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Mechanical Strength and Surface Microstructure of Partially Crystallised Glasses

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The influence on the mechanical strength of lithia-silica glasses of heat-treatment in the temperature range (400 to 600° C), where the degree of crystallisation is small, has been studied. It was shown for a binary Li_2O–SiO_2 glass that heat-treatment led to a significant increase in the mechanical strength and that similar but less marked effects were observed for a Li_2O–SiO_2–P_2O_5 glass. From observations of the effects of abrasion upon the mechanical strength of the heat-treated glass it appeared that the strengthening effect arose from a change in surface structure of the glass. Examination by electron microscopy and X-ray diffraction revealed that a surface layer of lithium silicate crystals is formed during heat-treatment. The mechanical properties are discussed in relation to the surface structure of the glass.

1. Introduction

During the course of investigations into the preparation of glass-ceramics (which are made by the controlled crystallisation of special glasses) it has been observed for some compositions that increases of mechanical strength occur after heat-treatment at temperatures which are too low to permit a significant degree of crystallisation. It was considered of interest to investigate this effect and in order to simplify the interpretation of the results it was decided to confine the investigation to glasses basically of the Li_2O–SiO_2 type. Also the effect of including a small proportion of P_2O_5 was of interest since the latter constituent is known to influence strongly the microstructure and mechanical strengths of glass-ceramics [1]. It has been shown, using a hot stage microscope, that the growth velocities of lithium silicate crystals (disilicate and metasilicate) in Li_2O–SiO_2 glasses were very much higher than those observed for similar glasses containing a small proportion of P_2O_5. Also measurements of electrical resistivity indicate that the production of these crystals is inhibited when P_2O_5 is present in the glass [2].

2. Experimental Techniques

Two glasses with molecular percentage compositions as follows have been studied:

Glass 70: SiO_2 70, Li_2O 30
Glass 70P: SiO_2 69, Li_2O 30, P_2O_5 1

Crushed Brazilian quartz and reagent grade lithium carbonate and lithium phosphate were used in the preparation of the glasses. The compositions were melted in 600 g quantities in lidded platinum crucibles in an electric furnace. Both glasses were refined for 2 h at the melting temperature (1400° C) after the last traces of the raw materials had disappeared. The samples for mechanical strength measurements were prepared by drawing rods (4 mm diameter) from the melts. Thin plates for microscopic examination were produced by pressing small quantities of the molten glass between cold metal surfaces.

Heat-treatments of rod and plate samples were carried out for 1 h at various temperatures between 400 and 600° C. Similar sets of samples were heat-treated at 525° C for periods up to 8 h. The heat-treatments were carried out using small, electrically heated furnaces with auto-

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matic temperature control which maintained the temperature to within ± 5° C of the nominal heat-treatment temperature. The rod samples (5 cm long) were held vertically by their ends in a stainless steel holder during the heat-treatments while the small plate samples were placed on platinum substrates.

The mean moduli of rupture of sets of 10 specimens were determined with a Hounsfield Tensometer using three-point loading. Some sets of rods were subjected to a standard abrasion treatment either before or after heat-treatment. This involved tumbling the rods with four times their weight of No. 80 mesh Carborundum powder for 15 min in a 17.8 cm diameter mill-jar rotating at 1680 rph.

Electron microscopy was employed to examine both the interior and the surface of the heat-treated glass. For this, specimens were prepared using conventional metallographic techniques to a final 1 μm diamond finish. The specimens were then etched for 15 sec in a $\frac{1}{2}$% hydrofluoric acid solution and platinum-carbon replicas were prepared, self-shadowed at an angle of 2:1. The replicas were examined using a Siemens Elmiskop I electron microscope. In order to identify the crystals which were developed in the glasses during heat-treatment, glancing angle X-ray diffraction analysis using CuKα radiation was employed. In addition, X-ray diffraction was carried out on the fractured surfaces of the specimens.

