JOURNAL OF MATERIALS SCIENCE 25 (1990) 1347–1352

# Fracture toughness and hardness of zinc sulphide as a function of grain size

D. TOWNSEND*, J. E. FIELD,
*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK*

The erosion properties of brittle materials depend upon plastic deformation and crack generation at an impact or indented site. Vickers indentations have been used to investigate the plastic processes and crack systems in chemical vapour deposited zinc sulphide of different grain sizes. The hardness, $H$, and the "local" fracture toughness $K_c$, are dependent upon the grain size of the material. For small grain size material (<50 μm) the Vickers hardness was found to increase with decreasing grain size in accord with the Petch mechanism, i.e. $H = H_0 + kd^{-1/2}$ where $k$ and $H_0$ are constants and $d$ is the grain diameter. A maximum hardness of ca. 4 GPa has been observed for material with an average 0.5 μm grain diameter. In large grain size material, hardness anisotropy within the grains causes significant experimental scatter in the hardness measurements because the plastic impression formed by the indenter (load 10 N and 100 N) is smaller than the grain diameter. The values of $K_c$ obtained using an indentation technique show that for grain sizes less than 8 μm $K_c$ decreases with decreasing grain size. For materials with a grain size in the range 500 μm to 8 μm, well developed median cracks were not observed, however, the radius of the fracture zone was measured in order to estimate an "effective" $K_c$. The "effective" $K_c$ was found to increase approximately linearly with the reciprocal root of the grain size. Consideration of the models for elastic/plastic impact and micromechanics of crack nucleation in conjuction with the variation of $K_c$ and $H$, indicate that zinc sulphide with a mean grain size of 8 μm will give the optimum solid particle and rain erosion resistance.

## 1. Introduction

With the growth in the use of brittle materials for vital components, in for example the aerospace industry, the problems of strength degradation and material removal caused by crack growth under erosive conditions are of importance. The contact of erosive particles, including both solids and liquid drops, generates intense local stress concentrations which give rise to characteristic indentation fracture patterns. Erosion studies of brittle materials are directed towards the understanding of the role of plastic deformation in producing these crack systems [1–4]. In soda-lime glass, inhomogenous shear lines formed below the indented or impacted site interact and nucleate the crack systems [2, 5, 6]. The cracks propagate into the surrounding elastic hinterland. For crystalline solids, deformation processes may also be required for the propagation of non-cleavage, e.g. radial cracks in ionic crystals.

For polycrystalline ceramics, the nucleation and propagation of the median, radial and lateral cracks around plastic indentations is influenced by the grain size and operating temperatures both of which can significantly affect the erosion behaviour. Changes in grain size and in temperature can transfer deformation and cracking modes from within the grain itself to events at the grain boundary such as sliding and voiding, thus providing deformation modes for both crack nucleation and propagation.

A model of the initiation of microfracture beneath sharp indenters by Lawn and Evans [7] assumed the presence of inherent flaws in the bulk. Hagan [5] discussed the possibility that the deformation processes can generate the necessary defects for crack growth. Van der Zwaag *et al.* [8] in a study of the contact damage in fine grained zinc sulphide provided further evidence of the important role of plastic deformation in creating the stress field and forming the crack initiation defects. They also observed a porous zone directly beneath the contact area due to the formation of voids by the relative shearing motion of grains past each other. Crack systems emanate from the porous zone and are nucleated from the voids. Crack propagation was found to be intergranular.

