oxygen enters the lattice substitutionally. According to a theory by Lidiard,[6] substitutional impurities diffuse in ionic crystals by forming complexes with vacancies on the same sublattice. One may therefore expect oxygen to diffuse into CaF_2 by forming complexes with fluorine vacancies.

One may further question whether the penetration is limited by the extrinsic or intrinsic diffusion rate of oxygen into CaF_2.[7] On the basis of Lidiard's theory, the activation energy for intrinsic diffusion, Q_i, in CaF_2 should be given by

$$Q_i = U + {}^{1}\!/_{2}F \qquad (4)$$

in which U is the activation energy for the mobility of complexes and F is the formation energy of an anti-Frenkel defect. The intrinsic activation energy would be obtained when the oxygen concentration at the penetration interface is much smaller than the intrinsic vacancy concentration. In the extrinsic limit, the diffusion activation energy, Q_e, should be given by

$$Q_e = U \qquad (5)$$

The extrinsic diffusion activation energy would be expected to control oxygen penetration if the oxygen concentration at the interface is much greater than the intrinsic fluorine vacancy concentration.

Ure[4] has determined that $F = 65 \pm 5$ kcal per mole in CaF_2, so it remains to estimate U. If the mobility of complexes is limited by the ability of fluorine vacancies to circulate about the oxygen ion, one may expect U to be about equal to the 12 kcal per mole activation energy for fluorine vacancy mobility in CaF_2.[4] If this hypothesis is valid, $Q_i \cong 45$ kcal per mole and $Q_e \cong 12$ kcal per mole. The experimental activation energy for oxygen penetration is 46 kcal per mole, consistent with the value estimated for the intrinsic-diffusion-limited case. The intrinsic vacancy concentration in the temperature range studied varies from 0.02 to 1.33%.[4] The oxygen concentration was 0.2% behind and about 0.002% in front of the penetration interface. At the highest temperature, even the oxygen concentration behind the interface satisfies the condition for intrinsic diffusion. Since no break from an Arrhenius relation was observed in the temperature range studied, the writers concluded that the penetration was intrinsic-diffusion-limited throughout. This conclusion was further supported by the fact that the penetration rate was the same in air and in oxygen in spite of the fact that the oxygen concentration behind the diffusion front was an order of magnitude greater for oxygen.

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[6] (*a*) A. B. Lidiard, "Impurity Diffusion in Polar Crystals," *Phil. Mag.* [7], **46**, 815–23 (1955).
(*b*) A. B. Lidiard, "Impurity Diffusion in Crystals (Mainly Ionic Crystals with the Sodium Chloride Structure)," *Phil. Mag.* [7], **46**, 1218–37 (1955).

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Sintering of Zinc Oxide

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Sintering studies have been conducted with single crystal spheres of zinc oxide in air at total pressures of 10^{-3} to 1.0 atm over the range 1050° to 1250°C. Quantitative observations were made on the rate of growth of a neck between the spheres. No change in the distance between the geometrical centers of the spheres was observed. An analysis of the kinetic data shows that sintering was predominantly achieved by distillation through the surrounding gas phase. At 1150° the rate of welding was inversely influenced by the total pressure when the latter was changed from 0.003 to 0.75 atm. No conclusion could be reached on the effect of the oxygen partial pressure at constant total pressure. A brief summary of the various sintering mechanisms of zinc oxide from 700° to 1250°C is presented.

I. Introduction

PREVIOUS studies on the welding together of monocrystalline microspheres of nonstoichiometric zinc oxide (quenched from a zinc vapor environment) showed that volume diffusion of the excess zinc ions is responsible for the observed sintering in the range 700° to 900°C, the driving force for the process being supplied by the surface oxidation of the excess zinc.[1] Whenever the required excess of zinc has been oxidized, this mechanism of sintering (a type of chemical sintering) ceases to operate and the welding of zinc oxide microspheres occurs by a process characterized by a different driving force. In this paper the writers report some experiments aimed at clarifying the nature of physical sintering mechanisms operative with zinc oxide.

II. Experimental Method and Results

To minimize the effects of chemical sintering the present experiments were carried out at higher temperatures than previous experiments on zinc oxide microspheres whose composition had been equilibrated with the surrounding gas phase.

Sintering data were obtained by measuring the growth rate of the neck formed between two contacting microspheres of zinc oxide. The spheres were obtained by crushing clear,

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[1] V. J. Lee and G. Parravano, "Sintering Reactions of Zinc Oxide," *J. Appl. Phys.*, **30** [11] 1735–40 (1959).

