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SILICON NITRIDE FOR GAS TURBINE
APPLICATIONS. A COMPARISON OF SELECTED
STRATEGIC MATERIALS TECHNOLOGIES IN
THE U.S. AND U.S.S.R.

Battelle Columbus Laboratories

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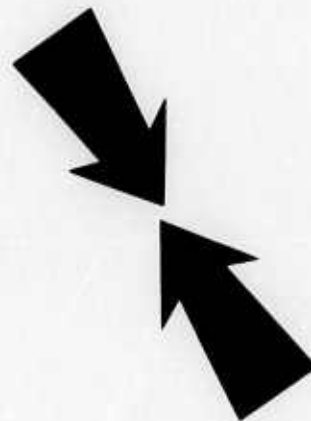
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*A Comparison of Selected Strategic Materials Technologies
in the US and USSR*

SILICON NITRIDE FOR GAS TURBINE APPLICATIONS

TECHNICAL SUMMARY

Gas turbine engines operating at inlet temperatures of 2500 F or higher would be much more efficient than comparable present engines, which are limited by their materials of construction to a maximum inlet temperature of 2000 F. The promise of higher efficiency has stimulated US and British research on ceramic engines; because of its desirable properties, silicon nitride has been chosen as the primary material to be evaluated for engine applications in programs at Ford and Westinghouse. The objective of the work described in this report was to determine whether or not ceramic-engine development involving silicon nitride was also being pursued in the Soviet Union, and, if so, to evaluate the Soviet program. The method of approach was a survey of Soviet literature.

The results of the survey indicated that the Soviets have a strong capability for basic research on silicon nitride; however, there was no evidence that they are pursuing a program to evaluate silicon nitride in gas turbine engines. Indeed, there was no evidence in their literature that the Soviets are working on ceramic engine components of any kind.

Recent interest in the US and UK has shifted toward silicon carbide as the material of construction for ceramic engines. A systematic study of Soviet research on silicon carbide, similar to the present one on the nitride, might reveal some evidence that ceramic-engine research in the USSR, if it exists, is concentrated on the use of silicon carbide.

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SILICON NITRIDE FOR GAS TURBINE APPLICATIONS

V. J. Tennery

INTRODUCTION

The development of gas turbine engines with gas inlet temperatures near 2500 F or higher will provide significant improvement of the efficiency compared with that obtained in present engines, where inlet temperatures are limited to a maximum of about 2000 F. Major materials requirements for such engines are for high strength and toughness, coupled with oxidation resistance at the operating temperature. Resistance to thermal-shock weakening or fracture is also of paramount importance. Refractory materials are required for the stator vanes that direct the hot gases to the turbine wheel blades and for the turbine wheel itself. The turbine wheel represents the rotating part of the machinery and consists of the turbine vanes or blades and the hub assembly. Presently, superalloys are used for these components in high-temperature gas turbines and critical components usually are cooled by a coolant gas flowing through internal passages within the blades.

Silicon nitride has shown considerable promise for possible use in uncooled turbine engine components due to its relatively good high-temperature strength, its thermal shock resistance, and its resistance to oxidation. Extensive work in the United Kingdom on this ceramic material helped to identify the properties which showed that the nitride might be usable in the form of uncooled high-temperature engine components.

The material property requirements for the stator and rotor components of the turbine depend upon the specific component design and the start-up and cool-down profile for the engine. The US effort in this area currently is centered in the AMERC-ARPA Ceramic Gas Turbine Program. Ford and Westinghouse

both have current contracts under this program. Ford is concentrating on using essentially state-of-the-art ceramic material in an automotive gas turbine while Westinghouse is concentrating on stator vanes of a large gas turbine for central-power or marine use. Ford's rotor is designed for fabrication from a material capable of withstanding a maximum tensile stress in service of about 60,000 psi, hot pressed Si_3N_4 . Stator blade stresses will rise to the order of 20,000 to 25,000 psi about one minute after combustor ignition. These stresses will subside rapidly to about 5,000 to 10,000 psi after engine warm-up. Oxidation resistance and absence of or minimal static fatigue effects are essential for silicon nitride ceramics to function in these applications due to the magnitude of the operating stresses and the limitations on strengths achieved to date.

