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► To cite this version:

E. Sato, C. Carry. Sintering and yttrium grain boundary segregation in sub-micron grain size alumina. Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-1335-C7-1340. 10.1051/jp4:19937205 . jpa-00251839

HAL Id: jpa-00251839

<https://hal.science/jpa-00251839>

Submitted on 1 Jan 1993

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Sintering and yttrium grain boundary segregation in sub-micron grain size alumina

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ABSTRACT

Sintering behavior with and without external stress was investigated using undoped and doped (1500 ppm yttria) sub-micron α -alumina powders. The yttria doped alumina showed anomalous behavior with grain size around 0.9 μm , a second peak in densification rate during free sintering and a stagnation followed by a steep increase in flow stress during sinter forging. These were thought to correspond to the creep rate plateau regime and to the saturation of grain boundary with yttrium. Yttrium segregation retarded the densification during free sintering, and made the flow stress higher during sinter forging. It also lowered the grain size at which the transition occurred in the rate controlling mechanism of deformation from grain boundary diffusion to interface reaction.

INTRODUCTION

It is well known that grain boundary segregation and precipitation can strongly affect the macroscopic properties of ceramics [1,2]. Generally, grain boundary solute content is thermodynamically calculated from both the material solute content and an apparent free energy for segregation, without any consideration to the microstructure of the material [3]. The density of grain boundary area, however, must be considered in the case where the solubility limit in the bulk is quite small.

Recently, one of the authors proposed a simple geometrical model of segregation where all of the solute is considered to locate at grain boundaries [4]: the solute content at grain boundary is in proportion to the inverse of a grain size until it becomes over-saturated and a new phase is formed. The model was established using dense alumina ceramics doped with 500 ppm yttria [4]. Yttrium grain boundary content varies linearly with a grain size below a given dimension, and it is independent of this above the same value, as schematically shown by the solid line of 500Y in Fig.1 (a). In the latter regime, inter-granular precipitation occurs. This transition strongly affects macroscopic creep behavior [5]: just below the grain-size related transition, a constant strain rate—plateau—regime is observed instead of decreasing in strain rate with increasing in grain size, as shown by the solid line of 500Y in Fig.1 (b).

The model predicts an inverse relationship between the grain size for saturation and the doping level when the solubility limit of the material is quite small. According to the relationship, it could be

possible to obtain sub-micron or nano-grain ceramic materials [6] with a much higher doping level without grain boundary precipitation; for example, more than 1% of yttria in alumina with a grain size lower than 100 nm could be considered. Such highly doped ceramics with a high density of grain boundaries that exhibit solute segregation could show interesting properties at room temperature as well as at high temperature.

The purpose of this paper is to examine the effect of yttria doping into alumina with a sub-micron grain size. The expected segregation behavior of alumina doped with 1500 ppm yttria is shown as the broken line of 1500Y in Fig.1 (a), and a creep rate plateau regime is expected to be observed in the grain size region from 0.5 to 0.8 μm . The behavior of dense ceramics with such a fine microstructure has not been studied because of grain growth during hot pressing of commercial powders. Using powder compacts doped with 1500 ppm yttria, the present authors have already observed an anomalous peak of densification rate during non-isothermal stress-free sintering at almost the same grain size with the expected transition [7]. The technique of sinter forging [8] on partly pre-sintered specimens was adopted in this work in order to observe the mechanical behavior in sub-micron grain size range. Microstructure and flow stress evolution was analyzed to reveal the effect of yttrium grain boundary segregation on the macroscopic mechanical behavior.

Fig.1 Schematic Diagrams of yttrium content at grain boundary $C_{gb}\delta$ (a) and creep rate $\dot{\epsilon}$ (b) as functions of the grain size obtained by Gruffel *et al.* [4,5]. Here C_{gb} denotes the average concentration of yttrium at grain boundary and δ the width of grain boundary. Broken lines are extrapolated from the experimental data shown by solid lines, and dashed-and-dotted lines are drawn based on the present results.

EXPERIMENTAL

Commercially prepared sub-micron α -alumina powders [Criceram, Jarrie, France] were used. The powders were doped with magnesia (500 mass ppm) and yttria (0, 500 or 1500 mass ppm) by the supplier; they are referred as 0Y, 500Y, or 1500Y, respectively. The main impurities are sodium, silicon and potassium, each of which is less than 50 mass ppm. Green compacts with a cylindrical shape of 15 mm height and 10 mm diameter were machined after cold-isostatic-pressing under a pressure of 250 MPa. They were all pre-sintered in a constant heating rate of $1^\circ\text{C}/\text{min}$ up to 1450°C to avoid rapid microstructural change at the beginning of the succeeding processes.

The specimens were sinter forged at 1400°C up to several strains under air atmosphere using Instron machine; they were deformed in a constant crosshead speed condition so as to make the initial strain rate $4.5 \times 10^{-5} \text{ s}^{-1}$. Some of them were sintered at 1400°C without external stresses in a dilatometer. After these treatments, the final density was measured, and the microstructure was observed by scanning electron microscopy on fractured surface to avoid grain growth due to thermal etching.

