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Influence Of Oxygen Activity On The Sintering Of MgCr₂O₄

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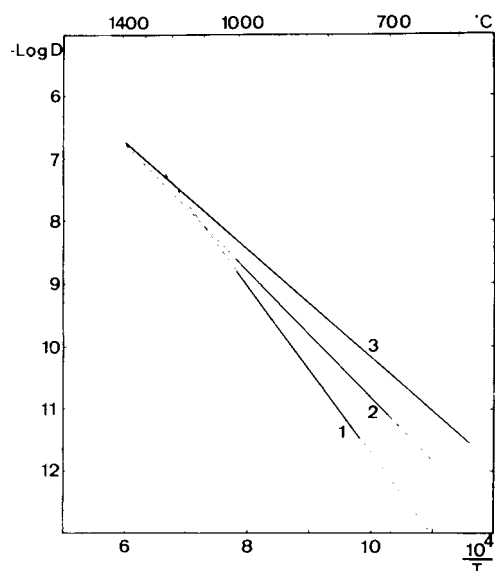


Fig. 7. Oxygen self-diffusion coefficients in (1) 83 mol% SiO_2 potassium silicate (Ref. 24) and in (2) 74 mol% SiO_2 potassium silicate (Ref. 24) and (3) binary interdiffusion coefficients of Si in 78 mol% SiO_2 potassium silicate (present work).

Acknowledgments

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Influence of Oxygen Activity on the Sintering of MgCr_2O_4

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The sintering behavior of MgCr_2O_4 powder compacts was investigated as a function of temperature, time, and oxygen activity. The results show that MgCr_2O_4 cannot be densified to >70% of theoretical density at temperatures up to 1700°C if the oxygen activity exceeds 10^{-6} atm. The oxygen activity must be decreased to $<10^{-10}$ atm before densities exceeding 90% of theoretical can be achieved. Weight loss and X-ray data indicated that maximum density occurred at an oxygen activity just above that where MgCr_2O_4 becomes unstable.

I. Introduction

OXIDES with high Cr contents are in general difficult to sinter to high densities without the use of pressure. However, a study of the sintering of Cr_2O_3 by Ownby and Jungquist¹ showed that high density can be achieved when the oxygen activity is near that specified by the $\text{Cr}/\text{Cr}_2\text{O}_3$ phase boundary. The densification of Cr_2O_3 is thought to be related to the stabilization of the Cr ion in its trivalent state.² At oxygen activities higher than those specified by this equilibrium, $\text{Cr}_2\text{O}_3(s)$ is unstable to volatilization as $\text{CrO}_2(g)$ and $\text{CrO}_3(g)$ as a result of oxidation of the Cr ion.

Because of the success of the work of Ownby and Jungquist,¹ a study of picrochromite was initiated. It was anticipated that densification of MgCr_2O_4 would show a dependence on oxygen activity similar to that observed for Cr_2O_3 . Since Mg has a stable divalent form, densification can again be expected to occur through stabilization of Cr ion in the trivalent state. Therefore, the oxygen-activity dependence can be assumed to be related to the reaction



The equilibrium O_2 partial pressure at 1600°C was calculated from thermodynamic data^{3,4} to be $\approx 10^{-12}$ atm, about the same as the pressure calculated for Cr_2O_3 .¹

II. Experimental Procedure

Picrochromite powder was prepared by a process developed by Pechini.⁵ Chromium nitrate* and MgCO_3 * were dissolved in separate solutions containing citric acid and ethylene glycol. Each solution was carefully analyzed for Cr and Mg content.

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*Certified, Fisher Scientific Co., Pittsburgh, PA.

