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Effect of Volatilization on the Conduction Behavior of Acceptor-Doped Chromium Oxide

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The effect of volatilization on the conduction behavior of Li- or Mg-doped Cr_2O_3 was studied. The P_{O_2} dependence on conduction changed from $\frac{1}{4}$ to $\frac{3}{8}$ when volatilization occurred. The high-temperature conduction mechanism of Cr_2O_3 may be dominated by the formation of Cr vacancies due to the volatilization effect. [Key words: chromia, electrical conductivity, lithium, magnesium, volatilization.]

I. Introduction

CHROMIUM OXIDE exhibits a high melting temperature, excellent corrosion resistance under severe environments, and good electrical conductivity at high temperatures. All of these make Cr_2O_3 an attractive material for high-temperature electrode applications.¹ As a result, the conduction behavior of this compound has been extensively studied¹⁻¹⁵ as a function of temperature, oxygen activity, and dopant concentration. Those studies have provided much valuable information on the conduction behavior of Cr_2O_3 .

It has long been recognized that at elevated temperatures Cr_2O_3 reacts with oxygen to form a gaseous CrO_3 phase¹⁶⁻²⁰ and that the effect is enhanced by the presence of moisture.¹⁸⁻²⁰ However, little is known regarding how the volatilization affects the defect structure, and hence the conduction behavior, of Cr_2O_3 . Since the fabrication and the potential applications of this compound need to be carried out at elevated temperatures, the influence of volatilization on the electrical properties of Cr_2O_3 cannot be ignored. Furthermore, previous studies have shown some discrepancies concerning the conduction mechanism,⁷⁻⁹ the conductivity dependence on oxygen activity,^{8,10} and the types of defects in Cr_2O_3 .^{7,11-15} These discrepancies may be related to the volatilization.

In this paper, the effect of volatilization on the electrical conductivity was studied as a function of temperature and oxygen activity. Based upon the conductivity and thermogravimetric data, defect models related to the volatilization of Cr_2O_3 are proposed. The conduction mechanism and the influence of moisture on the oxygen activity dependence of conductivity are examined.

II. Experimental Procedure

A series of Mg- or Li-doped Cr_2O_3 powders were prepared by an organometallic coprecipitation method. Details of this process have been described elsewhere.²¹ X-ray diffraction (XRD), scanning electron microscopy (SEM), and chemical analysis⁷ were used to identify the presence of phases and to determine the Mg and Li content. Results indicated that a second phase of MgCr_2O_4 exists in powders containing higher than 0.75 mol% of Mg.

These powders were used to prepare both dense and porous samples for conductivity measurements. Details of the porous sample preparation, the experimental techniques used for the conductivity measurements, and the solubility limit of Li in Cr_2O_3 were discussed previously.³ Porous samples, which could rapidly equilibrate to changing oxygen activity, were used to determine the dependence of the conductivity upon oxygen activity.

The dense samples were prepared by hot-pressing in a 3.8-cm-diameter graphite die at 10.3 MN/m² with temperatures up to 1793 K. The hot-pressed samples showed an average of 94% theoretical density. These dense samples were sliced into 1-mm-thick plates around which Pt wires were wrapped and painted with Pt past to form leads for conductivity measurements. Dense samples were used mainly to determine the total conductivity and its dependence upon the temperature.

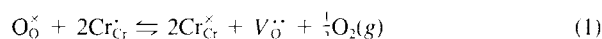
For both the porous and dense specimens, the conductivity was measured using four-point probes. The oxygen activity was controlled by CO_2 and forming gas (90% N_2 , 10% H_2) mixtures in conjunction with a zirconia oxygen sensor. Sufficient time was given so that a stable reading could be taken for each measurement point to ensure that the equilibration between samples and the ambient environments had been reached.

