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

Technical Progress Report

December 19, 1970 to December 18, 1971

Atomic Energy Commission

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TECHNICAL PROGRESS REPORT

December 18, 1971

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CONTRACT	AEC AT(11-1)-1591
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ABSTRACT

The effects of transition metal impurities and oxygen partial pressure changes on the creep of polycrystalline MgO and Al_2O_3 are discussed in this report and attached reprints. Most of the results are consistent with creep rates controlled by the lattice diffusion of cations. The role of impurities on the control of microstructure and hence creep behavior is also discussed.

Transient creep behavior in iron-doped polycrystalline MgO is analyzed in terms of transient diffusional creep theories. The effects of temperature, grain size, and impurities on the transient are discussed. Tentative evidence is presented to support the claim that transient behavior in the diffusional creep of iron-doped MgO can be predicted from a knowledge of the steady state creep properties and vice versa.

A general mass transport theory for the diffusional creep of ionic solids is described. The effects of transition metal impurities, temperature, grain size, and oxygen partial pressure on the relative roles of cation lattice and anion grain boundary diffusion in the creep of polycrystalline MgO and Al_2O_3 are analyzed.

Finally, a redesign of the hot pressing facility, which allows for the high temperature fabrication of doped, polycrystalline Al_2O_3 and MgO, is described.

I. INTRODUCTION

The research activities under contract AT(11-1)-1591 during the period December 19, 1970 to December 18, 1971 are described in this report and in the attached preprints.⁽¹⁻⁴⁾

Major effort was devoted to the following:

- 1) Completion of the studies on the effect of oxygen partial pressure changes on the steady state creep of polycrystalline magnesium oxide doped with iron. This work is described in a preprint⁽¹⁾ (presently under review by the American Ceramic Society) attached to this report and in the finished Ph.D. thesis of R. T. Tremper.⁽⁵⁾
- 2) Extensive studies on the effect of transition metal impurities (Cr, Fe, and Ti) and oxygen partial pressure changes on the steady state creep of polycrystalline Al_2O_3 . This work is described in a preprint⁽²⁾ (presently under review by the American Ceramic Society) and in the finished Ph.D. thesis of G. W. Hollenberg.⁽⁶⁾
- 3) An analysis of transient creep in polycrystalline MgO doped with Fe_2O_3 . This work is described in a paper (preprint)⁽³⁾ which is attached to this report. This paper has been accepted for publication in the Journal of the American Ceramic Society with minor revisions which are presently being made.
- 4) A theoretical analysis of mass transport and diffusional creep in ionic solids, pure and doped with variable valent cation impurities. This paper⁽⁴⁾ was presented at the fall 1971 meeting of the Basic Science Division of the American Ceramic

Society and is attached to this report.

- 5) A preliminary thermogravimetric study on Fe and Ti-doped Al_2O_3 involving weight changes as a function of oxygen partial pressure. This work is described in the Bachelor's thesis of Mr. Paul Lessing.⁽⁷⁾
- 6) A successful change of hot press design to allow for heating by an R.F. induction power supply. This design change will permit hot pressing to be accomplished in atmospheres which are considerably less reducing than in the present hydrogen-atmosphere, molybdenum-wound unit.

Finally, two papers^(8,9) have been published or accepted for publication this year:

- 1) "Calculation of Stresses and Strains in Four-Point Bending Creep Tests," G. W. Hollenberg, G. R. Terwilliger, and R. S. Gordon, J. Amer. Ceram. Soc., 54 (4), 196-199 (1971).
- 2) "Grain Size Distributions and Grain Growth in MgO and MgO- Fe_2O_3 Solid Solutions," D. D. Marchant and R. S. Gordon, J. Amer. Ceram. Soc., 55 (1) (1972).

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.

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. Since most of the work has been incorporated into reprints (attached to this report) which have been prepared for publication, only a brief summary of the major results and conclusions will be given in this progress report. The details concerning the experimental procedures of hot pressing and creep testing have been described extensively in previous reports and will not be included in the present summary.

A. Effect of Oxygen Partial Pressure on the Steady State Creep of Polycrystalline MgO-FeO-Fe₂O₃ Solid Solutions

A rather complete picture is now available on the creep properties of polycrystalline MgO doped with iron under a wide range of conditions (i.e., temperature, stress, oxygen partial pressure, and grain size). These results and their significance will be reviewed briefly in this section.

Creep experiments were performed on polycrystalline (hot pressed) magnesia (95-99.8% dense) doped with 0.1-10.0% by weight Fe₂O₃. Creep tests were conducted under four point bending at stresses between 70 and 250 kg/cm², temperatures between 1300 and 1425°C, in oxygen partial pressures between 1 and 10⁻¹⁰ atmospheres, and with grain sizes (linear intercepts) between 10 and 65 μm.

Viscous, steady state creep was always observed when the grain size (GS) was stable. In the 0.10% Fe₂O₃ specimens grain growth occurred during creep testing and a true steady state creep rate was never achieved. These results confirm earlier experiments by

Terwilliger, et al.⁽¹⁰⁾ under this contract which associated grain growth with transient creep behavior.

Creep rates ($\dot{\epsilon}$) increased significantly with increasing oxygen partial pressure. In all experiments it was observed that, except for transient effects, the steady state creep rates, observed for a given oxygen pressure, stress, temperature, and grain size, were reversible and reproducible. Two important features were noted in the creep rate-oxygen partial pressure (P_{O_2}) dependence. In oxidizing atmospheres ($P_{O_2} > 10^{-1}$ - 10^{-4} atm) the creep rate was nearly independent of the oxygen partial pressure. In reducing atmospheres ($P_{O_2} < 10^{-1}$ - 10^{-4} atm) the creep rate was approximately proportional to $P_{O_2}^{1/6}$.

In addition to P_{O_2} effects the steady state creep rate at a given P_{O_2} increased with increasing iron concentration. This impurity dependence was much stronger in oxidizing ($P_{O_2} \sim 1$ atm) than in reducing ($P_{O_2} \leq 10^{-6}$ atm) atmospheres.

The oxygen partial pressure was also found to have a marked effect on the activation energy for viscous steady state creep. In oxidizing atmospheres (i.e., $P_{O_2} \sim 1$ atm) the activation energy varied between 60-80 kcal/mole depending on the iron concentration. In reducing atmospheres ($P_{O_2} < 10^{-1}$ - 10^{-4} atm when $\dot{\epsilon} \propto P_{O_2}^{1/6}$) the activation was significantly higher ($\sim 112 \pm 8$ kcal/mole). The increase in activation energy in reducing atmospheres was attributed to the incorporation of oxygen in the lattice resulting in the formation of cation lattice vacancies and oxidation of some of the iron in solid solution from the divalent to the trivalent state.

The grain size dependence of the steady state creep rate was determined

for the 1% Fe_2O_3 samples over the grain size range between 10 and 65 μm and was found to be consistent with a Nabarro-Herring creep mechanism (i.e., $\dot{\epsilon} \propto (\text{GS})^{-2}$). These results were consistent with earlier results by Terwilliger et al.⁽¹⁰⁾ on 0.10% samples tested over a comparable range of grain sizes.

