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Strengthening soda–lime–silica glass by a low-expansion coating applied by melt dipping

TIAN HE WANG, P. F. JAMES
School of Materials, University of Sheffield, Elmfield, Northumberland Road, Sheffield S10 2TZ, UK

A method of strengthening glass by application of a low-expansion glass coating is described. Soda–lime–silica glass rods were dipped vertically into a low-viscosity borate glass melt at 1140 to 1200 °C and rapidly withdrawn. Uniform well-bonded coatings, 100 to 200 µm in thickness, were produced. The modulus of rupture (MOR) of unabraded rods coated with a 60 ZnO–40 B_2O_3 (wt %) glass (glass 1) was 548 MPa, compared with 225 MPa for a control set of uncoated rods; coated rods after abrasion gave 343 MPa compared with 110 MPa for abraded uncoated rods. Rods coated with glass 1 fractured uniformly into small pieces in a manner similar to thermally toughened glass. Approximate calculated axial stresses, using thermal expansion and other data, were 233 MPa (compressive) in the coating (glass 1) and 56 MPa (tensile) in the substrate rod. The magnitude of the calculated axial compressive stress in the coating was in good agreement with the increase in average strength of the rods after melt dipping. The results indicate that the fracture origin was probably at the outer coating/air surface and not at the substrate/coating interface, and that the flaw length was less than the coating thickness. Severe flaws on the original rod surfaces were probably filled during melt dipping, rendering them inoperative.

1. Introduction

The mechanical strength of glass has become an increasingly important factor in governing its practical applications. Despite intensive studies of the strength of glass, there are still many unsolved problems. Observed strengths under normal conditions are only a fraction of the theoretically calculated values of approximately 4×10^4 MPa [1, 2]. It is well known that the much lower values of the observed strengths are caused by submicroscopic flaws on the surface and the brittle nature of glass. The strength of glass can be effectively improved by eliminating the surface flaws or rendering them inoperative. In practice, this may be achieved by producing a layer in compression at the glass surface by physical or chemical treatments. Various methods have been used including thermal toughening by rapidly chilling the glass surfaces, ion exchange of larger ions for smaller ions in the glass surface and surface crystallization to produce a low-expansion phase. Many years ago, Schott reported a strengthening process involving overlay of a low-expansion cladding glass on a high-expansion core glass. Upon cooling, the cladding glass contracted more than the core glass, resulting in a compressive stress in the former [3]. Similarly Krohn and Cooper [4] strengthened borosilicate glass fibres by cladding them in a low-expansion high-silica glass. Also Corning, using the same principle, developed high-strength laminated glass articles by a continuous process [5]. In principle, low-expansion glass layers could be applied to glassware by glazing methods long established in the ceramics industry but there appear to be few reports of the use of such techniques to strengthen commercial soda–lime–silica glasses [1, 6]. However, compressive glazes have been used to strengthen glass-ceramics [7], and recently the strengthening of glass tubes and containers using glazes applied by flame spraying has been reported [8].

In the present work, the approach used was to produce glass coatings in compression on soda–lime–silica glass rods. The coating glasses were low-expansion compositions. The coatings were produced by a method involving direct dipping in a low-viscosity melt and by more conventional glazing methods. One of the main difficulties with the use of glazing techniques to produce coatings on conventional soda–lime–silica glassware is the possibility of serious deformation by viscous flow at the relatively high operating temperatures required. However, for the melt-dipping method using soda–lime–silica glass rods and a low-viscosity coating glass, the deformation of the rods proved negligible. Impressive increases in strength of the glass rods were achieved even after abrasion, demonstrating that the melt-dip coating method is a possible alternative to established strengthening methods such as ion exchange or thermal toughening.