To determine the volatilization of Cr_2O_3 , the nonreversible weight change of each powder specimen was measured as a function of temperature and oxygen activity. The apparatus and procedures for the thermogravimetric measurements were shown elsewhere.²²

III. Results and Discussion

(I) Effect of Volatilization on the Conductivity Dependence on Oxygen Activity

Undoped Cr_2O_3 has been found to exhibit a p -type electronic conduction behavior^{2,5,6} except under very reducing conditions at low temperature (573 K), where n -type behavior was observed.² In the case where the monovalent or divalent ions are substituted onto the Cr sites, electron holes will be created on the normal Cr ions to maintain the electrical neutrality of the compound.⁴ If the extrinsic defects caused by the acceptor dopants exceed the intrinsic defect concentration, then the conductivity will be controlled by the dopant levels in the high P_{O_2} region.⁴ Under reducing conditions, the oxygen can be lost and the two electrons produced by the oxygen vacancy will compensate the electron holes created by the acceptor dopants, thereby reducing the hole concentration. This reaction can be expressed as



Since the ionic conduction due to $\text{V}_\text{O}^\bullet$ is much smaller than the electronic conduction of an electron hole,¹³ the conductivity decreases with decreasing oxygen activity. According to the proposed defect models,³ the conduction in the high P_{O_2} region is controlled by the dopant level and no P_{O_2} dependence can be seen. In the low P_{O_2} region, where the formation of oxygen vacancies dominates the defect structure, a P_{O_2} dependence of $\frac{1}{4}$ is expected. The conduction behavior of Li-doped Cr_2O_3 had been previously studied using the porous samples.³ Although the measured conductivity data followed the proposed models well, a de-

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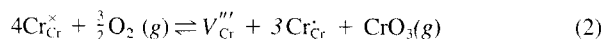
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viation from the predicted $\frac{1}{4}$ dependence of P_{O_2} was observed in the intermediate P_{O_2} range. In an effort to confirm the predicted P_{O_2} dependence, the conductivities of high-density Mg-doped samples were measured. Typical results are shown in Fig. 1 and are compared with the data for porous Li-doped specimens. In this figure, the conductivity of the porous specimens is plotted relative to that in air, since absolute values were not obtainable. As can be seen, the porous specimen data showed a region of $\frac{3}{8}$ power P_{O_2} dependence, but the high-density specimen did follow the predicted P_{O_2} dependence and no deviation was observed. Therefore, the higher P_{O_2} dependence found for the porous samples in the intermediate P_{O_2} range came from other defects.

Previous studies have shown that Cr_2O_3 reacts with oxygen at high temperatures¹⁶⁻²⁰ to form gaseous CrO_3 and that the effect is greatly enhanced by the presence of moisture.¹⁸⁻²⁰ The influence of the formation of a volatile CrO_3 phase on the defect structure of Cr_2O_3 can be expressed as



The equilibrium constant of Eq. (2) is

$$K_2 = [V_{\text{Cr}}'''] [\text{Cr}_{\text{Cr}}^{\cdot}]^3 / P_{\text{CrO}_3} P_{\text{O}_2}^{3/2} \quad (3)$$

With the neutrality condition of

$$3[V_{\text{Cr}}'''] = [\text{Cr}_{\text{Cr}}^{\cdot}] \quad (4)$$

the carrier concentration can be written as

$$[\text{Cr}_{\text{Cr}}^{\cdot}] = (3K_2 / P_{\text{CrO}_3})^{1/4} P_{\text{O}_2}^{3/8} \quad (5)$$

Therefore, the concentrations of both Cr vacancies and electron holes, hence the conductivity, are expected to increase whenever volatilization occurs. Furthermore, a P_{O_2} dependence of $\frac{3}{8}$ on the conductivity is also expected if the volatilization-induced electron holes dominate the charge-carrier concentration.

