JOURNAL OF MATERIALS SCIENCE 3 (1968) 158-164

Surface-Diffusion Studies on UO_2 and MgO*

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Received 27 October 1967

An optical interferometric technique has been used to study the growth of grain boundary grooves and the decay of surface scratches on UO_2 and MgO at temperatures in the range 1100 to 1700° C. The results were interpreted using equations derived by W. W. Mullins and it was found that surface-diffusion was the predominant material transport process for both oxides under the experimental conditions used. Surface-diffusion coefficients and activation energies were calculated, and gave the following equations for the variation of the mass transfer surface-diffusion coefficient D_s with temperature.

$$UO_{2.005},\quad D_s = 1.3 \times 10^8 \exp^{-110000 \pm 15000}/RT \text{ [1200 to 1400° C]}$$

$$MgO,\quad D_s = 8 \times 10^4 \exp^{-88500 \pm 15000}/RT \text{ [1200 to 1500° C]}$$

It was found that for UO_2 the rate of grooving increased markedly as the oxygen content of the oxide increased.

1. Introduction

The measurement of surface-diffusion coefficients is generally difficult, and as pointed out by Blakely [1], the data currently available on them is very meagre. The derivation by W. W. Mullins of equations showing how surface features would develop and change their dimensions at a given temperature under the effect of surface tension forces indicated a convenient method of measurement. Expressions were derived relating the rate of growth of a grain boundary groove to surface-diffusion [2] and volume-diffusion [3] mechanisms, and recently King and Mullins [4] have published similar equations describing the decay of surface scratches. These relationships have been used to obtain diffusion data for metals [5-7], but only one application to ceramic materials has so far been noted [8]. The work reported here describes thermal grooving and scratch healing experiments carried out on UO_2 and MgO, and the subsequent use of Mullins' equations to calculate surface-diffusion coefficients.

2. Experimental

2.1. Materials

The UO_2† was obtained as a large grain size fused product with an O:U ratio of 2.05, and <0.1 wt % total metallic impurity content. Two samples of MgO were used, one being a high-density, warm-pressed polycrystalline product and the other a large crystal-fused material from which single crystals of about 1 cm across were cleaved. The MgO samples contained <0.5 wt % total metallic impurities.

2.2. Theory of the Method

Mullins [2] showed that under the action of surface tension forces, with surface-diffusion as the process by which matter was transported, a grain boundary groove would assume the shape shown in fig. 1, and the distance w between the humps would increase as

$$w = 4.6\,(Bt)^{\frac{1}{4}} \qquad (1)$$

with t = experimental time, and $B = D_S.\gamma.\Omega^2.n/kt$, where D_S = surface-diffusion coefficient,

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*First read at an International Symposium on Reaction Mechanisms of Inorganic Solids, a meeting arranged by the Chemical Society and held at the University of Aberdeen, 11-16 July 1966.

†The symbol UO_2 will be used throughout as an abbreviation for the compound uranium dioxide without particular reference to its composition. Where the stoichiometry is referred to it will be written as e.g. $UO_{2.00}$.

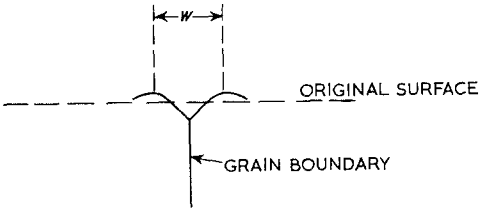

Figure 1 Grain boundary profile.

γ = surface energy, Ω = molecular volume of diffusing species, and n = number of molecules/cm^2 of surface.

In deriving this equation he assumed that γ did not vary with orientation, and that the groove which developed had a small slope with respect to the original flat surface.

A similar equation

$$w = 6.9\,(Bt')^{\frac{1}{4}} \qquad (2)$$

was derived by King and Mullins [4] to describe the decay of a single symmetrical surface scratch. In this equation t' is not the experimental time, but is related to it by the equation

$$t' = (t + t_0)$$

where t_0 is a fictitious time, the significance of which is discussed in King and Mullins' original work [4].

The experimental results were analysed according to equations [1] and [2] by plotting log w versus log t, or w^4 versus t as appropriate, and if they conformed with the theoretical exponent of $\frac{1}{4}$ then B and hence D_S was obtained.

