IMPURITY EFFECTS ON THE CREEP OF
POLYCRYSTALLINE MAGNESIUM AND
ALUMINUM OXIDES AT ELEVATED TEMPERATURES

MASTER

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December 19, 1969 to December 18, 1970

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TECHNICAL PROGRESS REPORT

December 18, 1970

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Magnesium and Aluminum Oxides at Elevated Temper-
atures

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CONTRACTOR: University of Utah
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ABSTRACT

The creep of iron doped polycrystalline magnesium oxide and iron and chromium doped polycrystalline aluminum oxide between 1300 and 1550°C is discussed in this report. The creep of iron doped MgO is viscous and very sensitive to changes in the oxygen partial pressure. With decreasing P_{O_2} the creep rate decreases and the creep activation energy increases. However, in iron doped Al_2O_3 the creep rate increases and the creep activation energy decreases with decreasing P_{O_2} . Possible mechanisms to explain these effects are discussed. The creep of iron and chromium doped Al_2O_3 is non-viscous with a creep exponent of 1.3. The creep of chromium doped Al_2O_3 is insensitive to changes in oxygen partial pressure.

Finally transient creep in $MgO-Fe_2O_3$ solid solutions is analyzed in terms of two concurrent mechanisms:

- 1) An exponential (partially recoverable) viscoelastic decay process which can be described by a Kelvin solid, and
- 2) "Steady state" creep which will show transient behavior if simultaneous grain growth is occurring.

Anelastic grain boundary sliding is tentatively proposed as the mechanism for the exponential decay process.

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I. INTRODUCTION

The research activities under Contract AT(11-1)-1591 during the period December 19, 1969 to December 18, 1970 are described in this report and in the attached preprints^(1,2). *(Preprints removed)*

Major effort was devoted to the following:

- 1) Extensive experimental work on the effects of oxygen partial pressure on the creep of polycrystalline magnesium oxide doped with Fe_2O_3 .
- 2) Preliminary experiments on the creep of Cr_2O_3 and $\text{FeO-Fe}_2\text{O}_3$ doped polycrystalline aluminum oxide.
- 3) Analysis of transient creep in polycrystalline $\text{MgO-Fe}_2\text{O}_3\text{-FeO}$ solid solutions and magnesium oxide.

In addition to these activities, which are described in this report, two studies were completed and are described in two attached preprints;

- 1) The Calculation of Strains and Stresses in Four-Point Bending Creep Tests⁽¹⁾,
- 2) Grain Size Distributions and Grain Growth in MgO and $\text{MgO-Fe}_2\text{O}_3$ Solid Solutions⁽²⁾.

A complete listing of the bibliography of papers and theses prepared under this contract to date is given at the end of the report in Section VI.

II. EFFECT OF OXYGEN PARTIAL PRESSURE ON THE CREEP OF POLYCRYSTALLINE $\text{MgO-FeO-Fe}_2\text{O}_3$ SOLID SOLUTIONS

In this section a summary of the results to date is given on studies relating to the effects of oxygen partial pressure, stress, and temperature on the creep of Fe_2O_3 doped magnesium oxide. In addition lattice parameter, microprobe and scanning electron microscope studies are briefly described.

A. Experimental

1. *Hot Pressing* - During this contract year it became apparent that, due to problems encountered with the high frequency generator, temperatures sufficient for hot pressing polycrystalline MgO and Al_2O_3 could not be attained by induction heating. Consequently it was decided to construct a resistance heated hot press, using a heating element made of molybdenum wire cast in alumina. Using the basic furnace shell which had been used on the induction unit, the new hot press has been constructed and is operational. Temperatures of 1450 - 1700°C have been reached to hot forge samples of polycrystalline MgO and Al_2O_3 between graphite plungers at pressures up to 5000 psi. The pressing can be accomplished either in vacuum or in a reducing atmosphere. Samples of both MgO and Al_2O_3 doped with iron have now been produced in which theoretical density has been nearly achieved.

2. *Sample Characterization* - Samples of polycrystalline MgO (containing 0.1, 1.0, 5.0, and 10.0% by weight Fe_2O_3 (0.056, 0.56, 2.8, 5.6 cation % Fe)) have been successfully hot pressed. After pressing, the billet is cut to approximately the desired size of the creep specimen (2 x 4 x 30 mm). These

samples are then annealed at 1450°C in air for 160 hours prior to creep testing to insure homogeneity of the iron and to stabilize the grain size.

After annealing, density and initial grain size measurements are made on representative samples in the usual manner. Values for several of the samples are given in Table 1, along with values of the grain size of the specimens after creep testing.

A precision lattice parameter study⁽³⁾ was conducted on various samples of iron-doped MgO which were equilibrated in air at 1400°C. A Debye-Scherrer back reflection camera was used with a chromium target X-ray tube. The values of the lattice parameters, which were determined, are given in Table 1. The lattice parameter remained essentially unchanged over the range of dopant levels encountered in this study. The lattice parameters were used in the calculation of the theoretical density of each of the samples. These values are also given in Table 1.

Electron microprobe studies⁽³⁾ were conducted on samples of MgO containing 0.1%, 1.0%, and 10.0% Fe₂O₃ by weight. Representative microprobe image patterns are given in Figures 1B and 1D along with the corresponding optical photomicrographs in Figures 1A and 1C. In the 0.1% and 1.0% samples, the iron dopant is apparently evenly distributed throughout the sample. In the 10% Fe₂O₃ sample, about 5% of the grains were an iron-rich second phase. The composition of this phase was: Fe - 50%; Mg - 10%; and O - 40%. Throughout the remainder of the sample, the iron was evenly distributed. No noticeable iron segregation at the grain boundaries was observed in any of the samples.

3. *Creep Testing* - After polishing the annealed specimens through 15 μ m diamond, they are creep tested under dead-load, four-point bending

Table 1
Characterization of Fe-Doped MgO Samples

wt % Fe_2O_3	Density gm/cm^3	Porosity %	Initial Grain Size (μ)	Final Grain Size (μ)	Lattice Parameter ($\text{\AA}$)	*Theoretical Density (gm/cm^3)
0	---	---	---	---	4.213	3.584
0.1	3.579	0.2	18	22	4.2127	3.585
1.0	3.583	0.3	14	14	4.2122	3.594
5.0	3.578	1.5	12	12	---	3.632
8.0	---	---	---	---	4.2125	3.661

* Calculated on basis of Fe in lattice in trivalent-state.

A. Optical - 1% Fe_2O_3 - 200X

B. Microprobe - 1% Fe_2O_3 - 200X

C. Optical - 10% Fe_2O_3 - 200X

D. Microprobe - 10% Fe_2O_3 - 200X

Figure 1. Electron Microprobe Analyses of Magnesium Oxide Doped with 1 and 10% Fe_2O_3 .

conditions in a molybdenum wound resistance creep testing facility which has been described previously⁽⁴⁾. One addition has been made to the furnace; a solid-state galvanic cell has been introduced to measure the oxygen partial pressure in the sample chamber. The cell consists of a calcia-stabilized zirconia tube with platinum electrodes attached to both sides of the closed end of the tube. Since the zirconia is an oxygen-ion conductor, an emf (E) is generated across the end of the tube which is related to the difference in the oxygen partial pressure in the atmosphere on either side of the zirconia; i.e.,

$$E = -\frac{RT}{4F} \ln \frac{P_{O_2}}{P_{O_2(\text{ref})}} \quad (1)$$

The inside of the tube is vented to the surrounding atmosphere, so $P_{O_2(\text{ref})}$ is 0.18 atm. F is the Faraday constant.

As has been done previously⁽⁵⁾, the stresses reported are the maximum (outer) fiber stresses; i.e.,

$$\sigma = \frac{3 (L - a) P}{2 b h^2} \quad (2)$$

in which

σ = stress

L = distance between support points

a = distance between load points

P = load

b = width of sample

h = thickness of sample.

It has been shown⁽¹⁾ that this is the correct expression for stress in situations where the stress exponent N equals one (in the relation $\dot{\epsilon} = k\sigma^N$) which is nearly always the case in this study.

Strain rates are calculated using the elastic expression

$$\dot{\epsilon} = \frac{6h}{(L - a)(L + 2a)} \dot{\gamma}_L \quad (3)$$

where

$\dot{\epsilon}$ = strain rate

$\dot{\gamma}_L$ = deflection rate of the load points.

This equation is valid for viscous creep (i.e., $N = 1$) in the limit of small strains⁽¹⁾, which are nearly always observed in this work.

B. Results

In the course of this research several areas of interest have been explored concerning the creep of polycrystalline MgO doped with Fe_2O_3 . Among these are the occurrence of steady state viscous creep; the effects of atmosphere, dopant level, and temperature; the mechanism of creep; and the analysis of transient creep (which is discussed in Section IV).

1. $1.0\% \text{ Fe}_2\text{O}_3$ in MgO - As reported earlier⁽⁴⁾, preliminary creep experiments were conducted on samples of MgO containing 1.0% by weight Fe_2O_3 . The tests were conducted at 1400°C over a stress range between 200 and 270 kg/cm^2 . The atmospheres used were air, commercially pure nitrogen, and nitrogen passed over a heated titanium metal getter to remove nearly all traces of oxygen.

