On Si nitriding kinetics and mechanisms

Reaction-sintered Si_3N_4 has potential applications as components in gas turbine engines owing to its fabricability and low cost. Considerable research has been devoted to investigating the reaction-sintering kinetics, but an understanding of the mechanisms is still far from complete. The reason for this is that the reaction-sintering process is complex and probably encompasses more than a single mechanism. For example, previous investigators have reported the following kinetic rate laws: erratic behaviour [1, 2], linear [3–5], parabolic [3, 6, 7], logarithmic [1, 3, 6], and continuously diminishing kinetics [8, 9].

The objective of this communication is to show that the kinetic data from many of the above investigators fit a linear rate law initially, followed by slower kinetics (in most cases). The results will be correlated with possible rate-determining mechanisms. This communication re-analyses previously published data on the per cent nitridation of Si as a function of time. The kinetics are determined from the time exponents n and m for a general exponential relation and nucleation/growth relation [10] in Equations 1 and 2, respectively, as shown below:

$$X = k_1 t^n \qquad (1)$$

$$V_V = 1 - \exp - k_2 t^m, \qquad (2)$$

where X is the weight per cent Si_3N_4 formed in time t, k_1 and k_2 are constants, V_V is the volume per cent Si_3N_4 formed in time t. In Equation 1 n is calculated from the slope of the data on log X–log t graphs. On rearranging Equation 2 and taking the double (natural) logarithm of $1/(1 - V_V)$ the slope m is determined.

The plotted data and calculated slopes are shown in Figs. 1 to 4. These plotted data were taken from both experimental data points and smoothed kinetic curves. The slopes were determined from linear regression curves fitted to the data points. The correlation coefficients of the regression lines were $\geqslant 0.99$. The 95% confidence intervals of the slopes were typically less than ±15% of the calculated values.

The results of the curve fitting indicate that the initial kinetics follows an approximately linear rate law ($n \approx 1$) for at least 5 to 25% nitridation.

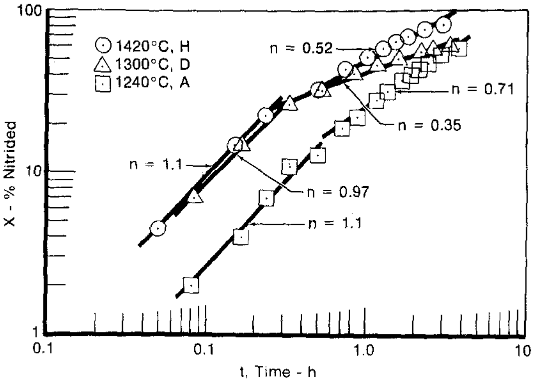

Figure 1 Plot of log X versus log t for Popper and Ruddlesden [2].

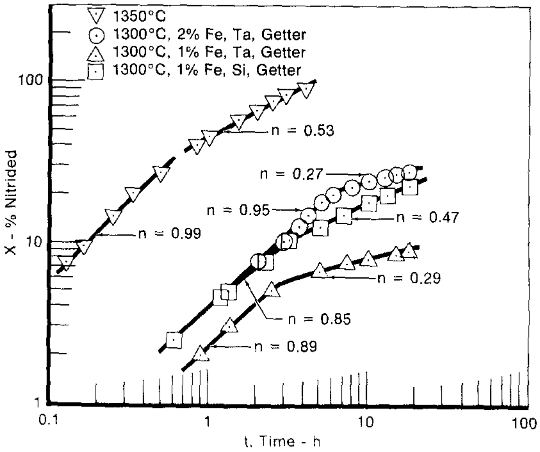

Figure 2 Plot of log X versus log t for ▽ (Billy [3]) and ○, △, □ (Messier and Wong [7]).

For longer times, in Figs. 1 to 3, the kinetics usually slows down to either an approximately parabolic ($n \approx 0.5$) or diminishing rate ($n \lesssim 0.5$). The nucleation/growth relation in Equation 2 fits the data in Fig. 3. This also fits other investigator's [2, 7] data in Figs. 1 and 2. Although not shown, the diminishing rate data in Figs. 1 to 3 could be fitted by linear curves when plotted as a logarithmic function, e.g. X versus log $(t + 1)$.

