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

Ronald S. Gordon
Principal Investigator

Technical Progress Report
December 19, 1971 to December 18, 1972

Atomic Energy Commission
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Division of Materials Science and Engineering
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Salt Lake City, Utah 84112

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December 18, 1972

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ABSTRACT

The research described in this report covers work on

- 1) transient creep in iron-doped, polycrystalline MgO,
- 2) an evaluation of oxygen grain boundary diffusion in the creep of iron-doped, polycrystalline MgO, and
- 3) the synthesis, hot pressing, and creep testing of high purity Al_2O_3 .

Some of the significant findings include the following:

- 1) Two relaxation times are required to properly describe the transient creep properties of iron-doped, polycrystalline MgO. Transient deformation, which is observed upon initial loading of a specimen, was found to be about 4-5 times that observed for subsequent loadings at the same stress.
- 2) Oxygen grain boundary diffusion (i.e., Coble creep) has been identified as the rate controlling mechanism in specimens doped with large amounts of iron (≥ 2.65 cation %) and tested in oxidizing atmospheres.
- 3) Slightly non-viscous creep (i.e., $\dot{\epsilon} \propto \sigma^N$; $N = 1.4$) has been observed in high purity, polycrystalline Al_2O_3 possessing an equiaxed microstructure.

This non-viscous creep behavior with an activation energy of ~ 130 kcal/mole appears to be characteristic of deformation in polycrystalline Al_2O_3 and unrelated to the morphology of the grain structure.

I. INTRODUCTION

The research activities under Contract AT(11-1)-1591 during the period December 19, 1971 to December 18, 1972 are described in this report and in the attached preprints^(1,2) and reprints.^(3,5)

Major effort was devoted to the following:

- 1) A paper has been published⁽³⁾ on preliminary transient creep studies. This year work has focused on equipment redesign and a more thorough evaluation of the parameters which are required to specify the transient creep properties of this system.
- 2) In view of the theoretical analysis⁽⁴⁾ which was conducted last year on mass transport, the creep properties of heavily doped (≥ 2.65 cation % Fe) MgO in oxidizing atmospheres were re-evaluated. It is now believed that oxygen grain boundary diffusion is the rate controlling process in this regime. This analysis is described in a preprint⁽¹⁷⁾ (presently under review by the American Ceramic Society).
- 3) Using high purity Al metal (99.999% Al) Al_2O_3 powders have been synthesized by autoclave and organometallic techniques.
- 4) Polycrystalline Al_2O_3 , possessing a normal, equiaxed microstructure, has been fabricated from high purity powders by vacuum hot pressing. Subsequent heat treatments have produced specimens, pure and doped with Cr and Fe, with a range of grain sizes without the complication of discontinuous (or exaggerated) grain growth.
- 5) Preliminary creep tests have been conducted on the new hot pressed material to evaluate the stress and temperature dependencies of the steady state creep rate. The creep properties of this high purity Al_2O_3 are characterized by slightly non-viscous stress exponents (i.e., $\dot{\epsilon} \propto \sigma^N$; $N \sim 1.4$) and an activation energy of ~ 130 kcal/mole.

Five papers have been published^(3,5) or accepted^(2,4,6) for publication this year:

- 1) "Grain Size Distributions and Grain Growth in MgO and MgO -Fe₂O₃ Solid Solutions," D. D. Marchant and R. S. Gordon, J. Am. Ceram. Soc. 55 (1) 19-24 (1972).
- 2) "Transient Creep in Fe-Doped Polycrystalline MgO," R. S. Gordon and G. R. Terwilliger, J. Am. Ceram. Soc. 55 (9) 450-455 (1972).
- 3) "Mass Transport in the Diffusional Creep of Ionic Solids," R. S. Gordon, J. Am. Ceram. Soc. 56 (3) (1973).
- 4) "Effect of O₂ Partial Pressure on the Creep of Polycrystalline Al₂O₃ Doped with Cr, Fe, or Ti," Glenn W. Hollenberg and R. S. Gordon, J. Am. Ceram. Soc. 56 (3) (1973).
- 5) "Origin of Anomalous High Activation Energies in the Sintering and Creep of Impure Refractory Oxides," G. W. Hollenberg and R. S. Gordon, J. Am. Ceram. Soc. 56 (1973).

