Effect of liquid-forming additives on low-temperature superplastic deformation of alumina

L. A. XUE
Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109, USA

It has recently been reported that in the Y_2O_3-stabilized tetragonal zirconia phase (TZP) system the addition of a small amount of transition-metal oxides (e.g. CuO, MnO and ZnO) which form a liquid or amorphous grain boundary phase significantly enhances superplasticity [1, 2]. In CuO-added 2Y-TZP abrupt changes have been found in the stress exponent and activation energy across the melting temperature, which are consistent with the proposed deformation mechanism that the superplasticity in these cases is diffusion-controlled below the melting temperature and is interface-controlled above that [1]. Similar deformation characteristics have also been observed in an 80 wt% 2Y-TZP/Al_2O_3 composite doped with liquid-forming additives [3].

The deformation of transition-metals-doped alumina has been studied before [4–10]. Due to the coarse-grained (usually of the order of 10 μm) samples used in these studies, deoformation has always been conducted in the creep range with strain rates $<10^{-5}$ s^{-1} and to small strains. Creep enhancement by the dopants has generally been observed, especially in alumina simultaneously doped with compensating dopants, e.g. $Ti^{4+} + Cu^{2+}$ [4], $Ti^{4+} + Fe^{2+}$ [5] and $Ti^{4+} + Mn^{2+}$ [6]. The influence of the transition-metal additives in these studies has been interpreted in terms of defect chemistry [10], although liquid phases may be present in systems doped with $Ti^{4+} + Cu^{2+}$ [4]. We have recently shown that, when doped with 2 mol% liquid-forming additives containing compensating dopants, a commercial alumina powder can be sintered to a dense ultrafine-grained (0.3 μm) ceramic at a temperature as low as 1070 °C [11]. Such a fine-grained microstructure should enable us to conduct the deformation study in the superplastic flow region at relatively low temperatures. In this letter we report the superplastic deformation behaviour of low-temperature sintered alumina doped with 2 mol% liquid-forming additives which shows a greatly enhanced superplasticity and a similar temperature-dependent characteristic to that found in CuO-added 2Y-TZP.

A commercial high-purity ($> 99.99\%$) alumina powder (TM-D, Taimei Chemicals, Tokyo, Japan) was used as the starting material, which was subsequently doped with a liquid-forming additive (0.9 mol% TiO_2 + 0.9 mol% CuO + 0.1 mol% B_2O_3 + 0.1 mol% MgO). Details of the material preparation were described in [11]. Specimens with densities greater than 98.5% theoretical (which was achieved by sintering at 1070 °C for 1 h) were used in

the deformation study. Specimens for testing were cut from sintered samples into square bars of aspect ratio 2.2. Deformation was conducted in uniaxial compression in air, between 950 and 1200 °C, with strain rates from 3×10^{-6} to 5×10^{-3} s^{-1}. Other experimental details were similar to those reported in [1].

The as-sintered doped alumina features an ultrafine microstructure with an average grain size of 0.3 μm, as can be seen from Fig. 1a. As discussed previously [11], abnormal elongated grain growth

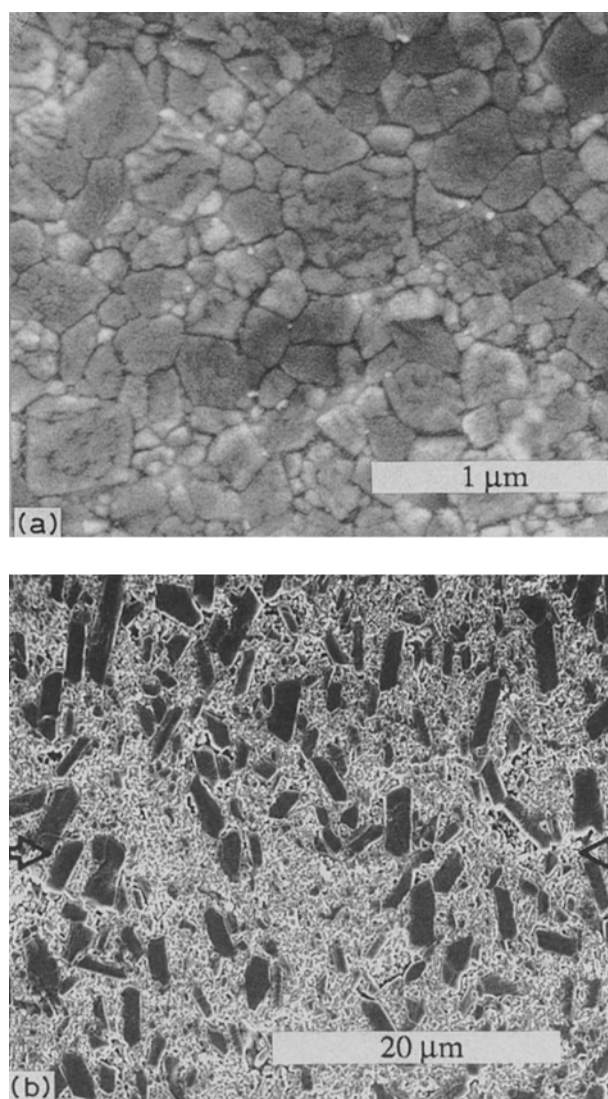*Figure 1* Scanning electron micrographs of alumina doped with 2 mol% liquid-forming additives: (a) before deformation and (b) after deformation at 1200 °C to a true stain of −0.6. The compression axis is indicated by the hollow arrows.

