Cr GRAIN BOUNDARY DIFFUSION IN Cr₂O₃

A. Sabioni, B. Lesage, A. Huntz, J. Besson, C. Dolin, C. Monty

► To cite this version:

A. Sabioni, B. Lesage, A. Huntz, J. Besson, C. Dolin, et al.. Cr GRAIN BOUNDARY DIFFUSION IN Cr₂O₃. Journal de Physique Colloques, 1990, 51 (C1), pp.C1-611-C1-616. 10.1051/jphyscol:1990196 . jpa-00230365

HAL Id: jpa-00230365

<https://hal.science/jpa-00230365>

Submitted on 1 Jan 1990

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cr GRAIN BOUNDARY DIFFUSION IN Cr_2O_3

A.C.S. SABIONI⁽¹⁾, 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

*E.N.S.M.P., 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 Cr_2O_3 a été mesurée en utilisant l'isotope stable ^{54}Cr . 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 D_j sont respectivement de $1,03.10^{-15}$ et $4,72.10^{-14}$ $\text{cm}^2.\text{s}^{-1}$ en prenant 1nm comme largeur de joint et en utilisant les valeurs de coefficient de diffusion en volume mesurées dans les monocristaux ($1,0.10^{-18}$ $\text{cm}^2.\text{s}^{-1}$ à 1200°C et $4,8.10^{-18}$ $\text{cm}^2.\text{s}^{-1}$ 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 Cr_2O_3 using ^{54}Cr 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 $4.72.10^{-14}$ $\text{cm}^2.\text{s}^{-1}$ 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 ($1.0.10^{-18}$ $\text{cm}^2.\text{s}^{-1}$ at 1200°C and $4.8.10^{-18}$ $\text{cm}^2.\text{s}^{-1}$ 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 Cr_2O_3 presents a great technological interest because its knowledge is necessary to interpret the mechanism of Cr_2O_3 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 Cr_2O_3 , 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 ^{51}Cr 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 Cr_2O_3 using an original technique. It consists of using the ^{54}Cr , 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 Cr_2O_3 was prepared by hot-pressing at 1450°C, 48 MPa during 40 min., using high purity Cr_2O_3 powder, (impurity contents < 10 ppm), obtained from Johnson Matthey Corp.

⁽¹⁾Supported by University of Ouro Preto and CNPq (BRAZIL)

The volumic mass of the hot-pressed Cr_2O_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 $3 \times 5 \times 1 \text{ mm}^3$ from the hot-pressed compacts. The largest surface was used as diffusion surface after diamond polishing .

Fig. 1- Microstructure of the polycrystalline Cr_2O_3 after thermal etching at 1100°C , 15 min., air .

Single crystals of Cr_2O_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

CHEMICAL ANALYSIS OF THE TRACER				
Isotopic composition				
Isotope	50	52	53	54
%	0.4	10.9	10.1	78.6

Chemical Impurities

Element	Ni	Cu	Ca	Fe	Si	Pb	Sn	Al	Mn	Mg
%	<0.01	0.01	0.02	0.05	0.02	0.05	0.01	0.02	<0.005	0.03

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 $250 \times 250 \mu\text{m}^2$. The concentration was determined from the ^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr signals using the expression $C = I_{54} / (I_{50} + I_{52} + I_{53} + I_{54})$, 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 ($5.10^{-5} \text{ atm O}_2$) . The concentration profile of ^{54}Cr in polycrystalline Cr_2O_3 for one of these experiments is shown in Fig.2 .

Fig.2- ^{54}Cr concentration profile in polycrystalline Cr_2O_3 after the diffusion annealing .