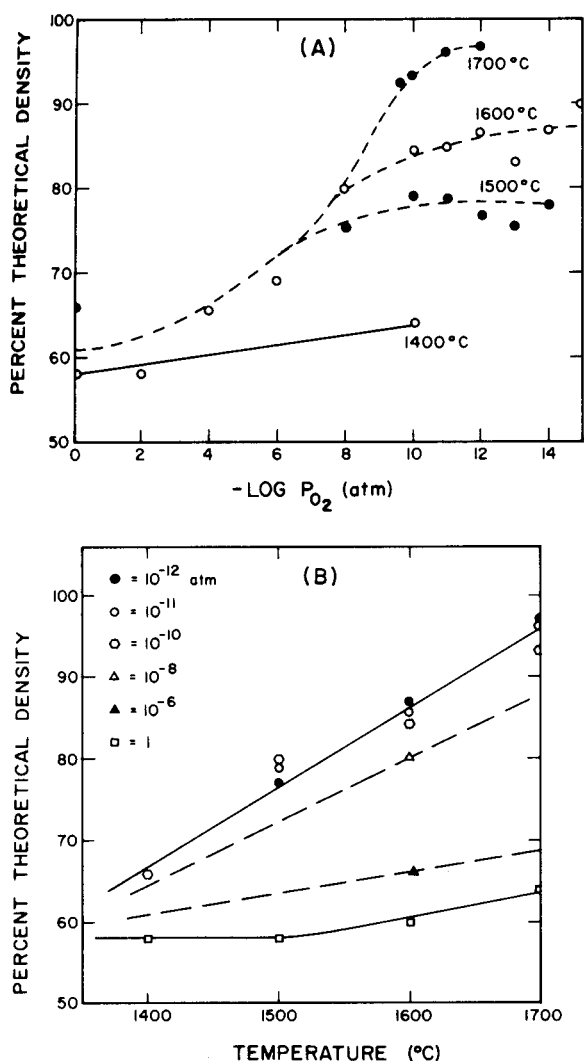


Fig. 1. Density of $MgCr_2O_4$ compacts as a function of (A) oxygen activity and (B) sintering temperature. Theoretical density = 4.42 g/cm³; time = 1 h.

The solutions were then quantitatively mixed in the ratio of 1 atom Mg to 2 atoms Cr. The resulting solution was heated and slowly evaporated to dryness. As the solution evaporated polymerization occurred, and an amorphous substance resulted. Since the Mg and Cr ions were randomly mixed in the solution, they remained well mixed in the glassy solid. When the solid was heated to 800°C, it was converted to powder with an average particle size of $<0.1 \mu m$. X-ray diffraction of the calcined powder proved that the oxide thus prepared was single-phase picrochromite. The only impurities present should be those of the starting components, which would yield a purity $\geq 99.9\%$.

The powder was isostatically pressed into compacts $\frac{1}{2}$ in. in diameter and $\approx \frac{1}{4}$ in. thick at 30,000 psi. The densities of the green compacts were 58 to 61% of theoretical. The theoretical density calculated from X-ray data is 4.42 g/cm³. The compacts were sintered at 1400° to 1700°C in an Mo-wound tube furnace in a controlled O_2 atmosphere which was established by using mixtures of CO and CO_2 with a total flow rate of 1 cm/s, in accord with Darken and Gurry.⁶

The bulk density and open porosity were determined by the Archimedes method. Specimen dimensions were measured before and after sintering to ± 0.001 in. with a micrometer. Weight loss was ascertained by weighing the specimens before and after sintering on an analytical balance.* X-ray diffrac-

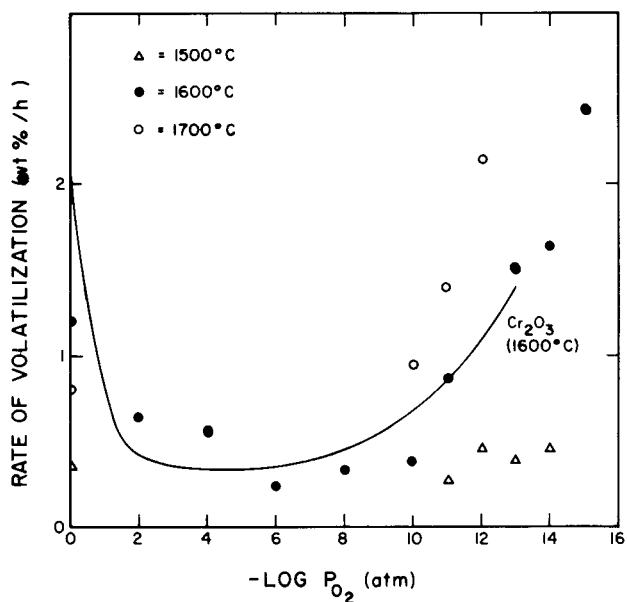


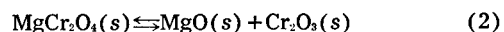
Fig. 2. Rate of volatilization of $MgCr_2O_4$ compacts as a function of oxygen activity.

tion data were taken on powder samples before and after sintering. Scanning electron micrographs of selected sintered specimens were obtained.

