

Improved tensile creep properties of yttrium- and lanthanum-doped alumina: a solid solution effect

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The tensile creep behavior of yttrium- and lanthanum-doped alumina (at dopant levels below the solubility limit) was examined. Both compositions (100 ppm yttrium, 100 ppm lanthanum) exhibited a uniform microstructure consisting of fine, equiaxed grains. The creep resistance of both doped aluminas was enhanced, compared with undoped alumina, by about two orders of magnitude, which was almost the same degree of improvement as for materials with higher dopant levels (in excess of the solubility limit). In addition, measured creep rupture curves exhibited predominantly steady-state creep behavior. Our results, therefore, verified that the creep improvement in these rare-earth doped aluminas was primarily a solid-solution effect.

I. INTRODUCTION

Oxide ceramics have recently become promising candidate materials for fiber-reinforced ceramic-matrix composites (CMCs) for use in various applications including hot exhaust components in advanced engines and aircraft.^{1,2} However, the creep properties have limited their applicability. Given this constraint, it is of interest to identify oxides having superior creep resistance. We note that significant progress toward this goal has been achieved after it was discovered that the tensile creep rate of aluminum oxide (α -Al₂O₃) was reduced by approximately two or three orders of magnitude by the addition of rare-earth ions (e.g., Lu³⁺, Y³⁺, Nd³⁺, and La³⁺).³⁻⁶ Furthermore, a small amount of Zr⁴⁺ was shown to enhance creep resistance of alumina by a factor of about 15.⁷ In these promising doped aluminas, emerging evidence suggests that grain boundaries play a dominant role in this behavior. One such observation is that oversized cation dopants strongly segregate to grain boundaries.⁸⁻¹⁰ Therefore, it has been suggested that oversized segregants selectively block rapid grain boundary diffusion paths and ultimately reduce creep rate.³

Previous studies on 1000 ppm yttrium (Y)- and 500 ppm lanthanum (La)-doped alumina, however, have shown that second-phase precipitates (i.e., Y₃Al₅O₁₂ and LaAl₁₁O₁₈, respectively) were present in the microstructure. As a result, it was not clear whether these precipitates played a major role in the creep retardation. Wakai *et al.*⁷ showed creep improvement from the Zr⁴⁺ doping in alumina even below the solubility limit. Therefore, the objective of the present work was to measure the creep

rate of Y- and La-doped alumina samples doped below the solubility limit to discriminate solid-solution from second-phase effects.

II. EXPERIMENTAL PROCEDURE

Y- and La-doped aluminas used in this study were prepared from commercial powders of α -Al₂O₃ (AKP-53, Sumitomo Chemical America, New York, NY). The α -Al₂O₃ powder was dispersed in methanol approximately with equal mass of liquid and solid. The dopant ions were added to the suspension in the form of yttrium (or lanthanum) nitrate methanol solution. The amount of the dopant can be nominally controlled by weighing. The inductively coupled plasma atomic emission spectroscopy (ICP) analysis of the doped powder indicates that by this method the doping concentration can be controlled with a deviation range of $\pm 15\%$. For the present samples, the dopant level of 100 ppm (dopant-Al ion) for both Y and La was chosen. Both Y- and La-doped aluminas were hot pressed at 1450 °C and 45 MPa under vacuum, in a graphite-resistance furnace. The resultant grain size was approximately 1.5 μ m, and bulk density was >99% for both materials.

Dog bone-shaped tensile specimens fabricated from hot-pressed 3-inch billets¹¹ were tested at various temperatures and stresses, as described elsewhere.^{3,12} To evaluate the grain size effect on creep, the specimens were annealed in the creep furnace at 1450 °C to grow the grains under a low applied stress (<5 MPa). This was followed by immediate loading.¹³ Strain rates were

measured from a well-defined steady-state regimen. The strain rate variation between the different sets of specimens for a given condition was <20%.

III. RESULTS

The microstructures of the as-hot-pressed materials of the 100 ppm Y- and La-doped aluminas are shown in Fig. 1(a) and 1(b), respectively. Both systems contain equiaxed grains that have been confirmed by observations taken at low-magnification micrographs ($\times 1000$).¹³ More importantly, both compositions did not show second-phase precipitates, indicating that the dopant level was below the solubility limit.