TABLE I Compositions of coating glasses (wt %)

Glass no.	ZnO	B_2O_3	Li_2O	BaO	MgO	Al_2O_3	V_2O_5	CaO	P_2O_5	α ($\times 10^7$ °C^{-1}) (mean value 100 to 400 °C)
1	60	40								46.0
2		79.2	2.5	2.5	14.8	1.0				57.3
3	57	28.5				5.0	9.5			62
4	45.7	38.2				1.3		7.3	7.4	68–77 [11]

2. Experimental procedure

2.1. Selection of glass compositions for coating

Suitable glasses for coating by melt dipping and glazing must have lower thermal expansion coefficients and preferably lower softening points than the base glass. Moreover, compared with the base glass they should have comparatively low viscosities and low melting temperatures. In general, with silicate glasses it is difficult to achieve the necessary combination of characteristics for satisfactory coating of soda–lime–silica glass. However, various borate glasses do possess these characteristics.

After some preliminary studies and examination of the literature on low softening point glasses [9–12], a number of compositions were selected for coating experiments. The results for four of these compositions (listed in Table I) are reported here. The glasses were melted in a platinum crucible at 1200 °C although it was found later that Glass 2 caused serious attack of the platinum. The following laboratory reagent-grade raw materials were employed; ZnO, B_2O_3, $Al(OH)_3$, SiO_2, Li_2CO_3, $MgCO_3$, Na_2CO_3 and $CaH_4(PO_4)_2H_2O$ and 250 g of each glass was prepared. Each melt was stirred with a platinum blade for 1 to 2 h to achieve homogeneity. All the compositions formed stable glasses on natural cooling in air and the melts were very fluid in the temperature range 1100 to 1200 °C.

Glass 1 had a liquidus temperature of 892 °C. According to the available literature [9–12], all the glasses in Table I have lower thermal expansion coefficients than standard commercial soda–lime–silica glasses. Measurements were made in the range 30 to 400 °C on an automatic self-recording fused silica dilatometer using 10 cm long rod samples. The heating rate was 5 °C min^{-1} and readings were taken every minute. The expansion coefficients (mean values 100 to 400 °C) determined for compositions 1 to 3 are summarized in Table I. The range of values quoted for composition 4 are those given in [11]. For comparison, the corresponding measured value for soda–lime–silica glass rods was 92.7×10^{-7} °C^{-1} (Fig. 1).

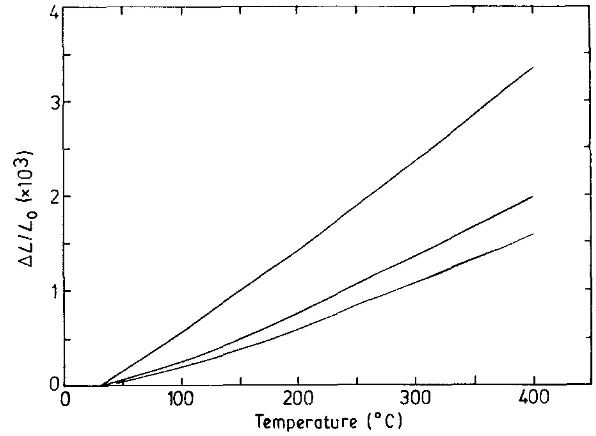

Figure 1 Thermal expansion results for glass 1 (bottom curve), glass 2 (middle curve) and soda–lime–silica glass rods (top curve). Plots of $\Delta L/L_0$ against temperature, where L_0 is the original length and ΔL is actual length minus original length.

2.2. Coating methods and strength measurements

Two simple coating methods were used. The first coating method was simply to dip vertically a preheated soda–lime–silica glass rod (3.5 mm diameter) into a low-viscosity glass melt and remove it after a short time (approximately 2 sec) at a constant withdrawal speed (in the range 50 to 200 mm sec^{-1}). The melt was contained in a mullite crucible placed in a small vertical electric furnace. The thickness of the glass coating produced depended on a number of factors, including the viscosity of the glass melt, the temperature of the preheated rods and the withdrawal speed from the melt. In the present experiments the melt temperature was maintained in the range 1140 to 1200 °C to ensure a low-viscosity melt of less than 10 Pa sec, and thus obtain a thin uniform coating (about 200 μm thickness). It was found that the higher the temperature of the preheated rods the thinner was the coating after withdrawal from the melt. Too low a temperature resulted in thicker coatings than required (greater than 200 μm), too high a temperature in slight elongation (viscous deformation) of the rods after coating. In practice, preheating for a few minutes at a temperature between 500 and 600 °C produced negligible deformation of the rods after coating.

