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Post-treatment of Pre-sintered Silicon Nitride by Hot Isostatic Pressing

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SUMMARY

The results of three different types of experiment are discussed: 1. Density, flexural strength and fracture toughness data at room temperature for different materials after post-hipping. The starting materials varied concerning the type and amount of sintering additive, as well as the pre-sintering conditions. 2. The post-densification behaviour by hipping of pre-densified starting materials, which were produced under well-defined conditions and in which various parameters were systematically changed: the residual porosity, the amount and viscosity of the liquid phase, and the silicon nitride phase composition ratio (α/β). *3. Results of model experiments: the behaviour of incorporated artificial macropores and cracks, as well as the change of the grain orientation in hot pressed silicon nitride (HPSN) with different degrees of texture.*

Positive effects of post-hipping are a slight density increase, particularly the filling of residual macropores or the reduction of the pore size, and the enhanced healing of cracks. Negative effects may be grain coarsening and grain globularization, as well as surface defects caused by vaporization of the liquid phase and/or decomposition of silicon nitride during hipping. As a result, a marked increase of strength is not observed. However, the scatter of strength values can be reduced and fracture toughness is often improved. The latter observation seems to depend on a more intensive interlocking of the elongated β-Si_3N_4 *grains, supported by local plastic deformation at the contact points of the grains. Which effect is dominant depends on the morphology and arrangement of the* β-Si_3N_4 *grains and the characteristics of the liquid phase in the starting pre-sintered materials, as well as on the hipping conditions.*

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1. INTRODUCTION

Hot isostatic pressing (hipping) is an advanced and promising processing technique which has become more and more important during the past years. The reason for this is that hipping combines the possibility of improving mechanical and thermo-mechanical properties with the possibility of producing complex-shaped components. Up to now this technique has been used for the processing of various material groups, e.g. metals and hard metals, and also ceramic materials such as some oxides, carbides and nitrides, as well as several composites.[1-3] Many applications showed that not only the physical and mechanical properties of these materials but also those of the ceramic components may be improved, reliability increased and costs reduced compared with conventional processes. Based on these positive results, it was thought that hipping was also a suitable method for the production of ceramic components made from high-temperature structural materials such as silicon nitride. For this reason, during the past years special hipping equipment has been developed to allow hot isostatic pressing at temperatures higher than 1700°C.[1-3]

In the case of silicon nitride, several advantages are expected from this technique. As for other ceramic materials, the main advantage for silicon nitride is that the nearly net-shaping possibility eliminates post-machining of the densified part, except for surfaces with extremely close tolerances. Thus, this technique offers a potential for the production of advanced ceramic components. Besides that, material properties are expected to be improved; for example, the uniform way of applying the high pressure results in fully isotropic material properties. The pressure increase by more than one order of magnitude over uniaxial hot-pressing enhances the densification process of silicon nitride. As a result, dense silicon nitride parts with powder compositions containing only small amounts of consolidation aids, or with more refractory additives, may be produced. Furthermore, the high pressure applied is thought to result in a more uniform and fine-grained microstructure under optimized hot isostatic pressing conditions, which may lead to improved strength. Healing of cracks under high pressure can result in an additional improvement both of the absolute values and of the reduced scatter of mechanical properties. Moreover, this technique gives the opportunity of joining silicon nitride parts produced by different techniques (diffusion bonding or gas pressure bonding). Therefore, hipping offers the possibility of producing near net-shaped components and a good opportunity for further improvement of the strength and high-temperature properties, as well as a reduction of the scatter of properties.

During hipping high pressure is applied via a gas to consolidate a porous compact after canning, or to remove the residual porosity from pre-sintered uncanned materials, which contain only closed pores. In the case of silicon nitride, the latter technique of post-treating pre-sintered silicon nitride by post-hipping is not yet well understood. Open questions are, in particular, the influence of microstructural characteristics of the pre-sintered materials, the influence of the type and amount of additives, and the influence of defect healing on the mechanical properties of the hipped materials. This paper attempts to answer these questions. In this context the results of three types of experiments are presented:

1. Density, flexural strength and fracture toughness data at room temperature for different materials after post-hipping. The starting materials varied concerning the type and amount of sintering additives, as well as the pre-sintering conditions.
2. The post-densification behaviour by hipping of pre-densified starting materials which were produced in the laboratory under well-defined conditions and in which various parameters were systematically changed: the residual porosity, the amount and viscosity of the liquid phase, and the silicon nitride phase composition ratio (α/β).
3. Results of model experiments: the behaviour of incorporated artificial macropores and cracks (induced by Knoop hardness indentation), as well as the change of the grain orientation in hot pressed silicon nitride (HPSN) with different degrees of texture.

2. HOT ISOSTATIC PRESSING OF SILICON NITRIDE

In order to produce nearly dense ceramic parts from silicon nitride via the hipping technique, three routes can be followed (Fig. 1):

(i) Hipping of silicon nitride powder compacts, moulded by any appropriate technique to the final shape; the shrinkage occurring during densification, however, has to be considered.
(ii) Hipping of reaction bonded silicon nitride (RBSN), also preformed to the final shape, taking into account shrinkage; this means starting with silicon powder and producing RBSN in a first step.
(iii) Hipping treatment of sintered silicon nitride (SSN) or sintered reaction bonded silicon nitride (SRBSN) as starting material. The two steps, sintering and hipping, were combined into one sinter-hipping cycle.

For all three techniques a certain amount of consolidation aid has still to be added in most cases. Using the first two techniques, the starting material has to be coated with a temperature- and pressure-resistant barrier against the high-pressure gas, to prevent the gas penetrating into the porous body. The starting material for the third technique usually has almost no open porosity, which makes encapsulation unnecessary.

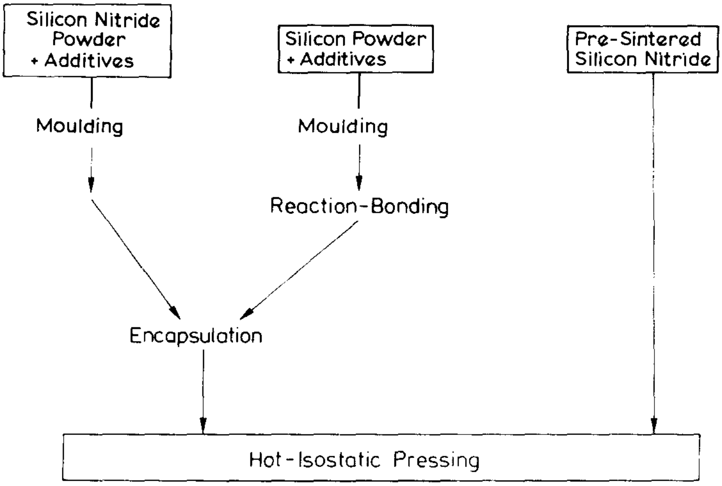

Fig. 1. Different routes for hipping silicon nitride.

Though hipping is a promising technique and many workers have started activities in this field, only a few papers have been published up to now. As this technique, however, is undergoing rapid development, important results are to be expected during the next few years.

The state of the art may be summarized as below.

2.1. Encapsulation

The encapsulation ('canning') of complex-shaped components, particularly parts with sharp edges and corners, still presents serious problems.[4-7] Different prerequisites for successful canning need to be fulfilled:

- The encapsulation material must have sufficient thermal stability at the hipping temperature, but is simultaneously required to have a certain amount of plasticity in order to transfer the applied gas pressure uniformly to the part to be consolidated. This restricts the selection of materials to refractory metals (tantalum, molybdenum, tungsten), glasses with high softening temperatures (silica glass, 'vycor' glass), or certain ceramic materials.
- Chemical reactions between the capsule and the ceramic parts must not occur; this often requires an additional barrier layer.
- The coefficients of thermal expansion of the container material and the material to be consolidated have to match well in order to avoid cracking during heating and cooling.
- Decapsulation of the densified parts has to be mechanical or chemical without any damage to the parts.

