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Fracture of single crystal $MgAl_2O_4$

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The fracture of single crystal, stoichiometric $MgAl_2O_4$ spinel, was investigated for the (1 0 0), (1 1 0), and (1 1 1) from room temperature to 1500° C. Two regions of fracture behaviour were observed; a low temperature elastic region where K_{Ic} decreased with increasing temperature, and an elevated temperature region where K_{Ic} increased rapidly with increasing temperature. The elastic region is explained primarily by the decrease of elastic modulus with increasing temperature, whereas the rapid increase of K_{Ic} at elevated temperature is attributed to plastic flow in the vicinity of the crack tip

1. Introduction

Utilization of brittle ceramic materials at elevated temperatures depends on their overall mechanical behaviour; and often, specifically on their fracture characteristics at these temperatures. The effects of temperature on the strengths of numerous polycrystalline ceramics and several single crystal materials have been extensively reported; however, the effects of temperature on single crystal fracture parameters are not as well documented. Three exceptions are the studies of St. John on silicon [1], Wiederhorn *et al.* on sapphire [2] and Henshall *et al.* on silicon carbide [3]. St. John propagated cleavage cracks in Si on the (1 1 1) at room temperature and elevated temperatures, while the sapphire study was on the $(1 0 \bar{1} 0)$, and the SiC investigation involved cracks on the $(1 1 \bar{2} 0)$. These studies suggest that the single crystal cleavage process at low temperatures is fundamentally that of the simple rupture of bonds without the presence of associated dislocation processes at the crack tip. However, at elevated temperatures, > 800° C in silicon, > 600° C in sapphire, and > 800° C in SiC, it appears that dislocation processes become active at the crack tip and cause a marked increase in both the fracture toughness, K_{Ic}, and the fracture surface energy, γ_f. A form of brittle to ductile (less brittle) transition occurs. This paper reports and analyses the effect of temperature on fracture on the (1 0 0), (1 1 0), and (1 1 1) planes of stoichiometric $MgAl_2O_4$ spinel, a brittle ceramic which exhibits plastic flow only at elevated temperatures [4].

2. Experimental procedure

The $MgAl_2O_4$ single crystals fractured in this study were transparent commercial boules [5], approximately 3 cm in diameter with ⟨1 0 0⟩, ⟨1 1 0⟩, and ⟨1 1 1⟩ growth directions. The reason these orientations were specifically chosen for study is that $MgAl_2O_4$ has a Zener Ratio of 2.43 with the Young's elastic modulus a minimum in the ⟨1 0 0⟩ and a maximum in the ⟨1 1 1⟩ [6]. The cubic structure of $MgAl_2O_4$ readily permitted the preparation of specimens to be fractured on (1 0 0), (1 1 0), and (1 1 1) from the corresponding growth directions. Individual specimens were diamond sawed and ground to rectangular prisms (~ 3 cm × 0.25 cm × 0.25 cm), whose lengths were coincident with the growth directions. X-ray diffraction, back reflection Laue method, was used to establish the orientations of the sides; {1 0 0} for the (1 0 0); {1 1 1}, and {2 1 1} for the (1 1 0); and {1 1 0} and {1 1 2} for the (1 1 1) specimens, respectively.

Fracture toughness measurements were made using the controlled surface microflaw technique popularized by Petrovic *et al.* [7]. Knoop indentations (1000 g) were made with the long diagonal of the indenter perpendicular to the sample lengths, parallel to: ⟨1 0 0⟩ for the (1 0 0), ⟨2 1 1⟩ for the (1 1 0), and ⟨1 1 0⟩ for the (1 1 1) specimens. Indent residual stresses were removed by polishing with 6 μm diamond paste in the manner described by Petrovic *et al.* [8]. Indented specimens were broken in three-point bending (1.8 cm span, 0.254 cm min^{-1} cross-head speed) on a commercial testing machine. Some (1 1 0) specimens were also tested

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at 2.54×10^{-2} and 5.08×10^{-3} cm min^{-1}. Fractures propagated in a ⟨1 0 0⟩, ⟨1 1 1⟩, and ⟨1 1 2⟩ on the (1 0 0), (1 1 0), and (1 1 1) respectively. For elevated temperature measurements, specimens were tested in a vertical furnace by raising the specimen into the furnace hot zone, and testing immediately on thermal equilibration. K_{Ic} was calculated from the following equation:

$$K_{\mathrm{Ic}} = 2.06\,\sigma_{\mathrm{f}}(a/\pi)^{1/2}, \qquad (1)$$

where (σ_{f}) is the measured fracture strength and (a) is the flaw depth. It has been shown to apply to nearly semicircular cracks whose depth is much less than the specimen thickness [9]. Fracture surfaces were examined microscopically to determine fracture origins, to estimate the sizes and shapes of the flaws, and to observe subsequent fracture paths. Other details are contained elsewhere [10].