The results of a creep test in an air atmosphere are given in Figure 2. Stress change experiments were conducted to determine the stress exponent N

Figure 2... Creep of 1% Fe₂O₃ Specimen at 1400°C in Air

in the relation $\dot{\epsilon} \propto \sigma^N$. The first stress change yielded a value of $N = 1.0 \pm 0.1$ which indicated creep was occurring by a viscous mechanism. The second stress change yielded a value of $N = 4.5$, an indication of a strong non-viscous contribution to creep. Shortly thereafter, creep proceeded into the tertiary stage with fracture occurring after 75 hours.

It is noted that steady state creep occurred throughout the first two stress levels, following an initial and rapidly decaying transient period.

Similar tests were conducted in dry nitrogen and gettered nitrogen atmospheres. In both of these tests, viscous steady state creep was observed⁽⁴⁾. The results of all three tests are given in Figure 3. This graph illustrates conclusively two very important facts. First, viscous creep ($\dot{\epsilon} \propto \sigma^1$) is occurring in all three cases. (Note - straight lines pass through the origin). Also, the dramatic effect of atmosphere on the creep rate is apparent. It can be seen that the creep rate decreases significantly with decreasing oxygen partial pressure. In fact, in a very reducing atmosphere, (i.e., $P_{O_2} \sim 10^{-9}$ atm) the sample is six times more resistant to creep than in an oxidizing atmosphere!

2. $0.1\% \text{ Fe}_2\text{O}_3$ in MgO - Similar tests were conducted on samples containing 0.1% by weight Fe_2O_3 . The results of a test run in an atmosphere of dry nitrogen are given in Figure 4 as a representative example. In these tests viscous creep was again observed, but completely steady state creep was not. The composite results of these tests are given in Figure 5. (Note: For the test in gettered nitrogen 850 is the temperature of the titanium getter). Again the effect of oxygen partial pressure was observed, but to a smaller extent as would be expected for a lower dopant level.

Figure 3. Creep of 1% Fe₂O₃ Alloys - Effects of Stress and P_{O_2}

Figure 4. Creep of 0.1% Fe₂O₃ Specimen in Nitrogen

Figure 5. Creep of 0.1% Fe₂O₃ Alloys - Effects of Stress and P_{O₂}

3. 5.0% Fe_2O_3 in MgO - The first sample containing 5.0 w/o Fe_2O_3 was tested in air, and the results are presented in Figure 6. These results indicate that for stresses up to 196 kg/cm^2 at 1400°C , viscous and steady state creep is observed. In Figure 7, the strain rate is plotted against stress. The linearity of this plot again illustrates the viscous behavior of this sample. (Note the low stress experiments which confirm the extrapolation to the origin).

The results of a test during which a 5% sample was subjected to a number of different test conditions are given in Figure 8. During this test, while the stress was kept at a constant 200 kg/cm^2 , the temperature was varied between 1300 and 1400°C in both reducing (gettered nitrogen) and oxidizing conditions. Besides showing the effect of temperature, this experiment shows the reversibility of the oxidation-reduction reaction. Each time parameters were reached which had been previously used, the creep rate returned to the previous value. For the reducing atmospheres in gettered nitrogen the temperatures on the plot refer to the temperature of the titanium getter.

4. *Summary* - A compilation of the absolute and relative creep rates for all the samples tested at 1400°C and 200 kg/cm^2 is given in Table 2. In the 0.1% Fe_2O_3 samples, going from oxidizing to reducing conditions caused the creep rate to decrease by a factor of 1.9. In the 1.0% samples, the decrease was by a factor of 6.0. In the 5.0% samples, the reduction factor was again 6.0, but in this case two observations should be made. This sample contained a significant amount of porosity ($\sim 1.5\%$), which perhaps would affect the absolute creep rate. Also, it was discovered after the test that completely

Figure 6. Creep of 5% Fe_2O_3 Specimen at 1400°C in Oxygen

Figure 7. Creep of 5% Fe_2O_3 Alloys - Effect of Stress

Table 2
Relative Creep Rates for Each Dopant Level

$$\sigma = 200 \text{ kg/cm}^2$$

$$T = 1400^\circ\text{C}$$

<u>Atmosphere</u>	<u>$\dot{\epsilon} \times 10^4 \text{ (hr}^{-1}\text{)}$</u>	<u>Relative Rate</u>
	<u>0.1% Fe₂O₃</u>	
Air	1.85	1.9
N ₂	1.26	1.3
scrubbed N ₂	0.97	1.0
	<u>1.0% Fe₂O₃</u>	
Air	2.68	6.0
N ₂	1.31	2.9
scrubbed N ₂	0.45	1.0
	<u>5.0% Fe₂O₃</u>	
O ₂ + H ₂ (P _{O₂} ~ 10 ⁻⁴)	3.63	6.0
N ₂ + H ₂ (P _{O₂} ~ 10 ⁻¹⁷)	0.62	1.0

Table 3
Calculated Diffusivities (1400°C)

wt % Fe ₂ O ₃	Atmosphere	$\dot{\epsilon} \times 10^4$ (hr ⁻¹)	D (cm ² /hr) Nabarro-Herring	D _b ^w (cm ³ /hr) Coble
0.1	Air (P _{O₂} = 0.18)	1.9	6.6 x 10 ⁻⁹	5.6 x 10 ⁻¹²
0.1	scrubbed N ₂ (P _{O₂} ~ 10 ⁻¹⁰)	1.0	3.6 x 10 ⁻⁹	3.0 x 10 ⁻¹²
0.1 ⁽⁵⁾	Air		1.3 x 10 ⁻⁸	1.3 x 10 ⁻¹¹
1.0	Air	2.68	4.5 x 10 ⁻⁹	2.7 x 10 ⁻¹²
1.0	scrubbed N ₂	0.45	7.9 x 10 ⁻¹⁰	4.7 x 10 ⁻¹³
5.0	O ₂ + H ₂ (P _{O₂} ~ 10 ⁻⁴ -10 ⁻⁷)	3.63-1.60	(7.3-2.1) x 10 ⁻⁹	(4.7-1.1) x 10 ⁻¹³
5.0	N ₂ + H ₂ (P _{O₂} ~ 10 ⁻¹⁷)	0.62	8.0 x 10 ⁻¹⁰	4.1 x 10 ⁻¹³
<u>Tracer Diffusivities</u> ⁽⁵⁾		Magnesium	4.61 x 10 ⁻⁸	
		Oxygen	7.23 x 10 ⁻¹¹	
<u>Oxygen Grain Boundary Diffusivity</u> ⁽⁵⁾				5.1 x 10 ⁻¹² - 5.1 x 10 ⁻¹³

oxidizing conditions were never achieved due to a hydrogen leak from the furnace into the sample chamber, which, after reaction with the oxygen, yielded a P_{O_2} of approximately 10^{-4} atm. Therefore, the creep rate at $P_{O_2} = 1$ atm. should be higher than that reported.

Finally it is apparent from the data presented in Table 2 that both the creep rate in air increases and that the effect of P_{O_2} on the creep rate becomes more and more significant as the Fe_2O_3 concentration increases.

C. Discussion

1. *Viscous Creep* - It has been the aim of this research to study creep in the regime of temperature, stress, and grain size where viscous modes of deformation are predominant. It has been shown that at $1400^\circ C^{(4,5)}$, viscous creep occurs in the system being studied at stress levels up to $\sim 250 - 400 \text{ kg/cm}^2$.

2. *Steady State Creep* - Prior to this study, steady state creep had never been observed in a polycrystalline magnesium oxide system⁽⁵⁾. Terwilliger, et al.⁽⁵⁾ have shown that, except for the initial transient creep, grain growth that is occurring during the creep test can account for the steadily decreasing creep rate which is frequently observed⁽⁶⁾. It was, therefore, felt that steady state creep could be achieved in creep tests in which no grain growth was occurring. This prediction was verified. In tests on pre-annealed samples containing 1.0 and 5.0% Fe_2O_3 , no additional grain growth occurred during creep, (Refer to Table 1) and steady state viscous creep was observed. During the creep of the 0.1% Fe_2O_3 sample, additional grain growth did occur, and a steadily decreasing strain rate was observed.

3. *Effect of Impurities, Atmosphere and Temperature* - Two major conclusions can be drawn concerning the effect of impurities and atmosphere on the creep of iron-doped MgO from the experimental results summarized in Table 2. These are that (1) viscous creep in $\text{MgO-Fe}_2\text{O}_3$ is enhanced in an oxidizing atmosphere and (2) the effect increases with total iron content. These results indicate that the creep rate increases with increasing concentrations of trivalent iron. Since increasing the amount of Fe^{3+} increases the concentration of cation vacancies in the lattice, these results are consistent with the proposition that the viscous creep of $\text{MgO-Fe}_2\text{O}_3$ solid solutions is controlled by cation diffusion.

A summary of the diffusivities which were calculated from the creep data using both the Nabarro-Herring bulk diffusion and the Coble grain boundary diffusion models is given in Table 3. It is to be noted that all the diffusivities reported fall between the values of the tracer diffusivities of magnesium and oxygen ions. Most of the previous studies on the creep of undoped magnesium oxide have reported diffusivities higher than magnesium ion tracer values. These abnormally high values are due probably to the presence of non-viscous creep and transient effects⁽⁵⁾.