McLean[1] has reviewed the materials requirements for ceramics in small gas turbines and illustrated the specific strengths of candidate turbine materials of various temperatures as shown in Figure 1. The specific strengths are given in units of σ/ρ where σ = strength in psi and ρ = density in lb/in.³. Table 1, also from McLean, lists some of the basic properties of selected ceramics and superalloys that are pertinent to gas turbine applications. As Figure 1 and Table 1 show, hot-pressed silicon carbide and silicon nitride both have properties that make them serious contenders for applications in gas turbines. The present report deals only with silicon nitride.

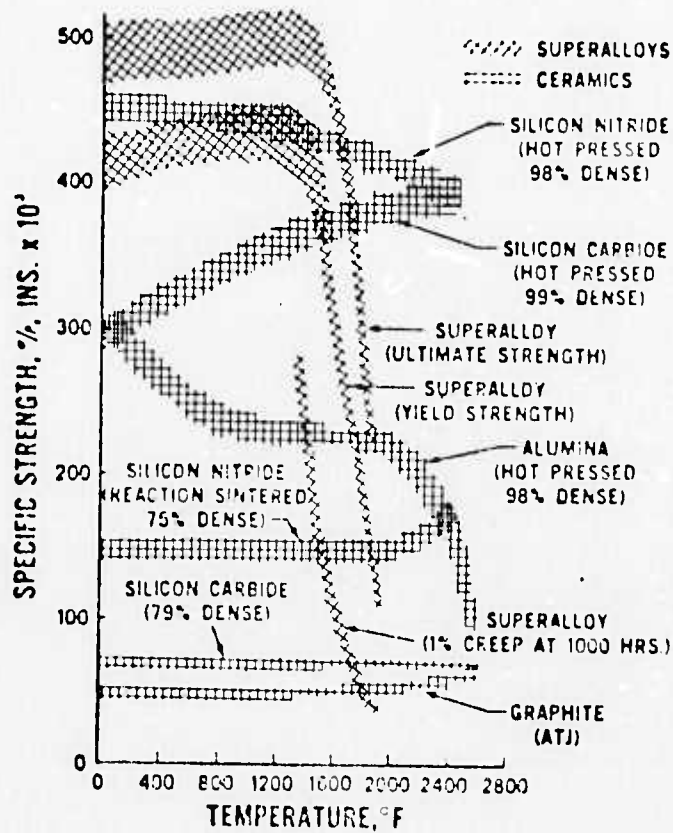


FIGURE 1. SPECIFIC STRENGTH OF HIGH-TEMPERATURE MATERIALS[1]

TABLE 1. BASIC PROPERTIES OF SOME SELECTED HIGH-TEMPERATURE CERAMICS AND SUPERALLOY METALS [1]

Material	Melt Point °F	Coeff. of Thermal Expansion x 10 ⁻⁶ /°F	Density (LB/INS. ³)	Thermal Conductivity (BTU-IN/ FT ² -HR-°F)	Specific Heat (BTU/LB/°F)	Young's Mod. (PSI x 10 ⁶ at 70°F)
<u>Ceramics</u>						
Al ₂ O ₃ Alumina (Commercial grade)	5660	5.7 (70-500 F)	.150	74	.19	40.2
SiO ₂ Fused Silica (Slip cast)	5100	0.29 (70-400 F)	.067	2	.15	3.8
G (ATJ Graphite)	6560 (Sublimes)	2.2	.062	725	.17	1.1
SiC Silicon carbide (Recrystallized)	4080 (Dissociates)	2.8 (70-100 F)	.090	115	.20	25.0
SiC Silicon carbide (Hot pressed)	4080 (Dissociates)	2.8 (70-400 F)	.112	700	.20	56.0
Si ₃ N ₄ Silicon nitride (Reaction sintered)	5450 (Dissociates)	1.1 (70-1800 F)	.090	28	.26	25.0
Si ₃ N ₄ Silicon nitride (Hot pressed)	5450 (Dissociates)	1.4 (70-1800 F)	.112	105	.26	31.0
Lithium-alumina- silicate (Glass ceramics)	2400	0.6 (750-1650 F)	.06	7	.20	12.0
3Al ₂ O ₃ ·2SiO ₂ Mullite (Pressed & sintered)	5320	2.8 (70-212 F)	.097	28.5	.23	22.5
<u>Metals</u>						
INVAR M 245 Hastelloy-X	2450 2470	7.24 9.0 (70-1600 F)	.305 .298	117 76	.10 .116	29.8 28.6
Inconel 713C	2550	8.3 (80-1600 F)	.286	146	.10	29.9

CONCLUSIONS OF ANALYSIS

- (1) The Soviets have a strong capability for determining the chemical-physical properties of refractory materials at high temperatures. They have not reported any high-temperature mechanical properties studies that would indicate their intent to use silicon nitride for turbine applications, and apparently are not presently pursuing this goal.

