JOURNAL OF MATERIALS SCIENCE 5 (1970) 96-99

An Electron Microprobe Study of Internal Oxidation in a Silver-Manganese Alloy

J. LÉVY,* P. NIESSEN
Materials Laboratory, Department of Mechanical Engineering, University of Waterloo, Ontario, Canada

A quantitative study of internal oxidation in a silver-10 at. % manganese alloy was performed. This alloy does not exhibit any external oxide layer after oxidation in air at high temperatures and its high manganese content allowed accurate microprobe analysis. The experimental results are in very good agreement with the predictions of Wagner's theory and yield values for the diffusion coefficient of manganese in silver consistent with previous determinations. Experiments performed on silver/silver - 10 at. % manganese diffusion couples have shown that this is true over a wide range of concentrations.

1. Introduction

Much consideration has been given to the internal oxidation of noble metals [1-5] as a possible strengthening mechanism. However, in most of the previous investigations the oxide-forming solutes were kept at very low levels, for two reasons: either their solubilities in the nobler metals were small or, if their concentrations were high, surface oxides formed which interfered with the internal oxidation process. This is not the case for the silver-manganese alloys where even at 14 at. % manganese, the solubility limit at room temperature, no external manganese oxide forms under atmospheric oxygen pressure. These alloys are therefore very convenient for a quantitative study of the distribution of manganese during internal oxidation because with the relatively high concentrations of manganese that may be used, accurate electron probe microanalysis is possible.

2. Experimental Procedure

A silver-10 at. % manganese alloy was prepared by melting 99.999 % silver and 99.9 % electrolytic manganese in sealed, argon-filled quartz tubes. The melt was allowed to solidify in the tube. The resulting ingot was annealed for 60 h at 850° C for homogenisation. Specimens were cut with a jeweller's saw and subsequently etched in dilute nitric acid to remove the deformed layers. One face of each specimen was ground flat on 600-mesh carbide paper and chemically polished in 10 vol % hydrochloric acid saturated with Cr_2O_3. (Many attempts to electropolish this alloy have been unsuccessful.) This polished face was later taken as a reference plane for thickness measurements of the internally oxidised layer. The samples were oxidised in air at various temperatures and for various times, quenched, sectioned and polished perpendicular to the oxidation front.

In addition to the internal oxidation experiments on the 10 at. % manganese alloy, it was also desirable to follow the variation of the thickness of the oxidised layer with initial manganese concentration. Instead of preparing a series of alloys of different compositions, diffusion couples were made, of silver/silver-10 at. % manganese and of cylindrical shape, 10 mm in diameter and 15 mm high, using an experimental procedure described elsewhere [6]. The concentration profiles of manganese were measured with the electron microprobe along the axis of the samples. The couples were then oxidised in air. Considering the short oxidation times, the couples could be assumed to behave like a pack of "slices" of different compositions, being independently oxidised.

---

*Now at École des Mines, Saint Etienne, France.

3. Experimental Results

3.1. Metallography

Generally, the oxidised layer was visible after polishing because of its reddish colour, and the interface between the oxidised layer and the unoxidised part of the sample was well-defined. This interface became more difficult to locate when the manganese content was below 1 at. %; only a very deep electroetching in a potassium cyanide electrolyte could then reveal the oxidation front. The manganese oxide particles in the oxidised layer were too small to be resolved under the optical microscope. Electron microscopy on carbon replicas of a sample containing 10 at. % manganese and oxidised 2 h at 910° C (fig. 1) showed spherical particles of 1000 to 1500 Å diameter.

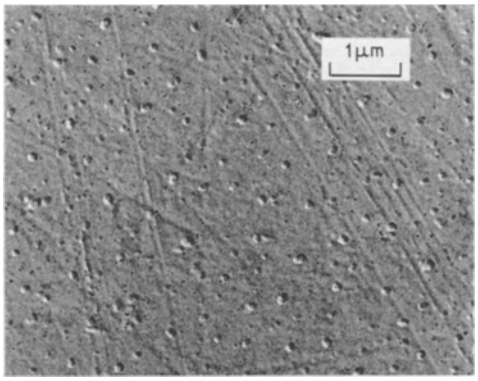

Figure 1 Electron micrograph of a carbon replica of the oxidised layer in a sample oxidised 2 h at 910° C.