At the present time, the exact defect structure of the $\text{MgO-Fe}_2\text{O}_3$ solid solution is under speculation. In last years Technical Progress Report⁽⁴⁾, a model was proposed which assumed that the iron ions substituted for magnesium and that the trivalent cations (i.e., Fe^{+3}) were compensated by unasociated magnesium ion vacancies. The incorporation of the oxygen into the lattice was described by the following quasi-chemical reaction, using the Kroger-Vink notation:

Figure 8. Creep of 5% Fe₂O₃ Alloy - Effects of Temperature and P_{O₂}

which leads to the following equilibrium constant (K) equation:

$$\frac{[Fe_{Mg}^{\circ}]^2 [V_{Mg}''] [O_o^x]}{[Fe_{Mg}^x]^2 P_{O_2}^{1/2}} = K \quad (5)$$

in which

- $[Fe_{Mg}^{\circ}]$ = concentration of trivalent iron
- $[Fe_{Mg}^x]$ = concentration of divalent iron
- $[V_{Mg}'']$ = concentration of cation (magnesium) vacancies
- $[O_o^x]$ = concentration of oxygen lattice sites.

If, in fact, the creep rate is controlled by cation diffusion, then

$$\dot{\epsilon} = k[V_{Mg}''] \quad (6)$$

This assumption led to the following expression which relates the creep rate to the partial pressure of oxygen:

$$\frac{(\dot{\epsilon})^3}{(A - \dot{\epsilon})^2} = B P_{O_2}^{1/2} \quad (7)$$

in which

$$A = \frac{k[Fe]_T}{2}$$

$$B = kK$$

k is a constant related to the vacancy diffusion coefficient, stress and grain size and other parameters in the diffusional creep theories. $[Fe]_T$ is the total concentration of iron (i.e., $[Fe_{Mg}^{\circ}] + [Fe_{Mg}^x]$).

From the data on hand last year for the 1% Fe_2O_3 creep samples, the partial pressure of oxygen in the titanium-gettered nitrogen was calculated from the above model to be 9×10^{-10} atmospheres⁽⁴⁾. After installation of the galvanic cell, the partial pressure was measured under identical conditions, and a value of 1.7×10^{-9} atmospheres was obtained. This would indicate the possible success of the model.

On the other hand, the equilibrium data of Alcock and Iyengar⁽⁷⁾ which relate P_{O_2} , total iron, $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, and temperature were used to calculate the equilibrium constant K in equation (5). For a given temperature, different values of K were found for various combinations of P_{O_2} , $[\text{Fe}]_T$, and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, indicating that the present model is incorrect. They postulated the defect structure to be an associated complex, or "micro-domain", consisting of two trivalent iron ions associated with each cation vacancy. It must be remembered, however, that their work was conducted between 900 and 1200°C, which are much lower temperatures than those used for this work (i.e., $T > 1300^\circ\text{C}$). A random vacancy model may be more appropriate at higher temperatures. Additional equilibrium data are needed in a higher temperature range.

The activation energy for creep in both oxidizing and reducing conditions was determined on a sample containing 5% Fe_2O_3 . The Arrhenius plots for this experiment (Refer to Figure 8) are given in Figures 9 and 10. The activation energies in oxygen partial pressures of 1 and 10^{-10} atmospheres are 75 and 123 kcal/mole, respectively. The increase of the activation energy in reducing conditions is reasonable. The expression for the creep rate for the oxidizing case is

Figure 9. Arrhenius Plot - 5% Fe₂O₃ Alloy - Creep Tested in Oxygen

Figure 10. Arrhenius Plot - 5% Fe₂O₃ Alloy - Creep
Tested in Gettered Nitrogen

$$\dot{\epsilon} = k [V_{Mg}^{''}] \approx k [Fe]_T \quad (8)$$

It has a temperature dependence only in k , which contains the cation diffusivity. Thus the activation energy is for the mobility of the cation vacancies.

In the reducing case, the creep rate expression from the model proposed earlier is

$$\dot{\epsilon} = k [V_{Mg}^{''}] = k [Fe]_T^{2/3} \left(\frac{K}{4}\right)^{1/3} p_{O_2}^{1/6} \quad (9)$$

This expression has a temperature dependence in both k and K . Therefore, the activation energy is related to the formation of cation vacancies as well as to their mobility. This same qualitative argument would hold true for any other defect model that could conceivably be proposed.

Although the evidence is strong for the conclusion that the creep rate of $MgO-FeO-Fe_2O_3$ solid solutions is controlled by the concentration of cation vacancies, the actual dependence of the creep rate and the activation energy on the oxygen partial pressure will depend on the exact nature of the defect structure. Whether or not the cation vacancies are distributed randomly over the cation lattice or associated in defect complexes remains to be determined by additional creep experiments over a broader range of oxygen partial pressures.

The proposal that the creep rate is controlled by the concentration of cation vacancies is intriguing in that it implies that somehow the anions with their lower bulk diffusivity (i.e., lower mobility and anion vacancy concentration) must find a rapid diffusion path. A proposal which has

been frequently⁽⁵⁾ given for creep and sintering results in oxides is that the anion migrates in or near grain boundaries to keep up with the faster moving cation with its relatively high bulk diffusivity. This mechanism would seem at first glance to be impossible unless there was an accommodation for the local charge imbalance which would be set up by having the anion and cation diffuse along different paths separated roughly by the radius of the grains.

In the $\text{MgO-FeO-Fe}_2\text{O}_3$ system this charge imbalance could perhaps be compensated for by holes which the multi-valent iron introduces into the structure. Referring to Figure 11A, the holes could possibly migrate with the negatively charged cation vacancies (maintaining local electrical neutrality) to the grain boundaries where they react with oxygen ions to form neutral oxygen atoms which in turn migrate along the grain boundaries.

Depending on the grain size, dopant level, and P_{O_2} either the volume (cation vacancy) or boundary (oxygen) diffusion processes could be controlling leading to either Nabarro-Herring or Coble type diffusional creep (or both). Terwilliger, et al.⁽⁵⁾ in their recent simultaneous grain growth and creep studies in air have postulated that grain boundary diffusion is rate controlling (i.e., $\dot{\epsilon} \propto \text{GS}^{-3}$) in small grain size specimens (i.e., $5 \mu\text{m} < \text{GS} < 15 \mu\text{m}$) while volume or bulk diffusion (i.e., $\dot{\epsilon} \propto \text{GS}^{-2}$) was predominant in large ($\text{GS} > 15 \mu\text{m}$) grain size samples. The grain size range in the present studies will have to be extended to test the various grain size dependencies for different values of Fe_2O_3 doping, P_{O_2} , and temperature.

Finally if a stable trivalent ion (such as Al^{+3} or Cr^{+3}), which does not introduce holes into the structure, is added to MgO as a dopant, both ions might have to migrate along the same path in order to maintain local charge

Figure 11. Possible Cation and Anion Diffusion Paths

neutrality, as shown in Figure 11B. In this case the creep rate might be controlled by the diffusivity of the slower moving specie (i.e., oxygen in the volume diffusion process). Thus, with increasing amounts of aluminum which will depress the oxygen vacancy concentration, the creep rate might decrease if volume diffusion kinetics are controlling.

Finally experiments, which are presently under way, to answer some of these questions include:

1. Effects of impurities with a single stable valence such Al^{+3} , Cr^{+3} , or Li^{+1} . Do transition metal impurities give different effects than stable valence species?
2. Extension of the range of oxygen partial pressures to more completely specify the creep rate - P_{O_2} dependence for four dopant levels (0.1, 1, 5 and 10% by wt. Fe_2O_3).
3. Extension of the grain size range of the present experiments to determine the relative importance of grain boundary and volume diffusion to viscous creep.
4. *Grain Boundary Sliding* - In recent years several investigators^(8,9,10) have interpreted the creep of polycrystalline ceramics (particularly Al_2O_3) in terms of grain boundary sliding (GBS). However, some confusion exists in the literature in that some grain boundary sliding (i.e., relative motion of one grain past another along a grain boundary) is required for diffusional creep mechanisms. Ashby and Raj⁽¹¹⁾ recently have made a thorough and informative theoretical study of grain boundary sliding in terms of mechanisms which must occur to accommodate it. If grain boundary sliding occurs without accommodation, then voids or intergranular separations must necessarily occur

along grain boundaries. In their recent study Ashby, and Raj have shown that when the accommodation of grain boundary sliding is by volume or grain boundary diffusion, these processes are identical to the classical diffusional creep mechanisms of Nabarro-Herring and Coble, respectively. In these cases GBS is controlled by diffusional accommodation processes.

Other modes of accommodation can be either elastic (giving rise to an-elastic (recoverable) deformation) or plastic deformation. If GBS occurs too rapidly for accommodation to take place then intergranular voids and separations should become visible.

Scanning electron microscopy is an excellent tool by which to check for the presence of intergranular voids, spearations, or other evidence of GBS occurring without accommodation. Preliminary observations in the scanning electron microscope have been conducted on both the tensile and unstressed surfaces (i.e., end of beam) of the 5 wt. % Fe_2O_3 creep specimens. Representative photomicrographs are presented in Figures 12 and 13.

The nature of the magnesium oxide surface was found to be markedly dependent upon the etching, polishing, and cooling (from the creep temperature) procedures. The samples in Figure 12 were slow cooled, polished, and etched while that in Figure 13 was quenched and etched. Samples which were cooled and observed without etching appeared to have contaminated surfaces compared to those surfaces which were either etched or polished. Etching was found to be necessary to remove this surface condition. Quenching was performed on some samples to inhibit precipitates from forming on cooling. However, a comparison between Figures 12 and 13 reveals that the quenching and polishing procedures were unnecessary.