Geometrically simple-shaped components (discs, bars, etc.) may be encapsulated in glass tubes or metal containers, which are sealed off by softening or welding under vacuum. For more complex parts other methods are necessary. For example, small parts like turbine blades may be encapsulated in glass tubes or metal containers under vacuum. However, to avoid tearing-off or other damage to the glass layer at the thin, sharp trailing edges of the blades, such parts were additionally embedded into a powder, e.g. boron nitride.[8,9] This powder acts as a pressure transmitter and simultaneously prevents chemical reactions and the building up of thermal stresses due to differences in expansion characteristics between the part to be consolidated and the capsule material ('powder-bed-canning technique'). Furthermore, decapsulation is easy and subsequent machining may often be avoided. For example, this technique has been applied to produce turbine blades for rotors with a metallic hub.[9]

For the production of larger, more complicated parts like turbo-chargers or monolithic turbine rotors, possible encapsulation methods comprise, up to now, the construction of equally complex metal housings,[3,10] the 'glass-particle-canning technique'[4,5,11,12] or the 'sinter-canning technique'.[6,13,14] The first one is a very costly method as refractory metal sheets have to be welded. In the second method, the 'glass-particle-canning technique', the ceramic part is coated with one or more layers of glass particles and is heated up under vacuum until the glass (or one layer of glass) softens, thus sealing off the body. This method has been applied especially in Sweden. It has been reported that complete turbine rotors, shaped by injection moulding of silicon nitride powders, have been produced of near theoretical density without subsequent machining.[4,5,11,15] The third method, the 'sinter-canning technique', comprises coating of the parts with a fine-grained ceramic powder or powder mixture, which is sintered under vacuum to gas tightness. It is relatively easy to adjust similar thermal expansion characteristics of the capsule and the silicon nitride part by using silicon nitride powders for the capsule. In order to prevent any reaction between the layer and the silicon nitride component, an interlayer may be used. This technique was, for example, successfully applied to the consolidation of cutting tools, turbine blades and monolithic rotors made from RBSN.[9,14,16]

2.2. Processing routes and material properties

The first two routes for hipping (see Fig. 1) show large differences in the shrinkage of the components. Starting with silicon nitride powder compacts, which usually have a green density of about 2·0 $\mathrm{Mg\,m^{-3}}$ (i.e. about 60 % theoretical density) after moulding, results in a volume shrinkage of nearly 40 %. With RBSN the starting density may be up to about 2·6 $\mathrm{Mg\,m^{-3}}$

($\sim$80% theoretical density). As a result, the volume shrinkage during hipping is much lower. The linear shrinkage of only 6–7% facilitates the production of complex-shaped components with close dimensional tolerances. This relatively low shrinkage is one advantage of the second route. Besides this, the combination of the easy shaping possibility of RBSN and the high strength data of dense silicon nitride is a further advantage of this technique.

For the hipping of silicon nitride powder compacts, the results show that density and mechanical properties are dependent on the purity of the starting powder and the type and amount of consolidation additive.[4,5,17–20] Using commercial silicon nitride powders, density values higher than 94% theoretical density were achieved without any additives. In this case the density of hot isostatically pressed silicon nitride (HIPSN) is dependent on the characteristics of the silicon nitride starting powder, primarily on the phase composition and the impurity content. Using highly pure silicon nitride powder,[20] the maximum density achieved was 94% theoretical density, but self-bonding between the grains was weak; in the case of starting materials containing a relatively high amount of impurity, complete densification was reached. To obtain fully dense materials with high-purity silicon nitride powders, only small additions of sintering aids are necessary. Mechanical properties are completely isotropic. High room-temperature strength data and high values of the Weibull modulus, m, have been observed. Improved high-temperature strength and creep behaviour were found. Nevertheless, it has not been possible up to now to develop materials with high room-temperature strength and simultaneously excellent high-temperature properties. Parts of cylindrical, conical and flat sections, and also complex-shaped components for gas turbines, have been fabricated to final shape without any or little post-machining. It has been reported[3,4] that the tolerances of the finished products are rather good and that shaped parts can be processed with tolerances and surface quality acceptable even for turbine blades.

Using a suitable encapsulation technique with the hipping of RBSN, fully dense materials have been achieved, even with low amounts of additives. Compared to hot-pressed materials and/or sintered grades, the yttrium oxide doped and hipped materials displayed similar or even superior high-temperature properties.[6,8,9,16,21]

Applying the 'sinter-canning technique' to RBSN, cutting tools, turbine blades, welding nozzles and monolithic rotors have been produced. Now the goal has to be to transfer the material properties, which have already been achieved in test specimens, to complex-shaped components, and to develop economical production techniques.

Because of the technical problems associated with the encapsulation technique and the relatively high costs in mass production, the third route, the post-treatment of pre-sintered silicon nitride by hipping without using a container, may be expected to gain wide acceptance on a short-term basis. This route, especially the combined sinter–hipping technique, is thought to be promising for the future and will therefore undergo rapid development supported by further progress in the sintering techniques. Up to now only a few results have been reported which indicate that the hipping of pre-sintered silicon nitride is strongly dependent on various microstructural characteristics of the sintered starting materials (density, grain size, grain morphology, grain boundary characteristics). Results of some systematic investigations have been published by a Japanese group.[7,22,23] These experiments were carried out in the temperature range between 1700 and 1900°C under a pressure of 100 MPa using argon or nitrogen. Some interesting results were achieved; a density increase was only observed if the density of the pre-densified silicon nitride was higher than about 93% theoretical density. In any case, nitrogen as pressure gas led to higher densities and higher strength values compared to an argon atmosphere because high nitrogen gas pressure suppresses the decomposition of silicon nitride. One of the reasons for the strength reduction after argon hipping is thought to be a formation of pores, especially near the specimen surface. After nitrogen hipping the improvement in strength for some materials was accompanied by an increase in Weibull modulus. The strength after hipping was dependent on the type of pre-sintered silicon nitride. The α/β-silicon nitride phase composition and the grain morphology of the pre-densified material seem to be decisive parameters for improving strength values. It is thought that a certain amount of α-phase and the existence of needle-like crystallites in the pre-sintered starting materials are necessary to improve the strength by nitrogen hipping. Moreover, the improvement in strength depends not only on the sintering conditions but also on the process parameters during hipping (type of gas, pressure, temperature, time). In addition, healing of relatively large internal defects, originated during cold-pressing or sintering, was observed after nitrogen hipping.

Recent investigations of the authors about fracture strength, fracture toughness and microstructural changes after post-hipping of pre-sintered silicon nitride permit the conclusion to be drawn that the microstructure of the pre-sintered starting materials and the healing of cracks and flaws are key parameters in the post-hipping process.[24,25]

There is one more point which should be discussed here: the solution of nitrogen during post-hipping. Following the third route, the high-pressure gas directly contacts the pre-sintered materials. Thus, solution of gas molecules in the silicon nitride compact is a possible phenomenon. So, for sintered silicon nitride containing 2·2 wt% aluminium oxide, 1·3 wt% magnesium oxide and 2 wt% silicon dioxide as densification aids, an increase in nitrogen of 0·6 wt% (and a decrease in oxygen content) was observed during hipping when the specimens were kept in a graphite crucible at 126 MPa and 1750 °C for 14 h.[26] The density increased slightly and the strength was improved. The authors think that nitrogen gas dissolves in the silicon nitride compact, which contains a liquid phase, and that nitridation of the silicon dioxide component takes place during hipping when the cycle runs for 10 h or more. The density increase after long soaking, and the improvement of strength, too, are thought to be partly caused by this effect. When heating up these specimens to high temperatures under atmospheric pressure, the dissolved nitrogen may be released, which results in the formation of pores.

2.3. Densification mechanism and microstructural development

The basis for the discussion of the properties of hipped materials is the understanding of the densification mechanism and the microstructural development. As for sintering and hot-pressing, densification by hipping occurs by a liquid phase sintering process involving rearrangement, solution–diffusion–reprecipitation and coalescence. However, the contribution and the rate of the different densification steps are changed by the application of pressure. Moreover, by enhancing different processes during densification, like dissolution, formation of β-nuclei and growth of β-silicon nitride crystals, fine-grained microstructures can be achieved. Thus, the microstructure of these HIPSN materials consists mainly of the two hexagonal phases α- and β-silicon nitride and a largely amorphous silicate or nitride oxide grain boundary phase (5 to 20 vol %), which is arranged in thin layers of about 1–5 nm thickness and in larger concentrations at grain triple junctions. One typical feature of all dense silicon nitride materials is the difference in the grain morphology; the α-grains are equiaxial ($\sim$0·1 to 2 μm), the β-silicon nitride phase reveals an elongated grain structure ($\sim$5 to 10 μm) with aspect ratios (= length to thickness ratios) of between 5 and 10.