3. Preparation of Specimens, Heat Treatment and Measurement

Flat specimen surfaces were prepared, polished on papers, and finally on a rotating lap with 0 to 1 μm diamond powder, and were then cleaned by ultrasonic vibration in trichlorethylene. Scratches were made by a Vickers diamond indenter in a Tukon hardness tester. The rotatable stage allowed scratches to be made in any desired direction. It was found that better scratches were produced if, after polishing, the specimen was heated for some hours at 1200 to 1400° C, and this became standard practice with the MgO. With the UO_2 specimens it was always necessary to heat them at the temperature, and in the atmosphere, which was going to be used for the experiment. This allowed the O:U ratio to reach a constant value. For the grain boundary grooving experiments this meant that a final, polish had to be given to obtain a flat surface for the start of the experiment.

Heating to 1600° C was carried out in an alumina tube furnace, the specimens being supported in closed crucibles of either MgO or UO_2. The heating rate was 15 to 20° C/min with the test temperature controlled at $\pm 10°$ C. At the end of a run the power was turned off, and the specimen cooled at 25° C/min to 1000° C, and then to room temperature over about 1 h. The experiments at 1700° C were performed in an induction furnace using a tantalum susceptor, the heating and cooling rates being approximately 50° C/min. The furnace atmosphere was provided by passing dry air over the specimen in the case of MgO, and either dry high purity argon or dry hydrogen in the case of the UO_2. These two gases were used with UO_2 to vary the oxygen partial pressure, and hence to study the effects of different O:U ratios.

With each specimen of UO_2 several smaller pieces were introduced, and used to check the stoichiometry of the UO_2 as the experiment proceeded. The O:U ratio was found by oxidising the specimen to U_3O_8 at 850° C in air. Generally the gases were dried by passing through magnesium perchlorate, although with MgO three experiments were performed in air which was moistened by bubbling through water before entering the furnace.

The widths of grooves and scratches were measured from an image of the specimen surface obtained with a Nomarski interferometer attached to the objective of a Reichert metallurgical microscope; this type of interferometer gives a double image of the groove, one of which is inverted. In the image produced, the depth of the groove is greatly exaggerated compared with the width. Photographs of the pattern were taken on 35-mm film, and measurements of groove or scratch width made with a travelling microscope on an enlarged print. The magnification was accurately found by photographing a 10 μm scale with each series. In general three photographs of each specimen were taken, as in fig. 2, and the groove width found from measurements made on twenty symmetrical profiles. Observations were made on two or three grain boundaries, and if any asymmetry developed, measurements on the boundary affected were discontinued.

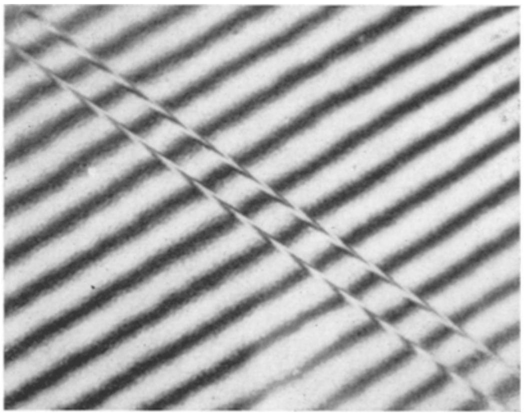

Figure 2 Typical interference pattern showing grain boundary groove on UO_2 after 10 h at 1300° C in dry argon (×400).

4. Results

Measurements made on the interference patterns indicated that the slope of the grain boundary profile made $\tan^{-1} < 0.3$ with respect to the flat surface, and so it was considered that the small slope approximation of Mullins [2] was justified. In order to calculate the surface-diffusion coefficient (D_S) a value of the surface energy $\gamma = 1000$ erg/cm^2 was assumed for both materials; this point will be discussed later. The volume of the diffusing species Ω cm^3/mole was taken as molecular weight/density $\times$ N, where N is Avogadro's Number, and n was taken as being equal to $\Omega^{-\frac{2}{3}}$mole/cm^2. Estimates of the accuracy of measurement of the profiles indicated a possible error of $\pm 40\%$ in B. Hence if errors in γ and Ω are neglected, this is also the error in D_S. The relative error in the derived ΔH values is then about $\pm$15000 cal/mole and it is worth noting that these ΔH values do not depend on γ and Ω [8]. The results for the two oxides will be given separately.