The linear rate law ($n = 1$) has been correlated with the following mechanisms: N_2 gas transport to the Si particle surfaces [6, 11], gas–solid phase-boundary reaction [5, 12], growth of Si_3N_4 nuclei [8, 9] and growth of whiskers [13]. The gas-transport mechanism may be rate-controlling for the fine particle sizes, e.g. 3 to 11 μm Si in

0022–2461/79/071752–03 $2.30/0

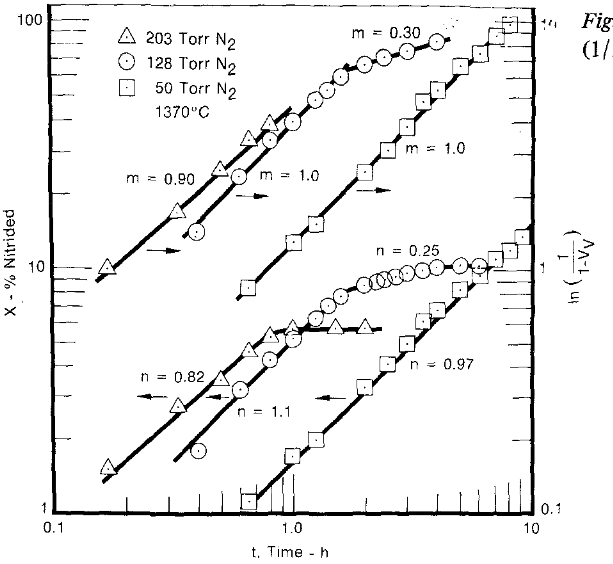

Figure 3 Simultaneous plots of log X and log log $(1/1-V_V)$ versus log t for Atkinson *et al.* [8].

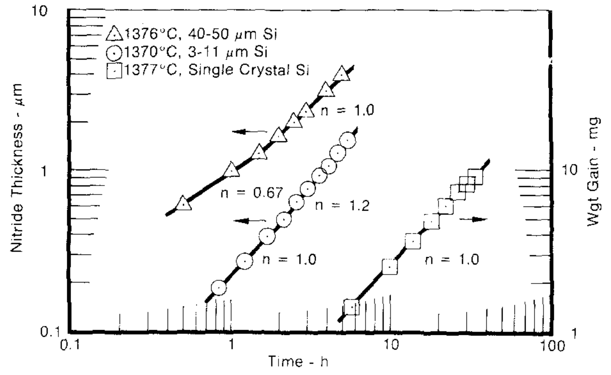

Figure 4 Simultaneous log–log plots of nitride thickness and weight gain versus time for △, ○ (Huttinger [4]) and □ (Huttinger [5]).

Fig. 4, where small pore diameters restrict N_2 penetration into the powder compact [11]. However, since most of the presented data are based on coarser particle sizes, gas transport probably is not rate-controlling.

The phase-boundary reaction can occur due to gas adsorption or molecular dissociation at the particle surfaces. The dependence of the nitriding kinetics on P_{N_2} (Fig. 3) in the range 128 to 400 Torr [8, 9] is consistent with Langmuir adsorption. Adsorption has been reported [5] to be dominant in the nitriding of single-crystal Si (Fig. 4). Also, since the initial oxidation of single-crystal Si [14] has been observed to occur by gas adsorption without molecular dissociation, N_2 adsorption is expected to be rate-controlling if nitridation and oxidation occur by similar mechanisms.

Classical nucleation and growth models have been developed for Equation 2 according to Fine [10] to explain various experimentally determined m values. For example, by assuming instantaneous Si_3N_4 nucleation on Si particle surfaces and diffusion-controlled radial growth of disc-shaped nuclei of constant thickness, a value of $m = 1$ is obtained. Also, one-dimensional growth of thin Si_3N_4 whiskers extending into pores (where long-range diffusion is not required), either by vapour transport or a vapour–liquid–solid mechanism [13] yields a linear growth rate. Other models for combined nucleation and growth give $m > 1$ [10] and are not compatible with experimental observations [8, 9].

The parabolic rate low ($n \approx 0.5$) in Figs. 1 and 2 can be explained by two mechanisms: thickening of Si_3N_4 nuclei and radial growth of a surface layer on the Si particle surfaces. For instantaneous nucleation of Si_3N_4 and one-dimensional diffusion-controlled growth of the disc-shaped nuclei, the thickness has been shown to give $m = 0.5$ [10]. Also radial diffusion-controlled growth of a Si_3N_4 mat or surface layer on Si particles has been reported to obey Janders' relation [15] for $n = 0.5$ [7].