Using this simple dipping method, a good quality, even glass coating of uniform thickness and high transparency was readily produced. With practice, the dipping and withdrawal of the rods could be conveniently performed by hand to produce a reproducible coating thickness on a series of rods. After coating the rods were cut into short lengths for mechanical testing. Examination of a sectioned, dipped rod with a high-resolution optical microscope revealed no evidence of a sharp interface between the soda–lime–silica glass core and the coated layer. This indicated that interdiffusion had occurred and the bonding between the two glasses was well-established.

In the second coating method, the soda–lime–silica glass rods were first heated to approximately 500 °C and then rolled, while still hot, in dry fine powder (less than 70 μm particle size) of the coating glass to enable a thin uniform layer of powder to adhere to the rod surfaces. The rods were then reheated to 500 °C and immediately transferred to an electric furnace at 1400 °C for a few seconds, a time short enough to prevent significant viscous deformation of the rods. Powders of glass 1 could be fused on to the rod surfaces forming layers of reasonable transparency, 10 to 20 μm thick and, if the whole glazing procedure was repeated, a thicker glaze could be produced. However, these layers were not as transparent or as even in thickness as the coatings produced by melt dipping, and optical microscopy revealed that they contained some fine pores. Glazing was also performed using firing in a gas flame, but because of the non-uniform firing temperature distribution, the glaze produced was not as even as in the furnace firing method.

A standard four-point bending method was used for flexural strength (modulus of rupture) measurements [2]. At least eight specimens were tested and the strength reported in each case in the following text is based on the average value.

3. Results and discussion

3.1. Coating with glass 1

At temperatures between 1100 and 1200 °C this composition formed a very fluid melt. The soda–lime–silica glass rods were first preheated to 550 °C and then dipped directly into the melt at 1150 °C for 2 sec. By removing a rod at an approximate speed of 100 mm $\sec^{-1}$ from the melt and allowing it to cool to room temperature, a clear and transparent coating, 200 μm thick, was obtained. Depending on the preheating temperature of the rod, and the withdrawal speed, the thickness of the coating varied by ±50 μm. However, careful operation reduced this variation to less than 20 μm.

The mean modulus of rupture (MOR) measured on the coated rods without abrasion treatment was 548 MPa (Table II) compared with a value of only 225 MPa for the as-received uncoated and unabraded rods (Table III). It was very interesting to observe that the coated rods fractured uniformly into small pieces during testing in a similar manner to the breakage of thermally toughened glasses. This indicated that a tensile stress had been produced in the interior of the coated rods. The thermal expansion curves measured for both the soda–lime–silica rods and for a rod of glass 1 are plotted in Fig. 1. Clearly the high MOR value obtained is consistent with the large difference in thermal expansion between the two glasses, and the consequent development of a compressive stress in the coating layer.

In order to test further the strength increase of the coated rods, a special, harsh abrasion treatment was used. The rods were placed in a plastic bottle containing steel balls, 1 to 3.5 mm diameter. The bottle was rotated on rollers at 90 r.p.m. The rods which had been coated with glass 1 and then heavily abraded by this method for 30 min had an average MOR of 343 MPa, representing a drop of only 37% from the coated but unabraded rods (Table II). For comparison, the strength of uncoated soda–lime–silica rods given exactly the same abrasion treatment was only 110 MPa (Table III).