RESULTS

Free Sintering

Figure 2 shows the densification curves in stress-free sintering at 1400°C. The relative density ρ (upper) and its time derivative dp/dt (lower) are calculated from the final density and the continuously measured shrinkage. Here, $t=0$ denotes the instant when the temperature reaches 1400°C. The fact that yttria doping retards densification [7] is the reason why 1500Y has a lower initial density than 0Y after the same pre-sintering.

While the densification rate of 0Y shows a single maximum, that of 1500Y shows double maxima. Such double maxima are also observed in a constant heating rate sintering of 1500Y [7]. Because the pre-sintering of 1500Y has just stopped at the summit of the first peak in a constant heating rate sintering, the first maximum at the beginning of the subsequent isothermal sintering corresponds to the remaining tail of the first peak in the pre-sintering. The second maximum in Fig.2, therefore, corresponds to the second peak observed in constant heating rate sintering. The anomalous second peak was interpreted an effect of the transition in yttrium grain boundary state [7].

Sinter Forging

Figure 3 shows the development of the density ρ (upper) and the grain size d (lower) during sinter forging at 1400°C with an initial strain rate of $4.5 \times 10^{-5} \text{ s}^{-1}$. The densities and grain sizes measured by individual specimens are shown by circles, while the solid lines show the fitted curves which will be used in further calculations. The density changes during free sintering are also shown in Fig.3 by broken lines.

The external stress during sintering accelerates densification strongly so as to obtain almost 98% density after 6 ks for both 0Y and 1500Y. The specimens sinter forged for more than 6 ks are, however, easy to break. This implies that many micro cracks must be introduced during the last stage of sinter forging, and that either lower strain rates or higher temperatures are needed to obtain dense ceramics.

Figure 4 shows the flow stress σ as a function of strain ϵ or time t during sinter forging. The stress is calculated from the recorded load P as follows:

Fig.2 Isothermal densification curves in free sintering at 1400°C. The upper and lower curves are the relative densities ρ , and their time derivatives dp/dt , respectively.

$$\sigma = \frac{P}{S_0(1 + \dot{\epsilon}_0 t)} \left(\frac{\rho}{\rho_0} \right)^{2/3}, \quad (1)$$

where $\dot{\epsilon}_0$, S_0 , ρ_0 , and ρ are the initial strain rate, the initial cross section, the initial density, and the density obtained from the fitted curves in Fig.3, respectively. The barreling observed in the specimens sinter forged more than 6 ks is ignored.

Although 1500Y has a larger initial grain size and a lower initial density than 0Y, it has an initial flow stress higher than 0Y. This implies that for the same grain size and density 0Y would deform more easily than 1500Y. The increase in stress of 1500Y slows down slightly at a strain of -0.17 followed by a steep increase after a strain of -0.21 : this phenomenon is highly reproducible. Such a stress evolution is not observed in 0Y, whose stress increases constantly. The steep increase in stress of 1500Y starts at the grain size of $0.9 \mu\text{m}$, which is close to the predicted grain size, $0.8 \mu\text{m}$, where a transition in the yttrium grain boundary state could occur (see Fig.1 (a).) The stress evolution of 1500Y proves the existence of a creep plateau regime in the grain size range from 0.7 to $0.9 \mu\text{m}$.

DISCUSSION

In order to analyze the mechanical behavior obtained from the creep and sinter forging experiments, it is necessary to convert them into a constant strain rate condition at the same temperature. High temperature creep behavior is usually expressed by a phenomenological constitutive equation, as follows:

Fig.3 The densification (ρ , upper part) and grain growth (d , lower part) behavior in sinter forging at 1400°C and $4.5 \times 10^{-5} \text{s}^{-1}$. The measured points are shown by circles. The densification behavior in free sintering at the same temperature is also shown by broken lines for comparison.

Fig.4 True stress-true strain curves in sinter forging at a temperature of 1400°C with an initial strain rate of $4.5 \times 10^{-5} \text{s}^{-1}$.

$$\dot{\epsilon} = A \sigma^n d^{-p} \exp \frac{Q}{RT}, \quad (2)$$

where n is the stress exponent, p the grain size exponent, Q the apparent activation energy, R the gas constant, and A a constant. The values of n , p and Q were measured by Gruffel [5] and they are summarized in Table I. The creep diagram shown in Fig.1 (b) is converted into a constant strain rate diagram at 1400°C and is drawn as broken lines in Fig.5.

The forging data are also converted into a constant strain rate diagram using the value of $n=1.1$ and 1.6. In Fig.5, the circles correspond to the specimens whose grain sizes are measured while the solid lines connecting them are obtained from fitted lines in Fig.3.

