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Strength of glass with vacuum-deposited metal films: Cr, Al, Au and Ag

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Fracture strength of acid-etched glass with vacuum deposited metal films is investigated. The strength of the etched glass having an initial value of 1696 ± 39 MN m^{-2} reduces to 265 ± 10 MN m^{-2} with 69 nm thick Cr film coating. Al film coating also causes the strength reduction, but the reproducibility of the strength is not found even under strictly controlled evaporation conditions. In ambient air, the strength of Au- and Ag-coated glasses maintains the initial high strength value and slightly increases with film thickness. From strength reduction behaviour of Cr-coated glass and dynamic fatigue characteristics for Ag-coated glass, it is highly probable that rupture of the metal film takes place before fracture of the glass occurs, and the flaw formed in the film propagates under loading into the glass to act as a Griffith crack.

1. Introduction

The thin metal film coatings on the glass surface have been widely used to obtain various useful optical properties for mirror and solar energy reflecting glasses. Although many studies have been made only on their optical properties [1], the mechanical properties of glasses coated with thin metal films are not yet well understood.

Generally thin inorganic film coatings on glass have a detrimental effect on its breaking strength, but the degree of the strength reduction varies over a wide range because of differences in materials and process of coating. Although some investigations on the fracture of coated glasses have been made [2, 3], their mechanisms are rather complicated because of various factors influencing the strength. Ohta *et al.* [3] have investigated the fracture strength of etched glasses coated with SnO_2 and TiO_2 films by chemical vapour deposition (CVD). Their conclusion is that the strength weakening by film coating is due to stress concentration at the surface irregularities in the films when breaking. In the CVD process, the glass substrates are normally heated up to $\sim 600^\circ$ C, so the strength decrease of etched glass by heating [4] seems no longer to be ignored.

Lambert *et al.* [5], on the other hand, have studied fracture behaviour of coated glasses using a simpler system, i.e. etched glasses coated with metal films by vacuum deposition, and shown that the metal films on the surface have a detrimental effect on its strength. However the mechanism of the strength lowering behaviour and the relations between the strength of film-coated glass and properties of the metal film itself have not been clarified.

Previously we reported briefly on the influence of vacuum-deposited metal films on the fracture strength of etched glasses having high strength levels [6], in which it was shown that the fracture strength clearly depends on the kind of metal film and a correlation was found between the effect of film materials on the strength of glass and the adhesive force of metal films to the glass surface and internal stresses present in them.

In the present work, we investigated further the detrimental effect of vacuum deposited Cr, Al, Au and Ag films on the fracture behaviour of etched glasses in detail, and examined the possible mechanism of fracture in the thin metal film coated glasses.

2. Experimental procedure

The soda-lime specimens were laths of commercial float glass of dimensions 80 mm × 50 mm × 2.5 mm thick. In order to avoid ambiguity and scattering

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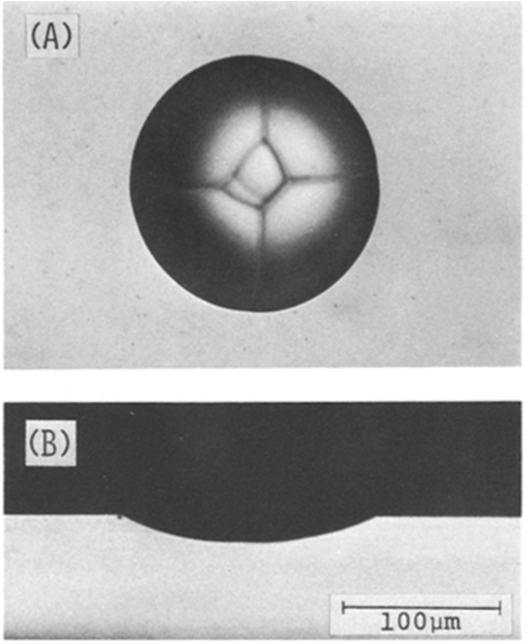

Figure 1 A dish-like etch pit (A) and its cross-sectional view (B).

of the measured strength value, a well-defined flaw was introduced at the centre of the top surface of the glass specimens using a Vickers diamond indenter under a load of 300 gf [7].

