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STUDY OF PHENOMENA RELATED TO THE SINTERING PROCESS
OF SILICON NITRIDE AT ATMOSPHERIC PRESSURE

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Sinterizzazione a Pressione Atmosferica del Nitruro di
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16. Abstract

A new procedure was perfected at the FIAT Research Center, for the production of components used in engineering applications of silicon nitride.

The method makes it possible to obtain particles of complex geometry that combine remarkable mechanical properties with a high density.

The process developed, in contrast to the "hot pressing" method, does not use external pressures; in contrast to the reaction bonding method, it makes it possible to obtain final densities close to the theoretical value.

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STUDY OF PHENOMENA RELATED TO THE SINTERING PROCESS OF SILICON NITRIDE AT ATMOSPHERIC PRESSURE*

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SUMMARY. A new procedure was perfected at the FIAT Research Center, for the production of components used in engineering applications of silicon nitride.

The method makes it possible to obtain particles of complex geometry that combine remarkable mechanical properties with a high density.

The process developed, in contrast to the "hot pressing" method, does not use external pressures; in contrast to the reaction bonding method, it makes it possible to obtain final densities close to the theoretical value.

One of the problems in developing this process is the obtention of sinterized products free of surface inhomogeneities that cause either reductions in density or in mechanical-physical properties.

To eliminate this problem a specific study of the phenomenon of diffusion of the sintering additives inside the sinter was performed; the results show that the main additive, MgO, is removed from the sample by diffusion, and that this fact is responsible for the inhomogeneities observed.

To be able to control that process, the diffusion

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* Eugenio Lubatti Prize 1979

coefficient of MgO in silicon nitride was measured.

This made it possible to modify the process, obtain-
ing samples perfectly homogeneous both in structure
and properties.

INTRODUCTION

Among the ceramic materials, silicon nitride is currently one of
the best considered for engineering applications in structural
components operating at high temperatures [1-4].

Among the characteristics that make it particularly interesting
for this type of application are its low specific mass, its op-
timum mechanical resistance up to temperature levels of 1250°C
and above, its high thermal and chemical stability, in addition
to a considerable resistance to mechanical impact, and to oxida-
tion.

Even though these are the properties that made it so attractive,
to date, leading to continuous improvements in the material, to
make it usable in the production of components be it for turbines
or diesel engines (blades, rotors, stators, combustion chambers,
pistons, etc.), it has other characteristics that make it inter-
esting for a number of applications.

Its high chemical stability even at elevated temperatures (the
nitride sublimes at approximately 1900°C), with the possibility
of resisting the attack of the common acids, render it suitable
to the construction of reaction vessels, tubing, nozzles, heat
exchangers, rotating parts for pumps in the chemical industry.

In fact, silicon nitride has resisted the attack of hydrochloric,
nitric, sulphurous and phosphoric acid for at least 500 hours of
immersion, but it is attacked by liquid NaOH at 500°C after 5 h.

In the industry of light and low-melting metals, the nitride is used in the construction of thermocouple sheeths, nozzles, extruders and even pumps with rotating parts, because the material does not react with molten light metals (Al, Zn, Sn), nor do they wet it and it has a good resistance to thermal shock.

In regard to its use in copper metallurgy, there are some limits, as it is partially attacked by molten copper in the presence of air: in this respect small quantities of tin act as stabilizer and substantially reduce the tendency of copper to attack the nitride.

Silicon nitride is not suited, however, to use in iron-works, partially because of the higher temperatures involved but particularly because the carbon present in steel and pig iron react with the free silicon in the material, forming silicon carbide, which is harmful both to the final product and to the nitride component.

The main processes used to date to produce Si_3N_4 particles are those of "reaction bonding" and "hot pressing".

Reaction bonded silicon nitride (RBSN) is a material obtained by the nitration of silicon powder sinters of the desired shape. These are obtained by traditional methods of ceramic production and their transformation into Si_3N_4 occurs according to the reaction $3 Si + 2 N_2 \rightleftarrows Si_3N_4$ by means of appropriate thermal treatment between 1000 and 1400°C, for a time varying from 50 to 100 h, and working in a nitrogen atmosphere.

The density of the material produced by the above method is modest (80% of theoretical) and consequently, because of the high porosity, its mechanical properties and its resistance to corrosion and erosion are somewhat limited.

