

The reasons for the differences between lines 1 and 2 are unknown at present. The major known difference between group I and group II experiments is the inclusion of compacts prepared from fine silicon powders in group II experiments and the influence of one type of silicon powder compact upon another during nitriding may be important.

The fact that we have observed differences between groups of experiments is of importance and indicates that caution must be exercised when comparing data obtained from different groups of experiments. The inclusion of control samples in comparative experiments appears necessary, although even this approach may not be entirely satisfactory due to the possibility of interaction between experimental and control materials.

In our earlier paper [1] we discussed the observation that compacts of powder P nitrided to weight gains greater than 60% frequently have mean strengths which fall below the values expected from the strength/density relationship. This observation was based on data accumulated at this laboratory from experiments in different furnaces, using various nitriding schedules and variable furnace contents. We suggested [1] that the explanation for this might be the existence of a flaw other than the largest effective pore which becomes strength controlling at higher weight gains when the pores are becoming small. Whilst such an explanation cannot be disregarded, attention is drawn to line 3 in Fig. 1 which represents the lower bound of the data. Lower than anticipated strength values are most probably the consequence

of a change in the previously derived strength/density relationship [1] caused by as yet unidentified variable parameters in the nitriding process. These low values are probably related to another strength/density relationship pertinent to the particular conditions existing during the experiments concerned.

It is interesting to speculate that if the variation of unidentified parameters can lead to a lower strength/density relationship than that recorded for group I experiments [1], then other conditions may be attainable when a higher strength/density relationship applies. Consequently, identification of the parameters which cause the observed changes in the relationship could lead to the development of stronger reaction sintered silicon nitride.

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#### References

1. B. F. JONES and M. W. LINDLEY, *J. Mater. Sci.* **10** (1975) 967.
2. *Idem*, *Powder Met. Int.*, to be published.

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#### *Plastic deformation of $Ni_{0.66}Fe_{2.34}O_4$ spinel ferrite single crystals*

Plastic deformation of oxides with the spinel structure has so far been studied through the example of  $(Al_2O_3)_n MgO$ . Some consistent results begin to appear [1, 2]. It is for example well accepted that glide directions are  $\langle 110 \rangle$  and that glide planes depend on the stoichiometric ratio  $n$ ; glide on  $\{111\}$  planes seems to occur for stoichiometries  $n = 1$  and  $n = 3$  whereas  $\{110\}$  glide planes are activated for  $n \sim 2$  [3–5]. In the present note, preliminary results are given of an

extensive investigation of the mechanical properties of an alternative spinel compound  $NiFe_2O_4$ .

Single crystals of  $Ni_{0.66}Fe_{2.34}O_4$  ( $8 \times 3 \times 3$  mm<sup>3</sup>) with  $\langle 001 \rangle$ ,  $\langle 011 \rangle$  and  $\langle 111 \rangle$  large axes have been strained between 1190 and 1516°C (0.73 to 0.9  $T_M$ ) in compression under constant strain-rate ( $\sim 2.5 \times 10^{-4}$  sec<sup>-1</sup>). After deformation, slip lines were observed either directly on suitably polished faces (Fig. 1) or after etching a few seconds in boiling HCl. Specimens were found to deform on  $\{111\}$  slip planes. An electron microscopic complementary study has shown

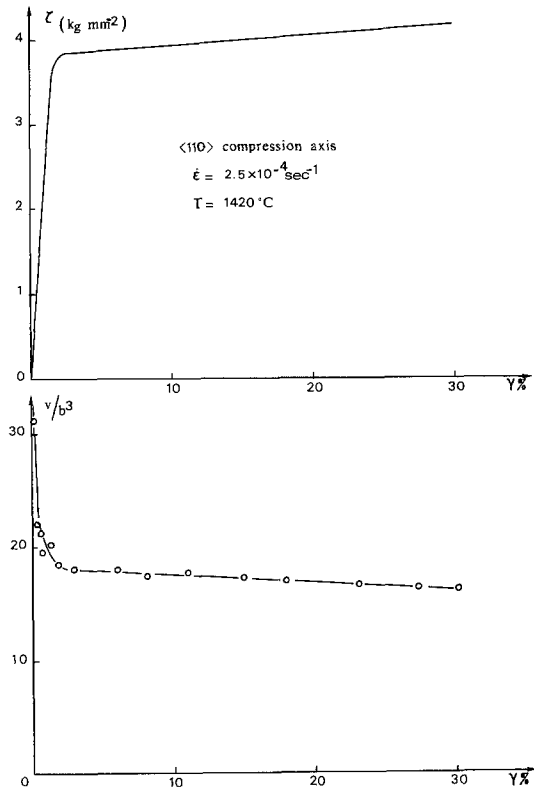


Figure 1 Typical stress-strain curve and variation of the associated activation volume.