The processes taking place during post-hipping of pre-sintered materials, however, are not yet completely understood. It seems that grain rearrangement is possible by grain-boundary sliding, that solution may occur at the highly stressed particle contact points, and that coalescence processes may take place.

3. EXPERIMENTAL PROCEDURE

3.1. Sample preparation

Besides samples which were prepared for systematic sintering studies and which contain different types and amounts of sintering additive (for details see Refs 24 and 25), various sets of starting materials and special pre-treated samples were prepared for hipping experiments. With these sets an attempt was made to evaluate parameters which determine the densification behaviour during hipping and to obtain information about the processes and mechanisms that are effective. These materials are characterized in Table 1.

In order to study the influence of the density of the starting material on the final density after hipping, sets of materials with different levels of density were prepared by compaction-limited hot-pressing (set I). Additionally, the influence of high and low amounts of sintering additive to the starting powder composition was investigated. The influence of the silicon nitride phase composition ratio α/β was studied with materials which were prepared by varying the hot-pressing time (set II).

In set III artificial pores were introduced by incorporating disc-shaped wax particles at a distance from the surface of about one-third of the specimen width. The average diameter of the pores was about 500 μm. These experiments were conducted with two materials, again with different

TABLE 1

Starting Materials for Hipping Experiments

Set	*Objective*	*Variations*	*Processing*
Systematic investigations			
I	Influence of starting density and additive concentration	– Starting density ~ 95–$\sim 98\%$ theoretical density – Additive amount low → high – Softening temperature low → high	Compaction-limited hot-pressing
II	Influence of α/β-phase composition	α-content ~ 70–$\sim 10\%$	Varying of hot-pressing time
Model experiments			
III	Filling of pores	Additive amount low → high	Incorporation of an artificial 500 μm pore, sintering
IV	Rearrangement/change of grain orientation in HPSN	– Additive amount/ softening temperature low → high – α-content ~ 70–$\sim 0\%$	Hot-pressing
V	Healing of cracks	Additive amount/ softening temperature low → high	Hot-pressing, Knoop hardness indentation

amounts of additive in order to change the characteristics of the liquid phase: 5 wt % yttrium oxide + 1·1 wt % aluminium oxide and 15 wt % yttrium oxide + 3·4 wt % aluminium oxide.

To study the rearrangement of the β-silicon nitride grains during post-hipping, hot-pressed materials with different types and amounts of additive were prepared, which showed large differences in orientation.[27] In all materials complete $\alpha \rightarrow \beta$-silicon nitride phase conversion had occurred (set IV).

Crack healing effects were studied with specimens where artificial cracks were introduced by Knoop hardness indentation (load 50 kg). The damaged surface zone was removed before hipping. The experiments were carried out with two materials fluxed with different additives: 5 wt % yttrium oxide and 8 wt % yttrium oxide + 2 wt % aluminium oxide + 4 wt % silicon dioxide, respectively (set V).

3.2. Hot isostatic pressing

The pre-sintered materials were post-treated by hipping without canning. Only one set of specimens was encapsulated before hipping. The pre-sintered samples were hipped in a boron nitride crucible. Boron nitride powder was used to prevent reaction between the specimens. In most cases hipping was carried out in the small-scale hipping equipment, 'HIP 2000' of National Forge, in nitrogen; some experiments were performed in the ASEA press 'QIH32' in argon. The temperature was varied between 1750 and 1980 °C. In all cases a pressure between 180 and 200 MPa was applied.

3.3. Characterization methods

Materials were characterized before and after hipping by density measurement, X-ray diffraction (silicon nitride phase analysis, orientation for different hot-pressed silicon nitride materials) and microstructural analysis, as well as by fracture strength and fracture toughness measurements. Quantitative microstructural analysis was performed on etched microsections. Following the method described in Refs 25 and 28, the thickness, $\bar{d}$, and length, $\bar{l}$, of the elongated β-silicon nitride grains were measured and the aspect ratio, $\bar{a} = \bar{l}/\bar{d}$, was determined.

Fracture strength was determined with specimens (3·5 × 4·5 × 45 mm) in 4-point bending (span 10/20/10 mm). Fracture toughness was measured by the Vickers hardness indentation technique, applying a 20 kg load and using the equations:[29]

$$K_{\mathrm{Ic}} = 0{\cdot}111 \times P \times b^{-1{\cdot}5}; \qquad b = \frac{(\Sigma\bar{l} + 2\bar{d})}{4}$$

The size and location of the artificial pores in the starting material, as well as in the post-hipped samples, were determined by a microradiographic method, described in Ref. 30. The size of the induced cracks by Knoop hardness indentation was analysed using a procedure described in Ref. 31.

4. EXPERIMENTAL RESULTS

4.1. Summary of results of various post-hipping treatments

Figures 2, 3 and 4 summarize the data of density, flexural strength and fracture toughness at room temperature for different materials which were prepared and post-hipped. These materials contain different types and amounts of consolidation additives and were pre-densified by pressureless sintering or by hot-pressing using various processing conditions. These data indicate some results which have been achieved by applying post-hipping to various pre-densified silicon nitride materials.

Figure 2 gives the density values after hipping as a function of the density of the starting material. For most materials an increase in density is observed, which ranges for the materials with $\rho > 90\%$ theoretical density from 0 to a maximum of 5%. The average density increase for these

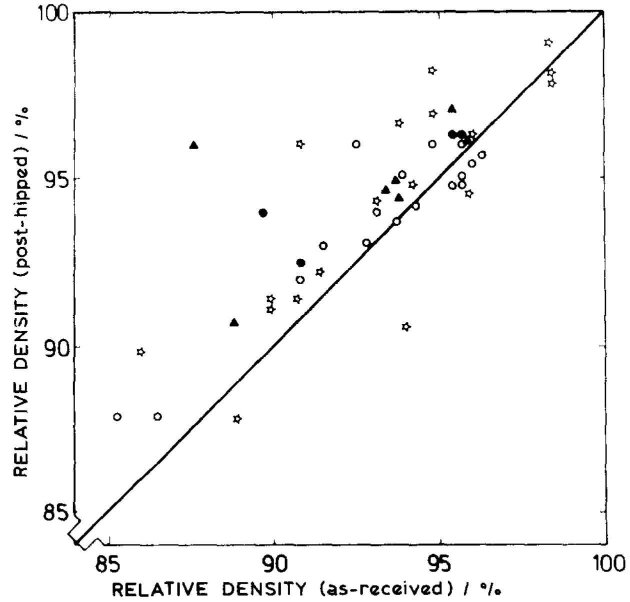

Fig. 2. Density values of post-hipped materials as a function of the relative density of the starting materials. ○, Argon; ●, encapsulated; ▲, argon + powder bed; ☆, nitrogen.

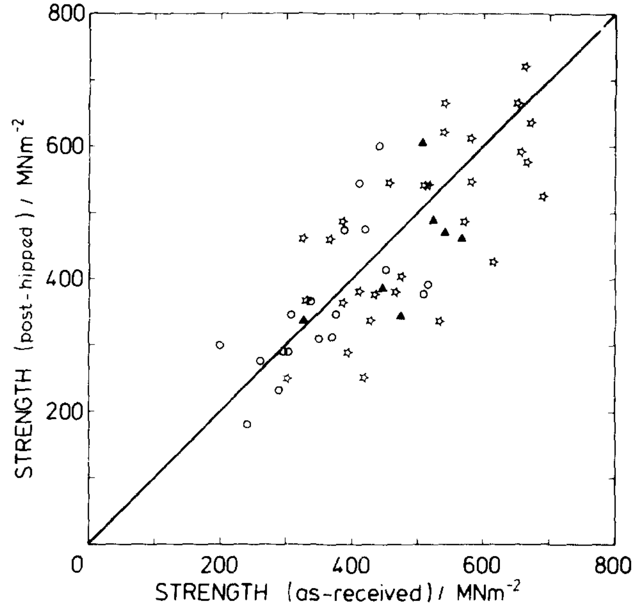

Fig. 3. Flexural strength data of post-hipped materials as a function of the strength values of the starting materials. ○, Argon; ▲, argon + powder bed; ☆, nitrogen.

pre-sintering conditions, however, is only about 1–1·5%. In no case is the theoretical density approached. Here it should be noted that a decrease or only a slight increase in density was observed for hipping in argon but also in some cases for hipping under high pressure nitrogen for some relatively dense materials. The reasons for this are the decomposition of silicon nitride in argon, and the vaporization of the liquid phase in the surface area of relatively dense materials or from the bulk of less dense silicon nitride grades (which still exhibit open porosity) due to the high hipping temperatures. The amount of vaporization mainly depends on the quantity and composition of additives (not shown here) which determine the properties of the liquid phase, especially its refractoriness. In contrast to this density reduction, a density increase can be observed in some cases with materials which still reveal a certain amount of open porosity. These materials contain additives which lead to further sintering at the hipping temperatures ($T_{\mathrm{hip}} > T_{\mathrm{s}}$).

