Structural State of the Strengthened Surface of Severely Tempered Glass

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The present investigation reveals the development of flaws and a considerable change in the structural state of a commercial glass, due to severe tempering in different liquid media.

It is shown that during severe tempering in silicone liquids, molten metals and alloys, strengthening takes place simultaneously with destructive degradation of the surface layers of the glass which depends on the cooling rate and the composition of the glass.

Increase in cooling rate causes the compressive stresses near the glass surface to increase but at the same time the temperature gradient gives rise to new microflaws and to the growth of small flaws into large ones. The modification of the structural state of the glass surface affects the mechanical properties of glass. Surface microflaws, degradation of glass structure, and temporary stresses are shown as contributory factors to the loss in strength of severely tempered glass.

1. Introduction

Features of the structural state of industrial glasses after tempering in various liquid media (polyorganosiloxanes and melts of fusible metals and alloys) were investigated. The influence of the degradation of the surface layers, the presence of microflaws (both those initially present and those formed on tempering), and of the compressive stresses within the surface layers on the strength of tempered glass was also studied.

During tempering of glass, compressive stresses are formed in the surface layers. These stresses are greater the more severe the cooling of the glass [1-3]. During the quenching of glass, microflaws, which are the centres from which brittle failure occurs, are formed on the surface as a result of thermal shock [4], and a more disrupted structure is formed in the surface layers, this structure being different to the glass structure in the annealed state [5-7].

These phenomena have very characteristic features at the high rates (instantaneous) of cooling which occur in the case of tempering of glass in liquid media. Methods of studying these were developed in the glass technology department of

the Mendeleev Institute of Chemical Technology [8, 9].

Under the given conditions these phenomena are more interesting in combination than individually, and the influence of the combined phenomena on the thermomechanical properties of the glass tempered in liquid media is particularly interesting. The influence of the individual factors (degradation of the glass structure, presence of microflaws in the surface layers, tempering stresses) on the strength of tempered glass was systematically studied for the present paper because major discrepancies exist in the literature on this subject.

2. Experimental

Plates (1.3 to 5 mm thick) and cylindrical rods (4 to 5 mm diameter) of some industrial glasses were used in this investigation. The glass specimens were tempered in polyethylsiloxanes N1(PE–1), N2(PE–2), N4(PE–4), N5(PE–5) and melts of tin and Wood's alloy. Chemical etching of glass specimens, which takes place in a discontinuous manner, was carried out using specially prepared solutions of hydrofluoric acid.

Other properties of tempered glass were determined by means of standard methods.

The change of density through the bulk of the tempered glass (fig. 1) shows that considerable differences exist between the structural states of the surface and inner layers. The greatest structural change is associated with the most severe tempering and takes place in the glass which is more easily tempered (BD-1)). The curves in fig. 1 which show how the density increases from the surface of the tempered glass also show that the density reaches its maximum value after removal of 150 to 200 μm of the surface layers. Determination of the volume concentration of silicon through the surface layers using an X-ray microanalyser technique also showed that the zone of degradation of the glass structure in the tempered glass ranges from the surface to approximately 200 μm into the glass.
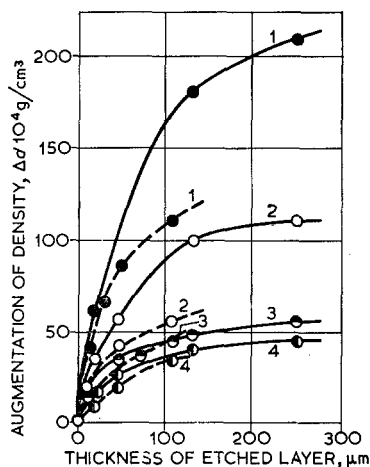

Figure 1 Change of the density in the surface layers of the BD-1 glass and Pyrex (dotted line) tempered in polyethylsiloxanes PE–1/1/, PE–2/2/, PE–4/3/ and PE–5/4/.

The loosening of the structure in the surface layers of severely tempered glass explains the important changes which occur in its physical properties. For example, the dielectric losses of the tempered glass are 35 % greater than those of the annealed glass. During the annealing of the glass its structure is stabilised and its dielectric losses decrease. The coefficient of thermal expansion also shows anomalous deviations from that of the annealed glass; this deviation increases as the severity of quenching during tempering in a liquid, and the degradation of the glass structure increases [10]. The increased rate at which chemical etching removes the surface

layers and the decrease in the speed of supersonic waves also show that the tempering of the glass has disrupted its structure in the surface layers [11]. It was, of course, expected that such a large degradation of the surface structure would exert a marked influence on its strength.

