

Cation Self-Diffusion in Cr₂O₃

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Self-diffusion of ⁵¹Cr was measured both parallel to and perpendicular to the c axis in single crystals of Cr₂O₃ as a function of oxygen partial pressure at 1490° and 1570°C. The oxygen-partial-pressure dependence of the diffusivity indicates that cation self-diffusion occurs by a vacancy mechanism. The values of the self-diffusion coefficients determined in this experiment are about 10⁴ times smaller than those previously reported in this temperature range.

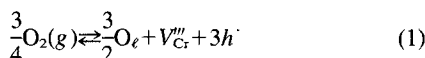
INTRODUCTION

CHROMIUM oxide plays an important role in the high-temperature corrosion resistance of many chromium-rich alloys. It is, therefore, highly desirable to know the mechanism for Cr diffusion to understand the oxidation process and to interpret the adhesion of Cr₂O₃ scales to the base metal. Like α-Al₂O₃ and Fe₂O₃, chromium sesquioxide Cr₂O₃ has the corundum structure. Although the deviation from stoichiometry in Cr₂O₃ at high temperature has not been determined definitely, it is generally recognized that the extent of nonstoichiometry is very small.^{1,2}

The diffusion of ⁵¹Cr in Cr₂O₃ has been studied by several investigators.³⁻⁵ Recently, Kofstad and Lillerud² have analyzed the experimental data measured by Hagel and Seybolt⁴ on the self-diffusion of ⁵¹Cr in both sintered and hot-pressed specimens; they suggested that self-diffusion occurs by an interstitial mechanism. Their

recent studies of the oxidation of chromium have also supported this diffusion mechanism.^{6,7} On the other hand, Walters and Grace have measured the ⁵¹Cr-tracer diffusion in Cr₂O₃ single crystals at 1300°C in H₂+H₂O gas mixtures within the narrow oxygen-partial-pressure range 1×10⁻¹¹ to 5×10⁻¹¹ Pa; they interpreted their results on the basis of a Cr-vacancy defect model.⁵

If the predominant point defects in Cr₂O₃ are triply charged vacancies, the formation of these vacancies can be expressed by the reaction^{1,5}



where O₂(g) is gaseous oxygen, O_e an oxygen-lattice ion, V_{Cr}^{'''} a triply charged cation vacancy, and h⁺ a positive electron hole. With the electroneutrality condition [h⁺]=3[V_{Cr}^{'''}], where the brackets indicate concentrations in mole fraction per mole of Cr₂O₃, the equilibrium concentration of chromium vacancies is given by

$$[V_\text{Cr}'''] = (K_1/27)^{1/4} p_{\text{O}_2}^{3/16} \quad (2)$$

where K₁ is the equilibrium constant for Eq. (1), and p_{O₂} is the equilibrium oxygen partial pressure. From a similar consideration for triply charged interstitial defects, the concentration of chromium interstitials [Cr^{•••}] is proportional to p_{O₂}^{-3/16} (Ref. 2). If the predominant defect for self-diffusion of Cr is either a triply charged vacancy or a triply charged interstitial, the diffusivity at a given temperature will be proportional to either p_{O₂}^{3/16} or p_{O₂}^{-3/16}, respectively. Since the previous measurements of the diffusion of ⁵¹Cr in Cr₂O₃ show considerable scatter, these suggested mechanisms are neither confirmed nor denied by the existing experimental results.³⁻⁷

In this communication, the self-diffusion of ⁵¹Cr has been measured both parallel to and perpendicular to the c axis in single crystals of Cr₂O₃ as a function of

oxygen partial pressure to confirm the cation-diffusion mechanism.

EXPERIMENTAL PROCEDURES

Single crystals of pure Cr₂O₃* underwent mass spectrographic chemical analysis; no impurities above the detection limits were observed (typically 0.005 at.%). Impurities sought but not detected included Ag, Al, Be, Bi, Co, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Si, Ti, and Zr. Crystals ≈5 by 5 by 2 mm with the large surface both parallel to and perpendicular to the c axis were cut from crystal boules oriented within 2° of the indicated directions by X-ray diffraction. The samples were polished and examined to ensure that they were parallel and flat. The finished samples were preannealed at 1490° and 1570°C in a given oxygen partial pressure established by a flowing CO₂/CO gas mixture, as described previously.^{8,9} The time of preannealing was longer than that of diffusion annealing to ensure that the sample was well characterized with respect to a given temperature and oxygen partial pressure. The ⁵¹Cr isotope was obtained[†] in the form of CrCl₃ in 0.5M HCl. The ⁵¹Cr tracer was converted to the sulfate form and picked up in distilled water. The tracer was deposited by drying a drop of the solution on the sample surface. The specific activity of ⁵¹Cr was sufficiently high that the thickness of the deposited layer was estimated to be less than one atomic layer. After the radioisotope had dried, pairs of samples were bound tightly together with platinum wire with their tracer-deposited surfaces together to prevent evaporation of the tracer during the diffusion anneal.