Figure 3 summarizes the flexural strength data before and after hipping. These data indicate that an improvement of strength, but also a strength degradation, can be obtained, independent of the strength level of the starting material. Figure 4 shows the fracture toughness values before and after hipping. Also in this case, an increase but also a reduction in fracture toughness was observed for different materials. Here it is interesting to note that the K_{Ic} values of those materials that already had a relatively high K_{Ic} value in the pre-sintered state are clearly increased.

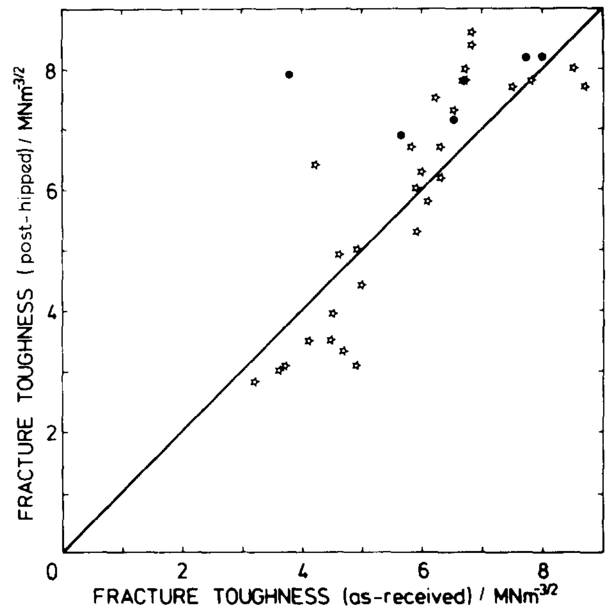

Fig. 4. Fracture toughness data of post-hipped materials as a function of the fracture toughness values of the starting materials. ●, Encapsulated; ☆, nitrogen.

As an example, Fig. 5 shows changes in density, flexural strength and fracture toughness by post-hipping of various materials, in relation to the additive composition. This demonstrates that neither are the property changes simply related to the type and amount of additive.

In order to interpret these results, some systematic investigations and model experiments were carried out (see Table 1) to evaluate the influence of certain characteristics of the starting material on the post-densification behaviour by hipping.

4.2. Results of systematic investigations

4.2.1. Influence of the density of the pre-sintered starting materials

Figure 6 shows the influence of the density of the starting material on the final density after post-hipping for two material groups with 1 and 5 wt % yttrium oxide (set I, Table 1), i.e. different amount and viscosity of the liquid phase. Each material group was prepared with a starting density $<95\%$ and $>95\%$ theoretical density. These results demonstrate that a density increase can only be observed if the starting materials contain no open pores. In the case of the 1 % yttrium oxide fluxed sintered silicon nitride, the change from open to closed porosity occurs at about 94 % theoretical density. Below this value a decrease in density takes place, probably

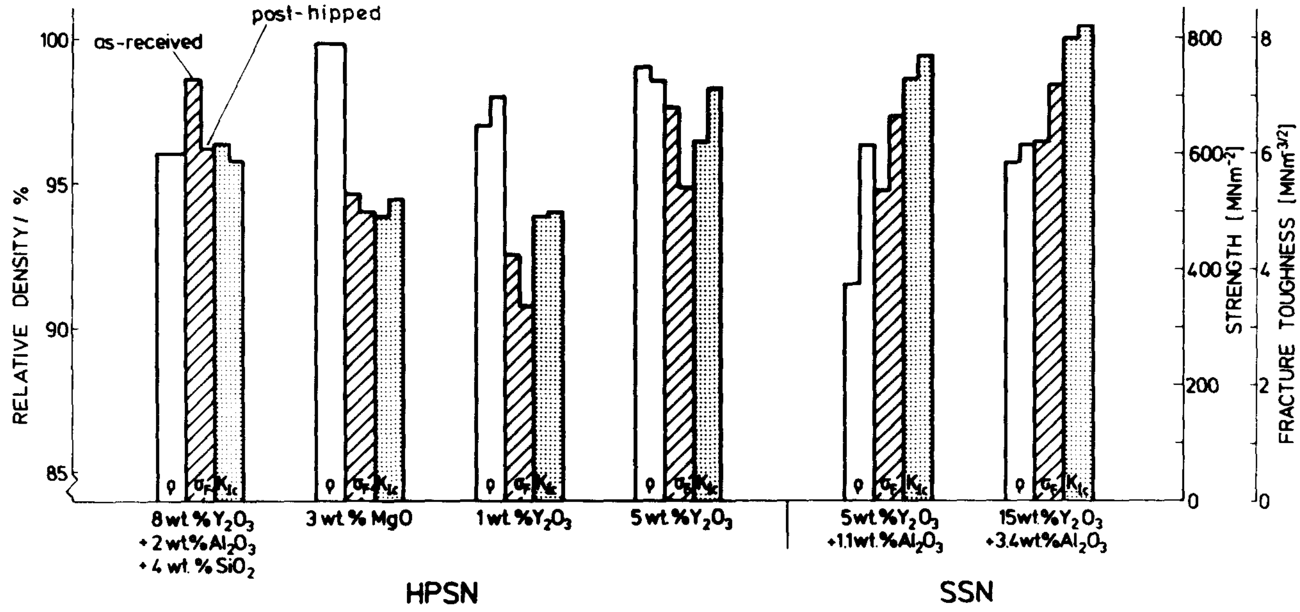

Fig. 5. Changes in density (ρ), fracture strength (σ_F) and fracture toughness (K_{Ic}) by post-hipping of various materials containing different amounts of additive.

caused by the vaporization of the liquid phase. Here, however, it should be mentioned that the density at which a material changes from open to closed porosity cannot be specified accurately because the theoretical density of the materials is usually not known exactly due to insufficient knowledge of the density of the secondary phases. The density increase for the high-density materials is about 1–1·5 % of theoretical density. For many materials investigated the density gains get smaller as the density of the starting materials approaches the theoretical density. In no case was the theoretical density reached for materials pre-sintered in nitrogen.

For purposes of comparison, Fig. 6 (left) presents the densification behaviour of a pre-sintered low-density material by post-hipping, which was encapsulated. In this case, nearly theoretical density was achieved. The high densification was caused by a real pressure-assisted sintering effect, similar to the densification process occurring during hot isostatic pressing of powder compacts or RBSN, and probably by the control of the equilibrium partial pressure of all components, thus avoiding vaporization.

As can be seen from Fig. 6, the amount of additive does not markedly influence the post-hipping behaviour. To prove this, samples with different amounts of additives were prepared in order to obtain an increasing viscosity of the liquid phase. Again, two groups of materials were used, the

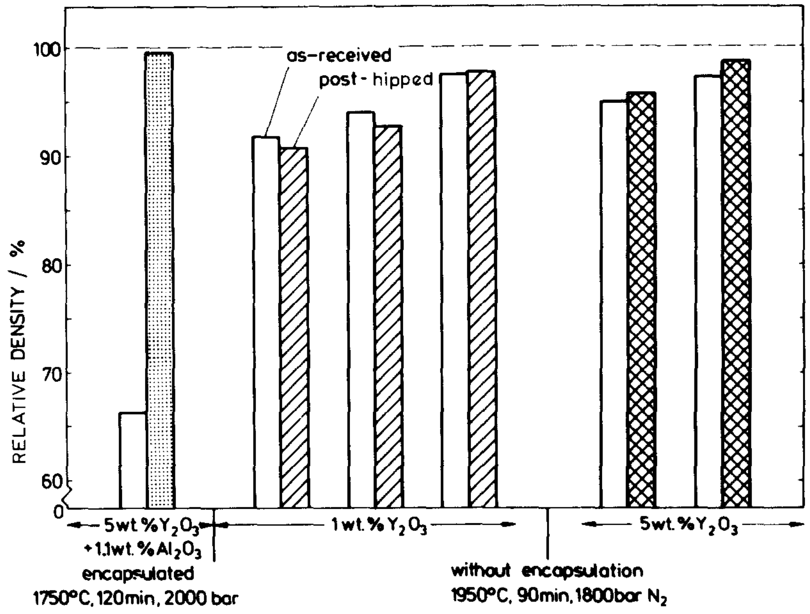

Fig. 6. Influence of the density of the starting materials on the final density after post-hipping for two materials with different amounts of yttrium oxide (for comparison, the final density of an encapsulated low-density starting material is given on the left).

