JOURNAL OF MATERIALS SCIENCE 13 (1978) 1199–1205

The α/β silicon nitride phase transformation

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The literature on the α/β silicon nitride transformation is reviewed briefly. Data are presented on the kinetics of the tranformation of 1600° C on low and high purity silicon nitride powders. The addition of magnesia increased the rate of transformation while the addition of yttria had no effect. Scanning electron photomicrographs show clearly the morphology changes that accompany the transformation. It is concluded that the transformation occurs via a solution-precipitation mechanism and that α and β are probably low and high temperature forms of silicon nitride.

1. Introduction

It has long been established that the α crystallographic form of silicon nitride can be converted to the β modification by heat treatment at temperatures exceeding 1500° C [1–3]. Although the importance of the phase transformation to the fabrication of high-strength hot-pressed silicon nitride has been recognized [4], its exact role has remained obscure. Coe *et al.* [4] reported that, although α-silicon nitride powder could be densified without transformation, high strength was only obtained on material that had transformed. Lumby and Coe [5] further emphasized the importance of the transformation to the hot-pressing process. It has been suggested that the strengthening is due to transformation-induced grain refinement [6, 7], but little information exists concerning details of the transformation mechanism.

Since there has been some disagreement on the crystal structures of α- and β-silicon nitride, crystallographic considerations that relate to the tranformation should be considered briefly. Ruddlesden and Popper [8] published the first complete determinations of these crystal structures. Both were found to be hexagonal with the unit cell of α-silicon nitride ($Si_{12}N_{16}$) being approximately twice as large as that of β-silicon nitride (Si_6N_8). Although it has been proposed that α-silicon nitride is actually an oxynitride of approximate composition $Si_{11.5}N_{15}O_{0.5}$ [9–12], recent observations [13–18] do not support this conclusion. It therefore appears that any proposed mechanism of transformation must consider α and β to be true polymorphs of silicon nitride.

The role of oxide additives such as magnesia in the hot-pressing of silicon nitride was first elucidated by Wild *et al.* They showed that magnesia reacted with silica (invariably present to some extent in silicon nitride) to form magnesium silicates that are molten at temperatures (1600° C to 1800° C) typically used in hot-pressing. They considered the transformation to involve decomposition of the oxynitride (α) to form the true nitride (β). The silica that was released by the decomposition was thought to be absorbed by the liquid phase. As was noted above, however, it is unlikely that α is an oxynitride, and this decomposition mechanism is therefore improbable.

There exist few published data on the kinetics of the α/β transformation, and it is only recently that quantitative data have been reported [19]. Coe *et al.* [4] found a linear relationship between per cent β and log time for silicon nitride powder hot-pressed with 1 wt% magnesia at 1740° C. A few results have been given by other investigators,

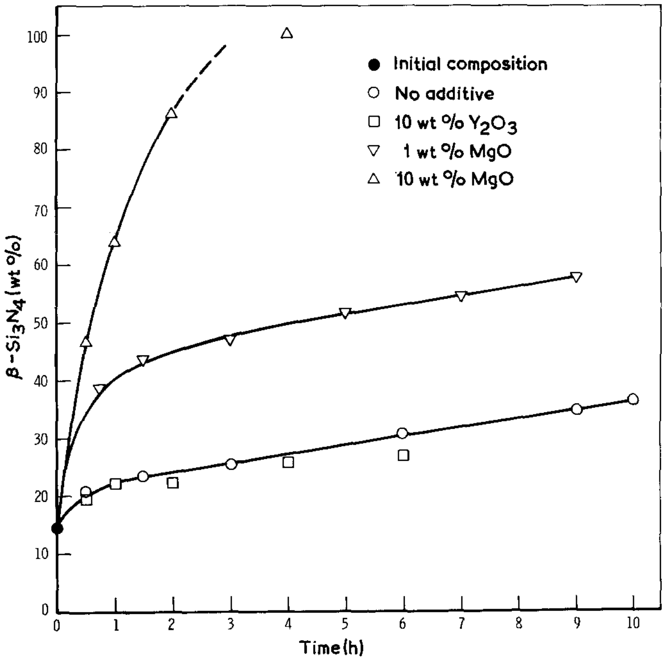

Figure 1 Effects of additives on the rate of transformation of 85% α-silicon nitride powder in flowing nitrogen at 1600° C.