In this paper, the influence of grain size on the plastic deformation and crack processes around Vickers indents in chemically vapour deposited (CVD) zinc sulphide is considered. The dependence of hardness, $H$, and fracture toughness, $K_c$, as determined by an indent technique, are found to be dependent upon the grain size of the material. Zinc sulphide is of particular interest because the combination of thermal and optical properties makes

* *Present address*: British Aerospace, Sowerby Research Centre, Filton, Bristol BS12 7QW, UK

0022–2461/90 $03.00 + .12 

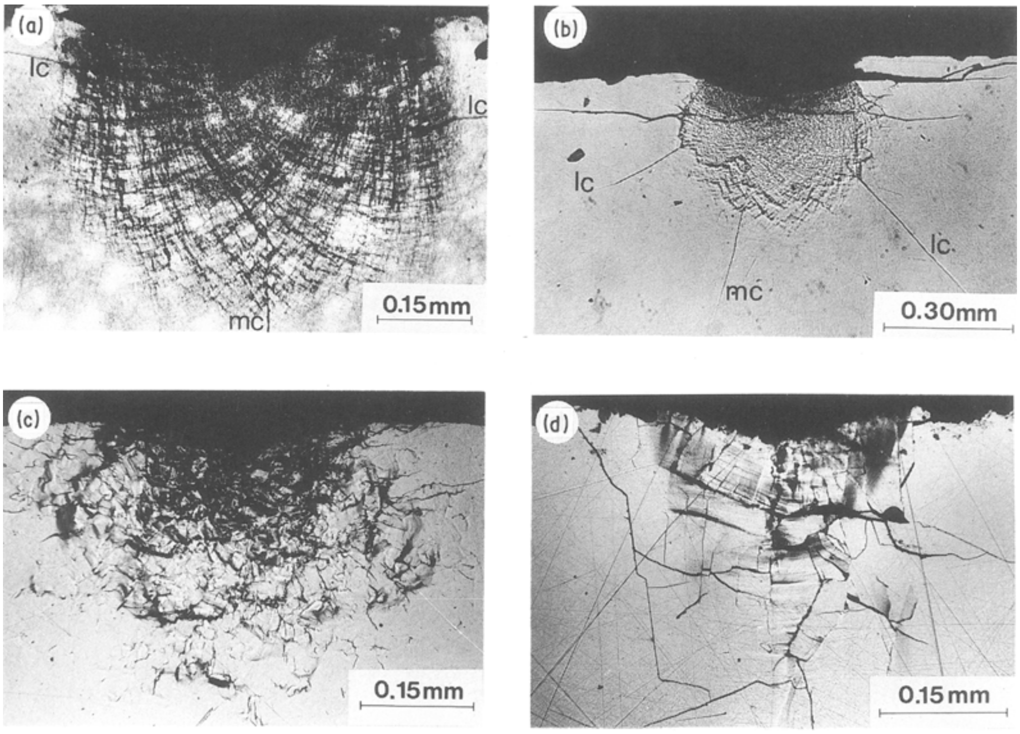


*Figure 1* Grain size dependence of the subsurface deformation mode for Vickers indentations on zinc sulphide (a) 300 N indentation for 0.5 $\mu$m grain size, (b) 75 N for 2 $\mu$m, (c) 150 N for 16 $\mu$m and (d) 100 N for 140 $\mu$m.

this material suitable as a protective window for infra red imaging systems [9]. Erosive environments lead to severe degradation of the mechanical and optical properties of the material. The variation in crack growth resistance and hardness indicates that material with a grain size of approximately 8 $\mu$m will give the optimum solid particle and rain erosion resistance.

## 2. Experimental details

The zinc sulphide specimens were experimental material provided by the Royal Signals and Radar Establishment (RSRE), Malvern and commercially available material. A CVD process was employed to produce the zinc sulphide: the growth conditions and in particular the deposition temperature largely determine the grain size. Deposition temperatures in the range 550° to 1050° C were used to produce a series of specimens with grain sizes ranging from 0.5 to greater than 500 $\mu$m. Disc specimens (25 mm diameter and 2 mm nominal thickness) for indentation studies were cut from the deposits and lapped and polished using 1 $\mu$m diamond paste. The specimens were prepared such that the faces of the disc were perpendicular to the growth direction. Grain size, $d$, was measured on the surface by the linear intercept method after etching the material in a bromine methanol solution (1 to 10 by volume). A characteristic of zinc sulphide produced by the CVD process is the columnar grain structure, [8] the axis of the grains being parallel to the growth direction. In this paper the grain size quoted for each specimen is the average diameter of the columnar grains.