TABLE II Strength results for soda–lime–silica glass rods coated by melt dipping

Dipping condition	Abrasion treatment	MOR (MPa) (mean)	No. of samples measured	Standard deviation (MPa)
In glass 1 at 1150 °C	Not abraded	548	10	115
In glass 1 at 1160 °C	Heavily abraded (30 min)	343	18	32
In glass 2 at 1140 °C	Not abraded	347	10	67
In glass 3 at 1140 °C	Not abraded	368	8	65
In glass 3 at 1140 °C	Heavily abraded (20 min)	277	9	43
In glass 4 at 1200 °C	Not abraded	419	14	109
In glass 4 at 1200 °C	Heavily abraded (30 min)	271	12	33

TABLE III Strength results for uncoated soda–lime–silica glass rods

Types of samples	Abrasion treatment	MOR (MPa)	No. of samples measured	Standard deviation (MPa)
Untreated rods (as-received)	Not abraded	225	12	38
As above	Heavily abraded (30 min)	110	13	9
Rods given similar thermal history to coated rods	Not abraded	234	15	44
As above	Heavily abraded	120	9	8

Clearly, high strengths can be obtained by the simple dipping method. However, it is important to note that after the dipping operation at 1150 °C the coated rods were allowed to cool rapidly in air to room temperature without being annealed. Although the rod specimens were small in diameter (3.5 mm) it was considered possible that thermal toughening might still contribute in part to the strength increase achieved. In addition, some healing of surface flaws on the rods might occur during dipping. To clarify these points, a more elaborate control experiment was also performed in which the uncoated (as-received) rods were given as similar a thermal history to the coated rods as possible. The rods were preheated to 500 °C and then inserted into a furnace maintained at the same temperature as the glass 1 melt (1150 °C) for approximately 10 sec, then removed immediately and allowed to cool to room temperature. The rods were not abraded. The measured MOR value in this case was 234 MPa. This was not significantly different from the 225 MPa obtained from the uncoated and unabraded rods. Moreover, after the same heat treatment followed by the same abrasion treatment, the strength dropped from 234 MPa to only 120 MPa (see Table III). This is not significantly different from the 110 MPa for the uncoated and abraded rods. Such a control experiment must be viewed as tentative because of the difficulty in obtaining exactly the same thermal history as that of the dip-coated rods. Nevertheless, the results do suggest that the strengthening effects cannot be attributed to thermal toughening.

In view of the large strength increase achieved by the dipping method, the simple glazing method described earlier (Section 2.2) was also performed using powder of glass 1. The mean MOR measured on the glazed rods was 207 MPa which is similar to that of the untreated rods. A similar glazing method but using a gas flame for firing gave comparable results. Because no increase in strength was achieved using such glazing methods with glass 1, no further powder firing experiments were performed for the other compositions (Table I).

3.2. Coating with glass 2

The same method of dipping was employed to coat soda–lime–silica rods with glass 2. This composition had a liquidus temperature below 1000 °C and the dip coating was operated at 1140 °C at which temperature the melt was sufficiently fluid. The measured thermal expansion coefficient was $57.3 \times 10^{-7}\ °C^{-1}$ and the expansion curve is shown in Fig. 1. The dipped rod samples had coatings with a thickness of approximately 200 μm and had good transparency. However, the strength measured was not as high as that obtained for rods coated with glass 1, being 347 MPa (Table II). Also, when the rods were tested, they did not break into very small pieces, as in the case of the rods coated with glass 1.

3.3. Coating with glasses 3 and 4

Similar dipping experiments were carried out with glasses 3 and 4, which were modified zinc borate compositions (see Table I). Both of the compositions had excellent fluidity at temperatures above 1100 °C and reasonably low thermal expansion coefficients. In addition, glass 4 was reported to possess good chemical durability [11]. Therefore, from a practical point of view, it was interesting to see how far the strength might be improved with these compositions.