A. Unstressed - Slow Cool - Polish and Etch - 500X

B. Unstressed - Slow Cool - Polish and Etch - 4900X

C. Tension Surface - Slow Cool - Polish and Etch - 500X

D. Tension Surface - Slow Cool - Polish and Etch - 2000X

Figure 12. Scanning Electron Microscope Photomicrographs
5% Fe₂O₃ Alloys

A. Tension Surface - Quench - Etch, 500X

B. Tension Surface - Quench, Etch, 5000X

Figure 13. Scanning Electron Microscope Photomicrographs

The microstructures typical of tensile surfaces can be compared with an unstressed surface by referring to Figures 12 and 13. The tensile axis on the stressed specimens corresponds to north and south on the photomicrographs. Although the 5% sample was porous prior to creep testing ($\sim 1.5\%$), a comparison between the tensile and the unstressed surfaces reveals possibly the presence of additional porosity in the tensile areas. This observation will have to be checked in future experiments by examining microstructures of initially (i.e., before creep testing) dense materials and by careful checks on the specimen density before and after creep.

An interesting feature of the voids in the tensile areas is their elongated shapes along certain grain boundaries. In Figure 12D a high magnification photomicrograph of one of these pores is shown. The smooth shape of the pore is noted. No evidence of cracks or intergranular separation emanating from the pore is evident. Another example of smooth elongated pores is given in Figure 13B. In this case two pores have almost coalesced and are separated by a thin grain boundary section. Again no cracks are observed in this area. In Figure 12B an enlarged photomicrograph of a pore in an unstressed area is given. In this case the pore is nearly spherical.

This tentative evidence clearly indicates that pores tend to elongate on those boundaries with a shear stress component on them. No evidence of intergranular fracture emanating from intergranular porosity is seen. The pores, possessing no sharp discontinuities, appear to have elongated by a diffusional process. Additional work is needed to determine if pores are formed during creep and if so how large is their contribution to deformation.

Finally these microstructures (i.e., Figures 12 and 13) are strikingly different than those reported recently by Sugita and Pask⁽⁹⁾ for the compressive creep of polycrystalline alumina. In this study scanning microscope photomicrographs revealed evidence of intergranular separation. It is clear that studies of this type are particularly useful in identifying unaccommodated grain boundary sliding.

D. Conclusion

Evidence is mounting that the steady state creep of polycrystalline MgO-FeO-Fe₂O₃ alloys is controlled by a cation diffusion process. Additional work on characterizing further the grain size, P_{O_2} , and temperature dependencies of the creep rate should clarify the situation regarding the actual creep mechanism.

Scanning electron microscopy is useful in determining the characteristics of intergranular porosity and its connection to unaccommodated grain boundary sliding.

III. EFFECT OF Fe₂O₃-FeO AND Cr₂O₃ IMPURITIES ON THE CREEP OF POLYCRYSTALLINE Al₂O₃

In this section preliminary results on the creep of polycrystalline doped Al₂O₃ will be discussed. These initial experiments were conducted between 1350°C and 1550°C on fully dense specimens. Two dopants were used: 1.0 cation % Fe and 1.0% cation Cr. As would be expected from previous literature⁽⁸⁾, a stress exponent of 1.3 was found (i.e., $\dot{\epsilon} \propto \sigma^{1.3}$). The most dramatic experiments, however, showed the steady state creep rate of iron doped alumina to be very sensitive to the partial pressure of

oxygen (P_{O_2}) between 1 and 10^{-4} atm. There was also a distinct change in the activation energy for creep, between the oxidized and reduced atmospheres. The creep of Cr_2O_3 doped alumina was not affected by changes in P_{O_2} .

After a discussion of the method of sample preparation, the results of the various creep experiments which illustrate the effects of stress, P_{O_2} , and temperature will be presented along with some of the theoretical aspects.

A. Fabrication and Characterization of Creep Specimens

Theoretically dense samples were prepared by hot forging alumina powder with 1 cation % Fe or Cr. Linde A alumina was used for the starting material. Although this is not the most chemically pure material available, its availability and fine grain size make it desirable. The impurities were added in the form of Fe_2O_3 powder and chromium acetate. Hot distilled water was added to the chromium acetate-alumina mixture; this was milled for two days, and then calcined at $800^\circ C$ in order to form Cr_2O_3 . The iron-doped powder was simply ball milled for two days.

Two inch diameter disks were pressed at room temperature and biscuit fired at $1200^\circ C$. After placing a disk in the hot press, it was hot-forged at a pressure of 5000 psi at $1500 - 1700^\circ C$ for approximately 4 hours. In most cases, the billets were not deformed enough to reach the die wall; thus hot forging is a more appropriate term than hot pressing which infers the restriction of lateral deformation by the die walls.

The forged billets were dark grey. It was found that long anneals (one or two weeks) at 1650°C were required to give the Fe_2O_3 -doped specimens a uniform, light green color typical of trivalent iron. Cr_2O_3 doped specimens appeared homogeneously purple after only two days at 1500°C in oxygen.

The density of the annealed specimens was found to be comparable to the expected theoretical density. Density measurements are recorded in Table 4. It is clear that the measured densities are greater than the accepted density of corundum (3.971). This is due to the fact that the heavier impurity ions replace aluminum in the lattice. Simple solid solution model calculations lead one to expect the densities which are observed. The grain sizes (all below 7 μm) are tabulated in Table 4.

B. Results

Creep experiments were conducted in an apparatus which has been described previously⁽⁴⁾. Four-point bending was the method of test with sapphire rods used as load and support points. Load point deflections were measured on a recorder connected to a LVDT. Three basic types of creep experiments were conducted. These included changes in stress, oxygen partial pressure (P_{O_2}), and temperature. The effects of these parameters on the creep of iron and chromium doped Al_2O_3 are discussed in this report.

1. *Stress Change Experiments* - A typical stress change experiment is shown in Figure 14. Before discussing the stress dependence of the creep rate several characteristics of the creep curve should be noted. First, transient creep, in which the strain rate decays rapidly with time, was observed. Secondly, steady state creep was consistently observed. Decaying strain rates due to simultaneous grain growth^(5,6) were not encountered in this study.

Table 4
Hot Pressing of Al_2O_3

Billet	Impurity	Temp (°C)	Pressure (psi)	G.S. (μm)	Density (gm/cm^3)
Fel-1A	Fe	1500	5000	4	3.98
Fel-1B	Fe	1600	5000	7	3.98
Fel-1B	Fe	1700	5000	---	4.00
Fel-2A	Fe	1450	5000	---	3.98
Cr1-1A	Cr	1700	5000	6	3.98
Cr1-1B	Cr	1600	5000	---	3.98

Figure 14. Stress Change Experiments in Chromium Doped Al_2O_3 at 1400°C in an Oxygen Atmosphere

As discussed in the attached preprint on the calculation of stresses and strains⁽¹⁾, the stress exponent, N , in the constitutive creep law, i.e.,

$$\dot{\epsilon}(t) = J(t)\sigma^N \quad (10)$$

can be obtained from the slope of a line on a log-log plot in which the load point deflection rate ($\dot{Y}_L$) is plotted against the applied load (P). In Figure 15 such a plot is constructed for the stress dependence of the steady state creep rate in oxygen ($P_{O_2} \sim 1$ atm.) of iron and chromium doped Al_2O_3 . These data, which were obtained in stress change experiments at 1400 and 1500°C, give straight lines corresponding to a stress exponent N of 1.3 for both doped aluminas. The stresses in these experiments were varied between 100 and 1000 kg/cm².

This stress exponent of 1.3 is consistent with most of the previous work on the creep of fine grained Al_2O_3 (8-10) in that values of N ranging between 1.0 and 1.67 have been reported.

2. *Variable Atmosphere (P_{O_2}) Experiments* - The objectives in selecting iron and chromium as the impurities in this study are two-fold. First, the impurity must be soluble in Al_2O_3 to a reasonable degree over the range of experimental variables (i.e., temperature and P_{O_2}). Secondly, in order to measure the effect of a changing oxygen partial pressure (P_{O_2}) on the creep rate it is desirable to have one impurity (Cr^{+3}) with a stable valence and a second (Fe^{+2} , Fe^{+3}) with a variable valence.

In view of the studies on Fe_2O_3 doped magnesium oxide it was hoped that significant changes in the defect structure (i.e., changing Fe^{+3}/Fe^{+2} ratio) of doped alumina could be effected by changes in the equilibrium oxygen partial pressure. This change, as in the case in iron doped magnesia, should reflect itself in a P_{O_2} dependent creep rate. On the other hand, the creep

Figure 15. Determination of Creep Stress Exponent in Iron and Chromium Doped Al_2O_3

rate of chromium doped alumina was not expected to depend on the oxygen partial pressure.