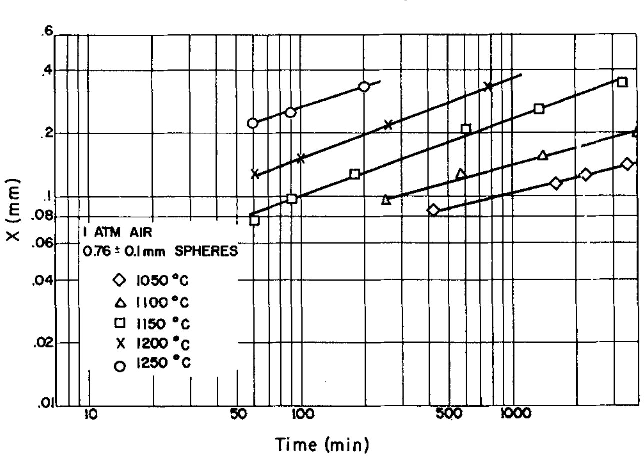

Fig. 1. Radius of bridge between particles (x) vs. time in sintering of zinc oxide microspheres.

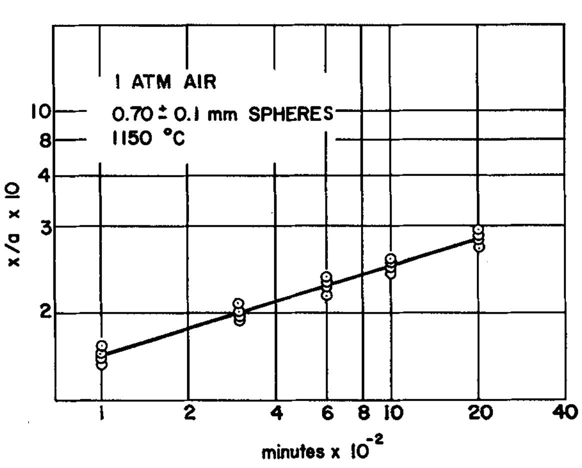

Fig. 2. Width of neck between spheres over sphere diameter (x/a) vs. time in sintering of zinc oxide microspheres.

single crystals of zinc oxide into smaller crystals which were ground and polished using air-grinding techniques previously discussed.[1] Final diameters of the spheres were on the order of 0.5 mm. The chemical composition, X-ray data, and spectroscopic analyses of the zinc oxide specimens, as well as the average value of their electrical conductivity, have already been reported.[1]

The microspheres were placed in a groove cut in a Pt10Rh rod which formed the heating element of a totally closed hot stage.[2] Observations were made through an optically flat quartz window. A creep-test microscope, equipped with a filar eyepiece micrometer, was vertically mounted above the heating rod, enabling direct observations of the growth of the bridge between the spheres at sintering temperatures. Measurements of the distance between spheres were used to check for shrinkage.

The current to the heating rod was supplied through a stepdown transformer, Variac, and voltage stabilizer. Temperatures were measured by means of a potentiometer and a Pt–PtRh thermocouple welded to the rod adjacent to the location of the zinc oxide microspheres. Temperatures were kept at a constant value (±2°C) by a stepless controller connected to a saturable reactor.

Sintering studies were made in air and in mixtures of electrolytic oxygen with purified helium or nitrogen. A dynamic gas system was used throughout. For runs made in air a flow rate of approximately 22 cm^3 per minute was maintained. Preliminary runs showed no effect of the gas flow rate on the rate of sintering with gas flow rates from 0 to 75 cm^3 per minute. Flow rates at subatmospheric pressure were obtained by means of a vacuum pump and capillary tubings on each side of the hot stage.

Typical results for sintering in air at 1 atm and at 1050° to 1250°C are shown in Fig. 1. The reproducibility of the data can be gaged from Fig. 2 which includes results from four runs under similar conditions. The effect of total gas pressure was studied by conducting experiments at air pressures from 3×10^{-3} to 1 atm. There was evidence that at higher pressures the rate of welding was inversely influenced by the pressure. Experiments aimed at detecting the effect of the oxygen partial pressure at constant total pressure were inconclusive.

Long, needle-shaped crystals developed on the surface of the spheres at temperatures greater than 1150°C. They showed no preferential region of growth on the spheres. At 1250°C crystallite formation posed experimental difficulties by growing across the neck region and obscuring observation. In some cases a crystallite bridge, produced by interlocking crystallites, was formed before substantial sintering occurred.

Measurements of end-to-end distances for two sintering spheres in air generally showed no change during sintering. Occasionally an increase in the end-to-end distance was observed. Metallographic examination of spheres exhibiting this behavior revealed the presence of a whisker embedded in the neck region.

