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Enhancement of the diffusional creep of polycrystalline Al_2O_3 by simultaneous doping with manganese and titanium

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The effect of simultaneous doping with manganese and titanium on diffusional creep was studied in dense, polycrystalline alumina over a range of grain sizes (4–80 μm) and temperatures (1175–1250° C). At a total dopant concentration of 0.32–0.37 cation %, diffusional creep rates were enhanced considerably such that the temperature at which cation mass transport was significant was suppressed by at least 200° C compared to that observed in undoped material. The Mn–Ti (and Cu–Ti) dopant couple was far more effective in enhancing creep rates and suppressing sintering temperatures than the Fe–Ti couple. The enhanced mass transport kinetics are believed to be caused by significant increases in both aluminium lattice and grain-boundary diffusion. When aluminium grain-boundary diffusion is enhanced by increasing the concentration of divalent impurity (Mn^{2+}, Fe^{2+}) or by creep testing at low temperatures, creep deformation is Newtonian viscous.

1. Introduction

Ample evidence abounds in the literature that either quadrivalent (e.g. Ti^{4+}) or divalent (e.g. Fe^{2+}, Mn^{2+}) ions, when present in substitutional solid solution, enhance mass transport processes in polycrystalline alumina. This enhancement manifests itself as increases in both the sintering kinetics [1–3] and diffusional creep rates [4, 5]. Furthermore, when alumina is simultaneously doped with these impurities (e.g., Mn–Ti, Fe–Ti, and even Cu–Ti), the enhancement in sintering [6, 7] and creep [8–10] kinetics (i.e., reduction in temperature for significant mass transport) is far more significant than in the case where each dopant is added separately.

Preliminary creep studies at low stresses (~ $10\,MN\,m^{-2}$) and moderate grain sizes (20–40 μm) by Lessing [9] on polycrystalline Al_2O_3 doped* simultaneously with either Cu–Ti or Mn–Ti revealed the presence of significant *viscous* creep rates ($\dot{\epsilon}$) with a strong reciprocal grain size (GS) dependence (i.e. $\dot{\epsilon} \propto (GS)^{-m}$ with $m \approx 4$) at very low temperatures (~ 1250° C). These results were confirmed by one of the present authors [10] for the Mn–Ti couple with anomously high grain-size exponents ($m = 4.5$–5.2). At these low temperatures (1150–1250° C), transient creep is significant and dominates the deformation process for long periods of time. It is currently suspected that the anomously high grain-size exponents (i.e. $m \gg 3$) are the result of transient creep behaviour. However, whatever the explanation, it is clear that creep rates, which have a strong inverse dependence on the grain size, are significantly enhanced at very low temperatures in these double-doped systems.

Another interesting observation, which was made by both Lessing [9] and Ikuma [10], concerns the presence of true viscous creep (i.e. $\dot{\epsilon} \propto \sigma^N$; $N = 1$) in these double-doped systems. The only other examples of viscous creep in polycrystalline alumina were those reported for iron-doped material (1–2 cation %) tested under conditions of small grain size and low stress [5] or under conditions where the concentration of

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*~ 1/2 cation % total impurities, equimolar concentration of each ion in the pair.

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divalent iron was large [5] (i.e. low oxygen partial pressures). In all other situations, the creep of polycrystalline alumina, doped or undoped, is slightly non-viscous with stress exponents (N) ranging between 1.1 and 1.4 [5].

To gain additional insight on the role of dopants such as Mn and Ti on mass transport processes in polycrystalline alumina at low temperatures (1150–1250° C), *steady state* creep experiments were designed and conducted at low stresses over a range of grain sizes. The results of these studies are reported here.

2. Experimental details

High-purity (> 99.99%) alpha-alumina powder was prepared by an organo-metallic synthesis [5]. Dopants (Mn and/or Ti) were introduced by a precipitation method [10]. Dense (> 99% theoretical density) specimens were prepared by hot-pressing [10]. A range of grain sizes (4–80 μm) was obtained by annealing hot-pressed specimens at elevated temperatures (1250–1750° C) followed by annealing at the creep-testing temperature (1100–1400° C). Three compositions were studied*: 0.05% Mn, 0.25% Mn + 0.12% Ti, and 0.075% Mn + 0.24% Ti. Four-point, dead-load creep tests were conducted on beams 2 mm x 5 mm x 30 mm in size at stresses between 2 and 17 MN m^{-2}.