The creep-rupture behavior of 100 ppm Y- and La-doped alumina was examined at 1300 °C with a constant stress of 50 MPa (Fig. 2). These specimens were preheated at the same temperature with a 13-h annealing treatment in the creep furnace under a stress of 5 MPa.

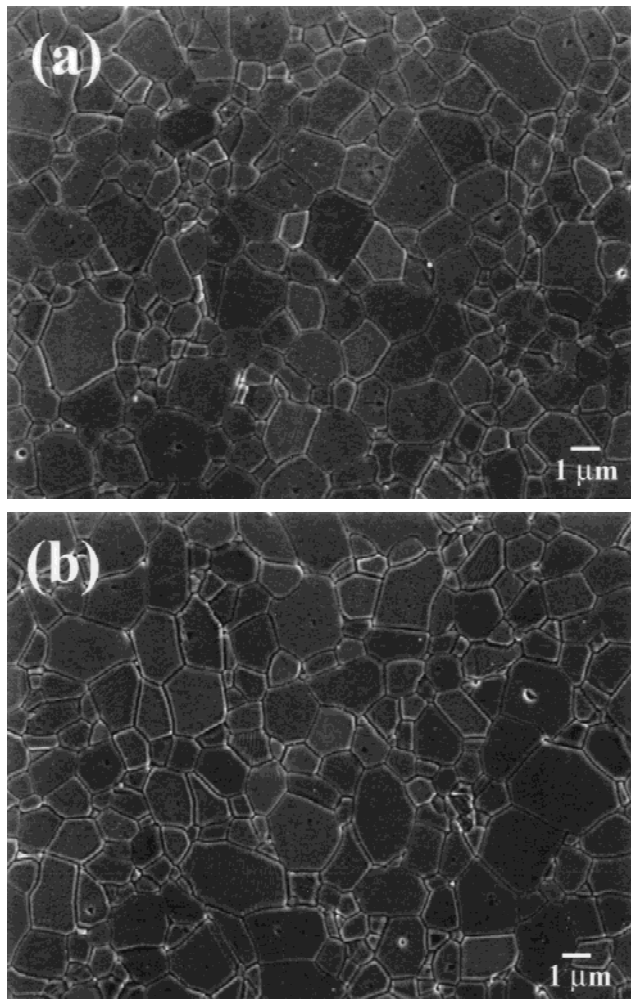


FIG. 1. Microstructures of as-hot-pressed Y- and La-doped alumina: (a) $\text{Al}_2\text{O}_3 + 100 \text{ ppm Y}$ and (b) $\text{Al}_2\text{O}_3 + 100 \text{ ppm La}$.

The beneficial effect of preannealing has been previously determined.³ The average grain size for both 100 ppm Y- and 100 ppm La-doped materials was approximately 1.5 μm . The creep responses of the two compositions were very similar and showed an extensive steady-state creep regimen with no indication of primary creep. However, the Y-doped alumina showed a slightly higher creep rate than the La-doped alumina after a 5% elongation. Both specimens were elongated >10%, and the testing was interrupted before failure. Total strains were much higher than those exhibited by the 1000 ppm Y-doped system that had shown a final strain of about 5.5% under the same conditions.¹³

Figure 3 shows the steady-state creep strain rate as a function of temperature for a constant applied stress of 50 MPa for both La- and Y-doped alumina as well as the undoped alumina. To assess the creep behavior of these doped alumina systems, the steady-state creep strain rate was normalized with a grain size exponent of 3 to account for differences in the grain size of different materials. A grain size exponent of 3 implies that a grain boundary diffusion-controlled creep model (Coble creep) is applicable and the reason for this is discussed in Sec. IV. Figure 3 reveals three notable features. (i) the steady-state strain rate shows no obvious dependence on the dopant concentration above 100 ppm for both Y and La. (ii) the creep rates of both Y- and La-doped aluminas were very similar and reduced by about two orders of magnitude in comparison with the undoped material. (iii) all doped aluminas show a much higher activation energy than the pure alumina.