3. Results

3.1. Mechanical Strength Tests

The heat-treatments referred to in the following sections were each carried out for 1 h. Rod samples of Glass 70 were totally transparent in the "as-drawn" condition but became slightly opalescent after heat-treatment at 550° C, the degree of opalescence increasing with increase of the heat-treatment temperature. A heat-treatment was carried out at 650° C during which the samples became slightly crazed and very brittle and therefore unsuitable for mechanical testing. The rods of Glass 70P in the "as-drawn" condition were slightly opalescent and became more so with rise in temperature until after heat-treatment at 550° C the rods were almost opaque. At higher temperatures there was some slight deformation of the rods and a skin effect was apparent on the surface. This effect was evident after heat-treatment at 600° C. After heat-treatment at 650° C the rods were completely opaque and highly deformed so that as in the case of Glass 70, mechanical strength testing could not be applied to the specimens.

The mean values of the moduli of rupture for unabraded samples after each heat-treatment are shown in table I. Statistical analysis was carried out to investigate real changes in mechanical strength with heat-treatment. The results show a significant increase in strength for the specimens heat-treated at 600° C as compared with the "as-drawn" specimens for both Glasses 70 and 70P. After heat-treatment at 600° C the modulus of rupture fell markedly. Slight deformation of the rods occurs at this temperature, however, and the corresponding moduli of rupture values may be inaccurate for this reason.

A comparison of Glasses 70 and 70P shows that after heat-treatment at low temperatures (400° C) the glasses have similar strengths. On increasing the temperature of heat-treatment, Glass 70 shows a faster rate of change of strength and a larger overall increase in strength than Glass 70P.

Rod samples which had been abraded after heat-treatment gave values of the modulus of rupture shown in table I. The strength of both

TABLE I The effect of heat-treatment for 1 h at various temperatures on the moduli of rupture of Glasses 70 and 70P

Heat-treatment temperature for 1 h	Modulus of rupture kg/cm^2			
	70		70P	
	unabraded	abraded	unabraded	abraded
As-drawn	1850 (322)	944 (106)	1834 (542)	849 (79)
400° C	2037 (349)	799 (85)	1884 (416)	798 (35)
480° C	2640 (514)	969 (86)	1623 (318)	881 (83)
500° C	2523 (555)	—	1858 (518)	1011 (58)
525° C	2440 (545)	911 (62)	1245 (398)	834 (72)
550° C	3444 (1120)	—	2328 (274)	910 (45)
575° C	3891 (626)	1078 (79)	2777 (736)	1139 (148)
600° C	3553 (1007)	1043 (133)	1791 (385)	1162 (215)

Standard deviations are given in parentheses.

glasses is considerably reduced by abrasion for all heat-treatments. A small increase in strength is found after heat-treatment at higher temperatures, and although this is less than that demonstrated for the unabraded rods, it is statistically significant.

The effects of duration of heat-treatment at 525° C are given in table II and it will be seen that both Glasses 70 and 70P generally show increasing strengths for longer heat-treatments. However, the initial rate of rise of strength appears to be faster for Glass 70.

TABLE II The effect of duration of heat-treatment at 525° C on the moduli of rupture of Glasses 70 and 70P.

Hours of heat-treatment at 525° C	Modulus of rupture kg/cm² 70	70P
0 h	2056 (442)	1966 (542)
¼ h	2505 (197)	2171 (500)
½ h	2679 (492)	2193 (368)
¾ h	2711 (343)	2146 (769)
1 h	2801 (462)	2238 (458)
1½ h	2904 (578)	2300 (985)
2 h	3060 (675)	2410 (260)
3 h	3537 (616)	2789 (515)
4 h	3865 (819)	3110 (729)
6 h	4236 (552)	3529 (1000)
8 h	3716 (523)	3956 (914)

