HIGH MODULUS LAYERS AS PROTECTIVE COATINGS FOR 'WINDOW' MATERIALS

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ABSTRACT

Theoretical and experimental studies have been made on the effect of thin hard coatings on the stress fields generated by indentation and impact onto a flat half space. The theoretical work uses finite element techniques and shows that a thin hard coating can have a significant effect on the maximum tensile stress generated in the substrate providing there is a good bond at the coating/substrate interface. As it is technically difficult to deposit layers of thickness greater than a few microns without residual stresses causing debonding and peeling; double layer and multilayer systems have also been examined. Hertzian indentation on hard carbon coated germanium has shown that such coatings do offer protection against indentation damage. High speed liquid impact on coated germanium and zinc sulphide has shown, however, that although the quasi-static performance of the material may be improved the impact resistance of the coated material is not significantly affected. Reasons for this are discussed. In conclusion, although it is still to be hope that coatings that do improve the impact performance of materials can be manufactured, current coatings offer better protection against handling damage rather than against impact.

SINGLE LAYER COATING SYSTEMS

The effects of both elastomeric and thin hard coatings on the elastic response of materials have previously been investigated in this laboratory (1). Work on thin hard coatings provides a basis for the current study and therefore the major results of this work are described here.

A finite element model developed, using the PAFEC finite element package, of a Hertzian indent (sphere on flat) was used to model a single layer hard coating (2) on a substrate. The coating layer was thin, being no more than 20% of the contact radius of the indent. Vertical displacements were used to specify the Hertzian boundary conditions.

Van der Zwaag et al (3) showed that although the presence of a thin hard coating increased the axial stress in the substrate at the interface the radial and circumferential stresses were decreased (in comparison to the stresses at such a depth for a uniform half-space) (see figure 1). For impact problems the important feature is the reduction of the radial tensile stresses at the edge of the contact area.

Figure 1. Stresses in the substrate at the coating interface for a single layer hard coating. Full line gives the analytic solution at this depth for a uniform halfspace. Dots give the finite element solution for the coated system. a) Axial stress, b) Circumferential stress, c) Radial stress.

(after van der Zwaag et al (3))

In this study Young’s modulus, Poisson’s ratio and the thickness of the coating were varied. The results for the maximum tensile (radial) stress generated at the interface are summarised in figure 2. If the half space were a uniform material then the stress would be as given by the dotted line. Overall it was found that the higher the Young’s modulus of the coating the greater the reduction of the maximum tensile stress at the interface. Increasing the Poisson’s ratio of the coating also had a beneficial effect. It should be noted, however, that the maximum tensile stress at the coating surface increases with increasing Young’s modulus and thus it is necessary to have a coating material that is capable of withstanding higher stresses than the substrate material. Reducing the thickness of the coating reduces the amount of protection offered to the substrate.

Figure 2. Variation of the maximum radial stress in the substrate with normalised coating thickness for a single layer coating. (After van der Zwaag et al.)

Figure 3. Variation of the maximum radial stress in the substrate with normalised coating thickness for monolayer and double layer coatings. In the case of double layer coatings \( t_1 = t_2 \). (After van der Zwaag et al.)

DOUBLE LAYER COATING SYSTEM

As it is technically difficult to deposit layers with a thickness greater than a few microns without residual stresses resulting in debonding of the layer, double layer systems, where each layer has different elastic properties were then investigated. The mesh for single layer systems was slightly modified for this work.

With a double layer system, similar results were found. The effects of having different moduli in the two coating layers compared to a uniform thick layer were studied by van der Zwaag et al. The individual coating layers were taken as having equal thickness in this work. A combination of layers was found to be less effective than a thick layer with a modulus equivalent to the greater of the two moduli of the two coating layers. It was found that the order of these coating layers (ie. whether the top or the bottom layer had the higher modulus) made no difference to the resultant stress in the substrate at the interface between the coatings and the substrate (see figure 3). Again the effectiveness of the coating is reduced as the total coating thickness is reduced. There were differences, however, on both the stresses at the top surface of the coating and the interface between the coatings. The stresses in the interlayer are reduced, for example, when the higher modulus layer provides the outer layer of the coating. The surface stresses were again found to be increased for the coated material; the precise value depending on the combination chosen.
Real optical coating systems may consist of more than two layers both in an attempt to overcome the problem of residual stresses and to achieve the desired optical performance of the component. A finite element mesh again using the PAFEC system has therefore been developed for a 5 layer coating system. The top layer of this system is assumed to be a thin antireflection layer. The bottom, bonding, layer of this system is also assumed to be thin: both layers are assumed to be 1μm thick. Although even thinner layers might be more realistic, this would require a substantial increase in the number of elements and thus a greater increase in the amount of computing time required (for example doubling the number of elements approximately quadruples the amount of computer time required). The intermediate layers have been assumed for simplicity to all be 5μm thick. A new mesh had to be developed for these thinner elements as modifying the previous mesh resulted in many distorted elements which produced incorrect solutions in the analytic (pure Hertzian) case. This mesh, which is shown in figure 4, has the advantage that it is easy to insert additional layers into the coating system and to vary the thickness of the layers. It may thus be used to model a wide range of possible coating systems.