Prior to coating, the glass samples were etched in a stirred solution of 5 wt % HF and 5 wt % H_2SO_4 to remove the surface layer of 150 μm, washed in distilled water, rinsed in ethylalcohol and then dried in dry N_2 gas. All minute flaws which existed beforehand on the glass surface were etched away in this treatment, and the flaw of semicircular shape formed by the indentation developed into a dish-like etch pit of 160 μm diameter as shown in Fig. 1. The fracture of the etched specimens in static bending always originated from this dish-like etch pit and the measured value of the bending strength was found to be 1700 $\mathrm{MN\,m^{-2}}$ in air at 24° C, 43% R.H.

We evaporated Cr, Al, Au and Ag films on the side of the dish-like etch pit. Evaporations were made using a commercially available evaporator* and the twelve specimens were simultaneously coated in one operation. 99.999% pure Au and Ag wire evaporants were evaporated from beryllia crucibles placed in tungsten helical heaters. 99.999% pure Al and 99.9% pure Cr slugs as evaporants were deposited from alumina-coated tungsten conical basket heaters. The distance between the evaporation source and the specimens was 25 to 30 cm. Evaporations were carried out at the residual gas pressure of about 10.7×10^{-6} Pa. Monitored deposition rates were 0.7 to 1 $\mathrm{nm\,sec^{-1}}$ for Au, Ag and Cr coatings and 1.4 to 2.3 $\mathrm{nm\,sec^{-1}}$ for Al-coating. The film thickness after deposition was measured using a profilometer Talystep I†.

After film deposition, we immediately caused the specimens to fracture from the dish-like pit side under static bending. Strength measurements were made in three-point bending over a span of 60 mm by use of an Instron type testing machine‡ with a traverse rate of 5 $\mathrm{mm\,min^{-1}}$ in air at 24° C, 43% R.H. or in dry N_2 gas at 22° C, 0.03% R.H. The strength value of the specimen was determined after correcting the data for the large deflection of beams [8].

3. Results and discussion

3.1. Cr-coated glass

Fig. 2 shows the relation between film thickness and bending strength for Cr-coated glasses measured in air and in dry N_2 gas. Data points with error bars represent the mean strength and 95% confidence limits for twelve specimens. The strength lowering effect is remarkable in Cr film deposition onto glass: non-evaporated glasses gave a strength of 1696 ± 39 $\mathrm{MN\,m^{-2}}$ in ambient air, while strengths of the specimens with a Cr film 25 and 69 nm thick were 588 ± 20 and 265 ± 10 $\mathrm{MN\,m^{-2}}$, respectively. Similar detrimental effects of Cr-coatings on the strength of etched glasses were observed through the measurements in dry N_2 gas as shown in this figure. Open symbols in Fig. 2 show the strength of glasses heated in the evaporator by radiant heat from the tungsten heater without the evaporant, during the time corresponding to the formation of each film thickness. Obviously no thermal damage due to the evaporation source alone on the strength was found, so the decrease in strength is attributable to the film coating.

Fig. 3 shows a fracture surface of 69 nm thick Cr-coated glass failed in bending. The fracture mirror was observed just beneath the bottom of

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* NEVA-VI-502, Nippon Electric Varian Co Ltd, Tokyo, Japan.

† Rank Taylor & Hobson Co Ltd, London, UK.

‡ Tensilon UTM-1-500, Toyo-Baldwin Co Ltd, Tokyo, Japan.