Since the volatilization effect was expected to play an important role in the conduction behavior of Cr_2O_3 , the influence of temperature and the buffer gas system on the volatilization was investigated. The effect of temperature was determined by meas-

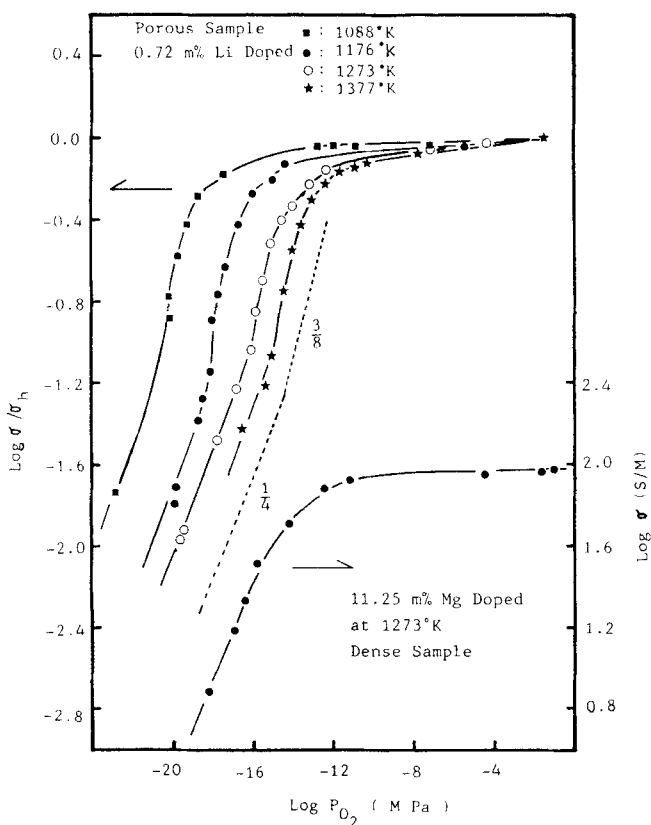
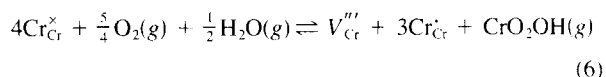


Fig. 1. Electrical conductivity dependence on P_{O_2} for porous and dense samples. σ_h is the conductivity measured in air.

uring the weight loss of powders occurring in a flowing oxygen atmosphere with respect to heating time and temperature. The results are shown in Fig. 2. As can be seen, Cr_2O_3 volatilized at constant rates when heated at temperatures higher than 1473 K, with no significant weight loss occurring at lower temperatures. This behavior is in agreement with previous studies.^{18,19} Thus, in order to minimize any possible volatilization due to temperature, the P_{O_2} dependence measurements must be carried out at temperatures below 1473 K.

To determine the influence of the buffer gas system (CO_2 and forming gas) on the volatilization, the weight changes occurring for Cr_2O_3 powders were measured at a constant temperature as they were subjected to reduction-reoxidation cycling using different gas mixture ratios. Typical weight change results due to cyclings are shown in Fig. 3. Theoretically, unless volatilization occurred, the weight change observed with reduction-reoxidation cycling should be reversible. However, as can be seen, the reversibility did not occur, indicating the occurrence of volatilization. It is apparent that the largest irreversible weight loss occurred in the gas combination of forming-gas-to- CO_2 ratios near 1. Significant amounts of water were found to condense in the gas outlet for these gas compositions. The water was coming from the reaction of oxygen and hydrogen, which came from the dissociated CO_2 and forming gas, respectively. The weight loss in the intermediate P_{O_2} range is unexpected, as little volatilization should occur in this low P_{O_2} region. Judging from the presence of water in this region, the weight loss must be coming from a moisture-enhanced volatilization process. The possible mechanisms for this moisture-enhanced process had been studied previously,¹⁸⁻²⁰ and the enhancement is thought to be caused by the formation of a gaseous CrO_2OH phase. For samples containing MgCr_2O_4 as a second phase, the effect of possible volatilization of MgCr_2O_4 needs to be considered. The volatilization of MgCr_2O_4 was studied by Anderson.²³ His results indicate that MgCr_2O_4 is stable at oxygen activities above 10^{-11} MPa at 1973 K. Since the weight-loss measurements were carried out in high P_{O_2} or at temperatures much lower than 1973 K, the influence of MgCr_2O_4 volatilization in this study is minimal.

