Indentation and liquid impact studies on coated germanium

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[Received 20 January 1983 and accepted 29 April 1983]

ABSTRACT

The effect of thin coatings on the damage to brittle materials due to static and dynamic loading has been examined for hard carbon layers on germanium. For quasi-static ball indentations a significant increase in the load for ring-crack formation was observed. The increase depends strongly on the ratio of coating thickness to ball radius. The results are in good agreement with theoretical predictions. Examination of the impact damage caused by a high-velocity liquid jet showed only a small increase in rain-erosion resistance. Coating debonding, leading to a local loss of protection, was a serious problem.

§ 1. INTRODUCTION

Germanium is an important lens material for optical systems designed for use in the infrared part of the spectrum since it combines good optical properties with a reasonably high mechanical strength (Marsh and Savage 1974, Donald and McMillan 1978). However, as in other brittle materials, contact with either sharp or blunt particles can lead to crack formation and hence strength reduction. The type of damage depends on the applied load and the radius of curvature of the indenting particle (Dick 1970). For elastic-plastic contact, as occurs for sharp particles, several crack systems (radial, median and lateral cracks) can form at different stages of the loading cycle. In the literature there is some controversy over the precise origin of these cracks. Evans and co-workers (Lawn and Evans 1977, Chiang, Marshall and Evans 1982) assume that the nuclei for these cracks already exist, while Hagan and others (Hagan and Swain 1978, Hagan 1979, Hockey and Wiederhorn 1979, van der Zwaag, Hagan and Field 1980) have stressed the possibility of crack nucleation due to plastic deformation processes in nominally brittle materials. For germanium the relation between plastic deformation and associated cracking around sharp indents has been examined by Bannerjee and Feltham (1974) and Lankford and Davidson (1979).

In purely elastic contact, as occurs with indentation by a ball of large diameter, a ring crack is formed around the contact area which, upon further loading, propagates into a cone crack (see Lawn and Wilshaw (1975) for an extensive review). The surface defects inherent in brittle materials form the nuclei for these cracks. The driving force for the propagation of these defects

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is provided by radial tensile stresses which exist in a shallow surface layer outside the contact zone.

Recently, it has been shown theoretically (van der Zwaag and Field 1982) that the maximum radial stress generated in the substrate by a spherical indentation can be reduced by applying a thin rigid coating. Certain hard, anti-reflection coatings are of interest with germanium since they do not interfere with infrared transmission, as would soft (for example elastomeric) coatings. In particular, for coating materials with a very high Young's modulus a significant increase in the fracture load for the substrate is predicted. The reduction in maximum tensile stress also depends strongly on the effective coating thickness, i.e. the ratio of coating thickness to contact radius. Therefore, in the present work we have examined the critical load for ring-crack formation in carbon-coated germanium as a function of coating thickness and radius of curvature of the indenting particle.

Furthermore, we have examined the beneficial effects of thin carbon coatings on the amount of damage due to high-velocity rain-drop impacts. This form of dynamically elastic loading can cause significant damage to brittle forward-facing aircraft components. (For a general review of this field see Adler 1979, Field 1979, Preece 1980.)

§ 2. EXPERIMENTAL

The effect of thin, hard coatings on the fracture load for ball indentations was examined for specimens of germanium (25 mm in diameter, 2 mm thick) provided with hard carbon coatings of 1 and 3 μm thickness. Tungsten carbide balls (0.4 and 1.0 mm in diameter) and hardened steel balls (2.0 and 4.0 mm in diameter) were used as indenters. The load was applied with an Instron testing machine. The cross-head speed during loading was 0.05 mm min⁻¹. The maximum load was applied for about 10 s. The occurrence of ring-crack formation was determined by examining the surface with an optical microscope after unloading.

The improved liquid-jet impact technique which was used to simulate high-velocity ($> 100 \text{ m s}^{-1}$) rain-drop impact has been described in detail elsewhere (Field, Gorham and Rickerby 1979, Field, Gorham, Hagan, Matthewson, Swain and van der Zwaag 1979). In this technique a lead slug is fired from a modified 0.22 calibre air rifle into the rear of a water-filled stainless steel chamber. The forward motion of a sealing neoprene disc extrudes a coherent jet of water with a smoothly curved front profile through the orifice section at the front of the chamber. By varying the gas pressure in the reservoir, velocities of up to 1000 m s⁻¹ can be reached. In the present work jets were produced using a 0.8 mm diameter orifice. The damage produced by these jets simulates that caused by 5 mm diameter rain-drop impacts over a wide velocity range (van der Zwaag and Field 1983). The impact damage to both coated and uncoated specimens was assessed by optical microscopy.