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.

2.1 Transient Creep Studies in Iron-Doped, Polycrystalline MgO

Recently, Gordon and Terwilliger⁽³⁾ have reported that transient creep in fine-grained, iron-doped MgO follows an exponential time relation,

$$\dot{\epsilon}_t = \dot{\epsilon}_I e^{-t/\tau}.$$

In addition to the exponential time behavior for the strain rate, the pre-exponential ($\dot{\epsilon}_I$) appeared to have a stress dependence and the relaxation time, τ , appeared to be thermally activated. Several mechanisms for the transient were considered and it appeared as if a transient diffusional creep mechanism⁽³⁾ was the most promising. In their analysis, Gordon and Terwilliger suggested that the relaxation time for the transient might be described by the following relation:

$$\frac{1}{\tau} = \frac{A \Omega D E}{kT (GS)^2} \quad (1)$$

The similarity between Equation (1) and the Nabarro-Herring diffusional creep equation, i.e.

$$\dot{\epsilon} = \frac{13.3 \Omega D \sigma}{kT (GS)^2} \quad (2)$$

was recognized and it was suggested that there might be a reciprocal correlation between long-time, steady-state creep and the relaxation time which describes transient creep behavior.

In view of the foregoing, the objectives of the present study were threefold:

- 1) modification of the existing creep apparatus to allow careful measurement of transient and steady state creep behavior during either loading or unloading experiments;
- 2) development of a computational method for reliably separating transient from steady state creep data and for expressing the transient in exponential form;
- 3) examination of preliminary data in order to determine the reproducibility of the observed transients.

2.1.1 Experimental Apparatus

To adequately analyze transient creep which follows an exponential behavior, it is necessary to be able to resolve slopes from the measured deflection versus time curves at times which approach the moment of loading. In addition, it is important to be able to unload and reload the specimen without perturbing the test geometry (in the 4-point bend test, the centering and alignment of the load points should remain undisturbed).

Previous work, supported by this contract, has produced a creep-testing apparatus which will allow resolution of very small steady state strain rates ($\dot{\epsilon}_{ss} = 1-3 \times 10^{-9} \text{ sec}^{-1}$). However, due to the design of the apparatus, loading and unloading procedures perturb the measurement of creep rates for periods up to one hour after loading. In order to avoid disturbing the creep apparatus, a device was designed and constructed which allows the loading and unloading of test weights from a remote station. The remote-loading procedure avoids having to open the constant-temperature chamber which contains the measuring LVDT, thereby allowing proper resolution of the creep rate from very nearly the moment of loading.

2.1.2 Computational Methods

The analysis of Gordon and Terwilliger has suggested that the overall measured strain rate, $\dot{\epsilon}_m$, can be represented by

$$\dot{\epsilon}_m = \dot{\epsilon}_{ss} + \dot{\epsilon}_T \quad (3)$$

where $\dot{\epsilon}_{ss}$ is the steady state strain rate and $\dot{\epsilon}_T$ is the transient strain rate. Expressing Equation (3) in terms of the exponential for the transient yields

$$\dot{\epsilon}_m = \dot{\epsilon}_{ss} + \dot{\epsilon}_I e^{-t/\tau} \quad (4)$$

Evaluation of the pre-exponential $\dot{\epsilon}_I$ and the relaxation time τ can be accomplished by rewriting the above as a linear equation

$$\ln(\dot{\epsilon}_m - \dot{\epsilon}_{ss}) = \ln \dot{\epsilon}_I - t/\tau \quad (5)$$

and analyzing $\ln(\dot{\epsilon}_m - \dot{\epsilon}_{ss})$ versus time. However, the linear analysis method requires that a steady state be determined graphically, a process which is frequently difficult where the measured strain rate might be decaying very slowly and/or where small experimental fluctuations prevent a completely unambiguous determination of the steady state.