- (2) Although the Soviets appear to be behind the US and UK in developing high-temperature, high-strength materials, they possess sufficient basic technical depth in materials to conduct an independent development of silicon nitride related to gas-turbine applications if they should decide to do so.

BACKGROUND

The United States and United Kingdom both have been actively considering the use of silicon nitride in gas turbines. Coe, et al.[2] discuss the design of a two-shaft gas turbine using silicon nitride. Current US work on gas turbines is reported in AMMRC report CTR 72-3[3] and subsequent issues. This work is unclassified.

Two forms of silicon nitride have been studied in the US and UK. These are: (1) a hot-pressed high-density form, and (2) a relatively porous lower density reaction-sintered form. Densification of the hot-pressed form is usually achieved with the use of additives, such as MgO, to silicon nitride powder prior to fabrication; this process is patented in the UK. The fabrication of reaction sintered material is accomplished by fabricating a shape from silicon powder and subsequently reacting the silicon with nitrogen at elevated temperatures to transform the part into silicon nitride. The dense form offers the advantage of higher strength, in accord with the general strength-density curve of Figure 2. Reaction sintering offers ease of fabrication of a variety of shapes, and usually is more economical.

Ford has investigated both hot-pressed and reaction-sintered forms for use in vehicle-turbine components, while Westinghouse has concentrated on the fabrication of stator vanes machined from billets of hot-pressed silicon nitride. Due to the relatively small size of vehicle-turbine components, a significant economic advantage exists for reaction-sintered components if they can be fabricated, have sufficient strength at high temperatures, and be sufficiently oxidation resistant.

The open Soviet literature on silicon nitrides refers to applications for the material in three principal areas: (1) as a refractory container material for containment of molten metals, (2) as an electrical insulator for the passivation and isolation of electronic circuits, and (3) as a fiber material for use in unidentified types of composites.

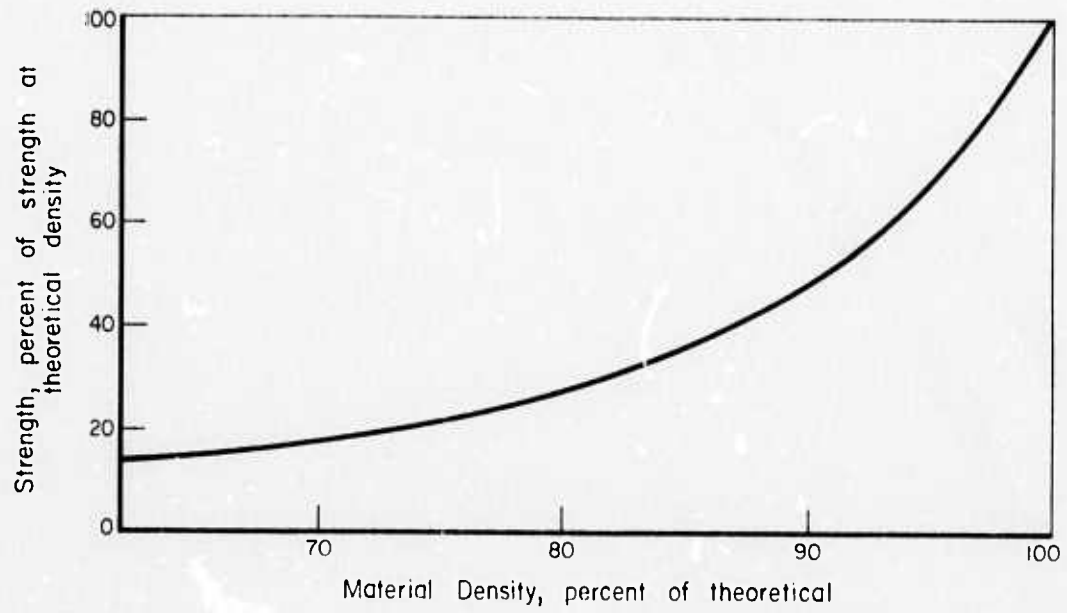


FIGURE 2. CERAMIC MATERIAL STRENGTH VERSUS DENSITY[1]

Research on the nitrides of silicon in the USSR and US does not and has not compared in volume with the work done on these materials in the UK. Work in the US primarily has been developmental and limited to contractual efforts on the ARPA High-Temperature Turbine Program. Other work supported by the US Navy has recently provided some insight into the causes of loss of strength in hot-pressed silicon nitride at high temperatures.