The figure 3 shows a penetration plot for ^{54}Cr in Cr_2O_3 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 δ the width of the grain boundary, is given by the following expression :

$$D'\delta = 0.661 \left(\frac{d \ln c}{dx^{6/5}} \right)^{-5/3} \left(\frac{4D}{t} \right)^{1/2}$$

where D is the lattice diffusion coefficient .

$$\text{This relation is valid if the parameter } \beta = \frac{D'}{D} \frac{\delta/2}{\sqrt{Dt}} \text{ is } > 10$$

The D values used to deduce $D'\delta$ 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, $D = 4.8 \cdot 10^{-18} \text{ cm}^2 \cdot \text{s}^{-1}$ /6/ and experimental data from Fig.4 , it was found $D'\delta = 4.72 \cdot 10^{-21} \text{ cm}^3 \cdot \text{s}^{-1}$ and $\beta = 907.6$. For the experiments at 1200°C, it was found the following values : $D = 1.0 \cdot 10^{-18} \text{ cm}^2 \cdot \text{s}^{-1}$, $D'\delta = (1.03 \pm 0.38) \cdot 10^{-22} \text{ cm}^3 \cdot \text{s}^{-1}$ 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 $x^{6/5}$. C_{∞} is the natural concentration of ⁵⁴Cr in Cr₂O₃ . 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 Cr₂O₃ . 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 - ● $D'\delta$ calculated by King et al. /9/ from Caplan and Sproule's oxidation data /10/.
 x $D'\delta$ measured in sintered Cr_2O_3 /5/ ■ $D'\delta$ in low angle boundaries /4/.
 o This work .

Fig.6- Arrhenius plot for lattice and grain boundary diffusion (using $\delta = 1\text{nm}$) in Cr_2O_3 .

IV- CONCLUSIONS

The Cr diffusion along grain boundaries in Cr_2O_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 $(1.03 \pm 0.38) 10^{-15} \text{ cm}^2.\text{s}^{-1}$ and $4.72.10^{-14} \text{ cm}^2.\text{s}^{-1}$, respectively, considering the grain boundary width equal to 1 nm . The results obtained with polycrystals confirm the low diffusivity of Cr in Cr_2O_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

- /1/ W.C. HAGEL and A.V. SEYBOLT. "Cation diffusion in Cr_2O_3 ", J. Electrochem. Soc. 108(12) (1961) 1146.
- /2/ L.C. WALTERS and R.E. GRACE. "Self diffusion of ^{51}Cr in single crystals of Cr_2O_3 ". J. Appl. Phys. 36(7) (1965) 2331.
- /3/ K. HOSHINO and N.L. PETERSON. "Cation self diffusion in Cr_2O_3 ", J. Am. Ceram. Soc. 66(11) (1983) C 202.
- /4/ A. ATKINSON and R.I. TAYLOR. "Diffusion of ^{51}Cr tracer in Cr_2O_3 and growth of Cr_2O_3 films" NATO-ASI Ser. B 129 (1984) 285.
- /5/ J.H. PARK, W.E. KING and S.J. ROTHMAN. "Cation tracer diffusion in Cr_2O_3 and in Cr_2O_3 -0.09 wt% Y_2O_3 ", J. Am. Ceram. Soc. 70(12) (1987) (880).
- /6/ A.C.S. SABIONI, B. LESAGE, J.C. PIVIN, C. DOLIN and C. MONTY. "Comparison of ion implantation and thick film methods to study Cr self diffusion in Cr_2O_3 " Proceedings of the NATO-ASI Conference on "Diffusion in Materials", Aussois (France), March 1989. (To be published).
- /7/ L.G. HARRISON. Trans. Faraday Soc. 57(1) (1961) 74.
- /8/ A.D. LE CLAIRE. "The analysis of grain boundary diffusion measurements", Brit. J. Appl. Phys. 14(1963) 351.
- /9/ W.E. KING, K.S. GRABOWSKI, D.F. MITCHELL and P.M. BALDO. "Rutherford backscattering study of high temperature oxidation of Y-implanted Fe-24Cr", Oxid. Met. 31(3-4) (1989) 181.
- /10/ D. CAPLAN and I. SPROULE. "Effect of oxide grain structure on the high temperature oxidation of Cr", Oxid. Met. 5(5) (1975) 459.
- /11/ W.E. KING and J.H. PARK, Proceedings of IIB 89, Paris, Les Editions de Physique .