Al_2O_3 melts) with the position of the calculated miscibility gap indicates that in this case liquid immiscibility occurs as a precursor to the observed metastable mullite crystallization, as discussed in the paper in question.[3]

We believe that the miscibility gap which we calculated from the phase diagram liquidi represents a metastable equilibrium condition between the separated glassy phases.[2] This metastable equilibrium may be circumvented by kinetic phenomena when rapid cooling techniques are used. Thus, rapid quenching can suppress the miscibility gap. Furthermore, because of the resulting highly energetic state of the glass, subsequent heating can cause decomposition reactions at temperatures $<T_{g(eq)}$. Our experimental quench-cooling rates were slow enough to provide essentially metastable equilibrium conditions. The cooling rate used by Jantzen and Herman[1] considerably suppressed the miscibility gap. Their questions emphasize the importance of considering metastable transformations[9] in the development of ceramic microstructures and reemphasize[2] the difficulty of experimentally defining the detailed miscibility gap in the system SiO_2-Al_2O_3.

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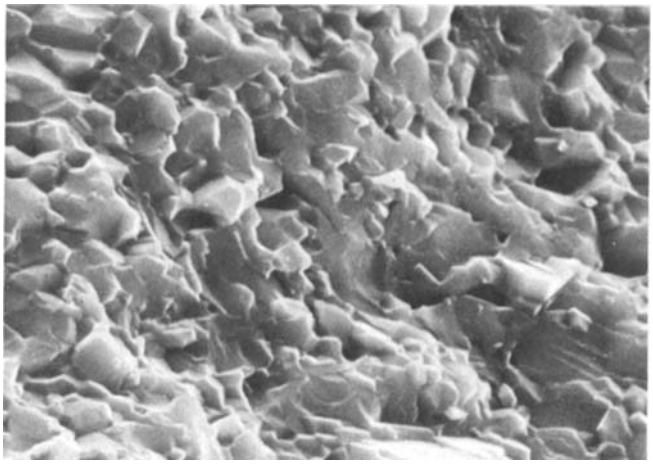

Fig. 1. Microstructure of as-hot-pressed Al_2O_3, average grain size ≈2 μm.

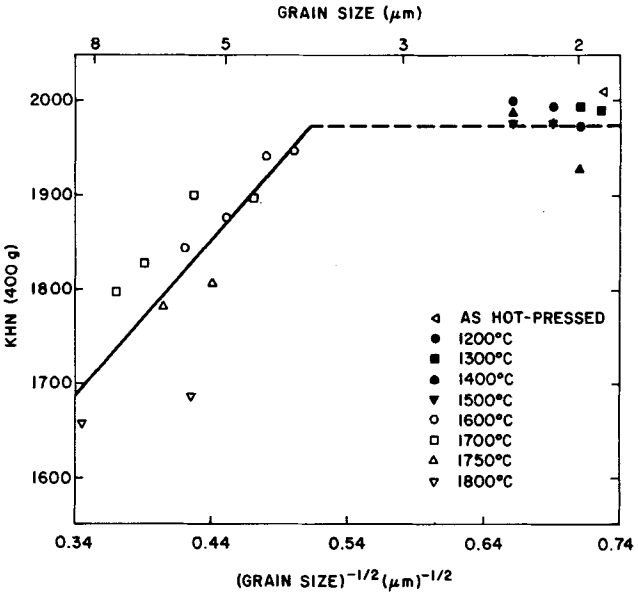

Fig. 2. Variation of microhardness with average grain size.

Microhardness of a Fine-Grain-Size Al_2O_3

S. D. SKROVANEK* and R. C. BRADT*

THE hardness of ceramics, which is important in many abrasive and wear applications, is related to the properties of the material and to the indenter, its geometry, the sample preparation, and the measurement technique.[1] The present note reports the variation with grain size of the microhardness of a dense hot-pressed polycrystalline Al_2O_3. Two microhardness regions are observed: a classic Hall-Petch region at larger grain sizes and a region where microhardness is independent of grain size at fine grain sizes.

Commercial α-Al_2O_3 with 0.5% MgO, hot-pressed at 1600°C, was used. Density, as measured by Archimedes' method, was 3.99 g/cm^3. The as-hot-pressed microstructure is shown in Fig. 1. Specimens (≈1 cm cubes) were annealed at 1200° to 1800°C, yielding a range of grain sizes which were measured by the linear intercept technique on fracture surfaces observed in an SEM. Microhardness was measured on diamond-polished surfaces, using a 400-g load on a Knoop indenter with a commercial microhardness tester.* The load was applied automatically over a 15-s interval and allowed to remain on the sample for an additional 30 s. The 50-μm indentation traversed several grains and grain boundaries. Indentations were repeated until 20 distinct, symmetrical, uncracked indentations were achieved. Averages were calculated and the variation determined as the 95% confidence limits using the t distribution. Other details are described elsewhere.[2]

Figure 2 shows the variation of microhardness with average grain size on the classic Hall-Petch plot. For clarity, error bars are not included; however, the 1-h anneal at 1600°C typically yielded $(KHN)_{400}=1943\pm20$ kg/mm^2. Two distinct regions of microhardness/grain size behavior are evident: Hall-Petch behavior at large grain sizes and a fine-grain-size region where hardness is independent of grain size. Regression analysis of the Hall-Petch region yielded:

$$(KHN)_{400}=1118+1673(gs)^{-1/2} \quad (1)$$

where the grain size is in micrometers and the microhardness is in kg/mm^2. Comparable Hall-Petch behavior has been found in a PZT,[3] a directionally solidified MgO·$MgAl_2O_4$ eutectic,[4] a sintered Al_2O_3,[5] and a crystallized glass-ceramic.[6] Constant microhardness/grain size regions have been reported at very fine grain sizes for MgF_2 and ZnS (Ref. 7) and again for a glass-ceramic.