The advantages this material has over the hot-pressed material are based on its ability to be shaped into components of complex

geometries.

In the alternative, "hot pressing" technology, the silicon nitride powder, containing appropriate densifying additives, are pressed at high temperatures in an inert atmosphere, in induction-heated graphite molds.

The pressing parameters vary according to the type of powder and additive(s) used, in an operational field that normally includes temperatures between 1550 and 1800 °C, forming pressures between 150 and 500 kg/cm^2 and times varying to a maximum of 5 hours.

The material obtained by this process has good mechanical characteristics; there are, however, some geometrical limitations that make the production of complex forms expensive in terms of machine time and limit its use in industrial applications.

At the FIAT research center an alternate silicon nitride densification process was developed, by means of sinterization at atmospheric pressure [6-7], which eliminates a good portion of the problems connected with the two preceding methods.

It had been believed, to date, that covalent solids were practically unsinterable, in the sense that it was not thought possible to obtain, by thermal treatment in the absence of external pressure, appreciable densification and shrinkage from the starting powders; the covalent nature of the silicon-nitrogen bond, with its remarkable chemical stability in fact entails a high activation energy for solid state diffusion, which is the main operating densification mechanism.

This implies an activation of sinterization that can occur either by means of the use of fine powders [8] (which reduces the diffusion path), or by additives that promote the formation of a liquid phase at the grain boundary [9]. In this regard, particularly efficient systems are those based on the oxides of magnesium or rare

earths such as Y_2O_3 or CeO_2, in which the silicon nitride is in the form of a powder with an average granulometry below 5 micron. The research mentioned has dealt primarily with these systems.

In regard to sinterization, silicon nitride presents, besides the problem of its covalent nature, also the phenomenon of thermal dissociation at the densification temperature, according to the reaction

$$Si_3N_4 \rightleftarrows 3Si + 2N_2\uparrow$$
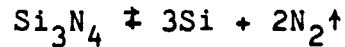
The procedure adopted to date to inhibit such decomposition consists in performing the sinterization at high nitrogen pressure (in an autoclave), in order to reduce the partial pressure of free silicon in the equilibrium.

The process developed at the CRF [Centro Ricerche FIAT = FIAT Research Center] consists, contrariwise, in conducting the sinterization of the Si_3N_4 powders in a protective environment consisting in a bed of powders of appropriate composition, that causes the required partial pressure of nitrogen for the equilibrium at that temperature.

Such a method has obvious technological advantages over the preceding one, in that it allows operation at atmospheric pressure, but it does not guarantee obtaining final sinters of good structural homogeneity.

The problem of Si_3N_4-base sinter homogeneity constitutes the main reason for the study being reported. The study, beyond determining the diffusion coefficient for MgO in the Si_3N_4 matrix, made it possible to show the necessity of performing the densification in some protective packs containing sintering additives; it has also made it possible to formulate interesting considerations regarding the obtention of homogeneous, sintered silicon nitride sinters.

SAMPLE PREPARATION

In the development of the silicon nitride sinterization method at atmospheric pressure, the main additive considered was magnesium oxide: its addition to the nitride powders has been determining for the densification of Si_3N_4, as had already been shown for the case of hot pressing. The procedure for the preparation of typical samples containing MgO involves several phases; the Si_3N_4 powder (the composition of which is shown in Table I, below) is ground

TABLE 1

O	C	Al	Ca	Fe	Mg	Ti	Ni	Cr	Cu	N	Si
0.9	0.11	0.12	0.26	0.8	0.05	0.01	0.01	0.05	0.04	37.5	1.2

dry for 60 h in order to reduce the average particle size to approximately 5 micron size; milling then continues for 50 hours, in iso-propanol containing 5% of MgO.

The powder so obtained is dried and then compacted by isostatic compression into cilinders of 30 mm diameter and a height of 40 mm, at 35 MPa. The density obtained in this phase is of 2.0 Mgm^{-3} (green density).

These compacts are then immersed in one volume of silicon nitride powder and the sinterization procedure is continued in an induction furnace, at atmospheric pressure and at a temperature of 1800 °C, for variable times, working in a nitrogen atmosphere.