The measured strengths for the soda–lime–silica glass rods coated with glasses 3 and 4, together with the coating conditions and abrasion treatments, are summarized in Table II. Examination of the coated rods with optical microscopy showed no significant difference in the thicknesses of the coatings for glasses 3 and 4 (both were approximately 200 μm). The unabraded modulus of rupture values for glasses 3 and 4 were 368 and 419 MPa, respectively. Clearly there was no significant difference statistically between these results, in fact the MOR for glass 3 was not significantly higher than that for glass 4 (the average strength was actually lower), in spite of the somewhat lower expansion coefficient of glass 3. It may be significant that according to Clinton and Coffeen [11] P_2O_5 can greatly improve the chemical durability of zinc borate glasses. Thus glass 4 should have a better chemical durability than glass 3. Moreover, the strength tests were carried out 3 days after the coatings had been produced for glasses 3 and 4. Consequently, it may be speculated that in the case of the glass 3 coating, some submicroscopic deterioration of the external coating surface could have occurred as a result of the reaction with water vapour in the atmosphere, thus causing a decrease in the average strength observed.

4. Further discussion

It has been demonstrated that impressive increases in strength of soda–lime–silica glass rods can be achieved by applying a low-expansion glass coating using a simple melt-dipping method. The average modulus of rupture of the coated (unabraded) glass rods was up to a factor of 2.4 times higher than the uncoated (unabraded) rods. Even more impressively, after surface abrasion the coated rods were up to a factor of 3.1 times stronger than the abraded uncoated rods. The largest increases in strength were achieved with the coating glass 1 which had the lowest thermal expansion coefficient. Considerable increases in strength were also observed for the other coating glasses. After abrasion the average strengths of the coated rods decreased for the coating glasses 1, 3 and 4 by only 37, 25 and 35%, respectively. On the other hand, the strength of the uncoated rods decreased by 51% after abrasion.

4.1. Approximate calculation of stresses in glass coating and substrate using elastic analysis

These results clearly indicate that the observed strength increases are caused by the difference in expansion coefficients between the substrate and coating glasses. This difference gives rise to a compressive stress in the coating layer when the rods are cooled below the effective "setting temperature" of the system. The magnitude of the stress in the glass coating depends primarily on the differential free contraction, δ, between coating and substrate, the geometry of the coated specimen, the elastic properties of the materials involved and the coating thickness. In the present case, a composite cylinder or "bead" seal model represents the most appropriate geometry for the purpose of calculating the surface compressive stress in the glass coating.

According to the Hull–Burger–Poritsky theory of the bead seal [13–16] for a coated rod, the axial stress is substantially constant throughout the coating thickness, although both the radial and circumferential (hoop) stress decrease with increasing radius in the coating, the former falling to zero at the external surface. The magnitude of the compressive axial stress in the coating, σ_{zz}, can be expressed as

$$\sigma_{zz} = [E_2\delta/(1 + \gamma + \gamma\beta R)][(2\nu a^2/b^2) + (1 + \gamma + \gamma\beta R)/(1 + \beta R)] \quad (1)$$

where E_2 and E_1 are the Young's moduli of the coating glass and substrate glass rod, respectively; $R = E_2/E_1$; $\gamma = a^2(1 - 2\nu)/b^2$; $\beta = (b^2 - a^2)/a^2$; a and b are the radii of the uncoated rod and coated rod, respectively; ν is Poisson's ratio, which is assumed the same for both glasses. The magnitude of the compressive hoop stress, $\sigma_{\theta\theta}$ at the external surface of the coating is also given by

$$\sigma_{\theta\theta} = [E_2\delta/(1 + \gamma + \gamma\beta R)][2a^2/b^2] \quad (2)$$

More complicated expressions for σ_{zz} and $\sigma_{\theta\theta}$ have also been derived for the case when the Poisson's ratio for the coating glass is not equal to that of the substrate [15]. Both these expressions and Equations 1 and 2 were used in the present analysis.