The data for a changing partial pressure experiment (Fe1-1A-6) are plotted in Figure 16. The creep test was conducted at 1500°C under a constant stress of 306 kg/cm². The oxygen partial pressure was varied between 0.18 and 9.6 x 10⁻⁶ atm. One of the intermediate P_{O₂} values (i.e., 2.8 x 10⁻³) was obtained by mixing air (P_{O₂} ~ .18) and nitrogen (P_{O₂} ~ 10⁻⁵) in an appropriate ratio. The other two pressures (i.e., 2.0 x 10⁻⁴ and 9.6 x 10⁻⁶ atm.) were obtained by using commercially prepared nitrogen-oxygen gas mixtures. Relatively high gas flow rates (i.e., 17 cc/sec) were used to insure that the furnace atmosphere was controlled by the gases and not influenced by any small hydrogen leaks from the molybdenum part of the furnace or oxygen leaks from the bottom of the furnace.

The creep rate of iron doped Al₂O₃, as expected, is very sensitive to the oxygen partial pressure. As the P_{O₂} decreases the creep rate increases. It is noted that this behavior is exactly opposite to that observed in iron doped MgO. Referring to the data in Figure 16 the steady state creep rate increases by a factor of about two and five between an air atmosphere (P_{O₂} ~ 0.18 atm.) and reducing atmospheres of P_{O₂} = 2.8 x 10⁻³ atm. and P_{O₂} = 2.0 x 10⁻⁴ atm., respectively. Thus the creep rate of iron doped Al₂O₃ is more sensitive to the oxygen partial pressure than is iron doped MgO for comparable dopant levels and oxygen partial pressure changes.

When the oxygen pressure was reduced further to 9.6 x 10⁻⁶ atm. the creep rate increased enormously. It had reached a value over an order of magnitude faster than the previous rate (i.e., at P_{O₂} = 2 x 10⁻⁴ atm.)

Figure 16. Effect of Oxygen Partial Pressure on Creep Rate of Iron Doped Al_2O_3 at 1500°C

before air was introduced into the furnace chamber. In other experiments, the sample fractured in the low oxygen pressure atmosphere before reaching steady state creep.

Since the creep rate is so rapid in highly reducing atmospheres, additional experiments are being designed for thicker samples and lower stresses so that smaller deflection rates can be measured for these apparently high strain rates.

In Figure 17 a plot of $\log \dot{Y}_L$ versus $-\log P_{O_2}$ is shown for the data presented in Figure 16. The deflection rate is related to the oxygen partial pressure by the relation

$$\dot{Y}_L = k_p P_{O_2}^{-m} \quad (11)$$

An m value of 0.24 gives a good description to the data.

It should be emphasized that these experiments are only tentative. All of the deflection rates plotted in Figure 17 may not correspond to steady state conditions. Additional experiments of this type over a wide range of P_{O_2} and T are planned.

Finally similar atmosphere change experiments were conducted on chromium doped alumina. The data from these experiments are shown in Figure 18. The steady state creep rate was essentially insensitive to oxygen pressure changes between 1 and 10^{-6} atm. These results are also plotted on Figure 17 as a comparison with the iron doped samples. The atmosphere change experiment on the chromium doped samples acts as a control. It indicates that the increase in the creep rate of iron doped alumina with decreasing oxygen partial pressure is due probably to a corresponding increase in the Fe^{+2}/Fe^{+3} ratio.

Figure 17. Creep Rate - P_{O_2} Dependence in Iron and Chromium Doped Al_2O_3

Figure 18. Effect of Oxygen Partial Pressure on Creep of Chromium Doped Al_2O_3

3. *Temperature Change Experiments* - Preliminary experiments were conducted between 1400 and 1550°C in 50° intervals on both iron and chromium doped Al_2O_3 . In Figure 19 an Arrhenius plot summarizes the temperature dependence of the steady state deflection rates. In these experiments on the same creep specimen the stress and microstructural features (e.g., grain size) are held constant. The activation energy for the creep of chromium doped Al_2O_3 was 122 kcal/mole and is similar to values (116 - 142 kcal/mole) obtained by previous investigators⁽⁸⁻¹⁰⁾ for the creep of Al_2O_3 .

From the data in Figure 19 it is clear that the activation energy for the creep of iron doped alumina is strongly dependent on the partial pressure of oxygen. With the data presently available at only two temperatures for oxygen atmospheres of 1 and $\sim 10^{-6}$ atm. it is not possible to calculate any meaningful activation energies. However, the present data indicate tentatively an activation energy in pure oxygen higher than that observed in chromium doped Al_2O_3 . For reducing pressures (i.e., $\sim 10^{-6}$ atm.) the creep rate is almost independent of temperature in comparison with the dependence in an oxidizing atmosphere. Further data are needed to establish the activation energy and its dependence on P_{O_2} . It is noteworthy that the dependence of the creep activation energy for iron doped Al_2O_3 is completely opposite to that reported earlier for iron doped magnesia. In the latter the activation energy increased significantly with decreasing oxygen partial pressure.

C. Discussion

In this section the present results on the creep of chromium and iron doped aluminum oxide will be compared briefly with previous work. In

Figure 19. Arrhenius Plot - Chromium and Iron Doped Al_2O_3

addition, possible mechanisms to account for the observed oxygen partial pressure dependence of the creep rate will be discussed.

1. *Stress Dependence* - As stated earlier a stress exponent of 1.3, which was found in the present work for creep in an oxygen atmosphere of chromium and iron doped alumina, is consistent with previous research. Stress exponents ranging between 1.00 and 1.67 have been observed in previous studies depending upon the grain size (GS), temperature, and stress. Most of the results of previous studies have been interpreted in terms of the following general relation for the strain rate ($\dot{\epsilon}$).

$$\dot{\epsilon} \propto \frac{\sigma^N e^{-\Delta H/RT}}{(GS)^M} \quad (12)$$

For the case of diffusional or viscous creep $N = 1$ and M can have values equal to 2 or 3 depending on the particular mechanism⁽⁶⁾. Values of M ranging between 2 and 2.5 have frequently been observed^(8,10). Thus the evidence is substantial that diffusional mechanisms (either by volume or grain boundary) are important in the creep of polycrystalline Al_2O_3 . However, the consistent appearance of non-viscous stress exponents suggest that some concurrent non-viscous mechanism is operating. Several workers⁽⁸⁻¹⁰⁾ have proposed that grain boundary sliding is responsible for this non-viscous behavior. Transmission and scanning electron microscope evidence is available for the presence of intergrannular displacements^(8,9) and for the formation of intergrannular voids⁽⁸⁾. Evidence for the accommodation of grain boundary sliding by localized dislocation movements is also available⁽¹⁰⁾. Further work is needed in these areas to determine (1) if GBS is important, and (2) how it is accommodated (i.e., void formation, dislocation motion, etc.)

Finally all of the stress change experiments in the iron-doped alumina have been conducted in an oxygen atmosphere where the creep rate is relatively slow. Similar experiments are planned under reducing conditions. It will be of interest to see if the exponent decreases or remains the same as the overall creep rate increases significantly under reducing conditions.

2. *Effects of Impurities and Oxygen Partial Pressure* - Evidence that diffusional mechanisms are important in the creep of polycrystalline aluminum oxide is substantial. For the purpose of argument let us assume that the creep of Al_2O_3 is controlled by volume diffusion (i.e., Nabarro - Herring Creep). In this model the creep rate is proportional to a diffusion coefficient. In alumina, unlike MgO , three possible defects might control the creep (i.e., diffusion) rate. These are oxygen vacancies ($V_O^{\circ\circ}$), aluminum vacancies ($V_{\text{Al}}^{\text{''}}$), and aluminum ion interstitials ($\text{Al}_I^{\circ\circ\circ}$) (a possible defect in view of the empty octahedral positions in the lattice). The diffusion coefficient could, in principle, be proportional to the concentration of any one of these three defects (i.e., $[V_O^{\circ\circ}]$, $[V_{\text{Al}}^{\text{''}}]$, and $[\text{Al}_I^{\circ\circ\circ}]$).

The problem which will be considered is the following: If the iron impurity is assumed to substitute for aluminum ion in the lattice, what is the expected oxygen pressure-creep rate dependence for the following cases in which the concentration of different defects is assumed to be rate controlling?

$$\begin{array}{ll} \text{Case I} & \epsilon = k_A [V_O^{\circ\circ}] \\ \text{Case II} & \epsilon = k_B [V_{\text{Al}}^{\text{''}}] \\ \text{Case III} & \epsilon = k_C [\text{Al}_I^{\circ\circ\circ}] \end{array} \quad (13)$$

Since there are two possible positive defects (i.e., oxygen vacancies ($V_O^{\circ\circ}$) and aluminum ion interstitials ($Al_I^{\circ\circ}$), two possibilities exist for the incorporation of oxygen from the gas phase into iron doped Al_2O_3 .

In these quasi chemical reactions (using Kroger-Vink notation), Fe_{Al}^x and $Fe_{Al}^{\cdot}$ are trivalent and divalent iron ions, respectively, on cation sites, O_O^x is a normal oxygen lattice site and V_I is a vacant interstitial site.

For the purpose of illustration the oxygen partial pressure dependence of the creep rate will be calculated on the assumption that oxygen is incorporated into the lattice by reaction (14) (i.e., the predominant defects in pure Al_2O_3 are Schottky defects - cation and anion vacancies). Using the law of mass action, the following expression can be written for the equilibrium constant of reaction 14:

$$K_{IV} = \frac{[Fe_{Al}^{\cdot}]^2 [V_O^{\circ\circ}] P_{O_2}^{1/2}}{[Fe_{Al}^x]^2 [O_O^x]} \quad (16)$$

For Fe-doped Al_2O_3 the overall electrical neutrality condition is

$$[Fe_{Al}^{\cdot}] = 2[V_O^{\circ\circ}] \quad (17)$$

For a mass balance of iron one can write

$$[Fe_{Al}^x] = [Fe_T] - [Fe_{Al}^{\cdot}] \quad (18)$$

in which $[Fe_T]$ is the total concentration of iron.

