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The influence of dopants and complexion transitions on grain boundary fracture in alumina

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ABSTRACT

The fracture of micro-cantilever Al_2O_3 specimens containing single grain boundaries is quantified via in situ bending experiments performed in the transmission electron microscope. The type of grain boundary complexion plays a dominant role in determining the fracture response, while the dopant chemistry has a secondary effect for the same complexion type. More 'ordered' complexions, those containing sub-monolayer adsorbates, are tougher than the undoped material. The behaviors of SiO_2 and Y_2O_3 doped Al_2O_3 with different complexions are compared and contrasted. In general, grain boundaries exhibiting more 'disordered' complexions types, those with multilayer adsorbates, are embrittled relative to undoped Al_2O_3.

1. Introduction

Predicting and controlling fracture remains a key focus of structural ceramic science. Hall-Petch scaling often provides a basis for tailoring mechanical properties of deformable polycrystalline materials [1–8]. The phenomenon generally extends to many brittle ceramics, although the mechanisms may be distinct. However, some aspects of the grain size dependence of mechanical properties in many ceramics remain anomalous. Experiments as diverse as mechanical tension [9], compression, three-point bending [10], acoustic emission [11], and dry sliding wear [12] all reveal a discontinuous change in properties as a function of grain size for a wide range of structural ceramics such as α-Al_2O_3, β-Al_2O_3, SiC, TiO_2 B_4C, $MgAl_2O_4$, Si_3N_4 and UO_2 [9,10,13]. At larger grain sizes the systems tend to be embrittled relative to Hall-Petch extrapolations from finer grain sizes. α-Al_2O_3 is amongst the most studied structural oxides and a discontinuity in its mechanical properties with grain size has been reported in a number of individual studies [9–15]. This general trend emerges in key reviews of the subject, and has been also appreciated in individual studies since at least the early 1970's [9–15]. Despite numerous investigations, a lack of a satisfactory fundamental understanding of the phenomenon persists. A common feature in these materials is that the plot of strength (σ) versus inverse root grain size ($G^{-1/2}$) is said to have two branches. The coarse grain branch of the data tends to extrapolate towards zero strength with increasing grain size rather than the single crystal value anticipated by the Hall-Petch relation. The response persists across a wide range of temperatures; for example in α-Al_2O_3 between −196 and 1000 °C. Fig. 1 reproduces an example plot from Rice [9] for α-Al_2O_3 flexural σ-$G^{-1/2}$ data from the literature with the approximate single crystal value highlighted.

The published literature provides several potential explanations for the deviation from the Hall-Petch behavior towards embrittlement at coarser microstructures [9,13]. (I) It was suggested that using the average grain size, rather than the grain size at the crack initiation point, where an abnormal grain is often located, introduces an error in the analysis. However, detailed treatments suggest that this cannot account for all of the experimental results [9]. (II) Flaw sensitivity has been proposed as an explanation, where the two branches on the σ-$G^{-1/2}$ plot intersect at the value grain size being equivalent to a critical flaw size, C. In the coarse grain regime, the size of internal flaws such as pores scales with grain size. In the fine grain regime, the largest flaws result from surface and other grain size independent processing defects. In this case, the σ-$G^{-1/2}$ slope in the coarse grained regime corresponds to K_{IC} and the fine grain slope is closer to 0 and most sensitive to sample

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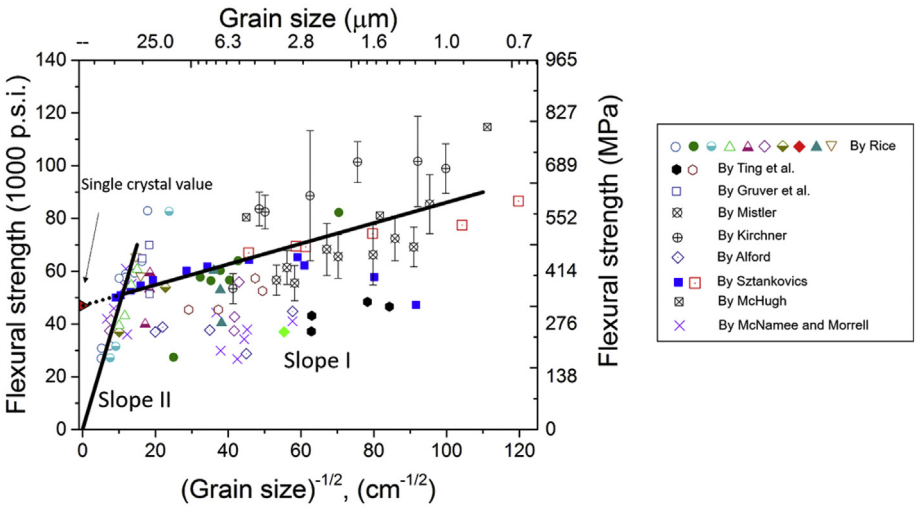