4.1. Uranium Dioxide

Figs. 3 and 4 are plots of log w versus log t for grain boundary grooving experiments carried out in argon and hydrogen respectively, and fig. 5, shows plots of w^4 versus t for scratch decay experiments in a hydrogen atmosphere. In each of these experiments agreement with the theoretical equations indicated that surface-diffusion was the dominant transport process and values of B and D_S were calculated. The D_S values found are summarised in table I, which shows that at constant temperature D_S was reduced as the O:U ratio became less. From an Arrhenius plot of the data given in fig. 6, an activation energy $\Delta H = 110000 \pm 15000$ cal/mole was found and the pre-exponential term

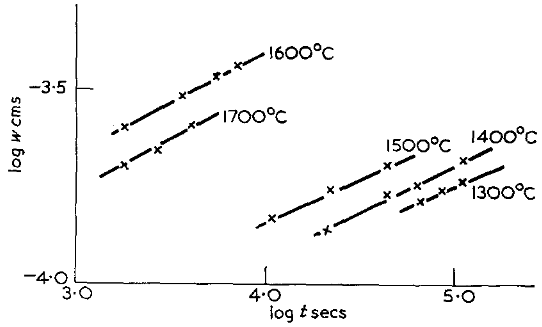

Figure 4 Log/log plot of grain boundary groove width versus time for UO_2 in dry hydrogen.

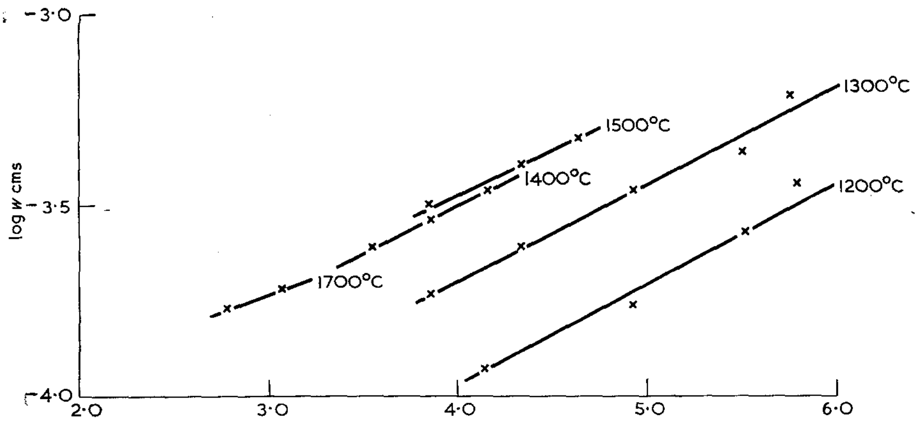

Figure 3 Log/log plot of grain boundary groove width versus time for UO_2 in high purity argon.

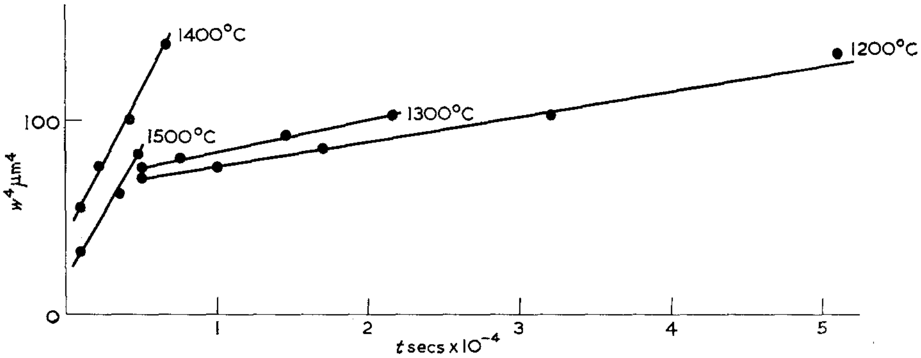

Figure 5 Plot of (scratch width)^4 versus time for UO_2 in dry hydrogen.

TABLE I D_s values for UO_2 (assuming $\gamma = 1000$ erg/cm^2).

