Observations of contact damage in MgO and LiF crystals by cathodoluminescence

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Cathodoluminescence (CL) studies in a scanning electron microscope of the static and dynamic contact damage in MgO and LiF crystals are described. The main luminescence for both MgO and LiF was found to be associated with the plastically deformed zone at and around the contact site, although there were differences of details in the CL behaviour of the two materials. It was also found that in MgO the intensity of luminescence from screw dislocations was markedly higher than that from the edge dislocations for all possible orientations of the specimen. It is proposed that this simple and rapid technique can be used for assessing the mechanical state of a surface.

1. Introduction

Recent studies of the photoluminescence [1] and cathodoluminescence (CL) [2–5] from plastically deformed MgO crystals have shown that the enhanced luminescence from deformed regions is associated with the dislocations created during the deformation. There is, however, a controversy about the exact mechanisms responsible for this phenomenon, and several suggestions have been made: Velednitskaya *et al.* [2] believe that the source is the interstitials in the deformed zone, whereas Chen *et al.* [1] have proposed the origin to be the clusters of deformation-generated vacancies. On the other hand, Pennycook and Brown [3] have suggested that the dilatation around a dislocation is high enough to cause a substantial decrease in the band gap, and thus cause the emission of visible radiation from the recombination of electrons and holes.

In spite of the uncertainty about the origin of the CL, we believe that it provides us with a simple technique which has several advantages over the existing methods for detecting plastic flow and damage caused by contact, abrasion, scratching, erosion, etc., in a wide variety of materials ranging from ionic solids and semiconductors to the hardest material, diamond. A special feature of this technique is that dislocations which are several micrometres below the surface can also be detected. Here we report CL studies of the static and dynamic contact damage in single crystals of MgO and LiF caused by spherical particle indentations; studies of the pointed static indentations are described by Velednitskaya *et al.* [2] and Pennycook and Brown [3].

2. Experimental details

MgO and LiF single crystals were obtained from BDH Chemicals Ltd. The former was grown in air by the carbon arc fusion technique, while the latter was vacuum grown. The impurity contents of the powders from which these crystals were grown are shown in Table I.

Indentations were made on (1 0 0) cleaved surfaces using tungsten carbide and glass spheres of diameter 0.4 to 0.7 mm; the loading was static or dynamic, the latter was achieved by impacting the particles on the test surface at speeds of up to 250 m sec^{-1} using the methods described elsewhere [6]. After inducing the damage, some crystals were etched to reveal dislocations. All crystals were sputter-coated with a thin silver film to avoid charging effects.

Cathodoluminescence studies were made in a Cambridge Stereoscan S4-10 electron microscope operating at 30 kV, the emitted radiation was collected by a quartz lens which focused it on to the photocathode of an EMI 9558 photomultiplier. The details of the apparatus are given elsewhere [7]. LiF was found to be very sensitive