Vickers indents were made using micro- and macro hardness testing machines at loads in the range 10 N to 100 N. Care was taken to ensure that the axis of the indenter was perpendicular to the face of the disc. Immediately after indenting, the surfaces were examined using an optical microscope and the dimensions of the plastic impression and crack systems recorded. Sections through the Vickers impressions were achieved by indenting across the interface of two highly polished blocks held rigidly together in a cold mounting plastic [10]. The specimens were orientated such that the longest axis of the grains was normal to the interface between the specimens. Following the indentation the composite specimen was prised apart thus enabling the subsurface damage to be examined. This technique and sectioning of bulk material were used by Van der Zwaag *et al.* [8] for studying contact damage in zinc sulphide. The subsurface damage observed in both cases was identical.

## 3. Results

### 3.1. Subsurface deformation

The deformation and cracking processes underneath Vickers indentations have been studied in zinc sulphide as a function of the grain size. Figure 1a shows the deformation for a 300 N indentation on 0.5 $\mu$m grain size zinc sulphide. Within the deformed zone, a large number of well-defined spiral flow lines can be distinguished which follow the maximum shear stress trajectories as predicted for an isotropic plastic material [11]. The deformation in zinc sulphide with a grain size of 2 $\mu$m is illustrated in Fig. 1b. The flow lines are still discernible, but are less well-defined than in the previous figure. Detailed examination of the sub-surface deformation in these fine grained materials [8] has shown that intergranular voids are formed along the flow lines due to a grain boundary sliding process. The deformation is mainly concentrated in the spiral flow lines. Some deformation, however, does occur within the grains. For the coarser grain sizes, the