In the simultaneously doped (Mn–Ti) compositions, creep tests could only be conducted at low temperatures ($\leqslant$ 1250° C). At higher temperatures, creep rates were so fast that tertiary creep leading to fracture occurred directly after an initial transient lasting a few hours. However, at these low temperatures, transient or primary creep was a problem in that it lasted more than 200 h. In order to induce steady state creep behaviour, specimens had to be annealed at the test temperature and in the test atmosphere for long periods of time (8–14 days) prior to beginning the creep test.

In the specimens doped with 0.05% Mn, steady state creep was routinely observed at 1400° C after a short (~ several hours) transient. At this composition, creep tests were performed over a range of oxygen partial pressures (0.86–10^{-10} atm).

All grain sizes, based on 800–1000 linear intercepts, are reported as 1.5 times the average intercept length. Outer fibre stresses and strains were calculated using standard viscoelastic relations [4, 5].

3. Results

3.1. Transient creep

In Fig. 1 creep data are presented for long-term tests (200–250 h) which clearly illustrate the transient nature of creep deformation in the Mn–Ti doped system at low temperatures (< 1200° C) and low stresses. Extensive and long-lasting transient creep was observed in test specimens which were annealed in air† prior to creep testing in pure oxygen. However, when specimens were annealed in *air* at temperatures higher than the test temperature prior to creep testing, steady state creep was observed (in *air*) after a transient lasting about 60 h. Finally, relatively short transients (~ 20 h) were observed in creep tests when specimens were annealed for 8–14 days in air at the test temperature prior to creep deformation in air. Steady state creep characteristics which are reported in this paper, were achieved by annealing test specimens in this manner.

It is believed that these transients are associated with an internal chemical homogenization, as the specimen establishes an equilibrium with the surrounding atmosphere. The time required for defect equilibration, which will involve some lattice or grain-boundary diffusion over a distance at least of the order of the grain size, could easily

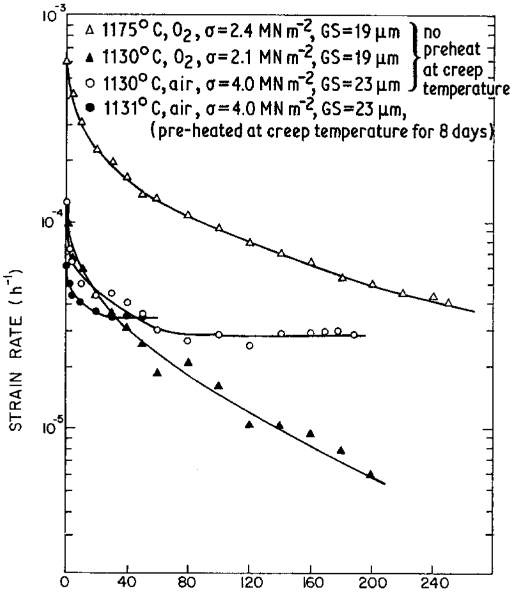

Figure 1 Transient and steady state creep in polycrystalline alumina doped with Mn and Ti.

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*All compositions are expressed in cation %.

†To stabilize the grain size.

exceed 100 h at temperatures below 1250° C. Other factors possibly responsible for the transient such as (1) grain growth, (2) strain or work-hardening by dislocation motion, (3) diffusional creep transient, (4) precipitation effects, (5) dopant volatization were all eliminated on the bases of various experimental considerations [10].