[12, 20–22], but none of these studies was intended to examine the transformation kinetics in any detail.

Drew and Lewis [3], from observations by transmission electron microscopy on partially transformed hot-pressed material, concluded that the transformation occurs via a solid/liquid/solid mechanism. They have also proposed [24] that β'-silicon aluminium oxynitride forms by the same mechanism. Additional results that are consistent with such a mechanism include evidence for the solubility of silicon nitride in molten magnesium silicates [25–27] and proposals that sintering in the silicon nitride–magnesia system occurs via a liquid phase mechanism [26, 28, 29].

All of the previous data on the α/β transformation were obtained as by-products of studies concerned primarily with the sintering of silicon nitride. The experiments reported herein were done by simply heat treating loosely packed powders with the objective of examining the transformation kinetics with as few complications as possible. In addition to reporting new experimental data on the transformation, it is an objective of this paper to evaluate all existing data within the framework of knowledge regarding the general subject of phase transformations.

2. Experimental procedures

Most of the experiments were done with silicon nitride powder[*] containing 85 wt % of the α phase. This powder was nominally 99% pure and its surface area was $1.57\,m^2\,g^{-1}$. Several experiments were done with high-purity, 100% α powder obtained by pulverizing thin slabs of chemically vapour-deposited (CVD) material[†]. Magnesia[‡] and yttria[§] were added as required, and mixtures were formed by shaking the combined powders in plastic containers.

Heat treatments were done in a system comprising a high-purity alumina muffle tube within a graphite susceptor. The heating atmosphere comprised flowing nitrogen. Specimens were contained in graphite crucibles with lids of the same material. Portions of the specimens that were removed after heating for desired time intervals were used for X-ray analysis.

The phase contents of the specimens were determined by a quantitative X-ray diffraction technique [30]. CuKα radiation was used and powder specimens were contained in aluminium holders. Specimens were also examined by scanning electron microscopy using standard techniques

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[*] AME-C.P. silicon nitride powder, AME Ltd., Gateshead, Durham, UK.

[†] United Technologies, Corp., East Hartford, Ct, USA.

[‡] "Specpure" MgO, Johnson and Matthey Co. Ltd., UK.

[§] BDH Ltd., Poole, Dorset, UK.

TABLE I Phase transformation data at 1600° C on phase-pure α-silicon nitride powder prepared by CVD

Run No.	Total time (h)	wt % β-Si_3N_4	Other phases	Remarks
9	2.0	0.0	2H SiC(w to m)*	No additive
	6.0	0.0	2H SiC(s)*	
10	0.5	3.5	–	10 wt % magnesia added;
	1.0	3.7	–	sintering occurred
	2.0	3.8	2H SiC?	
	4.0	4.3	–	
	8.0	4.5	2H SiC(m)*	

* w = weak; m = medium; s = strong.

3. Results

Fig. 1 shows transformation data at 1600° C for the 99% pure silicon nitride powder as received and with various additives. Note that the transformation rate is highly dependent upon the amount of magnesia added. The final part of the curve for the specimen containing 10 wt % magnesia is dashed because transformation was complete at an unknown time between 2 and 4 h. It should be also noted that the addition of 10 wt % yttria had no effect on the transformation rate.

Several minor phases were observed by X-ray diffraction in the various reaction products. The specimens that were heated as received and with 1 wt % magnesia contained small amounts of 2H silicon carbide [31]. Some "J" phase [32] was found in the specimen containing 10 wt % yttria. A few unidentified peaks in the specimen containing 10 wt % magnesia may have come from crystalline magnesium silicate phases [6]; they did not match with any compound likely to be present, and no attempt was made to index them.