It was also found that Young's modulus of the glass decreases with tempering, this decrease being proportional to the severity of the quench (fig. 2). This phenomenon can also be connected
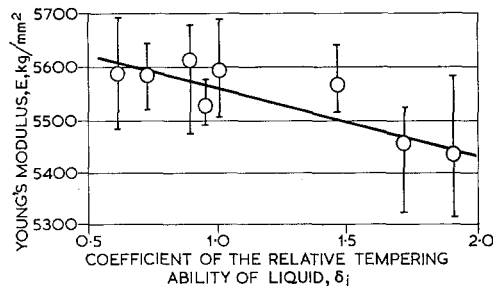

Figure 2 The dependence of Young's modulus of ZS–5K glass on the intensity of cooling during tempering in liquid polyorganosiloxanes (the relative tempering ability of liquid).

with a degradation of the glass structure. According to Orowan's [12] well-known principle, the decrease of Young's modulus which occurred during liquid tempering indicates that the structural degradation of the tempered glass decreases its practical strength. The data obtained in the present work on the influence of liquid tempering and subsequent low temperature annealing show that the glass strength is decreased after the tempering stresses are reduced, and that deeper degradation of the glass structure takes place during the tempering process. As to the influence of surface defects, comparison of the strength of glass containing flaws which were originally present and glass containing microflaws produced by chemical etching after annealing, tempering or a combination of the processes, shows that defects initially present in the particular glass (acquired during production and subsequent handling) have the greatest effect (table I).

The strength of glass containing the initially introduced flaws and the strength of glass containing flaws after tempering reach a maximum after removal of a layer 45 to 135 μm thick using chemical methods. However, the strength of glass containing microflaws introduced by chemical etching prior to tempering reaches a maximum

TABLE I Influence of defective glass surface on the strength

| N	Surface of glass	Bending strength (kg/mm²) BD–1 glass tempered in polyethylsiloxanes with different relative tempering ability			
		PE–5 $\delta_i = 1.0$	PE–4 $\delta_i = 1.46$	PE–2 $\delta_i = 1.72$	PE–1 $\delta_i = 1.92$
1.	Tempering without chemical treatment	44	54	63	67
2.	Chemical etching (45 μm) before tempering	52	56	65	69
3.	Chemical etching (45 μm) after tempering	65	92	124	147
4.	Chemical etching before tempering (45 μm) and after tempering (45 μm)	89	111	131	134
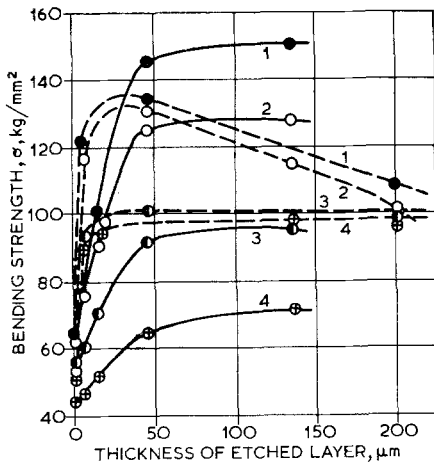
Figure 3 The dependence of the bending strength of BD–1 glass (containing original flaws and microflaws introduced by chemical etching) tempered in polyethylsiloxanes PE–1 (1) PE–2 (2), PE–4 (3), and PE–5 (4) on the thickness of chemically etched layers. The dotted lines show the results for BD–1 glass containing microflaws.

after the removal of a layer 10 to 45 μm thick (fig. 3). The flaws in the surface arising from liquid tempering increase steadily with the relative severity of the quench on the glass (δ_i) but the additional increase in strength as the glass is put through a preliminary etching process falls off. The coefficient of relative tempering ability of a liquid (δ_i) is a comparative characteristic of polyorganosiloxanes. This estimation is used as the basis for the comparison of the effects of the tempering of different glasses in such media. In connection with the influence of structural degradation and flaws on the surface layers of highly tempered glass the removal of these layers by etching causes the strength to increase on both static and dynamic loading (fig. 4).

