of d.c. operation, while those cut perpendicular to the rolling direction broke, also at the anode, but after an average time of 12.5 h.

The d.c. current intensities necessary to hold the central region of the specimens at 1460° C were: $I_{\parallel} = 28$ A in the rolling direction and $I_{\perp} = 21$ A perpendicular to the rolling direction. This measurement permits an evaluation of the resistivity anisotropy. Noting resistivities in the [100] and [110] directions, $\rho_{\parallel}$ and $\rho_{\perp}$ respectively, we have

$$\frac{\rho_{\perp}}{\rho_{\parallel}} = \frac{I^2_{\parallel}}{I^2_{\perp}} = 1.7\,.$$

This result confirms reports in the literature for the same alloy [6].

An attempted comparison of the matter fluxes in both directions was made from these experiments. The ratio of the fluxes should equal the reciprocal of the ratio of current passage times until rupture. $\dot{m}_{\parallel}$ and $\dot{m}_{\perp}$ are the matter fluxes in the [100] and [110] directions respectively, therefore

$$\dot{m}_{\parallel} \simeq 25\,\dot{m}_{\perp}\,.$$

There is, therefore, a marked anisotropy of matter transport between both specimen directions. The matter flux ratio is much higher than the ratio of resistivity (apart from being in the opposite direction). Bulk electromigration is theoretically proportional to the resistivity [1], but our experiments show that resistivity anisotropy cannot explain, even qualitatively, the observed electromigration anisotropy. A quite high anisotropy of the diffusion coefficient is also implied.

Bulk electromigration suffices to explain that the final rupture was systematically found near the anode: vacancies accumulate at this point in a transition region which is at a somewhat lower initial temperature. The accumulation of vacancies and their condensation, as internal voids or at the surface, reduces the useful cross-section of the specimen and increases either the macroscopical resistivity, or microscopic local current density, which accelerates the electromigration process until rupture occurs either by matter depletion, or by overheating.

A remarkable aspect of electromigration in silicon steel is its marked anisotropy, the rolling direction being preferred. The reason for this, and especially grain-boundary migration anisotropy, is not evident, neither grain shape nor grain substructure are isotropic; alignment of defects of solute, or of impurities as dipoles may also play some role. Whichever is the cause, it is even more remarkable that this anisotropy is not destroyed by diffusion itself, even quite near to the melting point.

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Oxygen content of α—Si_3N_4 Single crystals

It was proposed by Wild *et al.* [1] from structural and thermodynamic data that α-Si_3N_4 had a composition of $Si_{11.4}N_{15}O_{0.3}$ (0.90 wt % oxygen content) or $Si_{11.5}N_{15}O_{0.5}$ (1.48 wt % oxygen conent). Priest *et al.* [2] analysed a sample of pure α-Si_3N_4 prepared by chemical vapour deposition for oxygen content using a 14 MeV neutron activation analysis technique; the result was 0.30 ± 0.005 wt %. Edwards *et al.* [3] also analysed various samples of reaction-bonded Si_3N_4 and reported that the calculated oxygen content of α-silicon nitride lay between 0.45 ± 0.05 and 0.61 ± 0.06 wt %. The studies cited above were all carried out using polycrystalline samples or a mixture of α and β forms.

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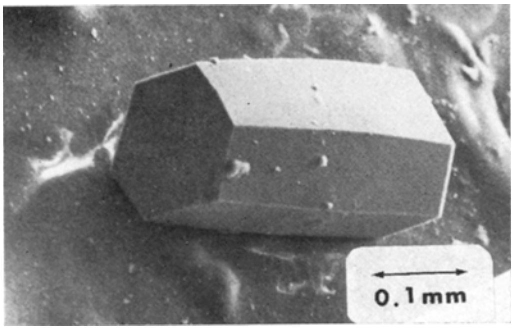

Figure 1 Example of a prismatic single crystal used for oxygen content analysis.

We prepared single crystals of α-Si_3N_4 by chemical vapour deposition on a graphite susceptor using a mixture of $SiCl_4$, N_2, and H_2 gases, and examined them for oxygen content by 14 MeV neutron activation analysis. Details of the apparatus and procedure employed for preparation are given elsewhere [4, 5]. The equilibrium oxygen partial pressure during crystal growth at high temperature was calculated as 6.9×10^{-20} atm [5]. Fig. 1 shows an example of a hexagonal prismatic single crystal obtained by this method. For the analysis two types of samples, A and B, were prepared. Sample A was prepared by collecting well developed single crystals, such as shown in Fig. 1, under an optical microscope, from the products of 30 growth experiments. Sample B consisted of inter-grown or less clear crystals. The result of oxygen determinations from sample A was 0.05 wt %, with an estimated standard deviation of 0.03 wt %, while sample B contained 0.09 wt % oxygen, with an estimated standard deviation of 0.02 wt %.

One of the well developed single crystals, as shown in Fig. 1, was also examined by X-ray diffraction [6]. The unit-cell dimensions of the crystal were $a = 7.818 \pm 0.003$ and $c = 5.591 \pm 0.004$ Å. The determined Si–N distances were between 1.715 and 1.759 Å, and the occupancy parameters for the sites N(1) and N(4) were within the range $1 \pm 2\sigma$.

It is concluded from the results of oxygen content analysis and of structure measurement, using α-Si_3N_4 single crystals prepared under well controlled conditions, that α-Si_3N_4 is a polymorph of Si_3N_4 and not a kind of oxynitride such as $Si_{11.5}O_{0.5}N_{15}$. The possible existence of a new phase between Si_3N_4 and Si_2ON_2 is another question.

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