An alternative method of separating transient creep from steady state creep is to consider the non-linear strain rate equation (Equation (4)) and numerically calculate a set of parameters ($\dot{\epsilon}_{ss}$, $\dot{\epsilon}_I$, $1/\tau$) which minimize the error in describing the measured strain rates. By numerically calculating all three parameters, it is possible to avoid the overestimation of the steady state creep rate which might occur during periods where the creep rate was decaying very slowly (e.g., if $\tau \geq 2$ hours, the total time

for a single creep experiment might become very long before a correct steady state could be determined accurately).

A computer program which employs the Marquardt⁽⁷⁾ algorithm for the least-squares estimation of non-linear parameters was written in order to describe measured creep rates (Equation (4)). The function $\dot{\epsilon}(t, B)$ is linearized by a truncated Taylor's expansion and rewritten as a function of incremental parameter values. The B parameters represent terms like $\dot{\epsilon}_{ss}$, $\dot{\epsilon}_I$ and $1/\tau$.

$$\dot{\epsilon}(B + \Delta B) \approx \dot{\epsilon} B + \Delta B_1 \frac{\partial \dot{\epsilon}}{\partial B_1} + \dots + \Delta B_r \frac{\partial \dot{\epsilon}}{\partial B_r} \quad (6)$$

then

$$\dot{\epsilon}(B + \Delta B) = \Delta B_1 \frac{\partial \dot{\epsilon}}{\partial B_1} + \dots + \Delta B_r \frac{\partial \dot{\epsilon}}{\partial B_r} \quad (7)$$

from which the ΔB_i 's can be determined.

The least-squares solution is modified to force convergence in that the newly-determined set of ΔB_i are used to arrive at a new estimate of B

$$B_{k+1} = \hat{\Delta B}_k + B_k \quad (8)$$

The process of forcing convergence has the feature⁽⁸⁾ that the step ΔB gradually rotates (vectorally) toward the negative gradient direction to the sum of squares surface. The process is a simple one, requiring only that the diagonal elements of the sum of squares matrix be doubled.⁽⁷⁾

The program has been successfully used in order to describe measured creep data in terms of a five parameter expression of the form

$$\dot{\epsilon}_m = \dot{\epsilon}_{ss} + \dot{\epsilon}_1 e^{-t/\tau_1} + \dot{\epsilon}_2 e^{-t/\tau_2} \quad (9)$$

In addition to describing the strain rate behavior, the calculated parameters can be used in the integration of Equation (9) to yield the total strain (ϵ_{tot}) at any time.

$$\epsilon_{tot} = \dot{\epsilon}_{ss} t - \dot{\epsilon}_1 \tau_1 (e^{-t/\tau_1} - 1) - \dot{\epsilon}_2 \tau_2 (e^{-t/\tau_2} - 1) \quad (10)$$

Agreement between total measured strain and the calculated strain has been excellent.

2.1.3 Results

A graphical analysis of some preliminary transient data in iron-doped MgO (0.53 cation % Fe) indicated that the total decay of the strain rate could not properly be described by a single exponential (Equation (4)). A plot of $\log (\dot{\epsilon}_m - \dot{\epsilon}_{ss})$ versus time revealed that perhaps a second exponential might be used in order to describe the decay of the strain rate at times near the moment of loading. Data from several transient creep experiments are summarized in Table 1 in terms of the calculated parameters for a two-exponential relation describing the measured load-point deflection rates ($\dot{Y}$)

$$\dot{Y}_m = \dot{Y}_{ss} - \dot{Y}_1 e^{-t/\tau_1} + \dot{Y}_2 e^{-t/\tau_2} \quad (11)$$

In addition to the calculated parameters, Equation (11) was integrated to give calculated load-point deflections (Y) which could be compared directly with the measured strip-chart recorder trace.