A certain amount of sintering that occurred in the specimens containing magnesia had no apparent effect on the transformation rate. In one experiment the amount of transformation that occurred on a sintered part of a specimen was the same as that on another, pulverized part of the same specimen.

Table I summarizes results on the transformation kinetics of the CVD powder. Note that, without the magnesia additive, no transformation whatsoever occurred and that relatively large amounts of silicon carbide were formed.

Considerable silicon carbide formation was also observed in early experiments (not shown in Fig. 1) on the 99% silicon nitride powder in a system which was leaking and known to be contaminated with oxygen. It was anticipated from the results of Colquohoun *et al.* [33] that the formation of silicon carbide would be promoted by the presence of silica in the silicon nitride powder: 99% silicon nitride powder containing 5 wt % silica was therefore heated for 1 h at 1600°C in a graphite crucible. Surprisingly, silicon oxynitride was the only extraneous phase observed in the product.

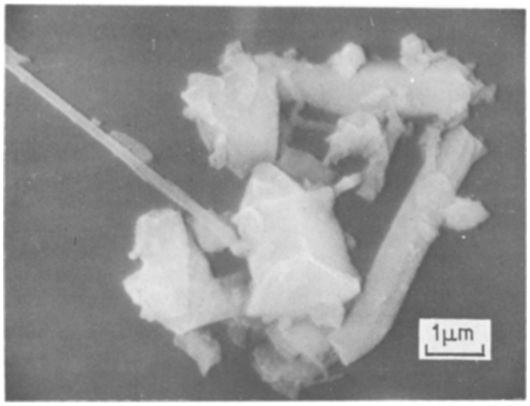

Figure 2 99% pure, 85% α-silicon nitride powder as-received.

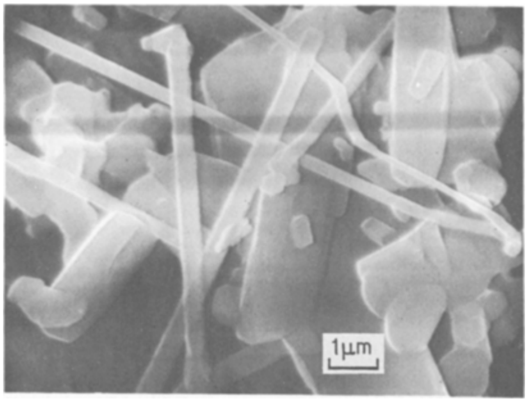

Figure 3 Silicon carbide whiskers in silicon nitride powder after heat treatment at 1600° C in a system contaminated with oxygen.

Fig. 2 shows the appearance of the 85% α-silicon nitride powder as-received. This figure shows the three types of morphology that are typically observed: whiskers, elongated particles, and equiaxed particles.

Fig. 3 shows whiskers such as are found in specimens contaminated with silicon carbide. Lower magnification photomicrographs (not shown) indicate aspect ratios for these wiskers in the range of from 50 to 100:1.

Fig. 4 is a series of scanning electron photomicrographs of silicon nitride powder containing 10 wt% magnesia at various stages of transformation at 1600° C. The changes in morphology as compared to the starting powder (Fig. 2) are striking. The hexagonal shapes of many of the grains and their increased definition as the transformation progresses are noteworthy.

4. Discussion of results

4.1. Silicon carbide formation

Our observations concerning the formation of silicon carbide, particularly in the absence of oxide additions, are consistent with the results of Colquohoun *et al.* [33]. Those authors explained that, when silicon nitride is heated, the surface silica that is invariably present volatilizes to form silicon monoxide which reacts with the graphite