§ 3. RESULTS

3.1. *Ball indentations on coated germanium*

Examination of the contact damage at high loads on both coated and uncoated germanium showed an approximately hexagonal 'ring' crack. The

ring cracks were usually visible on the coating surface. However, in a very limited number of cases at low loads only subsurface cracking could be detected, suggesting that for these coated specimens crack propagation started in the substrate. For 0.4 mm ball indentations, radial cracks as well as cone cracks were formed. Plastic deformation and occasionally coating debonding were also observed for this ball diameter. These results therefore fall outside the scope of the present work, which is concerned with the effect of coatings for purely elastic contact.

Detecting the onset of cracking in an optically transparent material is relatively easy since the contact area can be viewed directly. The procedure adopted here was to determine the load at which 50% of the indents showed partial or complete ring cracks after loading. This load is plotted in fig. 1 as a function of the indenter radius for both uncoated and coated specimens. The results are based on about 30 indents per data point. In particular for the larger ball sizes complete shattering of the specimen occurred frequently making it impossible to measure the fracture load accurately. Figure 1 shows that a carbon coating can lead to a significant increase in the fracture load. For the 1 μm coating the increase is about 100%, while for the 3 μm coating it is at least 200%.

Fig. 1

Variation of the load at which ring cracks are formed, as a function of ball radius, for both uncoated and coated germanium.

3.2. Liquid-jet impact damage

Figure 2 shows the damage caused by single and multiple liquid-jet impact at 260 m s⁻¹ to uncoated germanium. The damage is typical of that in brittle materials and consists of a central undamaged zone surrounded by an annular region with short circumferential cracks. The damage is due to the interaction of the Rayleigh surface wave generated by the impact and surface defects (Bowden and Field 1964). The influence of the {111} cleavage plane orientation on the fracture pattern is well illustrated in fig. 2, which also shows the increase in impact damage with increasing number of impacts. For the first and

Fig. 2

Impact damage to uncoated germanium caused by a 0.8 mm diameter jet at an impact velocity of 260 m s^{-1} , showing damage after the (a) first, (b) second and (c) third impacts. The letter A marks a common feature in each figure to aid in the comparison.

Fig. 3

Impact damage on germanium with a $3\text{ }\mu\text{m}$ thick coating caused by a 0.8 mm diameter jet at an impact velocity of 260 m s^{-1} , showing damage after the (a) first, (b) second and (c) third impacts. Letter A marks a common feature.

Fig. 4

Damage caused by three consecutive impacts at 220 m s^{-1} on (a) uncoated and (b) $3 \mu\text{m}$ coated germanium.

second impact, cleavage fracture is the most important mode of erosion. During the third impact the lateral outflow of water dislodged already existing raised cleavage edges and caused gross removal of material. Such a sequence of erosion mechanisms has also been observed in multiple rain-drop impact experiments on polycrystalline and single-crystal germanium (Hooker 1977).

Figure 3 shows the impact damage for a specimen with a $3\text{ }\mu\text{m}$ coating, also impacted at 260 m s^{-1} . The light area in this figure is the debonded region caused by the outflow of water. For the first and second impacts the number of cracks formed is smaller than on the uncoated specimen. At the third impact the increase in damage is considerable, particularly in the debonded areas where there is a local loss of protection.

A more favourable influence of thin coatings on the jet impact damage was observed at lower impact velocities. Figures 4 (a) and 4 (b) show the damage caused by three successive impacts at 220 m s^{-1} for an uncoated and a $3\text{ }\mu\text{m}$ -coated specimen, respectively. For the uncoated specimen an almost complete ring of cracks was formed at each impact. However, on the coated specimen only a few isolated cracks could be detected in the coating. No subsurface cracking was observed (for these thin coatings subsurface cracking would easily have been detectable). At this lower impact velocity there were no signs of incipient coating damage.

At an impact velocity of 260 m s^{-1} , the $1\text{ }\mu\text{m}$ thick coating lead to less reduction in damage than the $3\text{ }\mu\text{m}$ coating. However, no significant coating debonding occurred. At the lower impact velocity there was no significant differences between the damage to 1 and $3\text{ }\mu\text{m}$ coatings.

§ 4. DISCUSSION

4.1. Ball indentations on coated germanium

Here we compare the measured increase in the fracture load of coated specimens with the results of our recent theoretical study on the effect of thin hard coatings on the Hertzian stress field (van der Zwaag and Field 1982). To enable the comparison to be made, we have replotted in fig. 5 the data of fig. 1 in the form of fracture pressure versus contact radius. The contact radius was calculated using the well-known Hertzian equation

$$a^3 = \frac{4}{3} FR \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right), \quad (1)$$

where a is the contact radius, F the applied load, R the ball radius, and ν_1 , ν_2 and E_1 , E_2 the Poisson ratios and Young's moduli of the indenter and substrate, respectively. We have taken $E_2 = 140\text{ GPa}$ and $\nu_2 = 0.20$ as the average values of the elastic constants for germanium. It has been shown theoretically that for these thin coatings eqn. (1) gives a good approximation of the true contact radius on coated specimens. For the uncoated specimens the fracture pressure (and hence the fracture stress) decreases continuously with increasing ball size (and hence with contact radius). This indenter size effect arises from an increase in the probability of stressing a flaw of sufficient size with larger sampled area.