Several interesting features of the transient can be seen in Table 1. Let us consider sample 1.0-4-4 which was loaded and unloaded three

Table 1.

SUMMARY OF TRANSIENT CREEP PARAMETERS⁽¹⁾

$$\dot{Y} = \dot{Y}_{ss} + \dot{Y}_1 \exp(-t/\tau_1) + \dot{Y}_2 \exp(-t/\tau_2)$$

Specimen	Temp°C	Loading	$\dot{Y}_{ss}$	$\dot{Y}_1$	τ_1	$\dot{Y}_2$	τ_2	$Y_{\text{calculated}}^{(2)} \text{ transient}$	$Y_{\text{calculated}}^{(2)} \text{ total}$	$Y_{\text{measured}}^{(2)} \text{ total}$
1-4-4	1425	1	3.94	21.9	0.21	6.44	2.85	21.8	61.4	62.3
1-4-4	1425	2	3.19	3.28	0.34	2.23	1.76	5.06	36.9	37.6
1-4-4	1425	3	3.03	4.88	0.35	1.11	3.35	5.2	35.5	35.8
1-4-4	1425	Recovery	--	~ 12	~ 0.3					3.5
1-4-1	1375	1	0.69	89.7	0.077	7.33	2.38	24.9	31.3	28.0

- (1) Deflection rates are given in microns/hr.
Deflections are given in microns.
Relaxation times are given in hours.
- (2) Calculated or measured 10 hours after loading.

times; the purpose of the reloading was to check the reproducibility of the transient behavior. It can be seen from either the measured or the calculated total deflections (Y_{TC} or Y_{Tm}) that considerably more deformation of the sample occurs during the initial loading than during subsequent reloadings; the second and third loadings result in essentially the same total deformation. Another feature of the reloading experiments can be seen by comparing the time constants which were obtained from the transient; the relaxation times are essentially unchanged from one loading to another. The large total deformation encountered during the first loading is primarily reflected by higher initial deflection rates ($\dot{Y}_1$ and $\dot{Y}_2$). The constancy to the relaxation times and the variance of the initial decay rates implies that perhaps some sort of exhaustion or hardening process is occurring during the transient.

It should be noted that the recovery, measured after each of the loadings, was almost identical and the total recovered deformation was approximately 60% of the transient deformation which occurred during either the second or the third loadings.

The analysis of transient creep by Gordon and Terwilliger⁽³⁾ suggests an analogy between the reciprocal of the relaxation time and the Nabarro-Herring strain rate equation (Equation (2)). If we assume the geometry factor (A) in Equation (1) to be the same as for steady state creep (13.3), then it can readily be seen that the relaxation time should be related to the steady state creep rate and the stress in the following manner:

$$\frac{1}{\tau E} = \frac{\dot{\epsilon}}{\sigma} \quad (12)$$

or

$$\frac{\dot{\epsilon} \tau E}{\sigma} = 1$$

For the case of sample 1.0-4-1, the term $\frac{\dot{\epsilon} \tau E}{\sigma}$ was found to be 1.3 (if the second or long-time constant is used), indicating there may indeed be an intimate relationship between the transient which occurs during viscous creep and the eventual steady state creep rate.

In summary, several interesting features have been observed in the transient creep of iron-doped, polycrystalline MgO.

- 1) Two relaxation times are required to completely describe the transient.
- 2) Transient deformation which is observed upon initial loading of a specimen, was found to be about 4 to 5 times that observed for subsequent loadings at the same stress.
- 3) A correlation may exist between one of the relaxation times and the steady state creep rate.