For diffusional creep, the creep strain rate, $d\epsilon/dt$, can be expressed as

$$d\epsilon/dt = A(\sigma^n/d^p)\exp(-Q/RT) \quad (1)$$

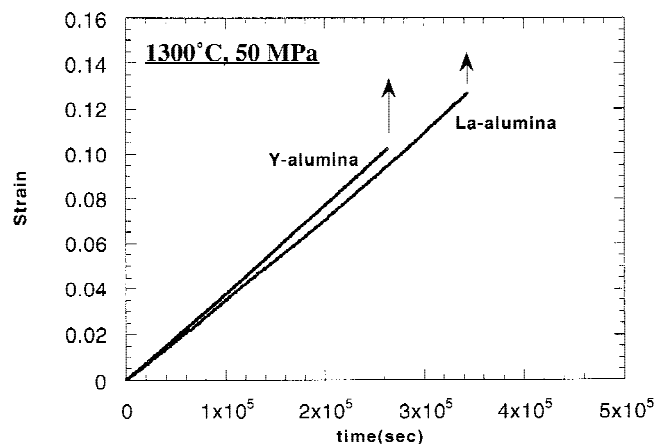


FIG. 2. Stress rupture behavior of Y- and La-doped alumina at 1300 °C under a 50 MPa. The specimen was preannealed for 13 h under a stress of 5 MPa at the same temperature. The grain size for both materials was approximately 1.5 μm .

where A is a constant determined by the slowest diffusing species along the most rapid diffusion path, σ is the applied stress, n is the stress exponent, d is the grain size, p is the inverse grain size exponent, Q is the activation energy, and T is temperature. The effect of applied stress and grain size on the steady-state creep rate is shown in Fig. 4(a) and 4(b), respectively. The results for both systems in the temperature range studied (1250–1350 °C) were again very similar, where the stress exponent (n) and inverse grain size exponent (p) were measured to be close to 2 and 3, respectively.

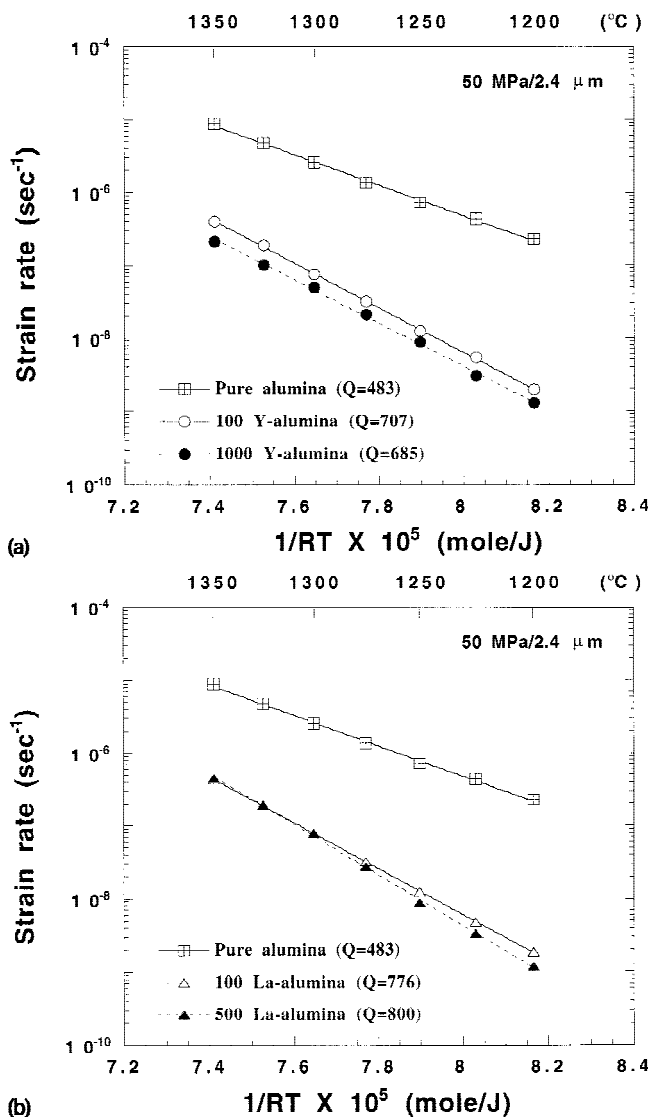


FIG. 3. Arrhenius plot of strain rate for 100 ppm Y- and La-doped alumina along with undoped alumina at 50 MPa. For comparison, the strain rate of 1000 ppm Y-doped alumina and 500 ppm La-doped alumina are also plotted. The strain rate for different materials are all calibrated to a grain size of 2.4 μm according to a grain size exponent 3. Q represents the activation energy (kJ/mol).