Fig. 5

Variation of the pressure at which ring cracks are formed as a function of contact radius for both uncoated and coated germanium (same data as in fig. 1).

Fig. 6

Ratio of the fracture pressure for coated and uncoated specimens as function of the normalized coating thickness (see the text).

The rapid decrease in fracture pressure with contact radius for the coated specimens is due to a combination of two effects: (1) the usual decrease in fracture pressure with contact radius as observed for the uncoated specimens and (2) the simultaneous decrease in the effective coating thickness (ratio of layer thickness d to contact radius) which determines its degree of protection. To separate the two effects and to obtain a good indication of the protection provided by the coating, we have plotted in fig. 6 the ratio of the fracture pressure for coated specimens, P , and that for an indentation *with the same contact radius* on an uncoated specimen, P^* , versus the normalized or effective coating thickness d/a . This procedure was followed to correct for the increase in contact area (and hence the decrease in fracture pressure because of the effects of flaw statistics) at the increased loads for the coated specimens. The error bars in this figure are related to the uncertainties in the fracture loads indicated in fig. 1. Figure 6 shows an approximately linear increase of the normalized fracture pressure with effective coating thickness. The increase in fracture pressure for the 0.4 mm ball indentations (where elastic-plastic contact takes place) is considerably smaller than predicted from the linear dependence observed for the larger ball sizes.

To compare the measured increase with theoretical predictions, we have to estimate the elastic properties of the carbon film since no experimental values are yet available. It has often been found that the Young's modulus of disordered systems is about 80% of that of the crystalline state (Weaire, Ashby, Logan and Weins 1971). Taking diamond as the reference state, we expect a Young's modulus of about 800 GPa. On the other hand, it has been found experimentally that the Young's modulus of thin amorphous films of germanium and silicon (which have the same structure as diamond) is only 30% of the crystalline value (Testardi and Hauser 1977); for the present coating material this would give a Young's modulus of about 300 GPa. In fig. 6 we have plotted (dashed lines) the theoretically predicted increase in the fracture pressure for three different values of Young's modulus of the coating (300, 500 and 800 GPa) while assuming that the critical pressure is determined by substrate failure. Poisson's ratio for the coating was taken as 0.20. Ignoring the two data points for 0.4 mm balls, where plastic deformation took place, a surprisingly good agreement between theory and experiment is obtained.

4.2. *Liquid-jet impact experiments on coated germanium*

The threshold damage velocity for 0.8 mm jets is 150 m s^{-1} (Blair 1981). Optical examination of the surface damage due to liquid-jet impact has shown that there is some protection provided by the carbon coating. As the number of specimens available was limited, we were unable to determine quantitatively the increase in threshold velocity for impact damage as a function of coating thickness. However, the similarity of damage patterns on coated and uncoated surfaces suggests that only a modest increase in the threshold velocity is obtained by coating. Furthermore, the observations have shown a rapid loss of protection at higher impact velocities as the coating is debonded by the shearing action of the radial outflow. This phenomenon, which has also been observed for drop impact experiments on coated zinc sulphide (Hackworth 1978) will be a major problem for real rain erosion conditions where the number of impacts per unit area will be high. Finally, it was noted that the thin

coating seemed almost as effective as the thick coating, but less susceptible to debonding. Two points are likely to be significant here. The first is the practical problem of depositing thick coatings without leaving residual stresses which make the coatings prone to debonding. The second is that liquid-jet impact is a particularly severe form of loading, combining high normal and shear stresses. In particular because of the outflow of water the shear stresses generated at the interface will be very much higher than under identical solid particle impact conditions.

§ 5. CONCLUSIONS

It has been shown that the critical load for spherical indentations to form ring cracks in germanium can be significantly increased (by up to 200%) by means of a thin carbon coating. The increase in the fracture load depends strongly on the effective coating thickness. The results are in good agreement with theoretical predictions. For liquid-jet impact the reduction in impact damage was more modest. Coating debonding due to lateral outflow was a major limitation of the coating system, particularly for thicker coatings. Although a coating may provide only a low degree of protection during liquid-jet impact, it can still assist in maintaining the pristine state of the surface so that the material performs better when impact does take place. The coating also has an important role as an anti-reflection layer. The rather different behaviour of the coating in ball indentation and in liquid-jet impact experiments has shown that care should be taken in making quantitative predictions about the performance of a coating under dynamic loading conditions from quasi-static experiments.

ACKNOWLEDGMENTS

We thank Dr. N. S. Corney for comments on the manuscript and Dr. A. Lettington of RSRE, Malvern, for providing the specimens. The research was supported by the Ministry of Defence (Procurement Executive) and by the U.S. Air Force Office of Scientific Research under grant number 78-3705.

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