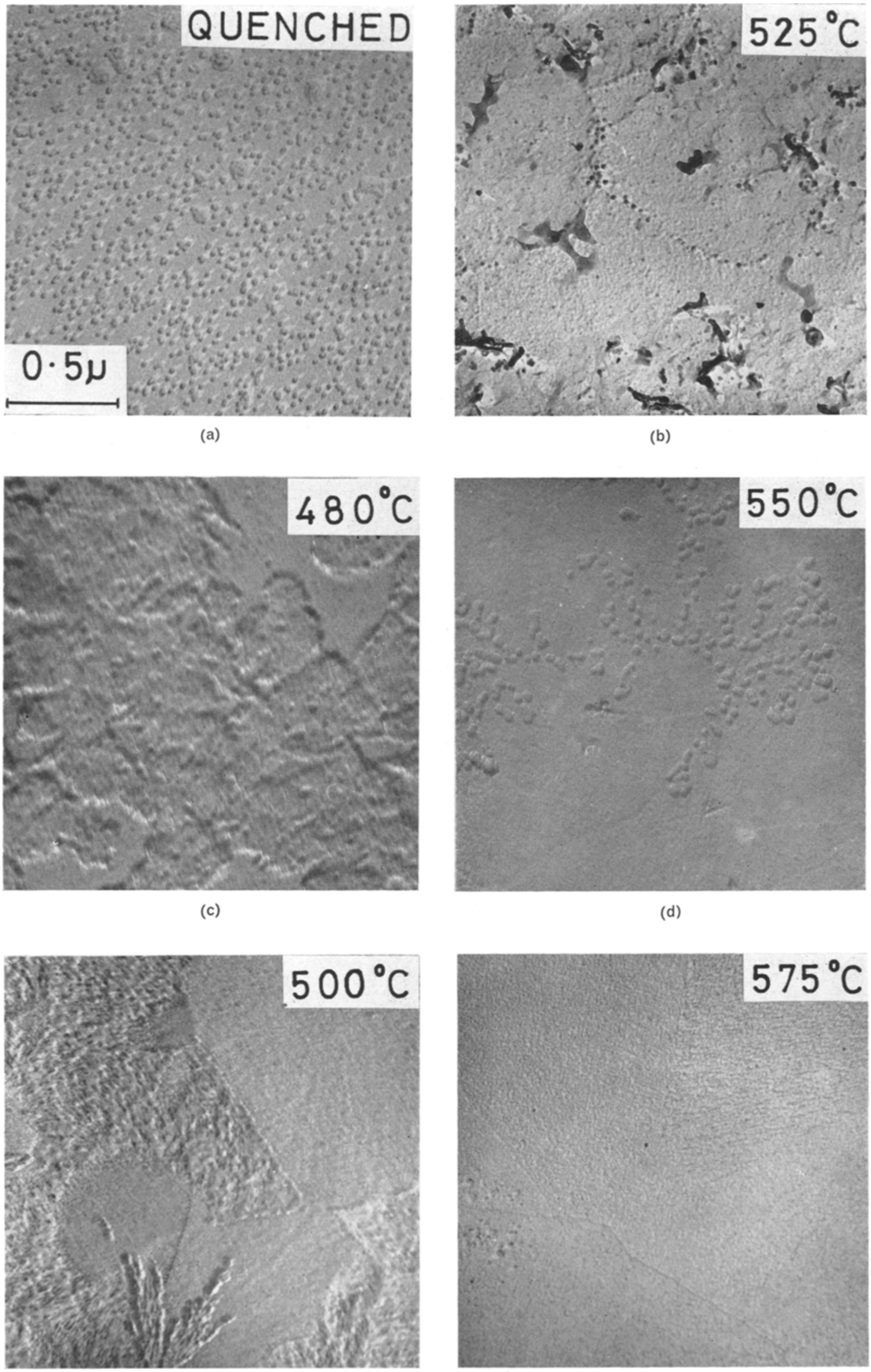
3.2. Electron Microscopy

Electron microscopy of the interior of both Glasses 70 and 70P showed phase separation. The second phase which appears after heat-treatments at temperatures below 575° C takes the form of dispersed globules. This is thought to be vitreous rather than crystalline since X-ray diffraction analysis yielded no pattern. Heat-treatments at temperatures above 600° C show a small proportion of lithium disilicate crystals. However, as far as effects on mechanical strength are concerned, phase separation was not considered significant, since evidence from the mechanical strength tests suggested that changes in surface structure are principally responsible for the mechanical strengthening. Therefore, the interior structure of the glasses is not discussed further in the present paper.

Electron micrographs exhibiting the effect of increasing heat-treatment temperature up to 575° C for periods of 1 h on the surface structure of the glasses, are shown in figs. 1 and 2. Glass 70 in the quenched condition shows uniformly distributed particles (mean diameter 250 Å) which are possibly crystals formed during the pressing process. Heat-treatment at 480° C results in aggregates of small crystals and large single crystals. With increasing heat-treatment temperature, the extent of crystallisation is increased until after heat-treatment at temperatures above 500° C, large crystal grains (1.5 to 4 μm diameter) are seen. For Glass 70P, the surface of the quenched glass appears virtually structureless (fig. 2) but with heat-treatment at temperatures in the range 480 to 575° C there is a progressive development of a crystalline phase. After heat-treatment at 575° C, the surface structure appears to be composed of crystalline grains which are between 0.25 and 0.5 μm long although the grain boundaries are only faintly discernible. The second phase takes the form of dispersed well-defined crystals or globules which are near-circular in shape and 250 to 500 Å in diameter.