III. Discussion

The conclusions which can be derived from the experimental data presented in the previous section are: (*a*) neck growth between single crystal zinc oxide microspheres occurred readily in air in the range 1050° to 1250°C; (*b*) at constant temperature and pressure, the experimental results could be fitted to an equation

$$x^m = kt \qquad (1)$$

x = width of neck between spheres.
t = time.
m,k = constants.

(Fig. 1), the average value of m being 3. This value was obtained by averaging the results of about 40 runs whose deviation never exceeded ±0.6. There was a tendency, however, for the higher values of m to predominate at the lowest temperature whereas with increasing temperature the value of m showed a tendency to decrease; (*c*) at constant temperature and air pressures of 0.003 to 0.75 atm the rate decreased as the total pressure increased; at higher pressures this effect was not observed; (*d*) the rate of neck growth varied exponentially with temperature; (*e*) over the whole range of experimental conditions investigated, the rate was independent of the flow velocity of the gas stream.

The results under (*b*) can be explained by assuming that the rate of growth of the neck is controlled by distillation of matter from the sphere surfaces to the neck region since, according to previous derivations,[3] the rate of mass transported to the neck by distillation is given by

$$\frac{x^3}{a} = \frac{3\pi M\gamma p}{\rho^2 RT}\left(\frac{M}{2\pi RT}\right)^{1/2} t \qquad (2)$$

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[2] H. M. O'Bryan, Jr., and G. Parravano, "Sintering of Titanium Dioxide"; pp. 191–99 in Powder Metallurgy—Proceedings of an International Conference, New York, 1960. Edited by Werner Leszynski. Interscience Publishers, Inc., New York, 1961. 847 pp.; *Ceram. Abstr.*, **1962**, August, p. 203*b*.

[3] W. D. Kingery and M. Berg, "Study of Initial Stages of Sintering Solids by Viscous Flow, Evaporation-Condensation, and Self-Diffusion," *J. Appl. Phys.*, **26** [10] 1205–12 (1955); *Ceram. Abstr.*, **1956**, February, p. 45*c*.

a = sphere diameter.
M = molecular weight of solid species.
γ = surface tension.
p = equilibrium partial pressure.
ρ = density.

It is to be noted that equation (2) refers to distillation in vacuum. Neglecting this condition and applying equation (2) to the present results by the use of experimental values of x^3/a averaged over several runs conducted at total pressures well below 1 atm (<0.04 atm) at 1150°C with $\rho = 5.61$ g cc^{-1} and $\gamma = 1000$ dynes cm^{-2}, it is possible to calculate a value of $p = 0.082$ mm Hg. This value is in satisfactory agreement with the literature value of 0.062 mm Hg.[4] Assuming a characteristic transport distance, L, in the present system of $\sim$ 0.5 mm and since the mean free path, l, in the vapor phase under the foregoing conditions is $\sim$0.05 mm, the ratio $l/L \cong 0.1$, indicating that the flow around the zinc oxide spheres was in the transition range between viscous and molecular.[5] This illustrates the extent of the simplification in using equation (2) in the present instance. In addition, taking the neck volume equal to $\pi x^4/16a$, where x and a are neck and sphere diameters, respectively, and assuming that all zinc oxide which was evaporated was condensed in the neck area, the evaporation rate from two spheres can be found equal to 3.11×10^{-8} g hr^{-1} from runs completed at 1150°C and 2.7×10^{-3} atm. In a study of the rate of formation of zinc aluminate from zinc oxide and alumina, in the same temperature range used in the present sintering experiments, the rate of evaporation of zinc oxide was found to be[6]

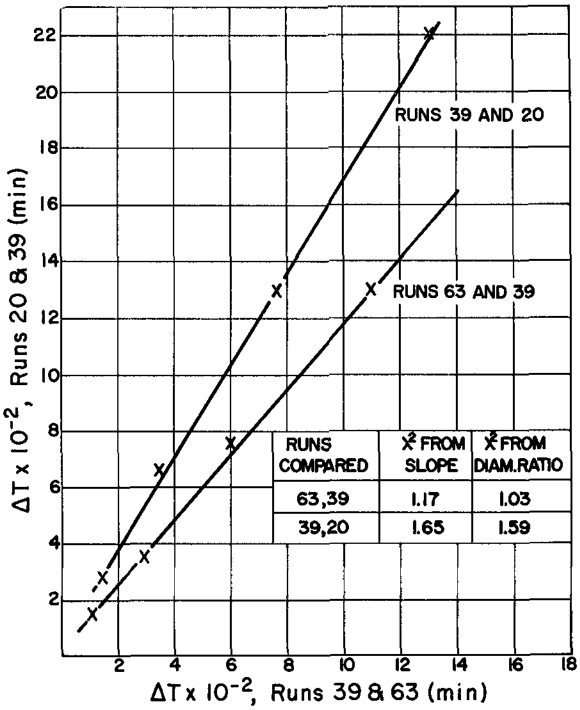
$$R = 6.3 \times 10^9 \exp\left(-\frac{95{,}000}{RT}\right) \text{ g cm}^{-1}\text{ hr}^{-1} \qquad (3)$$