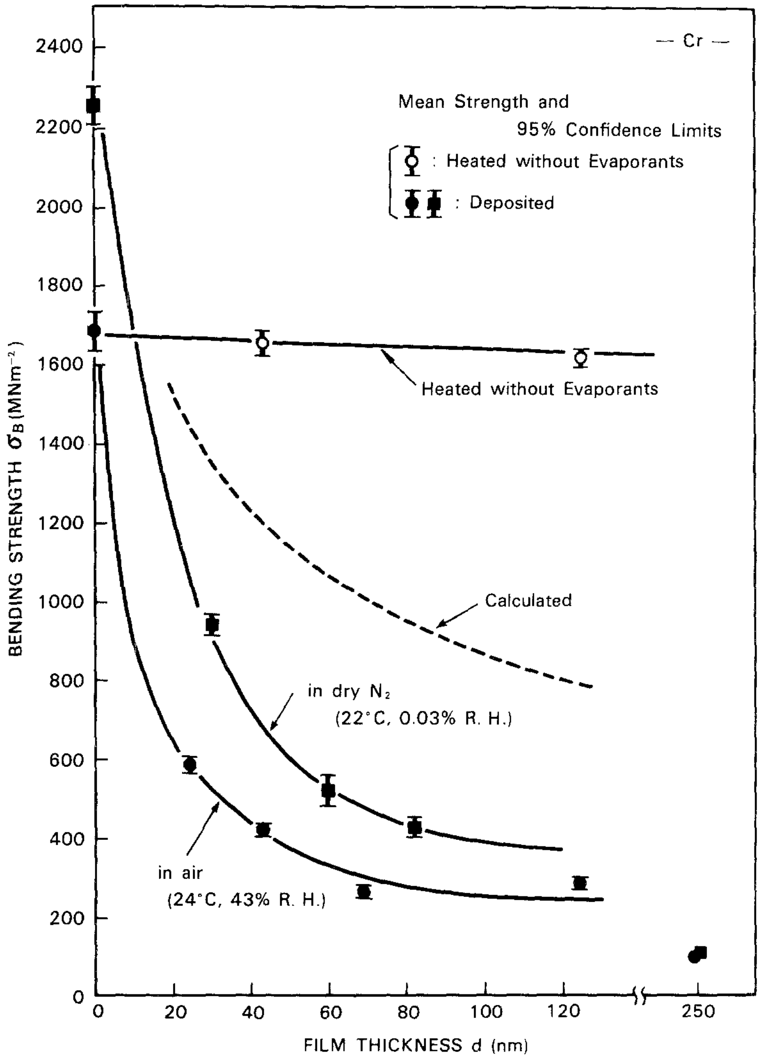

Figure 2 Relationship between bending strength and film thickness of Cr-coated glass.

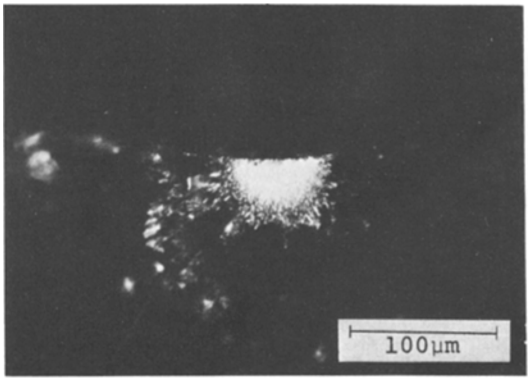

Figure 3 Fracture surface of 69 nm thick Cr-coated glass failed in bending.

the etch pit indicating that the fracture was initiated from the pit where the maximum stress concentrated.

The bending strength of the specimens with a 110 nm thick Cr film after removing the film was measured to examine the degree of mechanical damage on the glass surface produced by coating. The Cr films on the glass surface were removed by electrolytic etching: the specimen was suspended in a glass vessel and a lead wire was carefully bonded to the coated Cr film, a potential of 6 V d.c. was applied between the Cr film and a stainless steel plate, and a 10 wt % oxalic acid solution (2.2 N, pH 6.8 at 25° C) as an electrolytic solution was dropped little by little from a burette

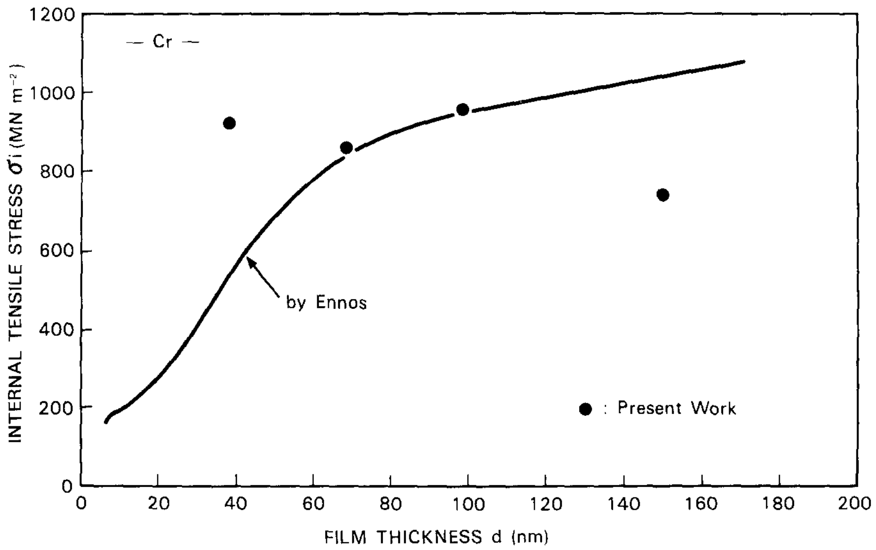

Figure 4 Internal stress in vacuum-deposited Cr film (solid line from Ennos [10]).

into the vessel. The bending strength of Cr film coated glasses having an initial value of 215 MN m^{-2} recovered up to 1628 MN m^{-2} after removal of the Cr film. However, fracture initiating sites were not in the etch pits but edges or other portions in the surface of samples where minute remnants of Cr film still remained. This means that the strength lowering behaviour of Cr-coated glasses is attributable to the film side.

