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NEUTRONS**

**ARMY MATERIALS AND MECHANICS RESEARCH CENTER
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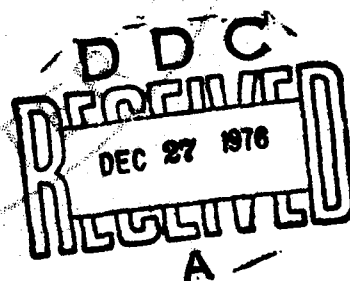
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CHARACTERIZATION OF SILICON NITRIDE USING 14 MeV NEUTRONS

FORREST C. BURNS, HOMER F. PRIEST, and GRACE L. PRIEST
MATERIALS SCIENCES DIVISION

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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ABSTRACT

There is special interest in the ceramic Si_3N_4 because it is a light-weight material having high-temperature oxidation and corrosion resistance, thermal shock resistance, and strength at both high and low temperatures. Such a material is needed for application in high temperature gas turbines.

Experimental techniques required to prepare samples of Si_3N_4 for analysis and the preparation of both low-oxygen-containing-nickel and polystyrene holders for these samples and their respective standards are described. Results are presented for total oxygen content of both hot-pressed and reaction-bonded Si_3N_4 subjected to oxidation at 2200 F, characterization of amorphous silicon nitride, the oxygen content of alpha silicon nitride, and the silicon-oxygen analysis of various other Si_3N_4 samples. (Authors)

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INTRODUCTION

Silicon nitride is a new, high-temperature ceramic which has many potential applications. The one with which we are principally concerned is its use in hot flow path components in gas turbines where high-temperature operation will give greatly improved efficiency.

There is already considerable literature on silicon nitride, mainly on processing studies, but with many conflicting findings. There were two commonly accepted crystallographic modifications: alpha, an oxygen-stabilized form considered to be a low-temperature form with the formula $\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$ (1.48% O),¹⁻³ and beta Si_3N_4 , the high-temperature form. Alpha was transformed irreversibly to beta at temperatures above 1400 C.

Silicon nitride bodies are most commonly prepared by one of two manufacturing procedures which give quite different products.⁴

a. *Reaction-bonded silicon nitride* is produced by making a ceramic body from silicon powder using conventional ceramic production techniques such as slip casting, injection molding, etc., followed by nitriding in a nitrogen atmosphere just below the melting point of silicon. The product is porous, of moderate strength, very resistant to thermal shock, and has the advantage that complex shapes such as turbine blades are easily made since there is no volume change in nitriding and the silicon powder is easily molded in complex shapes.

b. *Hot-pressed silicon nitride* is prepared at 1750 C in a graphite die hot press using high alpha powder with a densifying agent such as magnesium oxide. The material has a density close to theoretical density (3.2 g/cc), is hard, very strong, and has excellent thermal shock resistance. It is usually pressed in blocks, and complex shapes must be diamond machined from the blocks, which is a very expensive process.

Stoichiometry, cation impurity content, and oxygen content were all unknown when we first became interested in silicon nitride, so we decided to adapt our system using our Kaman 14 MeV neutron generator to look at this material.

EXPERIMENTAL TECHNIQUES

The equipment, described in Reference 4, was designed for cylindrical metal samples 0.305" in diameter and 1.500" long. It was not practical to obtain silicon nitride samples in this configuration, and many samples were in the form of powders. Therefore, accurately machined polystyrene sample holders with the required outside dimensions and with inside dimensions of 0.250" in diameter and

1. GRIEVESON, P., JACK, K. H., and WILD, S. *The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides*. Special Ceramics 4. Edited by P. Popper, British Ceramic Research Association, Stoke-on-Trent, 1972, p. 237-238.
2. WILD, S., GRIEVESON, P., and JACK, K. H. *The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides*. Special Ceramics 5. Edited by P. Popper, British Ceramic Research Association, Stoke-on-Trent, 1972, p. 385-393.
3. COLQUHOUN, I., WILD, S., GRIEVESON, P., and JACK, K. H. *Thermodynamics of the Silicon-Nitrogen-Oxygen System*. Proc. Brit. Ceram. Soc., no. 22, 1973, p. 207-227.
4. PRIEST, H. F., BURNS, F. C., and PRIEST, G. L. *An Irradiation, Transfer, and Counting System for Neutron Activation Analysis of Short-Lived Components in Inhomogeneous Samples*. Analytical Chemistry, v. 42, 1970, p. 499-503; also Army Materials and Mechanics Research Center Technical Report, AMMRC TR 70-21, August 1970.