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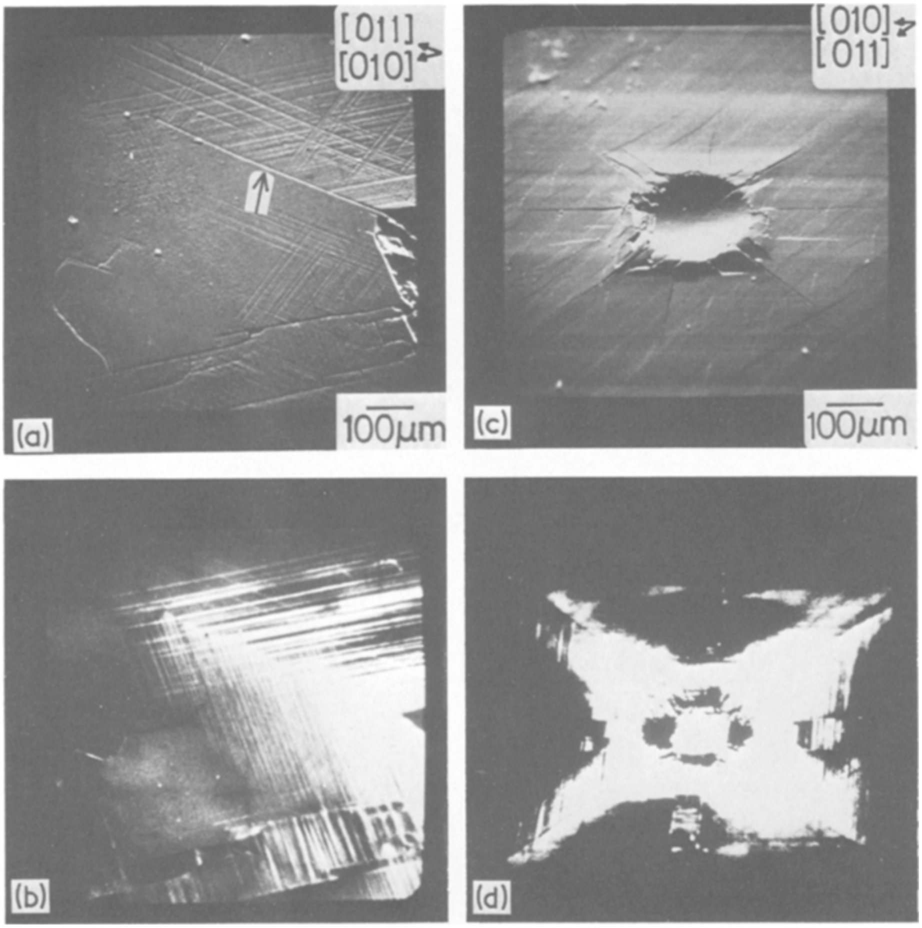

Figure 1 Secondary electron (a and c) and cathodoluminescence (b and d) micrographs of damage on the (1 0 0) surface of MgO crystals caused by the impact of spherical particles. The crystal in (a) and (b) was etched after the inducement of the damage, while that in (c) and (d) was not. (a, b) 0.7 mm diameter tungsten carbide sphere at 160 m sec^{-1}; ϵ = 12% (only one quarter of the damage is shown). The arrow shows a crack formed by the dislocation interactions. (c, d) 0.7 mm diameter tungsten carbide sphere at 34 m sec^{-1}; ϵ = 6.9%; there is significant luminescence from the contact zone.

to electron irradiation damage, especially for high-energy beams; this resulted in spurious CL. Therefore, the secondary electron (SE) images of the surfaces were taken with the accelerating voltage turned down to 3 kV; typically, the CL micrographs of a damage site were taken with the very first 30 kV electron beam scan of the surface.

3. Results

Fig. 1 shows the SE and the CL micrographs of spherical particle impact damage in MgO crystals; the crystal in (a) and (b) was etched, whereas that in (c) and (d) was not. Dislocations in these crystals lie on planes which are inclined to the indented (1 0 0) surface at angles of 45° and 90° and these planes are referred to as $\{1\,1\,0\}_{45}$ and $\{1\,1\,0\}_{90}$, respectively. Etch pits on the (1 0 0) surface along rows parallel to ⟨1 0 0⟩ are due to the screw dislocations on $\{1\,1\,0\}_{45}$ planes, while those along ⟨1 1 0⟩ are due to the edge dislocations on $\{1\,1\,0\}_{90}$ planes. Dislocations on two $\{1\,1\,0\}_{45}$ planes can interact to cause cracking along ⟨1 1 0⟩ as shown in Fig. 1a; the extent of these dislocation-induced cracks marks the size of the plastic zone. It is clear from Fig. 1b that the CL is associated with the deformed zone since there is very little emission from the region beyond the dislocation-induced crack tips. We have also found that contrary to previous observations from diamond pyramidal inentation damage [2, 3], there is some CL from the contact zone (Fig. 1d) when the damage was caused by spherical particles.

