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The effect of silica on the nitridation of silicon

The sensitivity of the reaction between high purity silicon and nitrogen to the nature of the surrounding alumina reaction tubing has been reported [1]. Observations based on the use of four types of alumina suggested that contaminants released from the alumina at nitridation temperature influenced the course of the reaction to favour formation of the beta-phase of silicon nitride. Nitridations have now been carried out using commercial grades of silicon powder in similar reaction environments. These confirm that the alumina must be regarded as a reaction variable (Fig. 1), but also suggest that the action of these contaminants may be more complex than had previously been assumed.

The characteristics of the silicon powders are given in Table I. Nitrogen gas was purified using an acidified aqueous chromous chloride scrubber, and phosphorus pentoxide. Small (approximately

TABLE I Characteristics of silicon powders used

Contaminant (wt %)	Powder B	Powder D
Iron	0.76	0.42
Aluminium	0.67	0.42
Sodium	0.04	0.01
Calcium	0.03	0.02
Magnesium	0.01	0.00
Oxygen	1.60	0.30
Median particle diameter (μm)	23	20

10 mm diameter \times 10 mm length) compacts of silicon powder were nitrided inside short inner tubes of two types of commercial sintered alumina (designated A and B), the ends of which were packed with discs of zirconium foil. The reaction system was evacuated to 10^{-6} bar at temperature and then nitrogen filled before the inner tube and specimens were drawn magnetically into the hot zone. Pellet green densities were approximately 1600 kg m^{-3} , and the nitrogen flow rate was 10 ml min^{-1} . The extent of nitridation was determined by measurement of initial and final weights, and the proportion of alpha- and beta-phases in the product by means of Philips diffractometer.

Results from nitridations in tubes of alumina B for which reaction time was varied at constant temperature (1365°C) are shown in Fig. 2. It is apparent that almost all the alpha-phase forms in the initial stage of the reaction, and that the bulk of the beta-phase is formed later, in conjunction with the characteristic slight upturn in the reaction-time curve. That prolonged nitridation may lead to a decreased alpha/beta ratio of the products is a common observation [2, 3], but the possibility of dividing the nitridation process into two fairly clearly defined stages has apparently not been commented on.

If the oxygen is assumed to be present initially as a uniform silica film on the silicon grains a

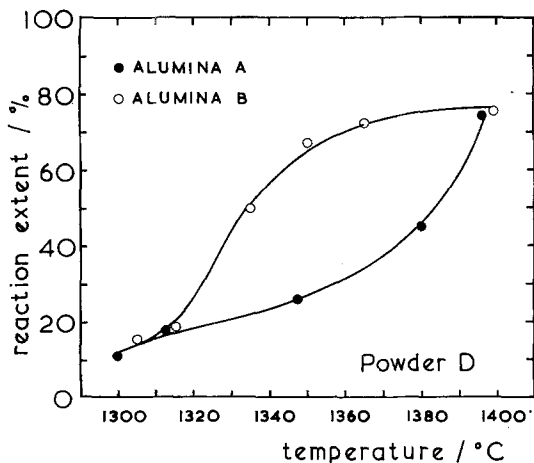


Figure 1 Reaction extent after 6 h for silicon powder D, plotted against temperature, using two grades of alumina reaction tube.

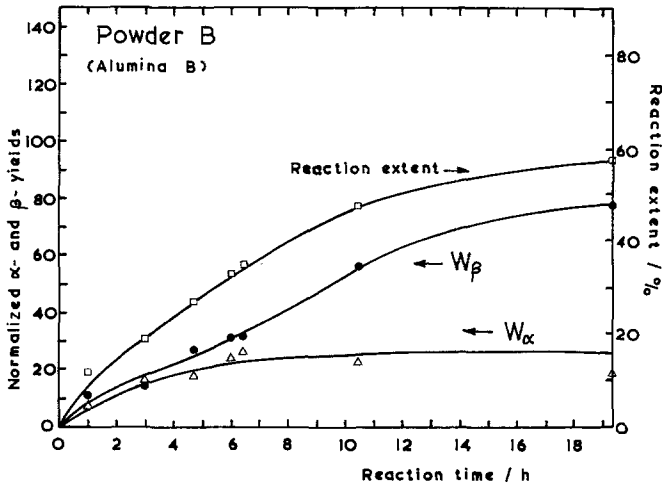
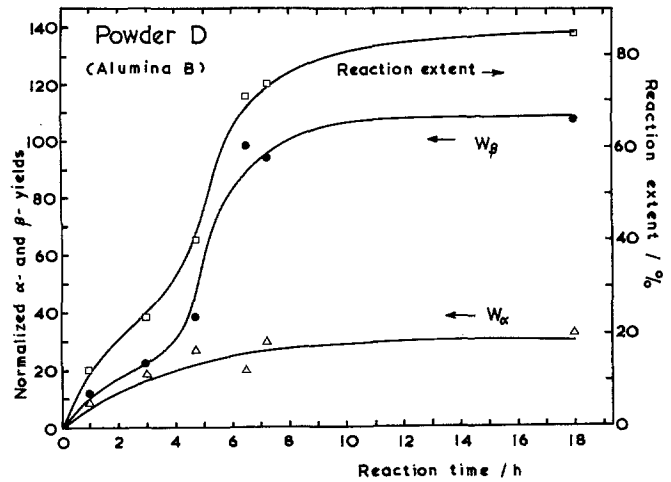
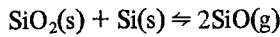


Figure 2 Reaction extent and product yield for two grades of silicon powder, plotted against time of reaction at 1365°C.



thickness of the order of 2 nm would be required. At 1365°C the reactions



provide equilibrium partial pressures of silicon monoxide and oxygen of approximately 4×10^{-3} and 10^{-20} bar respectively. Evaporation of silica would be expected to occur provided the oxygen pressure were maintained below approximately 2×10^{-3} bar and the silicon monoxide were continuously removed. These values will of course be only a guide to the actual pressures because of the essentially non-equilibrium nature of the system, and the small percentage of other oxides and silicates present.