Temperature (° C)	D_s in argon g.b. grooving (cm^2/sec)	O:U ratio	D_s in dry H_2 g.b. grooving (cm^2/sec)	O:U ratio	D_s in dry H_2 scratch decay (cm^2/sec)	O:U ratio
1200	4.0×10^{-9}	2.007			8.0×10^{-10}	2.001
1300	6.2×10^{-8}		3.7×10^{-9}		3.0×10^{-9}	
1400	3.6×10^{-7}	2.005	6.3×10^{-9}	2.001	1.5×10^{-8}	
1500	5.3×10^{-7}		1.6×10^{-8}		1.0×10^{-8}	2.000
1600	1.3×10^{-6}		1.1×10^{-6}			
1700	5.4×10^{-7}	2.000	4.5×10^{-7}	1.996		

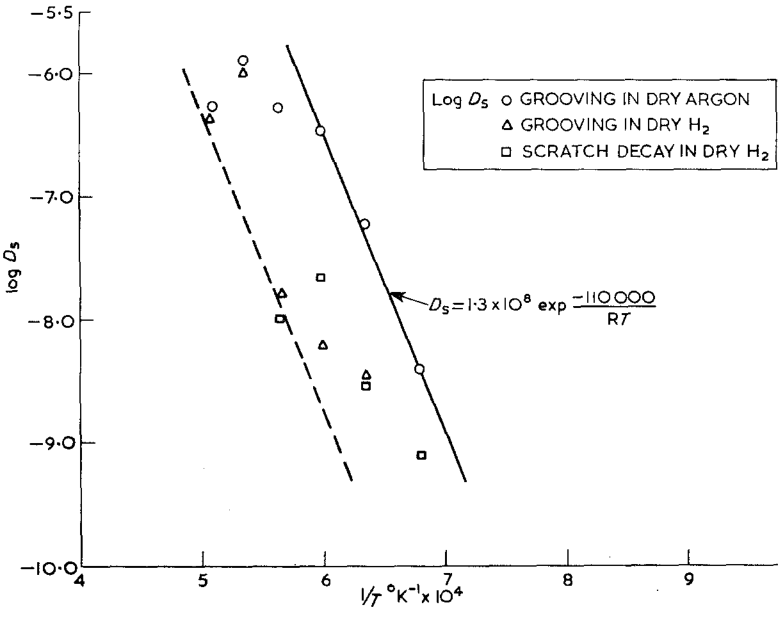

Figure 6 Plot of $\log_{10} D_s$ versus $1/T$ for UO_2.

$D_0 = 1.3 \times 10^8$ cm^2/sec. The results indicate that as the O:U ratio is lowered, D_0 decreases, with ΔH remaining approximately constant.

4.2. Magnesium Oxide

Plots of log w versus log t for the polycrystal are shown in fig. 7, and were found to be in agreement with the theoretical slope of $\frac{1}{4}$ for surface-diffusion. The large crystal MgO was cleaved to give (100) planes and then ground to give faces near (110) and (111). These faces were scratched in known directions. Plots of

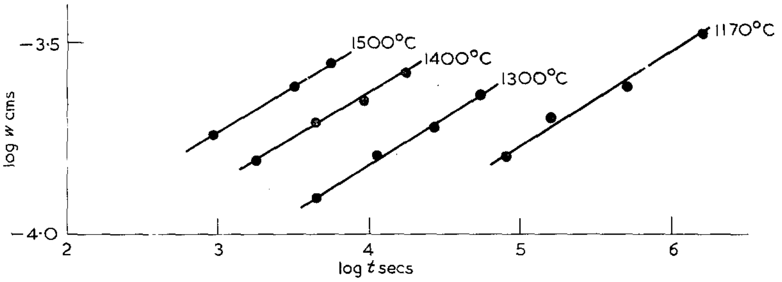

Figure 7 Log/log plot of grain boundary groove width versus time for MgO in dry air.

w^4 versus t for the scratches were generally found to be straight lines; no dependence of rate of scratch decay on direction was noted, but it was observed that the rate of scratch decay was slowest for orientations near the (111) plane. The calculated values for D_S are summarised in table II, and a plot of log D_S versus $1/T°$ K is given in fig. 8. This figure includes results of three experiments carried out on the polycrystal in moist air, indicating that the presence of moisture reduced the rate of grain boundary grooving. An activation energy $\Delta H = 88500$ cal/mole with $D_0 = 8 \times 10^4$ cm²/sec was calculated for the MgO polycrystal heated in dry air.