3.2. Quantitative Measurements

The thickness X_p of the oxidised layer was measured under a travelling microscope with a precision estimated to be ±5 μm. The concentrations of manganese were measured with the electron microprobe, using as a reference the original alloy containing 10 at. % manganese. On samples of this alloy and, after internal oxidation, the manganese concentration profiles were measured along the direction 0x perpendicular to the oxidation front. Considering that internal oxidation is a diffusion-controlled process, each experimental curve $C_{\mathrm{Mn}}(x)$ was transformed into a standard curve $C_{\mathrm{Mn}}/C_2{}^0 = C(\lambda)$*, where $\lambda = (x/\sqrt{t})$ and $C_2{}^0$ is the original concentration of manganese (0.1 in the present case). As expected, only one standard curve corresponded to a given temperature and, in particular, the position λ_p of the interface was fixed in λ-space. Each curve can be divided into two parts (fig. 2). C is roughly constant and equal to 1 in the oxidised layer ($0 < \lambda < \lambda_p$). It increases from a very low value to 1 when λ becomes greater than λ_p, exhibiting a discontinuity at the interface, and revealing a zone depleted of manganese ahead of the oxidation front. In this connection, it should be remembered that, because of the finite electron beam size, the analysed manganese profiles would be slightly distorted. The distortion becomes higher with steeper concentration gradients.

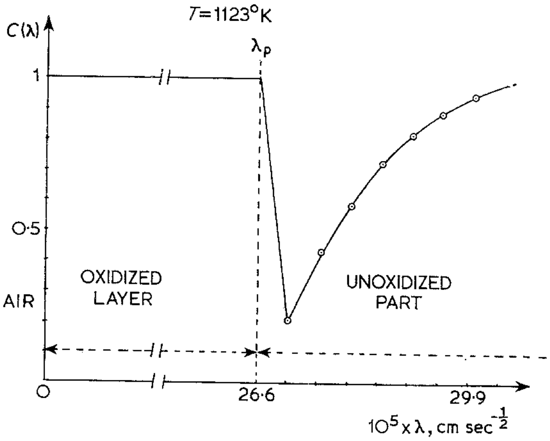

Figure 2 Standard concentration profile of manganese measured in a direction perpendicular to the oxidation front. Note the constant concentration in the oxidised layer and the zone depleted of manganese ahead of the interface.

When the temperature decreases, λ_p decreases according to an Arrhenius law, the width of the manganese-depleted zone shrinks and can no longer be detected by the probe in samples oxidised at 500° C and below.

The diffusion couple experiments gave the variation of λ_p with the initial concentration of manganese $C_2{}^0$. More precisely, the product $A = \lambda_p \times (C_2{}^0)^{\frac{1}{2}}$ was found to be constant over a large range of concentration. However, this was not true in the vicinity of the couple's interface; the imperfect welding modified the conditions of oxidation. Neither was it true at manganese concentrations below 2 at. %. Moreover, for manganese contents lower than

---

*The suffix 1 refers to oxygen concentrations and the suffix 2 to manganese concentrations.

0.5 at. % (estimated from extrapolation of the diffusion profiles) the thickness of the oxidised layer was constant, suggesting that below 0.5 at. % the manganese interferes very little with the diffusion of oxygen in the silver matrix.

We should mention here a special aspect of the behaviour of the grain-boundaries which has not yet been explained satisfactorily. A crack appears where a grain-boundary reaches the outside surface, and its depth and width increase with the severity of the oxidation conditions. Also, as shown in fig. 3, in the deeper parts of the oxidised layer the grain-boundary is surrounded by a zone depleted of manganese. Preferential diffusion of manganese is not sufficient to explain the width of the depleted zone and the very small quantity of precipitate visible at the boundary. The same depletion occurs at sub-boundaries.