Taking all of these results into consideration it was concluded that the predominant mechanism of deformation in iron-doped, polycrystalline MgO over the range of variables (i.e., iron concentration, P_{O_2} , T, stress, and grain size) utilized in this study was Nabarro-Herring creep controlled by the lattice diffusion of cation vacancies. Remarkably good agreement existed between diffusivities calculated from the Nabarro-Herring equation and recent experimental magnesium tracer measurements on single crystals.⁽¹¹⁾ In conclusion, these studies have established clearly that effects of non-stoichiometry on the steady state creep rate give information not only on the mechanism of creep of iron-doped, polycrystalline MgO (a well defined extrinsic system) but also on the nature of its defect structure.

It is appropriate at the conclusion of these studies to summarize briefly the major findings of all the research under this contract on the role of iron in solid solution on the creep of polycrystalline MgO. The effects of iron have been clearly established. They include the following:

- 1) Doping with Fe_2O_3 (0.1-10% by weight) promotes viscous creep behavior (at least up to stress levels of $\sim 250\text{-}300 \text{ Kg/cm}^2$).
- 2) Iron in solid solution inhibits grain growth⁽¹²⁾ and thus permits a stabilization of the microstructure over a range

of grain sizes, depending on the temperature of the creep test.

- 3) In the viscous creep regime increasing amounts of iron in solid solution enhance the creep rate, particularly in oxidizing atmospheres when most of the iron is in the trivalent state.
- 4) It is clear that as the cation lattice is made more defective (high iron dopant levels and oxygen partial pressures) the viscous creep of iron-doped MgO is enhanced. Thus, strong evidence is now present that the creep of this material is controlled by the lattice diffusion of cations for grain sizes larger than about 10-15 μm . This result implies a rapid transport mechanism for oxygen ions which will be discussed later in the report.
- 5) In a smaller grain size regime (5-15 μm) the earlier results of Terwilliger et al.⁽¹⁰⁾ under this contract are consistent with a Coble diffusional creep (i.e., $\dot{\epsilon} \propto (\text{GS})^{-3}$) mechanism (i.e., grain boundary diffusion control). Even in this regime iron doping enhances the steady state creep rate. A theoretical explanation for the transition between a Coble and Nabarro-Herring creep mechanism as the grain size (and temperature) is increased is given later in the report and discussed in the attached preprint.⁽⁴⁾
- 6) Finally, some conclusions can be drawn concerning the creep resistance of iron-doped, polycrystalline MgO in the low stress regime (i.e., stresses below 300 Kgm/cm^2). For maximum creep resistance three variables need to be considered; (1) iron dopant level, (2) grain size, and (3) oxygen partial pressure. The iron concentration should be high enough to

suppress non-viscous creep but not too high because of increased diffusion kinetics. Dopant levels between 0.1 and 1% Fe_2O_3 meet these criteria. Since the creep of Fe-doped MgO is viscous, the grain size should be reasonably large for high creep resistance (i.e., 50-100 μm). Finally, to compensate for the increased diffusion kinetics in iron-doped samples creep tests should be conducted in low oxygen partial pressure atmospheres ($< 10^{-6}$ atm) to obtain maximum creep resistance. Iron-doped MgO creep tested under these conditions at temperatures over 1300°C can, in principle, creep at rates up to several orders of magnitude slower than polycrystalline undoped MgO of comparable grain size.

In conclusion, the original objectives of this contract in relation to the effect of iron on the steady state creep of polycrystalline MgO in the low stress regime have been successfully accomplished. Two Ph.D. theses, three senior theses, and six papers have resulted from these studies.

B. The Effect of Oxygen Partial Pressure Changes on the Creep of Alumina Doped With Transition Metal Impurities (Cr, Ti, Fe)

With the experience and knowledge gained from the studies on iron-doped MgO the scope of the research under this contract was expanded to a study on the influence of impurities on the creep of polycrystalline Al_2O_3 .

As will be seen, a number of similarities exist between the creep of doped Al_2O_3 and that of doped MgO. However, as opposed to the MgO studies, microstructural abnormalities (i.e., non-equiaxed grains and discontinuous grain growth) and slightly non-viscous creep behavior

made the creep behavior of doped polycrystalline Al_2O_3 distinctly different than that observed in the creep of iron-doped MgO .

In this section the effects of temperature, stress, P_{O_2} , and grain size on the steady state creep of polycrystalline Al_2O_3 , doped with transition metal impurities, will be discussed briefly.

Nearly dense ($\geq 99\%$) polycrystalline alumina (Linde A) was hot pressed with 0.2 and 1 cation % Fe, 1% Cr and 1/2% Ti additions. Creep tests were conducted under four point bending at stresses between 10 and 500 kgm/cm^2 , temperatures between 1375 and 1525°C , and in oxygen partial pressures between 1 and 10^{-11} atmospheres.

1. Chromium-doped Al_2O_3

Stress change experiments were conducted on $6 \mu\text{m}$ Cr-doped Al_2O_3 at 1400 and 1500°C between 50 and 500 kg/cm^2 . The stress exponent N (i.e., $\dot{\epsilon} \propto \sigma^N$) was found to be 1.3 and was distinguished easily from viscous creep behavior (i.e., $N = 1$) as it extended over an order of magnitude in stress.

The origin of this slightly non-viscous behavior is not understood. It may be due to the nature of the microstructure of these materials which consists of elongated grains rather than a collection of equiaxed grains (typical of those in the $\text{MgO-Fe}_2\text{O}_3$ system). The factors which are responsible for this type of microstructure are not known at this time but it is expected that they are related either to impurities in the Linde A raw material or to the method of hot pressing. Efforts are presently underway to produce equiaxed, polycrystalline Al_2O_3 of significantly higher purity. These are discussed in the proposal for next year.

Single sample (Dorn type) activation energy experiments were conducted between 1400 and 1500°C on 3 and 6 μm material. These experiments yielded a creep activation energy of 115 kcal/mole. In addition, the creep rate of the 3 μm material was approximately four times faster than the 6 μm material (i.e., $\dot{\epsilon} \propto (\text{GS})^{-2}$).

Attempts to increase the range of grain sizes for creep studies were repeatedly foiled by the occurrence of discontinuous grain growth in high temperature anneals ($T > 1650^\circ\text{C}$). It is believed that impurities in the Linde A Al_2O_3 are responsible for the anomalous growth behavior at elevated temperatures.

One of the principal objectives for the creep studies on Cr-doped Al_2O_3 was to establish a reference base for the subsequent experiments with Fe and Ti dopants. In view of the variable valent nature of Fe and Ti, it was expected that the creep rate of Al_2O_3 doped with these impurities would be very sensitive to changes in oxygen partial pressure. However, the creep of Al_2O_3 doped with a stable +3 valence impurity (e.g., Cr) should be insensitive to changes in P_{O_2} and thereby serve as a convenient reference for the creep studies with variable valent impurities. This objective was achieved in the present studies in that the creep rate of Cr-doped, polycrystalline Al_2O_3 was found to be independent of P_{O_2} in the range between 1 and 10^{-6} atm.