The differential free contraction, δ, on cooling from T_Q, the effective setting point of the glass to glass seal combination, to room temperature, T_R, can be expressed [17, 18] as

$$\delta = \int_{T_Q}^{T_R} (\alpha_2 - \alpha_1)\,dT = (\bar{\alpha}_2 - \bar{\alpha}_1)(T_R - T_Q) \quad (3)$$

where α_1 and α_2 are the thermal expansion coefficients of the substrate glass and coating glass, respectively, at temperature T, and $\bar{\alpha}_1$ and $\bar{\alpha}_2$ are the mean expansion coefficients over the range from T_R to T_Q. The value of δ can be determined graphically by making the expansion curves (plots of $\Delta L/L_0$ against T) for the two glasses coincide at T_Q, and measuring the $\Delta L/L_0$ differential at T_R [2, 17, 18].

The problems in calculating the stresses in a bead seal have been fully discussed [2, 15–23]. One of the main problems is assigning a value to the set point T_Q. Ideally [18] during cooling from a high temperature, any stress "build up" is instantaneously relaxed down to T_Q and completely "frozen" below T_Q. In practice, glass has no sharp transition from liquid to solid, its viscosity increasing smoothly on cooling. The set point for a given glass may be quoted by manufacturers as 15 °C below the annealing point (corresponding to a viscosity of 10^{12} Pa sec) or at the annealing point itself. Varshneya [18] has shown, using stress relaxation theory, that T_Q depends on the cooling rate after seal formation and for higher rates it can be well above the annealing point; typically for a cooling rate of 10 K sec^{-1} T_Q may correspond to a viscosity of 10^{11} Pa sec. Recently, Scherer and Rekhson [19–23] in a series of papers have demonstrated the importance of using viscoelastic analysis in the accurate calculation of stresses in various types of seals. Consequently, in view of the uncertainty in T_Q in the present case and the use of the elastic theory, the following calculation of the stresses can only be regarded as approximate.

In order to calculate the stresses in the coating, the following data were used. The annealing point of the ZnO–B_2O_3 coating glass 1 was obtained from a fit of the Fulcher equation to the viscosity data of Sack *et al.* [24] for a glass of identical composition. The result was 553 °C, which is in good agreement with other data [25]. The glass transformation temperature determined by differential thermal analysis for the soda–lime–silica substrate glass used was 560 °C, which may be taken as approximately the annealing point. The set point T_Q of the glass seal combination may be expected to be higher than the annealing point of that glass which sets at the lowest temperature, because of the relatively high cooling rate after seal formation (coating the rods). Consequently, T_Q may be above 553 °C, the annealing point of the coating glass. However, for the purposes of calculation T_Q was taken as 553 °C. The value of δ was calculated from Equation 3 using the mean expansion coefficients for the temperature range (50 to 400 °C) covered in Fig. 1, and T_Q and T_R as 553 and 20 °C respectively, the result being $\delta = 2.51 \times 10^{-3}$.

The radii of the uncoated and coated rods were taken as 1.75 and 1.95 mm, respectively, corresponding to the coating thickness of 200 μm.

The Young's modulus (E_2) and Poisson's ratio (ν_2) of the coating glass were taken as 8.594×10^{10} N m^{-2} and 0.30, respectively, these being the measured values of Hamilton *et al.* [26] for a glass of nearly identical composition. The Young's modulus (E_1) and Poisson's ratio (ν_1) of the substrate glass were taken as 7.0×10^{10} N m^{-2} and 0.22, respectively, based on values quoted for commercial soda–lime–silica glasses of similar composition [17, 25]. In practice, the stress calculations in the present case were sensitive to the values of the elastic constants chosen for the coating glass but not strongly dependent on the values used for the substrate glass.