Substitution of equations (18) and (17) into (16) gives the following expression for the concentration of oxygen ion vacancies:

$$[V_0^{\circ\circ}] = \left[\frac{K_{IV}}{4} \right]^{1/3} \left[[Fe_T] - 2[V_0^{\circ\circ}] \right]^{2/3} P_{O_2}^{-1/6} \quad (19)$$

For highly oxidizing conditions $[Fe_{Al}^x] \gg [Fe_{Al}^I]$ and $[Fe_T] \gg [V_0^{\circ\circ}]$.

Equation (19) can then be simplified to

$$[V_0^{\circ\circ}] = \left(\frac{K_{IV}}{4} \right)^{1/3} [Fe_T]^{2/3} P_{O_2}^{-1/6} \quad (20)$$

In order to determine the oxygen partial pressure dependence of the remaining two defects (i.e., $V_{Al}^{''''}$ and $Al_I^{\circ\circ\circ}$) equilibrium constant expressions are required for Schottky (K_S) and Frenkel (K_F) defect formation, i.e.,

$$K_S = [V_{Al}^{''''}]^2 [V_0^{\circ\circ}]^3 \quad (21)$$

$$K_F = [V_{Al}^{''''}] [Al_I^{\circ\circ\circ}] \quad (22)$$

Substitution of equation (20) into (21) and (22) gives the following expressions for the concentration of aluminum ion vacancies and interstitials as a function of P_{O_2} in the oxidizing limit (i.e., $[Fe_T] \sim [Fe_{Al}^x]$)

$$[V_{Al}^{''''}] = \left[\frac{4K_S}{K_{IV}} \right]^{1/2} [Fe_T]^{-1} P_{O_2}^{1/4} \quad (23)$$

$$[Al_I^{\circ\circ\circ}] = K_F \left[\frac{K_{IV}}{4K} \right]^{1/2} [Fe_T] P_{O_2}^{-1/4} \quad (24)$$

In Table 5 the various partial pressure and $[Fe_T]$ dependencies of the creep rate for different combinations of predominant and rate controlling defect situations are summarized. These dependencies are valid only in the oxidizing limit. In addition they do not take into account any possible clustering or association of defects.

For highly reducing conditions (i.e., $[Fe_T] \sim [Fe_{Al}^I]$) it is expected that the values of m in equation (11) will be less than those predicted in

Table 5

Summary of P_{O_2} and $[Fe_T]$ Dependencies of
Creep Rate in Al_2O_3 under Oxidizing Conditions

$$\dot{\epsilon} = A P_{O_2}^{-m} [Fe_T]^P$$

	Creep Rate Con- trolling Defect	Predominant Defect (controlling O_2 incorporation)	m	P
Case I	$V_O^{\bullet\bullet}$	$V_O^{\bullet\bullet}$	1/6	1
Case II	$V_{Al}^{\bullet\bullet\bullet}$	$V_O^{\bullet\bullet}$	-1/4	-1
Case III	$Al_I^{\bullet\bullet\bullet}$	$V_O^{\bullet\bullet}$	1/4	2/3
Case I	$V_O^{\bullet\bullet}$	$Al_I^{\bullet\bullet\bullet}$	1/8	1/2
Case II	$V_{Al}^{\bullet\bullet\bullet}$	$Al_I^{\bullet\bullet\bullet}$	-3/16	-3/4
Case III	$Al_I^{\bullet\bullet\bullet}$	$Al_I^{\bullet\bullet\bullet}$	3/16	3/4

Table 5. Under these conditions little partial pressure dependence is expected and

$$[V_0^{\circ\circ}] \approx [Fe_T] + f(P_{O_2}) \quad (25)$$

$$[Al_I^{\circ\circ}] \approx [Fe_T] + f(P_{O_2}) \quad (26)$$

Comparing equations (25) and (26) with equations (20) and (24) it is easy to see why the activation energy under reducing conditions is less than that in an oxidizing atmosphere. Under oxidizing conditions the concentration of the rate controlling defect is a function of equilibrium constants involving the formation of defects while under reducing conditions it is essentially only a function of the total iron concentration (except $[V_{Al}^{\circ\circ}]$). Under the latter condition the activation energy for creep should involve primarily that for the mobility of the defect and not its formation.

By comparing Table 5 with the results in Figure 17 aluminum vacancies can be ruled out as the rate controlling defect. The present data tend to support aluminum interstitials as opposed to oxygen vacancies as the rate controlling defect. However, the differences in the pressure and $[Fe_T]$ dependencies are very small and require more extensive data than are presently available.

Depending on whether Schottky or Frenkel defects are predominant in Al_2O_3 , aluminum ion interstitials may or may not be the predominant defect. If they are predominant then a multiple path mechanism may have to be invoked which is similar to that used in iron doped magnesia (Refer to Figure 11). Only in this case electrons would be the charge compensating electronic defect. Similar arguments would hold for oxygen ion vacancies as predominant and rate controlling.

Finally a comparison between the results of this study and those of other workers on MgO doped Al_2O_3 is interesting. In this study increasing amounts of divalent iron increases the creep rate. Hewson and Kingery⁽¹²⁾ and Beauchamp⁽¹³⁾ concluded that MgO decreased the creep rate. Mocellin⁽¹⁴⁾ recently found a contrary result in that increasing amounts of MgO enhanced the creep rate. Finally, Heur⁽⁸⁾ and Cannon⁽¹⁰⁾ found no enhancement of the creep rate with increasing amounts of MgO doping. It is difficult to resolve these differences due to the many variables involved (temperature, grain size, stress, etc.) and to the possibility of multiple creep mechanisms, each of which may predominate in specific grain size, temperature or stress ranges. The results of this study are consistent with those of Mocellin.

D. Summary

Based on the present results some tentative conclusion can be drawn.

1) A stress exponent of 1.3 was found for the steady state creep of chromium and iron doped Al_2O_3 in an oxygen atmosphere.

2) The creep rate of iron doped Al_2O_3 increases as the oxygen partial pressure decreases. This oxygen pressure effect is greater and opposite to that found in iron doped MgO. The creep rate of chromium doped Al_2O_3 is essentially insensitive to changes in P_{O_2} .

3) The creep activation energy of chromium doped Al_2O_3 is 122 kcal/mole. For iron doped Al_2O_3 the activation energy decreases with decreasing oxygen partial pressure. This behavior is opposite to that observed in iron doped MgO in which the activation energy increases with decreasing oxygen pressure.

IV. ANALYSIS OF TRANSIENT CREEP IN POLYCRYSTALLINE MgO AND MgO-Fe₂O₃ SOLID SOLUTIONS

Transient creep has been frequently observed in the creep of polycrystalline MgO^(5,15,16,18) and Al₂O₃^(13,17). In fact, strain rates which continuously decrease with time, have been the rule and not the exception particularly at low temperatures (i.e., 1000 - 1200°C in MgO and 1200 - 1300°C in Al₂O₃). In recent years some workers^(5,16), including those on this contract, have been able to account for some of the decay in strain rate in terms of simultaneous grain growth. This procedure has been confirmed in recent work described in Section II of this report. In these studies MgO-Fe₂O₃ creep specimens were preannealed to stabilize the grain size. After a rapidly decaying initial transient, true steady state creep was observed (Refer to Figures 2 and 6). In this system whenever grain growth occurs during a creep test steady state creep is never achieved in that there is always a steady decrease in the creep rate^(5,6) (Refer to Figure 4).

Evidence is therefore substantial that simultaneous grain growth will account for some of the transient creep in MgO and MgO-Fe₂O₃ alloys at temperatures over 1200°C. However, at relatively low temperatures (1000 - 1200°C in MgO and MgO-Fe₂O₃), at which grain growth is almost insignificant, transient creep has been observed to proceed for long periods of time (i.e., up to and past 10 - 15 hours) in both MgO, Al₂O₃ and related systems. Obviously grain growth cannot account for the magnitude of these transients and some other explanation is needed.

A. Exponential Decay

If a typical creep curve (i.e., $\dot{\epsilon}$ versus time) is examined (e.g., Figures 2, 4, 6, 14), it is seen that the strain rate undergoes a very rapid decay in the first 1 - 10 hours depending upon the temperature. This behavior is similar to that observed in many metal systems⁽¹⁹⁾ in which the creep rate in the transient decays exponentially with time. In order to see if the initial decay in the strain rate was exponential, plots were made of $\log (\dot{\epsilon} - \dot{\epsilon}_{ss})$ versus time for a number of creep experiments on MgO-Fe₂O₃ alloys. $\dot{\epsilon}_{ss}$ is the steady state or long time creep rate. These experiments were conducted either at low temperatures (1100 - 1200°C) where the rate of grain growth is small or on specimens in which the grain size was stabilized. Attention is drawn to the creep data at 1100°C and 1134°C on Figure 20 and to the data at 1400°C in Figure 21.