In summary, the steady state creep rate of fine grained (3-6 μm) Cr-doped Al_2O_3 is slightly non-viscous ($\dot{\epsilon} = k\sigma^{1.3}$), proceeds with an activation energy of 115 kcal/mole, is independent of P_{O_2} , and varies inversely with the square of the grain size.

2. Iron-doped Al_2O_3

The stimulus for the present study on the creep of iron-doped

polycrystalline Al_2O_3 was twofold:

1) Due to the success of the creep studies on iron-doped MgO in which the steady state creep rate increased with increasing oxygen partial pressures, it was expected that iron doping would have the opposite effect on the creep of Al_2O_3 (i.e., decreasing creep rates as P_{O_2} increased). Thus, creep experiments in different oxygen partial pressures would be instructive in gaining knowledge of diffusion mechanisms and defect structures which are important in the high temperature creep of Al_2O_3 .

2) By taking advantage of the fact that the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio in Al_2O_3 is a function of the oxygen partial pressure, it is possible to vary the concentration of divalent iron on a single specimen and thus determine the effect of divalent impurities (and resulting charge compensating lattice defects) on the creep rate and mechanism. Previous experiments^(13,14) with fixed valence impurities (i.e., Mg^{+2}) have been contradictory due probably to the low solubilities (i.e., MgO in Al_2O_3) and fairly high levels of background impurities in the Al_2O_3 starting material. These experiments also depend on comparisons of creep rates between different samples doped at different impurity levels. Cross sample comparisons of this type frequently are clouded by experimental scatter between specimens due to microstructural differences (i.e., grain size, density) which are difficult to take into account in an accurate and reliable manner.

Creep experiments on iron-doped Al_2O_3 were conducted at two grain sizes: 28 and 10 μm . As in the Cr-doped material, discontinuous growth at elevated temperatures prevented the production of larger grain size

specimens to extend the grain size range of the creep studies. The microstructures of the iron-doped Al_2O_3 , although much coarser than the Cr-doped material, were similar in that the grains were slightly elongated and of irregular shape.

Stress change experiments were conducted on both materials. For stresses between 50 and 500 Kgm/cm^2 the stress exponent was 1.3 at 1400 and 1500°C for the 28 μm material. Similar experiments on the 10 μm material at 1500°C, but at lower stress levels (i.e., 10-150 Kgm/cm^2) yielded viscous creep behavior (only case observed in all of the alumina creep experiments in the present studies). Whether or not this viscous behavior was due to the smaller grain size or lower stress levels or both is not known at this time.

The activation energy for creep as determined by the Dorn method between 1400 and 1525°C was 148 Kcal/mole and independent of oxygen partial pressure between 1 and 10^{-5} atm.

Comparing creep rates for comparable stresses (50 Kgm/cm^2) and temperatures, the creep rate-grain size dependence as determined from data at the two grain size levels was consistent with $\dot{\epsilon} \propto (\text{GS})^{-2}$.

Extensive experiments were conducted on the effect of oxygen partial pressure ($1-10^{-10}$ atm) on the steady state creep rate of iron-doped Al_2O_3 . As expected, the creep rate increased significantly as the oxygen partial pressure decreased. This behavior was opposite to that found in iron-doped MgO . It is noted that high P_{O_2} values give rise to lattice defects (i.e., Fe^{+3}) in iron-doped MgO while low P_{O_2} values create lattice defects (i.e., Fe^{+2}) in iron-doped Al_2O_3 .

At low partial pressures ($P_{\text{O}_2} \sim 10^{-6}-10^{-7}$ atm) the creep rate

became insensitive to further reductions in oxygen pressure. This behavior was attributed to the precipitation of an iron rich phase. On the high pressure end (i.e., $P_{O_2} > 10^{-2}$ atm) the creep rate was also somewhat insensitive to changes in oxygen partial pressure. It is believed that in this regime most of the iron is in the trivalent state and background impurities in the Al_2O_3 are either in excess or approximately the same as the concentration of divalent iron. This effect was confirmed in the 0.2% Fe Samples in that the creep rate- P_{O_2} insensitive region extended to much lower pressures ($\sim 10^{-7}$ atm); i.e., lower P_{O_2} had to be reached before enough divalent iron was formed to overshadow the background impurities. It is noted in passing that the presence of background impurities, causing the nearly pressure independent creep rate at high P_{O_2} in Fe-doped Al_2O_3 , probably is responsible for the confusion on the effect of slightly soluble Mg^{+2} on the creep rate of Al_2O_3 .^(13,14)

For the 1 cation % specimens the maximum sensitivity in the creep rate occurred in the oxygen partial pressure range between $\sim 10^{-2}$ and 10^{-6} - 10^{-7} atm. In this regime the creep rate was described by $\dot{\epsilon} \propto P_{O_2}^{-m}$ with $m = 0.18 \pm 0.01$. Decreasing P_{O_2} from 1 to 10^{-6} atm increased the creep rate nearly an order of magnitude between 1425 and 1525°C. In addition, for all $P_{O_2} \geq 10^{-6}$ atm the creep rate- P_{O_2} effects were completely reproducible and reversible. These experiments have established without question that increasing amounts of a divalent impurity (Fe^{+2} in this study) enhance the creep rate of polycrystalline Al_2O_3 .

In summary, several features of the creep of polycrystalline Fe-doped Al_2O_3 have been determined in this study:

- 1) Relatively large grained material (28 μm) exhibits slightly non-viscous stress-strain behavior (i.e., $N \sim 1.3$) when tested between 50 and 500 kg/cm^2 .
- 2) Smaller grain size material (10 μm) will deform viscously at stresses below 150 kg/cm^2 .
- 3) Decreases in oxygen partial pressure (i.e., $1\text{-}10^{-6}$ atm) will increase the creep rate of 1 cation % Fe-doped Al_2O_3 by nearly an order of magnitude at 1425-1525°C.
- 4) The activation energy for creep between 1400 and 1500°C is 148 Kcal/mole and is independent of oxygen partial pressure down to 10^{-5} atm.

3. Titanium-doped Al_2O_3

In view of the effect of Fe^{+2} on the creep rate of polycrystalline Al_2O_3 , it was natural to speculate on the possible effect of a tetravalent (+4) cation impurity. This idea led to the study of the effect of Ti (Ti^{+3} , Ti^{+4}) on the creep behavior of polycrystalline Al_2O_3 .

In this section creep experiments on hot pressed Al_2O_3 (28 and 42 μm) doped with 1/2 cation % Ti will be discussed briefly.