Chromium is a brittle metal and vacuum-deposited Cr has high adhesive force to glass surfaces because of the oxide layer formed at the film/glass interface [9]. If breaking of the Cr film precedes the rupture of the glass, a crack formed in the film will act as a "dominant flaw" and penetrate into the glass to induce the failure of the specimen.

On the basis of the above discussion, the fracture strength of Cr-coated glasses can be estimated using the Griffith–Irwin equation, assuming that the thickness of Cr film is substituted for the depth of the penny-shaped crack. The broken line in Fig. 2 represents the calculated fracture strength for the Cr-coated glass. It is clearly shown that the calculated strength was much higher than the experimental one, e.g. the calculated value was 1177 MN m^{-2}, while the measured one was 265 ± 10 MN m^{-2} for 69 nm thick Cr-deposited glass.

To explain this discrepancy, the internal stress in as-deposited Cr film was estimated, because Ennos [10] reported that the vacuum-deposited Cr film possesses a high internal tensile stress. The value of the internal stresses was also determined by us from the deflection of Cr-coated glass microsheet strip* of 60 mm x 5 mm x 0.08 mm thick which was clamped at one end by an aluminium block. Fig. 4 shows the relationship between the Cr film thickness and the internal stress determined by Ennos [10], together with our data, which qualitatively correspond to the former. Our experimental results show that Cr film 68 nm thick exhibits an internal tensile stress of 863 MN m^{-2}, which is the same order as the difference between the measured and calculated strengths in Fig. 2; accordingly the reduction in strength is attributable to the internal stress stored in the Cr film. Thus, it is concluded that the internal stress acts concentrically at a crack tip formed in the Cr film and causes strength lowering in Cr-coated glasses.

3.2. Al-coated glass

The variation of bending strength of Al-coated glasses with Al film thickness, in air at 24° C, 43% R.H., is shown in Fig. 4. No thermal damage to the strength, as a result of radiant heat from the evaporation source was found, since the high strength level of glass was maintained. Al-film deposition causes, generally, a decrease in strength of the glass; however, the reproducibility of this strength was not found, even though evaporation conditions were controlled strictly, e.g. 180 nm Al-coated glasses gave a strength of 1716 ± 49 MN m^{-2} and 1030 ± 59 MN m^{-2} for each coating.

The influence of the deposition rate on strength

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*Corning No. 0211, Corning Glass Works Inc., USA.