At the same time the preferential development of compressive stresses in the surface layers during tempering exerts the greatest influence on the increase in strength of the glass (fig. 5), in this case the dependency of strength on the magnitude of the compressive stresses, proposed by Bartenev,
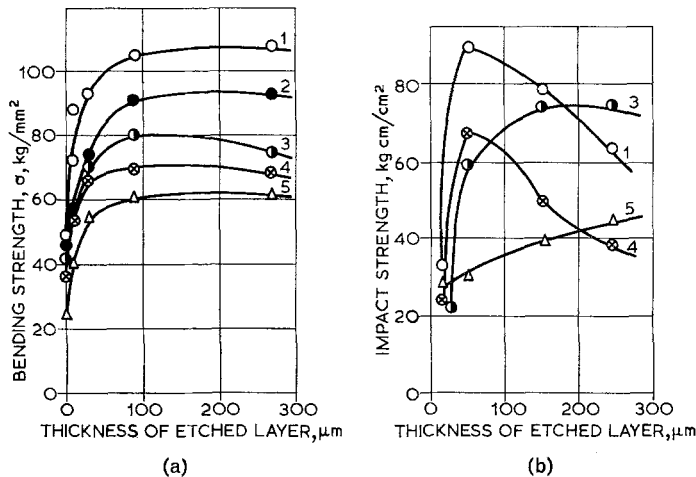
Figure 4 The dependence of bending strength (a) and impact strength (b) of BD–1 glass tempered in polyethylsiloxanes PE–1/1, PE–2/2/, PE–4/3/, PE–5/4/ and annealed at 530° C (5) on the thickness of etched surface layers.
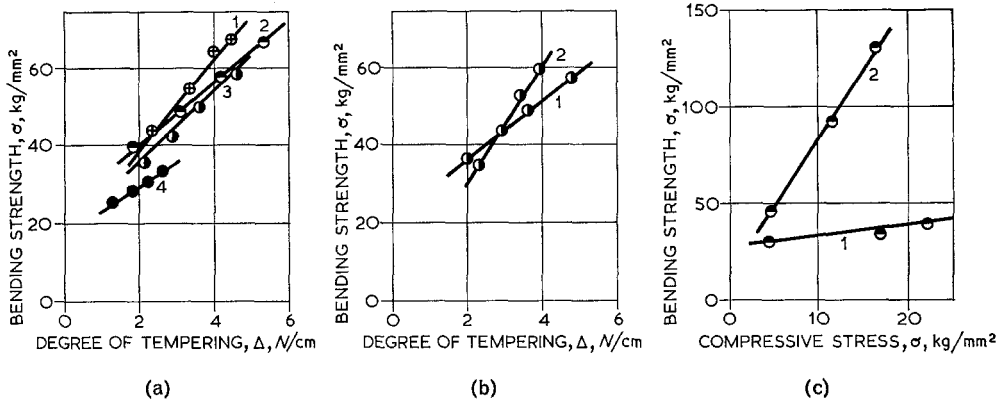
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Figure 5 The dependence of the strength of commercial glasses subjected to different tempering conditions on the degree of temper (a, b) and on the compressive stresses in the surface layers (c): (a) various glasses tempered in polyorganosiloxanes; (b) glass ZS–5K tempered in Wood's alloy (1) and molten tin (2); (c) plate glass 3 mm thick tempered (1) and tempered and chemically etched with 50 μm removed (2). $\oplus$ = BD-1; ◖ = V.V.; ◑ = ZS-5K; ● = Pyrex.

which is a linear relationship in the case of air tempering, can be used for tempering of glass in liquid media such as polyorganosiloxanes and in melts of metals, (the tempering in melts of fusible metals such as tin and Wood's alloy is achieved by immersion of very hot specimens of glass in the melt. This process is characterised by intensive isothermal cooling of the glass). The progressive increase in the thermal endurance of glass (by three to four times) with the increase of stresses on quenching which is achieved as a

Figure 6 The dependence of the strength of BD–1 glass on the degree of temper in polyorganosiloxanes PE–1/1/, PE–2/2/, PE–4/3/, PE–5/4/ for different depths of chemical etching.

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result of severe cooling during tempering, directly confirms this phenomenon [13, 14]. The data shown in fig. 6 give evidence that the strength of highly tempered glass is governed by a combination of all the factors given above (degradation of structure, flaws and stresses of different kinds). The strength of tempered glass steadily increases not only by increase in the compressive stress but also with the removal of the surface layers.

The compressive stresses in the surface of the glass introduced by tempering increase the ability of the surface of the glass to resist deformation, i.e. these stresses block the action of the factors leading to failure of the glass. This has been confirmed by tests carried out using a PMT–3 indentor (an apparatus with a diamond pyramid indentor similar to the Vicker's one). The load on the indentor leading to brittle failure of the glass was three to four times greater for the tempered glass than for the annealed or chemically etched (containing microflaws) glass (fig. 7). The microbrittleness of the tempered glass typically increases rapidly with the removal of some of the surface layers during chemical etching and this is connected with the reduction of the stresses introduced into the glass by quenching.