The strain rate-stress dependence, as was also the case in Cr and Fe doped material, again was found to be slightly non-viscous with stress exponents ranging between 1.1 and 1.3 for stresses between 10 and 200 kg/cm^2 . As in the case of iron-doped Al_2O_3 , the creep rate of Ti-doped material was dependent on the oxygen partial pressure. Only in this case the opposite effect was noted (i.e., enhanced creep rates in high oxygen partial pressures). The creep rate- P_{O_2} dependence was $\dot{\epsilon} \propto P_{\text{O}_2}^{0.10}$ and similar in nature to that observed in iron-doped MgO . The effect of P_{O_2} on the creep rate was not entirely reversible,

particularly in the high P_{O_2} region where the precipitation of a Ti-rich second phase was a factor. However, in these studies the experiments were started by equilibrating the specimens in very reducing atmospheres ($\sim 10^{-9}$ atm) prior to increasing the oxygen partial pressure. Performing the experiments in this manner assured that all of the impurity (primarily in the +3 valence) was in solid solution. Then as P_{O_2} increased, some of the Ti^{+3} oxidized to Ti^{+4} and the creep rate increased. Precipitation at higher P_{O_2} values (~ 1 atm) would not change the overall effect but just change the creep rate- P_{O_2} dependence.

Activation energies which were determined by the Dorn method between 1425 and 1525°C were 145 kcal/mole at $P_{O_2} = 10^{-9}$ and ~ 185 kcal/mole at $P_{O_2} = 1$ atm. The activation energy in reducing atmospheres was remarkably similar to that observed in Fe-doped Al_2O_3 . The anomalously high value at $P_{O_2} = 1$ atm was due probably to precipitation at the lower temperatures causing an excessive drop in the creep rate. Considerable scatter was present in these data.

In spite of the problems encountered with precipitation at higher oxygen partial pressures, these experiments definitely established that a +4 valence cation impurity in solid solution enhances the creep rate of polycrystalline Al_2O_3 .

With respect to the effect of grain size on the creep of Ti-doped Al_2O_3 , it can be concluded that the creep rate increases with decreasing grain size. However, the range of grain sizes (i.e., 28-42 μm) was too small to determine an accurate grain size dependence.

In summary, the results of the studies on the creep of polycrystalline Ti-doped Al_2O_3 reveal that:

- 1) Slightly non-viscous stress exponents (1.1-1.3) characterize the stress-strain rate behavior.
- 2) Increases in the oxygen partial pressure (10^{-10} to 1 atm) increase the creep rate nearly an order of magnitude according to the relation, $\dot{\epsilon} \propto P_{O_2}^{0.10}$. The effects of P_{O_2} on the creep rate were not entirely reversible particularly in the high P_{O_2} region.
- 3) An activation energy of 145 kcal/mole was obtained in reducing atmospheres ($P_{O_2} \sim 10^{-9}$ atm).
- 4) The irreversibility of the P_{O_2} dependence, the high activation energy in oxidizing atmospheres, and microscopic and X-ray evidence suggested that precipitation was an important factor in the high oxygen partial pressure experiments (i.e., as most of the Ti approached the +4 valence state).

4. Discussion

A major finding of the present study on the effects of transition metal impurities and oxygen partial pressure changes on the steady state creep of polycrystalline Al_2O_3 is that both a divalent (Fe^{+2}) and a tetravalent (i.e., Ti^{+4}) impurity in solid solution enhance the creep rate. Since the introduction of either Ti^{+4} or Fe^{+2} into the Al_2O_3 structure must necessarily lead to the creation of lattice defects, it is then possible to postulate several diffusion mechanisms which might be responsible for the creep of transition metal-doped Al_2O_3 .

For the purpose of argument, the creep data for all three dopants (i.e., Cr, Fe, and Ti) will be analyzed in terms of the Nabarro-Herring

volume diffusion creep mechanism. All of the creep rate-grain size data were consistent with a viscous mechanism and the data for the Cr and Fe doped aluminas supported the Nabarro Herring mechanism (i.e., $\dot{\epsilon} \propto (GS)^{-2}$). Although the slightly non-viscous stress exponents ($N = 1.1-1.3$) which were observed frequently in this study, are not entirely consistent with a diffusional creep mechanism, viscous behavior was found to be predominant at low stresses in fine grained ($\sim 10 \mu\text{m}$) iron-doped Al_2O_3 . Thus it is likely that, at least in the low stress regime, diffusional creep plays an important role in the creep of Al_2O_3 doped with transition metal impurities. In any case, however, it is clear that diffusion plays a significant role in the creep process, whether or not the mechanism is strictly viscous.

Using the Nabarro-Herring relation diffusion constants were calculated from the creep data taken at low stresses (i.e., $\sigma = 50 \text{ kg/cm}^2$). The results of the calculations were very interesting. In the case of Cr-doped Al_2O_3 calculated diffusivities agreed remarkably well with aluminum ion tracer values, not only with respect to absolute magnitude but also in their temperature dependence (i.e., activation energy = 115 kcal/mole). The diffusivities calculated from the creep data of Fe and Ti doped Al_2O_3 in all cases (i.e., high and low P_{O_2}) were higher than the aluminum and oxygen tracer values. At high oxygen partial pressure, when most of the iron is in the +3 valence state, the calculated diffusivities from the creep data on iron-doped Al_2O_3 approached the aluminum tracer values. Conversely, diffusivities calculated from the creep data on Ti-doped Al_2O_3 approached the aluminum tracer value as the oxygen partial pressure decreased (i.e., reduction

of Ti^{+4} to Ti^{+3}). Thus, in the limit where all the impurities are in the +3 valence state, the creep rates of Cr, Fe, and Ti doped polycrystalline Al_2O_3 of the same grain size would be nearly identical.

With these results in mind we can now speculate on the defect mechanism responsible for the observed creep behavior. The most consistent explanation for these results is to assume that Frenkel defects on the cation sublattice are predominant in pure Al_2O_3 . Doping Al_2O_3 with Fe^{+2} (low P_{O_2}) creates aluminum ion interstitials which contribute to enhanced cation diffusion, while doping with Ti^{+4} (high P_{O_2}) creates aluminum ion vacancies which also enhance cation diffusion. Further support for this model comes from the nearly identical activation energies for the creep of iron and titanium doped Al_2O_3 (i.e., 148 and 145 kcal/mole, respectively) suggesting that the diffusion mechanisms in the two materials are similar (i.e., vacancy exchange and interstitialcy). The increase in activation energy for the creep of iron and titanium doped Al_2O_3 over that of chromium doped Al_2O_3 (115 kcal/mole) can be readily explained on the basis of endothermic defect creation reactions which are based on a Frenkel model for the defect structure of Al_2O_3 and involve changing the oxidation states of iron ($\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$) and titanium ($\text{Ti}^{+3} \rightarrow \text{Ti}^{+4}$).

Thus, as was the case in iron-doped MgO, the creep behavior of polycrystalline Al_2O_3 doped with transition metal impurities sheds additional light not only on the mechanism of creep but also on the nature of the defect structure of Al_2O_3 . It is noted that these foregoing conclusions based on a Frenkel defect are supported by recent electrical conductivity measurements on impurity-doped Al_2O_3 by Brook, Yee, and Kroger.⁽¹⁵⁾

It has, therefore, been concluded that the creep of Cr, Fe, and Ti-doped Al_2O_3 is most likely controlled by the lattice diffusion of aluminum ions which can diffuse in the structure either by a vacancy exchange or an interstitialcy-type mechanism, depending on the nature of the impurities which are present. This conclusion requires rapid oxygen transport along grain boundaries. Whether or not oxygen grain boundary transport can ever be rate controlling is presently an open question. Additional and more extensive grain size-creep rate data are needed to determine the relative roles of cation lattice and anion boundary diffusion in the creep of impurity doped Al_2O_3 .