3.2. Viscous creep

Slightly non-viscous creep of polycrystalline alumina was first reported by Heuer *et al.* [11] and later confirmed in subsequent studies [4, 5, 12, 13]. However, several reports can be found in the literature concerning the presence of Newtonian viscous deformation in doped polycrystalline alumina. Hollenberg and Gordon [4] reported viscous deformation for iron-doped (1 cation %) material with a reasonably small grain size (~ 15 μm) tested at very low stresses ($\leqslant 15\,\text{MN m}^{-2}$). Lessing and Gordon [5] also reported the existence of viscous creep in iron-doped alumina (2 cation %) which was tested in a reducing atmosphere (~ 10^{-6} atm) where the concentration of divalent iron (Fe^{2+}) was enhanced. Under these conditions, Coble creep (i.e. $\dot{\epsilon} \propto (\text{GS})^{-m}$ with $m \approx 3$) was observed. Viscous deformation seems to be related to the dominance of the creep kinetics by aluminium grain-boundary diffusion. Whenever cation lattice diffusion is dominant (i.e. Nabarro–Herring creep with $m \approx 2$), slightly non-viscous creep behaviour is prevalent (i.e. $\dot{\epsilon} \propto \sigma^N$ with $N = 1.1$–1.4). Finally, Lessing [9] reported viscous creep deformation for polycrystalline alumina doped simultaneously with Mn–Ti and Cu–Ti. It is believed, however, that these experiments were conducted in a transient mode of deformation.

In the present study, experiments were conducted to establish conclusively the presence of viscous deformation in the *steady state* creep of alumina doped simultaneously with Mn and Ti. The results of these experiments are shown in Fig. 2 along with the data of Lessing and Gordon [5] on iron-doped alumina tested in a reducing atmosphere. Newtonian viscous deformation ($\dot{\epsilon} \propto \sigma$) was characteristic of this doped system at low stresses and grain sizes up to about 60 μm. Thus it is clear that both transient and steady state creep are Newtonian viscous in the Mn–Ti doped system.

3.3. Apparent creep activation energy

The effect of temperature on the steady state creep of polycrystalline Al_2O_3 doped simultaneously with Mn and Ti is shown in Fig. 3. These data were obtained by temperature change experiments on the same specimen. Apparent

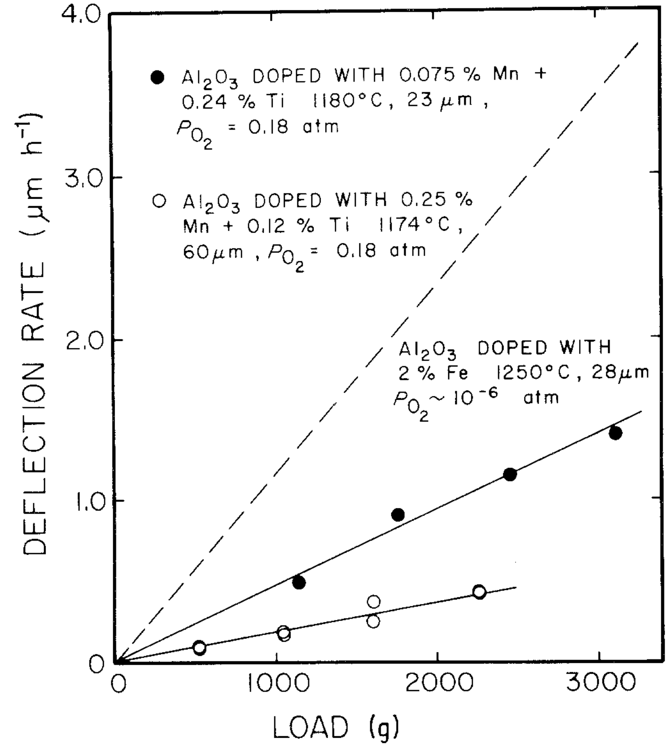

Figure 2 Viscous, steady state creep of polycrystalline alumina.