Since the gas compositions for which the conductivity dependence deviated on porous samples were the same as those for which a severe weight loss occurred, the deviation is thought to be related to enhanced volatilization due to moisture. This can be seen as



Because

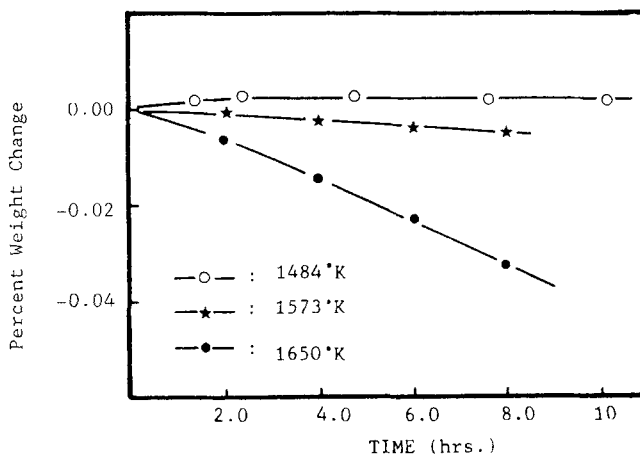


Fig. 2. Percent weight change with respect to time for different temperatures under flowing oxygen.

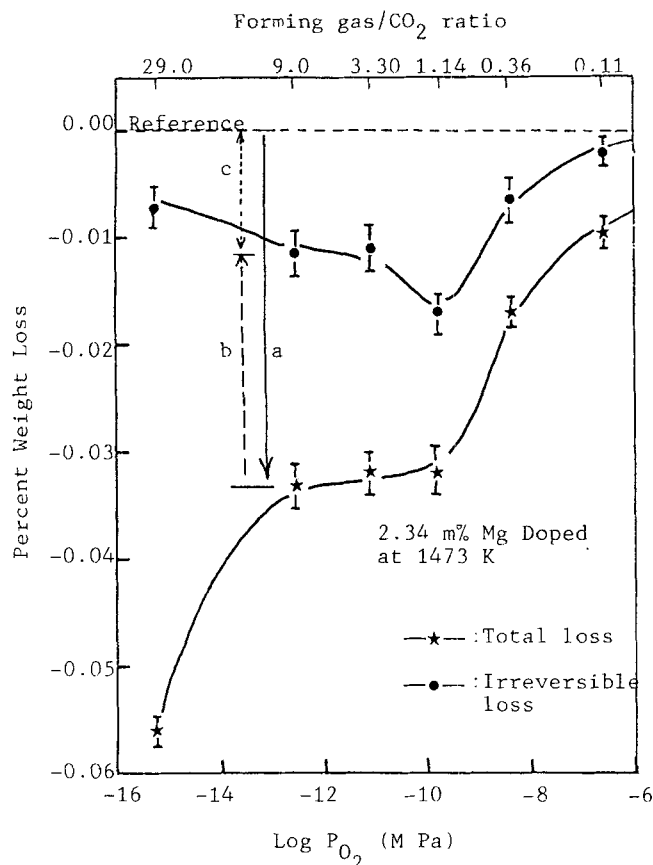
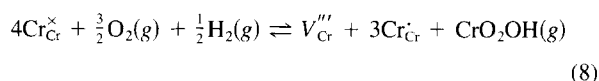


Fig. 3. Influence of buffer gas composition on weight loss behavior: (a) total loss at a given P_{O_2} , (b) reversible loss, and (c) irreversible loss. The reference point was taken as the weight in pure oxygen.

Eq. (6) can be rewritten as



Therefore, the electron hole concentration is

$$[Cr_{Cr}^{\times}] = A(P_{H_2}/P_{Cr_2O_3OH})^{1/4}P_{O_2}^{3/8} \quad (9)$$

where A is a temperature-dependent constant. Hence, like the dry condition shown in Eq. (2), a P_{O_2} dependence of $3/8$ is also to be expected for the moisture-enhanced volatilization of Cr_2O_3 . This is indeed what is shown in Fig. 1 for the conductivity of the porous samples. On the other hand, the dense samples, with much lower surface areas, have such low volatilization rates that the effect is negligible.