5. Discussion

Both UO_2 and MgO gave results which are in good agreement with Mullins' theory for surface-diffusion. No attempt has been made to subtract the contribution to grooving made by volume-diffusion; because of the close adherence to the $t^{\frac{1}{4}}$ relationship and the small groove widths

TABLE II D_s values for MgO in dry air (assuming $\gamma = 1000$ erg/cm²).

Temperature (° C)	Grain boundary grooving (polycrystal) (cm²/sec)	Scratch decay (single-crystal) (cm²/sec) (100)	near (110)	near (111)
1100		2.6×10^{-9}	5.0×10^{-9}	2.9×10^{-9}
1170	3.4×10^{-9}			
1200		3.2×10^{-8}	2.8×10^{-8}	1.1×10^{-8}
1300	5.4×10^{-8}	3.4×10^{-7}	2.6×10^{-7}	1.0×10^{-7}
1400	2.8×10^{-7}			
1500	1.1×10^{-6}			

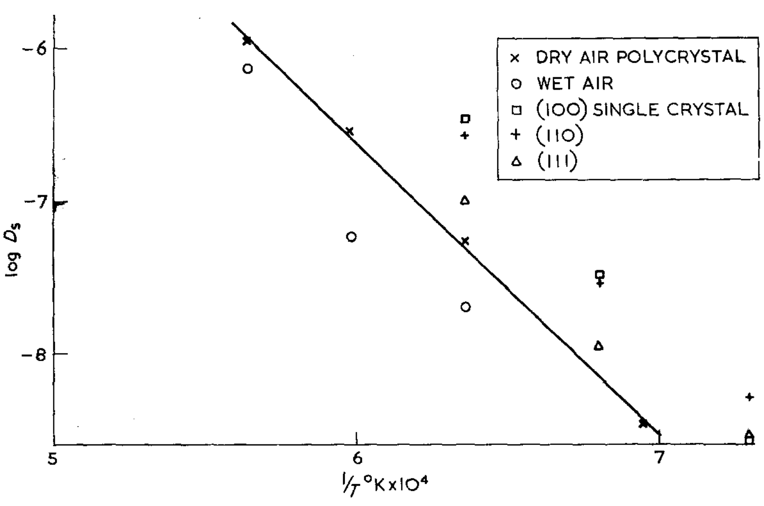

Figure 8 Plot of $\log_{10} D_s$ versus $1/T$ for MgO.

involved – the maximum was usually <5 μm – it was considered that volume-diffusion could be neglected.

The calculation of D_S depends on a knowledge of the surface energy γ. Values of γ for solids are not very well known and the methods of measurement and measured values that do exist have been criticised [9]. A value of $\gamma = 1030$ erg/cm^2 has been calculated for UO_2 by Benson [10], and for MgO both calculated and measured values of about 1000 erg/cm^2 have been published [11, 12]. Therefore, in the absence of other data the value $\gamma = 1000$ erg/cm^2 independent of temperature has been used in these experiments for both materials.

The results of the experiments on UO_2 show a marked dependence on the O:U ratio of the specimen, with the rate of grooving and scratch decay decreasing significantly as the oxygen content decreases. This makes it essential that the O:U ratio remains constant throughout any given experiment, otherwise the slopes of log w versus log t plots can be appreciably greater or smaller than $\frac{1}{4}$, possibly leading to the wrong interpretation of the process. Apparently the effect can be such as to suggest that D_S decreases with increasing temperature – for example in fig. 3, the rate of groove growth at 1700° C is slower than at 1600° C. This effect of stoichiometry on the transport properties of UO_2 has been observed in several studies [16]. Williams *et al* [17] found that the density of polycrystalline UO_2 showed a major increase as the compositions being sintered changed from $UO_{2.00}$ to $UO_{2.02}$, and Hawkins [15] has measured the coefficients for the volume self-diffusion of uranium in UO_2, and found an increase in D_V with increasing oxygen content. It is interesting to observe that an activation energy ΔH_V calculated from his values agrees reasonably well with that calculated for surface-diffusion. The reason for the increase of the diffusion coefficient with increasing oxygen content is not clear, but a theoretical explanation has recently been proposed by Lidiard [18].

