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

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Technical Progress Report
December 19, 1973 to December 18, 1974

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ABSTRACT

The research described in this report and the attached preprints covers work on

- 1) the non-viscous creep of large grain size MgO, doped with iron
- 2) viscous creep of fine-grained, high purity MgO
- 3) the effect of grain size on creep of polycrystalline Al_2O_3 , doped with iron
- 4) stress relaxation tests on polycrystalline MgO and Al_2O_3 , pure and doped with iron and chromium

Some of the significant findings include:

- 1) The power law creep (N^3) of iron-doped MgO is independent of the iron dopant level (creep rates nearly the same as undoped MgO), grain size and oxygen partial pressure. The creep activation energy is ~ 71 kcal/mole.
- 2) Viscous creep has been identified in fine grained (6-24 μ m) MgO by relating the transient creep behavior to simultaneous grain growth. Tentative results indicate that both magnesium lattice and grain boundary diffusion contribute to the overall creep rate. Iron doping appears to enhance magnesium lattice diffusion and suppress cation grain boundary diffusion.
- 3) Increased iron dopant levels and/or decreasing oxygen partial pressures increase cation lattice diffusion in polycrystalline Al_2O_3 such that oxygen grain boundary diffusion becomes rate-limiting in diffusional creep. Estimates have been made of both aluminum lattice and oxygen grain boundary diffusivities in iron-doped, polycrystalline Al_2O_3 .
- 4) Preliminary stress relaxation experiments on pure and doped polycrystalline Al_2O_3 and MgO have been performed. Stresses

up to 1000 Kg/cm^2 and strain rates up to 1 h^{-1} have been achieved without fracture. Well defined power law creep regimes (stress exponents between ~ 3 and 9) were identified in the high stress regime.

I. INTRODUCTION

The research activities under contract ATC(11-1)-1591 during the period December 19, 1973 to December 18, 1974 are described in this report and in the attached preprints⁽¹⁻³⁾.

Major effort was devoted to the following:

1. Stress, P_{O_2} , and temperature change (1500-1550°C) experiments were conducted on large-grained (97-154 μ m), iron-doped MgO. In agreement with previous work, power law creep ($N \sim 3$) was observed with an activation energy of ~ 71 Kcal/mole. In contrast with the diffusional creep regime in fine-grained material, creep rates were independent of grain size, P_{O_2} , and iron dopant levels.

2. The viscous creep of fine-grained (6-24 μ m) pure MgO was studied at 1350°C by relating the decay in creep rate to the occurrence of simultaneous grain growth. In this manner the relative contributions of cation lattice and cation grain boundary diffusion to the creep of pure polycrystalline MgO were evaluated. These data represent the first successful attempt in identifying viscous creep in undoped polycrystalline MgO.

3. A diffusional creep theory which takes into account the simultaneous occurrence of lattice and grain boundary diffusion for both anions and cations was developed further for a polycrystalline ionic compound.⁽²⁾ The effects of grain size, soluble cation impurities of variable valence, and oxygen partial pressure on the relative contributions of lattice and grain boundary diffusion of the different ionic species were analyzed. Several limiting conditions for diffusional creep were identified and compared with actual creep data on Al_2O_3 , MgO and BeO.

4. The effect of grain size on the creep of pure and doped

polycrystalline Al_2O_3 was determined in the low stress regime at 1450°C . Dopants studied were (in cation %) 0.2, 1 and 2% Fe and 1% Cr. For iron-doped Al_2O_3 (2% Fe) grain size effects were studied in both oxidizing ($\text{Po}_2 = 0.18 \text{ atm}$) and reducing atmospheres ($\text{Po}_2 \sim 10^{-7} \text{ atm}$). In general as the concentration of iron increased and/or the Po_2 decreased the contribution of oxygen grain boundary diffusion to diffusion creep increased.⁽¹⁾

5. Creep studies (1450 - 1550°C) by the method of stress relaxation were conducted on pure and doped polycrystalline MgO and Al_2O_3 . Dopants studied included iron and chromium. Strain rates up to 1h^{-1} and stresses up to 1000 kg/cm^2 were achieved without fracture. Well defined power law creep regimes (n values between ~ 3 and ~ 9 were observed) were identified in the high stress regime.