(2) Effect of Volatilization on the Conductivity Dependence on Temperature

The dependence of conductivity on temperature was determined by heating the well-annealed hot-pressed samples in air. Typical results are shown in Fig. 4 by a $\log \sigma T$ versus $1/T$ plot. The $\log \sigma T$ versus $1/T$ plots indicate two distinctive regions. In the low-temperature region (<1473 K), the conductivity increased slowly with the increase in temperature until 1473 K was reached. Above that temperature, the conductivity rapidly increased. It was found that the conductivity of specimens (both air-sintered porous samples and well-annealed hot-pressed samples) is reversible only in the low-temperature region. If the samples were kept at high temperatures for a period of time, a higher conductivity would be seen when cooling to the low-temperature region. The conduction mechanism in the high-temperature region has previously been suggested as an intrinsic behavior and that no P_{O_2} dependence on conductivity can be expected.^{7,11} Thus the activation energy observed in this region was attributed to the formation of intrinsic defects. This model, however, could not explain the data obtained from the thermoelectric measurements. Hay *et al.*⁵ used

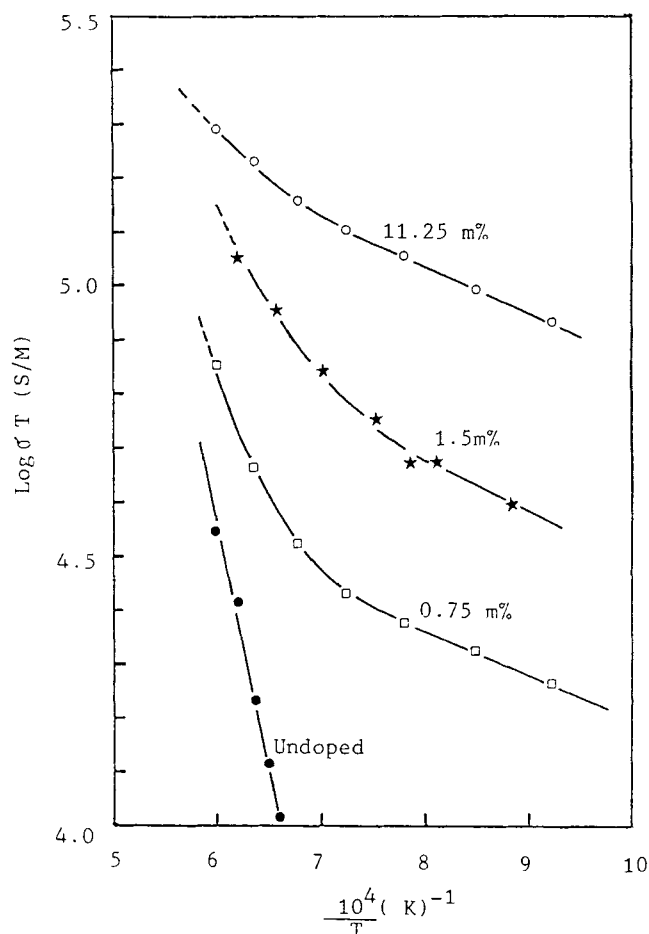


Fig. 4. Temperature dependence of electrical conductivity measured in stagnant air for Mg-Doped, hot-pressed samples.

the activation energy (173.4 kJ/mol or 1.8 eV) obtained from the high-temperature region to calculate the carrier concentration of Cr_2O_3 using the intrinsic-defect model. They found that the calculated carrier concentration was 2 orders of magnitude lower than the value obtained from the thermoelectric data. Meadowcroft *et al.*⁶ measured the Seebeck coefficient of Cr_2O_3 at high temperatures and observed a rapid increase of hole concentration in this region. The irreversibility of conductivities at high temperatures, the rapid increase of hole concentration observed in Seebeck measurements, and the instability of Cr_2O_3 toward volatilization above 1473 K suggest that the conduction behavior in the high-temperature region is probably dominated by the volatilization effect shown in Eq. (2). Because of the volatilization, extra electron holes can be generated; consequently, higher conductivity was observed when the sample was cooled from the high-temperature region. In the stagnant air environments, the hole concentration could increase until a concentration gradient of the volatilized phase was established around the sample,¹¹ which limited further volatilization to occur at that temperature.

