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Oxidation behaviour of a hot isostatically pressed silicon nitride material

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Abstract. — The oxidation behaviour of a dense silicon nitride material containing the minimum amount of additives was studied. A silicon nitride powder was hot isostatically pressed in the presence of 0.5 wt% Y_2O_3 and 0.025 wt% Al_2O_3 . The dense material obtained was oxidized for 24 hours, in an oxygen atmosphere within the temperature range 1475-1650 °C. The high oxidation resistance of this material may be related to the low amount of sintering aid initially introduced and consequently to the composition of the grain boundary phase. According to the temperature, the apparent activation energies for the oxidation processes, ranged from 355 to 680 kJ/mole.

1. Introduction.

Dense silicon nitride (SN) materials are usually obtained by pressureless sintering or by hot pressing (HP). Additives, which are necessary to attain complete densification, are located after sintering at triple points and along grains boundaries. Hot isostatic pressing (HIP) is a technique which allows the production, at high temperature and pressure, of denser components by using the minimum quantity of sintering aids.

The high temperature behaviour of silicon nitride ceramics has been studied extensively [1, 2] and is mainly governed by the amount and nature of the intergranular phase confined between the grains. Among the various oxides used as densification aids (MgO , Al_2O_3 , CeO_2 , Y_2O_3 , $BeAl_2O_4$, etc...), yttrium oxide yields improved oxidation resistance in high temperature environments. The preferential use of yttria as a densification aid for Si_3N_4 sintering results in the formation, at the grain boundaries, of a highly refractory secondary phase. Most studies to date indicate that the oxidation kinetics of hot pressed silicon nitrides are described by a parabolic dependence with time, which shows the diffusion nature of the oxidation process [3, 4].

G.E. Gazza [5] observed that a minimum amount of 5 wt% Y_2O_3 was required to complete the formation of an oxynitride boundary phase producing dense material and leading to a significant improvement in high temperature properties. In the same way, G.Q. Weaver [6] noticed that below a critical Y_2O_3 content (8 wt%), there was no degradation of properties. Improvements concern the flexural strength, the thermal shock and the oxidation resistance. In contrast, higher yttria content (> 11 wt%) silicon nitride materials, when oxidized at 1100 °C for 100 hours, showed the expected degradation. On a commercially available HPSN doped with 7 wt% yttria, severe degradation in strength was observed between 600 and 1000 °C, due to microcrack formation as a result of oxidation [7]. An 8 wt% Y_2O_3 , 2 wt% Al_2O_3 HPSN showed instability at 800-1000 °C, leading to a relatively small weight gain. At

1200 °C, the residual glass softening of the amorphous phase retarded or prevented micro-crack formation. For higher concentrations of Y_2O_3 , the continuous intergranular phase, which is viscous at high temperature, permitted inward and outward diffusion of reactants and additives species, leading to a gradient of depleted cations and the formation of Si_2N_2O . F.F. Lange [8] demonstrated that materials within the Si_3N_4 - Si_2ON_2 - $Y_2Si_2O_7$ triangle (Fig. 1) precluded the formation of unstable compounds and were extremely resistant to oxidation. This conclusion was confirmed by C.L. Quackenbush [9] who found it preferable – for optimal oxidation resistance – to maintain the Y_2O_3 - SiO_2 ratio in such a proportion that no $Y_2Si_3O_3N_4$ formed. Between 900-1350 °C, oxidation is believed to be controlled by oxygen diffusion through the surface silicate layer, but at 1350 °C, the surface oxide composition tends toward pure SiO_2 and the oxidation rate decreases. Two silicon nitride billets, with both 4 and 8 wt% Y_2O_3 , have been oxidized in air, in the temperature range 700-1000 °C [10]. The first composition led to the formation of phases, which were within the compatibility triangle (Fig. 1) and so, was highly resistant at intermediate temperatures. On the other hand, the material sintered with 8 wt% yttria contained unstable $Y_5N(SiO_4)_3$ which was outside the triangle. This behaviour was also described by J.B. Veyret [11] in the temperature range 800-1400 °C who proposed a model for the oxidation of a 9 wt% yttria HPSN, containing a crystalline grain boundary phase with apatite structure $Y_{10}(SiO_4)_6N_2$. At low temperature (800-900 °C) internal oxidation of the crystalline grain boundary phase occurs. The oxidation product: $Y_{4.67}(SiO_4)_3O$, is not protective, so the reaction progresses toward the bulk by oxygen diffusion through the largest grain boundaries. At temperature higher than 900 °C, silica layer formation is dominant, the grain boundaries are closed and internal oxidation stops. Between 1400 and 1590 °C, precipitation of an intergranular phase appears, which is located between the outside compact scale and the core [12]. This phenomenon has a temporary stabilizing effect because it inhibits the outward diffusion of impurities, which may be rate limiting.