PROCESS ANALYSIS

The weight loss of the samples treated as indicated was found to be a function of the sinterization temperature. Figures 1 and 2 (page 8) show, in comparison, weight changes and density changes as a function of temperature, for samples treated according to the proposed procedure and by other methods.
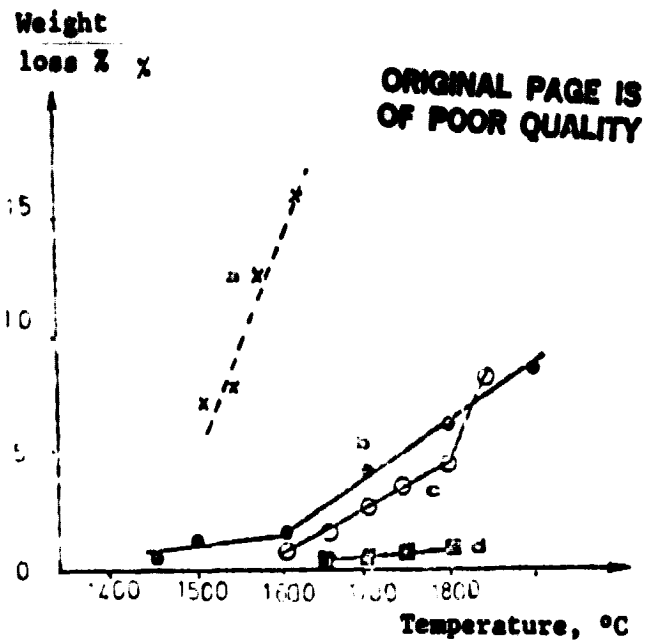
Weight
loss % χ

Figure 1. Weight loss during sintering as a function of
temperature. a: in N_2 at atmospheric pressure; b: in
N_2 at 10 atm; c: in N_2 at atmospheric pressure, in a
powder bed; d: as in c, but with MgO containing powder

The figures clearly show that the method of "packing" the samples
in a nitride powder bed seems particularly effective in inhibiting
silicon nitride decomposition: the density attained is, in fact,
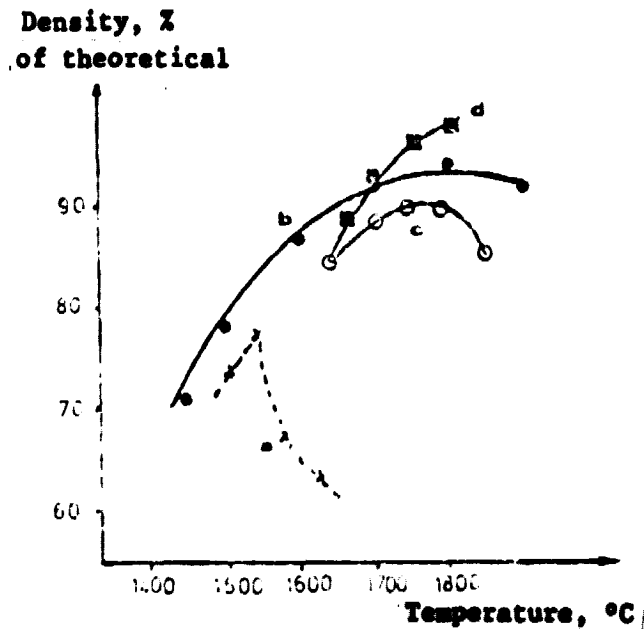of 2.85 Mgm^{-3}, or approximately 89% of the theoretical value.

Figure 2. Sample density with 5% MgO as a function of
temperature. a, b, c, and d as in Figure 1, above

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However, when these samples were submitted for structural and chemical analyses, it was observed that structural inhomogeneities still existed, with density and chemical composition differences between the surface layers and the interior.

Observation under the microscope, in addition to chemical and densimetric analyses have shown that the changes in density and porosity are related to variations in chemical composition in the external layer or "skin".

That layer is characterized by the absence or the diminished percentage of magnesium oxide. This leads to considering the weight variations during the treatment not only as a consequence of the decomposition of Si_3N_4, but also in part as due to a volatilization of the additive present in the samples.

In order to study this phenomenon, a series of samples were submitted for sinterization, varying the treatment time between 0.5 and 3 h.

The materials so obtained all show a "skin" of lower density than that at the center of the sample; its thickness grew with treatment time.