TABLE I Impurity contents of the materials from which the crystals were grown

Impurity	Content(ppm)	
	MgO	LiF
Al	15	–
Ba	–	100
B	5	–
C	10	–
Ca	100	50
Co	–	0.5
Cr	10	–
Cs	–	60
Cu	–	0.5
F	3	–
Fe	50	0.5
K	5	20
Mg	4	2
Mn	–	0.5
Na	5	200
Ni	3	0.5
P	2	–
Pb	–	0.5
Rb	–	30
Si	10	–
Sr	–	10
Ti	2	–
Zn	1	0.5

Moreover, examination of the cross-sectional cleavage through the indentation showed that the region immediately beneath the indentation also luminesces (not shown). CL was also observed from indentations caused by static loading (Fig. 2a and b) and by scratches produced by a spherical diamond stylus moving at 0.2 mm sec^{-1} (Fig. 2c and d).

An interesting feature of the CL micrographs is that the intensity is higher from screw dislocations than that from the edge dislocations for all possible orientations of the specimen. This is illustrated more clearly in Fig. 3 which shows high magnification SE and corresponding CL micrographs of rows of edge and screw dislocation pits taken from the region marked in Fig. 3a. The CL from the etch pits corresponding to the screw dislocations is much higher than that from the pits due to the edge dislocations. It was, however, found that, depending on the orientation of the specimen, the CL appeared to originate from the centre of the pits or from the material on either side of them; this effect is probably due to the refraction of the emergent light.

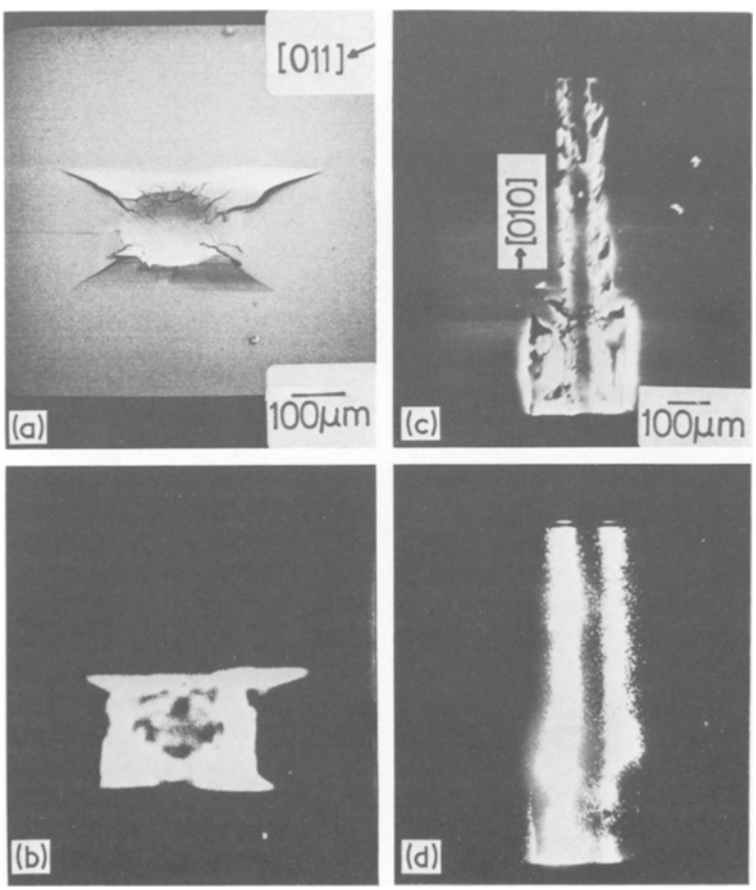

Figure 2 Secondary electron (a and c) and cathodoluminescence (b and d) micrographs of damage on the (1 0 0) surface of MgO crystals caused by static loading and by scratching. (a, b) 0.4 mm diameter tungsten carbide sphere loaded to 20 kg; $\epsilon = 9.1\%$. (c, d) Scratch produced by moving a hemispherical stylus on the surface at a velocity of 0.2 mm sec^{-1}. The crystals were not etched.

