Letters

Note on electromigration of grain boundaries in silicon iron

Electromigration (i.e. transport of matter under the influence of an electric field) has been studied in a great number of metals and alloys [1]. Accompanying this, a small displacement of crystalline defects, e.g. grain boundaries, takes place [2, 3]. In the present study, we report the results of a series of experiments on the electromigration of grain boundaries, in transformer sheet steel, under protective atmosphere in the 650 to 1460° C temperature range.

The material used was silicon iron (about 3.1 % Si), in the form of hot-rolled sheet, 0.35 mm thick. The substitutional alloy of this composition lies, over the whole temperature range in the α-region of the phase diagram [4]. Macroscopic examination of the sheet after chemical attack reveals grains of large size (2 to 3 cm long, 1.5 to 2.2 cm wide); boundaries are visible to the naked eye; these grain sizes were quite convenient for electromigration experiments. X-ray examination by transmission on numerous grain showed a strong (1 1 0) [1 0 0] texture in the rolling direction and also a substantial proportion of the grain boundaries is of the nearly pure tilt type, their tilt axes lying in the plane of the sheet, with a mean disorientation of about 2°.

The experiments were carried out using U-shaped specimens, (Fig. 1) cut in such a manner that the chosen rectilinear grain boundaries run across the centre of the U branches [5]. Specimens were first heat-treated at 1150° C under vacuum for 24 h, and electropolished.

A small amplitude of grain-boundary migration implies high temperature experimentation, involving fast diffusion and also fast oxidation. Therefore it was necessary to perform the experiments under a protective argon atmosphere, in a gas-tight chamber (Fig. 1). A vacuum port, argon entry and exit ports were fitted to the lower part of the chamber and also a transparent observation window, allowing specimen temperature measurement by means of an external optical pyrometer.

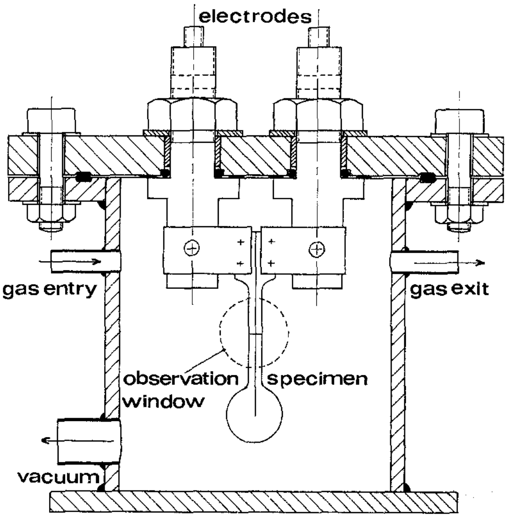

Figure 1 Experimental apparatus and specimen arrangement.

In the temperature range 650 to 1260° C, observations of grain-boundary migration were consistently negative for all specimens, with their length cut either along the rolling or the transverse direction of the sheet, even for periods amounting to 20 days. At 1260° C, however, no migration of grain boundaries could still be detected, but the specimens cut parallel to the rolling direction consistently broke near the anode after about 6 days, while the specimens cut perpendicular to the rolling direction did not break even after 20 days. There is, therefore, a marked anisotropy in the speed of transport of matter.

At 1460° C, i.e. only about 30° C below melting temperature, two distinct phenomena were observed. The first concerns electromigration of grain boundaries: for specimens cut parallel to the rolling direction, that is, near to a [1 0 0] axis, we observed a quite fast electromigration of grain boundaries, their average speed being 0.22 $\mu m\ sec^{-1}$, towards the cathode. This phenomenon is similar to that previously observed for various pure metals near to their melting points [2], except aluminium which, as we have shown [3], behaves in a quite different manner. For specimens cut perpendicular to the rolling direction, i.e. in the [1 1 0] axis, no migration of grain boundaries could still be detected.

The second phenomenon deals with the transport of matter along the specimen: the specimens cut parallel to the rolling direction broke at the anode after an average time of $\frac{1}{2}$ h 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.

References

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Received 17 July
and accepted 29 July 1974

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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.