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Cr GRAIN BOUNDARY DIFFUSION IN Cr₂O₃

A.C.S. SABIONI¹, B. LESAGE, A.M. HUNTZ, J. BESSON*, C. DOLIN** and C. MONTY*

ISMA, CNRS URA 1107, Laboratoire de Métallurgie Structurale, Bât 413, Université Paris XI, F-91405 Orsay Cedex, France
*BNRM, Centre des Matériaux, BP. 87, F-91003 Evry Cedex, France
**CNRS, Laboratoire de Physique des Matériaux, Bellevue, F-92195 Meudon, France

Résumé - La diffusion intergranulaire du chrome dans des polycristaux denses de Cr₂O₃ a été mesurée en utilisant l'isotope stable ⁵⁴Cr. Les profils de pénétration ont été établis par SIMS. A 1200 et 1300°C, sous une pression de 5.10⁻⁵ atm. (5 Pa), les valeurs trouvées pour Dj sont respectivement de 1,03.10⁻¹⁵ et 4,72.10⁻¹⁴ cm².s⁻¹ en prenant 1 nm comme largeur de joint et en utilisant les valeurs de coefficient de diffusion en volume mesurées dans les monocristaux (1,0.10⁻¹⁸ cm².s⁻¹ à 1200°C et 4,8.10⁻¹⁸ cm².s⁻¹ à 1300°C). Ces valeurs sont plus faibles que celles publiées précédemment dans le domaine de températures et de pression d'oxygène.

Abstract Cr grain boundary diffusion has been measured in dense polycrystals of Cr₂O₃ using ⁵⁴Cr as a stable tracer and depth profiling by SIMS. At 1200 and 1300°C, in an oxygen pressure of 5.10⁻⁵ atm. (5 Pa), it was found 1.03.10⁻¹⁵ and 4.72.10⁻¹⁴ cm².s⁻¹ respectively for the grain boundary diffusion, considering the width of the grain boundary equal to 1 nm and using lattice diffusion values obtained on single crystals (1.0.10⁻¹⁸ cm².s⁻¹ at 1200°C and 4.8.10⁻¹⁸ cm².s⁻¹ at 1300°C). These values are smaller than those previously published in the same range of temperatures and oxygen pressure.

I- INTRODUCTION

The study of self-diffusion in Cr₂O₃ presents a great technological interest because its knowledge is necessary to interpret the mechanism of Cr₂O₃ scale growth on chromium-rich alloys at high temperature. However, up to now, there is a lack of data in literature about chromium and oxygen diffusion in Cr₂O₃, especially with respect to grain boundary (GB) diffusion. This work deals with the Cr diffusion. In all earlier experiments /1-5/, the chromium radioactive isotope ⁵¹Cr was used. In such cases, the concentration profile of the tracer is determined by sectioning the sample in thin layers, mechanically or by ion beam sputtering, and counting the radioactivity remaining in the sample or in each layer. The purpose of this paper is to determine new values of the lattice and grain boundary diffusion coefficients in Cr₂O₃ using an original technique. It consists of using the ⁵⁴Cr, the less abundant of the natural chromium stable isotopes, and depth profiling by secondary ion mass spectrometry (SIMS). Our results are compared to literature data.

II- EXPERIMENTAL PROCEDURE

II-1 Material

Polycrystalline Cr₂O₃ was prepared by hot-pressing at 1450°C, 48 MPa during 40 min., using high purity Cr₂O₃ powder, (impurity contents < 10 ppm), obtained from Johnson Matthey Corp.

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The volumic mass of the hot-pressed Cr$_2$O$_3$ samples is quite equal to 100% of the theoretical volumic mass of this oxide, and its microstructure after thermal etching is shown in Fig.1. The diffusion samples were cut into small parallelepipeds of 3x5x1 mm$^3$ from the hot-pressed compacts. The largest surface was used as diffusion surface after diamond polishing.

Fig. 1- Microstructure of the polycrystalline Cr$_2$O$_3$ after thermal etching at 1100°C, 15 min., air.

Single crystals of Cr$_2$O$_3$ of 99.9% purity were purchased from Labelcomat (Belgium). These samples were used as disks of 2mm thickness and 5mm in diameter. The $^{54}$Cr used as stable tracer was obtained through CEA (France). Its chemical composition is given in Table 1.