Fig. 1. — Phase relations in the Si_3N_4 - SiO_2 - Y_2O_3 system [1].

The literature demonstrates that the use of high pressures (3000-7000 MPa) results in the formation of more highly resistant materials [13]. Hot isostatic pressing was applied as a post-treatment in order to complete the densification of silicon nitride ceramics having small amount of porosity (< 6%). This treatment permits pore filling, which is controlled by the viscosity and amount of the liquid phase and consequently improves the thermomechanical properties. RBSN samples, doped with 0.7 to 7 wt% Y_2O_3 , were post-hiped at 1750 °C, 200 MPa for 30 min. [14]. On subsequent oxidation at 1350 °C, the lowest value of the parabolic oxidation rate constant occurred for the material with the lowest amount of Y_2O_3 aid. Parabolic kinetics were also recorded during oxidation, between 1100 and 1425 °C, of a sinter-hip silicon nitride containing 6 wt% Y_2O_3 and 4 wt% Al_2O_3 [15]. The surface morphology of the oxide scale varied with temperature, composition and cooling rate. After rapid cooling, the main crystalline product was SiO_2 , while after slow cooling, crystals of $Y_2Si_2O_7$ precipitated out. Data points suggest a change of behaviour at about 1400 °C. An equilibrium composition for the formation of $Y_2Si_2O_7$ could be the explanation. Above 1400 °C, the oxidation rate decreased by precipitation of the phase below the silica layer. The activation energy values derived were different below and above 1400 °C i.e. 865 and 190 kJ/mole respectively.

A typical pressureless sintered Si_3N_4 based ceramic containing 5 wt% Y_2O_3 and 2.5 wt% Al_2O_3 , was subjected to hot isostatic pressing at 1700 °C and 180 MPa [16]. After hipping, the glassy pockets were reduced and the distribution of the secondary phases at grain boundaries was more regular. Oxidation was conducted in flowing oxygen from 1300 to 1500 °C. Up to 1400 °C, there was a minimization of the outward cationic (Al and Y) diffusion compared to the starting nitride. At about 1400 °C, YAG crystallisation restrained the outward cationic migration and counterbalanced viscosity changes. This phenomenon again resulted in different apparent activation energies according to oxidation temperature (800 kJ/mole up to 1450 °C and 440 kJ/mole above 1450 °C). Nevertheless, up to 1450 °C, the hiped material was more resistant to oxidation than the non-treated one.

There is no lack of agreement between all these investigations, which clearly demonstrate that the oxidation of silicon nitride depends on the amount and composition of additives.

2. Experimental.

The silicon nitride powder was supplied by UBE Industries, Japan. The powder was homogeneous and consisted of submicronic spherical grains. The specific surface area was about 14 m²/g. The average particle size was close to 0.6 μ m. The grains composition is listed in table I.

Table I. — *Chemical analysis of the starting powder (wt%).*

Si	N	O	Al	Ti	Fe	Ca	Mg	K	Na	C
60	38	1.2	0.24	0.05	0.02	0.09	0.01	0.02	0.28	0.1

X-ray diffraction analysis indicated that 95% of the powder was α - Si_3N_4 . The yttrium oxide powder was of high purity (99.999%). Silicon nitride was added to yttrium oxide and mixed for 6 hours in propan-2-ol with alumina billets. The alumina uptake induced by grinding was

about 0.025%. The mixed powders were cold isostatically pressed at 250 MPa. The relative density was close to 54%. The green moulded material was introduced into a silica container. A boron nitride diffusion barrier was necessary to prevent reactions between the capsule and the component. Degassing was carried out at 600 °C, in vacuum (10^{-3} MPa) for 6 hours. After sealing, the container was treated for 1 h at 1750 °C and at 170 MPa pressure.

Density measurements were carried out using Archimede principle. The microstructure was assessed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The α/β ratio was specified by means of quantitative XRD analysis. The oxidation resistance of cubic samples was examined in a dynamic flow of oxygen (20 l/h), at atmospheric pressure, using a setaram microbalance.

3. Results and discussion.

Under the above conditions, more than 99% theoretical density was achieved in confirmation of previous observations [17, 18]. The small residual porosity was obviously due to the difficulty of the elongated β -grains to rearrange: this is called the bridge effect. The specimen only contained 30% α - Si_3N_4 and this was proof of the liquid phase role in the α - β transformation kinetics. The dissolution of the α - Si_3N_4 phase and the β - Si_3N_4 reprecipitation is a function of the quantity and of the nature of the liquid phase. Due to the small amount of additive, the α - β transformation occurred mainly in the solid state at the working temperature. Figure 2a shows a homogeneous microstructure.