Finally, transition metal impurities in Al_2O_3 have another effect which is, perhaps, even more significant in its relation to the production of a creep resistant material. The presence of either iron or titanium promoted the formation of relatively larger grain size material (i.e., $\geq 10 \mu\text{m}$) during hot pressing than that found in the Cr-doped Al_2O_3 (i.e., 3-6 μm). Since the creep rate is proportional to some reciprocal power of the grain size, a greater creep resistance was found in general at a given temperature for coarse grained iron and titanium (low P_{O_2}) doped Al_2O_3 when compared to the creep behavior of fine grained (i.e., 3 μm) Cr-doped Al_2O_3 . The larger grain sizes of the former materials exerted a greater influence on the creep rate than the enhancement of the diffusivity by the impurity additions. Thus it is clear, as was also the case in iron-doped MgO , that impurities play roles in the creep behavior of a polycrystalline ceramic other than those related to changes in defect chemistry and hence enhanced diffusive properties. They also play a significant role in the control of grain size, which is perhaps the most important variable in the high temperature creep

of polycrystalline ceramics.

Iron and titanium additions appear to enhance grain growth in polycrystalline Al_2O_3 while iron additions in MgO inhibit grain growth. These factors are very important when the ultimate high temperature creep behavior of these impure polycrystalline ceramics is considered.

C. Analysis of Transient Creep in Polycrystalline, Iron-doped MgO

Transient behavior has been observed frequently in the creep of polycrystalline MgO . Creep rates which continuously decrease for long periods of time have been reported in several studies particularly at low temperatures (1000-1200°C) and for shorter periods at temperatures over 1200°C.

Due to the availability of steady state creep theories and to the relative ease of data analysis, which is required in the steady state regime, previous investigations on the creep of polycrystalline ceramics have focused primarily on steady state creep behavior and have to a large degree ignored transient effects. In fact, it is not uncommon to see transient creep data interpreted with steady state theories.

Since transient behavior becomes a predominant feature of the creep of polycrystalline MgO and other ceramics, for that matter (e.g., Al_2O_3 , BeO), as the temperature is lowered it is essential to understand its origin and the variables (i.e., temperature, grain size, impurities, and atmosphere) which affect it. From an engineering standpoint, an understanding of the transient creep behavior of ceramics is perhaps more crucial than that of the steady state regime, since most loading applications probably involve the primary or transient stage of creep,

particularly in short time loading situations.

With the foregoing in mind, studies on the transient or primary creep of iron-doped, polycrystalline MgO were initiated. A second objective to these studies was to see if a unified creep theory could be found for the creep of iron-doped, polycrystalline MgO, i.e., Can steady state behavior be predicted from transient creep data and vice versa? The iron-doped MgO system is ideally suited for this purpose since steady state creep is well documented and characterized.

1. Review of Experimental Results

Most of the effort to date in this contract period on studies of the transient creep properties of iron-doped MgO has focused primarily on a theoretical analysis of the data which have been accumulated previously. New experiments, which have been designed in light of this analysis, are presently underway and will be described in the proposal for the next contract period.

A paper on the transient creep of iron-doped, polycrystalline MgO has been written and accepted for publication in the Journal of the American Ceramic Society.⁽³⁾ In this report a brief summary will be given on the present state of understanding.

All of the creep data on iron-doped MgO can be described by the following equation in which it is assumed that the total strain rate, $\dot{\epsilon}$, is the sum of the transient strain ($\dot{\epsilon}_t$) and the steady state strain ($\dot{\epsilon}_{ss}$) rates, i.e.,

$$\dot{\epsilon} = \dot{\epsilon}_t + \dot{\epsilon}_{ss} \quad (1)$$

The transient strain rate ($\dot{\epsilon}_t$) at any time t can be determined by subtracting the long term steady state creep rate ($\dot{\epsilon}_{ss}$) from the total ($\dot{\epsilon}$). In iron-doped, polycrystalline MgO $\dot{\epsilon}_{ss}$ is given either by the Coble or Nabarro-Herring diffusional creep equations, depending on the grain size and temperature.

The foregoing procedure for the determination of $\dot{\epsilon}_t$ must be modified for creep tests in which grain growth is occurring simultaneously. In this case $\dot{\epsilon}_{ss}$ is no longer constant but also decays slowly with time because of its reciprocal grain size dependence (i.e., $\dot{\epsilon}_{ss} \propto (GS)^{-m}$, $m = 2$ or 3). Using the procedure of Terwilliger et al.⁽¹⁰⁾ which was developed under this contract, the decay of $\dot{\epsilon}_{ss}$ with time due to grain growth can be taken into account quantitatively. Once this is done, the true transient strain rate-time behavior can be obtained from equation (1).

Transient strain rates, obtained by the foregoing procedures, have been found to decay exponentially with time according to the relation

$$\dot{\epsilon}_t = \dot{\epsilon}_i e^{-t/\tau} \quad (2)$$

$\dot{\epsilon}_i$ is the initial transient strain rate which has been found to be linear with stress (up to approximately 300 kgm/cm^2) and τ is a characteristic relaxation time which describes the rate of decay of the transient strain rate. τ is thermally activated and depends on temperature as

$$\frac{1}{\tau} = \frac{1}{\tau_0} e^{-\Delta H/RT} \quad (3)$$

τ_0' is a constant and ΔH is the activation energy associated with the decay of the transient strain rate. It is clear that the rate of exponential decay of transient creep in iron-doped MgO is very sensitive to temperature (~ 75 minutes at 1400°C and ~ 8 hours at 1100°C). Thus at low temperatures transient creep behavior is very pronounced and extends to long periods of time.

Finally, preliminary experiments indicate that most of the transient creep which is observed is permanent and non-recoverable in nature.

2. Theoretical Analysis

Several mechanisms come to mind which can give rise to an exponential creep law (i.e., equation (2)). These include:

- 1) exhaustion and work hardening dislocation creep theories,
- 2) elastic accommodation of grain boundary sliding, and
- 3) transient diffusional creep.

Most dislocation theories predict a non-viscous stress-strain rate dependence, which is inconsistent with the observed viscous nature of both the transient and steady state creep properties of iron-doped, polycrystalline MgO.

The mechanism of viscous grain boundary sliding accommodated by elastic deformation was elucidated in the classical papers of Ke⁽¹⁶⁻¹⁸⁾ and was most recently analyzed by Ashby and Raj.⁽¹⁹⁾ For this mechanism, the elastic stresses at grain boundary intersections are capable of reversing the sliding after the load is removed so that the creep strain is slowly recovered. During the transient period the strain rate due to sliding slows down with time and finally goes to zero when the

elastic back stresses at the boundary intersections equal the applied shear stresses on the boundaries. If the sliding process is viscous, the decay of the transient creep rate will follow equation (2).

Thus all the strain for this process should be recoverable, and the relaxation time for recovery should be the same as that for the transient after loading. Finally, this mechanism is restricted to small strain ($\leq 10^{-5}$) situations.