The experiments at 1100 and 1134°C were conducted on MgO doped with 0.94 and 0.14% Fe₂O₃, respectively⁽²⁰⁾. Although these fine grained specimens were not preannealed, grain growth at these temperatures is very slow⁽²¹⁾. It is interesting that an exponential function describes most of the decay in the strain rate for periods up to about 8 hours. The creep data at 1400°C in Figure 20 were obtained on a constant grain size specimen (1% Fe₂O₃). In this case the exponential decay ($\sim$ order of magnitude) is confirmed up to 75 minutes and accounts for essentially all of the observed transient. Similar results have been obtained for a 5% Fe₂O₃ specimen creep tested at 1350°C.

This evidence suggests that two processes contribute to transient creep in polycrystalline magnesium oxide doped with iron: (1) An exponential decay

Figure 20. Exponential Decay of Transient Creep - $\text{MgO-Fe}_2\text{O}_3$ Solid Solutions

Figure 21. Exponential Decay of Transient Creep -
Preannealed $\text{MgO-Fe}_2\text{O}_3$ Specimen

process which accounts for most of the initial transient; (2) Simultaneous grain growth which accounts for some of the initial decay but extends for longer periods of time and causes a steady decrease in the strain rate.

The remaining transient data in Figure 20 between 1200 and 1300°C were obtained by taking into account simultaneous grain growth. (This procedure will be discussed later). Again the transient data follow an exponential decay law.

It is apparent that the rate of exponential decay is very sensitive to temperature (~ 75 minutes at 1400°C to ~ 8 hours at 1100°C). This observation helps to explain why grain growth could account for most of the transient at temperatures over but not under 1200°C. It also suggests that most of the low temperature creep behavior is transient or primary in nature.

B. Rheological Model

In this section a rheological model will be developed which is consistent with the observed transient and steady state creep behavior in polycrystalline MgO and MgO-Fe₂O₃ solid solutions.

The simplest viscoelastic model which will give rise to a strain rate which decays exponentially with time is the Kelvin (Voigt) solid which consists of a spring and dashpot connected in parallel (i.e., Figure 22). The expression for the stress σ in terms of the modulus (M_1) of the spring and the viscosity (η_1) of the dashpot is

$$\sigma = M_1 \epsilon + \eta_1 \dot{\epsilon} \quad (27)$$

When a Kelvin body is stressed, part of the deformation energy is stored in the spring, while the remainder is dissipated in the dashpot.

Figure 22. Rheological Creep Model - Combined Kelvin and Maxwell Bodies

If at time $(t) = 0$, $\epsilon = 0$ and a stress σ is applied, then solving the differential equation (27)

$$\epsilon = \frac{\sigma}{M_1} (1 - e^{-t/\tau}) \quad (28)$$

in which $\tau (= \eta_1/M_1)$ is a relaxation time.

In order to more closely approximate real creep behavior, a Kelvin and Maxwell body are combined in series (refer to Figure 22). In this case

$$\epsilon = \overset{\text{I}}{\frac{\sigma}{M_2}} + \overset{\text{II}}{\frac{\sigma}{M_1} (1 - e^{-t/\tau})} + \overset{\text{III}}{\frac{\sigma t}{\eta_2}} \quad (29)$$

The first term (I) corresponds to the instantaneous elastic strain. The second (II) is the Kelvin (anelastic) term and the third (III) is the Newtonian viscous (steady state) strain term.

Differentiating equation (29) with respect to time gives the following expression for the strain rate:

$$\dot{\epsilon}_t = \dot{\epsilon}_i e^{-t/\tau} + \dot{\epsilon}_{ss} \quad (30)$$

in which: $\dot{\epsilon}_i (= \frac{\sigma}{M_1 \tau})$ is the strain rate at $t = 0$ for the Kelvin element (i.e., initial transient strain rate) and $\dot{\epsilon}_{ss}$ is the steady state (viscous) creep rate.

It is apparent that if $\dot{\epsilon}_{ss}$ is constant, a plot of $\ln (\dot{\epsilon} - \dot{\epsilon}_{ss})$ versus t is linear with slope equal to $-1/\tau$. Thus the transient strain rate should decay exponentially with time.

If diffusional creep is operating and simultaneous grain growth occurs during creep, $\dot{\epsilon}_{ss} = f(\frac{1}{GS})$ and $\dot{\epsilon}_{ss}$ will also decrease with time^(5,6). Thus grain growth will contribute to the overall apparent transient behavior.

This simple viscoelastic rheological model assumes that only one relaxation time τ describes the exponential decay. It is common to use more than one τ to completely characterize actual creep data⁽²²⁾. However, for the purpose of illustrating the effect only one relaxation time will be used to describe the initial decay in the strain rate. It is apparent from the data in Figures 20 and 21 that a single relaxation time gives a fairly good description of the initial strain rate decay.

Finally the initial transient strain rate $\dot{\epsilon}_i$ should be linear with stress, if the transient mechanism is viscoelastic. The rate of exponential decay is independent of stress. In Figure 23 a exponential plot is made for 0.48% Fe_2O_3 specimens which were creep tested in air at 1300°C at different stress levels^(5,20). The plots are linear with nearly identical slopes. They are displaced by their different values of $\dot{\epsilon}_i$ which depend on stress.

In Figure 24 the stress dependence of $\dot{\epsilon}_i$ is checked for two series of tests (i.e., 0.10 and 0.48% Fe_2O_3 specimens creep tested in air at 1300°C). Except for one point at a high stress level $\dot{\epsilon}_i$ is essentially linear with stress as predicted by equation (30). The stresses on the plot are incremental values since, at the start of a creep test, the specimens are already subjected to the load of an alumina loading rod ($\sim 20\text{-}40 \text{ kgm/cm}^2$ depending upon specimen dimensions)⁽²⁰⁾.

C. Simultaneous Grain Growth and Steady State Creep

As has been discussed in previous progress reports⁽⁴⁾ and papers^(5,6) simultaneous grain growth will cause a steady decrease in the creep rate if a viscous (or diffusional) mechanism is contributing to the deformation.

Figure 23. Effect of Stress on Transient Creep of 0.48% Fe_2O_3 Specimens at 1300°C in Air

Figure 24. Effect of Stress on Initial Transient Creep Rate

In Figure 25 a log-log plot of the strain rate versus GS^{-2} and GS^{-3} is given for the creep of a 0.10% Fe_2O_3 specimen tested in air at $1300^\circ C$ ⁽⁵⁾. For the grain size range (i.e., 5-15 μm) the creep rate was found to be proportional to GS^{-3} except for the data in the first two hours. This observation supported the conclusion that creep was controlled by grain boundary diffusion (after a model by Coble⁽²³⁾). By combining the expressions for diffusional creep (i.e., grain boundary) with that describing grain growth in this system^(5,21) the following equation was obtained which describes the time dependence of steady state (viscous) creep, i.e.,

$$\dot{\epsilon}_{ss} (hr^{-1}) = \frac{26.7 \times 10^{-3}}{(t + 5.13)^{3/2}} \quad (31)$$

Values of transient creep rates ($\dot{\epsilon}_t$) at any time (t) can then be obtained by subtracting $\dot{\epsilon}_{ss}$ from the experimentally measured creep rate (i.e., $\dot{\epsilon}_t = \dot{\epsilon}_{actual} - \dot{\epsilon}_{ss}$) at any time.

In Figure 26 exponential plots of the total strain rate and the calculated transient strain rate (i.e., total - viscous) are given. Two important observations are to be made:

- (1) If grain growth is not taken into account a single relaxation time τ will not describe the decay in the strain rate.
- (2) The transient strain rate, which is obtained by correcting for grain growth assuming a grain boundary diffusion creep mechanism, does decay exponentially with time and is described by a single relaxation time. It is noted that if the Nabarro-Herring model (i.e., $\dot{\epsilon} \propto GS^{-2}$) is used to account for the grain growth, a single relaxation time will not describe the resulting data. Also the values of τ in this procedure will be too high

Figure 25. Creep Rate - Grain Size Correlation -
0.10% Fe₂O₃ at 1300°C.

Figure 26. Exponential Decay - 0.10% Fe_2O_3 - With and Without Grain Growth Connection.

in comparison with values at other temperatures in which no grain growth corrections were necessary.

Taking the value of τ from the slope and $\dot{\epsilon}_i$ from the intercept the following equation was derived to describe the transient creep rate, i.e.,

$$\dot{\epsilon}_t (\text{hr}^{-1}) = 5.2 \times 10^{-3} e^{-t/0.57} \quad (32)$$

Equations (31) and (32) were then combined to construct a theoretical creep time curve which is shown in Figure 27. The agreement between this curve and the actual strain rate data is excellent and indicates that transient creep in $\text{MgO-Fe}_2\text{O}_3$ alloys can be described by two terms:

- (1) An exponential decay term characterized by a single relaxation time.
- (2) A steady state term which will decay with time if simultaneous grain growth is occurring.

This procedure was then repeated on several creep tests conducted at 1200°C and 1300°C in which simultaneous grain growth occurred. In Figures 28 and 29 similar analyses for the 0.10 and 0.94% Fe_2O_3 creep specimens at 1200°C are presented. It was not always possible to obtain an excellent fit with a two term equation (refer to Figure 28). This fact may be due to a number of factors.

- (1) Grain Growth at high dopant levels and lower temperatures is very slow and difficult to characterize accurately⁽²¹⁾

- (2) A single relaxation time may not describe the transient particularly at low temperatures

- (3) The viscous or steady state portion may not correspond entirely to grain boundary diffusion as was assumed in all the calculations for grain sizes below 15 μm .