2.2 Evaluation of the Importance of Oxygen Grain Boundary Diffusion in the Creep of Fe-Doped, Polycrystalline MgO

The steady state creep of iron-doped polycrystalline MgO (dopant concentrations ≥ 2.65 cation %) can be characterized by two regimes:

Regime I: at low oxygen partial pressures ($P_{O_2} < 10^{-3} - 10^{-5}$ atm) the creep rate is very sensitive to changes in the oxygen partial pressure (P_{O_2}). Increasing the P_{O_2} and, hence, the concentration of trivalent iron enhances the steady state creep rate ($\dot{\epsilon} \propto P_{O_2}^{1/6}$). The activation energy in this regime is $\sim 122 \pm 5$ kcal/mole. Cation lattice diffusion via the Nabarro-Herring mechanism has been proposed as the rate controlling process for creep in this regime. This conclusion implies a rapid transport

of oxygen along the grain boundaries.

Regime II: at high oxygen partial pressures ($P_{O_2} > 10^{-3}$ atm) the creep rate is nearly independent of the oxygen partial pressure and the activation energy is significantly lower ($\sim 83 \pm 5$ kcal/mole).

Previously the second creep regime has been interpreted as being controlled by cation lattice diffusion in the limit where all of the iron is trivalent.⁽⁹⁾ However, after further analysis and a re-evaluation of the data, it has been concluded, tentatively, that the rate controlling process in this regime is oxygen grain boundary diffusion. This conclusion was based on the following observations:

- 1) In oxidizing atmospheres substantial divalent iron ($20 \pm 5\%$) is present at these dopant levels in the temperature range of interest (1300-1450°C).
- 2) The range of oxygen partial pressures over which creep regime II exists is markedly dependent upon both the grain size and the dopant level. Increasing either one or both of these parameters increases the extent of this regime (i.e., decreases the P_{O_2} for the initiation of Regime I).
- 3) The effect of grain size on the creep rate is much more pronounced in oxidizing ($\dot{\epsilon} \propto (GS)^{-m}$; $m \sim 3$) than in reducing atmospheres ($m \sim 2$).
- 4) The creep rate is nearly independent of iron concentration in regime II. However, in the high activation energy regime, which is controlled by cation lattice diffusion, the creep rate is approximately proportional to the iron dopant level.

These observations, in combination with the low activation energy and the O_2 pressure insensitivity, strongly suggest that oxygen grain boundary diffusion (i.e., Coble creep) is rate controlling in regime II and not cation lattice diffusion.

Finally, these results are consistent with the mass transport theory⁽⁴⁾ which has been developed under this contract in which oxygen grain boundary diffusion (i.e., Coble creep) is predicted in the limit when

$$\frac{GS}{\pi} D_{Mg}^{\ell} \gg \delta_o D_o^b$$

(i.e., large grain sizes, high iron dopant levels, and oxidizing atmospheres). In this limit cation lattice diffusion (D_{Mg}^{ℓ}) becomes too fast to be rate controlling and the mechanism shifts to kinetics controlled by oxygen grain boundary diffusion ($\delta_o D_o^b$). For a more thorough discussion of the foregoing, the reader is referred to the preprint attached to this report.⁽¹⁾

2.3 Studies on the Synthesis, Hot Pressing and Creep Testing of High Purity Al_2O_3

Previous research⁽¹⁰⁾ under this contract into the effect of impurities on the high temperature creep of polycrystalline aluminum oxide was hampered by problems with exaggerated grain growth. In addition to problems with grain growth, many of the alumina specimens, which were creep tested, had non-equiaxed grain structures. It was proposed⁽¹¹⁾ that the manufacture of specimens from high purity (low in silica and soda) alumina would allow for the generation of equiaxed, bubble type microstructures, and would eliminate the problem of exaggerated grain growth. It was also postulated that occurrence of a slightly non-viscous stress exponent ($N = 1.3$) in the creep equation ($\dot{\epsilon} = k \sigma^N$) might be related to microstructural morphology, and, as such, material with equiaxed grains might exhibit viscous creep ($N = 1$).

In view of the foregoing, three major objectives were pursued during the current contract year.

- 1) The synthesis of high purity, silica and soda free, alumina powders.
- 2) The fabrication by vacuum hot pressing and subsequent heat treatment of creep specimens which exhibit equiaxed microstructures and do not suffer from problems of exaggerated grain growth.
- 3) Preliminary creep tests to determine the strain rate-stress dependence and the activation energy for creep of fine-grained, undoped Al_2O_3 , which was fabricated from high purity powders.