While this process might be responsible for some of the observed transient behavior, it is not believed to be the major contributor in iron-doped, polycrystalline MgO for the following reasons:

- 1) Most of the transient strain is non-recoverable.
- 2) The transient strains ($> 10^{-4}$) are considerably larger than those normally found in anelastic creep experiments on metals and ceramics in which the (small) transient strain is completely recoverable.
- 3) The relaxation times are considerably longer than those observed in anelastic recovery.

However, to properly determine the role of anelastic grain boundary sliding, additional experiments to determine the amount of the transient which is recoverable are underway.

In view of the foregoing it is believed that the process which is responsible for the major portion of the transient is that which is intrinsic to diffusional creep itself.

Diffusional theories of creep were developed originally by assuming steady state conditions. Thus they represent solutions to the steady state diffusion equation:

$$\nabla^2 \mu = 0 \quad (4)$$

in which $\nabla^2 \mu$ is the Laplacian of the chemical potential μ . Herring⁽²⁰⁾ and later Lifshitz⁽²¹⁾ indicated that immediately after stressing vacancy diffusion would be very rapid in the vicinity of grain boundary intersections, because of relatively small diffusion paths. Therefore, a redistribution of stresses must occur so that the flux (i.e., vacancies) is uniform over all the faces of the grains. This redistribution results in a transient creep strain. During this period, the flux is described by the non-steady state form of Fick's second law of diffusion:

$$\nabla^2 \mu = \frac{1}{D} \frac{\partial \mu}{\partial t} \quad (5)$$

Equation (5) was solved by Lifshitz and Shikin⁽²²⁾ for the case of an array of idealized infinitely long square grains. The solution was found to have two limiting conditions depending on the importance of elastic strains. In both limits the transient strain followed an exponential decay law (i.e., equation (2)). The appropriate limit under which the transient is operating depends on the value of a dimensionless parameter λ which is defined as

$$\lambda = \frac{\Omega C_v E}{kT} \quad (6)$$

Ω is the molecular volume (1.86×10^{-23} cc in MgO), C_v is the site fraction vacancies, E is the elastic modulus, and kT has its usual meaning.

For $\lambda \gg 1$ elastic strains are not important and the relaxation time τ_0 for the transient is defined by equation (7):

$$\frac{1}{\tau_0} = C \frac{D_v}{(GS)^2} \quad (7)$$

D_v is the vacancy (defect) diffusion coefficient, (GS) is the grain size and C is a geometrical constant.

For $\lambda \ll 1$ elastic displacements are important and the relaxation time τ is defined as:

$$\frac{1}{\tau} = \frac{\lambda}{\tau_0} = C \frac{D_v C_v \Omega E}{(GS)^2 kT} \quad (8)$$

Equation (8) is very interesting in that the coefficient of the modulus (i.e., $C \frac{D_v C_v \Omega}{(GS)^2 kT}$) is identical to that of the stress in the Nabarro-Herring equation for steady state creep providing the constant C is chosen to be 13.3. Thus it appears that the rate of steady state creep and the relaxation time for the diffusional transient are intimately related.

In order to determine the appropriate limiting condition for the transient data, which are summarized in Table 1, the parameter λ was calculated for each specimen (Refer to Tables 2 and 3). In all cases, except one, (i.e., sample 5-A-4 at 1350°C), λ was less than unity.

In these calculations a high temperature modulus for polycrystalline $MgO^{(23)}$ was used (i.e., $E = (2.2-2.1) \cdot 10^{12}$ dynes/cm² at 1200-1400°C).

The vacancy (i.e., cation) concentration was assumed to be one-half of the total iron content (assuming all of the iron to be in the trivalent state).

For the purposes of calculation all of the transient data will be treated under the limit in which $\lambda < 1$, (i.e., elastic strains important). This limit is probably valid even for the 5% Fe_2O_3 specimen (5-A-4) for which the calculated λ is greater

Table 1. Transient Data - Doped MgO

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

Specimen	Grain Size (μm)	wt. % Fe_2O_3	σ (kgm/cm ²)	$\sigma - \sigma_L$ (kgm/cm ²)	τ (hr)	$1/\tau$ (hr ⁻¹)	$\dot{\epsilon}_i$ (10 ⁻³ hr ⁻¹)
<u>1100°C</u>							
P 37T1	~ 4	0.94	126	---	5.16*	0.19	0.54
<u>1134°C</u>							
P 23T1	~ 4	0.14	137	---	4.40*	0.23	0.87
<u>1200°C</u>							
P 30T2	4-6	0.10	178	---	1.77	0.57	3.00
P 37T2	5-9	0.94	137	---	1.56	0.64	1.25
<u>1300°C</u>							
P 30T5	5-15	0.10	228	199	0.57	1.75	5.20
P 30T8	5-15	0.10	294	271	0.46	2.19	5.50
P 30T6	5-15	0.10	473	436	0.48	2.08	10.15
P 28T6	5-12	0.48	214	187	0.70	1.44	3.90
P 28T5	5-12	0.48	291	262	0.70	1.44	5.20
P 28T8	5-12	0.48	301	278	0.55	2.31	6.60
P 28T3	5-12	0.48	445	420	0.59	1.68	14.80
<u>1350°C</u>							
5.0-A-4	12	5.0	124	102	0.39	2.56	---
<u>1400°C</u>							
P 30T4**	~ 13	0.10	169	---	0.37	2.7	---
1.0-A-4	14	1.0	209	---	0.38*	2.63	---

* No grain growth correction was necessary.

** A grain growth correction was made using the Nabarro-Herring equation. All other grain growth corrections were performed with the Coble Equation.

Table 2. Correlation Between Transient and Steady State Creep
Nabarro-Herring Model

Specimen	wt. % Fe_2O_3	Grain Size (μm)	λ	$\frac{\text{GS}^2}{\tau} (\frac{\mu\text{m}^2}{\text{hr.}})^{**}$	$D^{\lambda} (\text{cm}^2/\text{hr})$	
					Transient	Steady State
P 30T4	0.10	$\sim 13^*$	<u>1400°C</u> 0.044	1030	4.6×10^{-9}	$1.3 \times 10^{-8} \text{***}$
1-A-4	1.0	14	0.443	1160	5.2×10^{-9}	5.3×10^{-9}
5-A-4	5.0	12	<u>1350°C</u> 2.26	830	3.6×10^{-9}	2.4×10^{-8}

* Average grain size (estimated) during the transient period ($\pm 1 \mu\text{m}$).

** Grain sizes were multiplied by 1.5 in the calculation of diffusion constants.

*** Tremper⁽¹⁾ recently obtained a steady state value of $5.6 \times 10^{-9} \text{ cm}^2/\text{hr}$ for D^{λ} in 0.10% doped MgO .

