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DIFFUSION REACTIONS BETWEEN SILICON OXYNITRIDE AND SILICON NITRIDE DURING HIP-SYNTHESIS

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ABSTRACT

Recent advances in production processes for High Performance Ceramics have made it possible to produce fully dense net shape turbocharger and gas turbine rotors made of silicon nitride. These rotors must usually be attached to a metal shaft by some joining technique.

Solid state bonding by diffusion reactions is an attractive route to achieve joints that retain strength at high temperature. Intimate physical contact across the joint during bonding is important for the diffusion process. Hot Isostatic Pressing (HIP) can enhance the contact and thus produce a stronger joint at a lower bonding temperature than other methods.

Silicon oxynitride synthesized from a stoichiometric mixture of silicon nitride and silicon oxide by HIP has some interesting properties that might be useful as an intermediate layer in bonding silicon nitride to metals.

This work is a part of an assessment to develop solid state bonding methods for the joining of silicon nitride to superalloys by HIP. It presents the first steps in the development, namely the optimization of the synthesis of pure silicon oxynitride during densification by HIP and joining of the oxynitride to silicon nitride during synthesis and densification by HIP. The achievements in these areas and the direction of future work will be discussed.

1. INTRODUCTION

The introduction of engineering ceramics such as silicon nitride in demanding applications is often limited by the lack of adequate joining methods to other parts of the structure. This is especially true when one wants to take advantage of the superior high temperature properties of the ceramic. In those applications the large difference in thermal expansion characteristics makes it difficult to avoid thermal stresses that decrease the strength of the joint and might lead to complete failure of the component.

Silicon oxynitride, $\text{Si}_2\text{N}_2\text{O}$, is an interesting material often formed on the surface of a silicon nitride component during sintering. If machining of the joint area of the silicon nitride component is to be avoided, the bonding reactions of silicon oxynitride to i.e. a superalloy is as important as for the silicon nitride itself. Earlier work on silicon oxynitride compounds by Washburn (1) predicts that some important properties such as the coefficient of thermal expansion and Young's modulus differ less from those of a superalloy than the nitride and might therefore reduce thermal joint stresses. The earlier work was, however, performed on materials containing large amounts of sintering additives and remaining silicon nitride. More recent work by Huang et al (2) and Lewis et al (3) show a higher degree of conversion to silicon oxynitride, but this is still only possible by rather large amount of additives. This is due to the necessity to sinter at a relatively low temperature to avoid excessive dissociation during pressureless sintering. Hot Isostatic Pressing of glass encapsulated powder bodies has the ability to prevent dissociation, thereby making it possible to sinter at a higher temperature using very low amounts of additives (4). It was therefore considered to be both necessary and possible for the evaluation to develop a method to synthesize a dense material of almost pure silicon oxynitride.

2. SYNTHESIS OF SILICON OXYNITRIDE

Silicon oxynitride $\text{Si}_3\text{N}_4\text{O}$, henceforth called γ -phase, can be synthesized from a stoichiometric mixture of silicon nitride, Si_3N_4 , and silicon oxide, SiO_2 , during densification with Hot Isostatic Pressing using the following route:

- Mixing and ball milling of the stoichiometric powder mixture in petroleum ether or water for 100 h using milling media and jars made of silicon nitride and polypropylene. The initial powder mixtures were compensated for wearing residuals of 1 wt% Si_3N_4 emanating from the milling media.
- Drying of the powder using a thin-film evaporator and a heated vacuum chamber up to 250 C.
- Forming of green bodies by Cold Isostatic Pressing (CIP) at 300 MPa isostatic pressure of powder contained in PVC bags.
- Heat treatment of green bodies in a vacuum furnace up to 700 C and 10^{-2} Pa to remove water and other absorbed species from the powder surfaces.
- Densification using the proprietary ASEA CERAMA glass encapsulation and HIP technology. The process parameters were varied in order to optimize the conversion into silicon oxynitride. The highest oxynitride content was obtained by HIPing at 1900 C and 200 MPa for 4 h hold time.