The aspect ratio ($a = \Sigma l/d$, l : maximum length, d : maximum thickness) is about 9-10, the average grain thickness is close to 0.2-0.3 μm . Hexagonal compact grains and elongated needle-like grains were observed by TEM. The sintered material so obtained was composed of equiaxed crystal grains, between which was a small amount of glassy phase, mainly consisting of SiO_2 . The thin intergranular film merging into pockets at multigrain junctions is shown in figure 2b. The high aspect ratio of the β - Si_3N_4 grains developed in this material results in a high fracture toughness (10.2 MPa $\sqrt{\text{m}}$).

In order to establish the reactivity of this silicon nitrogen ceramic, a sample was exposed to oxygen at a linear increasing temperature of 2.5 °C/min. The temperature at which the reaction became noticeable was close to 1600 °C. Measurable weight gains were obtained after 24 hours oxidation at 1475 °C or higher. Isothermal curves were recorded between 1475 and 1650 °C over 24 hours. The oxidation kinetics were parabolic. A sample exposed during 24 hours at 1590 °C shows a conversion degree $\Delta m/\Delta m_\infty$ of 0.02 (Δm_∞ : weight gain corresponding to complete oxidation).

At the beginning of reaction, an alumino-silicate film containing additives and impurities is formed. In the present study the previously observed [11] low temperature oxidation process between 800 and 1000 °C, certainly occurred but could not be detected because of the small amount of intergranular phase produced.

XRD analysis, with a Guinier Hagg chamber, indicated, at 1475 °C, the presence of cristobalite and of two yttrium silicates: up to 1530 °C β - $\text{Y}_2\text{Si}_2\text{O}_7$ and above this temperature γ - $\text{Y}_2\text{Si}_2\text{O}_7$. The maximum $\text{Y}_2\text{Si}_2\text{O}_7$ intensity was observed at 1525 °C together also with the yttrium garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$, which certainly constituted the intergranular crystalline phase.

At 1475 °C, the surface was covered with needle like and platelet yttrium disilicate. At 1525 °C, the needle shape crystals were replaced by hexagonal grains and progressively, as temperature increased, the quantity of silica increased, such that the oxidized surface became more and more regular. The molten silica layer had flooded the yttrium silicate crystals. Due to silica enrichment, the specimen became progressively embedded in a protective scale,

Fig. 2. — Scanning electron micrograph of an etched surface (a). Transmission electron micrograph showing small amount of glassy phase (b).

which acted as a diffusion barrier. At 1600 °C, the microcracks observed on the surface may be induced by rapid cooling. Figure 3 shows yttrium X-ray mapping of oxidized surfaces at various temperatures.

EPMA analyses of the surface crystals showed an equivalent amount of yttrium and of silicon and confirmed the presence of $Y_2Si_2O_7$ up to 1575 °C. At 1590 °C, no more yttrium could be detected on the surface (Fig. 4). In the same way, yttrium depletion of the bulk, coupled with an increase of the amount of this element at the internal interface, was observed by microanalysis.

Diffusion is the most probable mechanism controlling the oxidation of Y_2O_3 -doped silicon nitride materials [1-4]. Cation diffusion through the grain-boundary phase to the nitride-oxide reaction interface is recognized as the probable rate-limiting step during oxidation

Fig. 3. — a) Secondary electron image; b) Y X-ray image of surface oxidized at 1475 °C; c) Secondary electron image and d) Y X-ray image of surface oxidized at 1525 °C.

at intermediate temperatures. In this study, this process occurred up to 1585 °C with an apparent activation energy of 355 kJ/mole (Fig. 5). At 1590 °C, large nitrogen bubbles disrupt the silica film and allow oxygen to penetrate the oxide layer and permeate to the oxide-nitride interface. Above 1600 °C, the thickness of the oxide layer increases more rapidly as also does its fluidity such that diffusion of gaseous species through this scale is probably the rate controlling mechanism with an apparent activation energy value of 680 kJ/mole (Fig. 5).

Fig. 4. — a) Secondary electron image of surface oxidized at 1590 °C and b) EDAX analysis of surface oxide layer showing absence of yttrium.

Fig. 5. — Temperature dependence of the parabolic rate constants K_p .

4. Conclusions.

This study has confirmed the possibility of obtaining by hot isostatic pressing, a high performance silicon nitride material. The use of sub-micron silicon nitride starting powder

favoured the densification process. In addition, minimization of the amount of an additive (0.5 wt% Y_2O_3) required for densification at working temperature and pressure, resulted in an improvement of the oxidation behaviour up to 1585 °C. Above 1600 °C, the oxidation rate increased as the molten silica layer permitted the easy diffusion of adsorbed oxygen and of nitrogen gas released.

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