The growth of α- and β-Si_3N_4 accompanying the nitriding of silicon powder compacts

Interest continues in the factors controlling the formation of α- and β-Si_3N_4 accompanying the nitriding of silicon, and in the transformation of α- to β-Si_3N_4 [1]. A brief report of some hitherto unpublished data is now presented which, we believe, contributes towards a better understanding of the topic. The observations were made during the course of a study [2, 3] of the mechanisms of bonding to form reaction-bonded silicon nitride, a study which drew heavily on the results, reported in full [4], of earlier research into the mechanism of the nitriding of high purity silicon.

High purity silicon powder, prepared in the manner described [4] (particle size: maximum 45 μm; mean 20 μm), was isostatically pressed (140 MN m^{-2}) into compacts (30 cm x 5 cm x 5 cm), no binders being used. The compacts were nitrided (1370° C in N_2 at 50 Torr) in a furnace similar to that used previously [4]. The extent of the reaction was determined by weighing and the phase composition by X-ray diffractometry. The data are summarized in Fig. 1.

It is believed that during nitriding below the melting point of silicon two parallel reactions occur, one involving the nitriding of volatilized silicon and the other the direct nitridation of solid silicon. The evidence in support of this is argued, in detail, in a comprehensive review [5]: for the present it is sufficient to note that, at 1370° C, the rate of evaporation of silicon [6, 7], and its subsequent nitridation in the vapour phase, can readily account for the fastest nitridation rates we have ever observed, and the evidence for the direct nitridation of solid silicon is strong [4, 8].

Drawing on the experience of those studying the formation of CVD S_3N_4 [9], we believe that vapour phase reactions between Si- and N-bearing species lead only to α-Si_3N_4 or amorphous Si_3N_4, but not β-Si_3N_4. From the arguments developed below we further believe that the direct reaction between solid Si and N_2 as well as reactions involving a suitable liquid phase, lead to β-Si_3N_4.

The linear part of the reaction kinetics (Fig. 1) corresponds to a situation in which the supply of nitrogen to the reaction sites is the rate-determining step: in this regime, nucleation and growth of nitride nuclei is occurring, the reaction eventually slowing as a coherent layer develops across the Si [4].

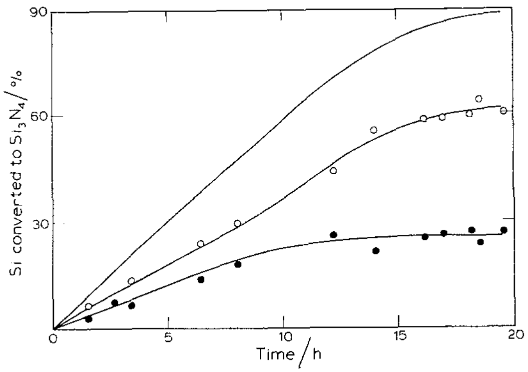

Figure 1 Growth kinetics of α-Si_3N_4 and β-Si_3N_4: 99.999% Si.– total conversion; ○ % Si converted to α-Si_3N_4; ● % Si converted to β-Si_3N_4.

Fig. 1 shows that the growth of β-Si_3N_4 stops when the overall reaction slows, the growth of α-Si_3N_4 continuing because vapour phase reactants can meet via the "chimneys" passing through the nitride layer.

Boyer and Moulson [10] have recently measured the amounts of β-Si_3N_4 developed in a nitriding compact of the high purity silicon powder to which Fe had been added. They were able to link the β-Si_3N_4 growth with the presence of an $FeSi_x$ phase. This growth of β-Si_3N_4 from a liquid phase would seem to be, in principle, the same process as that occurring during the hot-pressing of Si_3N_4, when the β-Si_3N_4 is believed to precipitate from the liquid, after the solution of α-Si_3N_4 in the silicate melt [11].

In our view, the weight of published evidence leads to the following simple hypothesis which, to date, adequately serves to interpret our own data:

(1) α-Si_3N_4 is a metastable polymorph of Si_3N_4, the stable form at all temperatures being β-Si_3N_4.

(2) α-Si_3N_4 is the polymorph which grows from vapour phase reactions, although the precise growth morphology ("massive" or "whiskers") depends upon the chemical nature of the reactants (Si, SiO, etc.).

(3) β-Si_3N_4 can form as a result of the direct nitridation between solid Si and N_2.

(4) β-Si_3N_4 readily forms through the agency of a liquid phase. (This is exemplified in silicon nitride technology by the many studies showing

preferential formation of β-Si_3N_4 at reaction temperatures above the silicon melting point.)

(5) α-Si_3N_4 cannot be directly converted to β-, at least under readily accessible conditions of temperature and pressure: the usual "transformations" observed involve a liquid phase in which β-Si_3N_4 precipitates following solution of α-Si_3N_4 [11, 12].

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On the opening and edge-sliding fracture toughness of aluminium–epoxy adhesive joints

Much work has already been done on the fracture mechanics and mechanisms of aluminium–epoxy adhesive joints for the opening fracture mode [1–4]. The critical strain energy release rate (G_{IC}) is usually used to characterize their crack propagation resistance. This follows from an energy balance approach of the fracture process which gives [5]

$$G_{IC} = \frac{P_c^2}{2B}\frac{dC}{da} \tag{1}$$

where P_c is the fracture load, B the specimen thickness, a the crack length and C the compliance. In the evaluation of G_{IC}, C is experimentally determined and hence includes all compliance contributions due to the adherend, the adhesive and any crack tip plasticity effects.

Little work however has been reported to date on the critical stress intensity factor, or equivalently the fracture toughness (K_{IC}) [6, 7], for these aluminium–epoxy adhesive joints, even though it is a much more useful design parameter from the stress analysis viewpoint. In homogeneous isotropic materials, K-expressions for a wide range of test-piece geometries and loading configurations have been computed and are readily available in published literatures [8, 9]. Thus, in the most general form,

$$K = \sigma\sqrt{a}\phi \tag{2}$$

where σ is the applied stress and ϕ is the shape correction factor. Equation 2 is however not directly applicable to two-phase materials such as aluminium–epoxy adhesive joints, and this explains why relatively few K_{IC} data exist. However, through some strenuous efforts and laborious finite element analyses, Trantina [6] and Stone *et al.* [7] have independently obtained an approximate K-expression for adhesive joints with very thin bond line thickness, which is related to the one-material solution of Equation 2. Thus,

$$\left(\frac{K_{al-ep}}{K_{al}}\right)^2 = \left(\frac{\phi_{al-ep}}{\phi_{al}}\right)^2 = \frac{E_{ep}\,G_{al-ep}}{E_{al}\,G_{al}}. \tag{3}$$

Trantina [6] has also shown that the strain energy release rates G_{al} and G_{al-ep} are equal* so that Equation 3 is reduced to

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*Without going through the finite element analysis one can easily obtain that for a very thin bond line the compliance contribution due to the adhesive is negligible. It follows from Equation 1 therefore that $G_{al} = G_{al-ep}$.