The conduction behavior in the low-temperature region is reversible because no extra charge carriers are created in this region. Therefore, the activation energy found in this region is strictly from the mobility term. The $\log \sigma T$ versus $1/T$ plot yields a straight-line relationship, and an activation energy of 16.0 ± 0.3 kJ/mol (0.17 eV) was obtained. The low activation energy suggests that the conduction is of the small polaron hopping type. The lack of temperature dependence for mobility reported by De Dogan *et al.*⁹ is probably due to the low temperature used in their study. As was pointed out by Wimmer *et al.*,²⁴ it is rather difficult to observe a temperature dependence for mobility at low temperatures. Seebeck measurements in the 973 to 1373 K range⁶ indicated the existence of an activated mobility, which also support the hopping process.

The solubility limits of Mg in Cr_2O_3 have been reported by

Ownby *et al.*²⁵ to be 0.37 mol% on samples prepared under strong reducing conditions, and by this study to be 0.75 mol%. More recently, Park *et al.*²⁶ found that the solubility limits of MgO in Cr_2O_3 varied between 0.6 and 1 mol% depending on the oxygen partial pressure and temperature when samples were prepared. They suggested that additional Mg atoms which came from the decomposition of MgCr_2O_4 may have occupied the Cr vacancy sites at high temperatures. In general, the conductivity of the samples should increase proportionally to the amount of dopants until its solubility limit is reached. Beyond that limit, no further increase can be expected. However, as shown in Fig. 4, the conductivity increases with increasing Mg content even though the solubility limit of 0.75 mol% which was determined using low-temperature (1173 K) calcined coprecipitated powders, had been reached in these samples. It is possible that the formation of chromium vacancies by volatilization during high-temperature annealing may allow additional Mg atoms to substitute onto these sites, in agreement with Park *et al.*'s suggestion.²⁶ As a result, higher conductivity was observed due to higher Mg solubility.

The activation energy obtained in the high-temperature region can be used to examine the proposed defect model based on the volatilization effect. The energy of 165.2 kJ/mol (1.7 eV) obtained in this region is in agreement with previous studies^{7,13} and should be the combination of energies needed for the mobility (16.0 ± 0.3 kJ/mol) and for the volatilization reaction shown in Eq. (2). Therefore, according to the model (Eq. (2)), the energy needed for the formation of a Cr vacancy and the associated electron holes and the formation of the volatilized CrO_3 phase is 596.8 ± 1.2 kJ/mol. The temperature dependence of oxidative vaporization of Cr_2O_3 was studied by Stearns *et al.*,¹⁷ and the activation energy for the formation of CrO_3 was calculated to be 233.0 ± 21 kJ/mol. Therefore, the formation energy of Cr vacancies and the associated electron holes is calculated to be 363.8 ± 22 kJ/mol. Within experimental error, this value is similar to the value of 372.5 kJ/mol reported by Greskovich²⁷ on the formation energy of a Cr vacancy and the associated defects in the high-oxygen activity region. This suggests that the high-temperature conductivity of Cr_2O_3 is controlled by the oxidative volatilization and not by an intrinsic band-to-band process. Furthermore, the band gap of Cr_2O_3 has been reported to be 462.3 kJ/mol (4.8 eV),²⁸ which would yield an activation energy of 231.2 kJ/mol (2.4 eV), not the commonly found value of 165 kJ/mol (1.7 eV), for the high-temperature region if it dominated the conductivity.