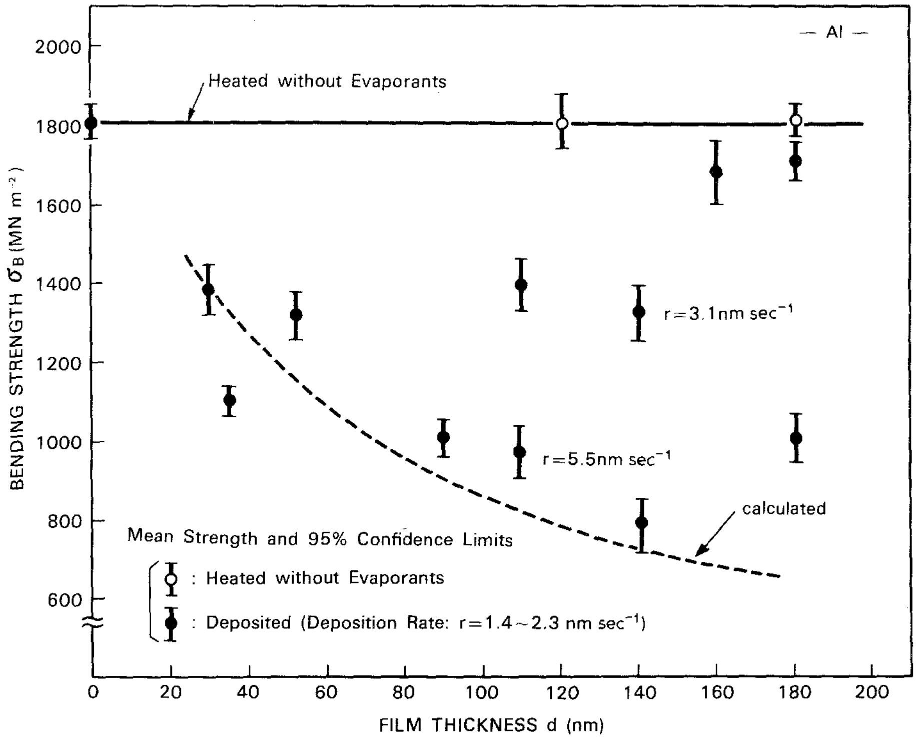

Figure 5 Variation of bending strength of Al-coated glass with film thickness.

was investigated as shown in Fig. 5, but a definite relationship between them was not found: for 110 nm Al-coated glass, the strength of glasses coated at a deposition rate of 5.5 nm sec^{-1} was lower than that of those coated at a rate of 1.8 nm sec^{-1}. In contrast, for 140 nm thick Al-coated glass, the strength of glasses coated at a rate of 3.1 nm sec^{-1} was higher than those of those coated at a rate of 1.6 nm sec^{-1}.

The broken line in Fig. 5 represents the estimated strength of Al-coated glass calculated in a similar manner to that previously mentioned (see Section 3.1) on the strength of Cr-coated glasses. As shown in this figure, the lowest strength values obtained fit this calculated curve.

The measured values of internal tensile stress in Al films deposited on glass microsheet strips were 35.9, 40.7 and 50.2 MN m^{-2} for 41, 92 and 150 nm thick Al films, respectively, which were much lower than those in Cr films. Therefore, the internal tensile stress in Al films seems to have less effect on the strength of Al-coated glass than that in Cr films affecting the strength of Cr-coated glass.

It is known that the structure of the film/glass interface is highly influenced by conditions in evaporation, such as evaporant materials, evaporation source, residual gas pressure, cleanness of substrate, substrate temperature, etc. It is presumed that some impurities like non-stoichiometric oxides are formed at the Al film/glass interface and/or in the film during evaporation and they play a part as "dominant flaws" thus causing the strength reduction of Al-coated glasses, even if the evaporation is carefully carried out under definite conditions. The large scatter in the strength of Al-coated glasses may be mainly due to some instabilities in the numbers and strength of adhesive joints per unit area made at the Al/glass interface, and partly due to the structural variations in the interfacial oxide layers for each coating.

3.3. Au- and Ag-coated glasses

In Figs. 6 and 7, the relationships between the bending strength and the film thickness of Au- and Ag-coated glasses are shown. The thermal damage on glass produced by radiation heating from the evaporation source was also not found here, as indicated by open circles in these figures, which will result in a strength reduction of etched glasses.

In ambient air, the strength of Au- and Ag-coated glasses did not decrease from that of etched glasses but slightly increased with film thickness ranging from 0 to 360 nm. In fact, a glass with Au