All samples were fully densified to the calculated theoretical density of each final composition. Most of the syntheses have been carried out without any sintering additives, but a few samples were made with an addition of 1 wt% Y_2O_3 for comparison purposes.

2.1. Analysis

Studies of the synthesized compositions after HIP have been made by semi-quantitative X-ray diffraction analysis using a Philips PW 1700 system equipped with PDF data base and pattern processing capability. An active dilution method was used to improve the accuracy in the determination of the low amounts of α - and β -phase in the samples.

2.2. Results

The relative amounts of α -, β - and γ -phase achieved by varying the process parameters HIP-temperature and hold time are presented in figure 1. The influence of a small addition of 1 wt% Y_2O_3 is shown in figure 2. Yttria seems to enhance the conversion to silicon oxynitride, especially at the lower temperatures where the viscosity in the liquid phase otherwise is too high to effectively promote the synthesis.

3. JOINING OF CERAMICS

The next step in the evaluation of silicon oxynitride as a bonding layer between silicon nitride and superalloys was to examine the diffusional bonding reactions between the oxynitride and the nitride during sintering. The joint was made by the following route:

- A stoichiometric powder composition of $\text{Si}_3\text{N}_4 + \text{SiO}_2$ without sintering additives was prepared as earlier described.
- A silicon nitride powder composition designated for gas turbine use containing 2.5 wt% Y_2O_3 was prepared in a similar way.
- A PVC container was filled with the oxynitride mixture up to half its height and then filled up with nitride powder. The sealed container was CIPed at 300 MPa to give a green body of the two compositions.
- The powder compact was glass encapsulated and HIPed using the ASEA CERAMA method at 1900 C and 200 MPa for 4 h hold time.

The powder compact converted to a fully dense body of silicon oxynitride joined to β -silicon nitride. The ceramic was sliced by diamond saw to make it possible to examine the reactions in the joint.

3.1. Analysis of joint area

A examination of the two materials joined reveals that a distinct joint reaction has taken place during synthesis and densification. The reaction zone extends from the initial powder border approx. 2.0 mm into the silicon nitride material, and in the opposite direction approx. 0.1 mm into the silicon oxynitride, see figure 3. The zone is optically very dark compared with the bulk materials, and especially so on the synthesized silicon oxynitride side. A cross section of the joint area was marked with parallel indents to make it possible to perform Energy Dispersive X-ray analysis (EDX) at chosen distances from the initial powder border. Then a thin area between each pair of indents was measured concerning the yttrium level at several points in the joint area compared to the level in the Si_3N_4 bulk material. No other element than silicon and yttrium could be detected by EDX. The yttrium level is plotted in figure 4.

The composition of crystalline phases in the reaction layer was determined by XRD using the following method. A 0.2 mm thick tungsten foil with a 2 mm slit was applied on the surface of the cross-section to make it possible to analyze a thin layer by concealing the surrounding areas from measurement. Then diffraction patterns was measured for the reaction layer and the bulk materials on each side in a range without tungsten peaks to determine the compositions.

3.2. Results

It was found that the reaction layer mainly consists of β -silicon nitride with a small amount of silicon oxynitride. No other crystalline phases could be detected by XRD. The patterns of the three areas are presented in figure 5.

4. DISCUSSION

The joint reaction during HIP can be described as follows: The powder body of the two compositions, one of the $\alpha\text{-Si}_3\text{N}_4 + \text{SiO}_2$ stoichiometric mixture and the other of $\alpha\text{-Si}_3\text{N}_4$ with a small Y_2O_3 addition, is heated up to HIP temperature with a heating rate of approx. 10 C/min. When it reaches the eutectic melting temperature in the system $\text{SiO}_2\text{-Y}_2\text{O}_3$ (5) at about 1660 C, the oxides near the initial powder border area form a low viscosity melt of high yttria concentration some minutes ahead of the other oxide-containing areas. The melt is then squeezed through the pore channels during local shrinkage due to the compressive isostatic pressure acting on the encapsulated body.