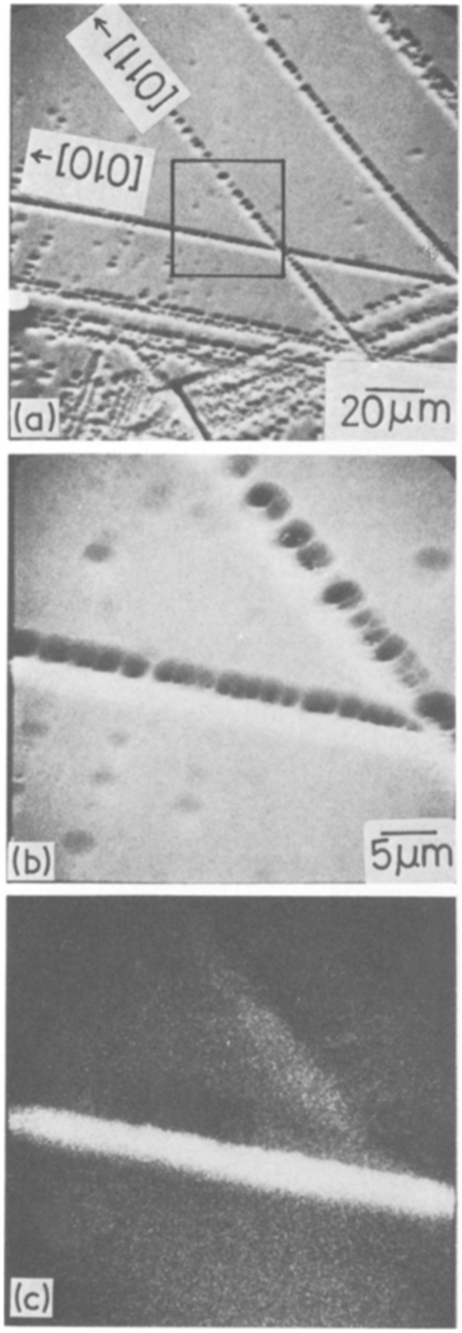

Figure 3 Magnified micrographs of the damage shown in Fig. 1a and b. Two rows of etch pits (b, c), one due to the screw dislocations and the other due to the edge dislocations, were selected from the region marked in (a). It is clear from (c) that the luminescence from the screw dislocations is much higher.

Enhanced luminescence at a damage site also appears in LiF crystals, though in details there are differences in its CL behaviour from that of MgO. Firstly, for both static and dynamic loading the luminosity from within the indentation is significantly stronger than that from the deformation zone outside the indentation (see Fig. 4a to d). Secondly, we did not observe any fine structure in the CL and the relative intensities of the luminescence from the screw and edge dislocations. Surface scratches also give CL and Fig. 4e and f shows SE and CL micrographs, respectively, of a scratch caused by a pointed indenter. Again the CL is greater from within the track than from the region outside it.

4. Discussion

As in previous investigations, the main CL has been found to be associated with dislocations in the deformed zone. We have also shown that in MgO the CL from screw dislocations on $\{1\,1\,0\}_{45}$ planes is considerably greater than that from edge dislocations on $\{1\,1\,0\}_{90}$ planes (see Fig. 3). A factor which may be of relevance here is that the screw dislocations produce steps on the surface whereas the edge dislocations do not; these steps may reflect light more efficiently. No such difference was observed for LiF.

One interesting observation was that the CL from the actual contact zone was noticeably more for spherical than Vickers pyramid indentations on the same surface. This difference cannot be explained on the basis of the total representative plastic strains in the two cases as the strains for spherical indentations are about the same or higher than that for the pyramidal indentations, i.e. $\epsilon = 8\%$. However, there is the possibility that the plastic strains very close to the indented surface are significantly different in the two cases; detailed knowledge of the strain distribution about the indentations is, as yet, not available, however. Another factor is that for the pyramidal indentations there is a severe rotation and distortion of the planes in the region directly beneath the indenter so as to accommodate its shape.