III. Results

The densification results (Fig. 1) showed that $MgCr_2O_4$ cannot be densified to $>80\%$ of theoretical density at oxygen activities above 10^{-8} atm even at 1700°C. The highest density ($\approx 97\%$) was obtained by sintering at 1700°C for 10 h at an oxygen activity of 10^{-11} atm. Equally high densities were obtained at 1600°C and 10^{-12} atm oxygen activity. Very little pressure dependence of densification was observed at oxygen activities from 10^{-10} to 10^{-12} atm. Within this range densities $>96\%$ of theoretical were obtained by sintering at either 1600° or 1700°C; the only difference was the time necessary to reach the desired density.

At oxygen activities below 10^{-12} atm, the densification results became erratic, and in many cases density decreased. To determine what was occurring, X-ray diffraction data were taken for several specimens. The X-ray results showed that $MgCr_2O_4$ is stable at oxygen activities above 10^{-12} atm, even at 1700°C. This result was expected from the free-energy data of Tretjakow and Schmalzried.³ For the reaction



these workers found that the free energy of reaction is +6600 cal/mol at 1 atm pressure and 1600°C. Thus reaction (2) should not occur at high oxygen activities.

When the oxygen activity was decreased to 10^{-13} atm, the X-ray data show that Cr_2O_3 began to appear at 1600°C as a second phase. Despite the fact that the sensitivity of the X-ray analysis for MgO was nearly the same as that for Cr_2O_3 , no MgO was detected, in agreement with the thermodynamic prediction that reaction (2) does not occur.

Figure 2 shows the weight-loss data for $MgCr_2O_4$. At 1500°C, the weight loss was <0.5 wt%/h at all oxygen activities. The data for 1600° and 1700°C are very similar to those observed for $Cr_2O_3(s)$. The solid line in Fig. 2 was taken from Ownby and Jungquist's data.¹ The rates at 1600°C are nearly identical to those observed by Ownby and Jungquist. The rates at 1700°C are shifted to higher oxygen activities. This shift can be accounted for by the movement of the Cr/ Cr_2O_3 phase boundary from 10^{-12} atm O_2 at 1600°C to 10^{-11} atm at 1700°C.

*Mettler Instrument Corp., Princeton, NJ.