The experiments with MgO indicate that the effects of orientation and direction are not very marked. Theoretical work has shown that only a weak dependence on orientation might be expected, and that in a cubic crystal directional effects would be absent in the (100) and (111) planes, but might occur in the (110) plane [14]. The experiments on UO_2 were carried out on faces within a few degrees of (111), and scratches made in random directions behaved alike. However, recent experiments have indicated that there might be a marked orientation effect with UO_2 and a possible change in D_S of $\simeq 10^1$ between "slow" and "fast" faces [19]. The faces studied in the experiments reported here can probably be regarded as "fast" faces.

The high values found for the activation energy are contrary to early speculations on surface-diffusion, when it was considered that the activation energy would be substantially smaller than that for volume-diffusion. The theoretical basis for the calculation of D_S is not yet well established, but Shewmon and Choi give the expression [20]

$$D_S = D_0 \exp^{-\Delta H_S/RT}$$

where $D_0 = n^1 \left(\frac{1}{4}\right) L^2 \nu \exp^{\Delta S_S/R}$, and n^1 is a constant having values between 1 and 2, L is the mean jump distance of the diffusing species, and ν is the vibration frequency. According to Shewmon and Choi $\Delta H_S \sim \frac{2}{3} L_S$, where L_S is the latent heat of sublimation. The values found for ΔH_S in this work are in reasonable agreement with this prediction. The high values found for D_S and ΔH_S lead to high values of D_0, and in the case of UO_2 an activation entropy ΔS_S of ~ 40 entropy units can be calculated (assuming $L = a_0$) which is approaching the entropy change for evaporation of UO_2 (~ 65 entropy units). The finding of high values of ΔS for surface-diffusion has led to the consideration that the diffusing species behaves as a two dimensional gas. However, it has been pointed out by Gjostein [14] that if this were the case then $L \gg a_0$ and D_0 (surface) would be much greater than D_0 (lattice) from this factor alone. Suffice it to say that the high values found here for ΔH_S and D_0 are in general agreement with some of the current ideas on surface-diffusion although the theory is not yet sufficiently well advanced to fully explain them. It should be remembered that the diffusion studied in this work refers to the transfer of mass in which the movement of different types of atoms is coupled to prevent composition fluctuations, and therefore comparison with tracer diffusion, or with mass transfer in pure elements, can be misleading.

A further point to consider is the state of the surface, and the effects of polishing and scratching in producing strain, which might affect the experimental measurements. It was found in scratch experiments that when MgO was heated for short times at relatively low temperatures

(<1200° C), then w decreased rather than increased, possibly because of the relaxation of induced strain; with longer heating times and higher temperatures the effect seemed to be unimportant. As far as the adsorption of gaseous impurities is concerned, at the temperatures used it might be expected that this would be negligible and the surface would be in equilibrium with the furnace atmosphere. The D_S values found refer to this condition.

6. Conclusions

(i) Thermal grain boundary grooving and scratch decay experiments carried out on UO_2 in dry hydrogen and high purity argon have shown that at temperatures of 1200 to 1700° C surface-diffusion is responsible for the material transport. The rate of grooving and scratch decay decrease markedly as the O:U ratio approaches 2.000. For $UO_{2\cdot005}$ the surface self-diffusion coefficient can be expressed by

$$D_S = 1.3 \times 10^8 \exp^{-110\,000 \pm 15\,000/RT} \quad [1200 \text{ to } 1400° \text{ C}]$$

For $UO_{2\cdot00}$ the activation energy remains about the same, but the pre-exponential factor is reduced to $\sim 1 \times 10^7$.

(ii) Similar experiments with MgO* have also shown that surface-diffusion is the dominant transport process, and for polycrystalline MgO heated in dry air the surface self-diffusion coefficient is given by

$$D_S = 8 \times 10^4 \exp^{-88500 \pm 15\,000/RT} \quad [1200 \text{ to } 1500° \text{ C}]$$

The presence of water vapour slightly reduces the rate of groove growth but the effects of orientation and direction are not very marked.

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20. See [1] p. 407.

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*Since this report was first written it has been drawn to the authors' attention that the results for MgO are in very good agreement with a similar study carried out by Dr W. M. Robertson of the North American Aviation Science Center. A paper describing this work was submitted to Proceedings, International Conference on Sintering and Related Phenomena (Notre Dame, 21 June 1965).