The diminishing kinetic rate ($n < 0.5$) in Figs. 1, 2 and 3 may be due to Si_3N_4 nuclei growth impingement [9]. The radial disc growths of Si_3N_4 nuclei (for $m = 1$) eventually impinge upon each other, "choking-off" the kinetics and reducing the rate law. Also, microcracks caused by the ~22% volume expansion during the phase transformation $Si \rightarrow Si_3N_4$ [6], can act as diffusion barriers to reduce the kinetics, yielding a logarithmic rate law [16].

At present, it is difficult to generalize about which mechanisms are rate-controlling during each stage of the nitriding kinetics. The difficulty arises due to investigators using different particle size distributions, green densities, Si powder purities, N_2 gas purities and sources of gas impurities (e.g. oxygen) in the furnace. Nevertheless, the initial nitriding kinetics can be consistently described by an approximately linear rate law, which subsequently is followed by multi-stage rate laws.

Acknowledgements

The author wishes to thank Dr M. Watson and Mr W. Forrester for their assistance in this work.

References

1. J. W. EVANS, and S. K. CHATTERJI, *J. Phys. Chem.* **62** (1958) 1064.
2. P. POPPER and S. N. RUDDLESDEN, *Trans. Brit. Ceram. Soc.* **60** (1961) 603.
3. M. BILLY, *Ann. Chim. (Paris)* **4** (1959) 795.
4. K. J. HUTTINGER, *High Temp. High Press.* **1** (1969) 221.
5. *Idem, ibid* **2** (1970) 89.
6. D. S. THOMPSON and P. L. PRATT, "Science of Ceramics", Vol. 3, edited by G. H. Stewart (Academic Press, New York, 1967) pp. 33–51.
7. D. R. MESSIER and P. WONG, *J. Amer. Ceram. Soc.* **56** (1973) 480.
8. A. ATKINSON, A. J. MOULSON and E. W. ROBERTS, *J. Mater. Sci.* **10** (1975) 1242.
9. *Idem, J. Amer. Ceram. Soc.* **59** (1976) 285.
10. M. E. FINE, "Introduction to Phase Transformations in Condensed Systems" (Macmillan, New York, 1964) pp. 62–78.
11. I. AMATO, D. MARTORANA and M. ROSSI, *Powder Met.* **18** (1975) 339.
12. A. ATKINSON, P. J. LEATT and A. J. MOULSON, *Proc. Brit. Ceram. Soc.* **22** (1973) 253.
13. R. S. WAGNER and W. C. ELLIS, *Trans. AIME* **233** (1965) 1053.
14. B. E. DEAL and A. S. GROVE, *J. Appl. Phys.* **36** (1965) 3770.
15. W. D. KINGERY, "Introduction to Ceramics", (Wiley, New York, 1960) p. 335.
16. U. R. EVANS, *Trans. Electrochem. Soc.* **91** (1947) 547.

Received 4 September
and accepted 6 December 1978

M. I. MENDELSON
Pratt & Whitney Aircraft Group,
West Palm Beach,
Florida 33402, U S A

Comments on "A model of fatigue crack growth in polymers"

Williams has proposed an interesting model to describe fatigue crack propagation (FCP) in polymeric solids and to account for a number of experimental observations [1]. The purpose of this communication is to (1) examine the basic assumptions underlying the model, (2) compare recent data with values predicted from the model, and (3) present alternative explanations for polymer fatigue behaviour.

The first assumption is that upon unloading and reloading a craze at the crack tip, some of the craze ligaments become damaged, thereby reducing the craze stress σ_c. From this a two-stage craze zone is envisioned in which the newly formed craze material at the craze tip experiences a stress σ_c while the remaining part of the craze sustains a lower stress, $\alpha\sigma_c$. Use of this assumption leads to values of σ_c and $\alpha\sigma_c$ for several polymers in the ranges 325 to 720 and 29 to 2016 MPa, respectively (see Table II in [1] and [2]). In contrast, use of the Dugdale plastic strip formulation leads to

0022–2461/79/071754–05 $2.50/0