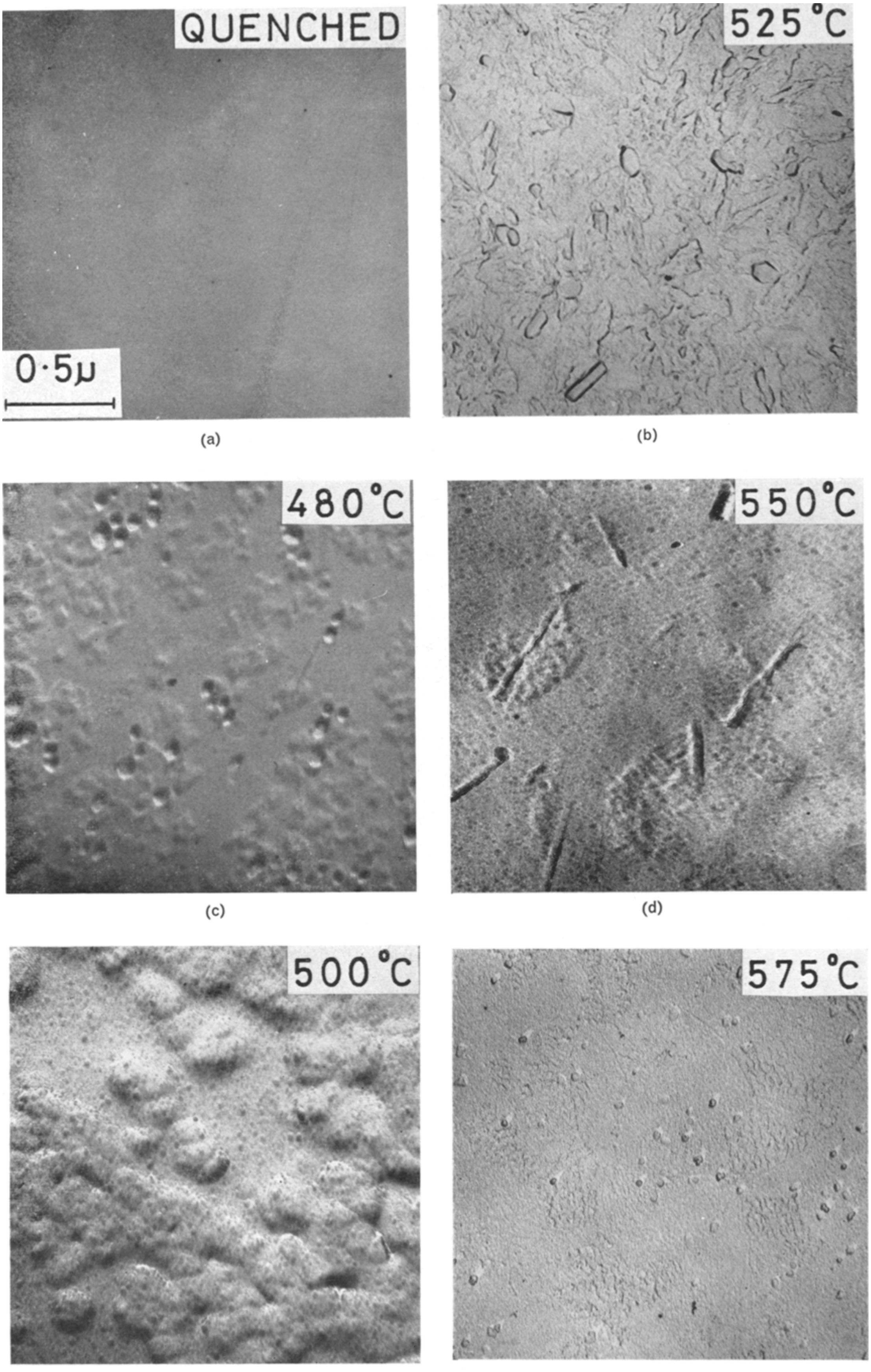
Fig. 3 comprises electron micrographs of the surface of Glass 70 in the quenched condition and after heat-treatment at 525° C for periods up to 8 h. After heat-treatment for 0.5 h, crystals are present on the glass surface. These have a mean diameter of about 500 Å and there are in the region of 5.4×10^9 crystals/cm² of surface. After 0.75 h, the mean diameter of the crystals increased to about 750 Å but they were fewer in number. For specimens heat-treated for 2 h the small isolated crystals are replaced by an overall fine structure which is believed to be crystalline. There are also some near-spherical particles present in this structure which may also be crystals, and these have a mean diameter of about 600 Å. After heat-treatment for 4 h, angular crystal grains are clearly seen, and the grain-boundaries enclose a fine structure. The length of these grains is from 1.0 to 1.5 μm and this increases to 1.5 to 2.5 μm after 8 h at 525° C.

Fig. 4 comprises electron micrographs of the surface of Glass 70P in the quenched condition and after heat-treatment at 525° C for periods of up to 8 h. While the surface of the quenched glass is relatively featureless, that of the heat-treated glass shows the presence of a fine crystalline structure which becomes progressively coarser as the heat-treatment is increased from 0.5 to 2 h. It is difficult to locate the boundaries of the crystal grains on these electron micrographs and therefore it is not possible to quote any crystal sizes. As the heat-treatment time is increased beyond 2 h the crystalline structure