Table 3. Correlation Between Transient and Steady State Creep
Coble Model

Specimen	wt. % Fe ₂ O ₃	Grain Size* (μm)	λ	$\frac{GS^3}{\tau}$ ($\frac{\mu m^3}{hr.}$) **	δD^b	
					Transient	Steady State
			<u>1200°C</u>			
P30T2	0.10	~ 5	0.050	241	2.4×10^{-14}	5.3×10^{-14}
P37T2	0.94	~ 6	0.473	465	8.1×10^{-14}	6.4×10^{-13}
			<u>1300°C</u>			
P30T5	0.10	~ 5	0.047	379	8.4×10^{-14}	8.8×10^{-13}
P30T8	0.10	~ 5	0.047	924	1.1×10^{-13}	4.1×10^{-13}
P30T6	0.10	~ 5	0.047	876	9.9×10^{-14}	3.5×10^{-13}
P28T6	0.48	~ 5	0.226	606	7.2×10^{-14}	7.2×10^{-13}
P28T5	0.48	~ 5	0.226	606	7.2×10^{-14}	6.6×10^{-13}
P28T8	0.48	~ 5	0.226	970	1.2×10^{-13}	8.8×10^{-13}
P28T3	0.48	~ 5	0.226	708	8.4×10^{-14}	1.7×10^{-12}

* Average grain size (estimated) during the transient period ($\pm 1 \mu m$)

** Grain sizes were multiplied by 1.5 in the calculation of diffusion constants

than unity. The steady state creep rate of 5% specimens is approximately 2-8 times faster than those doped at the 0.10% level instead of the expected factor of 50 times faster.⁽¹⁾ Hence the cation diffusivity is not proportional to the iron content and the calculated λ factors are probably overestimated.

It is noted that both equations (7) and (8) are based on a volume diffusion mechanism. Although Lifshitz and Shikin did not explicitly treat the case for grain boundary diffusion control, we can easily infer that the expression for $1/\tau$ in this case for $\lambda \ll 1$ would be

$$\frac{1}{\tau} = \frac{47 (\delta D^b) \Omega E}{(GS)^3 kT} \quad (9)$$

δD^b is the product of the grain boundary width and diffusivity. Again a direct relationship should exist between the value of τ and the magnitude of the steady state creep rate.

In order to test the usefulness of these theories on the present transient data, it will be assumed, for the purpose of calculation, that the mechanism of creep in the steady state regime (i.e., (GS) dependence) is the same as that in the transient (i.e., equation for $1/\tau$). This assumption must await further experimentation for verification. Therefore, for the large grained specimens (i.e., P30T4, 1-A-4, 5-A-4--See Table 2) at $T > 1300^\circ\text{C}$ for which evidence is presently available for a Nabarro-Herring mechanism in the steady state,^(1,10) equation (8) was used to estimate (cation) lattice diffusivities, $D^L (= C_V D_V)$. These estimates are compared in Table 2 with values calculated from the steady state creep rates using the Nabarro-Herring

relation. The two sets of values agree to within a factor of seven. This agreement is remarkably good in view of the approximations (i.e., (GS), E) and in one case a correction for simultaneous grain growth. The data in Table 2 indicate tentatively that the transients decay slightly faster as the iron content is increased. Similar effects have been found for the effect of iron content on the steady state creep rates. However, more transient data are needed to determine the effect of iron dopant level on the relaxation time. It is also noted in passing that the calculated diffusivities at 1400°C for the 0.10% specimens are in good agreement with the magnesium tracer value of $5.6 \times 10^{-9} \text{ cm}^2/\text{hr}$ (extrapolated).⁽¹¹⁾

In a similar fashion the transient data at $T \leq 1300^\circ\text{C}$ for the fine grained specimens ($\sim 5\text{-}6 \mu\text{m}$) were analyzed with equation (9). In this case the steady state regime is characterized by the Coble grain boundary diffusion equation.⁽¹⁰⁾ In Table 3 values of δD^b which were calculated from the transient data using equation (9) and from the steady state data using the Coble diffusional creep relation are compared. Again the agreement is relatively good (an order of magnitude or less) when one considers the assumptions and that grain growth corrections were made on all specimens.

The effect of the iron concentration on increasing the value of δD^b is quite pronounced at 1200°C and essentially non-existent for the data at 1300°C. However, more data are needed before a definite conclusion can be drawn on the effect of the dopant on the transient.

3. Summary

On the basis of the transient data presently available we can conclude that the transient creep behavior of polycrystalline iron-doped MgO is consistent with a mechanism based on a diffusional transient. The stress, temperature, and time dependencies of the transient are all proper for this mechanism. In addition, it seems possible that transient behavior (i.e., rate of relaxation) can be predicted from steady state creep rates and vice versa.

Additional and more extensive data are needed on the effects of iron concentration, oxygen partial pressure, and grain size on the relaxation time and initial strain rate for the transient. If the proposed theory is valid, grain size should have a very pronounced effect on the transient behavior due to its strong dependence.

Finally, the combined analysis of the "true transient" and steady state creep behavior gives further support to the thesis that the steady state creep at 1200-1300°C of fine grained (5-15 μm) iron-doped MgO occurs primarily by a grain boundary diffusion mechanism.

D. Theoretical Analysis of Mass Transport and Diffusional Creep in Ionic Solids

In most of the creep studies on polycrystalline ceramics (MgO, Al_2O_3 , BeO) in which Nabarro-Herring creep has been reported diffusion constants, which are calculated from the creep data, are frequently equal to or higher than reported cation tracer values and well in excess of anion diffusivities. In addition, impurity additions and related atmosphere effects (e.g., changes in oxygen partial pressure) which create cation lattice defects and hence enhance cation diffusivities

have also given rise to enhanced creep rates.

Possible explanations for anomalously high creep rates include

- 1) Treatment of non-viscous creep data with viscous diffusional creep theories,
- 2) Treatment of transient data with steady state theories.

However, even when viscous, steady state conditions are insured, calculated diffusivities and impurity-atmosphere effects support cation diffusion controlled kinetics in polycrystalline, doped MgO and Al_2O_3 .

Thus it becomes necessary to conclude that some rapid transport process for the "slower" moving (i.e., in the lattice) anion is available. Evidence is present that the mobility of anions in grain boundary regions is high in polycrystalline materials like NaCl, (24,25) Al_2O_3 , (26-28) and MgO. (29) With this in mind, it is frequently concluded that the creep is cation diffusion controlled with a rapid transport of anions along grain boundaries.

Little quantitative diffusion data have been available to test this hypothesis. Also, a generalized mass transport equation for diffusion in pure and doped ionic solids which takes into account parallel diffusion paths (i.e., lattice, grain boundaries, dislocations, etc.) has not been available.

During the present contract period a generalized mass transport equation for ionic solids, which takes into account parallel diffusion paths for anions and cations, was developed using the methods of Readey, (30,31) Ruoff, (32) and Howard and Lidiard. (33) This theory was applied to the creep measurements on iron-doped, polycrystalline

MgO described earlier in this report. Iron-doped MgO was used as a test system since most of the pertinent diffusion constants are known and, depending on the grain size, viscous Nabarro-Herring and Coble creep have been documented reasonably well. Finally, the role of anion grain boundary diffusion in the creep of polycrystalline Al_2O_3 , "pure" and doped with transition metal impurities (Ti, Fe, and Cr) was analyzed.