Figure 3 (page 10) shows the concentration of magnesium oxide as a function of the distance from the surface for some of the samples of Si_3N_4 prepared for this study.

The figure lines were obtained by points, with a laser microprobe (laser spectrometer) capable of performing qualitative and quantitative chemical analyses with a spatial precision of 40 microns and a sensitivity of 0.01% for the different materials.

The displacement towards the right of the concentration front as the treatment time increases - clearly visible comparing the curves in Figure 3 - leads one to suspect that the magnesium oxide is lost
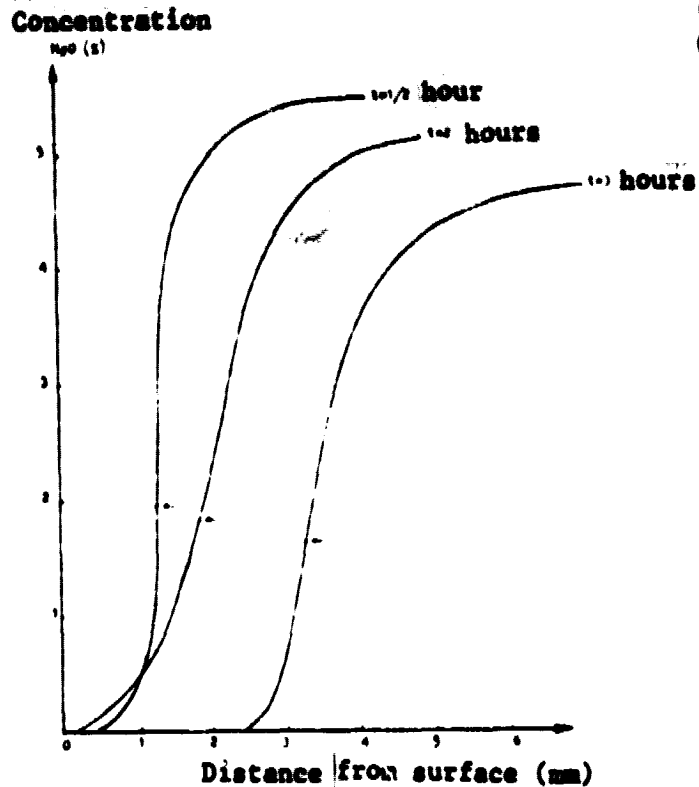
Figure 3. Variation in MgO concentration as a function of
depth; the arrows show 1/1 of initial concentration

by diffusion from the nitride packing.

In order to control the densification process and to optimize it
as a function of the sample mass itself, it hence became neces-
sary to determine the diffusion coefficient for the magnesium
oxide in silicon nitride.

EVALUATION OF THE DIFFUSION COEFFICIENT

In the case under discussion, the diffusion phenomenon – general-
ly studied for the case of the enrichment of a material in the
body of a different susbtance – here occurs as the inverse pheno-
menon, i.e., as the impoverishment in a material by diffusion out-
wards of one of its components.

The phenomenon of diffusion, whatever its boundary conditions,
obeys Fick's Second Law:

$$\frac{\partial^2 y}{\partial x^2} = D \, \frac{\partial y}{\partial t} \qquad\qquad (1)$$

where y is the concentration of the diffusing element, x the co-ordinate (unidimensional case), t is the time of diffusion and D the diffusion coefficient, in $cm^2 s^{-1}$ [10].

The boundary conditions for the case under examination can be stated as

$y = 0$ at $x = 0$ for all $t \neq 0$

$\lim_{x \to \infty} y = y_0$ for any finite time $\qquad\qquad (2)$

where y_0 = initial concentration of the diffusing element.

One solution of equation (1) that satisfies the boundary conditions (2) is

$$y = y_0 \, \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad\qquad (3)$$

where

$$\mathrm{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-v^2} \, dv$$

This solution, however, is not entirely acceptable in that it does not take into account the "displacement" of the concentration front that is evident in the figure. A solution - analytical or numerical - that does take into account that phenomenon is very complex.
It is possible from equation (3), however, to evaluate the diffusion coefficient D.