The very high practical strength of glass highly tempered in liquid media is determined by the blocking action of the compressive stresses in the surface layers. The strength of such glass remains unchanged even after the action of certain powerful agents (for example, treatment in an autoclave at 150° C and 1200 atm pressure) whilst the strength of chemically strengthened
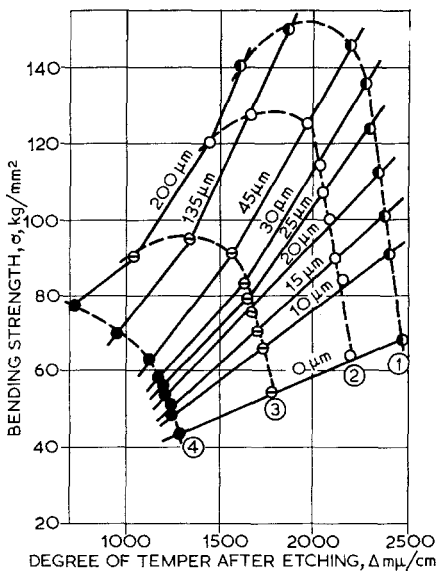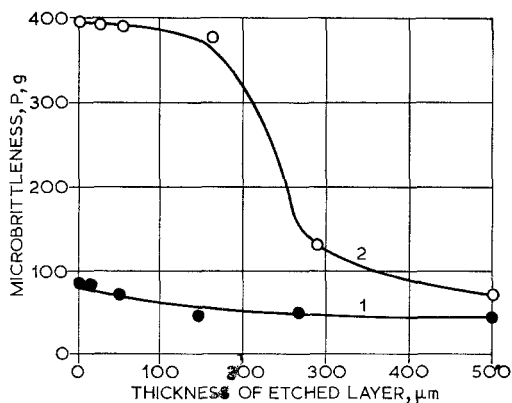
Figure 7 The dependence of the microbrittleness of the plate glass annealed (1) and tempered in PE–4/2/ on the thickness of etched surface layers.

glass sharply decreases under these conditions (fig. 8). The blocking effect of the compressive stresses within the surface layers of highly tempered glass stabilises its thermomechanical properties and also favourably affects the achievement of the necessary practical strength in this glass.
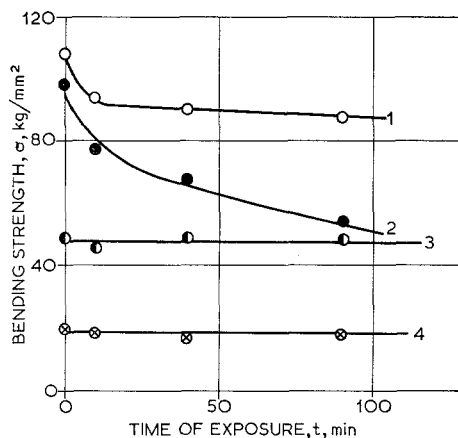

Figure 8 Influence of the hydrothermal conditions upon the strength of BS–1 glass tempered in PE–4 and chemically etched (1) only etched (2) tempered in PE–4/3/ and as usually annealed (4).

Statistical comparisons of the strength of different glasses strengthened by different methods shows that the optimum combination of high strength and low coefficient of variation of the strength is obtained most effectively by liquid tempering as shown in fig. 9. The data given in
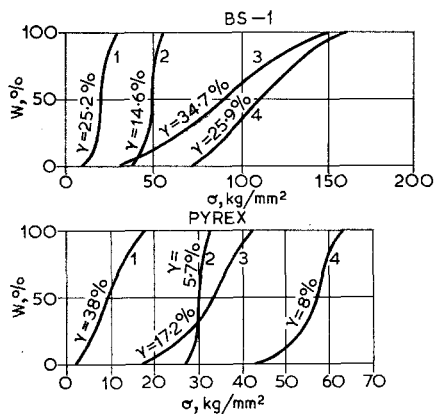

Figure 9 Probability of the failure ($W\%$) of BS–1 and Pyrex glasses subjected to different strengthening conditions: (1) as initially prepared; (2) tempered in PE–4 or PE–2 (Pyrex); (3) chemically etched (45 μm removed); (4) tempered and etched (45 μm removed).
(γ is the coefficient of variation of the strength.)

fig. 9 indicates that the coefficient of variation of the strength (γ) is least for the liquid tempered glass and is much higher for chemically toughened glass.

3. Conclusions

The results of the investigation are concerned with the nature of the surface layers of glass which has been severely tempered in liquid media and with the influence of various interdependent phenomena (thermal degradation of the glass structure, surface flaws and compressive tempering stresses) upon the strength of the surface of the glass. The biggest increase in strength of the glass surface is achieved by the controlled removal of surface flaws and the structurally degraded surface layers. The effective development of compressive stresses as a consequence of increase in the intensity of cooling of the glass during liquid tempering is the most important factor in increasing the practical strength of glass.

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