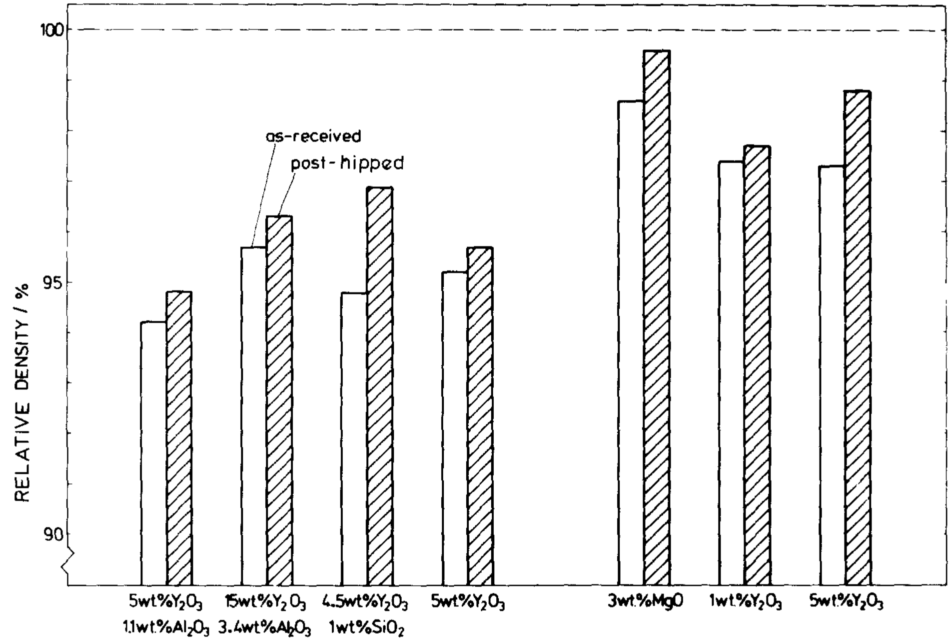

Fig. 7. Density values before and after post-hipping for materials with different type and amount of additive, arranged for two groups of similar starting density values.

first with a starting density of about 95 % theoretical density and the second with about 98 % theoretical density. The results are summarized in Fig. 7. The viscosity of the liquid phase is thought to increase within each group from left to right. These results again show neither a relation of the post-densification behaviour to the viscosity of the liquid phase nor to its quantity. Therefore, the conclusion may be drawn that besides density other microstructural characteristics exert a strong influence on the post-densification behaviour, whereas the amount and viscosity of the liquid phase is of secondary importance.

4.2.2. Influence of the silicon nitride phase composition ratio (α/β) in the pre-densified starting materials

Figure 8 shows the influence of the silicon nitride phase composition ratio (α/β) of pre-densified magnesium oxide fluxed starting materials on the final density and phase composition ratio, as well as on flexural strength and fracture toughness after hipping at 1850 °C in nitrogen (set II, Table 1).

The density of the hot-pressed starting materials increases slightly with higher β-phase content. The final density of all post-hipped materials rises by about 0·02 Mg m^{-3} and is independent of the β-phase content of the starting materials. The β-phase content of the post-hipped materials is dependent on the phase composition of the starting material. Only for high

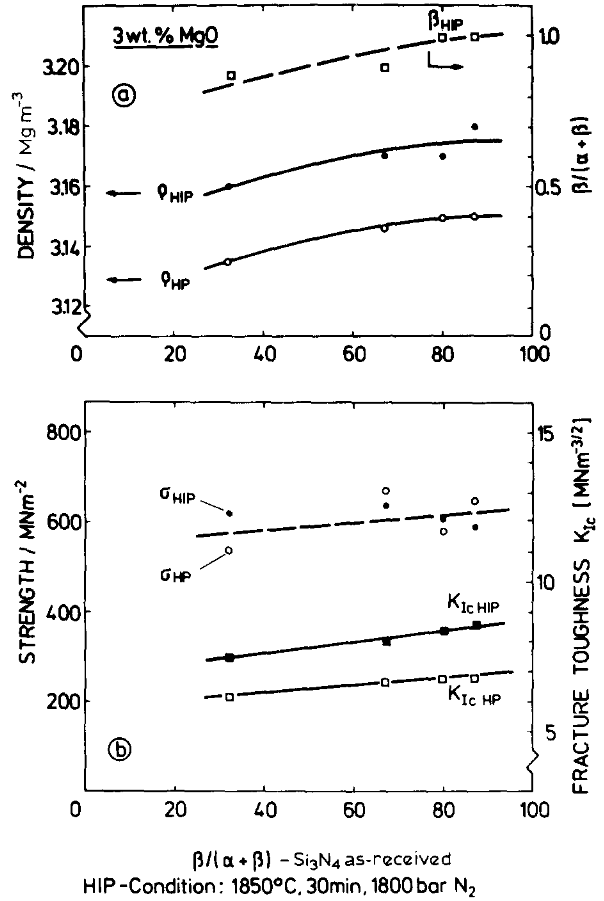

Fig. 8. Influence of silicon nitride phase composition ratio (α/β) of hot-pressed magnesium oxide fluxed (3 wt %) starting materials on: (a) final density (ρ_{HIP}) and phase composition ratio (α/β) (ρ_{HP} = density of the starting material); and (b) fracture strength and fracture toughness of post-hipped materials.

β-phase content in the pre-densified specimens does complete phase transformation occur during hipping under these conditions.

Fracture toughness increases for all materials after post-hipping. A slight improvement of K_{Ic} with higher β-phase content in the pre-densified materials was observed; this means that there is the same tendency as in the starting material. The strength data reveal no change.

4.3. Model experiments

4.3.1. Incorporation of artificial pores

The results given above show that in nearly all materials with closed porosity a slight reduction in total porosity was achieved by post-hipping. In order to

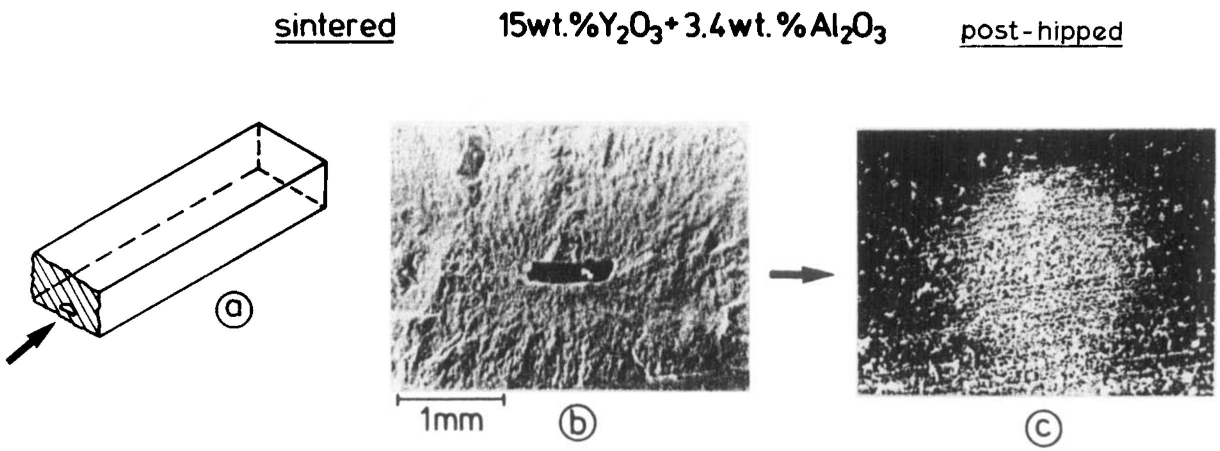

Fig. 9. Incorporation of artificial pores. (a) Location of pore (schematic); (b) artificial pore in the fracture surface; (c) pore filling detected in the cross-section.

study the mechanisms of porosity reduction, artificial pores were introduced (Fig. 9, set III, Table 1). These experiments were carried out with two materials containing different additive compositions, i.e. with different amount and characteristics of the liquid phase: 5 wt% yttrium oxide + 1·1 wt% aluminium oxide and 15 wt% yttrium oxide + 3·4 wt% aluminium oxide. In the case of a high amount of liquid phase, complete filling of the artificial pore was observed (Fig. 9(c)) as determined by microradiographic and SEM evaluation. The material in these pores is characterized by very fine grains, lower hardness and a somewhat higher silicon/yttrium ratio compared to the characteristics of the matrix. However, in the case of the material with a lower amount of liquid phase, the large artificial pore was not filled completely. This means that the effect of pore filling is dependent on the amount and probably on the viscosity of the liquid phase.