1.125" long were constructed as shown in Figure 1. The sample holders weigh less than a gram and can accommodate powders as well as round, square, rectangular and disk samples provided the diagonal measurement is 0.250" or less. Powders are packed in the holders by a combination of vibration and tamping. For irregular samples such as a turbine blade, a diamond core drill with 0.250" core diameter is used to cut disks which are combined in the holder to give the required length. Samples smaller than the required dimension had to be shimmed with polypropylene to hold them in position. In all cases, lucite or high purity silicon standards, of as close to the same configuration to the sample as possible, were used in a polystyrene sample holder. The oxygen content of polystyrene (0.15 wt% O) and the polypropylene (0.05 wt% O) shims was determined for the blank corrections.

In some cases it was necessary to analyze very small samples, and this was done in a low oxygen nickel holder (0.005 wt% O) with a cavity 3/16" by 3/16" as shown in Figure 2. The lucite or silicon standard was of the same size in an identical holder. With only a few milligrams of sample there was some loss in precision but the results were adequate.

The accuracy was checked frequently using a NBS reference standard SRM 356 versus titanium plus lucite rods for oxygen, and high purity, oxygen-free silicon for silicon. The relative mean error was less than 0.20% of the value 0.01069 g for oxygen and 0.07% of the value 1.5228 g for silicon.

RESULTS

Initially the problem was to screen a variety of commercially available silicon nitride samples. In general, oxygen analyses and silicon analyses were made. Gamma spectroscopy was used to detect major cation impurities. Tables 1 and 2 show a series of analyses on crystalline and amorphous commercial samples.