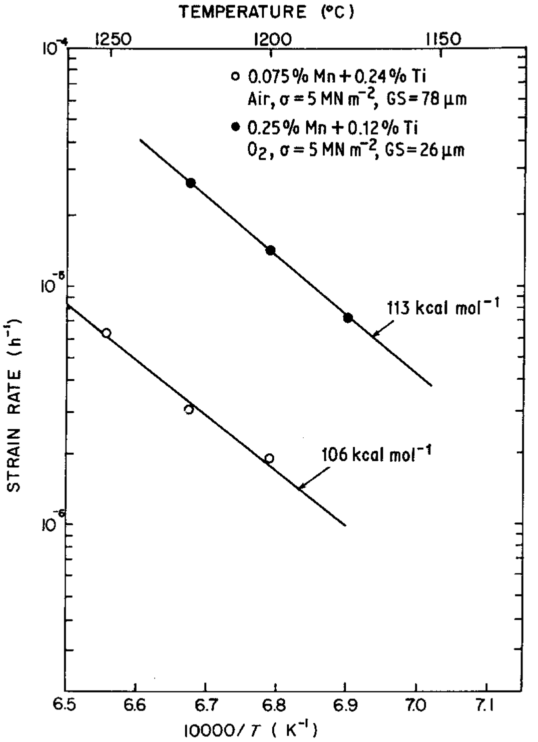

Figure 3 Temperature dependence of steady state creep of polycrystalline alumina doped simultaneously with Mn and Ti.

activation energies of 106–113 kcal mol^{-1} were obtained. These are comparable to those (94–100 kcal) reported by Lessing [9] and Ikuma [10] for Mn–Ti and Cu–Ti compositions in earlier transient creep studies.

The temperature range for determining the creep activation energy was restricted for two reasons: (1) at temperatures over 1225–1250° C, creep rates were so rapid that large strains accumulated early in the test leading to tertiary creep and fracture; (2) at lower temperatures ($<$ 1100–1150° C) creep rates were very slow and excessive times ($>$ 200 h) were required to achieve steady state conditions.

3.4. Atmosphere effects

In Fig. 4 the effect of oxygen partial pressure on the creep of polycrystalline alumina doped with 0.05% Mn is shown. For comparison, similar effects are shown for iron- and titanium-doped material using the data of Hollenberg and Gordon (H + G) [4] and Ikuma and Gordon (I + G) [8]. Decreasing the oxygen partial pressure to 10^{-10} atm increased the creep rate of Mn-doped Al_2O_3 by about a factor of three. The effect of Mn is similar to that of Fe in that increasing concentrations of divalent species (i.e. Fe^{2+}, Mn^{2+}) enhance the steady state creep rate (and sintering rates [2, 3]). Small amounts of Mn are more effective in enhancing the mass transport kinetics than a comparable concentration of iron dopant. The $[Mn^{2+}]/[Mn]_T$ concentration ratio is estimated from the creep data to be at least four times higher than the $[Fe^{2+}]/[Fe]_T$ concentration ratio at a given temperature and dopant concentration.

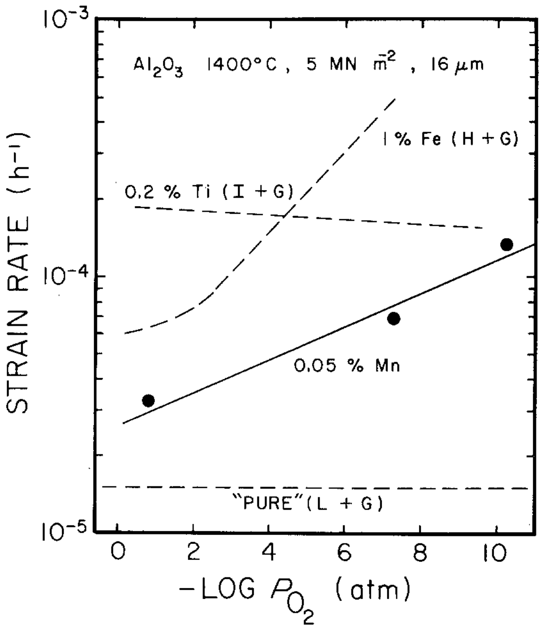

Figure 4 Effect of oxygen partial pressure on steady state creep of polycrystalline alumina doped with transition metal impurities.

Obtaining data on the effect of oxygen partial pressure on the steady state creep of polycrystalline alumina doped simultaneously with Mn and Ti was experimentally difficult in view of the long equilibration times required to achieve steady state conditions at the low temperatures characteristic of this study.

3.5. Grain-size effects

In Fig. 5 the effects of grain size on the *steady state* creep rate of polycrystalline alumina doped with Mn and/or Ti are compared at 1180° C with similar data for undoped, iron-doped, and Fe–Ti compositions. Except for the Mn–Ti and 2% Fe–0.15% Ti compositions, all data in Fig. 5 were extrapolated from creep tests conducted at higher temperatures (1400–1475° C).