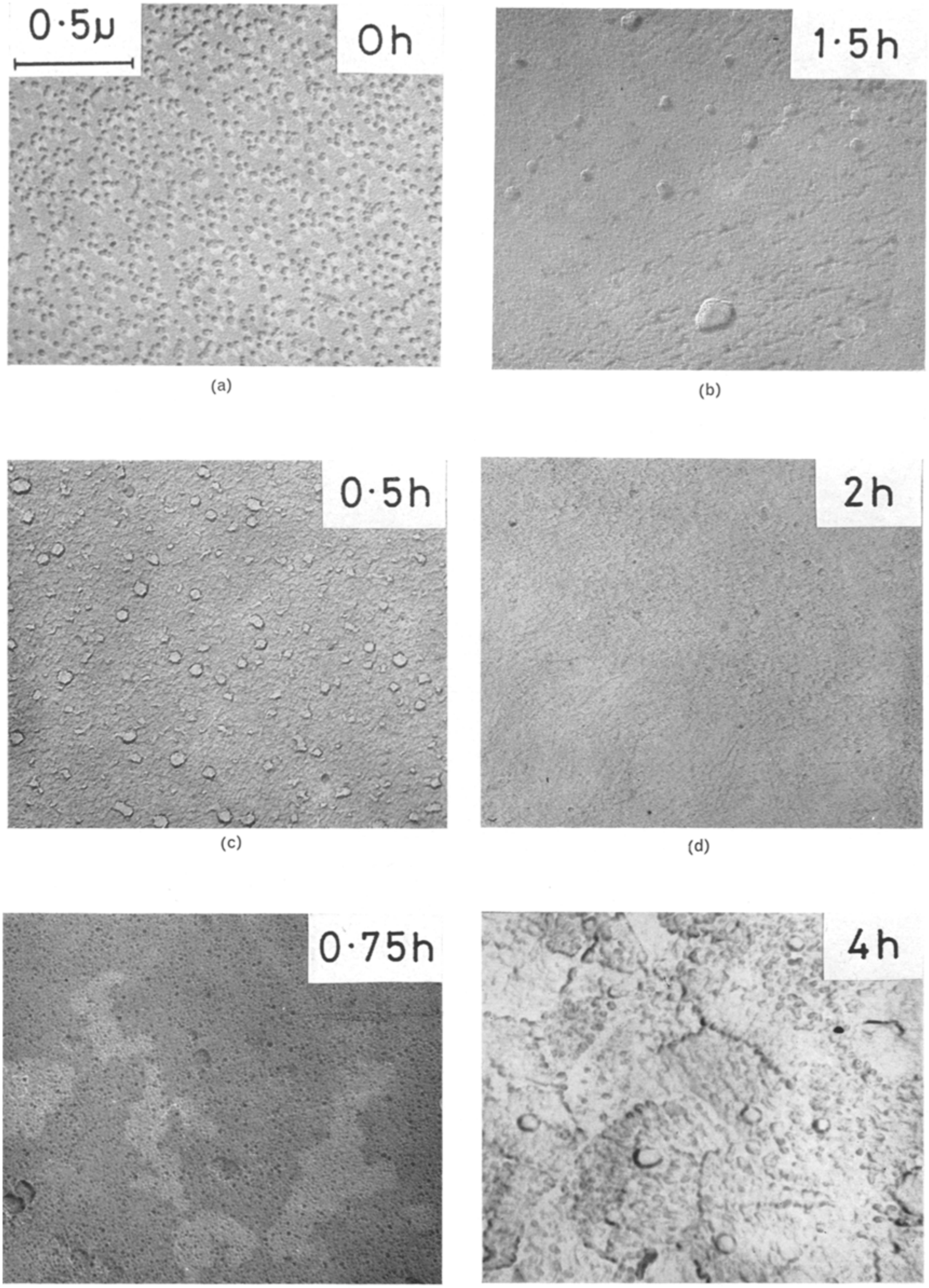
(a) (b) (c) (d) (e) (f)

Figure 1 Electron micrographs showing the effect on the surface structure of Glass 70 of heat-treatment for 1 h in the range 480 to 575° C.



(a) (b) (c) (d) (e) (f)

Figure 2 Electron micrographs showing the effect on the surface structure of Glass 70P of heat-treatment for 1 h in the range 480 to 575° C.