Four papers have been published⁽⁴⁾ or accepted for publication⁽¹⁻³⁾ this year. Copies of preprints and reprints are attached to this report:

1. "Creep of Polycrystalline $\text{MgO-FeO-Fe}_2\text{O}_3$ Solid Solutions", R.T. Tremper, R.A. Giddings, J.D. Hodge, and Ronald S. Gordon, J. Am. Ceram. Soc. 57 (10) 421-428 (1974).
2. "Analysis of Mass Transport in the Diffusional Creep of Polycrystalline $\text{MgO-FeO-Fe}_2\text{O}_3$ Solid Solutions" Ronald S. Gordon and J. D. Hodge, J. Mater. Sci. (in press)
3. "Ambipolar Diffusion and its Application to Diffusion Creep" Ronald S. Gordon, to be published in The Proceedings of the Ninth University Conference on Ceramic Science - Mass Transport Phenomena in Ceramics, Case Western Reserve University - June 1974.
4. "Impurity and Grain Size Effects on the Creep of Polycrystalline Magnesia and Alumina" Paul A. Lessing and Ronald S. Gordon, to be published in the Proceedings of the Symposium on "Plastic Deformation of Ceramic Materials" Pennsylvania State University, July 1974.

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 IV.

Finally the principal investigator attended two symposia this past summer and presented invited papers on:

1. Ambipolar Diffusion and its Application to Diffusion Creep - Case Western Reserve University.
2. Impurity and Grain Size Effects on the Creep of Polycrystalline Magnesia and Alumina - Pennsylvania State University.

II. REVIEW OF RESEARCH ACTIVITIES

In this section the research activities which have been conducted under the contract for the current period will be described briefly. This discussion will focus only on research not covered in the preprints attached to this report.⁽¹⁻³⁾

2.1 Non-Viscous Creep of Large Grain Size MgO, Doped with Iron

Diffusional creep is the dominant deformation mechanism in polycrystalline iron-doped MgO at low stresses ($\leq 100\text{--}300 \text{ kg/cm}^2$) and small grain sizes (8-100 μm). Three diffusional mechanisms have been identified as rate controlling in certain regimes:

- (1) Coble creep controlled by magnesium grain boundary diffusion
- (2) Nabarro-Herring creep controlled by magnesium lattice diffusion which is enhanced with increasing amounts of trivalent iron in solid solution and
- (3) Coble creep controlled by oxygen grain boundary diffusion

As the grain size is increased over 100 μm and stress levels exceed 100 kg/cm^2 , non-viscous creep is dominant ($T > 1425^\circ\text{C}$). In this regime strain rate-stress exponents (N) of ~ 3 and creep rates which are grain size independent have been observed.⁽¹⁾

Pure, polycrystalline MgO deforms by a power law ($N = 3$) mechanism in which the creep rate is independent of grain size and slightly faster than iron-doped material.⁽¹⁾

A complete discussion of power law ($N=3$) creep in polycrystalline MgO, pure and doped with iron, is given in the preprint attached to this report.⁽¹⁾ This work was presented at the Symposium on Plastic Deformation of Ceramic Materials at Pennsylvania State University this past summer.

In the interim additional work has been completed that further verifies the previous results of stress, P_{O_2} and temperature change experiments performed on Fe-doped, large grained MgO. (1)

Apparent (experimental) stress exponents of 2.5 and 2.8 were measured for samples with grain sizes of 97 and 154 μm (linear intercept) respectively, at 1500°C. An average activation energy of 71 kcal/mole was measured on the 154 μm sample using jump type temperature changes from 1500 to 1550°C. This is in good agreement with the tentative value of 71 kcal/mole reported earlier. (1)