When the temperature has risen to approx. 1700 C, a two-phase liquid form, consisting of a major low yttria, high viscosity phase of almost pure silica and a minor phase with higher yttria content and lower viscosity. The melt flowing in the oxynitride direction is soon depleted with aspect to yttria, and the flow front stops when the composition does not have a lower melting temperature than the surrounding silica. This can be observed by the continuous decrease of yttrium (see figure 5), combined with the optical appearance of a very dark zone close to the initial border gradually becoming lighter when moving into the pure Si_3N_4 . This can be explained by the decreasing nitrogen content and the larger grains observed in etched areas by SEM, see figure 6, 7 and 8.

The melt flowing in the nitride direction, on the other hand, has a large silica content and can therefore not be quickly depleted in a similar way. The low viscosity, high yttria phase flows in the front of the major low yttria phase through the pore channels, dissolving some of the yttria grains and impurities on the way.

The temperature continues to raise and the speed of the conversion from $\alpha\text{-Si}_3\text{N}_4$ to $\beta\text{-Si}_3\text{N}_4$ by dissolution-precipitation in the yttrium silicate melt made of the surface silica on $\alpha\text{-Si}_3\text{N}_4$ grains and yttria increases, especially in the area swept by the yttrium silicate melt flow.

The melt flow stops after covering approx. 2 mm into the silicon nitride body. This could be explained by two concurrent mechanisms. One possible mechanism is that the pressure difference between the low viscosity melt and the pore channels decreases due to higher contact forces between the grains in the initial powder border area during compression and due to the increasing melt formation in surrounding areas. Another mechanism that will stop the melt is the fast closing of porosity during sintering of the Si_3N_4 -2.5wt% Y_2O_3 mixture designated for HIPing at 1750 C for 1 h when the temperature quickly raises by 10 C/min. up to 1900 C.

Small amounts of silicon oxynitride are formed in the zone swept by the yttrium silicate melt. The earlier syntheses described in this paper show that silicon oxynitride is formed to a very high degree when silicon nitride and silicon oxide are in close contact at a temperature sufficiently high to promote the kinetics of formation. In this case the silicon oxide is, however, thermodynamically more stable in the yttrium silicate melt compared with the silicon oxynitride due to the higher concentration of yttria. Furthermore the conversion from α - Si_3N_4 to β - Si_3N_4 is a faster reaction than the oxynitride formation. Therefore the main crystalline phase in the swept reaction zone will be β - Si_3N_4 with only minor amounts of $\text{Si}_2\text{N}_2\text{O}$.

The volume relation between the thin (approx. 20 μm) glassy layer in the reaction front and the large layer of 2 mm thickness mainly consisting of β - Si_3N_4 can be explained by the relative amount of silica compared to yttria in the melt flow. The amount of glassy phases does not seem to be higher in the main part of the reaction zone compared with the bulk material of silicon nitride composition, because of the fast closure of the pore channels, thus limiting the amount of high silica melt to flow through the zone. The silica is then transformed to silicon oxynitride during the remaining time at high temperature.

The reactions described take place during the heating and the first minutes at the HIP temperature. Subsequently the silicon oxynitride is formed during the remaining time at 1900 C.

Grain growth occurred in the areas containing considerable amounts of the low viscosity yttrium silicate melt, mainly at the reaction front and at the initial powder border, see figures 6 and 7.

It can be assumed that the distance covered by the yttrium silicate melt into the silicon nitride powder body was mainly governed by the heating rate, i.e. a slower rate between 1660 C and 1720 C would allow the melt to flow a longer distance before being stopped by pore closure.