The lack of P_{O_2} dependence in the high-temperature region reported in previous studies^{7,13} could be due to the slow diffusion rate of oxygen. In measuring the conductivity dependence on P_{O_2} for dense samples, it was found that after extreme reduction, the initial conductivity could not be restored even after 2 d of reoxidation at 1000°C. However, if samples were heated 50° to 100°C higher for a short time and then cooled, the initial values were readily obtained. It appears that the kinetics are such that increasing temperature has a more profound influence in restoring the equilibrium than does increasing the oxygen partial pressure. Recently, Hoshino *et al.*¹⁰ observed a P_{O_2} dependence of $3/16$ for diffusion of Cr vacancies in Cr_2O_3 . Their experiment was carried out at 1550°C in the low P_{O_2} region using an undoped single crystal. The highly dense single crystal and low P_{O_2} reduced the chance of volatilization, and the high testing temperature could greatly enhance the equilibrium between the sample and the ambient conditions. Their data suggest that the conductivity in the high-temperature region should show a P_{O_2} dependence of $3/16$, since the concentration of cation vacancies is directly related to the hole concentration by the neutrality condition shown in Eq. (4); however, these measurements were not reported.

IV. Conclusions

The influence of volatilization on the electrical conduction behavior of acceptor-doped Cr_2O_3 were studied by conductivity and thermogravimetric analysis (TGA) measurements. Results indicate that both the defect structures and the conduction behavior of

Cr_2O_3 are affected by volatilization. The dependence of electrical conductivity on oxygen partial pressure can be altered from $1/4$ to $3/8$ on samples affected by the volatilization. The volatilization process is influenced by the temperature, the oxygen activity, and the moisture content in the ambient. It was observed that the volatilization of Cr_2O_3 can occur even in the low P_{O_2} region, due to a moisture-enhanced process.

TGA data have shown that volatilization occurs at temperature higher than 1473 K in high P_{O_2} regions. Strong evidence suggests that the formation of Cr vacancies and the associated electron holes induced by the volatilization may be the dominating factor for the conduction behavior of Cr_2O_3 in the high-temperature region rather than an intrinsic band-to-band process. The formation energy of the Cr vacancy and the associated holes was determined to be 363.8 ± 22 kJ/mol. The activation energy for the mobility term is 16.0 ± 0.3 kJ/mol, which indicates that the conduction is by the small polaron hopping process.