On the basis of P_{O_2} change experiments completed last year on a 170 μm 1% Fe sample, it was concluded that the non-viscous creep process had no P_{O_2} dependence. Recent studies confirm this conclusion. The oxygen partial pressure was cycled from 0.18 to approximately 10^{-7} atm at 1500°C on the 154 μm sample and no effect was found at a stress of $\sim 200 \text{ kg/cm}^2$. In the smaller grained sample (97 μm) a noticeable reduction in the creep rate was found upon reducing the sample. At a stress of 218 kg/cm^2 the strain rate dropped from $1.90 \times 10^{-3} \text{ h}^{-1}$ to $1.62 \times 10^{-3} \text{ h}^{-1}$ or a difference of $2.8 \times 10^{-4} \text{ h}^{-1}$. The estimated viscous contribution at this temperature, grain size, and stress is $2.5 \times 10^{-4} \text{ h}^{-1}$. The logical conclusion is that the reduction in creep rate comes from lowering of the viscous contribution to the strain rate in the ($\sim 10^{-7}$ atm) reduced state.

Oxygen partial pressure change experiments were conducted for long periods ($\sim$ one week). During this time at 1500°C a continual and very gradual decay in the strain rate was noted. Even though this problem of hardening was minimal in short time stress change experiments, it is noticeable at long times.

In summary the creep of coarse-grained MgO doped with iron proceeds by a power law ($\dot{N}=3$) mechanism with an activation energy of

~ 71 kcal/mole. In contrast to the diffusional creep regime in fine-grained material, creep rates are independent of grain size, oxygen partial pressure and iron dopant level. Work is progressing on the development of a model consistent with these results.

2.2 Viscous Creep of Fine-Grained MgO

Gordon^(2,5) has recently shown that in the limit of small stresses, small grain sizes and small cation lattice diffusivities, the creep rate of a binary ionic compound such as MgO should be controlled by cation grain boundary diffusion. Also, extrapolation of the non-viscous creep data of Lessing and Gordon⁽¹⁾ on polycrystalline MgO, pure and doped with iron, to low stresses ($< 100\text{kg/cm}^2$) and relatively low temperatures ($\sim 1350^\circ\text{C}$) revealed that the relative contribution of non-viscous mechanisms to the creep rate of polycrystalline MgO at these stress levels and temperatures should be negligible, particularly in fine-grained material. Despite these predictions, no evidence exists in the literature at this time to show that diffusional creep exists in high purity, polycrystalline MgO. Previous work^(6,7) has been complicated by high stresses and temperatures, where non-viscous components should become more and more important, and/or grain growth during the creep test. In this study, a method developed by Terwilliger⁽⁶⁾ was used to determine the grain size dependence of the strain rate at different stress levels. In this method, previously obtained grain growth data are used to assign grain sizes to the creep sample at various times during the test. Using this procedure, a plot of strain rate vs. grain size can be made, and the grain size dependence of the creep rate can be determined.

High purity (99.95-99.99%) MgO powder was mixed with 2% LiF and hot-pressed to full density at 850°C . The hot-pressed sample was subsequently annealed at 1000°C for 2 hrs. Benecke⁽⁸⁾ has shown that MgO containing LiF treated in this manner will lose all of the Li during pressing except for a very small ($\sim 75\text{ppm}$) residual amount. The grain size of these annealed samples was about $2\mu\text{m}$.

A grain growth study was performed on these samples at 1350°C . The annealed specimens were heated in air at various times ranging between

10 minutes and 7 days. The samples were polished and etched using a method described by Gardner and Robinson.⁽⁹⁾ Average grain sizes were determined on polished surfaces using the linear intercept method by counting approximately 500 grains. Final grain sizes of all creep samples were also measured in this manner. All data are reported as linear intercept values.

Creep testing was performed using a four-point dead-load apparatus described previously. Tests were conducted at 1350°C in air and at stresses ranging from 25 kg/cm² to 100 kg/cm². In most cases, tests lasted approximately 20 hours.

In Figure 1, the results of the grain growth study are shown. As can be seen, the samples follow a squared growth law very well except for some deviation at long times which would tend to indicate that the samples are not totally dense and some coalescence of pores is taking place. Similar results have been obtained by other workers.^(10,11) These data also indicate that grain growth in the creep specimens is comparable to that observed in the unstressed grain growth samples.