4.3.2. Influence of post-hipping on the grain orientation of hot-pressed materials

Though the elimination of residual macropores by the reduction of pore size occurs during post-hipping, the question still remains why, in most cases—even for as-received materials with residual α-phase content—complete densification cannot be achieved. A possible answer is that during post-hipping of pre-densified materials no essential rearrangement of the elongated β-Si_3N_4 grains takes place and, consequently, the reduction of porosity is limited ('bridge effect'). Thus, the microstructure and the pore structure of the post-hipped materials are mainly controlled by the microstructure of the starting materials (characteristics of the liquid phase and arrangement of the β-Si_3N_4 grains).

This hypothesis was proved by post-hipping HPSN with different types and amount of additive (set IV, Table 1). It is well known that hot-pressed materials exhibit a strong grain orientation. The reason for this is that the elongated β-Si_3N_4 grains crystallize during hot-pressing in such a way that their direction of elongation, which coincides with the crystallographic c-axis of the hexagonal β-phase, is oriented perpendicular to the hot-pressing direction. This preferred orientation results in a pronounced anisotropy of strength, fracture toughness and thermal properties.[32] The orientation effect was found to be dependent on the type and amount of additive.[27] This is demonstrated in Fig. 10 for materials with different magnesium oxide and yttrium oxide concentrations. In this graph the orientation effect is indicated by the X-ray intensity ratio $I(200)/I(002)$ of the hexagonal β-Si_3N_4 phase. This figure also demonstrates that post-hipping does not result in any marked change of the β-Si_3N_4 grain orientation. Only if starting materials with high residual α-Si_3N_4 phase are post-hipped (Fig. 11) does the average

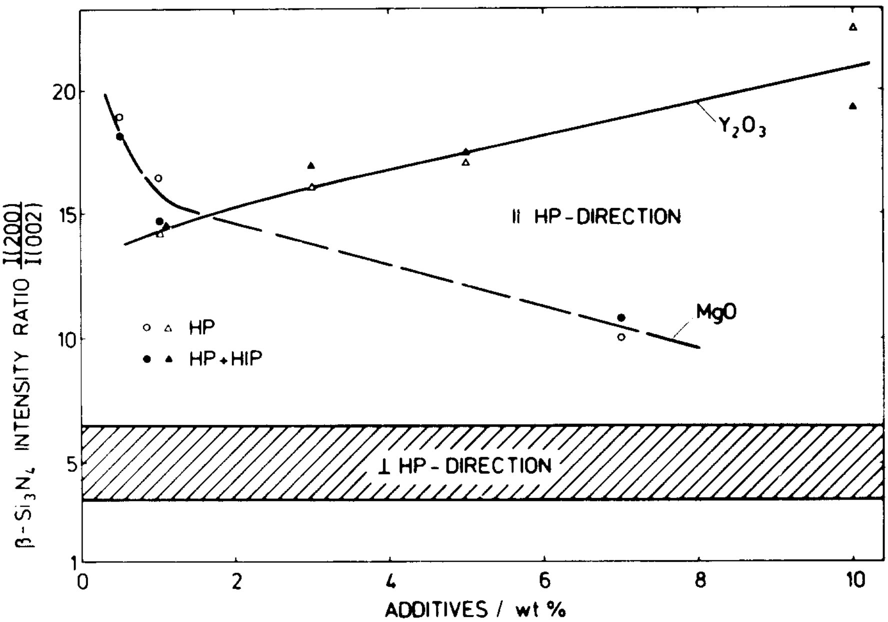

Fig. 10. Influence of post-hipping on the grain orientation of hot-pressed materials ($\beta/(\alpha+\beta)=1$): β-Si_3N_4 intensity ratio $I(200)/I(002)$ as a function of the additive concentration for hot-pressed (HP) and post-hipped (HP + HIP) materials. ||HP: measured parallel to the hot-pressing direction. ⊥HP: measured perpendicular to the hot-pressing direction.

orientation become smaller after hipping, because the newly-formed β-Si_3N_4 grains precipitate without orientation, due to the isotropic pressure.

4.3.3. Introduction of artificial cracks and crack healing experiments

In order to study the effect of enhanced crack healing during hipping, two materials with large differences in the viscosity of the liquid phase were precracked using the Knoop hardness indentation technique and the flexural strength was measured before and after hipping (set V, Table 1). Figure 12 shows the fracture strength for two materials fluxed with 5 wt % yttrium oxide (high viscosity of the liquid phase) and yttrium oxide + aluminium oxide + silicon dioxide additives (low viscosity of the liquid phase) in the uncracked and pre-cracked as-received state. Hipping results in an improvement of the fracture strength of both pre-cracked materials. The strength data are only limited by decompositional effects during hipping, as can be seen from the strength reduction of the uncracked material.

One important effect of post-hipping is the reduced scatter of strength data. This is demonstrated in Fig. 13 for three hot-pressed materials which were very badly machined. The improvement in data scatter after hipping is mainly caused by the healing of cracks; however, the elimination or reduction of residual pores may additionally contribute to this effect.

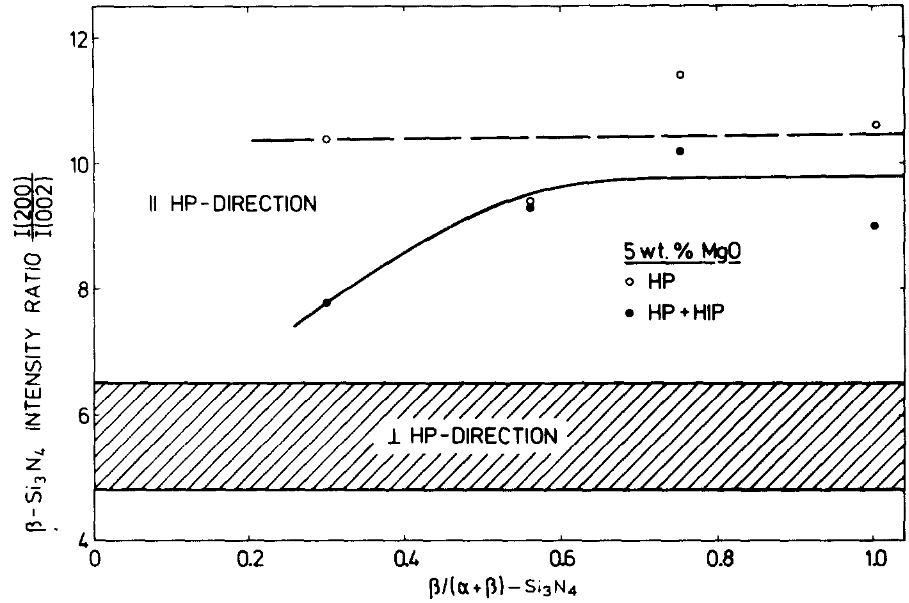

Fig. 11. Influence of post-hipping on the grain orientation of hot-pressed materials with different amounts of residual α-Si_3N_4 phase: β-Si_3N_4 intensity ratio $I(200)/I(002)$ as a function of the α/β-phase composition in the starting material for hot-pressed (HP) and post-hipped (HP + HIP) materials. ||HP: measured parallel to the hot-pressing direction. ⊥HP: measured perpendicular to the hot-pressing direction.