In fact, if in analogy to other cases of diffusion [10-12] we define the length of diffusion 1 (el) as

$$1 = 2\sqrt{Dt} \qquad\qquad (4)$$

as the distance at which the concentration is reduced to one e-th of the initial value, then we obtain, from (4):

$$D = \frac{l^2}{4t} \qquad (5)$$

Inserting into (5) the pair of values l_i, t_i obtained from the the experimental curve, we obtain the value of the diffusion coefficient D (Table II, below).

TABLE II				
Time (s.) × 4	l (cm)	D $\frac{cm^2}{s}$	Δ D	%
7.200	0.135	2.53×10^{-6}	2×10^{-7}	7.40%
14.400	0.168	1.9×10^{-6}	4×10^{-7}	5.2%
28.800	0.200	1.53×10^{-6}	7×10^{-7}	4.88%
36.000	0.308	2.63×10^{-6}	1×10^{-7}	4.90%
43.200	0.335	2.59×10^{-6}	8×10^{-8}	4.85%

The value, calculated by the χ^2 method, was $D_\chi^2 = 2.11 \cdot 10^{-6} cm^2/s$

Figure 4, below, shows a verification of the validity of the observations made, representing a comparison between experimental points and the curve $y = 2\sqrt{Dt}$, with $D = 2.0 \cdot 10^{-6}$
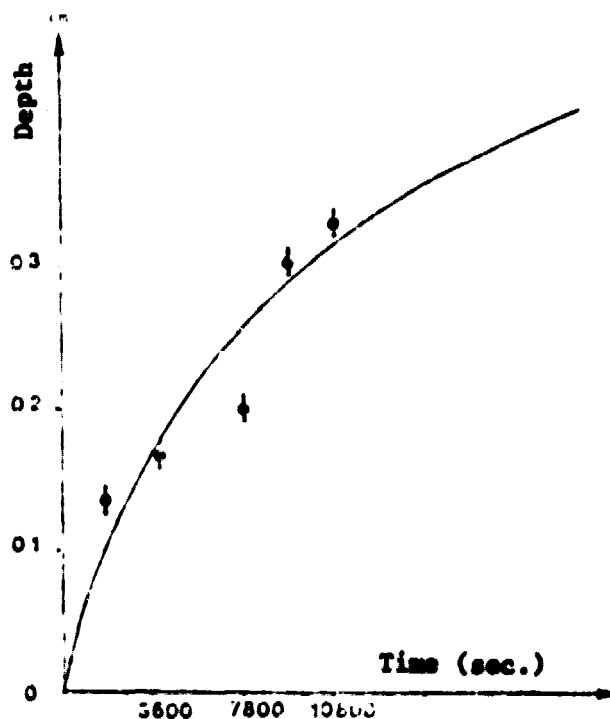

Figure 4. Comparison between experimental points and the curve $l = 2\sqrt{2.5 \cdot 10^{-6} t}$

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It can be seen that the values of D obtained are mutually compatible. The diffusion coefficients obtained are valid only for the treatment temperature used. The times considered are such that they guarantee a modest influence of material density variations on the diffusion coefficient [7].

CONCLUSIONS

During the development of the atmospheric pressure sinterization process for silicon nitride, in the presence of magnesium oxide as main densification activator, the fundamental role falls to the control of the additive's mobility inside the sample, as well as its tendency to diffuse out of it in the gas phase, at the treatment temperature.

The analysis of that phenomenon has led to some interesting conclusions that can be summarized as follows:

- it is possible to obtain homogeneous sinterized silicon nitride compacts by sinterization, at atmospheric pressure, of the system Si_3N_4-Y_2O_3MgO, acting in the presence of appropriate protective packing to inhibit the thermal dissociation;

- the structural inhomogeneities and consequent weight losses observed on sinterized Si_3N_4 samples are not only due to thermal dissociation of Si_3N_4 but also to the outward diffusion of the magnesium oxide;

- the loss of MgO occurs by diffusion, according to the model described by Fick's law;

- the relatively low values for the diffusion coefficient of MgO in the Si_3N_4 matrix indicate that the sinterization parameters (time and temperature) used may be considered acceptable on condition that the MgO loss be inhibited by reducing the concentration gradient between sample and treatment atmosphere by

mean of enrichment of the packing in the additive itself;

- the analysis of the phenomenon performed for the course of the sinterization treatment at atmospheric pressure, can be considered applicable also to densification processes that occur under pressure.

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