To check that the mesh would produce good results it was initially tested on a pure Hertzian situation: all the coating layers and the substrate were given the same mechanical properties. The results for pressure boundary conditions and for displacement boundary conditions are given in figures 5 and 6. These results are for the stresses at a depth equivalent to the surface of the substrate in a coated specimen. It can be seen that the pressure boundary conditions give the more accurate results although the discrepancy with displacement conditions is still only 5%.

As with the previous work, despite the reduced accuracy, displacement boundary conditions have been used. This more closely models the real situation where different pressures will be generated by impact on different materials.

**Results for coated systems**

Systems based on the following coating materials have been studied so far: zinc sulphide; zinc selenide and diamond like carbon (DLC). For the purposes of this work diamond like carbon has been assumed to have the properties of diamond averaged over all directions.

The results for a zinc sulphide coating on a zinc selenide substrate show relatively little difference from those assuming that the whole sample is made of zinc selenide. This is because the differences in moduli between these two materials are small.
Figure 5. Stresses in a uniform halfspace at a depth equivalent to the coating depth. Crosses indicate the finite element solution for the current mesh with pressure boundary conditions. Solid line gives the analytic solution.

Figure 6. Stresses in a uniform halfspace at a depth equivalent to the coating depth. Crosses indicate the finite element solution for the current mesh with displacement boundary conditions. Solid line gives the analytic solution.

It is only when a diamond like carbon layer is introduced that substantial differences in the substrate stresses are seen. The results are similar to those found in the work described above, namely the axial stresses are increased, but the radial and circumferential stresses are decreased (see figure 7). In a multilayer system it is the high modulus layers that are most important in reducing the contact stresses generated in the substrate. That this is the case even with quite thin layers is fortunate as it means that although thick layers may not be usable owing to the generation of large residual stresses or because the optical properties are unsuitable some measure of protection can still be afforded to the substrate.
Figure 7. DLC/ZnS/ZnSe system. Crosses indicate the finite element solution for the substrate stresses at the interface. Solid line gives the analytic solution for a uniform halfspace at this depth.

Figure 8. DLC/ZnS/ZnSe system with thermal deposition stresses. Crosses indicate the finite element solution for the substrate stresses at the interface. Solid line gives the analytic solution for a uniform halfspace at this depth (no thermal stresses).
Thermal stresses from deposition

Most practical coating systems will have residual stresses present in them resulting from the deposition process. The most readily calculable of these are thermal in origin: the deposition of a coating at an elevated temperature will result in thermal stresses being 'frozen into' the system on cooling owing to the thermal mismatch in the thermal expansion coefficients in the coating and the substrate. These stresses may be calculated using PAFEC for the mesh being studied. The resulting stresses may be superposed on those resulting from the Hertzian indent for the identical coating system. The stress distribution resulting from deposition at 300°C for the DLC/ZnS/ZnSe system previously discussed is shown in figure 8 (the solid line gives the solution for a uniform half space). It can be seen that such stresses introduce an additional tensile component into the stress distribution in the substrate. This is because diamond like carbon has a very low thermal expansion coefficient compared to the substrate and the diamond like carbon layer thus finishes in compression and the substrate in tension. These stresses may, therefore, result in damage to the substrate.

In addition to such residual stresses a component that is in flight may be subjected to thermal shock. The stresses generated in this fashion could also be expected to modify the performance of the material. Such effects are currently being studied.

EXPERIMENTAL WORK

Hard carbon on germanium

Experimental work on germanium samples protected by hard carbon layers is given in van der Zwaag et al. As predicted, films of 1µm and 3µm had significant effects and offered protection to indentation damage (see figure 9).

![Graph](image)

Figure 9. Variation of load at which ring cracks are formed, as a function of ball radius, for both coated and uncoated germanium (after van der Zwaag et al).