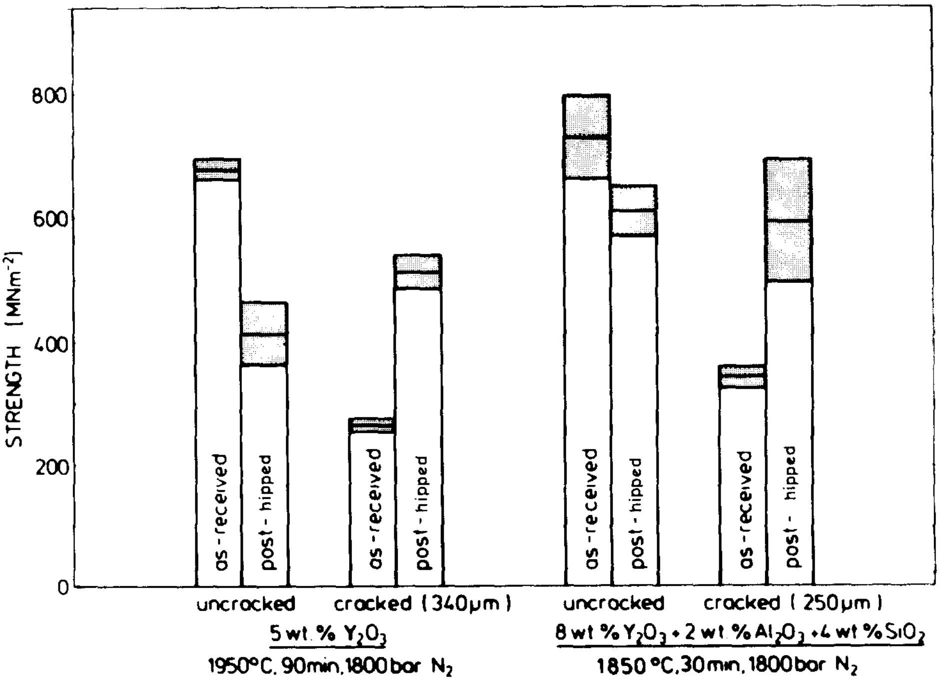

Fig. 12. Crack healing during post-hipping in two materials with different amount and composition of additive, i.e. different amount and viscosity of the liquid phase: flexural strength of uncracked and pre-cracked materials before and after hipping.

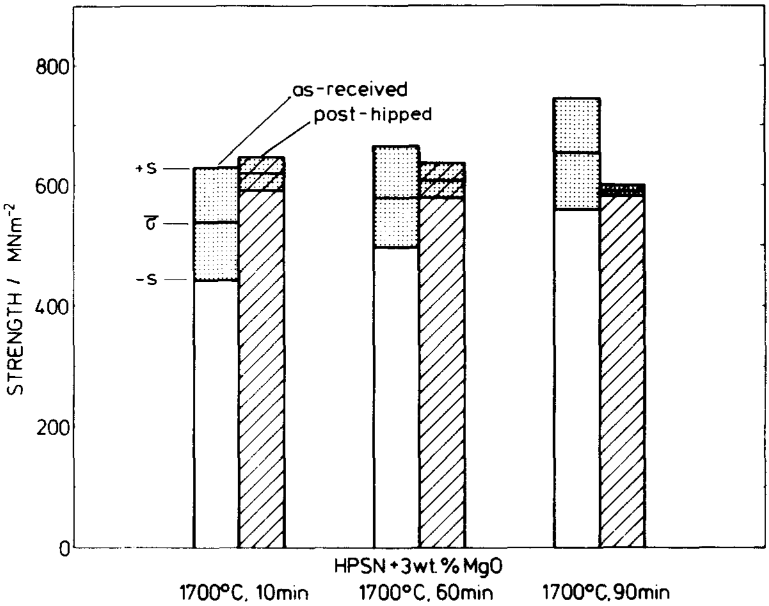

Fig. 13. Reduction of the scatter ±*s* in strength by post-hipping of badly machined hot-pressed materials.

5. DISCUSSION

The experimental results, particularly the systematic investigations and model experiments, permit some conclusions to be drawn about the microstructural changes which take place during post-hipping of pre-sintered materials and about the effect of these changes on the mechanical properties.

5.1. Microstructural changes

In nearly all materials with closed porosity sintered in nitrogen a slight reduction in total porosity was achieved by post-hipping. The change in density becomes smaller as the density of the pre-sintered material approaches the theoretical density. In the authors' experiments with holding times of ≤ 1 h at maximum temperature, theoretical density was not obtained. Here it should be noted, however, that for long holding times (≥ 6 h) theoretical density has been reached.[26] As the experiments with artificial pores indicated, the reduction of residual porosity is caused at least partially by filling of pores due to viscous flow of the liquid from two grain boundaries (or triple points) into the pores. Thus, pore filling is controlled by the viscosity and the amount of liquid phase. The difference between the compositions of the pore filling and the grain boundary phase might be caused by the silicon monoxide condensation, released by the liquid phase, and by the presence of silicon nitride whiskers within the pore which may be formed by a gas phase reaction during sintering or during the first stage of hipping.

One important reason for the limitation in porosity reduction, however, is that during the post-treatment of pre-densified materials by hipping no essential rearrangement of the elongated β-Si_3N_4 grains takes place, as demonstrated by post-hipping experiments of pre-hot-pressed materials. Even for starting materials with a certain amount of residual α-Si_3N_4 phase the density increase is controlled by the interlocking of the elongated β-Si_3N_4 grains in the pre-densified materials ('bridge effect' during the application of high pressure). This observation is independent of the type and amount of additive.

Although the arrangement of grains during post-hipping of pre-sintered (or pre-hot-pressed) materials is not changed considerably, in many cases globularization (indicated by the decrease in the aspect ratio of the elongated β-Si_3N_4 grains) and grain coarsening take place. Both microstructural changes are dependent on the microstructure of the pre-sintered materials and the hipping conditions. Two typical examples are shown in Fig. 14. Here, as in most cases, a decrease in the length, $\bar{l}$, and the aspect ratio, $\bar{a}$, of the elongated β-Si_3N_4 grains has been observed. In both materials these changes are associated with density gains and an increase in fracture strength and fracture toughness. This is unusual behaviour, as the change in grain morphology towards equiaxed grains, due to long soaking times and high temperatures, usually leads to a strength degradation, as shown schematically in Fig. 15. Therefore, other mechanisms seem to affect the mechanical properties of post-hipped pre-sintered silicon nitride materials, as will be discussed in Section 5.2. Apart from these examples, the globularization and coarsening of the β-Si_3N_4 grains often resulted in a reduction in fracture strength and/or in some cases in fracture toughness. Thus, the processing parameters, temperature, time, pressure and atmosphere, are important, and the optimum conditions depend on the type and concentration of the additives.

The choice of temperature and atmosphere is limited by the decomposition of the silicon nitride and the vaporization of the liquid phase at high temperatures. Both effects result in microcavities in the surface area and in pore formation in the sub-surface zone which lead to strength degradation. This means that the hipping temperature and atmosphere have to be optimized for the different additives to avoid these negative effects. In order to minimize the thermal decomposition of the silicon nitride, hipping of unencapsulated materials is preferably carried out under high nitrogen pressure, and/or the preforms have to be embedded in a powder bed consisting of a mixture of silicon nitride and sintering additives.