For some time, silicon nitride was thought to exist in two polymorphic forms designated (α) and (β). Work on these materials was of such an approximate nature that it was only as recently as 1972 that Wild, et al. [4] determined that the α form is actually an oxynitride, $\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$, and that the β form is Si_3N_4 . Another silicon oxynitride, Si_2ON_2 , is known, and the Soviets have reported considerable work on this material. The Soviets have not yet indicated an awareness that α -silicon nitride is actually an oxynitride, on the basis of literature surveyed in connection with this report.

DETAILED ANALYSIS OF PRESENT STATUS

The Soviets have a strong capability in refractory-materials development and have reported extensive work on the chemical and physical properties of silicon nitride. This work has apparently not been directed toward the development of advanced materials for turbine applications. Extensive work is being done by the Soviets on the use of silicon nitride for use as an electronic circuit passivation material, as a crucible refractory for containing certain molten metals, and as a whisker material for use in composites. The infrared spectra of various silicon nitrides has recently been reported and Soviet work on the sintering properties of various silicon nitride powders has indicated difficulty in achieving near-theoretical-density nitride by conventional sintering. Magnesia additives to serve as sintering aids in nitride powders have been reported by the Soviets, similar to their use in the US and UK.

No work was confirmed in which the Soviets have done extensive high-temperature strength tests, creep tests, nor oxidation resistance tests of either reaction-sintered or hot-pressed silicon nitride. Considerable Soviet work on the synthesis of silicon nitride powders and fundamental studies of reactions between the oxynitride Si_2ON_2 , SiO_2 and α and β silicon nitrides have been reported.

The Soviets do not appear to be as far along on the development of high-temperature, high-strength materials for turbine applications as the US and UK. Silicon nitride powder is commercially available in the USSR.

High-Density Hot-Pressed Silicon Nitride

At this time, the attainment of high bulk density in silicon nitride ceramics can be achieved only with the use of a sintering aid such as MgO, followed by hot pressing. This technology is covered in a British patent[5] issued to Plessey-UK, Ltd. and by patents to Joseph Lucas Co., Ltd. The only manufacturer of significant quantities of high-density silicon nitride in the US is the Norton Co., Worcester, Massachusetts; Norton is a licensee of the Lucas patents.

Lange and Terwilliger[6] have recently (1972) concluded that the relatively high room-temperature strength of hot-pressed silicon nitride is related to the transformation of the α phase to the β phase during hot pressing. The mechanism whereby magnesia functions in this process is not understood at present. Wild, et al.[7] discuss possible mechanisms for this process. Lange[8] has concluded that the high-temperature strength of dense silicon nitride is closely related to the microstructural morphology of the β -nitride grains in the dense ceramic and that these grains achieve their interlocking morphology during the conversion of α to β nitride. No information from the USSR was located concerning these factors influencing the strength of dense silicon-nitride ceramics.

Recent work of Norton reported by Torti[9] indicates that strengths of 100,000 psi at 1200 C (2190 F) have been achieved for dense silicon nitride consisting primarily of Si_3N_4 (previously designated as β form). An appreciable decrease in strength occurs above 1200 C, with a value of 40,000 psi at 1400 C (2550 F) in air being reported. No reports of such properties were found in the Soviet literature.

Coe, et al.[2] have reported on properties of hot-pressed silicon nitride made from powder, primarily of the α form, with 1 percent MgO added, and discussed the potential engine applications for this material.

Zabruskova, et al.[10], at Moscow Chemical-Technological Institute, have recently published data on the infrared spectra and synthesis of Si_3N_4 , and Samsonov, et al.[11], at the Institute of Materials Science, in Kiev, have discussed

process development oriented toward complete densification of Si_3N_4 and Si_3N_4 -SiC composites. Reference[10] also discusses the reaction sintering of both silicon nitride and silicon carbide. The ceramics being produced by Samsonov, et al., reportedly had 25-30 percent open porosity. Their reporting of X-ray crystal parameters indicates a full understanding of the role of the α and β forms of the nitride in producing strong ceramics. The silicon nitride powder used in most of the Soviet experiments was referred to as "commercially available" and produced by the Zaporozhe Abrasives Combine. The silicon carbide powders reportedly came from this same source.