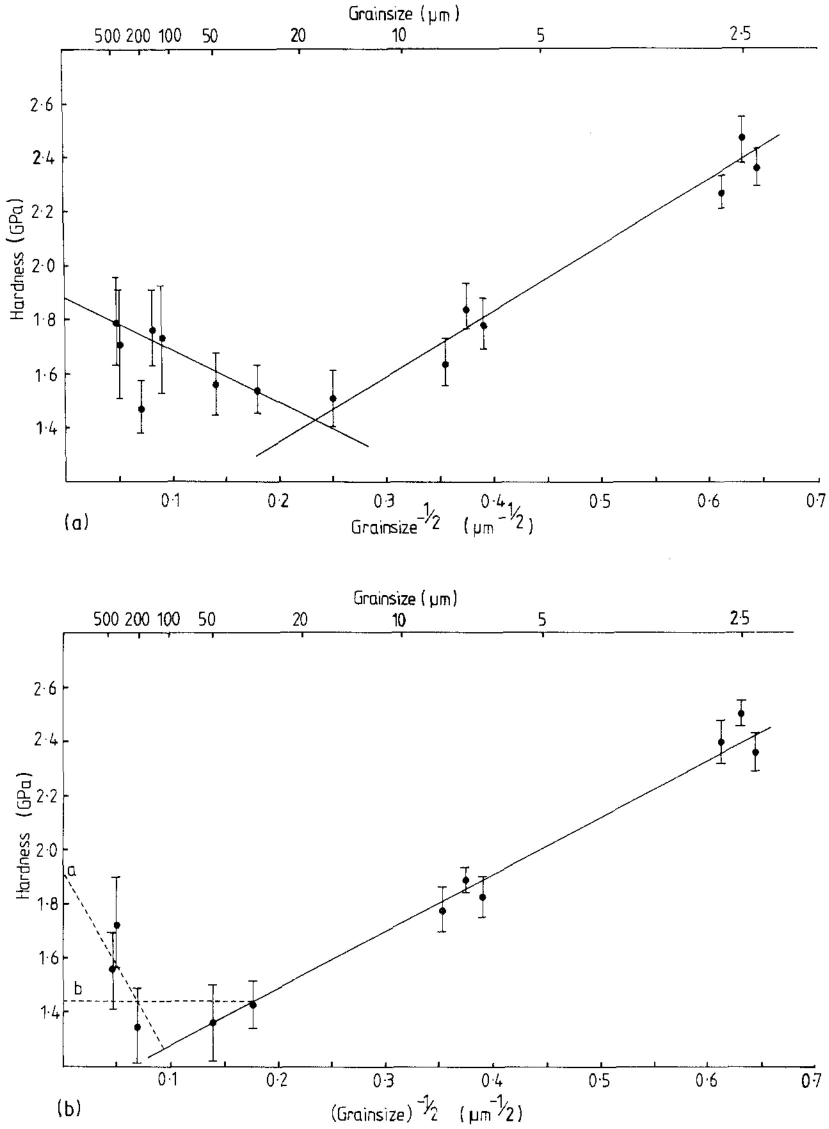


*Figure 2* (a) Vickers hardness against (grain size)$^{-1/2}$ for zinc sulphide. Indenter load 10 N. (b) Vickers hardness against (grain size)$^{-1/2}$ for zinc sulphide. Indenter load 100 N.

possibility of deformation along the grain boundaries is limited. The deformation therefore occurs principally within the grains. In this case the spiral flow lines are not formed as shown by Figs 1c and d. It is clear from Fig. 1d (grain size 140 $\mu$m) that the deformation is concentrated within the grain. The amount of slip in each grain depends on the orientation of the crystal with respect to the indentation stress field. For the 16 $\mu$m grain size material (Fig. 1c), the deformation has resulted in a large number of primarily intergranular cracks.

These changes in the mode of deformation also affect the various crack systems which form around the indentation. Well-developed median cracks, mc, are observed in the fine grained materials (Fig. 1a and b). Traces of lateral cracks, lc, formed in the unloading cycle are also present. The residual stress field, caused by plastic deformation at the indent, provides the driving force for these cracks. Voids formed at the intersection of the shear flow lines in the deformed zone directly beneath the plastic impression serve as nucleating sites for the crack systems. For the larger grain sized material ($> 8$ $\mu$m), the intergranular radial cracks showed a large scatter in length and fracture path. Furthermore, it was observed that at low loads the formation of lateral cracks in these materials was suppressed. Extensive cracking in the deformed zone reduces the residual stress field around the plastic impression leaving insufficient stored energy to propagate the lateral cracks into the surrounding matrix. The absence of lateral cracking could reduce the rate of material removal during solid particle erosion.

## 3.2. Hardness determination

Hardness measurements of the zinc sulphide specimens were made with a Vickers diamond pyramid indenter loads of 10 N and 100 N. The hardness is defined from the projected area as

$$H = 1.854P/a^2 \qquad (1)$$

where $P$ is the indenter load and $a$ the length of the indent diagonals. Figure 2a and b show the variation in hardness with grain size for indenter loads of 10 N and 100 N respectively. A minimum hardness is observed at 20 $\mu$m for the 10 N load and 60 $\mu$m for the 100 N loads. This factor of three difference in the grain size corresponds to the ratio of the indent diameters produced by the 10 N and 100 N loads. It appears that the minimum hardness occurs when the size of the indent is a few grain diameters. The increasing hardness towards smaller grain sizes is attributed to dislocation pile-ups at the grain boundaries. This is the Petch mechanism which predicts $H = H_0 + kd^{-1/2}$