For 0Y, the forging data are in fairly good agreement with the creep behavior. A slight change in slope is observed above 1 μm in the forging data, which corresponds the transition from deformation controlled by interface reaction to that by grain boundary diffusion. Although the transition is drawn as a sharp change in gradient in the schematic diagrams of Figs.1 and 5, the original creep data shows a gradual change in slope, similar to that observed in the forging data.

The forging stress of 1500Y shows a certain stagnation at grain sizes from 0.7 to 0.9 μm and a subsequent steep increase instead of a constant increase due to grain growth. The grain size region of the stagnation is a little higher than that of the predicted plateau regime, from 0.5 to 0.8 μm . This discrepancy can be explained by the lower densities in the forging specimens, since yttrium segregates more strongly on remaining pore surfaces than at grain boundaries [3].

The steep increase in the forging stress of 1500Y is in good agreement with the steep decrease in the creep rate observed just after the plateau regime for 500Y. The deformation in 500Y is controlled by grain boundary diffusion after the plateau as well as before [5]. Since the stress observed in the finest grain size region in 1500Y shows much lower dependency of grain size than that for the deformation controlled by grain boundary diffusion, it can be deduced that an interface reaction controls the high

Table I Parameters in the constitutive equation (eq.2) obtained by Gruffel *et al.* [5].

material	grain size region	n	p	Q
0Y	finer	1.8	1.0	520 kJ/mol
	coarser	1.1	3.0	520 kJ/mol
500Y	finer <1.4 μm	1.6	3.0	600 kJ/mol
	plateau 1.4–2.3 μm	1.6	0.0	600 kJ/mol
	coarser >2.3 μm	1.3	3.0	800 kJ/mol
1500Y	coarser >0.8 μm	1.3	3.0	800 kJ/mol

Fig.5 Deformation diagram at the temperature 1400°C and the strain rate $4.5 \times 10^{-5} \text{s}^{-1}$: the circles and solid lines show the present results, the broken lines the creep results [5], and the dashed-and-dotted line the deduced behavior in finest region.

temperature deformation of yttria doped alumina for grain sizes lower than 0.6 μm as indicated by dashed-and-dotted lines in Figs.1 and 5.

The deformation in these regions is considered to be superplastic where grain boundary sliding contributes mainly because the microstructure remains equiaxed before and after the deformation except the plateau regime [5]. The grain boundary sliding is accommodated and controlled by grain boundary diffusion except in finer grain size region where it is controlled by grain boundary reaction. Lartigue *et al.* [9] observed a certain activity of lattice dislocations only in the plateau regime, which these authors suggested were emitted from sliding grain boundaries for accommodation. The ability to emit lattice dislocations seems to be possessed only by the grain boundaries with yttrium just below the content of saturation. In free sintering, however, any lattice dislocation activity is not likely to contribute to densification, but the anomalous densification peak could correspond to an anomalous variation of the apparent diffusion coefficient.

CONCLUDING REMARKS

The alumina powder doped with 1500 ppm yttria shows anomalous behavior at high temperature with grain size around 0.9 μm : a second peak in densification rate during free sintering, and a stagnation followed by a steep increase in flow stress during sinter forging. These phenomena correspond to the creep plateau regime and to the saturation of grain boundary with yttrium. The grain boundary saturation occurs at a given grain size and it is inversely related to the doping level. This implies that finer grained alumina could be doped with higher yttria without grain boundary precipitation.

Yttrium segregation at grain boundary of alumina retards the densification in free sintering, and makes the flow stress higher in creep and sinter forging. It also lowers the grain size at which the transition in the rate controlling mechanism of deformation from grain boundary diffusion to interface reaction occurs.

REFERENCES

- [1] COOK R. F., *Acta Metall.*, **38** (1990) 1083.
- [2] LI C. W. and KINGERY W. D., *Adv. in Ceramics vol. 10*, Ed. Kingery W. D., Am. Ceram. Soc. (1985) 368.
- [3] HONDROS E. D. and SEAH M. P., *Metall. Trans.*, **8A** (1977) 1363.
- [4] GRUFFEL P. and CARRY C., *J. Europ. Ceram. Soc.*, **11** (1993) 189.
- [5] GRUFFEL P. and CARRY C., *Proc. 11th Riso Int. Symp. on Metallurgy and Materials Science*, Eds. Bentzen J. J. *et al.*, Riso Int. Lab. (1990) 305.
- [6] AVERBACK R. S., HOFER H. J., HAHN H. and LOGAS J. C., *Nanostructured Materials*, **1** (1992) 173.
- [7] SATO E. and CARRY C., submitted to *3rd Europ. Ceram. Soc. Conf.*, Madrid, (1993).
- [8] VENKATACHARI K. R. and RAJ R., *J. Am. Ceram. Soc.* **70** (1987) 514.
- [9] LARTIGUE S., PRIESTER L., DUPAU F., and CARRY C., *Mater. Sci. Eng.*, in press.