The samples were diffusion annealed for 6.5×10⁴ to 4.2×10⁵ s at the same temperature and under the same oxygen-partial pressure as was used for the preanneal. The furnace temperature was controlled to within ±2°C. Annealing temperatures were monitored with a Pt-Pt10Rh thermocouple calibrated periodically during the course of the experiments. After the samples were diffusion annealed, their edges were ground to eliminate the possibility of contributions of activity arising from diffusion from the sides of the samples. The concentration profile of the radioactive tracer was determined by a serial-sectioning technique

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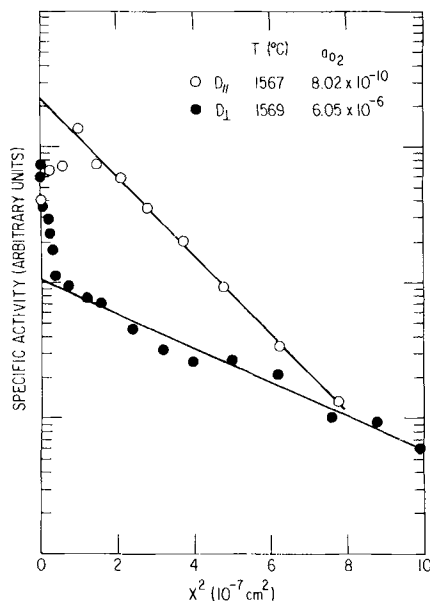


Fig. 1. Typical plots of log (specific activity) vs square of penetration distance.

Table I. Experimental Values of Cation Self-Diffusion Coefficient in Cr₂O₃

T (°C)	a _{O₂}	(10 ⁻¹³ cm ² /s)	(10 ⁻¹³ cm ² /s)	D /D _⊥
1490	8.40×10 ⁻⁶	1.0	0.72*	1.4
1567	8.02×10 ⁻¹⁰	1.1	0.63*	1.7
1570	1.21×10 ⁻⁷	2.5	1.3	1.9
1569	6.05×10 ⁻⁶		2.7	
1570	1.06×10 ⁻⁵	4.8	3.0	1.6

*Experimental errors of 10 to 20% may be included in these values because of the very small penetration depth.

*Cristal Tec, Grenoble, France.

†Purchased from New England Nuclear.

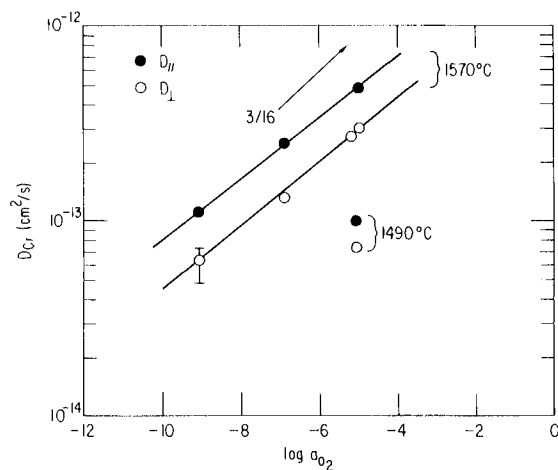


Fig. 2. Oxygen activity dependence of tracer-cation self-diffusion coefficient in Cr_2O_3 .

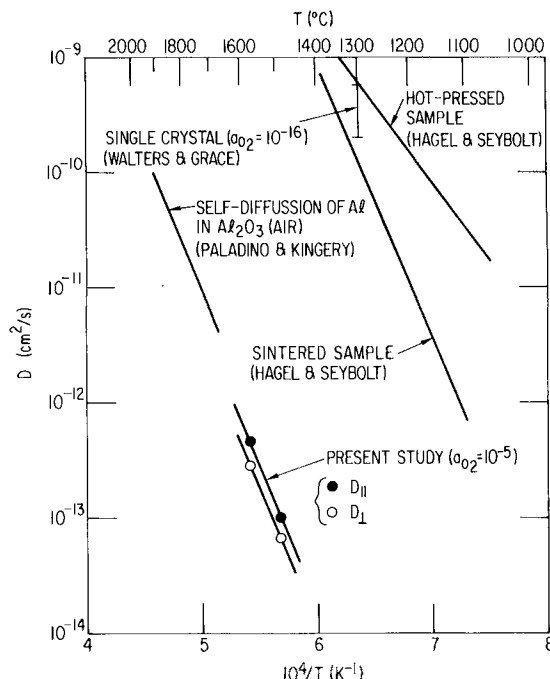


Fig. 3. Temperature dependence of Cr self-diffusion coefficient in Cr_2O_3 ; cation self-diffusion coefficient in Al_2O_3 is also shown.