3. Results and discussion

Room temperature K_{Ic}s for the three orientations are 1.18 ± 0.05 MN m$^{-3/2}$ for the (1 0 0), 1.54 ± 0.08 MN m$^{-3/2}$ for the (1 1 0), and 1.90 ± 0.06 MN m$^{-3/2}$ for the (1 1 1), where the intervals are the 95% confidence limits. These compare favourably with several literature single crystal K_{Ic}s for stoichiometric $MgAl_2O_4$: 1.6 [11], 1.7 [12], and 1.3 [13] MN m$^{-3/2}$; even though their specific orientations were not disclosed. Al_2O_3-rich spinel crystals, ($MgO \cdot 3Al_2O_3$), of ⟨1 0 0⟩ orientation have also been measured yielding K_{Ic}s of 1.5 MN m$^{-3/2}$ as grown, and 2.6 MN m$^{-3/2}$ after ageing at elevated temperature to produce fine precipitates [14]. Comparable to these single crystal values are several stoichiometric polycrystalline K_{Ic}s of 1.7 [11], 1.9 [10], 2.0 [15], and 2.2 [16] MN m$^{-3/2}$

From the values for K_{Ic}, the fracture surface energy, $\gamma_{\mathrm{f}} = f\{h\,k\,l\}$ was calculated from:

$$\gamma_{\mathrm{f}} = \frac{K_{\mathrm{Ic}}^2(1-\nu^2)}{2E} \qquad (2)$$

where $E = f\langle h\,k\,l\rangle$ and $\nu = f\{h\,k\,l\}$ were calculated from single crystal elastic constants and the appropriate transformations of axes [17]. Average values are 3.57, 4.07, and 4.85 J m^{-2} for the (1 0 0), (1 1 0), and (1 1 1) orientations respectively. These single crystal values compare favourably with other values quoted for polycrystalline spinel, 4 to 8 J m^{-2} [15].

Although each of the (1 0 0), (1 1 0), and (1 1 1) appears to fracture, the most distinct cleavage plane in $MgAl_2O_4$ at room temperature is the (1 0 0), as illustrated in Fig. 1, clearly showing {1 0 0} fractures. Both K_{Ic} and γ_{f}, as well as E, are the lowest for the (1 0 0), supporting the hypothesis of Gilman [18] that the favoured cleavage plane should be that requiring the least force to propagate a crack.

Fig. 2 illustrates the K_{Ic} for the (1 1 1) from r.t. to 1500° C. Two distinct regions are evident. From r.t. to about 1000° C, a low temperature region exists where there is a linear decrease of K_{Ic} with increasing temperature. This K_{Ic} decrease is about 10^{-4} MN m$^{-3/2}$ °C^{-1}. Wiederhorn *et al.* [2] also report a well-defined low temperature linear decrease for the $(1\,0\,\bar{1}\,0)$ of sapphire. It is about 10^{-3} MN m$^{-3/2}$ °C^{-1} to 600° C. Henshall *et al.* [3] observed a similar decrease of K_{Ic} for the $(1\,1\,\bar{2}\,0)$ of SiC from r.t. to approximately 800° C. It was also about 10^{-4} MN m$^{-3/2}$ °C^{-1}. They did not amplify these results, probably because of a paucity of data. Results of the above studies, as well as St. John's on Si [1], which reports no effect of temperature on K_{Ic} in the low temperature region, all suggest that fracture in the low temperature region is free from plastic deformation. Analysis applied here to $MgAl_2O_4$ confirms that this decrease is the result of brittle elastic fracture.