that, as expected, glide directions were  $\langle 110 \rangle$ . Since constitutional cation vacancies are not present in  $\text{Ni}_{0.66}\text{Fe}_{2.34}\text{O}_4$  ( $\text{Ni}_{0.66}^{2+}\text{Fe}_{0.34}^{2+}\text{Fe}_{0.34}^{3+}\text{O}_4^{2-}$ ) this result is fully consistent with those concerning  $\text{MgAl}_2\text{O}_4$ . Electron microscope observations also revealed that deformation was inhomogeneous since dislocations were absent in extremely large thin areas (tens of  $\mu\text{m}^2$ ), even after 30% deformation, as in the as-grown boules (dislocations are not mobile at temperatures where chemical thinning was carried out so that thin foils are believed to be representative of the bulk material). In areas where they were observed, dislocations generally form low-angle boundaries [6].

The stress-strain curve shown in Fig. 2 has been obtained at  $1480^\circ \text{C}$  ( $0.85 T_M$ ) and is typical of those obtained with the three compression axes ( $\langle 001 \rangle$ ,  $\langle 011 \rangle$ ,  $\langle 111 \rangle$ ) and in the above temperature range. The observation of only one stage in the work-hardening curve is con-

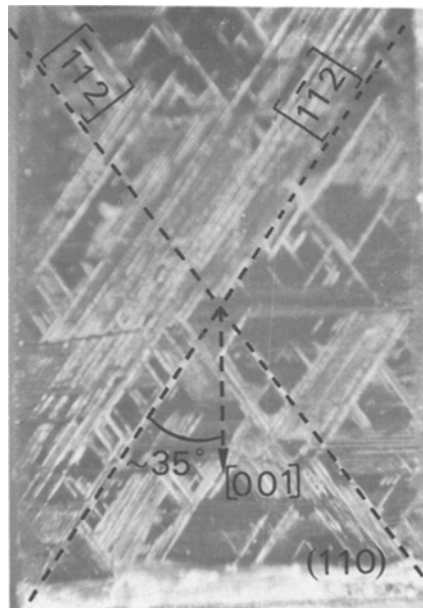


Figure 2 Glide lines of a  $(110)$  face of a  $\text{Ni}_{0.66}\text{Fe}_{2.34}\text{O}_4$  single crystal deformed at  $1420^\circ \text{C}$  along  $[001]$ .

firmed by stress relaxation determinations of apparent resolved activation volume  $v_a$  which is found to be approximately constant:  $v_a \sim 16b^3$ . Apparent activation enthalpy  $\Delta H_a$  has been calculated from conventional and differential tests, a value of  $4.5 \pm 0.5 \text{ eV}$  has been found. Determinations of  $\Delta H_a$  and  $v_a$  are consistent with dislocation glide controlled by climb as could be expected at such a temperature and as confirmed by electron microscope observations of low-angle subgrain boundaries the formation of which is controlled by climb [6].

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### References

1. G. R. TERWILLIGER and K. C. RADFORD, *Amer. Ceram. Soc. Bull.* **53** (1974) 172.
2. K. C. RADFORD and G. R. TERWILLIGER, *ibid* **53** (1974) 465.
3. M. H. LEWIS, *Phil. Mag.* **17** (1968) 181.
4. K. C. RADFORD and C. W. W. NEWWEY, *Proc. Brit.*

- Ceram. Soc.* 9 (1967) 131.  
 5. N. DOUKHAN, R. DUCLOS and B. ESCAIG, *J. Phys. C* 9 (1973) 379.  
 6. P. VEYSSIÈRE, J. RABIER, H. GAREM and J. GRILHÉ, *Phil. Mag.*, to be published.

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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 ( $\mu\text{m}$ )	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  $1600 \text{ kg m}^{-3}$ , and the nitrogen flow rate was  $10 \text{ ml min}^{-1}$ . 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 ( $1365^\circ \text{C}$ ) 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

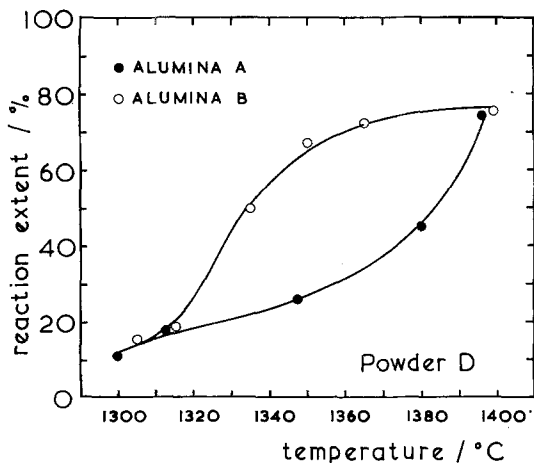


Figure 1 Reaction extent after 6 h for silicon powder D, plotted against temperature, using two grades of alumina reaction tube.