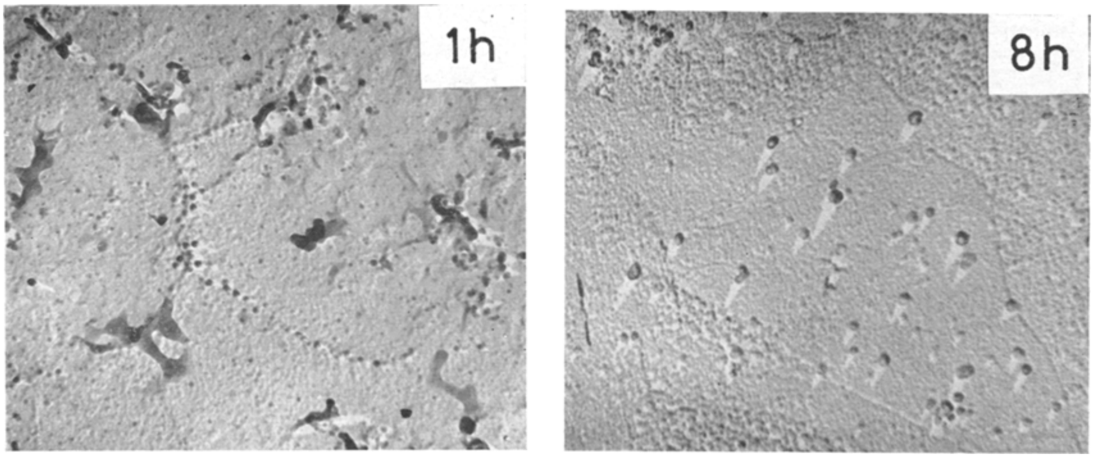


(a) (b)

(c) (d)

(e) (f)

cont.



(g) (h)

Figure 3 Electron micrographs showing the effect on the surface structure of Glass 70 of heat-treatment at 525° C for various times.

becomes progressively less distinct and after a time of 8 h no discrete crystals can be seen.

3.3. X-ray Diffraction

X-ray diffraction analysis showed a very weak pattern, with the result that positive identification was difficult. However, one strong line and a few weak diffuse lines were consistent with the crystals being lithium disilicate.