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Although evidence does exist for both types of microhardness/grain-size-dependence, these results for Al_2O_3 are the only ones showing both types of behavior in the same material.

The hardness/yield-strength correlation discussed by Chin *et al.*[8] provides a direct comparison. Brass,[9] titanium,[10,11] a 1010 steel,[12] and nickel[13,14] exhibit Hall-Petch regions at larger grain sizes. However, at very fine grain sizes (≈ 1 μm) the 1010 steel, as reported by Abrahamson,[12] and the nickel, as reported by Thompson,[13] both exhibit yield-strength trends analogous to that of the fine-grain-size Al_2O_3 microhardness behavior of Fig. 2. It has been suggested that a saturation in grain-size strengthening occurs and the grain size dimension as applied to any dislocation pileup length is no longer applicable. A source length related to the dislocation substructure should be used, as suggested in the models of Kuhlman-Wilsdorf.[15,16]

In the fully dense, hot-pressed Al_2O_3, the existence of dislocation substructure has been demonstrated, both indirectly[17] and directly.[18,19] This substructure apparently results in the departure from the grain-size-dependent Hall-Petch mechanism at very fine grain sizes. That it is the hot-pressing-induced substructure which is responsible for the microhardness behavior is strongly supported by the distribution of microhardnesses and their annealing temperatures in the two regions in Fig. 2. The Al_2O_3 was hot-pressed at 1600°C and presumably there was some annealing out of the less stable dislocation structure on cooling or during the brief hold at that temperature. On annealing, there was no microhardness decrease nor grain growth, until the 1600°C anneal, which may be interpreted as indicating a relatively stable substructure for the lower-temperature anneals. The present writers conclude that the microhardness of fine-grain-size, hot-pressed, dense, polycrystalline Al_2O_3 possesses two regions of microhardness variation with grain size. At large grain sizes, the classic Hall-Petch trend is followed. However, at finer ones, there exists a "constant" microhardness region where the hot-pressing dislocation substructure, rather than the grain boundaries, is the critical structural parameter for determining the microhardness.

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Observation of Viscoelastic Strain Recovery in Hot-Pressed Silicon Nitride

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It is generally agreed that the high-temperature (>1100°C) mechanical properties of magnesia hot-pressed silicon nitride are controlled by a viscous amorphous glass phase which resides at the grain boundaries and/or triple points.[1,2] This grain-boundary phase is the combined product of oxidation and hot-pressing additives[1,3–9] and is a magnesium calcium silicate.[10]

More specifically, uniaxial creep testing[11–13] shows that the activation energy for the creep process is in reasonable agreement with the activation energy for viscous flow of silicate glasses similar in composition to the grain-boundary phase and that the stress dependence of the creep rate is consistent with mechanistic models[11,13] of creep deformation via grain-boundary sliding and associated viscous grain-boundary glass flow. Further, dislocation activity is far too low to account for observed creep deformations.[14] These observations indicate that during creep magnesia hot-pressed silicon nitride behaves as an aggregate of elastic nondeformable grains, bonded by a viscous grain-boundary phase which controls creep deformation due to relative motion of the elastic grains.

It may then be assumed that such an aggregate of elastic grains and a viscous liquid would display interesting rheological effects and, in contrast with metals, might exhibit appreciable viscoelastic strain recovery when applied stresses are reduced after creep at high temperatures. Such recovery was observed in a lithium zinc silicate glass-ceramic.[15] Considering this possibility, interrupted uniaxial-tension creep tests were conducted in which applied stress was reduced to near zero after accumulation of varying degrees of creep strain. The immediate concern was to see if recovery occurred and, if so, its extent and the important parameters.

Figure 1 shows a representative recovery curve and displays the strain response for recovery from 0.962% strain at 1204±2°C and from a prior creep stress of 103.3 MN m^{-2}. As expected, recovery occurred and was characterized by an extremely high initial negative strain rate. After ≈3 h, the recovery rate slowed and after ≈24 h approached the experimental limit of strain rate resolution of 10^{-9} s^{-1}. Generally, the total recovered strain approached 0.1% absolute strain or roughly 5 to 10% of the previous creep strain.

We are confident that this recovery is a real phenomenon and not an artifact of extensometry; this conclusion is based on stability and resolution checks of our extensometry and equipment during tests

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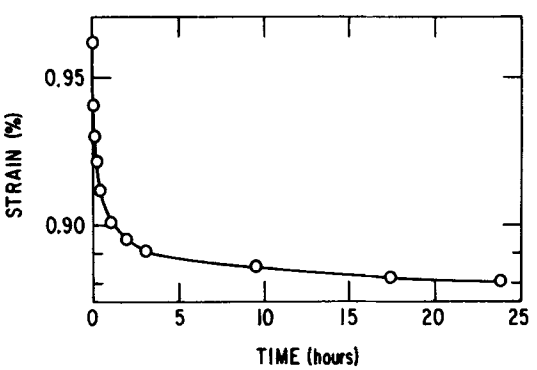

Fig. 1. Strain vs time curve for recovery at 1204°C; prior stress 103.3 MPa.