5. ACKNOWLEDGEMENTS

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7. FIGURES

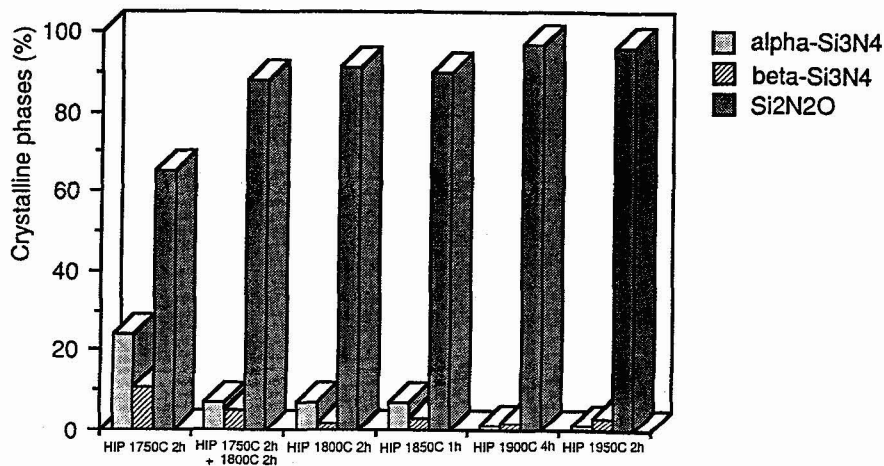


Figure 1. Synthesized ceramic compositions achieved by HIP of addition-free stoichiometric powder mixtures.

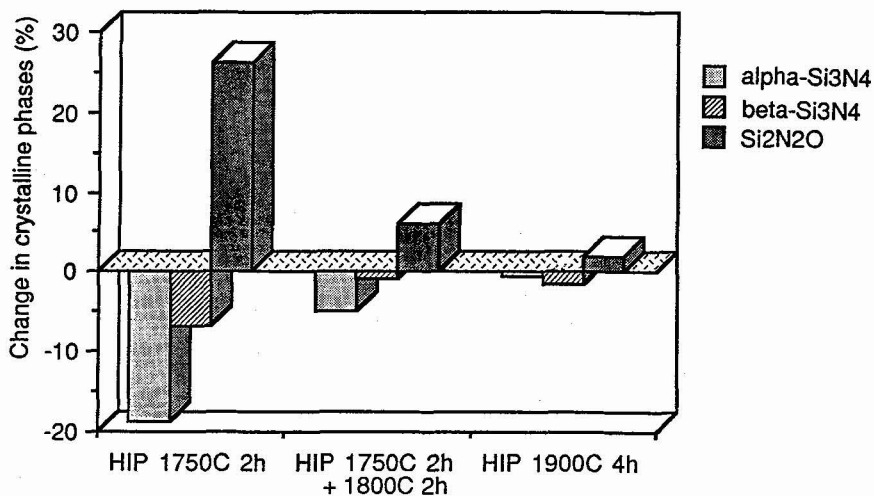


Figure 2. Influence of 1 wt% Y_2O_3 addition on synthesis.

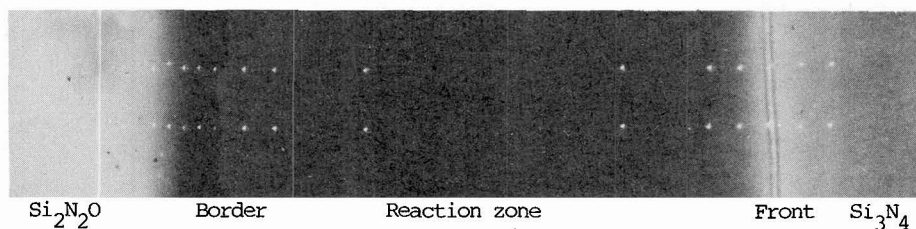
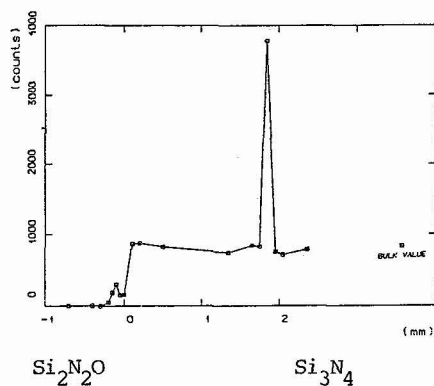
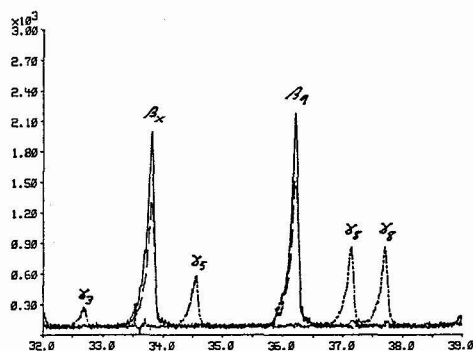