occurred during sintering at higher temperatures or for a prolonged sintering time. This kind of abnormal grain growth also developed during the deformation, which was especially pronounced at temperatures higher than 1100 °C. Fig. 1b shows the microstructure of a sample deformed at 1200 °C and at a strain rate of 2.4×10^{-3} s^{-1} to a true strain of -0.6, showing predominant abnormal grain growth. At low strain levels (about 0.05) at which the stress–strain rate data were taken, however, the volume fraction of these larger elongated grains was small, being $< 10\%$. According to Chen's continuum model for composites [12], this "inclusion phase" (i.e. these abnormal grains) would not alter the overall flow stress in any significant ways. The existence of these large abnormal grains does, nevertheless, introduce local stress concentrations and therefore cause cavitation at high strain rates even under compression. As a result, the obtainable tensile strain of this material has been found to be rather low, being only about 15%. In view of this, the tensile superplasticity of this doped alumina seems to be limited owing to the occurrence of the abnormal grain growth.

It is interesting to observe from Fig. 1b that during deformation these elongated grains align preferentially along the direction perpendicular to the compression axis. This preferred orientation has been found to be deformation strain-dependent; specimens deformed at the same temperature and strain rate, but to different strains, show that the higher the strain is, the higher the degree of the alignment. The phenomenon may be employed in the future as a viable technique to achieve preferred orientation of fibre/whisker in ceramic composites.

The superplastic flow behaviour of the doped alumina is summarized in Fig. 2. For comparison, the flow stress–strain rate relation at 1250 °C of a pure alumina with an average grain size of 0.5 μm is also shown [13]. It is obvious that the additive greatly enhances the superplasticity of alumina; it

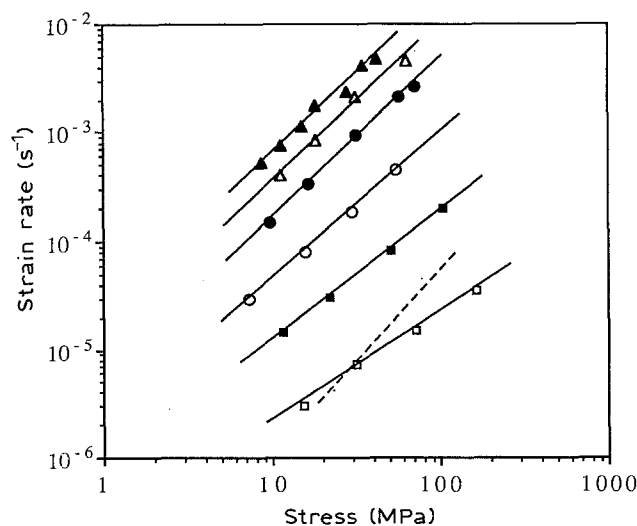lowers the deformation temperature by 300 °C, or (when extrapolating the 1250 °C pure alumina data to 1200 °C) increases the strain rate by four orders of magnitude. The apparent melting temperature for the liquid phase in this system seems to be in the range 1050–1100 °C, which is in agreement with the differential thermal analysis finding that shows the onset of an endothermic peak at approximately 1040 °C [11], but a significant deformation enhancement has already been found at a temperature as low as 950 °C. A similar observation has been made in the CuO-added 2Y-TZP system [1]. The degree of the enhancement by the dopants is in good agreement with that found (10^4) by Cannon [4] for alumina doped with 2 mol% Ti + 2 mol% Cu at 1200 °C in the creep range.