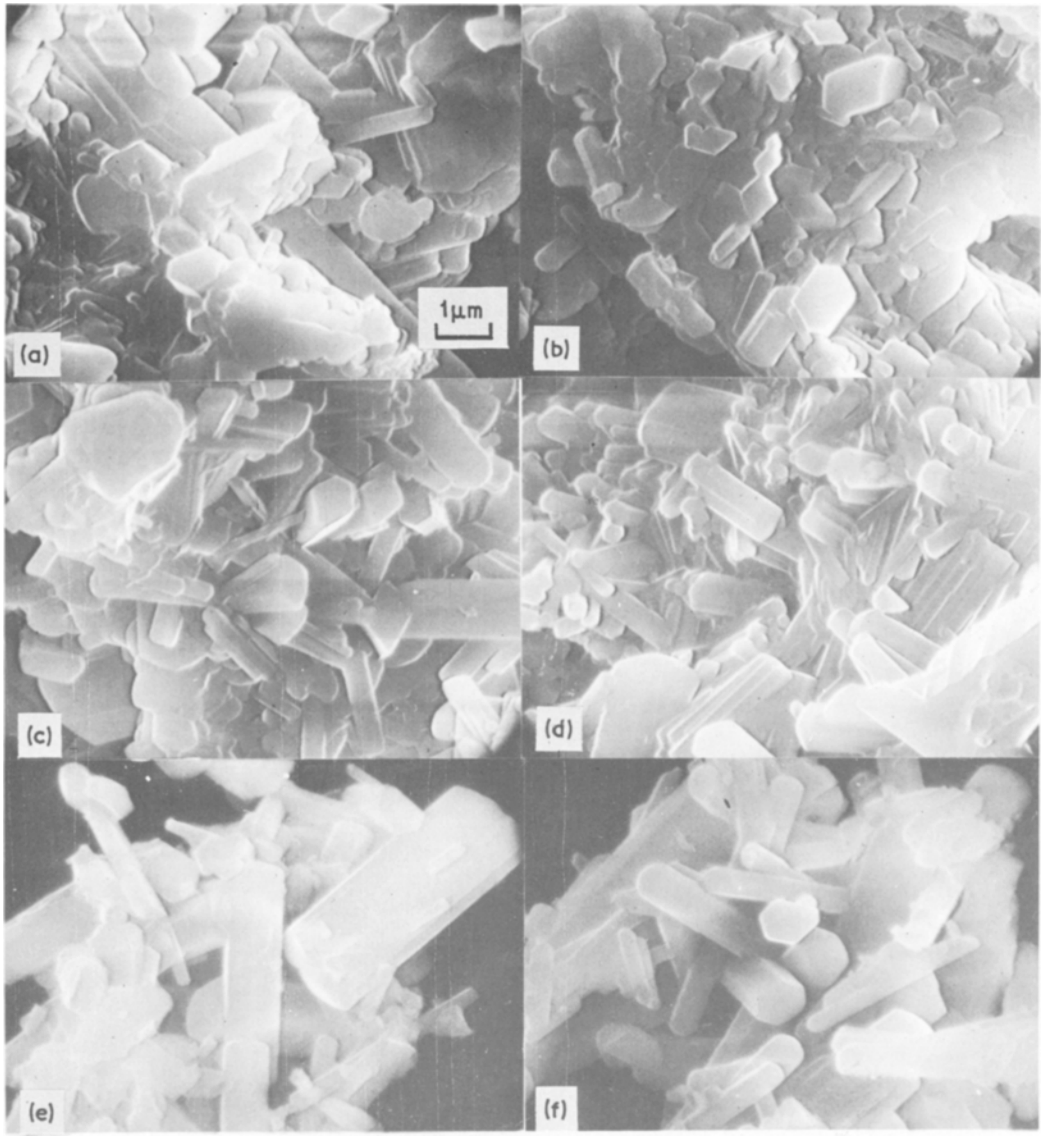

Figure 4 Silicon nitride powder containing 10 wt% magnesia at various stages of transformation after heat treatment at 1600° C. (a) and (b): 0.5 h, 46.8 wt% β. (c) and (d): 1.0 h, 64.1 wt% β. (e) and (f): 4.0 h, 100 wt% β.

container to form carbon monoxide. The silicon nitride is subsequently carburized as follows:

$$3CO(g) + Si_3N_4(s) =$$

$$2SiC(s) + 2N_2(g) + CO_2(g) + SiO(g).$$

The silicon monoxide that is formed reacts further with the graphite container to continue the cycle. When an oxide additive such as magnesia is present, however, it combines with the silica to form a magnesium silicate; the activity of the silica is thus reduced, carbon monoxide formation is minimized, and little or no silicon carbide is formed.