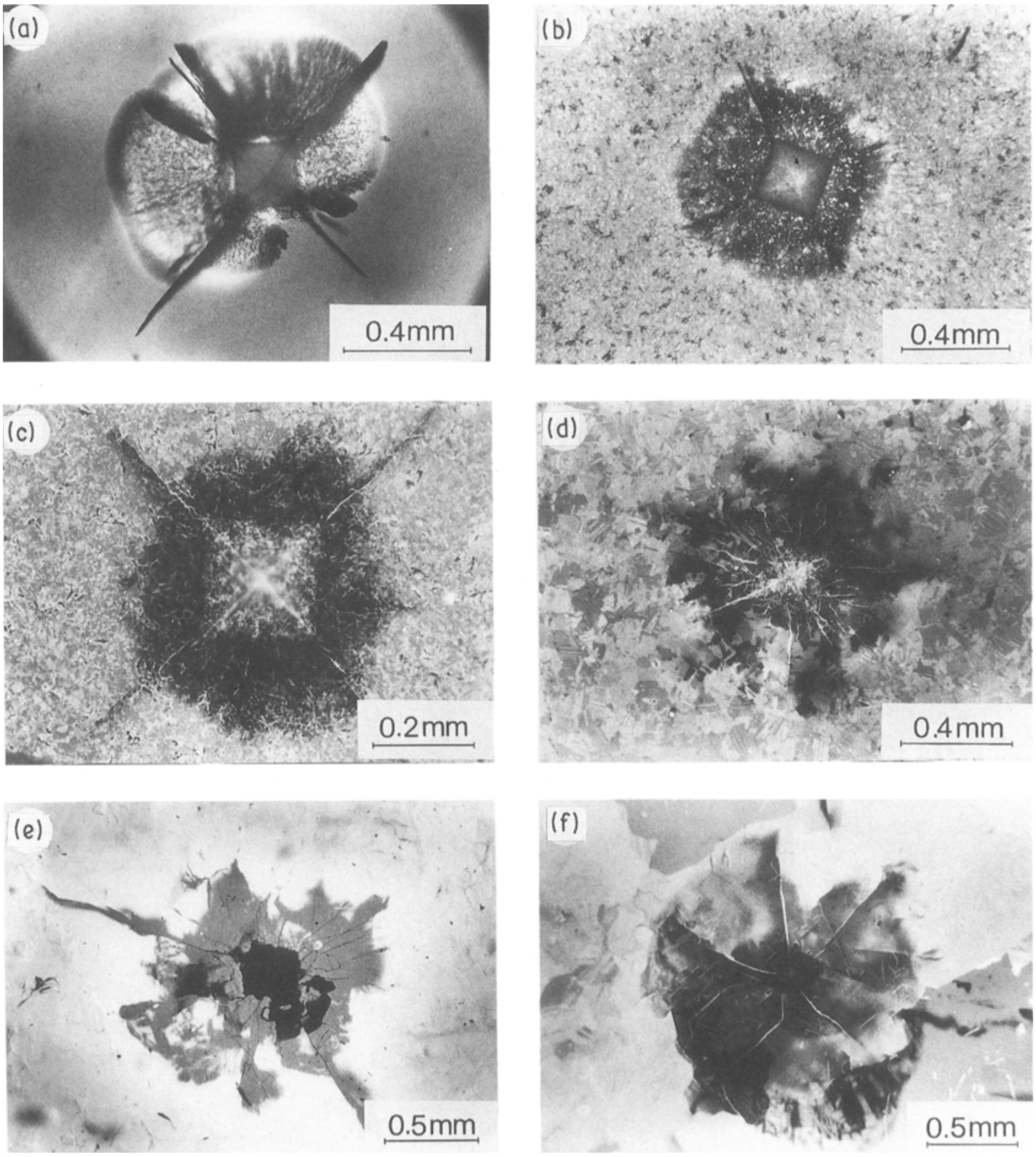


*Figure 3* Surface views of Vickers indents on zinc sulphide. All for loads of 100 N, (a) 2.5 $\mu$m grain size, (b) 6.5 $\mu$m, (c) 8 $\mu$m. (d) 32 $\mu$m, (e) 140 $\mu$m and (f) 400 $\mu$m.

where $k$ is a constant and $d$ is grain diameter. The data is plotted as hardness against $d^{-1/2}$ to test this relation. The Petch relation of increasing hardness with decreasing grain size is observed in many polycrystalline ceramics [12, 13]. In Fig. 2b considerable experimental scatter is observed in the hardness measurements of the large grain size material. This is because the indent size is less than the grain size, hence the hardness anisotropy within the grains contributes to the spread of the results [14]. The scatter in results for 100 N indentation on large grain size material is such that the variation in hardness with grain size can be represented by either curve a or b.