It would appear, therefore, that the formation of the alpha-phase of silicon nitride can be associated with the existence of silica (or silicon monoxide) within the nitriding compact. When loss of surface silica by evaporation is complete the reaction may accelerate, but due almost entirely to an increased rate of production of the beta-phase. It has been suggested that solid state diffusion processes are relatively insignificant in the silicon nitridation reaction, and that the dominant mechanism is that of the vapour phase transport of reactants, with interaction taking place at suitable nuclei, or nitride surfaces [4]. These results imply that when silicon is carried to the reaction site as silicon monoxide the alpha-phase develops; when the silicon is present as silicon vapour, only the beta-phase is produced.

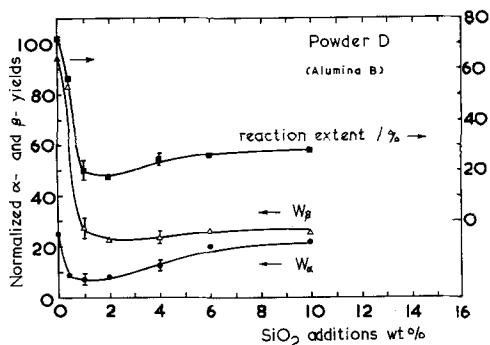


Figure 3 The effect of silica additions to silicon powder D on reaction extent and product yield, after 6 h at 1365° C.

Supporting evidence for a relationship between the presence of silicon monoxide and the formation of the alpha-phase is contained in the results of experiments in which small percentages of silica (B.D.H. precipitated grade) were incorporated in the silicon powder compacts, also nitrided in tubes of alumina B. The beta-forming reacting is markedly retarded although the alpha-forming reaction is relatively unaffected (Fig. 3). This effect is also seen in the reference compacts of silicon (without silica addition), placed alongside the mixed samples in the zirconium gettered reaction tube (Fig. 4). The probable explanation for the action of this added silica is that in providing background partial pressures of silicon monoxide and oxygen, it suppresses the evaporation of silica from the silicon surfaces, and prolongs the slower "alpha-stage" of the reaction. It is well-known that the alpha-phase can be prepared by the large scale reaction between silicon monoxide and nitrogen [5], and the involvement of silicon monoxide in powder nitridations has long been suspected [6].

This work indicates that the presence of oxygen aids the formation of the alpha-phase. Earlier results, however, have shown that the phase can be formed in gettered high purity systems in which only traces of oxygen were likely to have been present [7], and crystals have now been prepared having oxygen contents close to zero [8]. Taken together these facts suggest that the main function of the oxygen is that of a silicon carrier, and that it is the form in which the silicon arrives at a developing nitride surface which determines the crystal structure. This is additional evidence that the alpha and beta phases of silicon nitride should

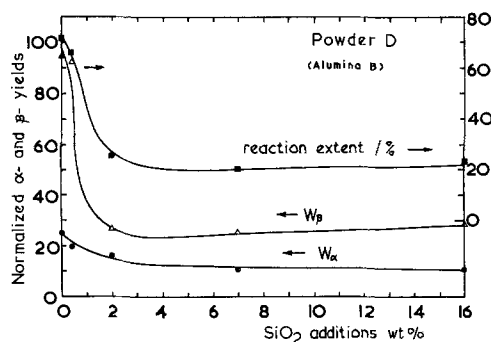


Figure 4 Reaction extent and product yield after 6 h for reference compacts of powder D, nitrided at 1365° C together with silica-containing compacts (Fig. 3).

be regarded as polymorphs, the beta phase having the slightly lower energy [9]. The concentration, and type, of impurity in the nitriding system, or the form in which silicon is supplied to the growing nucleus, appear to control which phase develops although only very small amounts of these other components may be incorporated in the crystal structure. In this respect silicon nitride would be showing features broadly similar to those of silicon carbide, for which vapour phase impurities have been found to favour strongly growth of hexagonal structures as opposed to that of the cubic structure [10]. Many other examples of this phenomenon are of course known [11].

Alternative mechanisms for the action of metallic impurities in affecting the proportions of alpha- and beta-nitride formed, besides the possible direct assistance of the beta-phase formation, now have to be considered. One possibility is that the oxides operate in part by accelerating the volatilization and ultimate disappearance of silica films. Another is that by combining with silica, silicon monoxide partial pressures are reduced relative to that of silicon vapour. It is clear that the overall course of the nitridation of a specific silicon powder is likely to be determined in a complex way by both oxygen and metallic impurity levels, and that these two factors are unlikely to operate independently.

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