In dead-load creep tests at 1350°C and stresses between 23 and 100 kg/cm², a continual decay in the creep rate was observed. Using the grain growth data in Figure 1, the creep rates were plotted against calculated grain sizes in Figure 2. These data indicate that grain growth can account for essentially all of the transient creep behavior. Furthermore the creep rates are strongly dependent on the grain size with the grain size exponent $m = 2.59$ (i.e. $\dot{\epsilon} \propto (GS)^{-m}$). Secondly, the relative insensitivity of the creep rate to stress is a strong indicator of viscous creep with little contribution of power law creep in this low stress regime. The reciprocal grain size dependence and the approximate viscous creep behavior indicate that creep is being controlled by a diffusional mechanism.

The value of the grain size dependence is one that is intermediate

Figure 1. Grain Growth Kinetics in High Purity Polycrystalline MgO

Figure 2. Effect of Grain Size on the Viscous Creep of Pure, Polycrystalline MgO

between Coble and Nabarro-Herring creep. Gordon^(2,5) has shown that this type of behavior will be expected when cation lattice and grain boundary diffusion are comparable and the grain size is reasonably small.

In the compound MgO the general diffusional creep equation is

$$\dot{\epsilon} = \frac{44\Omega_V\sigma}{kT(GS)^3} \frac{[(GS/\pi) D_{Mg}^l + \delta_{Mg} D_{Mg}^b]}{\left[1 + \frac{[(GS/\pi) D_{Mg}^l + \delta_{Mg} D_{Mg}^b]}{[(GS/\pi) D_O^l + \delta_O D_O^b]} \right]} \quad (1)$$

in which

$\dot{\epsilon}$ = strain (creep) rate

Ω_V = molecular volume of MgO

σ = stress

GS = grain size

T = absolute temperature

k = Boltzmann's Constant

D_{Mg}^l, D_O^l = magnesium and oxygen lattice diffusion coefficients

D_{Mg}^b, D_O^b = magnesium and oxygen grain boundary diffusion coefficients

δ_{Mg}, δ_O = effective grain boundary thicknesses, respectively, for Mg and O boundary diffusion

In this system the total oxygen ion mobility is high and dominated by grain boundary diffusion such that

$$\delta_O D_O^b \gg (GS/\pi) D_O^l \quad (2)$$

$$\delta_O D_O^b \gg [(GS/\pi) D_{Mg}^l + \delta_{Mg} D_{Mg}^b] \quad (3)$$

Equation (3) holds when the grain size is small and D_{Mg}^l is not too high as is expected in undoped MgO. Taking into account (2) and (3) the general creep equation for fine-grained MgO reduces to :

$$\dot{\epsilon} = \frac{44\Omega_V\sigma}{kT(GS)^3} [(GS/\pi)D_{Mg}^{\ell} + \delta_{Mg} D_{Mg}^b] \quad (4)$$

Equation (4) can be rewritten in the form

$$\dot{\epsilon} (GS)^2 = \frac{44\Omega_V\sigma D_{Mg}^{\ell}}{\pi kT} + \frac{44\Omega_V\sigma\delta_{Mg} D_{Mg}^b}{kT(GS)} \quad (5)$$

Equation (4) predicts that if $(GS/\pi) D_{Mg}^{\ell} \approx \delta_{Mg} D_{Mg}^b$, then the grain size exponent, m , will lie between 2 and 3 as is seen from the creep data in Figure 2.

Equation 5 can then be used to estimate the relative contributions of magnesium lattice (D_{Mg}^{ℓ}) and magnesium grain boundary ($\delta_{Mg} D_{Mg}^b$) diffusion in the diffusional creep of fine grained MgO. In Figure 3, $\dot{\epsilon} (GS)^2$ is plotted versus $(GS)^{-1}$ using computed values from a least squares analysis of the data in Figure 2. The slope (m) and intercept (b) of the line are given by

$$m = \frac{44\Omega_V\sigma \delta_{Mg} D_{Mg}^b}{kT} \quad (6)$$

$$b = \frac{44\Omega_V\sigma D_{Mg}^{\ell}}{\pi kT} \quad (7)$$

Least squares values for m and b are $0.45331 \mu m^3/h$ and $0.02794 \mu m^2/hr$ respectively. From these values we can estimate D_{Mg}^{ℓ} and $\delta_{Mg} D_{Mg}^b$ to be $1.53 \times 10^{-12} \text{ cm}^2/\text{sec}$ and $1.19 \times 10^{-15} \text{ cm}^3/\text{sec}$, respectively.