It can be noted from Fig. 2 that the slopes of these stress–strain rate data for the doped alumina, which are near unity at 950 °C, become steeper at higher temperatures. In all cases the slopes are less steep than that for the pure alumina. The change in the slope means that the stress exponent, n, increases with the temperature. As highlighted in Fig. 3, the value of n increases gradually as the temperature increases, then goes through a somewhat abrupt transition at a temperature around 1100 °C. The n-value (between 1 and 1.5) found in the present study is relatively low compared with that for pure alumina (about 1.7), and is characteristic of superplastic flow.

The temperature dependence of the superplastic flow undergoes a corresponding transition, becoming lower at higher temperatures (Fig. 4). The activation energy at lower temperatures (457 kJ mol^{-1}), which is comparable with that of pure alumina (460 kJ mol^{-1} [13]) decreases quickly to 243 kJ mol^{-1} at higher temperatures.

The transition in superplastic flow behaviour in the vicinity of the melting temperature of the liquid phases, i.e. increase in stress exponent and decrease in activation energy, has been identified in the CuO-doped 2Y-TZP system as the consequence of the grain boundary liquid phase formed [1]. The
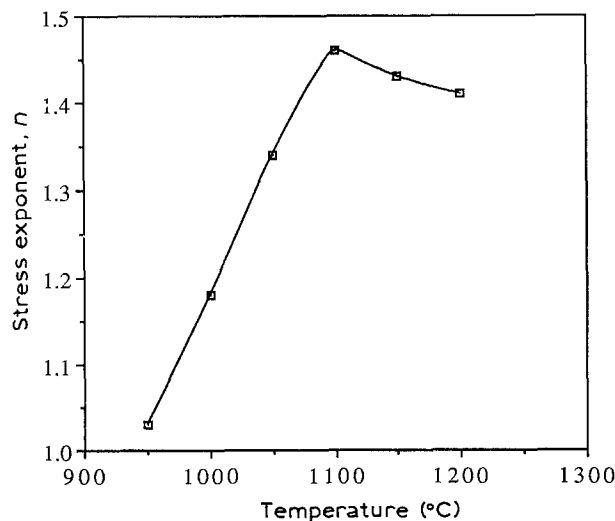

Figure 2 Flow stress–strain rate relationships for the doped alumina at various temperatures: (□) 950, (■) 1000, (○) 1050, (●) 1100, (△) 1150 and (▲) 1200 °C. The broken line is for a pure fine-grained (0.5 μm) alumina at 1250 °C [13].

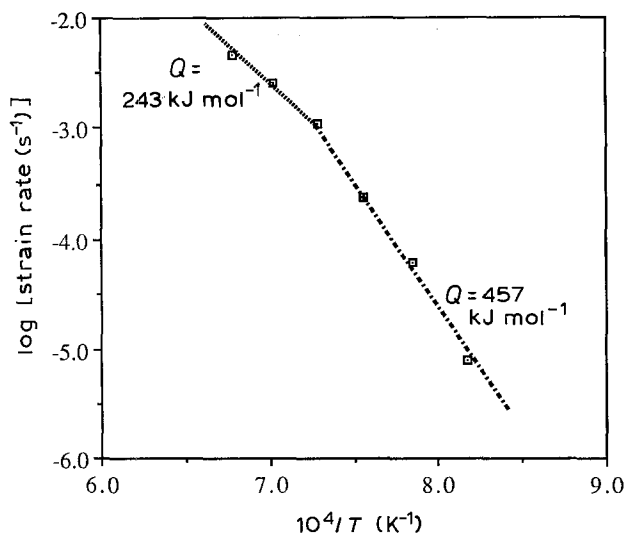Figure 3 Temperature dependence of the stress exponent, n, for the doped alumina.

Figure 4 Temperature dependence of strain rate for the doped alumina at 40 MPa. The values of the activation energy, Q are indicated for the two temperature ranges.

deformation mechanism there, which was dominated by a grain boundary phase-enhanced diffusion below the eutectic temperature, shifted to a liquid-enhanced interface-controlled one at higher temperatures [1]. The close similarities in the deformation characteristics between the CuO-doped 2Y-TZP and the doped alumina in the present study tends to suggest that these two deformation mechanisms are also operative in the latter system.

To summarize, 2 mol % liquid-forming additives containing compensating dopants enhances the deformation rate of alumina by four orders of magnitude. At low strain rates or high temperatures, elongated abnormal grain growth occurs during the superplastic deformation, which gives rise to cavitation at large strains and hence becomes the cause of rather limited tensile strain (about 15%) for the material. There are abrupt changes in the stress exponent and activation energy across the apparent melting temperature of the liquid phase, suggestive of a shift of the deformation mechanism from diffusion control below the melting temperature to interface control above that.

Acknowledgement

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