The results of the calculations are given in Table IV. In Calculation 1 the equations given by Redston and Stanworth [15] were used with Poisson's ratios of coating and substrate set at 0.30 and 0.22, respectively. The axial stress and hoop stress at the outer surface of the coating have similar values because of the relatively small thickness of the coating. In the more approximate Calculation 2, Equations 1 and 2 given

TABLE IV Calculated compressive stresses (MPa) in the glass coating using the bead seal model and the data given in the text

	Axial (σ_{zz})	Hoop, external surface ($\sigma_{\theta\theta}$)
Calculation 1 using $\nu_1 = 0.22$, $\nu_2 = 0.30$ (coating thickness 200 μm)	233	236
Calculation 2 using $\nu_1 = \nu_2 = 0.30$ (coating thickness 200 μm)	240	245
Calculation 3 using $\nu_2 = 0.30$, $b = a$, limit of zero-coating thickness	308	308

Note: from Calculation 1 the radial stress $\sigma_{rr} = 0$ at the external surface ($r = b$) and $\sigma_{rr} = 28.6$ MPa (tensile) at the interface ($r = a$); the hoop stress in the coating at the interface ($r = a$) is 265 MPa (compressive). In the substrate glass all the stresses are tensile and constant: $\sigma_{zz} = 56.3$ MPa, $\sigma_{\theta\theta} = \sigma_{rr} = 28.6$ MPa.

above were used with the Poisson's ratio of the substrate assumed equal to that of the coating (0.30). The stresses are only slightly higher than in the first case. Finally, in Calculation 3 the stresses were obtained in the limit of coating thickness tending to zero, where the magnitudes of both σ_{zz} and $\sigma_{\theta\theta}$ are given by

$$\sigma_{zz} = \sigma_{\theta\theta} = \delta E_2/(1 - \nu_2) \qquad (3)$$

The stress values were higher in this case, showing the significant effect of coating thickness on the calculation, even for a thin coating.

For comparison, in Table IV, the stresses in the substrate glass are also given. These were all tensile and much smaller in magnitude than the compressive stresses in the coating.

4.2. Comparison of strength results with stress calculations

It is generally assumed that the strength of glass under surface compression is given by the sum of the strength of the base glass, as determined by its population of flaws and the surface compressive stress. Thus the additional surface compressive stress must be overcome by the applied tensile stress before failure. This assumes that the flaw size is less than the depth of the surface compressive zone [1, 2, 27].

The axial stress is considered to be the most important under the present testing conditions and from Table IV the calculated axial compressive stress in the glass coating, σ_{zz}, is 233 MPa. Adding 233 MPa to the strength of the as-received rods (225 MPa, Table III) gives 458 MPa. This is in good agreement with the measured value of 548 MPa for the strength of the rods coated with glass 1 (Table II), when the standard deviation is taken into account. Moreover, when 233 MPa is added to the 110 MPa for the strength of the abraded rods, 343 MPa is obtained which is, perhaps fortuitously, in exact agreement with the measured value for the coated plus abraded rods. The validity of the latter comparison is not as obvious as that of the first because the rods were abraded after coating and not before. However, both comparisons are reasonable if it is assumed that the flaw distributions on the coated surfaces (abraded or unabraded) are similar to those on the corresponding surfaces of the uncoated rods.

Green [27] has analysed theoretically the compressive surface strengthening of brittle materials when the flaw size (a_0) is greater or less than the depth of the compression zone (t). He showed that for $t/a_0 < 1$ and a given surface compressive stress, strengthening still occurred but was less than that when the flaw was completely embedded in the compression zone ($t/a_0 > 1$), and decreased with decreasing t/a_0. The strengthening could still be increased by increasing the surface compressive stress but the effect saturated at high values of this stress, corresponding to the situation where the surface crack was partially closed at failure. The present results show that the strength of the glass rods was increased by an amount equal to the magnitude of the surface compressive stress. This indicates that the flaw length was less than the thickness of the surface compressive coating ($t/a_0 > 1$ where t was 200 μm) and that failure was initiated from the external surface of the coating.