The calculated value for D_{Mg}^{ℓ} is reasonable when compared with the tracer value⁽¹²⁾ extrapolated from measurements at higher temperatures ($0.95 \times 10^{-12} \text{ cm}^2/\text{sec}$). The value obtained for $\delta_{Mg} D_{Mg}^b$ ($1.19 \times 10^{-15} \text{ cm}^3/\text{sec}$) has not been reported in the literature except for some estimates calculated from creep data on iron-doped (≤ 0.5 cation %) polycrystalline MgO⁽¹⁾. These values ($\sim 5 \times 10^{-16} \text{ cm}^3/\text{sec}$) are significantly lower than those obtained in this study and indicate tentatively that iron doping depresses magnesium

(15)

Figure 3. Analytical Procedure for Determining Values of D_{Mg}^l and $\delta_{Mg} D_{Mg}^b$

grain boundary diffusion. This conclusion is supported by the experimental observation that at small grain sizes the creep rate of undoped MgO is significantly faster than the creep rate of material doped with 0.53 cation % Fe which has been shown to be controlled by cation lattice diffusion.

Further experiments are needed on the effect of iron dopant concentration on the relative contributions of cation lattice and grain boundary diffusion in the creep of polycrystalline MgO. If in fact iron doping increases D_{mg}^l but decreases D_{Mg}^b , then the transition grain size between cation lattice and grain boundary diffusion control will decrease with increasing iron concentration (e.g. $\sim 24\mu m$ for undoped and $\sim 16\mu m$ for 0.05 cation % Fe⁽³⁾).

2.3 Effect of Grain Size on Creep of Polycrystalline Al_2O_3 , Doped with Iron

Gordon^(2,5) has predicted for the system $\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{FeO}$ that in the limit of a large grain size and/or a high value of the aluminum ion lattice diffusivity (D_{Al}^{L}) that diffusional creep rates in the low stress regime will be rate-controlled by oxygen grain boundary diffusion because cation lattice diffusion becomes too fast. Aluminum lattice diffusion can be enhanced by increasing the iron dopant level and/or reducing the oxygen partial pressure. Both of these changes will increase the concentration of divalent iron leading to enhanced lattice diffusion⁽¹³⁾ via aluminum interstitials.

In work reported last year diffusional creep data at 1450°C were obtained at different grain sizes for polycrystalline Al_2O_3 doped with 1 cation % iron.^(1,2) These data which are reproduced in Figure 4 indicate a grain size exponent ($m=2.24$) which is intermediate to that expected from Nabarro-Herring ($m=2$) and Coble creep ($m=3$). Gordon⁽²⁾ using a procedure developed by Gordon and Hodge⁽³⁾ for MgO , extracted values for D_{Al}^{L} ($5.5 \times 10^{-12} \text{ cm}^2/\text{sec}$) and $\delta_0 D_0^{\text{b}}$ ($3.4 \times 10^{-14} \text{ cm}^3/\text{sec}$) from these creep data.

By doping at even higher concentrations (i.e. 2 cation % Fe) and reducing the oxygen partial pressure ($4.66 \times 10^{-7} \text{ atm}$) D_{Al}^{L} can be increased even further at 1450°C without the precipitation of a second phase. If Gordon's ambipolar diffusional creep theory is correct, these changes should lead to larger grain size exponents(m) and creep rates controlled more and more by oxygen grain boundary transport.