In view of the above considerations, the experiment in which 5 wt% silica was added to the silicon nitride powder should have yielded a product containing a significant amount of silicon carbide. The only extraneous phase found in that product, however, was silicon oxynitride. It seems likely, therefore, that the behaviour of this system is complex, and that the morphology and perhaps the distribution of the silica may determine which chemical reactions occur.

4.2. Transformation kinetics

Results of a pressure sintering study [19] indicate that the α/β transformation follows first order kinetics under such conditions, i.e., plots of log per cent α versus time are linear. The present data (Fig. 1) fit such a model reasonably well, but the data are insufficient to unequivocally establish that the model is correct. Quantitative interpretation of our data was therefore not attempted.

Because of the limited amount of transformation that occurred, the rate data for the CVD powder, Table I, were not given in a figure. It is noteworthy, however, that these data give no indication of an induction period as would be the case if nucleation were rate-controlling. That the transformation rate is slower on the CVD powder as compared to the lower purity powder may be because of the coarse particle size of the former. The CVD powder comprised more or less equiaxed particles of the order of 30 to 40 μm diameter as compared to the fine particles in the 99% pure powder (Fig. 2). It is also likely that impurities could affect the rate of transformation.

The solubility of silicon nitride in molten silicates is now well established [25–27], and the evidence obtained in this study supports the conclusion of Drew and Lewis [23] that the α/β silicon nitride tranformation occurs via solution-precipitation rather than a solid state mechanism [7]. Also improbable is a mechanism [6] involving "deoxidation" of an oxynitride (α) to form the "pure" nitride (β).

The strong dependence of the transformation rate on magnesia content, Fig. 1, suggests that the rate is proportional to the amount of magnesium silicate liquid that is present at 1600° C. It is also significant that, at the same temperature, the rate is unaffected by yttria, another common hot-pressing additive [34]. These circumstances are consistent with phase diagram data; the lowest eutectics occur at 1543° C in the magnesia–silica system [35] and at 1660° C in the yttria–silica system [36]. Liquid phase formation, and an enhanced rate of transformation would therefore not be expected with the yttria additive at 1600° C.

That transformation occurred in the 99% pure powder without additives must be attributed to impurities that react with silica to give some liquid phase formation, for Priest *et al.* [13] observed no transformation whatsoever in high purity CVD silicon nitride at 1800° C, and we only observed transformation at 1600° C when magnesia was added to our CVD powder. Although Jack [25] reported transformation without magnesia additions, his powder was similar to the lower purity powder used in this study.

4.3. Microscopy

Earlier suggestions [6, 7] that the α/β phase transformation produced strengthening in hot-pressed silicon nitride via grain refinement appear inconsistent with the present results. Although it must be remembered that our results were obtained on loosely packed powder, the particles in the transformed material, Fig. 4, are clearly as large as or larger than thoses in the starting powder, Fig. 2. It appears significant, however, that grains larger than a few μm are never observed; the high strength of hot-pressed silicon nitride could well be due to the development of a fine-grained microstructure in which grain growth is minimal.

Iskoe and Lange [38] have proposed that the aspect ratios of the β grains in hot-pressed silicon nitride are related to the β phase content of the starting powder, i.e., that existing β grains serve as nuclei for the growth of additional β-silicon nitride. In this investigation, however, β-silicon nitride was formed even in the case where phase-pure α-silicon nitride powder was the starting material. Such a circumstance precludes the presence of existing β

particles, and the transformation must have involved formation of new β nuclei.