About 1000° C, the (1 1 1) fracture initiates an elevated temperature region revealing a rapid increase of K_{Ic} with increasing temperature, characteristic of a brittle to ductile transition. This increase of fracture toughness has been

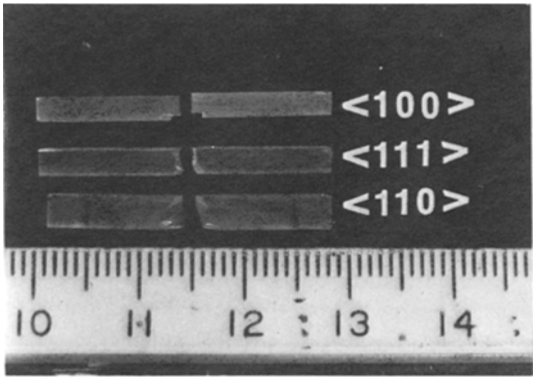

Figure 1 Room temperature fracture of ⟨1 0 0⟩, ⟨1 1 0⟩, and ⟨1 1 1⟩ crystals. Note the distinct cleavage of the {1 0 0} for the ⟨1 0 0⟩ crystal.

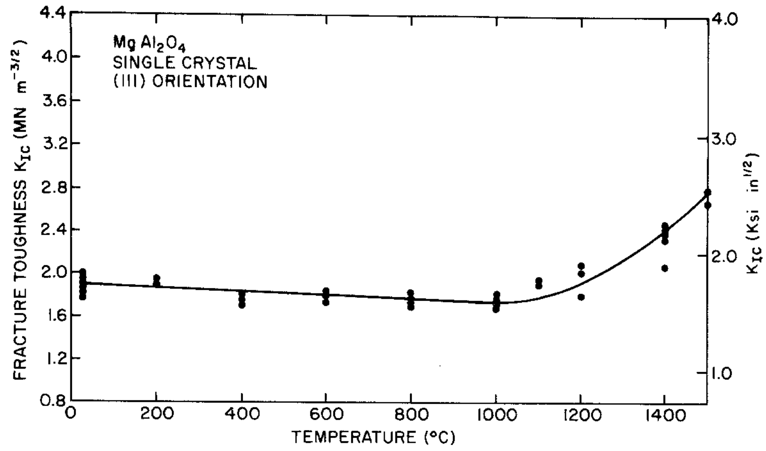

Figure 2 Variation of K_{Ic} for (1 1 1) of $MgAl_2O_4$ with temperature.

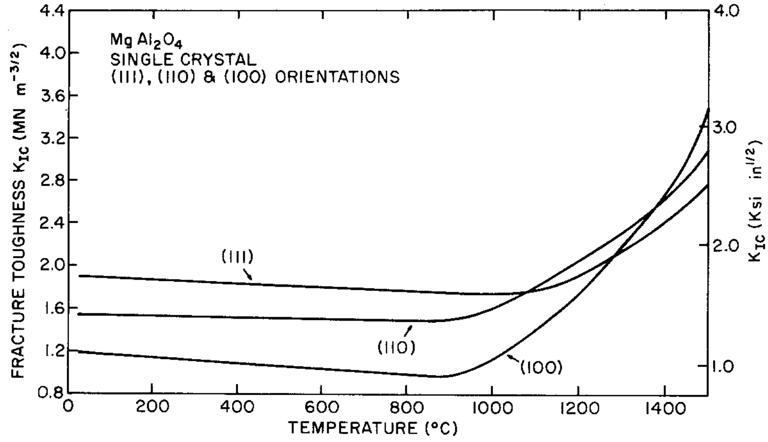

Figure 3 The variation of K_{Ic} with temperature for the (1 1 1), (1 1 0), and (1 0 0) of $MgAl_2O_4$.

generally attributed to an increase of plastic deformation in the vicinity of the crack tip. In this rapid increase high temperature region, St. John [1] presented direct X-ray topographic evidence of a plastic zone in Si, while Wiederhorn *et al.* [2] observed dislocation structures in sapphire. Henshall *et al.* [3] did not make direct observations, but suggested that local plastic flow contributed to the elevated temperature increase of K_{Ic}. The results discussed in the following sections confirm the role of dislocation plastic flow in promoting this rapid increase of K_{Ic} with increasing temperature.

The K_{Ic} variations with temperature for all three orientations are shown in Fig. 3. For clarity of comparison, individual data points are omitted. Analogous to the (1 1 1), the (1 0 0) orientation also exhibits a substantial decrease in K_{Ic} with increasing temperature. However, the (1 1 0) K_{Ic} decreases only slightly in the low temperature regime. The K_{Ic} rapidly increases with increasing temperature above 900° C for the (1 0 0) and (1 1 0), similar to the (1 1 1) above 1000° C. The (1 0 0) cleavage appears to exhibit a much greater increase in K_{Ic} with increasing temperature in the high temperature regime, so that above 1400° C, the (1 0 0) becomes the toughest orientation.