### 3.3. Fracture toughness

The fracture toughness of the polycrystalline zinc sulphide was determined from the size of the median cracks produced by the Vickers indent. An indentation technique was employed because it provided the only quantitative method of evaluating the variation in fracture toughness with grain size from the limited number of samples. Furthermore, the erosion properties of brittle materials depend upon crack generation around an indented or impacted site. The similarity between these cracks and those formed by the Vickers indenter, therefore, signifies that it is advantageous to measure $K_c$ by this method when evaluating the erosion resistance of brittle materials.

Fig. 3 shows the surface damage formed by 100 N Vickers indentations on different grain size material. There is a clear change in the pattern of fracture as the grain size varies. For the smallest grain size material, 2.5 $\mu$m, well-defined median cracks are formed (Fig. 3a). Essentially, the same crack pattern is observed for the 6.5 and 8 $\mu$m grain size material. Indentation in a material with a grain size greater than 8 $\mu$m did not, however, produce recognizable median cracks. In these materials, the surface damage consisted of multiple radial fractures. This difference in the crack pattern correlates with the changes observed in the deformed zone, described in the previous section. These observations are consistent with the comments

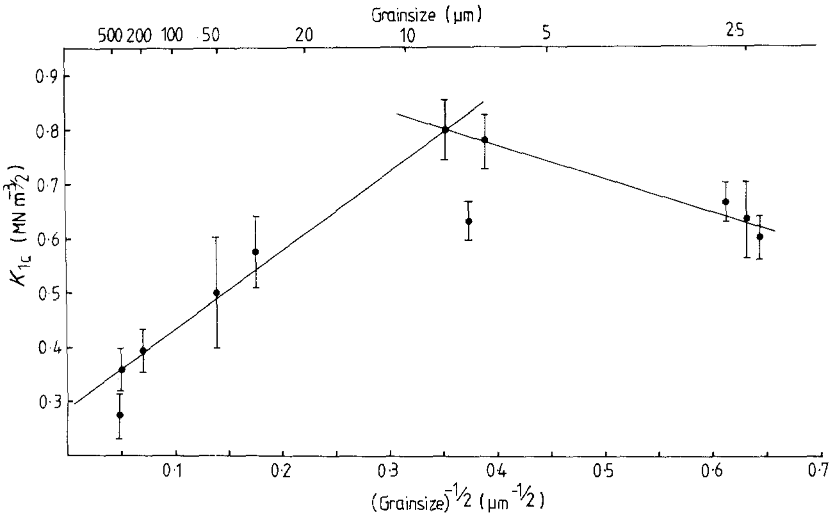


*Figure 4* $K_{Ic}$ against (grain size)$^{-1/2}$ for zinc sulphide.

of Antis *et al.* [15] and Evans [16], i.e. as the coarseness of the microstructure becomes comparable with the size of the indent, the fracture pattern is more susceptible to disruption from local grain failure events. In the limit of large grains, the fracture patterns tend to those for a single crystal.

The determination of fracture toughness from the median/radial crack systems that occur at hardness indentations in brittle materials has received considerable attention in recent years. In comparison with more conventional testing techniques, e.g. notched beam, double torsion, the advantages of the indentation test procedure are that it is simple, it can be applied to small specimens and it is capable of measuring the local crack growth resistance [16]. An early treatment of the indentation process by Lawn and Fuller [17], showed that the toughness, $K_c$, could be related to the indenter load, $P$, and the radius of the semi-circular median cracks, $c$ by

$$K_c = \chi_1 P/c^{3/2} \quad (2)$$

where $\chi_1$ is a numerical constant dependent upon the indenter geometry. For Vickers indents, $\chi_1 = 0.0726$. This treatment assumed, however, that the driving force for the cracks was derived from an elastic stress field.