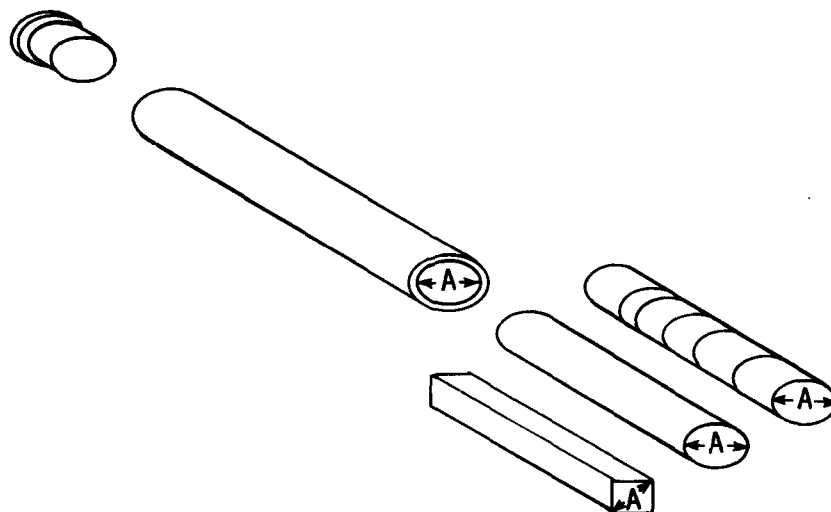


Figure 1. Polystyrene Sample Holder

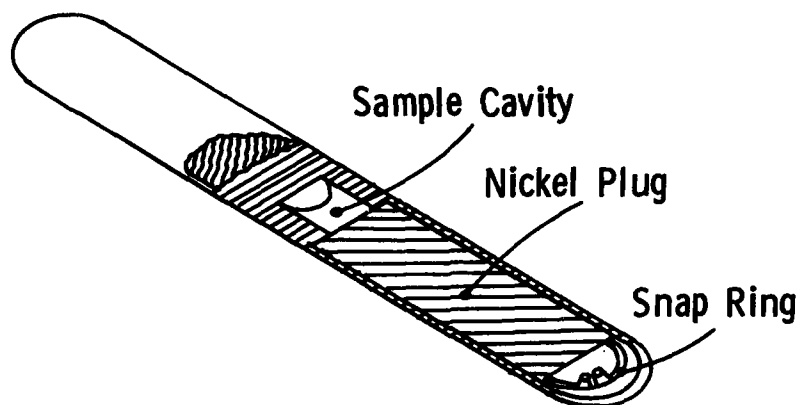


Figure 2. Nickel Micro Holder

It is obvious that many of the crystalline samples were badly contaminated with oxygen and that few approached theoretical stoichiometry. In the case of most of the amorphous samples, the analyses showed them to consist largely of diimide $\text{Si}(\text{NH})_2$, with very little silicon nitride, and many were severely contaminated with quartz.

Chemically vapor-deposited (CVD) silicon nitride,⁵ using the reaction of silicon tetrafluoride with ammonia at about 1500 C, is dense, 100% alpha-type and does not convert to beta on extended heating at 1800 C under 275 psig nitrogen pressure. Table 3 shows the results of a number of analyses on this material. This work showed conclusively that alpha does not have constitutional oxygen⁶ and has led to a reevaluation of the structure determination which shows that alpha silicon nitride is Si_3N_4 . The CVD form of silicon nitride is the purest available.

Unfortunately, despite its good properties, silicon nitride is susceptible to oxidation by either of the following reactions:



In the first case there will be a net weight gain resulting from oxidation, but in the latter there will be a loss so that weight change measurements are not easily interpreted. Table 4 and Figure 3 show data for oxidation of both injection-molded, reaction-bonded material (density 2.3) and hot-pressed material (density 3.2). The porous material oxidizes in its pores as shown by the fact that the oxygen content is not affected by grinding away the surface. Due to the MgO addition the initial oxygen content of the hot-pressed material is higher

5. GALASSO, F., KUNTZ, U., and CROFT, W. J. *Pyrolytic Si_3N_4* . J. Amer. Ceram. Soc., v. 55, no. 8, 1972, p. 431.

6. PRIEST, H. F., BURNS, F. C., PRIEST, G. L., and SKAAR, E. C. *Oxygen Content of Alpha Silicon Nitride*. J. Amer. Ceram. Soc., v. 56, no. 7, July 1973, p. 395.

Table 1. 14 MeV NEUTRON ACTIVATION ANALYSIS
OF CRYSTALLINE Si_3N_4

Sample	Material	Wt% Si	Wt% O	Exptl. Rel. Std. Dev. % Oxygen
1	High α	62.39	1.36	0.52
2	High $\alpha + \beta$	53.23	3.86	.39
3	High $\alpha + \beta$	54.46	4.58	.40
4	85% $\alpha + \beta$	60.85	1.31	.46
5	Mostly β	59.98	1.81	.41
6	95% $\alpha + \beta$	60.43	0.94	.52
7	$\alpha + \beta$	60.25	1.13	.54
8	$\alpha + \beta$	56.55	16.24	.33
9	HP 85% α	61.96	1.74	.44
10	High α	63.13	1.36	.49
11	$\alpha + \beta$	58.90	2.45	.42
12	$\alpha + \beta$	58.70	2.18	.58
Theoretical: Si_3N_4 - 60.06% Si				

Table 2. 14 MeV NEUTRON ACTIVATION
ANALYSIS OF AMORPHOUS Si_3N_4

Sample	Wt% Si	Wt% O	Exptl. Rel. Std. Dev. % Oxygen
1	50.35	29.55	0.36
2	52.09	31.21	.34
3	50.83	27.45	.17
4	52.08	3.02	.54
5	54.41	2.54	.49
6	49.66	12.12	.45
7	53.53	7.44	.47
8	52.59	2.81	.70
9	52.95	7.88	.48
10	51.10	6.98	.48
Theoretical: Si_3N_4 - 60.06% Si $\text{Si}(\text{NH})_2$ - 48.33% Si			

