10	1,35	0,40	0,47
1300	2,781	360	6	8	1,45	0,48	0,29
1400	2,783	272	8	6	1,51	0,49	0,28
Note, γ - pycnometric density; S - specific surface.							

The powders have low density values (~ 15% lower than that of silicon nitride and silicon carbide) and good agreement of the particle size according to the data of specific surface area measurements by the BET method and transmission electron microscopy (TEM). The oxygen content is, however, quite high. The resulting powders were then subjected to annealing. Annealing in argon led to crystallization of cubic (β-SiC (T = 1300 ° C), and annealing in an NH_3: H = 1: 1 mixture was accompanied by crystallization of α-Si3N4 (1400 ° C).

The residence time of the precursor-gas mixture at high temperatures in a reactor with a diameter of 25.4 mm and a length of ~ 200 mm was less than 0.1 s. The degree of conversion in the temperature range from 1100 to 1400 ° C increased from 30 to 51%. Within 30 min, it was possible to precipitate ~ 2 g of powder on a rotating drum cooled with liquid nitrogen. It is noted that to obtain non-agglomerated UFPs, a low concentration of the precursor in the carrier gas is required (which minimizes the probability of cluster coalescence under the condition of a short process duration), a rapid expansion of the gas flow at the exit from the thermal zone into an environment with a low inert gas pressure (102 - 5 · 103 Pa) and rapid cooling of the particles. Such installations are also equipped with special devices for collecting powder and its consolidation in situ at high pressures without contact with the environment.

CONCLUSION

Currently, the main methods for the synthesis of silicon nitride are self-propagating high-temperature synthesis (SHS). The SHS method is characterized by low energy consumption, high productivity, and simplicity of hardware design. There is a known method for producing α - Si3N4, including preparing a mixture consisting of silicon powder, an alkali or alkaline earth metal azide and a substance that increases the yield of the α-phase and increases the specific surface area of the final product (amorphous or crystalline silicon oxide) taken in a stoichiometric ratio of components, its ignition in a nitrogen atmosphere under pressure.

The disadvantage of the SHS azide technology is that sodium azide is highly toxic and more expensive than gaseous nitrogen. In addition, the use of halide salts in the initial mixture involves the use of an additional stage – purification of the product from sodium halide salts.

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