Evans and Charles [18] employed dimensional analysis and correlation with conventional fracture toughness measurements to obtain an unique characterization of the fracture caused by Vickers indentation. In this analysis a functional dependence on the ratio $E/H$ ($E$ = Young's modulus, $H$ = hardness) was introduced to account for the elastic/plastic stress field associated with the indentation

$$K_c = \chi_2(E/H)^{0.4} P/c^{3/2} \quad (3)$$

Detailed consideration of the interaction between the elastic matrix and the plastic impressions shows that $\chi_1$ (Equation 2) depends upon the ratio $E/H$ to approximately the one half power [19]

$$K_c = C_v(E/H)^{1/2} P/c^{3/2} \quad (4)$$

where $C_v$ is a material independent constant and for Vickers indent produced median cracks is equal to 0.016. Equations 3 and 4 are of similar form, differing only in the exponent of the ratio $(E/H)$. These equations can be applied to predict the intrinsic fracture toughness of the material to an accuracy of better than 30%.

Determination of the intrinsic fracture toughness of a brittle material by the indentation technique is best accomplished using Equations 3 and 4. In this investigation, however, the main aim is to predict the optimum grain size for erosion resistance. Erosion processes involve small scale elastic/plastic contact at an impact or indented site. The important consideration is, therefore, the extent of crack propagation in the material at a contact site. For this reason, Equation 2 was used to give a local fracture toughness which is a direct measure of the extent of the crack growth. Further, from the observed dependence of $H$ and $K_c$ on grain size, assuming that $E$ remains constant the variation of $K_c$ with the grain size would be greater if either of Equations 3 or 4 were used.

For each specimen studied the "local" $K_c$ was evaluated from a plot of $P$ against $c^{3/2}$. Figure 4 shows the variation in $K_c$ with grain size. In the range of 500 to 8 μm, $K_c$ increases approximately linearly with the reciprocal root of the grain size. For grains smaller than about 8 μm, $K_c$ decreases. Well-defined median cracks were not observed in material with a grain size greater than 8 μm. For these specimens, the radius of the multiple fracture zone was taken as the value of $c$ in the expression for $K_c$. The indentation fracture analysis cannot be applied to these large grain size materials [16]. The lower "effective" $K_c$ values, however, do indicate an important trend because they are a measure of the extent of fracture produced by a given load. The decrease in "effective" $K_c$ can be attributed to crack nucleation from dislocation pile-ups at the grain boundaries and to easy crack propagation along cleavage planes in the large grains [20].

For grain sizes less than 8 μm, well-defined median cracks were formed at indenter loads of 10 N to 100 N. The decrease in $K_{Ic}$ for small grain size zinc sulphide is attributed to void formation which arises from grain boundary deformation in the spherical zone under the contact area. These voids provide the nucleation sites for the median radial and lateral crack systems [5, 8]. In addition, the deformation at the crack tip may lead to a microscopic loss of coherence at the grain boundary, resulting in a decrease in fracture toughness.

## 4. Conclusions

The variation of hardness and local fracture toughness with grain size of CVD zinc sulphide has been measured by the Vickers indentation technique. In accordance with a Petch mechanism, the smallest grain size material has the maximum value of hardness. A peak value of fracture toughness is observed in zinc suphide with an 8 $\mu$m grain size.

The mechanisms of erosion and impact damage have received considerable attention in the literature and several suggestions have been made to relate the fracture toughness and hardness of a brittle material to the erosion resistance and impact performance [21]. Elastic/plastic contact considerations by Ruff and Wiederhorn [21] and analysis of solid particle erosion data for a number of brittle materials by Wiederhorn and Hockey [22] shows that erosion resistance increases with increasing fracture toughness and to a much lesser extent, decreases with increasing hardness. In the case of liquid impact, analysis of the Rayleigh wave interaction with surface defects [23] predicts that the threshold velocity for damage initiation increases in proportion to $K_{Ic}^{2/3}$. The micromechanics of crack nucleation [5] indicate that the load necessary to propagate a critical flaw will increase in proportion to $K_{Ic}^4/H^3$.