IV. DISCUSSION

A. Solid-solution effect

It has been well recognized that the microstructure of rare-earth oxide-doped alumina depends on the dopant concentration. Typically, when the dopant concentration is above the solid-solution limit, the microstructure shows a wide grain size distribution and the existence of a second phase. The 100 ppm doped alumina systems (dopant concentration below the solubility limit) result in more uniform, equiaxed microstructures compared with the same aluminas doped at levels above the solubility limit. It is significant that the tensile creep rates were similar to those exhibited for dopant concentrations, exceeding the solubility limit. This result shows that the creep improvement can be attributed to the oversized segregants acting in solid solution, rather than any influence of second-phase precipitates. In addition, the creep retardation was achieved in specimens with an equiaxed, fine-grained microstructure that was uniform throughout

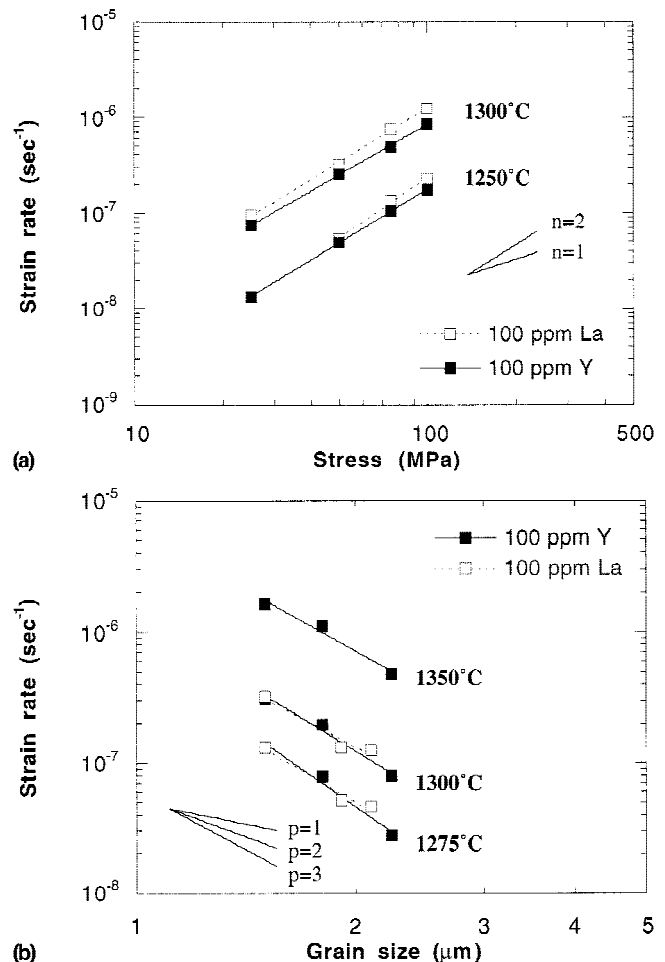


FIG. 4. Effect of applied stress and grain size on steady-state creep rate for 100 ppm Y- and La-doped alumina: (a) stress effect at 1250 °C and 1300 °C and (b) grain size effect from 1275 to 1350 °C under a 50 MPa.

the sample. Any possible purely microstructural influences (e.g., bimodal grain size or elongated grains) can, therefore, be ruled out. This view is also consistent with the previous result by Wakai *et al.*⁷ on Zr-doped alumina, which showed that creep resistance is enhanced even with a dopant level below the solubility limit. More recently, Li *et al.*⁵ studied Nd/Zr-codoped alumina by varying the Nd concentration and found that particles that were precipitated in excess of solubility limit did not influence the creep rate.