The linear decrease of K_{Ic} with increasing temperature in the low temperature region can be explained on the basis of an elastic model. Replacing γ_f in equation 2 by $E/a_0(\lambda/\pi)^2$, after Gilman [18] or Kelly [19] yields:

$$K_{Ic} = \frac{\sqrt{2E\lambda}}{\pi a_0^{1/2}(1-\nu^2)^{1/2}}, \qquad (3)$$

where E is Young's elastic modulus perpendicular to the crystallographic plane of interest, λ is the relaxation distance of attractive forces between ions, a_0 is the interplanar spacing between cleavage planes, and ν is Poisson's ratio. Differentiating with respect to temperature, treating λ as a constant, then rearranging, yields;

$$(\mathrm{d}K_{\mathrm{Ic}}/\mathrm{d}T) = \frac{\sqrt{2}\lambda}{\pi a_0^{1/2}(1-\nu^2)^{1/2}} \times \left[\frac{\mathrm{d}E}{\mathrm{d}T} - \frac{1}{2}E\alpha + \frac{E\nu}{(1-\nu^2)}\frac{\mathrm{d}\nu}{\mathrm{d}T}\right], \qquad (4)$$

where α is the linear coefficient of thermal expansion. The temperature variation of the elastic modulus is only available for ⟨1 0 0⟩ and ⟨1 1 1⟩, so those two orientations are the only ones that can be compared here.

In $MgAl_2O_4$, the bonds ruptured during fracture are most likely Mg–O [20]. Consideration of the unit cell shows that $a_0 = 1.01$ Å for (1 0 0) and 2.35 Å for (1 1 1); λ is assumed to be the sum of the Mg^{2+} and O^{2-} radii, 1.98 Å [21] for both cases, while $\alpha = 7.6 \times 10^{-6}$ ° C^{-1} [22] independent of orientation. The (dE/dT) values are $-$ 14.47 and $-$ 15.69 MN m^{-2} ° C^{-1} for the ⟨1 0 0⟩ and ⟨1 1 1⟩, respectively. An estimate of (dν/dT) of about 2×10^{-5} ° C^{-1} is available from other single crystal [17] and polycrystalline [10] data. Incorporating into (4) yields -1.3×10^{-4} and -1.0×10^{-4} MN m$^{-3/2}$ ° C for the (dK_{Ic}/dT) values for the (1 0 0) and (1 1 1) respectively. These values can be compared with the experimental results of -2.5×10^{-4} and -1.7×10^{-4} MN m$^{-3/2}$ ° C for the (1 0 0) and (1 1 1) respectively in the linearly decreasing range of (K_{Ic}) versus (T). The theoretical and experimental values agree in magnitude, and predict the correct order of decrease in approximately the experimentally observed ratios. The slight difference in magnitude might be partially attributed to treating λ as a constant, when it may decrease with an increase in temperature. However, no estimates of (dλ/dT) are available at the present.

The results of St. John on Si attribute the elevated temperature rapid increase of K_{Ic} to extensive plastic yielding in the vicinity of the crack tip. Resolution of the applied stress onto the reported slip system for stoichiometric spinel [4], explains the crystallographic differences in Fig. 3 and further substantiates this interpretation of the elevated temperature increase of K_{Ic}. The low to high temperature transitions for the different orientations are approximately 900° C for the (1 0 0) and (1 1 0), and about 1000° C for the (1 1 1). If the K_{Ic} increase is attributed to yielding on the {1 1 1}⟨1 1 0⟩ system [4], then the results of Fig. 3 for the (1 0 0) and (1 1 0) suggest yielding at a lower temperature for these orientations, and accordingly that the critical resolved shear stress should be greater for these orientations. Although the initiation of a plastic zone generated near the crack tip is governed by the orientation of the slip system and also the crack, as well as specimen and testing restrictions, a simple resolution of stresses, through the Schmid factor, explains the order of the resulting K_{Ic} increases with increasing T. For the ⟨1 0 0⟩ and ⟨1 1 0⟩ crystals, the Schmid factors are nearly equal, about 0.41 (actually 0.409 and 0.408), but the Schmid factor for ⟨1 1 1⟩ crystal is much smaller, only 0.28. Since the critical resolved shear stress for yielding is negligibly affected by the orientation of the applied stress, yielding should and does initiate earlier and at the same temperature, for the Schmid factors are equal for the ⟨1 0 0⟩ and the ⟨1 1 0⟩ crystals. The K_{Ic} of the ⟨1 1 1⟩ should, and does increase at a higher temperature because of its smaller Schmid factor.