using a precision parallel grinder. The radioactivity in each section was counted using a well-type NaI(Tl)-crystal scintillation counter. For these experimental boundary conditions, the distribution of the specific activity, C , of a tracer as a function of penetration depth, X , after diffusion annealing for a time, t , can be expressed in the usual exponential form,

$$C = C_0 \exp(-X^2/4Dt) \quad (3)$$

where D is the tracer-diffusion coefficient and C_0 is a constant.

RESULTS AND DISCUSSION

Some of the penetration plots ($\log C$ vs X^2) for the self-diffusion of ^{51}Cr , D_{Cr} , in Cr_2O_3 are illustrated in Fig. 1, where the symbols $D_{||}$ and D_{\perp} represent self-diffusion coefficients parallel to and perpendicular to the c axis, respectively. Except for the first few sections, all the penetration plots are straight lines over 1 to 2 orders of magnitude in specific activity. Surface hold-up was apparent for samples annealed at higher oxygen activity ($a_{\text{O}_2} \geq 10^{-7}$); here, a_{O_2} is the equilibrium oxygen activity defined as $a_{\text{O}_2} = p_{\text{O}_2}/p_{\text{O}_2}^0$, where $p_{\text{O}_2}^0$ is the reference oxygen pressure (9.8×10^4 Pa). Evaporation of the tracer was observed in the penetration plots of samples annealed at lower oxygen activity ($a_{\text{O}_2} = 10^{-9}$). However, the linearity in the region of deeper penetration in Fig. 1 is consistent with volume diffusion. The values of $D_{||}$ and D_{\perp} are listed in Table I. Both the temperature and the oxygen activity range of the diffusion measurements are severely limited by the small diffusion coefficient and the high vapor pressure of chromium oxide. Although a diffusion anneal was attempted at a higher oxygen activity ($a_{\text{O}_2} = 0.21$) at 1570°C , the measurements were unsuccessful because of excessive evaporation of the tracer.

In Fig. 2 the values of $\log D_{\text{Cr}}$ are plotted vs $\log a_{\text{O}_2}$ at 1490°C and 1570°C . A line with a slope of $3/16$ corresponding to diffusion by triply charged vacancies

(Eq. (2)) is also shown. The slopes of both the $\log D_{||}$ vs $\log a_{\text{O}_2}$ and the $\log D_{\perp}$ vs $\log a_{\text{O}_2}$ plots are ≈ 0.16 at 1570°C , a value quite close to $3/16$ ($= 0.188$). The difference in the slopes between the experimental value and the theoretical value estimated from Eq. (2) may be due to impurity-induced (extrinsic) defects in the low a_{O_2} region. Thus, it can be concluded that self-diffusion of Cr occurs predominantly by a triply-charged vacancy. The values of the ratio $D_{||}/D_{\perp}$ are ≈ 1.7 and independent of temperature and oxygen activity. This behavior indicates that diffusion both parallel to and perpendicular to the c axis occurs by the same mechanism, but the jump frequencies of the chromium ions for the two directions are different.

Figure 3 shows the temperature dependence of the Cr self-diffusion coefficient together with those determined by previous workers.^{4,5} The self-diffusion coefficients obtained by Paladino and Kingery¹⁰ for Al in polycrystalline Al_2O_3 in air are also shown in Fig. 3. The self-diffusion coefficients in the present work are 10^4 times smaller than those obtained in previous studies,^{4,5} and the activation enthalpy for self-diffusion at $a_{\text{O}_2} = 10^{-5}$ can be roughly estimated to be 500 kJ/mol. This result may be compared to the self-diffusion of Al in Al_2O_3 , where the activation enthalpy for self-diffusion has been determined to be 477 kJ/mol in the temperature range 1670° to 1905°C .¹⁰ Both the a_{O_2} dependence of D_{Cr} and the absolute value of D_{Cr} relative to cation self-diffusion in Al_2O_3 suggest that the present results are representative of intrinsic lattice diffusion, and the much larger values of D_{Cr} in the

previous studies may result from impurity effects^{4,5} and/or the polycrystalline nature of the samples.⁴ A reanalysis of the published penetration plots of Hagel and Seybolt⁴ in terms of grain-boundary diffusion ($\ln C$ vs $X^{6/5}$) supports the suggestion that their measurements are representative of grain-boundary diffusion.

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