References

- G. M. Crosbie, G. J. Tennenhouse, R. P. Tischer, and H. S. Wroblewa, "Electrically Conducting Doped Chromium Oxides," *J. Am. Ceram. Soc.*, **67** [7] 498–503 (1984).
- P. R. Champman, R. H. Coriffith, and J. D. F. Marsh, "The Physical Properties of Chromium Oxide–Aluminium Oxide Catalysts. II. Electrical Properties," *Proc. R. Soc. London, Sect. A*, **224**, 419–26 (1954).
- R. F. Huang, A. K. Agarwal, and H. U. Anderson, "Oxygen Activity Dependence of the Electrical Conductivity of Li-Doped Cr_2O_3 ," *J. Am. Ceram. Soc.*, **67** [2] 146–50 (1984).
- W. C. Hagel, "Electrical Conductivity of Li-Substituted Cr_2O_3 ," *J. Appl. Phys.*, **36** [8] 2586–87 (1965).
- K. A. Hay, F. G. Hicks, and D. R. Holmes, "The Transport Properties and Defect Structure of the Oxide ($\text{Fe}, \text{Cr}_2\text{O}_3$) Formed on Fe–Cr Alloys," *Werk St. Korros.*, **21** [11] 917–24 (1970).
- D. B. Meadowcroft and F. G. Hicks, "Electrical Conduction Processes and Defect Structure of Chromium Oxides," *Proc. Br. Ceram. Soc.*, **23**, 33–41 (1972).
- J. A. Crawford and R. W. Vest, "Electrical Conductivity of Single-Crystal Cr_2O_3 ," *J. Appl. Phys.*, **38** [8] 2413–18 (1964).
- L. N. Cojocaru, "Electrical Properties of Non-Stoichiometric Cr_2O_3 ," *Z. Phys. Chem. (Munich)*, **64**, 255–62 (1968).
- D. De Dogan and G. A. Loneragan, "Carrier Mobility in Cr_2O_3 ," *J. Phys. Chem. Solids*, **38**, 333–34 (1977).
- K. Hoshino and N. L. Peterson, "Cation Self-Diffusion in Cr_2O_3 ," *J. Am. Ceram. Soc.*, **66** [11] C-202–C-203 (1983).
- P. Kofstad and K. P. Lillerud, "On High Temperature Oxidation Mechanism of Chromium," *J. Electrochem. Soc.*, **127** [11] 2410–19 (1980).
- T. F. Kassner, L. C. Walters, and R. E. Grace, *Thermodynamics*, Vol. II, pp. 357–71. International Atomic Energy Agency, Vienna, Austria, 1966.
- W. C. Hagel and A. U. Seybolt, "Cation Diffusion in Cr_2O_3 ," *J. Electrochem. Soc.*, **108**, 1146–52 (1961).
- N. Toker and L. S. Darken, "Preparation of Cr_2O_3 Crucibles and the Defect Structure of Cr_2O_3 ," *Geochim. Cosmochim. Acta*, **39**, 847–52 (1975).
- D. Caplan, A. Harvey, and M. Cohen, "The Effect of Surface Preparation on Oxide Films on Cr and Fe–Cr Alloys," *J. Electrochem. Soc.*, **108**, [2] 134–39 (1961).
- K. P. Lillerud and P. Kofstad, "On High Temperature Oxidation of Chromium. I. Oxidation of Annealed, Thermally Etched Chromium at 800–1100°C," *J. Electrochem. Soc.*, **127** [11] 2397–409 (1980).
- C. A. Stearns, F. J. Kohl, and G. C. Fryburg, "Oxidative Vaporization Kinetics of Cr_2O_3 in Oxygen from 1000° to 1300°C," *J. Electrochem. Soc.*, **121** [7] 945–51 (1974).
- D. Caplan and M. Cohen, "The Volatilization of Chromium Oxide," *J. Electrochem. Soc.*, **108** [5] 438–42 (1961).
- H. C. Graham and H. H. Davis, "Oxidation/Vaporization Kinetics of Cr_2O_3 ," *J. Am. Ceram. Soc.*, **54** [2] 89–93 (1971).
- N. W. Kim, "Volatilization of Chromium Oxide in Oxygen and Water Vapor," Ph.D. Thesis. University of Pennsylvania, Philadelphia, PA, 1969.
- M. Pechini, "Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coatings Using the Same to Form a Capacitor," U.S. Pat. No. 3,330,697, July 1967.
- B. K. Flandermeier, M. M. Nasrallah, A. K. Agarwal, and H. U. Anderson, "Defect Structure of Mg-Doped LaCrO_3 Model and Thermogravimetric Measurements," *J. Am. Ceram. Soc.*, **67** [3] 195–98 (1984).
- H. U. Anderson, "Influence of Oxygen Activity on the Sintering of MgCr_2O_4 ," *J. Am. Ceram. Soc.*, **57**, [1] 34–36 (1974).
- J. M. Wimmer and I. Bransky, *Electrical Conductivity in Ceramics and Glass*, Part A: pp. 274–78. Marcel Dekker, New York, 1974.
- P. D. Ownby and G. E. Jungquist, "Final Sintering of Cr_2O_3 ," *J. Am. Ceram. Soc.*, **55** [9] 433–36 (1972).
- J. S. Park and H. G. Kim, "Electrical Conductivity and Defect Models of MgO-Doped Cr_2O_3 ," *J. Electrochem. Soc.*, **71** [3] 173–76 (1988).
- C. Greskovich, "Deviation from Stoichiometry in Cr_2O_3 at High Oxygen Partial Pressures," *J. Am. Ceram. Soc.*, **67** [6] C-111–C-112 (1984).
- G. V. Samsonov, *Oxide Handbook*; p. 214. IFI/Plenum Press, New York, 1982.