Several interesting conclusions can be drawn

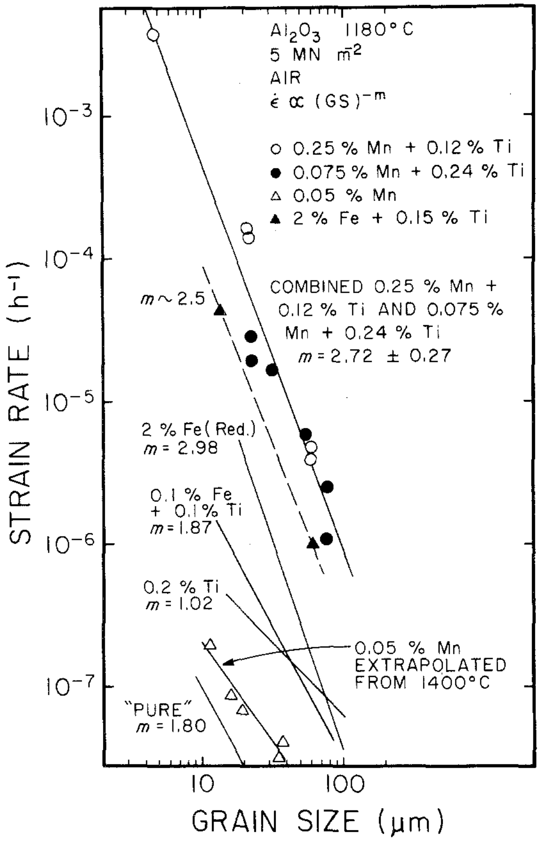

Figure 5 Effect of grain size on the steady state creep of polycrystalline alumina doped with transition metal impurities.

from the data: (1) at similar total dopant concentrations, the Mn–Ti couple is far more effective than the Fe–Ti couple in enhancing the steady state creep rate of polycrystalline alumina. The creep rate was enhanced over *three* orders of magnitude for total dopant concentrations of 0.32–0.37 cation%. To achieve comparable enhancements in the Fe–Ti system, iron concentrations must be approximately 2% with the titanium composition around 0.15%. This significant enhancement in mass transport kinetics permits the suppression of the temperature for significant creep rates (and densification rates in sintering) by at least 200° C; (2) the grain-size dependence for the Mn–Ti system is consistent with a substantial contribution of grain-boundary diffusion (i.e. $\epsilon \propto (GS)^{-m}$ with $m \approx 2.7$); (3) diffusional creep of Mn-doped polycrystalline alumina is controlled by a lattice diffusion process (i.e. $\dot{\epsilon} \propto (GS)^{-m}$ with $m \approx 2$); (4) small amounts of Mn are more effective in enhancing the creep rate of alumina than a comparable concentration of Fe indicating that the concentration of divalent species is higher in the case of Mn doping; and (5) at temperatures below 1200–1250° C, grain-boundary diffusion processes are enhanced as is evidenced by creep grain-size exponents over 2. At higher temperatures, grain-size exponents indicative of kinetics controlled by lattice diffusion (i.e. $m \sim 2$) are typical for the Fe–Ti system [8].

In the Mn–Ti system, the creep data in Fig. 5 at the two compositions indicated were treated together in terms of least squares analysis. Within experimental scatter, the creep rates at the two compositions were identical. Furthermore, at the relatively low temperature of 1180° C, it is suspected that the solubility limit of the dopant pair lies below that of the total dopant concentration, although some enhanced solubility might be expected for the pair over that of single dopants [14]. Some second phase was observed by electron microprobe examination. Thus it is likely that the concentration of impurities in solution is nearly identical for both sets of specimens.

The grain-size exponent of 2.5 for creep at 1180° C for the 2% Fe + 0.15% Ti composition should be considered a lower bound. The creep rate of the specimen with the 60 μm grain size was very slow and should be considered an upper bound.