Further confirmation that the rapid increase of K_{Ic} at elevated temperatures is due to the onset of extensive plastic deformation in the vicinity of the crack tip can be obtained by estimating the yield stress from the K_{Ic} value at the T-minimum for each of the three orientations. The elastic stress field at the crack tip can be expressed by:

$$\sigma_{r\theta} = \frac{K_{\mathrm{I}}}{(2\pi r)^{1/2}} \sin(\theta/2)\cos^2(\theta/2), \qquad (5)$$

as discussed in the text by Lawn and Wilshaw [23]. If one accepts that the onset of the increase of K_{Ic} is the initiation of plastic flow, then at that point $\sigma_{r\theta}$ can be replaced by σ_{ys} for the most favourably oriented slip system, and K_{I} can be replaced by the measured K_{Ic}. This cannot be done once extensive plastic flow commences. The value for r in Equation 5 is clearly argumentative; however, a minimum value might be the Burgers' vector on the {1 1 1}⟨1 1 0⟩ slip system [4], 5.7 Å. This approach yields σ_{ys} estimates of 6.0×10^3 MN m^{-2} for the ⟨1 0 0⟩ crystals and 6.8×10^3 MN m^{-2} for the ⟨1 1 0⟩ crystals, at 900° C, where their minimum exists. The ⟨1 1 1⟩ minimum is at the higher temperature, 1000° C, so it cannot be directly compared with the ⟨1 0 0⟩ and ⟨1 1 0⟩ because of the temperature dependence of the yield stress; however, a similar estimate of the σ_{ys} for the ⟨1 1 1⟩ crystal yields 1.1×10^3 MN m^{-2} at 1000° C, as expected, lower than the 900° C value for the ⟨1 0 0⟩ and ⟨1 1 0⟩ crystals. Mitchell *et al.*

TABLE I Effect of $\dot{\sigma}$ on the (1 1 0) K_{Ic} (MN m$^{-3/2}$)

Stressing rate (MN m^{-2} sec^{-1})	Temperature (° C)	
	1200	1500
2.39×10^6	2.16 ± 0.06	3.26 ± 0.04
2.39×10^5	2.28 ± 0.04	4.42 ± 0.03
4.78×10^4	2.69 ± 0.21	4.92 ± 0.33

[4] measured σ_{ys} values of "bulk" crystals of stoichiometric $\mathrm{MgAl_2O_4}$, which although measured above 1500° C can be extrapolated to 1000° C. Such an extrapolation results in macroyield stresses that are about an order of magnitude greater than those estimated here.

Other evidence supporting the role of extensive plastic flow in the rapid increase of K_{Ic} is that of the stressing rate effect. As mentioned in the experimental procedure, for a number of ⟨1 1 0⟩ crystals, K_{Ic}s were measured at three different cross-head speeds, some at 1200° C, and some at 1500° C, both well within the elevated temperature, rapidly increasing K_{Ic} region. The results are contained in Table I. The trends are consistent with those of St. John on Si, indicating higher apparent K_{Ic}s for slower testing speeds, indicative of a plastic flow type of energy dissipative process.

4. Conclusions

Room temperature and elevated temperature fracture toughnesses were measured for the (1 0 0), (1 1 0), and (1 1 1) of single crystal, stoichiometric $\mathrm{MgAl_2O_4}$ spinel. The K_{Ic}, γ_{f}, and E are a minimum for the (1 0 0) at room temperature, consequently distinct (1 0 0) cleavage occurs for favourably oriented crystals at that temperature. With increasing temperature, all three of the planes exhibit two regions of K_{Ic} variation, a low temperature region where K_{Ic} decreases with increasing temperature, and an elevated temperature region where K_{Ic} increases rapidly with increasing temperature. An elastic analysis of the low temperature region predicts the order of magnitude of $(\mathrm{d}K_{\mathrm{Ic}}/\mathrm{d}T)$ as well as the relationship between the (1 0 0) and (1 1 1). Analysing the high temperature, rapid K_{Ic} increase region on the basis of yielding in the vicinity of the crack tip, predicts the correct order of K_{Ic} versus T minima for the planes based on the Schmid factors, and also yields reasonable estimates of the yield stress. The effect of stressing rate on K_{Ic}, and a higher K_{Ic} for lower loading rates, confirm the effect of yielding at the crack tip as the mechanism of the K_{Ic} increase at elevated temperatures.

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