At this point some comment on the philosophy of the analysis is necessary. It is frequently asserted that predominant anion transport in grain boundary regions and cation transport in the lattice imply a separation of charges in the solid and hence a violation of local electrical neutrality. The fact that anion and cation fluxes may not be the same in any particular parallel diffusion path does not necessarily imply a separation of charge. The steady state fluxes of cations and anions across any particular volume element (i.e., lattice or grain boundary region) are, of course, related in part to the local concentrations of charged lattice defects which, in turn, are governed by conditions of local electrical neutrality. However, these concentrations are not affected by the steady state ion fluxes but are functions only of temperature, pressure, and composition. On the other hand, when all parallel diffusion paths between points of mass annihilation (compression boundaries) and creation (tension boundaries) are considered, then a zero net current (total) flow must, of course, be present to maintain the structure. This requirement, however, does not imply a zero net current flow along each parallel diffusive path, and, thus, allows for the possibility of unequal cation and anion fluxes over any particular path. The general mass transport theory was derived

on this basis.

The theory which was developed and applied to the diffusional creep of polycrystalline MgO and Al_2O_3 (pure and doped with transition metal impurities) gives a clear indication of the role of grain size and cation impurities (in solid solution) on the relative contributions of lattice and grain boundary diffusion of different ionic species. Depending on the temperature, grain size, impurity level, and oxygen partial pressure, several limiting conditions were found to be possible for the diffusional creep of ionic solids:

Condition I: At very small grain sizes and reasonably small cation lattice diffusivities the creep rate will be controlled by the slower moving ion in the grain boundaries (i.e., Coble Creep).

Condition II: For intermediate grain sizes and cation lattice diffusivities the creep rate will be controlled by cation lattice diffusion providing anion transport is significantly faster in the grain boundaries than in the lattice (i.e., cation controlled Nabarro-Herring creep).

Condition III: For an appropriate combination of large grain sizes and high cation lattice diffusivities the creep rate will be controlled by anion boundary diffusion (i.e., anion controlled Coble creep).

Well defined examples of Conditions I and II have been observed in the creep studies under this contract on iron-doped MgO . Tentative evidence is present for Condition III but more extensive grain size data are needed.

Most of the current creep studies at low stresses on transition metal doped Al_2O_3 fall within Condition II. However, more extensive

grain size-creep rate data are needed to properly evaluate the contributions of cation lattice and anion boundary diffusion in controlling the overall creep rate.

The theory which has been developed provides an explanation for much of the data in the literature in which creep rates correspond to cation lattice mobilities. It was concluded that in the creep of polycrystalline ceramics anion transport in the boundaries is rapid and can, under some circumstances, be rate controlling.

E. Thermogravimetric Studies on Fe- and Ti-Doped Al_2O_3

A Cahn microbalance was used in an exploratory thermogravimetric study on iron (1-3 cation %) and titanium (1 cation %) doped polycrystalline Al_2O_3 at 1400-1525°C. The results which at this stage are only qualitative, are consistent with the effects of P_{O_2} on the steady state creep of these same materials. In all cases samples gained weight upon oxidation (i.e., $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$ and $\text{Ti}^{+3} \rightarrow \text{Ti}^{+4}$) and lost weight upon reduction. The thermogravimetric data were not entirely reversible due to the very small weight changes which were involved, fabrication problems encountered in the specimens due to second phase formation, and in some cases relatively slow equilibration kinetics. However, these experiments were useful in laying the basis for future experimental work.

In addition to the equilibrium studies (i.e., $\text{Fe}^{+2}/\text{Fe}^{+3}$ and $\text{Ti}^{+3}/\text{Ti}^{+4}$ ratios as a function of oxygen partial pressure), the rate of approach to equilibrium after a change in oxygen partial pressure was also measured in both systems. It is clear that the oxidation and reduction kinetics in these systems are diffusion controlled and

dependent upon the direction of the reaction. In the iron-doped specimens the rate of reduction was slower than the rate of oxidation. The converse was true in titanium-doped specimens. Activation energies for diffusion in the $\text{Ti-Al}_2\text{O}_3$ system were about 130-136 kcal/mole.

For future studies a more sensitive microbalance should be used because of the small weight changes involved and small dopant levels which must be used to avoid problems associated with second phase formation. Particular care also needs to be exercised in controlling more precisely the oxygen partial pressure.

F. Redesign of Hot Pressing Facility

Prior to the redesign of the hot pressing facility, it consisted primarily of a graphite die enclosed in a steel tank and heated resistively with a molybdenum coil. Due to the molybdenum heating element, the hot press had to be operated in a hydrogen atmosphere. This very reducing atmosphere caused considerable problems in the fabrication of iron-doped Al_2O_3 and MgO . Second phase (sometimes metallic) precipitates were found frequently in the hot pressed bodies. They could be successfully removed by high temperature annealing in Fe-doped MgO . However, in Fe-doped Al_2O_3 this was not possible and suitable specimens had to be fabricated in a hot process facility at another location.

The original design problems⁽³⁴⁾ encountered in inductively heated dies have now been overcome and a new press has been designed, constructed, and placed into operation. The present induction heated, vacuum hot press consists of a 5" diameter by 12" long mullite tube that forms the vacuum chamber. The vacuum chamber is mounted in an external, 10 ton loading press. Currently, the system is capable of

operating at temperatures of at least 1500°C, gas pressures of 10^{-2} torr, and sample pressures of 6300 psi across a 2" diameter specimen. Refer to Figures 1 and 2 for schematic drawings of the entire facility and the inside of the press.

The design of the hot press is based on the principle of hot forging, i.e., hot pressing without die wall constraint. As such, the graphite die employed in the press is thin (1/4" thick); the primary purpose of the die is to act as a susceptor for the magnetic field. Currently, graphite plungers are being used in the press with pyrolytic spacers (.005" Graphfoil) actually in contact with the sample. The pyrolytic spacers minimize graphite contamination of the sample and act as lubricating surfaces for the free expansion of the sample during the forging process.

The new hot pressing facility will now allow for the fabrication of pure and doped polycrystalline MgO and Al_2O_3 without the problems of second phase formation since the ambient atmosphere in the die is considerably less reducing than in the former hydrogen atmosphere press.

Figure 1. Hot Press Schematic

Figure 2. Inside of Hot Press

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VI. PRINCIPAL INVESTIGATOR

The principal investigator, Dr. Ronald S. Gordon, has devoted two months full time effort to this project in addition to considerable supervisory activities related to the project personnel. Since September 13, 1971 Dr. Gordon has been on a leave of absence working in the Lighting Research Laboratory of the General Electric Company. Dr. Gordon makes frequent telephone contacts with the project personnel and has visited the University once during his absence. Dr. Gordon's industrial research activities on the microstructural characterization of polycrystalline Al_2O_3 are very relevant to the research activities conducted under the present contract.

During Dr. Gordon's absence from the University Dr. Ivan Cutler, Professor of Ceramic Engineering in the Division of Materials Science and Engineering, is Acting Principal Investigator.

Dr. Cutler's extensive experience on the effects of impurities on sintering and grain growth processes in polycrystalline Al_2O_3 make him ideally suited for his advisory role on this contract.