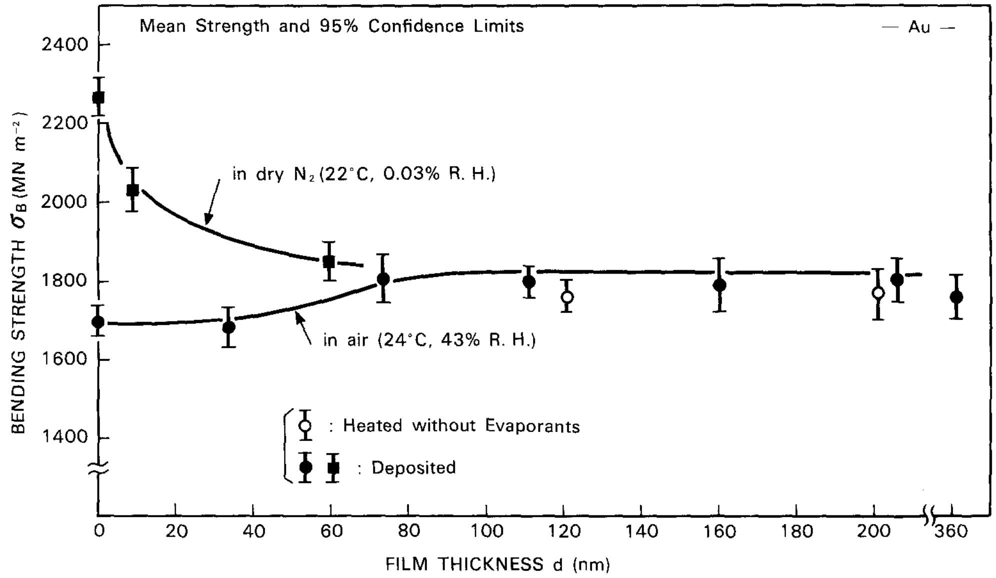

Figure 6 Relationship between bending strength and film thickness of Au-coated glass.

film 205 nm thick maintains a high strength value of 1775 ± 59 NM m^{-2}. This experimental result is different from that obtained by Lambert *et al.* [5]: they reported that Au- and Ag-coatings by vapour deposition induce a strength reduction in glass in ambient air. However, in dry N_2 gas, the detrimental effect of Au- and Ag-coatings on the strength of glasses was observed, and the difference in the strength of coated glasses measured in ambient air and in dry N_2 gas had a tendency to decrease with film thickness.

To explain this difference in strength under these two atmospheric conditions, we measured the effect of the stressing rate ($\dot{\sigma}$) on the bending strength (σ_B), i.e. dynamic fatigue effect of etched glass and 85 nm thick Ag film coated glasses in air at 24° C, 43% R.H. Fig. 8 shows the log–log plot of the experimental results. Ritter [11] showed that the dynamic fatigue of glass can be expressed by the following formula,

$$\sigma_f = k\beta^{1/(n+1)} \qquad (1)$$

where σ_f is fracture strength of glass, β is stressing

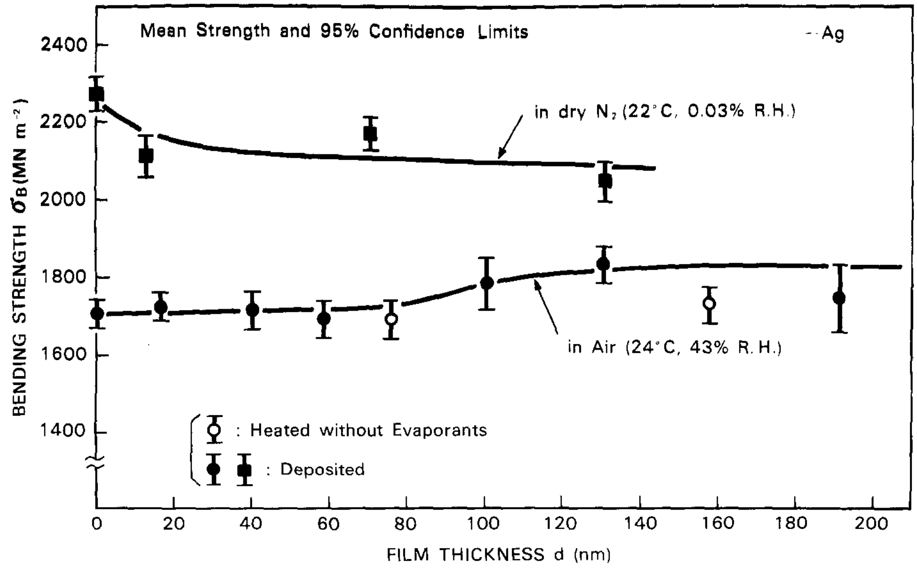

Figure 7 Relationship between bending strength and film thickness of Ag-coated glass.