Under the conditions of the present experiments equation (3) gives $R = 8.08 \times 10^{-7}$ g hr^{-1}. No condensation of zinc oxide was ever observed in the colder parts of the hot stage or in the connecting equipment. However, the assumption of the condensation of all zinc oxide vapor species in the neck region represents a simplification which results in an evaporation rate lower than the actual rate. Under these conditions the computation of the rate from equation (3) gives an upper limit for the value of the rate of evaporation. This is just the result obtained by comparing the values of the rate computed from the writers' experimental results and from those obtained in the other investigation.[6] The two values are within an order of magnitude indicating that sufficient evaporation is occurring to effect sintering, irrespective of the dynamic flow conditions and that the assumption of complete condensation of vapor species in the neck between spheres is not too unrealistic.

The tendency for the rate of welding to decrease with increasing air pressure at constant temperature may be the result of diffusional limitations to the evaporation flux. Since the flow rate of gas did not influence the observed growth rate of the neck at atmospheric pressure, the resistance to the flux of the evaporation species can be traced to natural convection through a density gradient in the vapor of zinc oxide adjacent to the solid surface. Under these conditions, the proper expression for the rate of sintering is[7]

$$\frac{x^3}{a} = \frac{6\pi D}{\delta}\left(\frac{M}{\rho RT}\right)^2 \gamma p t \qquad (4)$$

where δ and D are the thickness of the boundary layer and the diffusion coefficient for species in the gas phase, respectively. A rough estimate of $D = 2.0$ cm^2 sec^{-1} can be made[8] and from the value of the mean free path in the gas phase, δ is approximately 10^{-4} cm. Using these values in equation (4) and the present experimental data for runs at 1 atm and 1150°C, a value of $p = 0.093$ mm Hg is deduced. This value is again in good agreement with that obtained by direct measurements.[4] It should be noted that no agreement in the value of the equilibrium vapor pressure is observed for runs at 1 atm if the model based on the rate of evaporation as controlling step is used.



RUNS COMPARED	λ^2 FROM SLOPE	λ^2 FROM DIAM.RATIO
63,39	1.17	1.03
39,20	1.65	1.59

Fig. 3. Effect of change of sphere size on sintering time.

The effect of a change in size of the spheres on the sintering rate for the mechanisms discussed here shows[7, 9] that the ratio between the times required for the growth of similar neck width is the following function of the sphere diameters:

$$\lambda^2 = \Delta t_1/\Delta t_2 = (a_1/a_2)^2 \qquad (5)$$

Figure 3 compares values of (a_1/a_2) as obtained from observed times for equivalent amounts of sintering with values obtained directly from the ratios of the sphere radii. Although there is a large amount of scattering in the experimental points and the range of λ investigated was only from 1 to 1.4, Fig. 3 shows that the results are not inconsistent with relation (5).

The activation energy calculated from the experimental data (Fig. 4) is 105 to 110 kcal per mole. This result should be compared with the value of 95 kcal per mole of equation (3) and with the value of the evaporation energy of zinc oxide of 123 kcal per mole.[4] The observation that the center-to-center distance of spheres during sintering remained constant can be taken as further evidence for the operation of the distillation mechanism.

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[5] Saul Dushman and J. M. Lafferty, Scientific Foundations of Vacuum Technique, 2d ed., p. 81. John Wiley & Sons, Inc., New York, 1962. 806 pp.

[6] Bo Bengtson and Robert Jagitsch, "Untersuchung der Kinetik der Spinellbildung bei der Umsetzung zwischen Zink-und Aluminumoxyd" (Kinetic Studies on Formation of Spinel from Zinc Oxide and Alumina), *Arkiv Kemi*, **24A** [18] 1–16 (1947); *Ceram. Abstr.*, **1948**, June, p. 141g.

[7] J. B. Moser and D. H. Whitmore, "Kinetics of Sintering of Sodium Chloride in the Presence of an Inert Gas," *J. Appl. Phys.*, **31** [3] 488–93 (1960).