Several investigations of the thermal stability of Si_3N_4 and Si_2ON_2 have been reported by the Soviets and the work by Zabruskova, et al.[12], is one of the more recent reports. This work was oriented primarily toward the use of Si_2ON_2 as a bonding phase for SiC ceramics, but also included high-temperature mass spectrographic studies of the vapor species over Si_3N_4 . Samsonov and Kazakov[13] have reported on work of producing articles of various shapes from materials based on silicon nitride with MgO or Al_2O_3 , with subsequent partial sintering of the mixed powders while packed in boron nitride in a nitrogen atmosphere. Final sintering was accomplished at 1600-1700 C (2910-3090 F) in another charge also containing MgO. The report of this rather laborious process is a reasonable indication that the Soviets have chosen processing procedures for achieving densification of silicon nitride which are considerably different from those developed in the UK and utilized in the US. They have not reported on results of hot-pressing studies of silicon nitride, but Samsonov and Petrykina[14] have done a considerable amount of work on hot pressing of various metals, carbides, and oxides. Extension of this capability to silicon nitrides would be relatively simple. Samsonov, et al.[15] have reported the importance of carbide homogeneity to hot-pressing densification kinetics; homogeneity is also quite relevant to silicon nitride.

Extensive nitriding studies of various metals other than silicon have also been reported by the group under Samsonov at the Institute of Materials Science, Academy of Sciences of the Ukrainian SSR. Earlier work by Kashtalyan, et al.[16], at the same Institute included measurement of Young's modulus of Si_3N_4 -BN compacts at various temperatures and these results clearly showed that very little softening of high Si_3N_4 compositions occurred at temperatures to at least 1200 C (\sim 2250 F). The stability relations in the Si-O-N system were reported about the same time by

Krasotkina[17] and concentrated on the role of various oxide and fluoride additives in determining the nature of transformations of Si_3N_4 to Si_2ON_2 and cristobalite in air and carbon monoxide at temperatures to 1750 C (3180 F).

Reaction-Sintered Silicon Nitride

Reaction-sintered silicon nitride does not exhibit the loss of strength shown by hot-pressed nitride as temperatures near 1200 C (2190 F). Since this material is produced by reacting nitrogen directly with silicon, no sintering-aid additives are employed. The final disposition of the additives in the hot-pressed form is not clear at this time, but presumably they migrate toward the grain boundaries. It is possible that softening of this additive-rich grain boundary phase is responsible for the general weakening of the hot-pressed ceramic at high temperature. The strength of reaction-sintered silicon nitride is not strongly dependent upon temperature and remains relatively constant to 1400 C (2550 F). Room-temperature strengths of the order of 36,000 psi have been reported by Davidge and co-workers[18] for reaction-sintered material. Due to its open porosity, reaction-sintered silicon nitride oxidizes more readily than the hot-pressed form, but its strength remains relatively unaffected up to temperatures near 1200 C (2190 F).

Zabruskova, et al. [10] in their recent article cited earlier, reported some of the properties of silicon nitride materials formed by reactive sintering of silicon with SiO_2 in a nitrogen atmosphere. The Si_3N_4 content of the finished materials was determined from a 580 cm^{-1} absorption band that reportedly belongs to this phase. The use of this analytical technique for this material is new as far as the author is aware. The thermal expansion coefficient was 2.13×10^{-6} per centigrade degree (1.19×10^{-6} per Fahrenheit degree) from 20 to 800 C (70 to 1470 F) and the material withstood up to 100 thermal cycles between 1000 C (1830 F) and 25 C (75 F). Bend strengths of 25,000 to 30,000 psi were reported and the strength was relatively independent of temperatures to 1000 C (1830 F).

TECHNICAL FORECAST ANALYSIS

No indication was obtained that the Soviets are actively developing ceramic silicon nitride materials for gas turbine applications. As discussed previously, they have the technical ability to do so, but the data available at this time indicate

that they are working on these materials with the point of view of using them as special refractories in more customary applications. The Institute of Materials Science, Academy of Sciences of the Ukrainian SSR, Kiev, under Samsonov, would be the logical place where gas-turbine oriented work would be done if they decide to do so, and the activities of this group should be monitored for indications that Soviet work in silicon nitride has taken this new direction.

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