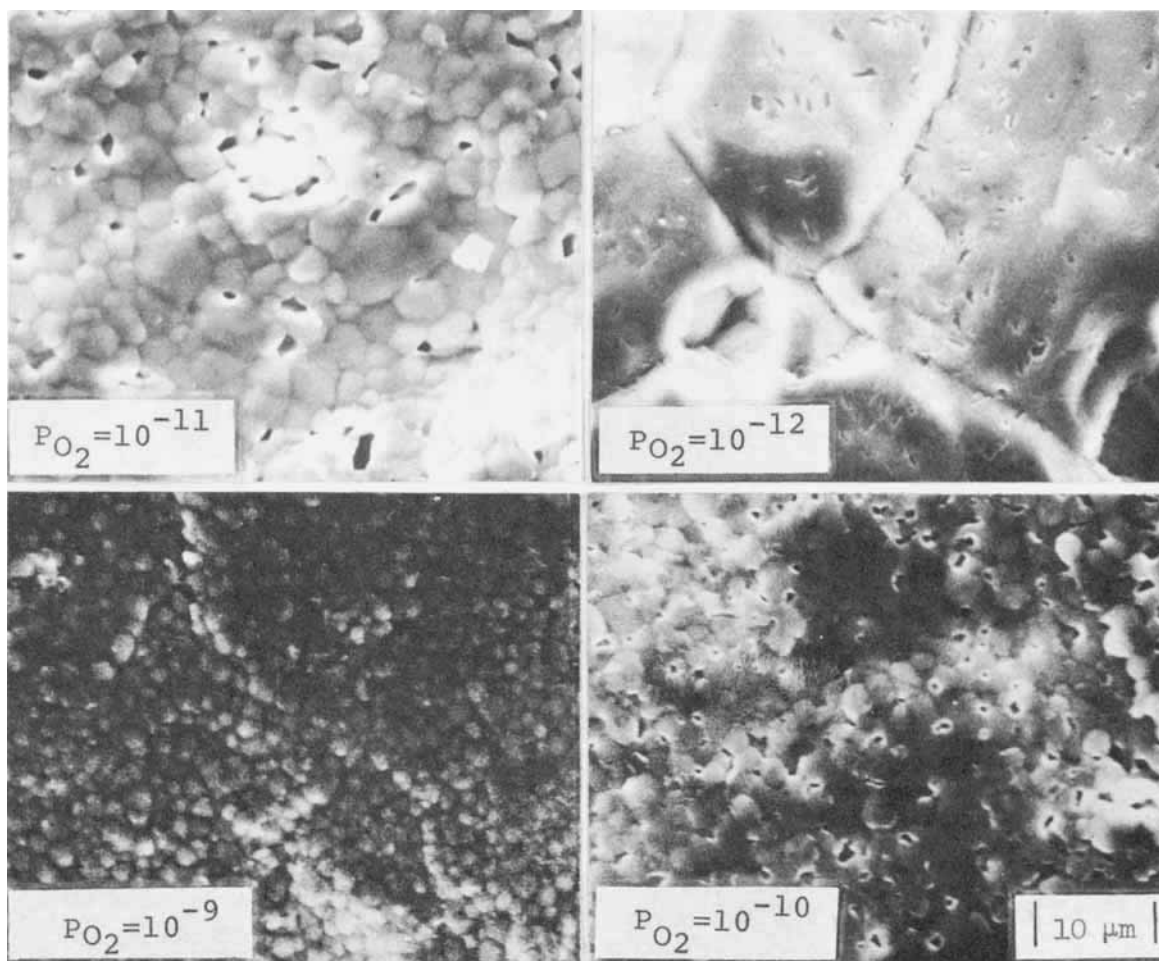


Fig. 3. Scanning electron micrographs of MgCr_2O_4 compacts sintered at 1700°C for 1 h.

Because of the similarity in the volatilization data, the explanation of Ownby and Jungquist' of the variation of weight loss with oxygen activity appears to be applicable to MgCr_2O_4 . These workers showed that the weight loss was the result of volatilization of $\text{Cr}(g)$, $\text{CrO}(g)$, $\text{CrO}_2(g)$, and $\text{CrO}_3(g)$. The partial pressure of each gas depends on oxygen activity. Ownby and Jungquist demonstrated that it was possible to calculate from thermodynamics the variation of the partial pressure of each of these gases with varying oxygen activity and to construct a weight-loss curve which is very similar to that shown in Fig. 2. Thus, the correct disproportionation reaction probably involves the formation of volatile Cr compounds; however, insufficient data are available to choose between the possible mechanisms.

In an effort to further delineate the disproportionation reaction and the sintering process, scanning electron micrographs were taken of surfaces of sintered specimens (Fig. 3). The average grain size of each microstructure is listed in Table I. Figure 3 and Table I show that exaggerated (discontinuous) grain growth occurred at 10^{-14} and 10^{-12} atm at 1600° and 1700°C , respectively. The grain growth at each temperature also depends rather strongly on oxygen activity.

The microstructure changes rather sharply when discontinuous grain growth occurs. Instead of being smooth and equiaxed, the grains become rough and irregular, indicating that either considerable volatilization or dissociation of the individual grains has occurred. Thus, the onset of irregular grain growth correlates well with the increased volatilization rate and the appearance of $\text{Cr}_2\text{O}_3(s)$. Grain growth at constant pressure was approximately proportional to the square root of time, as is typical for diffusional grain growth in solids.

Table I. Average Grain Size as a Function of O_2 Partial Pressure, Time, and Temperature

Temp. ($^\circ\text{C}$)	Time (h)	Grain size (μm) at given O_2 partial pressure (atm)						
		10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	10^{-15}
1500	1							1.4
1600	1			1.2	1.3	2	7	8
	5				3	7		
	8			3.5				
	10				4			
1700	1	1	1.6	3	20			
	10		5					

In addition to the temperature and time dependencies, the grain-growth kinetics also depended on oxygen activity, suggesting that more than one transport mechanism is operative. This behavior complicates the treatment of the sintering kinetics such that none of the current intermediate sintering models^{7,8} can be used. Before models can be successfully applied, much more data on densification rate and grain-growth kinetics as functions of temperature and oxygen activity are needed.

IV. Conclusions

(1) MgCr_2O_4 cannot be densified to $>70\%$ of theoretical density at temperatures up to 1700°C when the oxygen activity exceeds 10^{-6} atm.

(2) At 1700°C MgCr_2O_4 can be sintered to densities $>96\%$ of theoretical at oxygen activities below 10^{-10} atm.