[8] R. C. Reid and T. K. Sherwood, Properties of Gases and Liquids—Their Estimation and Correlation. McGraw-Hill Book Co., Inc., New York, 1958. 420 pp.

[9] Conyers Herring, "Effect of Change of Scale on Sintering Phenomena," *J. Appl. Phys.*, **21** [4] 301–303 (1950).

IV. Conclusions

It is instructive to summarize briefly the results of the studies on the transport mechanisms observed during the welding together of monocrystalline spheres of zinc oxide. At low temperatures a solid-state diffusional transport predominates.[1] The transport is the result of the nonstoichiometric nature of zinc oxide and involves a relatively low activation energy (~35 kcal per mole). There is evidence that the carriers are excess zinc ions. Oxygen partial pressure and impurity content of zinc oxide affect the rate of welding. Differences in chemical potential of the zinc ions may arise either as a result of surface oxidation (chemical sintering) or as a consequence of the presence of the small convex neck area (physical sintering). In both cases the bulk of the spheres is the source of the carriers, but their sink is represented by the surface of the sphere for the former, and by the neck area for the latter case. Between 700° and 900°C chemical sintering is predominant, whereas physical sintering through bulk diffusion is appreciable at about 1000° to 1050°C. At higher temperatures (1100° to 1250°C) the diffusional transport is greatly overshadowed by the transfer of matter through the surrounding gas phase. Sintering then becomes dependent on the rate of evaporation of zinc oxide. In principle, three cases are possible. The transport through the gas phase may not be slowed down by convective phenomena. The rate of transfer is then controlled by the rate of evaporation and is independent of total pressure and gaseous flow rate, and it involves a rather high activation energy (109 kcal per mole). This mechanism tends to occur at total pressures of less than 1 atm. At higher pressures, diffusive control of the rate of evaporation may set in. Sintering becomes dependent on the total pressure (natural convection) and, at high flow velocities, should be proportional to a fractional power of the flow velocity of the carrier gas (forced convection). The energy values involved in solid diffusion and evaporation are the factors which determine the type of sintering to be followed.

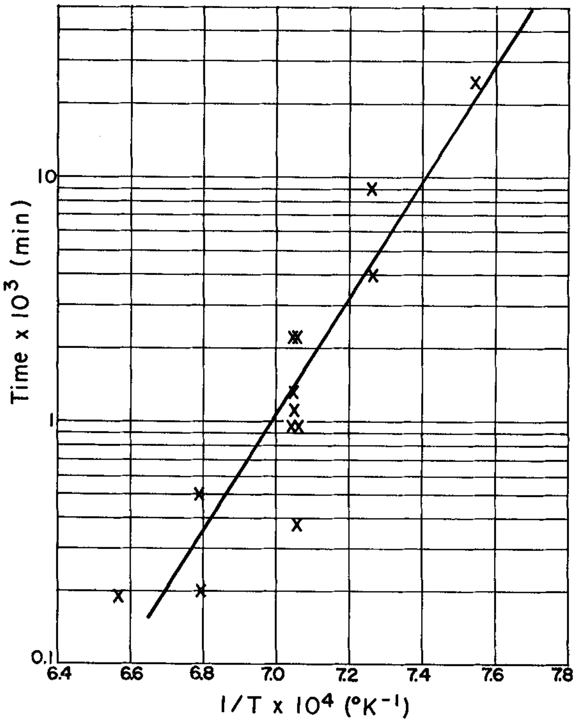

Fig. 4. Variation of the time to reach x/a = 0.3 vs. reciprocal of the temperature at 1 atm pressure.

Relation of Single-Crystal Elastic Constants to Polycrystalline Isotropic Elastic Moduli of MgO

by **DAE-HYUN CHUNG, JOSEPH J. SWICA, and WILLIAM B. CRANDALL**

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The three elastic compliance coefficients of synthetic periclase were determined in the kilocycles per second frequency range by a resonance method. Polycrystalline elastic moduli on dense-formed MgO were measured. The calculated isotropic elastic moduli for polycrystalline MgO obtained from the single-crystal constants are in good agreement with experimental values measured on the dense MgO at the theoretical density point. The measured Young's modulus and the shear modulus of polycrystalline MgO are found to be 30.50 and 12.90 × 10^{11} dynes per cm^2 respectively. The results of the present investigation are compared with the earlier work in the megacycles per second frequency range. A theoretical analysis is made to establish the validity of the present values. Schemes of averaging the single crystalline elastic constants for polycrystalline behavior are reviewed for crystals of cubic symmetry.

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