4.4. Nature of the α/β transformation

It has been suggested from structural considerations that the α/β transformation should be reconstructive [3, 39], and all available evidence indicates that it can be classified as a reconstructive transformation of secondary coordination [40]. Such transformations involve breaking bonds, but the first coordination is the same in each structure. Because of the structural rearrangement that is required, the kinetics of the process are sluggish, and a solvent is often needed to enable the transformation to occur [41]. Other examples of this type of transformation are the ones between any pair of the set quartz-tridymite-cristobalite, and the würtzite–sphalerite transformation [41].

The present results support the assumption that β-silicon nitride is the stable form at 1600° C. Ample evidence exists for the solubility of both forms of silicon nitride in molten silicates [25–28], and it would be expected that a solution sauturated with the unstable form (α) would be supersaturated with respect to the stable for (β) at a temperature above the transition point [41]. The proposed solution-precipitation transformation mechanism is thus entirely consistent with qualitative thermodynamic arguments regarding the stabilities of the two phases.

It seems pertinent to further consider the silicon nitride transformation in terms of what is known about other systems [41], specifically in regard to whether or not α-silicon nitride is metastable at all temperatures [39], and as to whether or not α is the low temperature, and β the high temperature form. In general, the high temperature form tends to be more symmetrical crystallographically than the low temperature form and such is the case of for β-silicon nitride [3]. (Point group 6/m as opposed to 3m for α-silicon nitride). From entropy considerations, one expects the high temperature form to have greater open spaces available for thermal motion and to have lower density. β-silicon nitride appears to satisfy the former criterion, but not the latter; the density of α ($3185\,\mathrm{kg\,m^{-3}}$) is slightly less than that of β ($3196\,\mathrm{kg\,m^{-3}}$).

If α- and β-silicon nitride are true polymorphs, questions arise as to the transformation temperature and as to why the β/α transformation never has been observed experimentally. The present results indicate that the transition temperature must be less than 1600° C but existing thermodynamic data are inadequate to establish what the exact temperature is. It is possible however, that the transition temperature could be so low that kinetics barriers could prevent the β/α transformation from ever occurring, especially in view of the considerable disruption necessary to go from one structure to the other. It should also be remembered that the present results, as well as those in the literature, apply almost exclusively to systems at atmospheric pressure. As has been demonstrated for silicon carbide, for example, there could be another pressure regime in which the transformation could occur reversibly [43].

In view of the foregoing discussion, the results of Clancy [43], who presented inferential evidence for the β/α transformation, are difficult to rationalize. In a thorough examination by optical and electron microscopy of silicon nitride crystals obtained from several sources, he found numerous examples of crystals which apparently contained both crystalline phases. Because those crystals had morphologies typical of the β phase, Clancy concluded that they had partially transformed to α-silicon nitride. It must be noted, however, that no data were reported on transformation kinetics, i.e., it was not shown that what was observed was indeed β transforming to α over a given period of time. It is therefore possible that the crystals as formed contained both phases, or that they actually represented an example of the reverse transformation. Careful examination of Clancy's data, however, makes the latter explanation appear unlikely.

5. Summary

(a) Silicon carbide whiskers form via reactions between silicon nitride and graphite containers at 1600° C. Silicon carbide formation is suppressed by magnesia and yttria additions, and the addition of silica gives a product containiing silicon oxynitride.

(b) The α/β transformation rate at 1600° C is enhanced by magnesia but not by yttria. This result is consistent with expected liquid phase formation in the former system, and with a transformation mechanism involving solution precipitation.

(c) Transformation occurs in high purity α-silicon nitride powder at 1600° C only when magnesia is added to the system.

(d) The β-silicon nitride obtained from the transformation comprises fine, log-shaped grains that typically have hexagonal symmetry.

(e) The α/β silicon nitride phase transformation is a reconstructive transformation of secondary coordination.

(f) Available evidence suggests that α- and β-silicon nitride may be true polymorphs with α being the low temperature form.

Acknowledgements

This work was supported by a Fellowship awarded to D. R. Messier by the Secretary of the U.S. Army. The capable assistance of Andrew F. Connolly in obtaining the photomicrographs that are a vital part of this work is greatly appreciated.

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Received 12 July and accepted 17 October 1977.