Fig. 1. Flexural strength of Al_2O_3 as a function of grain size reproduced from reference [9] The red symbol refers the approximate single crystal value of Al_2O_3. Rice's samples are hot-pressed and sintered 96% and 99% Al_2O_3, where solid symbols represent tensile strength (G) obtained based on average grain size, open symbols represent individual G or cluster size at origin, and half-filled symbols are G in a grain cluster from which failure originated [9]; Ting et al.'s sample are 99% sintered Al_2O_3 with no data correction (solid) and with correction (open) [45]; Gruver et al. for a commercial 96% sintered Al_2O_3 [46]; Mistler [47] and Alford [48] for sintered Al_2O_3; Kirchner for hot-pressed sample [49]; Sztankovics for hot pressed sample with (solid) or without data correction (open) [50]; McHugh for 0%–5.5% Mo–Al_2O_3 [51]; McNamee and Morrell for 99% sintered Al_2O_3 [52]. The readers are referred to reference [9] for detailed samples information and data correction procedures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

preparation. However, the fracture toughness values extracted from this analysis in the coarse grain branch are consistently lower than measured values. Additionally, it is also known from more recent work on nanograin ceramics that Hall-Petch strengthening continues to <10 nm grain sizes (i.e. the σ-$G^{-1/2}$ slope is not zero) [16]. (III) Environmental sensitivity could also play a role in the flaw sensitivity that impacts the σ-$G^{-1/2}$ trends. However, it has been found that for oxides such as Al_2O_3 exposure to H_2O only affects mechanical response in-situ and that pre-exposure has no measureable effect when subsequently tested in dry conditions [13]. The double branched σ-$G^{-1/2}$ behavior persists under a variety of environmental conditions and temperatures. (IV) The fracture toughness is hypothesized to vary as a function of grain size due to differences in the tortuosity of the crack fracture path and microcracking behavior [17]. This hypothesis is based on reanalysis of the fracture strength data used to construct the σ-$G^{-1/2}$ plots in Ref. [18] and has not been quantitatively verified through detailed geometric analysis of the experimental samples. Nevertheless, it is supported by comparison of the relative response of cubic and non-cubic systems [17].

Measurements of acoustic emission during Hertzian contact, as a function of grain size, indicate a transition to grain boundary microcracking in a similar grain size regime, where the σ-$G^{-1/2}$ curve tends to embrittle [11]. This loading state is not flaw sensitive, and the behavior was attributed to a transition between length scales where the matrix is effectively mechanically homogeneous or heterogeneous. Dry sliding wear experiments performed on Al_2O_3 also indicate an anomalous grain size dependent response, in a similar size regime, where the deformation mechanism transitions from plasticity and light erosion, to grain pull-out [14]. Qualitatively, grain pull-out tends to occur during polishing of coarse grained Al_2O_3, while it is less common in fine grained material. While the stress states during these experiments are complex and hard to define, they are less flaw sensitive and suggest that embrittlement may be more intrinsic to the grain boundary properties.

Annealing time and temperature have received little consideration in the interpretation of the σ-$G^{-1/2}$ response, where grain size is assumed to be an isolated variable. In fact, many published studies do not describe heat treatments making re-interpretation of the data challenging. Reported σ-$G^{-1/2}$ measurements in Al_2O_3 often extend to grain sizes in the range of 200–400 μm. To achieve ≈400 μm grain sizes in high purity Al_2O_3, where abnormal and discontinuous grain growth does not occur, samples must be annealed at, for example, 2020 °C for ≈100 h or 1900 °C for >1000 h [19]. Such high temperatures and long annealing times were not utilized in the literature [9,13]. Instead, large grain sizes were achieved via discontinuous or abnormal grain growth. Discontinuous and abnormal grain growth both break self-similarity associated with normal grain growth, but discontinuous growth results in a unimodal grain size distribution, whereas abnormal grain growth produces a bi-modal or multimodal distribution. In both cases, a change in grain growth mechanism typically occurs. The mechanisms for abnormal and discontinuous grain growth in Al_2O_3 have been investigated extensively since Coble's early work on controlled normal grain growth [20,21]. Abnormal grain growth in Al_2O_3 has been associated with grain boundary 'phase' transitions called complexion transitions [19]. Grain boundaries in this system can undergo an entropically induced transformation in the local equilibrium structure and chemistry as a function of temperature and chemical potential. Like in a bulk phase transition, the complexion transition produces a discontinuous change in the properties, such as grain boundary mobility, grain boundary diffusivity, grain boundary mechanical properties, grain boundary thermal conductivity, etc. [19,22,23] The distribution of high mobility boundaries surrounding a certain grain can allow it to grow abnormally fast relative to grains coordinated by different lower mobility complexions. The full details of the relationship between complexions and grain growth are beyond the scope of the current introduction and further explanation can be found in references [19,24–26]. Al_2O_3 undergoes a series of complexion transitions as a function of temperature and/or chemical potential, with 6 different general types of complexions having been observed. These 6 complexion types correlate with 6 different regimes of average grain boundary mobility. The complexion transitions occur in a manner analogous to layering