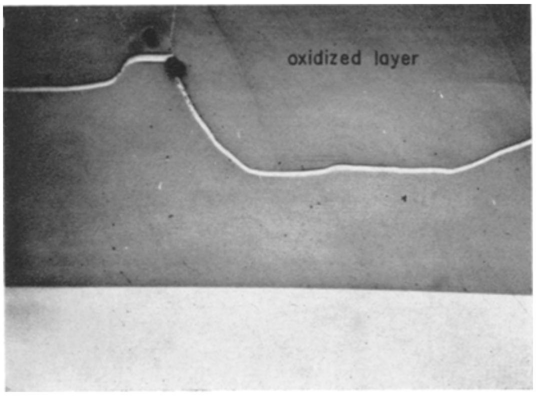

Figure 3 Micrograph showing the interface between the internally oxidised layer and the unoxidised part of the sample. Note in the oxidised layer the manganese depleted zone at a grain-boundary. Oxidation in air at 850° C for 6 h. Chemically polished (× 135).

4. Interpretation

The theory of Wagner [3] describes remarkably well most of the experimental facts. In this theory, the following assumptions are made: the concentration C_1 of *dissolved* oxygen is zero in the unoxidised part of the sample (i.e. for $\lambda < \lambda_p$); at the outside surface $C_1 = C_1^0$, the maximum solubility of oxygen in silver at the given temperature and pressure; oxygen is supposed to diffuse through the oxidised layer with the diffusion coefficient D_1 of oxygen in pure silver; the concentration C_2 of *dissolved* manganese is zero in the oxidised layer, because manganese is completely oxidised; $C_2 = C_2^0$ in the unoxidised part, far from the reaction interface (i.e. at $\lambda = \infty$); manganese diffuses in silver with a diffusion coefficient D_2.

Consequently there are two boundary conditions. First, the number of oxygen atoms reaching the interface from the outside and the number of manganese atoms from the inside are related in order to build up a stoichiometric compound MnO_n. This determines the position of the oxidation front. Secondly, all the atoms of manganese crossing the interface are oxidised. This fixes the molar concentration f of precipitates MnO_n in the oxidised zone.

From these assumptions, it is possible to assign mathematical expressions to some parameters which can then be computed and compared with the experimental values. If $\gamma = (\lambda_p/2\sqrt{D_1})$, $\phi = (D_1/D_2)$, and for the case when $\gamma \ll 1$, $\gamma\phi^{\frac{1}{2}} \gg 1$, then according to [3]

$$\gamma = \left|\frac{C_1^0}{2nC_2^0}\right|^{\frac{1}{2}} .$$

The concentration of dissolved manganese is:

$$\text{for } 0 < \lambda < \lambda_p\,,\quad C_2 = 0$$

$$\text{for } \lambda_p < \lambda\,,\quad C_2 = C_2^0\left|1 - \frac{\operatorname{erfc}(\lambda/2\sqrt{D_2})}{\operatorname{erfc}(\gamma\phi^{\frac{1}{2}})}\right| .$$

The concentration of oxide is $f \simeq C_2^0$.

Since the electron probe is unable to distinguish between dissolved and oxidised manganese, we must compare the experimental curve $C(\lambda)$ with the following theoretical relationship:

$$\text{for } 0 < \lambda < \lambda_p\,,\quad f/C_2^0 \simeq 1\,,$$

$$\text{for } \lambda_p < \lambda\,,\quad C_2/C_2^0 = 1 - \frac{\operatorname{erfc}(\lambda/2\sqrt{D_2})}{\operatorname{erfc}(\gamma\phi^{\frac{1}{2}})} .$$

In independent experiments, D_1, D_2 and C_1^0 have been measured to be:

$D_1 = 3.66 \times 10^{-3} \exp(-11\,000/RT) cm^2 sec^{-1}$ [5, 7]

$D_2 = 0.18 \exp(-42\,900/RT) cm^2 sec^{-1}$ [6]

$C_1^0 = 3.06 \times 10^{-2} \exp(-11\,800/RT)$ mole oxygen/g at. silver,

at atmospheric pressure of oxygen [5, 7].