Figure 27. Transient Creep - 0.10% Fe₂O₃ 1300°C

Figure 28. Transient Creep - 0.10% Fe₂O₃ 1200°C

Figure 29. Transient Creep - 0.94% Fe_2O_3 1200°C

However, in spite of these difficulties the values of τ generated by these corrections for simultaneous grain growth compare favorable with those obtained from experiments in which no significant grain growth occurred. The various values of τ will be compared in the next section.

Finally the data in Figures 20 and 23 at 1200 and 1300°C were also obtained after an analysis for simultaneous grain growth. The resulting transients creep rates obeyed the exponential decay law very well.

In retrospect the most adviseable procedure to obtain the grain size dependence of the steady state creep rate would be to first conduct an experiment on a specimen with a stabilized grain size and determine the transient (i.e., Figure 21). Then with this information available it would be relatively easy to determine in another experiment (with grain growth occurring) that portion of the apparent transient which is due to simultaneous grain growth and thereby the grain size dependence of $\dot{\epsilon}_{ss}$.

In Tables 6 and 7 the parameters τ and $\dot{\epsilon}_i$ describing transient creep in Fe_2O_3 doped and undoped MgO are summarized. The relaxation times vary between 6.7 and 0.23 hours over temperatures between 1000 and 1400°C. The long relaxation times at temperatures below 1200°C indicate that transient creep behavior will extend out to long periods ~~observed~~.

D. Temperature Dependence of Transient Creep

Since τ is a relaxation time it should be exponentially related to the absolute temperature, i.e.,

$$\frac{1}{\tau} = \frac{1}{\tau_0} e^{-\Delta H/RT} \quad (33)$$

Table 6
Transient Data - Doped MgO^(18,20)

$$\dot{\epsilon}_t = \dot{\epsilon}_i \exp(-t/\tau)$$

Specimen	wt % Fe ₂ O ₃	σ (kgm/cm ²)	$\sigma - \sigma_L$ (kgm/cm ²)	τ (hr.)	$1/\tau$ (hr. ⁻¹)	$\dot{\epsilon}_i$ (10 ⁻³ hr. ⁻¹)
1100°C						
P 37T1	0.94	126	---	5.16*	0.19	0.54
1134°C						
P 23T1	0.14	137	---	4.40*	0.23	0.87
1200°C						
P 30T2	0.10	178	---	1.77	0.57	3.00
P 28T2	0.48	143	---	1.44	0.69	---
P 27T2	0.94	137	---	1.56	0.64	1.25
1300°C						
P 30T5	0.10	228	199	0.57	1.75	5.20
P 30T8	0.10	294	271	0.46	2.19	5.50
P 30T6	0.10	473	436	0.48	2.08	10.15
P 28T6	0.48	214	187	0.70	1.44	3.90
P 28T5	0.48	291	262	0.70	1.44	5.20
P 28T8	0.48	301	278	0.55	2.31	6.60
P 28T3	0.48	445	420	0.59	1.68	14.80
1350°C						
5.0-A-4	5.0	124	102	0.39*	2.56	---
1400°C						
P 30T4	0.10	169	---	0.29±0.07	3.5±0.8	---
1.0-A-4	1.0	209	---	0.38*	2.63	---

*No grain growth correction was necessary

Table 7

Transient Data - Undoped MgO^(18,20)

$$\dot{\epsilon}_t = \dot{\epsilon}_i \exp(-t/\tau)$$

Specimen	Temperature (°C)	τ (hours)	Remarks
P25BC29	1007	6.68	good fit - 10 hours
P36BC32	1115	6.16	good fit - 7 hours
P36BC33	1119	3.78	good fit - 5 hours
P37BC46	1129	2.17	good fit - 6 hours
P21T2C19	1154	3.80	---
P21T4C21	1158	3.46	good fit - 3 hours
P21T3C20	1160	3.34	---
P38B2	1200	4.72	good fit - 7 hours
P43TB	1300	0.65	---

In Figure 30 the values of $\frac{1}{\tau}$ in Table 6 are plotted as an Arrhenius plot. Although there is some scatter, the fit to equation (33) is remarkably good in view of the assumptions involved in obtaining some of the values of τ . The values obtained without any grain growth corrections are so indicated. These fall on essentially the same line as the other values which may be slightly over estimated if viscous creep isn't entirely by grain boundary diffusion. A value of $\Delta H = 46 \pm 2$ kcal/mole gives a good description of the data. The scatter at 1400°C is due probably to the difficulty in making reliable measurements since the creep rate decays very rapidly. The fact that $\frac{1}{\tau}$ varies exponentially with temperature is a justification for the assumptions involved in obtaining the relaxation times. This dependence also gives a good explanation for the long transient periods which are observed as the temperature is decrease below 1200°C.

E. Mechanism of Initial Transient

The Kelvin solid, in addition to its exponentially decaying strain rate, will recover anelastically all of the strain once the stress is removed. Setting $\sigma = 0$ in equation (27) and solving for ϵ leads to equation (34)

$$\epsilon = \epsilon_0 e^{-t/\tau} \quad (34)$$

in which ϵ_0 is the strain when the stress is relieved. This equation predicts that once the stress is removed all of the strain will recover. In fact the same relaxation time τ will govern the exponential decay of the transient creep rate.

In order to test this feature a creep experiment was conducted at 1350°C on a 5% Fe_2O_3 specimen. After creep testing for about one hour, which was about the duration of the transient (i.e., exponential decay in strain rate),

Figure 30. A Temperature Dependence of Transient Relaxation Times

the load was reduced by about 82%. As can be seen from Figure 31 an elastic after effect was noted in that some of the inelastic strain was recovered. It is difficult to perform this experiment accurately with the present equipment because, upon unloading, the core in the LVDT is displaced leading to uncertainties in the absolute deflection. However, it is clear that some, if not all, of this initial transient is recoverable. The total deflection in this initial transient period is small and ranges between 3×10^{-3} and 10^{-2} cm (note $\sim 5 \times 10^{-3}$ cm at 1350°C in Figure 31). Recoverable anelastic deformation frequently has been observed in the primary region during the creep of metals⁽²⁴⁾. The behavior in polycrystalline MgO may be similar.

Zener⁽²⁵⁾ has proposed an anelastic grain boundary mechanism to account for internal friction and elastic after effects which are frequently observed in polycrystalline metals. In this model (refer to Figure 32), which is identical to the Kelvin solid, viscous grain boundary (i.e., dashpot) sliding commences with the application of a shear stress on the boundary. Sliding proceeds until an elastic (i.e., spring) back stress at grain intersections sets up to stop the process. On release of the stress the stored elastic energy causes the sliding to reverse itself. Therefore, all the deformation is elastic and recoverable. Ashby and Raj⁽¹¹⁾ have recently referred to this process as grain boundary sliding accommodated by elastic deformation. It is important in the initial stages of creep when the strain (deflection) is small.

Activation energies determined from internal friction studies in polycrystalline metals correspond in many cases to those for creep⁽²⁶⁾. It is even conceivable that they would be similar to those for grain boundary dif-

Figure 31. Elastic After Effect - 5% Fe_2O_3 Specimen - 1350°C

Figure 32. Anelastic Grain Boundary Sliding Model (after Zener)

fusion. In this study the activation energy, which was determined from the temperature dependence of τ , is 46 ± 2 kcal. This value is smaller than that observed in creep (Refer to Section II), and self diffusion^(27,28) by about 25-50%.

Finally using a reasonable approximation for the shear modulus of MgO ($\sim 12 \times 10^6$ psi), grain boundary viscosities ranging between 10^{15} and 10^{16} poise were calculated from the relaxation times (τ) between 1000 and 1400°C. It is noted that glasses⁽²⁹⁾ with viscosities above $\sim 10^{12}$ poise will deform in a fashion described by the Kelvin solid and similar to that observed in this study.

In conclusion a viscous grain boundary sliding process accommodated by elastic deformation seems, at this stage, to be a reasonable interpretation for the mechanism of the initial transient. Additional data are needed particularly with respect to the recoverable nature of the transient. Internal friction data related to grain boundary sliding in MgO and its alloys would also be useful. These data are available in polycrystalline Al_2O_3 ^(30,31) and may relate to transient creep which has been observed.

F. Summary

Transient creep in MgO and MgO-Fe₂O₃ alloys can be described in terms of two effects:

(1) An (anelastic?) exponential decay which is characterized in most cases by a single relaxation time (τ).

(2) A viscous (in the case of MgO-Fe₂O₃) contribution which will decay slowly with time if simultaneous grain growth is occurring.

The observed transient creep has many of the features associated with a Kelvin solid. The activation energy of 46 ± 2 kcal/mole is consistent with a grain boundary diffusion process. Finally grain boundary sliding accommodated by elastic deformation is a promising candidate to explain a good portion, if not all, of the rapidly decaying transient creep in MgO and its alloys.

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VIII. PRINICPAL INVESTIGATOR

The principal investigator, Dr. Ronald S. Gordon, had devoted approximately two months full time effort to this project in addition to normal supervisory activities related to the project personnel. For the remainder of the current contract period, Dr. Gordon will spend whatever supervisory effort is required in addition to time spent in the preparation of papers for publication.