Table 3. 14 MeV NEUTRON ACTIVATION ANALYSES OF CVD Si_3N_4

Sample	Material	Wt% Si	Wt% O	Exptl. Rel. Std. Dev. % Oxygen	Exptl. Rel. Std. Dev. % Silicon
1	α	60.87	0.30	1.00	0.31
2	α	-	.30	0.76	-
3	α	61.30	.30	0.76	0.14
4	α	-	.35	2.00*	-

*Sample size 0.071 g in Ni holder

Theoretical: Si_3N_4 - 60.06% Si, 39.94% N

$\alpha\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$ - 59.69% Si, 1.48% O, 38.83% N

Table 4. 14 MeV NEUTRON ACTIVATION ANALYSES OF Si_3N_4 OXIDIZED IN AIR AT 2200 F

Sample	Material	Wt% O Initial	Total Time at Temp Hr	Wt% O after Oxidation	Wt Gain (%)	Wt% O after Ground	Exptl. Rel. Std. Dev. %		
1	Inj. molded Reaction bonded	0.49	5	7.57	2.93		0.73	0.45	
2	↓	0.48	8	10.16	4.16		.73	.43	
3		0.46	24	12.38	5.19	12.42	.74	.44	0.42
4		0.52	48	14.51	6.19	14.14	.74	.45	.42
5		0.48	72	17.16	7.48	16.97	.74	.45	.41
6	Sample 4		119	19.94	9.17			.44	
7	Sample 5		143	19.37	8.83			.37	
8	Inj. molded Reaction bonded	0.48	144	20.76	9.19		.73	.41	
9	"	0.48	212	23.19	10.94		.73	.38	
10	Hot pressed	3.44	48.5	3.51	0.04		.42	.41	
10a	Sample 10		163	3.77	0.17			.39	

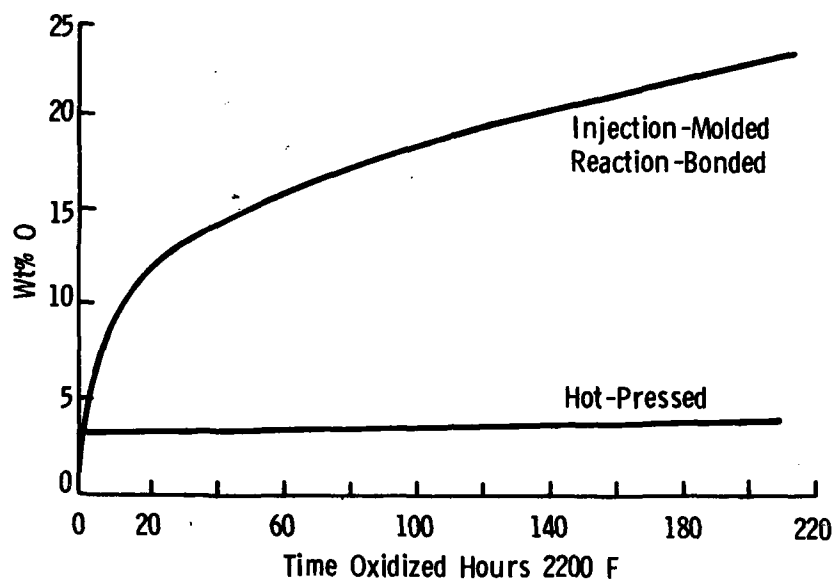


Figure 3. Oxidation of Silicon Nitride

than that of reaction-bonded material, but the hot-pressed material shows very small increase in oxygen due to oxidation as compared to the injection-molded, reaction-bonded material.

CONCLUSION

The 14 MeV neutron activation analysis for oxygen and silicon is a very powerful tool in developing the new, important ceramic material Si_3N_4 , both in characterizing starting materials and end products.