Another possibility is that of failure originating at the substrate/coating interface. This was suggested by Sozanski and Varshneya [8] to explain their results for the strengthening of glass tubes coated with low-expansion glazes by flame spraying, because the strength of the glazed tubes was not significantly decreased by abrading the outer glaze surface. However, in the present case severe abrasion did significantly reduce the strength of the coated specimens suggesting that the fracture origin was at the outer coating/air surface and not at the substrate/coating interface. Moreover, in the dip-coating process the glass rods were in intimate contact with the hot and fluid coating glass. Hence it seems likely that the severe flaws on the original surfaces of the glass rods were filled rendering them inoperative, so that the substrate/coating interface was no longer the main origin of failure. This is supported by microscopic examination where the interface had almost disappeared. Also, some healing of flaws on the original rod surfaces because of thermal effects cannot be ruled out, although this is not supported by the earlier thermal control experiment (Section 3.1).

In contrast, for the glass rods glazed by applying powder and firing (Section 3.1), where no increase in strength was observed, failure may have been initiated at the substrate/glaze interface. Further strength measurements after abrasion are needed to test this possibility.

5. Conclusions

1. A method of strengthening glass by the application of a low-expansion glass coating is described. The coating is applied by a simple melt dipping technique. Preheated soda–lime–silica glass rods were dipped vertically into a low viscosity glass melt at between 1140 and 1200 °C and removed, after a short time, at a constant withdrawal speed. Uniform well-bonded coatings up to 200 μm thick were produced depending on the temperature of preheating, the melt temperature and withdrawal speed. Various borate glasses, based on zinc or magnesium borate compositions, with low viscosities at the melt dipping temperature and low thermal expansion coefficients (in the range 46 to 57 $\times 10^{-7}\,°\mathrm{C}^{-1}$) were found to produce good coatings by melt dipping on soda–lime–silica glass rods.

2. MOR measurements using four-point bending on 3.5 mm glass rods after coating showed impressive increases in the average strength relative to the uncoated rods. The largest increase in MOR was observed for a 60 ZnO.40 B_2O_3 (wt %) glass coating (glass 1) which had the lowest expansion coefficient of $46 \times 10^{-7}\,°\mathrm{C}^{-1}$ (mean value 100 to 400 °C). As-received rods coated with this glass had a mean MOR of 548 MPa compared with 225 MPa for the uncoated, as received, rods (representing a factor of 2.4 times increase in strength). Similar rods coated and then heavily abraded still showed a high average MOR of

343 MPa, whereas the as-received, uncoated rods, given the identical abrasion treatment, gave only 110 MPa, this representing a strength enhancement of 3.1 times. Considerable increases in strength were also observed for the other coating compositions.

3. The rods coated with glass 1 fractured uniformly into small pieces during testing in a similar manner to the breakage of thermally toughened glass, indicating that a compressive stress had been produced in the coating and a tensile stress in the interior of the rods.

4. A control experiment was performed in which uncoated rods were given a similar thermal history to the dip-coated rods. These rods showed no significant difference in MOR from the uncoated, untreated rods, indicating that the strengthening effects produced by the melt dipping could not be attributed to thermal toughening as a result of the rapid cooling.

5. A simple glazing method was also used in which rods were covered with a thin layer of glass powder and fired at high temperature. Good transparent coatings 10 to 20 μm thick were produced, but the surfaces were slightly uneven, and some fine bubbles were observed. The MOR of these coated rods was similar to that of the untreated rods.

6. For the rods coated with the 60 ZnO.40 B_2O_3 (wt %) glass (glass 1), the stresses in the coating and substrate glass were calculated approximately from the Hull–Burger–Poritsky theory of the bead seal, using the measured thermal expansion coefficients of the glasses, and other property data from the literature. The calculated axial compressive stress in the coating was 233 MPa, and the axial tensile stress in the substrate was 56 MPa. The magnitude of the axial compressive stress in the coating was in good agreement with the increase in average strength of the rods after melt-dip coating.

7. The results indicate that for the coated rods the flaw length was less than the thickness of the applied coating, and that the fracture origin was probably at the outer coating/air surface and not at the substrate/coating interface. Severe flaws on the original surfaces of the glass rods were probably filled during melt dipping rendering them inoperative.

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