As indicated in Figure 4, doping with 2% Fe and creep testing in air resulted in higher strain rates and a larger grain size exponent ($m=2.55$). When creep tests were conducted in a reducing atmosphere ($P_{\text{O}_2} = 4.66 \times 10^{-7} \text{ atm}$), creep rates increased even further, although

Figure 4. Grain Size Effects on the Creep of Pure and Iron-Doped, Polycrystalline Al_2O_3

the relative increase was smaller at large grain sizes than in fine grained material. Under these conditions the creep grain size exponent was 2.98, its largest value and in excellent agreement with that predicted by Coble creep.

In Table 1, a summary is given for values of D_{Al}^l and $\delta_0 D_0^b$ computed from creep data at the 0.0, 0.2, 1.0 and 2.0% dopant concentrations.

Table 1

Cation Lattice and Anion Grain Boundary Diffusivities (1450°C) in Iron Doped, Polycrystalline Al_2O_3

$P_{O_2}(\text{atm})$	Cation % Fe	D_{Al}^l (cm^2/sec)	$\delta_0 D_0^b$ (cm^3/sec)	m
0.18	0*	6.9×10^{-13}	-	2
0.18	0.2*	1.7×10^{-12}	-	~ 2
0.18	1.0**	5.5×10^{-12}	3.4×10^{-14}	2.24
0.18	2.0**	3.4×10^{-11}	4.9×10^{-14}	2.55
4.66×10^{-7}	2.0***	-	5.9×10^{-14}	2.98
Tracer (Extrapolated)		1.0×10^{-13}		

*Calculated from Nabarro-Herring creep equation modified for an ionic compound⁽²⁾

**Calculated by a procedures similar to that reported by Gordon⁽²⁾ and Gordon and Hodge⁽³⁾

***Calculated from Coble creep equation modified for an ionic compound⁽²⁾

The data in Table 1 indicate that both D_{Al}^l and $\delta_0 D_0^b$ increase with iron doping, in particular the concentration of divalent iron. In addition as D_{Al}^l increases the relative contribution of oxygen grain boundary diffusion increases giving rise to increasing values of the creep rate grain size exponent. Both of these effects are in accord with that predicted by the ambipolar diffusional creep theory of Gordon.^(2,5)

2.4 Stress Relaxation Tests on Polycrystalline MgO and Al₂O₃, Pure and Doped with Iron and Chromium

In order to reach high strain rates ($\sim 1\text{h}^{-1}$) and stresses ($\sim 1000\text{ kg/cm}^2$), which are difficult to achieve in dead-load creep tests on brittle materials because of specimen fracture, a series of stress relaxation tests were conducted on pure and doped (Fe, Cr) samples of polycrystalline Al₂O₃ and MgO. By achieving these high strain rates and stresses it has been possible to investigate the transition in creep regimes between diffusion creep at low stresses and power law creep at higher stresses. In some cases this transition can be studied in a single relaxation test while in others a comparison can be made with dead-load creep data taken at low stresses.

Stress relaxation is also a convenient technique for studying strain hardening processes which are expected to be important in power law creep regimes involving dislocation generation and glide. The stress relaxation test is conducted under conditions of constant total strain and approximately constant plastic strain if the initial elastic strain on loading, which is converted to plastic strain during relaxation, is small. Conditions of nearly constant plastic strain imply constant hardness or dislocation structure. If no strain hardening is present, a second relaxation test at a higher strain level should result in a trace of the original $\dot{\epsilon}-\sigma$ plot. If, however, hardening is occurring, then the $\dot{\epsilon}-\sigma$ plot will lie below the original curve (i.e. lower strain rates for the same stresses). Therefore by performing multiple stress relaxation tests at different plastic strains one can study the strain hardening character of a material in addition to the transition between low and high stress deformation regimes. If these experiments are then conducted over a range of temperatures, the temperatures where recovery processes become important (i.e. no hardening) can be identified.

For these reasons a technique has been developed this past year for studying deformation processes in pure and doped, polycrystalline MgO and Al_2O_3 at temperatures between 1450 and 1550°C by the method of stress relaxation. Preliminary data will be reported and are subject to further refinement. However, distinct differences in deformation behavior have been observed over the range of materials studied.