All the various theories predict that erosion resistance should depend on $K_{Ic}$ and should be improved as $K_{Ic}$ increases. The predicted dependence on hardness varies between the different theories. However, with zinc sulphide, the variation of hardness in the region of 8 $\mu$m grain size is so small that this size is always predicted as optimum.

The conclusions from this study are that fracture toughness is the dominant material property in determining the erosion resistance of zinc sulphide and that material with a mean grain size of approximately 8 $\mu$m has the potential to give optimum solid particle and liquid erosion resistances. However, whether or not this potential is achieved will depend on a particular sample's growth and surface preparation. If either of these processes leave large defects (for example, grinding damage not removed by polishing) then these defects will reduce the sample's strength and act as sites for erosion [24].

## Acknowledgements

This work was supported in part by the MOD (Proc. Exec.) We thank Dr N. S. Corney of RAE, Farnborough and Dr J. A. Savage of RSRE, Malvern for useful discussions and for providing samples.

## References

1. B. R. LAWN and M. V. SWAIN, *J. Mater. Sci.* **10** (1975) 113.
2. J. T. HAGAN and M. V. SWAIN, *J. Phys. D: Appl. Phys.* **11** (1978) 2091.
3. A. G. EVANS, M. E. GUILDEN and M. E. ROSENBLATT, *Proc. R. Soc.* **A361** (1978) 343.
4. B. R. LAWN and D. B. MARSHALL, "Fracture Mechanics of Ceramics" Vol. 3, edited by R. C. Bradt, D. P. H Hasselman and F. F Lange (Plenum, New York, 1978) 205.
5. J. T. HAGAN, *J. Mater. Sci.* **14** (1979) 2975.
6. *Idem, ibid.* **15** (1980) 1417.
7. B. R. LAWN and A. G. EVANS, *ibid* **12** (1977) 2975.
8. S. VAN DER ZWAAG, J. T. HAGAN and J. E. FIELD, *ibid.* **15** (1980) 2965.
9. J. A. SAVAGE, "Infrared Optical Materials and their Anti-reflection Coatings" (Adam Hilger, Bristol, 1985) 95.
10. T. O. MULHEARN, *J. Mech. Phys. Sol.* **7** (1959) 85.
11. A. NADAI, "Plasticity" (McGraw-Hill, New York, 1931).
12. R. W. RICE, "Treatise on Materials Science and Technology", Vol. II, edited by R. K. MacCrone (Academic, New York, 1977) p. 199.
13. S. S. SMITH and B. J. PLETKA, "Fracture Mechanics of Ceramics", Vol. 6, edited by R. C. Bradt, A. G. Evans, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1983) 189.
14. E. LENDRAY and W. V. FOCK, *J. Mater. Sci.* **4** (1969) 747.
15. G. R. ANTIS, P.CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64** (1981) 533.
16. A. G. EVANS, "Fracture Mechanics Applied to Brittle Materials" ASTM STP 678, edited by S. W. Frieman (1979) 112.
17. B. R. LAWN and E. R. FULLER, *J. Mater. Sci.* **10** (1975) 2016.
18. A. G. EVANS and E. A. CHARLES, *J. Amer. Ceram. Soc.* **59** (1976) 371.
19. B. R. LAWN, A. G. EVANS and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **63** (1980) 574.
20. R. W. RICE, "The Science of Ceramic Machining and Surface Finishing" Vol. 2 (National Bureau of Standards Special Publication 562 1979) 429.
21. A. W. RUFF and S. M. WIEDERHORN, "Treatise on Materials Science and Technology" (Academic, New York) **16** (1979) 69.
22. S. M. WIEDERHORN and B. J. HOCKEY, *J. Mater. Sci.* **18** (1983) 766.
23. A. G. EVANS, Y. M. ITO and M. ROSENBLATT, *J. Appl. Phys.* **51** (1980) 2473.
24. S. VAN DER ZWAAG and J. E. FIELD, *J. Mater. Sci.* **17** (1982) 2625.

*Received 8 November 1988*
*and accepted 26 April 1989*