The value of n depends on the type of manganese oxide formed and can reasonably be assumed to be either 3/2 or 1. In table I, λ has been calculated from the measured λ_p and D_1 taken from [5] and [7] ($\gamma_{(obs)}$) or from its theoretical expression where C_1^0 is given by [5] and [7], C_2^0 is fixed and n is assumed ($\gamma_{(calc)}$). In table I, these data appear. We have also given the corresponding values of γ_{obs}, $\phi^{\frac{1}{2}}$, where ϕ is calculated from [5-7]. The results suggest that the oxide formed is MnO($n = 1$). A discrepancy appears at 1183° K which could be due to the fact that $\gamma\phi^{\frac{1}{2}}$ (table I) could no longer be considered much greater than one.

TABLE I

T°K	$\gamma_{(\text{obs})} \times 10^2$	$\gamma_{(\text{calc})} \times 10^2$ $n = 1$	$n = 3/2$	$\gamma_{(\text{obs})} \times \phi^{\frac{1}{2}}$
1183	2.43	3.16	2.6	2
1123	2.6	2.77	2.26	3.1
1073	2.38	2.45	2	3.6
1023	2.08	2.14	1.75	4.95

Regarding the manganese concentration profiles, the theory predicts the observed, almost constant, value of 1 for $C(\lambda)$ in the oxidised layer ($0 < \lambda < \lambda_p$). Assuming now D_2 unknown, for each temperature an "observed" value of D_2 can be calculated by adjusting the theoretical curve C_2/C_2^0 to the experimental curve $C(\lambda)$. D_2 thus determined agreed quite well with the results of previous diffusion couple experiments [6] as can be seen in table II and this implies a good agreement between the theoretical and observed concentration profiles beyond λ_p. For the foregoing determinations of D_2, the asymptotic expansion for erfc(z) [8] has been used.

TABLE II

T°K	$D_{2(\text{obs})} \times 10^9$, cm² sec⁻¹	$D_2[6] \times 10^9$, cm² sec⁻¹
1183	4.5	5.01
1123	2.1	1.89
1073	1.3	0.896
1023	0.45	0.259

Finally, from the oxidation of diffusion couples, the measured values of $A = \lambda_p \times (C_2^0)^{\frac{1}{2}}$ have been compared with their theoretical values $(2D_1C_1^0)^{\frac{1}{2}}$, and these appear in table III.

TABLE III

T°K	$A_{(\text{obs})} \times 10^4$, cm $\text{sec}^{-\frac{1}{2}}$	$A_{(\text{calc})} \times 10^4$, cm $\text{sec}^{-\frac{1}{2}}$
1183	1.28	1.18
1123	0.766	0.9
1073	0.67	0.7
1023	0.51	0.54

5. Conclusion

The quantitative microprobe analysis performed on a silver - 10 at. % manganese alloy has shown that the effective distribution of manganese after internal oxidation is quite accurately described by the theoretical treatment of Wagner [3]. A comparison between the experimental data and the theoretical predictions has been made, assuming values for the diffusion coefficient of manganese in pure silver as determined by binary couples experiments [6]. This assumption leads to consistent results.

Another confirmation of the validity of the theory has been provided by internal oxidation experiments on diffusion couples silver/silver - 10 at. % manganese. The observed variation of the thickness of the oxidised layer with the initial concentration of manganese is in good agreement with the theoretical law.

Acknowledgement

The authors wish to thank Professor J. S. Kirkaldy for stimulating discussions and valuable suggestions.

This work has been supported by the National Research Council of Canada.

References

1. F. N. RHINES and A. H. GROBE, *Trans. Met. Soc. AIME* **147** (1942) 818.
2. J. L. MEIJERING and M. J. DRUYVESTEYN, *Philips Res. Rep.* **2** (1947) 81; 260.
3. C. WAGNER, *Z. Electrochemie, Ber. Buns. Ges.* **63**, (1959) 772.
4. R. A. RAPP, *Acta Met.* **9** (1961) 730.
5. G. BÖHM and M. KAHLWEIT, *ibid* **12** (1964) 641.
6. R. S. BARCLAY and P. NIESSEN, accepted for publication in *Trans. Amer. Soc. Metals* (1969).
7. W. EICHENAUER and G. MULLER, *Z. Metallk.* **53** (1962) 321; 700.
8. E. JAHNKE and F. EMDE, "Funktionentafeln" (Teubner, Leipzig, 1938).

Received 25 August and accepted 2 October 1969.