2.3.1 Alumina Powder Synthesis

The preparation of high purity aluminum oxide was accomplished by two methods:

- 1) the reaction of high purity metal with steam in an autoclave,
- 2) the preparation of aluminum isopropoxide from high purity metal and the subsequent precipitation of aluminum hydroxide.

Starting materials for the two preparation techniques were the same, either A. D. Mackay, Inc. aluminum pellets or Alcoa Raffinal piglets. Reported purities for the two starting materials were 99.999% with the major impurities being Fe, Cu, and Si.

The production of alumina powder by reaction with steam was accomplished by autoclaving for times from four to five hours at approximately 380°C and 4000 psig. One run was performed for 88 hours in order to achieve a high content of alpha alumina.

A summary of the types of alumina produced and their approximate amounts is presented in Table 2. An X-ray diffractometer was used to scan the samples in order to detect the various phases. Standards of Linde-A alpha and gamma aluminas were mixed in different proportions varying from

Table 2. SUMMARY OF AUTOCLAVED ALUMINA POWDERS

Starting Material	Time-Pressure-Temperature	Phases Present	% Alpha Present
Consolidated Al 99.999% HCl etched Chunk	Five hours-4000 psi-380°C	Small alpha, small gamma Alpha monohydrate	less than 40%
	Calcined 600°C-two hours	Alpha, bigger gamma peak	---
	Calcined 1180°C-two hours	Big alpha	100%
Consolidated Al 99.999% HF etched Chunk	Five hours-4000+psi-380-400°C	Alpha, small gamma, alpha Monohydrate, small beta Monohydrate	41%
	Calcined 450°C-two hours	Alpha, larger gamma	42%
	Calcined 1180°C-two hours	Big alpha	100%
	Autoclaved and leached in HCl for several days	Alpha, small gamma, alpha monohydrate	---
Consolidated Al 99.999% HF etched Chunk	Five hours-4000 psi-380-400°C	Alpha monohydrate	0%
	Grey surface flakes	Alpha	100%
	Calcined 1180°C-two hours		
Consolidated Al 99.999% HF etched Chunk	88 hours-3600 psi-350°C	Alpha, small gamma peaks, alpha monohydrate, beta mono- hydrate, beta trihydrate, alpha trihydrate*	71%
	Calcined 450°C-two hours	Alpha, small gamma peak, alpha monohydrate, 1/3 smaller beta monohydrate, beta trihydrate, alpha trihydrate*	72%
	Calcined 600°C-three hours	Larger alpha, larger gamma	76%
	Calcined 1180°C-two hours	Alpha	100%

* Alpha monohydrate peaks are difficult to separate from alpha trihydrate.

0.1 to 100% alpha. The peak height intensity for one alpha peak ($d = 2.55 \text{ \AA}$) was integrated for the various standards and compared to the integrated intensity for the autoclaved and calcined powders.

As shown in Table 2, when the beta monohydrate phases disappeared (calcining to 600°C) the alpha peak increased in intensity. The change in intensity gives one some idea how much beta monohydrate was present. Also, the gamma phase is seen to increase in intensity as alpha monohydrate and the trihydrate decompose.

Important conclusions can be drawn from Table 2. Autoclaving for long times (88 hours) produced approximately 70% alpha and 5-7% beta monohydrate. Results were similar for AlAG powder or consolidated Al blocks. Short time autoclaving produced less alpha ($\sim 40\%$) and no beta monohydrate. Alpha monohydrate was found to be formed on the surface of the aluminum. (This layer is most likely formed at lower temperatures and pressures as the autoclave heats up.) Calcination to 1180°C always resulted in 100% alpha.

Microscopic examination indicates that all the powders are agglomerated, but individual particle sizes are small (on the order of 0.3μ).