It might be argued that larger segregating ions should be more effective in decreasing grain boundary diffusion. Sintering studies of Y- and La-doped aluminas indeed corroborated this prediction, where the densification rate of La-doped alumina was twice as slow as that of Y-doped alumina.¹⁴ However, the present study reveals a saturation of the creep improvement beyond some critical radius of the dopant ion. This is consistent with previous observations of creep rates in a series of rare-earth doped systems.^{3,5} In addition, secondary ion mass spectrometry (SIMS) mapping⁹ and scanning transmission electron microscopy (STEM) analysis¹⁰ did not reveal a higher level of segregation in the La-doped system versus Y-doped. It is interesting that a recent compression creep study by Yoshida *et al.*⁶ reported that the Y-doped system is more creep resistant than La-doped alumina. To further understand the dopant size effect, the segregating dopant environment at the boundaries has been studied by using both computer modeling¹³ and extended x-ray absorption fine structure (EXAFS).¹⁵

B. Strain rate retardation mechanism

It has been well established that Zr^{4+} and rare-earth dopant ions in alumina are mainly segregated to the alumina grain boundaries, but the mechanism by which these dopants affect the creep properties in doped alumina remains to be established. A clear understanding of the deformation mechanism in the fine grain-sized doped alumina is a key for identifying the mechanism by which dopant affects the creep properties. The deformation mechanism is normally inferred from the measured grain size and stress exponents as expressed in Eq. (1).

Our observation of $p = 3$ strongly supports a grain boundary diffusion-controlled creep mechanism, which is in a general agreement for the creep behavior of fine-grained alumina systems under the experimental conditions considered in this study.¹⁶ However, the experimental values of the stress exponent ($n \sim 2$) and (inverse) grain size exponent ($p \sim 3$) are difficult to reconcile because they predict different rate-controlling mechanisms. Instead, the exponent is consistent with either grain boundary sliding model¹⁷ or interface reaction-controlled creep.¹⁸ Such apparent contradictions, however, are not uncommon in the creep literature, e.g., see Refs. 19–21, and measurements conducted at Lehigh

on undoped alumina also showed similar exponent values.^{4,13} Sherby and Wadsworth^{19,20} resorted to a grain boundary diffusion model to explain a combination of $p = 3$ and $n = 2$, as found in many superplastic materials.

Although more definitive evidence is necessary to understand the relation σ^2/d^3 , overall, we are persuaded that the case for grain boundary diffusion control (versus interface control) is more compelling on the basis of the following. The study of Fang *et al.*¹⁴ showed that for Y- and La-doped alumina, the densification kinetics exhibited a grain size exponent of 4, which again is consistent with grain boundary diffusion being the predominant mechanism. In the absence of definitive evidence to the contrary, therefore, we believe that the primary effect of the rare-earth ions was to inhibit grain boundary diffusion, most likely by “site blocking” of rapid transport paths. The site blocking of rapid grain boundary diffusion paths by oversized ions is a reasonable model for the observed behavior, and intuitively preferable, because of its more straightforward physical basis. Furthermore, it is supported by recent atomistic simulations by Cho *et al.*¹³ that showed that segregated ions increased the migration energies considered with various paths at grain boundaries in alumina. We note that a similar mechanism for diffusive retardation, involving the “clogging” of important boundary paths by segregants, was proposed by others to explain the decrease in boundary diffusivity in Fe that attends Sn segregation.²²

Most recently, Ching *et al.*²³ conducted first-principles molecular orbital calculations of the bonding states in the Y–Al–O system. Although their calculations are based only on bulk crystal structures, they found that the relative bonding strength between Y–O and Y–Al depends on atomic environment. Similarly, Yoshida *et al.*²⁴ showed that the Al–O bond strength can be altered by doping, in that case with the lanthanides. From these results it was inferred that the enhanced creep resistance of rare-earth doped alumina may be attributed to a reduction in grain boundary diffusion caused by the stronger bonding at segregated grain boundaries.

We recognize that other deformation mechanisms may also participate in the creep deformation process of doped alumina. This may include dislocation sliding of both grain boundary and bulk lattice dislocations. However, microstructure observation and an extensive review of the creep data in the literature¹⁶ has indicated that this is not the dominant deformation mechanism.

V. SUMMARY

Both 100 ppm Y- and La-doped aluminas displayed a dramatic reduction in creep rate by about two orders of magnitude. Second-phase particles were not observed in the microstructures, thus showing that the creep improve-

ment is a solid-solution effect. In contrast to some instances for the higher dopant concentrations, the compositions studied did not exhibit any microstructural inhomogeneities. An extensive steady-state creep regimen was obtained, with total strain values significantly higher (>10%) than observed previously for higher dopant levels. Both the Y- and La-doped compositions resulted in a stress exponent (n) of 2 and an inverse grain size exponent (p) of 3.

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