Figure 3. Optical microscope picture of the reaction zone between $\text{Si}_2\text{N}_2\text{O}$ and Si_3N_4 . Scale: $\text{L} = 0.1 \text{ mm}$



$\text{Si}_2\text{N}_2\text{O}$

Si_3N_4



Reaction layer: ———
 $\text{Si}_2\text{N}_2\text{O}$ material: - - -
 $\beta\text{-Si}_3\text{N}_4$ material: - · -

Figure 4. Distribution of yttrium in joint area determined by EDX.

Figure 5. X-ray diffraction patterns from thin layer measurements.

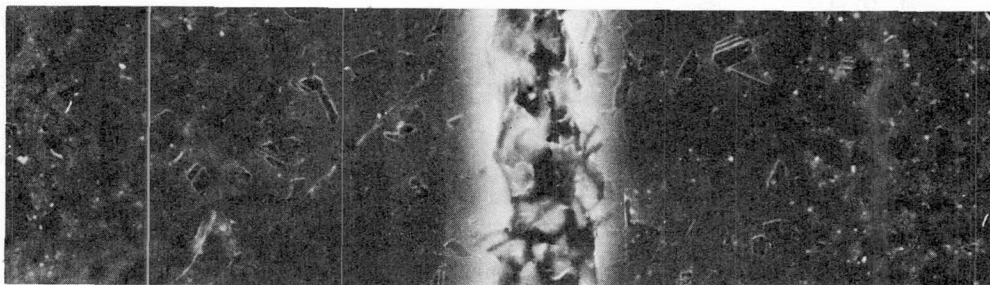


Figure 6. SEM picture of glassy layer in reaction front etched in $\text{HF} + \text{HNO}_3$. Scale: $\text{L} = 10 \mu\text{m}$

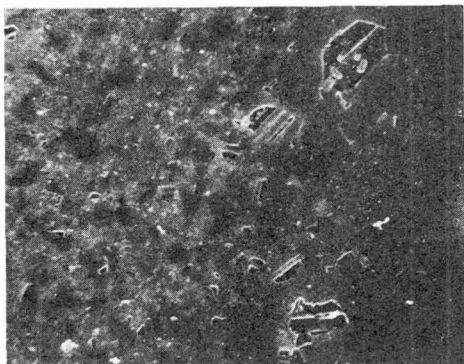
 Si_3N_4 $\text{Si}_2\text{N}_2\text{O}$

Figure 7. SEM picture of the initial powder border.

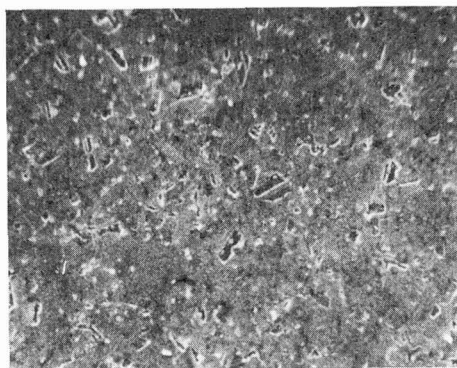


Figure 8. SEM picture of $\text{Si}_2\text{N}_2\text{O}$ bulk material.