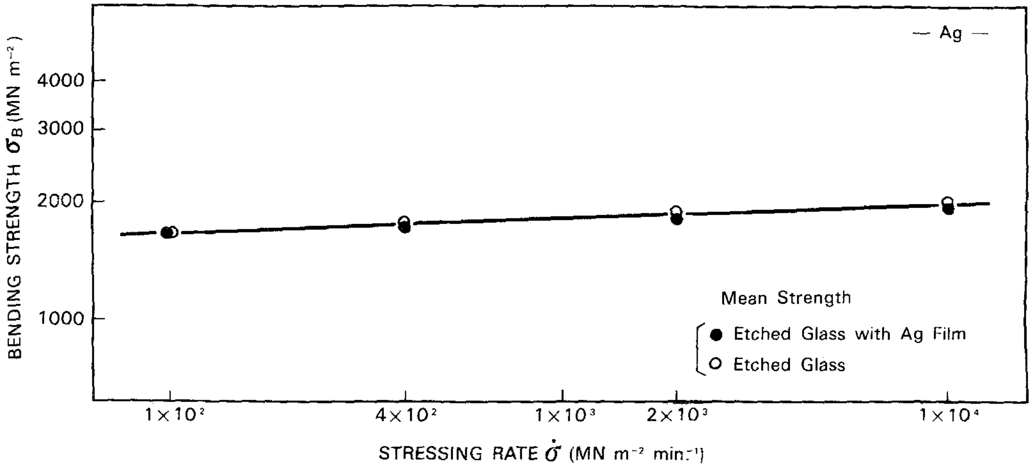

Figure 8 Dynamic fatigue characteristics of acid etched glass and 85 nm thick Ag-coated glass.

rate, k and n are strength constant and stress corrosion susceptibility constant, respectively. Applying this formula to the straight line in Fig. 8, a slope of $25.6^{-1} = (n+1)^{-1}$ for the etched glass was obtained by the least square method. The bending strength values of Ag-coated glasses fitted satisfactory to this line, which indicates that Ag film has no improvements on the dynamic fatigue characteristics of the etched glass. We consider this as follows: Beams [12] reported that the ultimate strain of vapour-deposited thin polycrystalline Ag films in tensile testing is not more than 1%. However, the ultimate strain of Au- and Ag-coated glasses estimated from our experimental results was 3 to 4% in bending. So it can be concluded that the rupture of the metal film precedes the fracture of glass, and the moisture in the ambient air penetrates into the crack of metal film to cause the dynamic fatigue effect on the strength of coated glasses. Since the attack of moisture on the glass surface can be obstructed by the metal film itself up to the time that the film breaks, the slight increase in the strength of Au- and Ag-coated glasses with film thickness is attributable to the fact that the time required for the breaking of the film increases with film thickness. The interfacial bondings between the glass surface and Au and Ag films are very poor, because these metals are considered to be bonded with glass merely by Van der Waals force [13] and their internal stresses are very low [14, 15]. Therefore, cracks formed in these metal films do not penetrate into the glass side under loading but diminish through displacement of the films, which results in no detrimental effect on the strength of etched glasses in the air containing moisture. The strength lowering effect of the Ag film coating, however, was observed in dry N_2 gas and the same trend was obtained for Au film. It is supposed that micro-cracks or minute surface damage produced by the impingement of metal atoms upon the glass surface during evaporation have some detrimental effect on the strength of etched glasses.

4. Conclusions

The effect of vacuum-deposited Cr, Al, Au and Ag films on the fracture strength of $HF–H_2SO_4$ acid etched glass was studied. The fracture strength of metal film coated glass depends on the type of metal film and a correlation is found between its strength and the adhesive force of metal films to the glass surface and the internal stress exhibited in them.

It is highly probable from the strength behaviour and dynamic fatigue characteristics for the film coated glasses that rupture of the metal film takes place before the fracture of glass occurs.

(1) The strength of etched glass was reduced from an initial value of $1696 \pm 39\,\mathrm{MN\,m^{-2}}$ when uncoated, to a strength of $265 \pm 10\,\mathrm{MN\,m^{-2}}$ for glass coated with a 69 nm thick Cr film. For Cr film which makes strong adhesive joints between the film and glass, rupture of the film can occur prior to fracture of the glass. This induces flaws in the film and they propagate under loading into the glass through the interface to act as Griffith cracks. The difference between the estimated strength values of coated glass calculated on this assumption and the experimental one coincides

with the internal tensile stress existing in the film. Thus the strength can be mainly determined by that of the film in this case.

(2) The strength reduction of Al-coated glass may be due to impurities such as oxides formed at the film/glass interface or in the film during evaporation, of which scatter of the data may be caused from some instabilities in the numbers and strength of adhesive joints per unit area at this interface.

(3) The strengths of Au- and Ag-coated glasses were found to be slightly higher than that of the acid etched glass in air containing moisture. This very high strength value of 1700 to 1800 MN m^{-2} was attributed to a lower adhesive force of Au and Ag films to the glass surface and lower internal stresses in these films, compared with Cr film. In dry N_2 gas, however, the strengths of glasses with Au or Ag films are lower than that of the non-coated glass, which indicates that the surface of etched glass may be minutely damaged during evaporation.

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