As mentioned in Section 1, the explanations of CL from dislocations are based on the generation of point defects [1, 2, 5] and on the reduction in the energy of the band gap at dislocations due to the dilatation [3]. On the latter model it is not clear why screw dislocations should give higher intensity CL than that from the edge dislocations as the dilatation around a screw dislocation is zero [8].

Finally, although the processes involved are

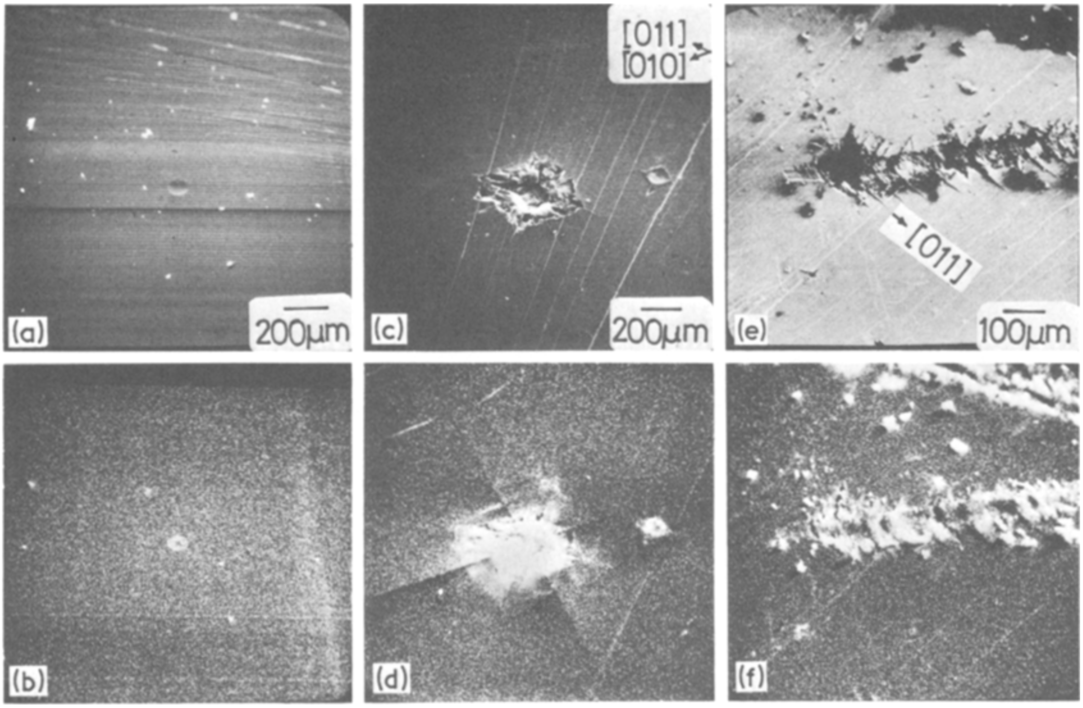

Figure 4 Secondary electron (a, c, e) and cathodoluminescence (b, d, f) micrographs of damage on the (1 0 0) surface of LiF crystals caused by static and dynamic loading, and by scratching. (a, b) Static loading by a 0.4 mm diameter tungsten carbide sphere under a load of 500 g. (c, d) Impact by a 0.44 mm diameter glass sphere of velocity 245 m sec^{-1}; $\epsilon = 12.2\%$. On the right of the main damage site there is another site which is due to the impact of a similar size particle at a much lower velocity. (e, f) Scratches by a sharp point. Note that in all cases there is a significant amount of luminescence from the actual contact zone.

very complex and further work is needed, the observation of CL from surfaces which have been subjected to contact stresses provides us with a simple, quick and versatile method for detecting and studying plastically deformed regions.

Acknowledgements
We would like to thank Drs L. M. Brown, Y. Enomoto, and S. J. Pennycook for discussions.

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Received 23 August and accepted 1 October 1979.