4. Discussion

The occurrence of viscous creep appears to be strongly related to the dominance or significant contribution of aluminium grain-boundary diffusion in the overall mass transport process (e.g. Mn–Ti double dopant or 2% Fe at $P_{O_2} \sim 10^{-6}$ atm). Slightly non-viscous creep exponents are normally encountered in situations where the creep grain-size exponent ($m \sim 2$) is consistent with a creep mechanism involving a strong contribution of aluminium lattice diffusion. Mass transport processes involving lattice diffusion can encounter problems with the efficient creation and/or annihilation of point defects at grain boundaries*, thus leading to stress exponents with values over unity. Complete dominance of the steady state

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*Limited defect mobility within the grain-boundary impedes boundary dislocation climb and hence the generation or absorption of point defects into or from the lattice.

creep rate by interfacial kinetics at grain boundaries was observed by Ikuma and Gordon [15] in studies on polycrystalline alumina doped only with titanium[*]. Dominance of the mass transport kinetics by grain-boundary (interfacial) defect reactions is believed to be caused by a combination of enhanced lattice and depressed grain-boundary transport of the cation. However, when aluminium grain-boundary diffusion is dominant or significantly enhanced (e.g. at increasing concentrations of Fe^{2+} or Mn^{2+}), interfacial defect creation/annihilation processes at grain boundaries are not likely to be a controlling factor since defect transport in the grain boundaries is expected to be rapid.

Aluminium grain-boundary diffusion in transition metal-doped polycrystalline alumina can be promoted by (1) increasing the concentration of divalent dopant (e.g. 2% Fe at $P_{O_2} \approx 10^{-6}$ atm), and (2) lowering the temperature. In the Mn–Ti system, the enhancement in mass transport is so significant that the temperature must be lowered from about 1400–1500° C to under 1250° C to obtain steady state creep rates which can be measured without the onset of tertiary creep and fracture. At these low temperatures, mass transport is dominated by aluminium grain-boundary diffusion because of its lower activation energy ($\sim 100 \pm 10\,\mathrm{kcal\,mol^{-1}}$) compared to that for lattice diffusion (> 120–$130\,\mathrm{kcal\,mol^{-1}}$).

In order to assess quantitatively the effect of the Mn and/or Ti dopants on mass transport in polycrystalline alumina, diffusion coefficients were calculated from appropriate diffusional creep equations. In the case of alumina doped simultaneously with Mn and Ti, Equation 1 was used to estimate values of $D^{\mathrm{l}}_{\mathrm{Al}}$ and $\delta_{\mathrm{Al}} D^{\mathrm{b}}_{\mathrm{Al}}$ using a method developed by Gordon and Hodge [16]. For Mn-doped alumina, the Nabarro–Herring relation (Equation 2) was used to estimate values of $D^{\mathrm{l}}_{\mathrm{Al}}$.

$$\dot{\epsilon} = \frac{22\Omega_{\mathrm{v}}\sigma}{kT(\mathrm{GS}^2)}\left[\frac{D^{\mathrm{l}}_{\mathrm{Al}}}{\pi} + \frac{\delta_{\mathrm{Al}}D^{\mathrm{b}}_{\mathrm{Al}}}{(\mathrm{GS})}\right] \qquad (1)$$

$$\dot{\epsilon} = \frac{22\Omega_{\mathrm{v}}\sigma D^{\mathrm{l}}_{\mathrm{Al}}}{\pi kT(\mathrm{GS})^2}. \qquad (2)$$

In Equations 1 and 2, Ω_{v} is the molecular volume of Al_2O_3, δ_{Al} is the width of the grain-boundary for aluminium ion transport, $D^{\mathrm{b}}_{\mathrm{Al}}$ is the aluminium grain-boundary diffusion coefficient, $D^{\mathrm{l}}_{\mathrm{Al}}$ is the aluminium lattice diffusion coefficient and kT has its usual meaning. In both of these relations, oxygen transport (via grain-boundaries?) has been assumed to be rapid and not rate-limiting in the overall transport kinetics.