![Table 1](image)

**Table 1**

<table>
<thead>
<tr>
<th>Isotopic composition</th>
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</thead>
<tbody>
<tr>
<td>Isotope</td>
</tr>
<tr>
<td>$^{54}$Cr</td>
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</table>

**Chemical Impurities**

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<th>Si</th>
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<tbody>
<tr>
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<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
<td>0.02</td>
<td>&lt;0.005</td>
<td>0.03</td>
</tr>
</tbody>
</table>

II-2 **Diffusion experiments**

The diffusion experiments were performed by the following procedure:

- Samples were preannealed in oxygen pressures corresponding to the diffusion test conditions, during a time longer than the diffusion time.
- Samples were polished again to eliminate the thermal etching at the surface.
- $^{54}$Cr was deposited by vacuum evaporation at 10$^{-4}$ Pa.
- Oxidation of the $^{54}$Cr film was performed by heating at 500°C, in air during 30 min.
- Diffusion annealing were then conducted in 5.10$^{-5}$ atm (5 Pa) $P_{O_2}$ at 1200 and 1300°C.
II-3 Depth profiling by SIMS

The depth profiles were determined by SIMS using a 10 KeV Cs⁺ ion source. The scanned area was 250x250 μm². The concentration was determined from the ⁵⁰Cr⁻, ⁵²Cr⁻, ⁵³Cr⁻ and ⁵⁴Cr⁻ signals using the expression \( C = \frac{I_{54}}{(I_{50} + I_{52} + I_{53} + I_{54})} \), where \( I_s \) are the count numbers of each chromium isotope. \( I_{54} \) is the count number on ion 54 corrected from a background obtained by calibrating the signal far from the diffusion zone. The penetration depths were obtained assuming a constant sputtering rate and measuring the final depth of the crater.

III- RESULTS

This paper presents the results obtained for experiments performed at 1200 and 1300°C in argon (5.10⁻⁵ atm O₂). The concentration profile of ⁵⁴Cr in polycrystalline Cr₂O₃ for one of these experiments is shown in Fig.2.

![Fig.2: ⁵⁴Cr concentration profile in polycrystalline Cr₂O₃ after the diffusion annealing.](image)

The figure 3 shows a penetration plot for ⁵⁴Cr in Cr₂O₃ single crystal /6/ at the same temperature and oxygen pressure. The comparison between the plots of figures 2 and 3 allows to know the region where lattice diffusion becomes negligible in our experimental conditions. Our diffusion experiments correspond to the type-B diffusion /7/. In this case, Le Claire /8/ has shown that the product \( D'\delta \), where \( D' \) is the GB diffusion coefficient and \( \delta \) the width of the grain boundary, is given by the following expression:

\[
D'\delta = 0.661 \left( \frac{4D}{dx^{6/5}} \right)^{5/3} \left( \frac{t}{\text{dx}^{6/5}} \right)^{1/2}
\]

where \( D \) is the lattice diffusion coefficient.

This relation is valid if the parameter \( \beta = \frac{8/2}{\text{D'}} \) is > 10

The D values used to deduce D'd were taken from the experiments performed on single crystals.
Fig. 3- Penetration plot of Cr in Cr2O3 single crystal after diffusion annealing /6/.

Using, at 1300°C, \( D = 4.8 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1} /6/ \) and experimental data from Fig.4, it was found \( D'\delta = 4.72 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1} \) and \( \beta = 907.6 \). For the experiments at 1200°C, it was found the following values: \( D = 1.0 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1} \), \( D'\delta = (1.03 \pm 0.38) \times 10^{-22} \text{ cm}^3 \text{ s}^{-1} \) and \( \beta = 205 \). No additional fast diffusion process was observed as in King and Park's experiments /11/.

Fig. 4- Plot of \( \log_{10}(C - C_\infty) \) versus \( x/5 \). \( C_\infty \) is the natural concentration of \( ^{54}\text{Cr} \) in \( \text{Cr}_2\text{O}_3 \). Its value is 2.4%.

In Fig. 5 our \( D'\delta \) values are compared with earlier data. Fig. 6 shows the comparison between grain boundary and lattice diffusion in \( \text{Cr}_2\text{O}_3 \). When there is more than one value at the same
temperature in a reference, only the smallest value is indicated, and for lattice diffusion data only from single crystals are shown.

Fig.5 - ○ D'δ calculated by King et al. /9/ from Caplan and Sproule's oxidation data /10/. x D'δ measured in sintered Cr₂O₃ /5/ □ D'δ in low angle boundaries /4/. © This work.

Fig.6- Arrhenius plot for lattice and grain boundary diffusion (using δ = 1nm) in Cr₂O₃.
IV- CONCLUSIONS

The Cr diffusion along grain boundaries in Cr$_2$O$_3$ has been measured successfully using $^{54}$Cr as a stable tracer and profiling by SIMS. The grain boundary diffusion coefficient at 1200°C and 1300°C in $5.10^{-5}$ atm O$_2$ was found to be $(1.03 \pm 0.38) \times 10^{-15}$ cm$^2$.s$^{-1}$ and $4.72 \times 10^{-14}$ cm$^2$.s$^{-1}$, respectively, considering the grain boundary width equal to 1 nm. The results obtained with polycrystals confirm the low diffusivity of Cr in Cr$_2$O$_3$ observed previously in experiments with single crystals /6/. New experiments are planned at different temperatures and oxygen pressures to know more about the role played by grain boundary diffusion in high temperature oxidation.

V- REFERENCES