The preparation of aluminum oxide from an organometallic followed a method similar to that used by Mazdiasni et al.⁽¹²⁾ for the production of yttrium oxide. Aluminum metal was reacted with 2-propanol to yield aluminum isopropoxide as shown in the following reaction

A small amount of (10^{-4} mole/mole Al) of Hg Cl_2 was needed as a catalyst.

After preparation of the organometallic, aluminum hydroxide was precipitated

by reaction with water, i.e.,

Attempts at stoichiometric precipitation (using only 3 H_2O to yield Al_2O_3 directly) did not result in complete reaction; excess water was always needed.

The precipitate had a very fine particle size, consistent with the findings of Harris and Sing,⁽¹³⁾ who report that the hydrolysis of aluminum isopropoxide gave a material similar to that of "activated" alumina, in that it had a surface area of 1130 m^2/g and a retained surface of 300 m^2/g on aging. Calcination of the precipitate at 1200°C resulted in complete conversion to alpha alumina.

2.3.2 Fabrication of Dense Polycrystals by Vacuum Hot Pressing

Using either the alkoxide or the autoclave powder as a starting material, creep specimens (undoped, Cr-, or Fe-doped) were vacuum hot pressed for 3 to 9 hours at temperatures from 1450 to 1600 and at pressures up to 5000 psi. Final densities ranged between 98 and > 99.5% of theoretical. In addition, specimens have been annealed at temperatures up to 1850°C. No problems of exaggerated grain growth have been encountered as long as sufficient attention has been paid to cleanliness during powder preparation.

Micrographs of typical grain structures are presented in Figures 1-A and 1-B for the alkoxide and autoclaved powders, respectively. In addition, a micrograph (Figure 1-C) is included, illustrating the microstructure which is found when a commercial powder was used (Ugine Kuhlmann of America, 99.995% pure). It can be seen by comparing the micrographs, the preparation of our own high purity powders has resulted in a substantial improvement in grain morphology over those which are possible from commercial materials.

Fig. 1-A Alkoxide 475x

Figure 1-B Autoclave 250x

Fig. 1-C Ugine Kuhlman 475x

Figure 1. Representative microstructures of hot-pressed autoclave, alkoxide, and Ugine Kuhlman powders

2.3.3 Preliminary Creep Tests

Four point bending, dead load, creep tests have been conducted on high purity autoclave and organometallic Al_2O_3 at temperatures between 1400 and 1525°C, at stresses between 35 and 400 kg/cm^2 , and for grain sizes between 6 and 33 μm . In these studies several important observations were made:

- 1) Slightly non-viscous creep behavior was observed with stress exponents N around 1.4 (i.e., $\dot{\epsilon} \propto \sigma^N$).
- 2) The activation energy for creep was ~ 130 kcal/mole in the range expected for kinetics controlled by cation lattice diffusion.
- 3) The grain size effects, although only limited data are available, were consistent with Nabarro-Herring creep (i.e., $\dot{\epsilon} \propto (\text{GS})^{-2}$).

The most important finding to date is the slightly non-viscous creep in high purity Al_2O_3 with a normal equiaxed microstructure. It is apparent that grain morphology has little to do with the strain rate-stress behavior and that slightly non-viscous stress exponents are characteristic of deformation in polycrystalline Al_2O_3 .

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1. "The Effects of Impurities and Atmosphere on the Creep of Polycrystalline MgO," Materials Science Division, Argonne National Laboratory, April 1971.
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3. "A Review of Mass Transport Processes in the High Temperature Creep of Polycrystalline Ceramics," Gordon Research Conference on Corrosion, July (1973).

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VI. PRINCIPAL INVESTIGATOR

The principal investigator, Dr. Ronald S. Gordon, has devoted considerable time, both in supervisory activities and in preparing talks and papers on work related to this contract. Since September 1971 Dr. Gordon has been on a leave of absence working in the Lighting Research Laboratory of the General Electric Company. Dr. Gordon makes weekly telephone contacts with the project personnel and has visited the University twice 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.