breaking of Si–O bonds. The outlined diffusion mechanism in SiO_2 also seems to hold for high temperature (1100 to 1500° C) corrosion of SiC and Si_3N_4 during which SiO_2 layers form. Activation energies of 20 to 30 kcal mol^{-1} were observed in the oxidation (parabolic regime) of SiC [15, 16] and around 25 to 35 kcal mol^{-1} for pure Si_3N_4 [17, 18]. The activation energy for the oxidation of impure Si_3N_4 increases with impurity content [19]. Instead of pure SiO_2, the impure Si_3N_4 forms silicate glass layers that presumably have higher activation energies of tracer oxygen diffusion.

Acknowledgement

This work was supported in part by NATO Research Grant 1019.

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Received 19 September
and accepted 1 November 1977

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Kinetics of solid state $NiFe_2O_4$ formation at 700 to 1400° C

Ferrites are fabricated by heating powders, and many processing variables, e.g. powder purity, size distribution, type, etc., effect the reaction rate [1]. Activation energies for $NiO + Fe_2O_3 = NiFe_2O_4$ have varied from 105 and 185 kJ mol^{-1} [2] and 225 to 293 kJ mol^{-1} [3]. In the present work spectrographically pure (J. Matthey) NiO and Fe_2O_3 with sieved particle sizes of 15.6 to 33.0 μm were used. Equimolar amounts were mixed by hand for over 1 h, pressed in a steel die without binder or lubrication to form a pellet 10 mm diameter and 4 mm thick, placed in a recrystallized alumina boat, and fired in air within a temperature variation of ±3° C. The amount of $NiFe_2O_4$ formed was measured by the force in a magnetic field. Chamfered pole pieces of an electromagnet gave a region of constant field gradient and a double pan chemical balance was used to measure the force. A phosphor bronze cantilever was used to prevent the specimen being attracted to either pole. Its stiffness could be neglected during weighing when the specimen returned (checked by a cathetometer) to a null position. A Cu specimen holder was used to hold about 100 mg powdered sample. The force per unit mass of sample versus mol% $NiFe_2O_4$ in a range of NiO, Fe_2O_3 and $NiFe_2O_4$ mixtures was linear and used to determine the unknown amount of $NiFe_2O_4$ in a sample.

Compacting pressures in the range 10 to 100 MPa did not affect the amount of $NiFe_2O_4$

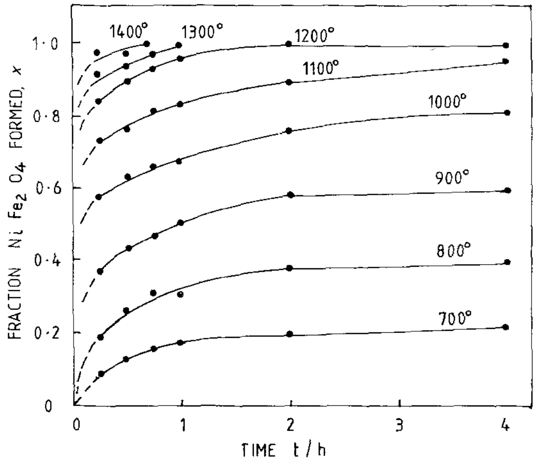

Figure 1 Amount of $NiFe_2O_4$ formed as a function of time at 700 to 1400° C.

formed after 30 min at 800° C, or at 1400° C, and 30 MPa was used on all further samples. The results are shown in Fig. 1. Jander [5] showed that for reacting spheres in which the reaction product formed a spherical diffusion barrier shell, the fraction x formed after time t follows the equation

$$\{1-(1-x)^{1/3}\}^2 = Kt$$

The results are shown as a Jander function in Fig. 2. Typically the data do not go through the origin and deviate at larger times [2–4], and the limitations of the Jander function have been discussed [4–6]. However, we consider that the results are consistent with a Jander-type model, not of spheres touching but of squashed spheres with a substantial area of contact. We consider the initial fast reaction to be due not so much to a higher intrinsic surface reactivity [7] but to a larger surface area because of particle surface micro-geometry. Surface peaks have a higher surface to volume ratio and react faster. Once a shell of reaction product has formed, the conditions for Jander's equation is approximated in most particles and it is closely followed for a time (Fig. 2). For a coordination number 12 (say) the probability of a NiO particle being surrounded by 12 Fe_2O_3 particles is only 12 $(0.5)^{12}$ and the probability of other configurations are given by other terms in the binomial expansion. The point is that there are many NiO and Fe_2O_3 groups, and these have a diffusion length much larger than a particle radius which slows the reaction rate compared to the value predicted on the basis of a uniform particle size. The Arrhenius function of the initial gradient of the Jander plot is shown in Fig. 3 and the least mean squares calculated activation energy is 97 kJ mol^{-1}. This is small compared with previous values, and it may be that impurities in the less-pure substances interact with diffusing species and make its motion more difficult.

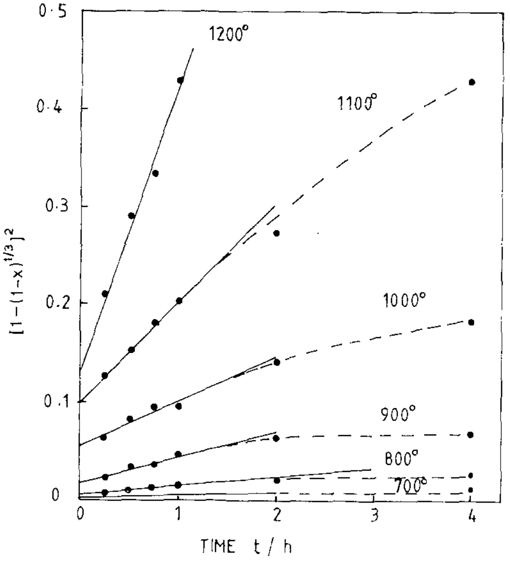

Figure 2 Jander plot of data. x is the fraction of $NiFe_2O_4$ formed. Points at 700° C not shown.

Acknowledgements

This work was submitted by JL as an undergradute project in a CNAA degree in Applied Physics.

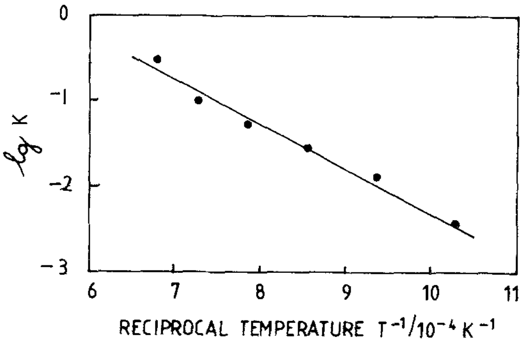

Figure 3 Arrhenius function of the initial linear gradient of Jander plot.

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Received 19 September
and accepted 1 November 1977.

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