This year a four-point bend stress relaxation apparatus has been designed and built that interfaces with a floor model 'Instron' Universal testing machine. The equipment consists of:

- (1) a water cooled, steel table to support the specimen pedestal and furnace.
- (2) water cooled adapters to attach the load cell to 'Instron' and the load rod to the load cell.
- (3) accurately machined dense alumina load rods and sample pedestal with single crystal sapphire support points.
- (4) a linear variable differential transformer (Shaevitz HR 050) and non rotating micrometer head readable to 0.00002 inch. These enable crosshead deflections to be recorded accurately.
- (5) a furnace and associated 'West PSCR' solid state proportional power supply, controller, and also a 2:1 step-down transformer. The furnace utilizes the latest design for compact furnaces. It features 6 MoSi_2 hairpin heating elements and fibrous zirconia insulation. It is capable of temperatures up to 1700°C in air.
- (6) platinum-rhodium thermocouples that measure sample temperature and provide input for furnace control.

In Figure 5 (5A and 5B) photographs are presented of the various components of the stress relaxation equipment.

Figure 5A. Loading rod and support pedestal.

Figure 5B. Assembled stress relaxation apparatus.

The load cell was calibrated and initial tests were made to test the stiffness (compliance) of the machine and loading linkages. An exceedingly thick sample of dense (99+%) 18 μ m grain size Al₂O₃ was cut and polished to ± 0.01 mm tolerances. Its width and height were 5.72 mm and 10.75 mm, respectively, compared to a normal sample of 5.00 mm and 1.50 mm. Measuring the slope of the loading curve at a fixed crosshead rate gave the compliance of the machine. This measurement was taken both at room temperature and at 1450-1500°C. At room temperature the compliance was 5.50×10^{-5} in/kg and at 1466°C it was 6.20×10^{-5} in/kg. These measurements reveal that the specimens (MgO and Al₂O₃) will always be softer than the machine and, thus, the data analysis is facilitated.

When in operation, the furnace temperature was ± 0.25 °C. Small fluctuations in room temperature contributed to scatter in low strain rate data (i.e. $\dot{\epsilon} < 10^{-3} \text{ h}^{-1}$).

A loading rate of 0.02 in/min. was used in loading the samples to a preset level, and then the decay of the load was recorded with time on a strip chart recorder. Elastic equations were used to convert loads to stresses and the slope of the load decay to strain rates. The deflection rate at the center of the beam is given by:

$$\dot{y}_c = \frac{dp}{dt} \cdot C \quad (8)$$

in which P is the load, t is the time, C is the compliance of sample, measured upon loading and assumed to entirely elastic (actually some plastic yielding on loading will make C lower and lead to overestimates of the strain rate. This problem will be checked in future experiments). The total plastic strain introduced into the test specimens during multiple stress relaxation tests was small ($\sim 0.2\%$ in pure and iron-doped MgO and $\leq 0.1\%$ in Al₂O₃ - based systems).

The strain rate is given by:

$$\dot{\epsilon}_{\text{max}} = \frac{(12)(h)}{3(L)^2 - 4(a)^2} \dot{y}_c \quad (9)$$

in which h is the height of beam, L is the distance between outer support points and a is the distance between inner load points.

The stress is given by:

$$\sigma_{\text{Max}} = \frac{1.5(L-a)P}{bh^2} \quad (10)$$

in which b is the width of beam.

Initial tests covered the gamut of samples to be studied in this program. Samples of a large grained ($\sim 140\mu\text{m}$) pure MgO , 0.53% Fe doped MgO ($328\mu\text{m}$), medium grained undoped Al_2O_3 ($\sim 29\mu\text{m}$), and small grained 1% Cr doped Al_2O_3 ($\sim 10\mu\text{m}$) were tested at temperatures between 1450 and 1550°C.

Strain rates corresponding to stresses below approximately 100 kg/cm^2 are subject to errors due to temperature fluctuations and instabilities found in the zero of the load recorder. Absolute values of the strain rates are probably high, perhaps as much as 8 times in some cases, due to overestimates of the sample compliance when plastic deformation takes place upon loading. Also, using elastic equations for the stress and strain values introduce errors by as much as 25-30%. Further refinements in calculations and experimental procedures are expected to minimize these errors.