The estimates of diffusion coefficients at 1180° C are summarized in Table I. Some of the values (probably lower bounds in the case of cation lattice diffusion) were extrapolated from higher temperatures as indicated in Fig. 5. These calculations indicate that both $D^{\mathrm{l}}_{\mathrm{Al}}$ and $\delta_{\mathrm{Al}} D^{\mathrm{b}}_{\mathrm{Al}}$ are significantly enhanced in polycrystalline alumina co-doped with Mn and Ti. The Mn–Ti dopant pair is far more effective than the Fe–Ti couple in enhancing cation lattice diffusion. In the Fe–Ti compositions, Ti^{4+} is dominant unless the iron concentration is well in excess of 2% [8]. Insuf-

TABLE I Aluminium diffusion coefficients in polycrystalline alumina at 1180° C

Composition	$D^{\mathrm{l}}_{\mathrm{Al}}$ (cm² sec⁻¹)	$\delta_{\mathrm{Al}} D^{\mathrm{b}}_{\mathrm{Al}}$ (cm³ sec⁻¹)
Undoped*	2.0×10^{-16}	–
Mn + Ti (= 0.32–0.37%)	3.4×10^{-13}	4.5×10^{-16}
	$(1.9 \times 10^{-14}$–$5.3 \times 10^{-13})$	$(2.3 \times 10^{-16}$–$7.9 \times 10^{-16})$
0.2% Ti‡	6.5×10^{-15}	–
0.05% Mn§	6.0×10^{-16}	–
0.2% Fe†	3.8×10^{-16}	–
0.1% Fe + 0.1% Ti†	5.0×10^{-15}	–
1% Fe†	9.1×10^{-16}	2.7×10^{-18}
2% Fe†	1.7×10^{-15}	3.8×10^{-17}
2% Fe ($P_{O_2} \sim 10^{-5}$)	–	1.8×10^{-16}

*Extrapolated from 1450° C [5].
†Extrapolated from 1450° C [8].
‡Extrapolated from 1475° C [15].
§Extrapolated from 1400° C, this study.

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[*] The reader is referred to the data of Ikuma and Gordon [15] in Fig. 5 for the creep of titanium-doped alumina where the grain-size exponent ($m = 1$) is indicative of interfacial dominated kinetics.

ficient data are available to conclude whether Ti^{4+} or Mn^{2+} is dominant in the Mn–Ti system. However, based on the effect of Mn doping, it is suspected that the concentration of Mn^{2+} is higher in the Mn–Ti couple than the Fe^{2+} concentration in the Fe–Ti couple at comparable compositions of total dopant. Since the aluminium lattice diffusion coefficient at the 0.05% Mn composition lies between those for the 0.2 and 1% Fe compositions, it can be concluded that the $[Mn^{2+}]/[Mn]_T$ ratio is at least four times higher than the $[Fe^{2+}]/[Fe]_T$ ratio in an oxidizing atmosphere.

Finally, some comments should be made concerning liquid phases and their possible role in enhancing sintering and creep rates in the Mn–Ti system. Cutler *et al.* [6] concluded that eutectic liquid formation might be responsible for the low-temperature densification of Al_2O_3 doped simultaneously with Mn–Ti or Cu–Ti. Some recent studies [17] in the system Al_2O_3–$MnTiO_3$ have shown that the eutectic temperature is 1320° C. Since the sintering studies of Cutler *et al.* were conducted at temperatures primarily above 1300° C and at higher total impurity concentrations, their conclusion is plausible. In recent years, Cutler [18] has been able to sinter to high density at 1200–1300° C polycrystalline alumina doped with either MnO–TiO_2 or Cu_2O–TiO_2 impurity pairs (0.5% by weight of each oxide). The creep experiments reported in this paper were conducted at temperatures below 1250° C where liquid formation is unlikely. The lower test temperatures and dopant concentrations, in combination with the observed activation energies and reciprocal grain size effects, strongly suggest that the enhancing effect of the mixed dopant is due to a diffusion effect in the solid state and not to the formation of a liquid phase.

5. Conclusions

Doping polycrystalline alumina simultaneously with small amounts of Mn and Ti leads to significant enhancement in both aluminium lattice and grain-boundary diffusion which permits viscous steady state creep to take place at very low temperatures, i.e. 200° C lower than that observed in undoped material. Newtonian viscous creep deformation is attributed to significant aluminium grain-boundary transport which is enhanced by the presence of divalent manganese.

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