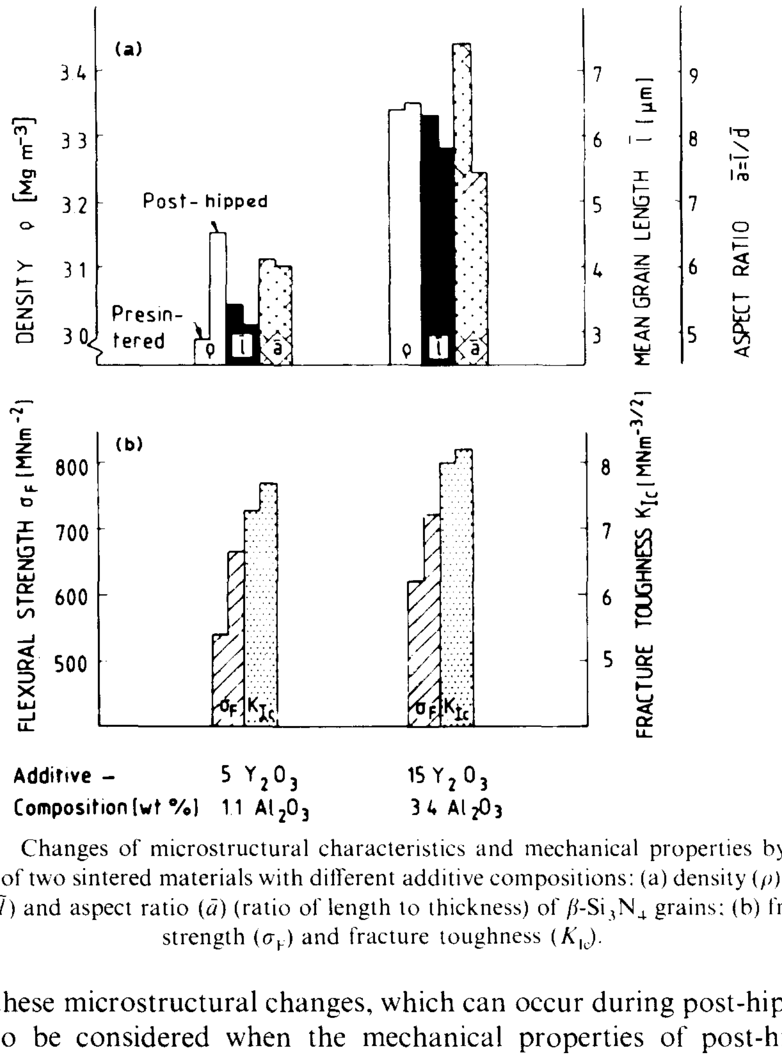

Fig. 14. Changes of microstructural characteristics and mechanical properties by post-hipping of two sintered materials with different additive compositions: (a) density (ρ), mean length ($\bar{l}$) and aspect ratio ($\bar{a}$) (ratio of length to thickness) of β-Si_3N_4 grains; (b) fracture strength (σ_F) and fracture toughness (K_{Ic}).

All these microstructural changes, which can occur during post-hipping, have to be considered when the mechanical properties of post-hipped materials are discussed.

5.2. Mechanical properties

A number of investigations show that the fracture strength of dense silicon nitride is generally controlled by various microstructural characteristics: the elongated β-Si_3N_4 grains frequently characterized by the aspect ratio, $\bar{a}$ ($\bar{a}\uparrow \rightarrow \sigma\uparrow$); the grain dimensions (grain size $\uparrow \rightarrow \sigma\downarrow$); and the residual porosity, P ($P\uparrow \rightarrow \sigma\downarrow$). Quantitative microstructural characterization of different types of dense silicon nitride, and the interdependence with mechanical properties, permit the conclusion to be drawn that the major factor controlling fracture strength (and fracture toughness) is the aspect

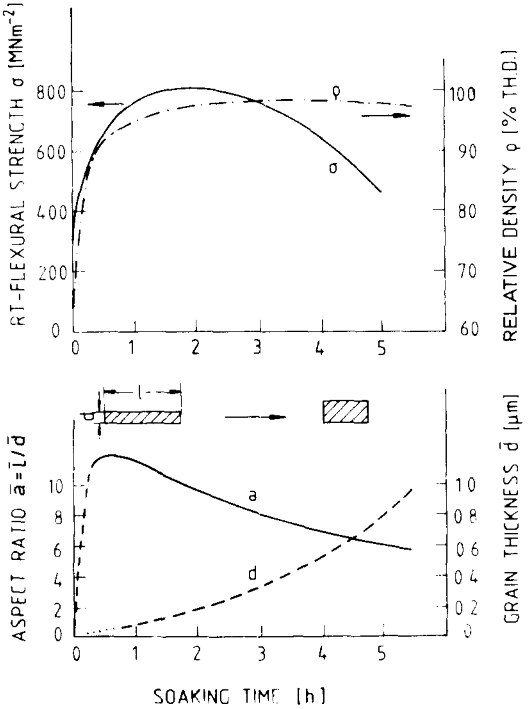

Fig. 15. Influence of soaking time on density, microstructural characteristics and the room-temperature flexural strength (schematic plot).

ratio of the β-Si_3N_4 grains.[24,25,28] The influence of grain size on fracture strength has been found to be essentially smaller. Nevertheless, there are some indications that other parameters, such as the amount and properties of the glassy phase, also have an influence on room-temperature strength.

The mechanical properties of silicon nitride after hipping are mainly controlled by the following changes: (i) the slight reduction of total porosity, (ii) the elimination or reduction of residual macropores, (iii) the healing of cracks, and (iv) the variation in grain size and grain morphology. Additionally, microcavities in the surface area may be created if during hipping in argon, or partly also in nitrogen, chemical decomposition cannot be avoided.

The slight reduction in total porosity and the filling of residual pores and other cavities result in an improvement of fracture strength, both of the absolute values and of the data scatter.

As is known from the literature, crack healing can occur in dense silicon nitride during post-annealing at temperatures higher than 900 °C, depending on the composition of the sintering additives.[31] Crack healing results in an improvement of mechanical properties, the absolute strength and data scattering. Annealing treatments in different atmospheres indicate that two mechanisms are mainly responsible for crack healing: (a) formation of cristobalite and silicates on the surface due to the effect of atmospheric oxygen and (b) the viscous flow of the liquid phase. The extent of crack healing is dependent on the viscosity and the amount of liquid phase. In the case of high viscosity and low amounts of liquid, as used for high-temperature materials, crack healing is limited. For these materials the healing of cracks is enhanced by applying high pressure at high temperature during post-hipping. In particular, the improvement of the scatter is one of the main advantages of post-hipping of pre-sintered silicon nitride.

The quantitative microstructural analysis of various materials before and after post-hipping clearly demonstrates that in many cases a globularization and coarsening of the β-Si_3N_4 grains takes place (see Fig. 14). Usually these effects result in a reduction of fracture strength and fracture toughness. Nevertheless, for the post-hipped materials no clear relationship was observed between fracture toughness, K_{Ic}, and the aspect ratio, $\bar{a}$; for example, K_{Ic} can be increased by post-hipping, though the aspect ratio is reduced. Consequently, other parameters must be effective. These results may be explained by the build-up of residual stress and by plastic deformation of the elongated β-Si_3N_4 grains during post-hipping, which strengthens the interlocking growth and leads to a stronger linking of the elongated β-Si_3N_4 grains. This assumption seems to be confirmed by observations in the literature.[17-19] TEM studies are under way to prove this effect.

In the case of fracture strength, no systematic interdependence was found to exist between strength data and the aspect ratio, $\bar{a}$. Usually, strength degradation is expected with decreasing $\bar{a}$ value; this result, however, was not observed in all cases. The reason for this is that fracture strength of post-hipped materials is determined by the improvement of fracture toughness, and additionally by the reduction of pore size effects and by crack healing. Which effect is dominant depends on the morphology and arrangement of the β-Si_3N_4 grains and the characteristics of the liquid phase as well as on the hipping conditions.

6. SUMMARY AND CONCLUSIONS

The systematic investigations and model experiments allow some conclusions to be drawn about the factors which determine the post-hipping behaviour of pre-sintered silicon nitride materials, the mechanisms being effective and the resulting properties:

(a) Post-hipping of pre-sintered silicon nitride without canning primarily demands materials which reveal only closed porosity. This is usually the case above about 94 % theoretical density of the starting material, otherwise encapsulation is necessary.

(b) In many cases only a slight increase in density was observed with materials pre-sintered in nitrogen. The reduction of residual porosity is caused by the filling of residual macropores, which may occur by squeezing out liquid phase from grain boundaries and triple junctions. A prerequisite is a sufficiently high amount of low-viscosity liquid phase.

(c) Though post-hipping may lead to an increase in density, in no case has theoretical density been achieved. One reason seems to be the rearrangement of the mainly elongated β-Si_3N_4 grains in pre-sintered silicon nitride compacts during hipping being prevented by a 'bridging' effect.

(d) The mechanical properties of hipped materials at room temperature are controlled by an overlapping of different effects. Essential positive effects are the slight density increase, particularly the filling of residual macropores or the reduction of the pore size, and the enhanced healing of cracks. Negative effects are the grain coarsening and grain globularization, as well as surface defects caused by vaporization of the liquid phase and decomposition of silicon nitride during hipping.

(e) As a result, a marked increase of strength levels is not observed. However, the scatter of strength values can be reduced and fracture toughness values often are improved. The latter observation seems to depend on a more intensive interlocking of the elongated β-Si_3N_4 grains, supported by local plastic deformation at the grain contact points. This is one more positive effect during post-hipping.

(f) Which effect is decisive depends on the morphology and arrangement of the β-Si_3N_4 grains and the characteristics of the liquid phase in the starting pre-sintered materials, as well as on the hipping conditions.

Therefore, an improvement of properties of pre-sintered silicon nitride by post-hipping demands optimized hipping conditions, as well as a well-defined microstructure of the pre-sintered starting material.

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