In Figure 6 stress relaxation tests at 1500°C are shown for a large grain size ($328\mu\text{m}$) MgO specimen doped with 0.53 cation % Fe. Stresses up to $\sim 600 \text{ kg/cm}^2$ were obtained. A slightly curved strain rate-stress dependence was found. For loads up to $\sim 400 \text{ kg/cm}^2$, N was 2.7 which compares favorably with $N=3.1$ found in dead load creep tests.⁽¹⁾ Above 400

Figure 6. Stress Relaxation at 1500°C. in Large Grain Size, Iron-Doped MgO

kg/cm², a higher N value (5.2) was observed; of course a composite least squares line would give an N value between these two limits. Raising the test temperature to 1550°C increased strain rates as shown in Figure 7. The same shape of the stress versus strain rate curve was found. The data in Figure 6 also indicate little hardening between the third and sixth loadings.

Twenty one different relaxation tests were completed at 1500°C on a sample of large grained, pure MgO (~145μm). Values of N were found to range from 4.02 in the first test to 3.08 in the latter ones as indicated in Figure 8. The $\dot{\epsilon}$ -σ lines for pure MgO were only slightly faster than those for the iron-doped material. This result was also found in the dead load creep studies.⁽¹⁾ Three power creep was also observed in dead load creep tests.⁽¹⁾ A small amount of hardening was found, however, not much strain was accumulated and more studies need to be done.

Medium grained, pure Al₂O₃ (~29μm) tested at 1450°C typically showed N values in the 5-6 range, in stress relaxation tests, with a slight curvature toward higher values as shown in Figure 9. When the temperature was raised to 1550°C the curvature disappeared and N dropped to 3.75. Stresses up to 1,000 kg/cm² were achieved in these tests; these are 3 to 4 times that achieved in the typical dead load creep test.

In stress relaxation tests on chromium (1 cation) - doped Al₂O₃ (~10μm), N values ranging from 5.8 to 9.24 were measured at stresses between 500 and 1200 kg/cm². It appears that there is a break to N values of approximately 1.0, below 400-500 kg/cm². This would indicate a viscous mode of deformation as found in dead load tests (stresses up to 280 kg/cm²).^(1,13) Absolute strain rates are in reasonable agreement with dead load studies, considering the errors involved. Both the stress relaxation and dead load creep data are shown in Figure 10. Considerable hardening was observed in multiple stress relaxation tests and warrants additional study.

Figure 7. Stress Relaxation at 1550°C in Large Grain Size, Iron-Doped MgO

Figure 8. Stress Relaxation at 1500°C in Large Grain Size, Pure MgO

Figure 9. Stress Relaxation in Pure, Polycrystalline Al_2O_3

Figure 10. Stress Relaxation in Chromium-Doped, Polycrystalline Al_2O_3

In summary, the preliminary stress relaxation tests on pure and doped, polycrystalline MgO and Al_2O_3 have met the desired initial objectives.

- 1) High stresses ($\sim 1000 \text{ kg/cm}^2$) and strain rates ($\sim 1\text{h}^{-1}$) have been achieved without fracture.
- 2) Transitions between low and high stress creep regimes have been observed (e.g. Fig. 10 for Cr-doped Al_2O_3)
- 3) Reasonable agreement (i.e. N values) exist between stress relaxation tests and dead load creep tests ($N \sim 3-4$ in iron-doped and pure MgO).

Additional work over a wider range of temperatures and grain sizes is needed. Furthermore the effect of pre-straining in the inhibition of dislocation creep modes (e.g. Cr-doped Al_2O_3 in Figure 10) is interesting and merits additional study.

The stress relaxation test appears to be promising and in conjunction with dead load creep experiments can generate data over five orders of magnitude ($10^{-5} - 1\text{h}^{-1}$).

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VI. PRINCIPAL INVESTIGATOR

In addition to full time research on the contract for a portion of the summer, Dr. Gordon spends time throughout the year in supervisory activities and preparing talks and papers on work related to this contract.