Coatings on ZnS

Damage resulting from liquid impact on brittle materials is a stress wave dominated phenomenon as the high 'water hammer pressures' generated during the initial compressible phases of the impact are of a short duration (typically ~0.01 - 0.1µs). In particular surface cracks are extended by interaction with the Rayleigh surface waves generated by the impact resulting in a circumferential crack pattern (see figure 10a). See also a related paper at this conference.

Liquid impact is conveniently studied in the laboratory using the single jet impact technique. It is possible to relate the damage caused by particular sized jets to that produced by an 'equivalent' (usually 2mm diameter) spherical drop. Quantitative assessment of any damage can be achieved by measuring the post-impact (residual) strengths using the hydraulic pressure test technique. A residual strength curve for zinc sulphide is shown in fig. 10b. It can be seen that there exists a threshold velocity below which the stresses induced by impact are insufficient to extend the pre-existing
surface defects. Once the threshold velocity is reached these defects are extended by interaction with the Rayleigh wave pulse.

The extent to which any flaw grows is dependent on both its initial size and its position relative to the impact site. This results in a bimodal transition region: in some of the samples no pre-existing flaws are significantly extended, whilst in others, with more serious flaws in the high stress region, they are. At high impact velocities many more of the flaws are extended and thus the strength of all the samples is reduced. The width of the bimodal transition region of the residual strength curve is reduced for multiple impact. Surface flaws are able to grow on each loading cycle (assuming the threshold velocity has been exceeded) and thus the probability that a flaw close to the impact site will be extended significantly is increased. The probability for a reduction in strength of a sample is therefore increased and hence there is a reduction in the width of the bimodal region (see fig. 10b).

![Typical liquid impact damage on zinc sulphide](image)

![Residual strength curve for zinc sulphide](image)

**Figure 10.** a) Typical liquid impact damage on zinc sulphide. b) Residual strength curve for zinc sulphide.

With several coatings studied, only a marginal increase of a few m s\(^{-1}\) in the threshold velocity for damage on zinc sulphide has been found although the quasi-static strengths have been increased significantly (see figure 11 for example).

![Residual strength curve for a typical coated zinc sulphide](image)

**Figure 11.** Residual strength curve for a typical coated zinc sulphide.
There are several possible reasons for this. Firstly, as the velocity of impact is increased the pressure generated during impact increases more than linearly with velocity. This is because, although the high pressures generated during the initial compressible stage of the impact are given by
\[ P = \rho C v, \]
where \( \rho \) is the density, \( C \) the shock wave velocity and \( v \) the velocity of the impacting liquid; the shock wave velocity also depends on the impact velocity
\[ C = C_0 + k v, \]
where \( C_0 \) is the sound wave velocity in the liquid and \( k \) is a constant equal to 2 for water. The duration of the high pressure (damaging) phase of the impact also increases with velocity. This has a subtle but important effect. It has to be remembered that the duration of the high pressure stage of liquid impact (\( \tau = 3R v / 2C^2 \)) is short (typically 50ns for 2mm diameter rain drops impacted at 100m s\(^{-1}\)), and the dynamic interaction of a stress pulse with a flaw has to be considered. If the pulse duration increases, a greater length of flaw is stressed as the penetration depth of the Rayleigh wave is dependent on the pulse width (inversely dependent on frequency), and thus the conditions for crack growth are more easily achieved. Finally the residual stresses in the coating and the substrate and the adhesion of the coating to the substrate become very important: all the above calculations assume that there is a perfect bond between the coating and the substrate. Figure 12 shows a case where the coating has debonded from the substrate during impact.

![Image of coating debonded from substrate](image)

It is still to be hoped that a suitable coating can be manufactured such that an increase in threshold velocity can be achieved. Until this is the case hard coatings will be of most in preventing handling damage to the component rather than enhancing its in-flight mechanical performance.

CONCLUSIONS

High modulus layers can be used as protective coatings for 'window' materials. They offer most protection against handling damage and may increase the quasi-static strength of the component. This has been shown both experimentally and theoretically. Under dynamic (impact) conditions experiments have shown that such coatings offer less effective protection to the substrate and reasons for this have been given. Of particular importance in the dynamic case is the adhesion of the coating to the substrate.

The deposition of such coatings can result in high residual stresses both in the coating and the substrate. These stresses can result in delamination of the coating and will modify the performance of the coating under any given loading conditions. Preliminary theoretical calculations show the effect that such stresses that are thermal in origin may have in a quasi-static loading case. It should be possible for residual stresses to act beneficially and this is one of the objectives of our present research.
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REFERENCES