- (3) At 1600°C MgCr₂O₄ is unstable at oxygen activities of <10⁻¹³ atm.
- (4) The weight loss at 1600° and 1700°C increases from about zero to several percent when disproportionation occurs.
- (5) The grain-growth kinetics are complex and probably involve several mechanisms operating simultaneously.
- (6) The volatilization rate of MgCr₂O₄ is similar to that observed for Cr₂O₃.

Acknowledgments

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Empirical Relation Between Self-Diffusion and Electrical Conduction in Mixed-Alkali Glasses

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An empirically modified Nernst-Einstein-type equation is proposed to relate the electrical conductivity of mixed-alkali glasses to the self-diffusivities of the alkali ions. Conductivities were calculated for 3 glass systems using measured self-diffusivities and the proposed equation. These calculated conductivities and those measured directly agree quite well.

I. Introduction

SEVERAL properties of mixed-alkali glasses do not conform to the additivity relation. In the electrical conductivity pronounced minima, as much as 5 to 7 orders of magnitude below the values for the end-member compositions, are observed. This effect, commonly termed the mixed-alkali effect,[†] has been investigated by several workers.²⁻⁹ No reasonably successful explanation for this effect has been given, although an electrodynamic model proposed by Hendrickson and Bray⁹ (hereafter termed the HB model) appears promising. Whereas most previous models of the mixed-alkali effect have been based on empirical ideas, the HB model uses virtually no empiricism.

In the HB model, the electrical conductivity (without correlation effects) is written in terms of a Nernst-Einstein-type relation.¹⁰ Contributions to the conductivity expression are derived from electrodynamically associated alkali ions and the remaining unassociated alkali ions. Support for the model is cited in terms of successful calculation of the tracer diffusivities of the alkali ions as a function of glass composition from the conductivity-vs-composition curves or vice versa. According to Hendrickson and Bray,⁹ the measured tracer mobilities differ from the true mobilities of each species because of electrodynamic interactions.

Although the present paper attempts to interrelate the conductivity of, and the diffusivities in, mixed-alkali glasses, it does not explain the mixed-alkali effect. In contrast to the HB model, it assumes the existence of a mixed-alkali effect such that the measured mobility of each ion at a particular composition is still the true mobility of that ion at that composition regardless of interactions. With this assumption, it is shown that the dc conductivity can be calculated at a given composition from the known tracer diffusivities at that composition, using an empirically derived modification of the Nernst-Einstein equation.

It should be emphasized that this work is primarily empirical. Thus, only a little effort has been exerted to justify the

expressions in the key equation (Eq. (2)), as discussed in Section IV. In Section III, measured conductivities in 3 systems (from the literature) are compared with those calculated using the present approach.

II. Conductivity-Diffusion Equation

The Nernst-Einstein relation between the electrical conductivity, σ , and the self-diffusivity, D , of ion A is

$$\sigma = [N_A e^2 / (kT)] (D_{(A)}) / f_A \quad (1)$$

where (A) = tracer of A, N_A = number of A ions/unit volume, f_A = a correction factor equal to the correlation factor for the motion of tracer ion (A) when unit transfer of mass is accompanied by unit transfer of charge, e = electronic charge, k = the Boltzmann constant, and T = absolute temperature.

The correlation factor, generally, is taken to account for the motion of the tracer ion relative to the regular ions. However, Haven and Stevels¹¹ have pointed out that in some types of diffusion mechanism, the jump distance for the conductivity is not identical to that for the diffusivity. For example, in the direct exchange (A)⁺ ⇌ A⁺, whereas the tracer ion hops over a unit distance, the charge does not move at all. The correlation factor, in such cases, should be modified to account for this difference. Another possible means for overcoming this problem is subtraction of the number of particles which do not take part in conduction from the total number of particles. The proposed relation between conductivity and the self-diffusivities in a mixed-alkali system is based on the latter method. It is suggested that, in a mixed-alkali system, a fraction C_{AB} (= $C_A C_B$; C_i = moles of i /total moles of alkali) does not take part in the conduction process. Thus, the modified Nernst-Einstein relation for mixed-alkali systems is

$$\sigma = \frac{Ne^2}{kT} \left[\frac{(C_A - C_{AB})D_A}{f_{OA}} + \frac{(C_B - C_{AB})D_B}{f_{OB}} \right] \quad (2)$$

where N = total number of alkali particles/unit volume, f_{oi} = correlation factor in "pure" i glass (end composition), and the measured self-diffusivity, $D_{(i)}$, is written as D_i for simplicity. Or, since $C_A + C_B = 1$,

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†A good review on this topic is given in Ref. 1.