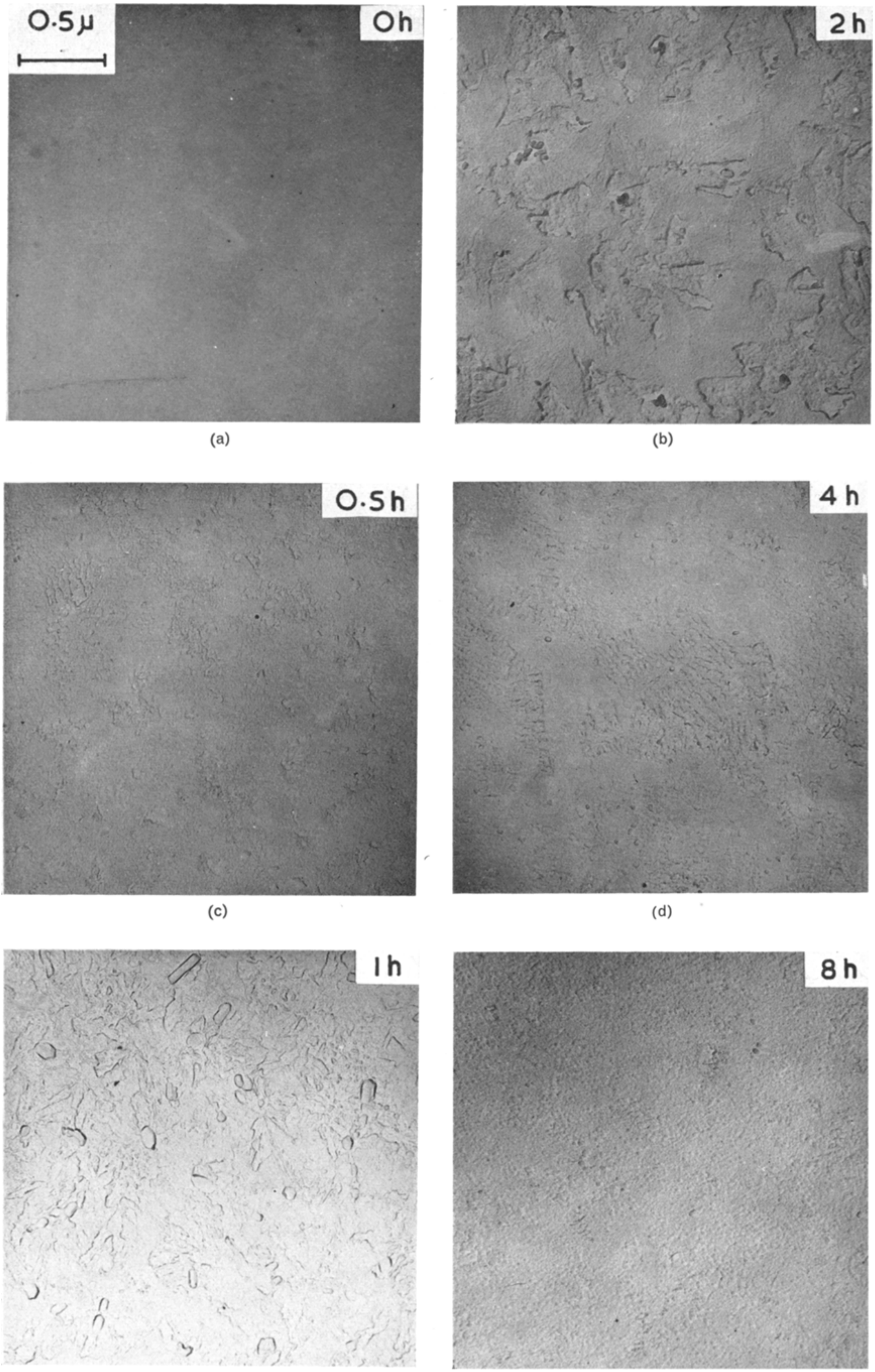
4. Discussion

It has been shown that heat-treatment of the glasses in the range 500 to 600° C results in significant increases of mechanical strength. Surface crystallisation of the glasses occurs during heat-treatment within this temperature range and it is thought that this is responsible for the increase in strength. The smaller increases in strength observed for the abraded specimens are consistent with the idea that the strengthening effect is associated with a change of surface structure of the glass. Also the generally smaller increases in strength observed for Glass 70P could be attributed to a slower development of the surface crystalline layer and this is consistent with the observed slower growth rates of lithium silicate crystals when a small proportion of P_2O_5 is present in the glass.

One possible explanation of the increase in mechanical strength associated with surface crystallisation is that the surface layer is stressed in compression, owing to a difference between the thermal expansion coefficients of the crystallised layer and the uncrystallised core of the glass rods. Examination of polished sections of the glass rods in a polarising microscope did not show any marked birefringence in the glassy core, suggesting that high internal (tensile) stresses were not present. This does not necessarily prove that surface compressive stresses were not present, however, since the nature of the stress distribution could be such that the internal stresses were low, even though high compressive stresses were present in a very thin surface layer.

If surface compressive stresses were present, this would imply that the thermal expansion coefficient of the crystallised layer was very much lower than that of the uncrystallised core. To investigate this, a glass of the disilicate composition was heat-treated in order to crystallise it completely to lithium disilicate, as shown by X-ray diffraction analysis. The thermal expansion coefficient (96×10^{-7} per ° C) was significantly higher than that of Glasses 70 and 70P after heat-treatment at 525° C (87×10^{-7} and 86×10^{-7} per ° C, respectively). This result might suggest that the surface crystallised layer has a higher rather than lower expansion coefficient in comparison with the uncrystallised core.

Further evidence was obtained from measurements of the thermal expansion of specimens made by sintering and heat-treating finely powdered glass. In this way the maximum surface area is available for crystallisation. Comparison of the thermal expansion coefficients of such specimens with those of the bulk glass heat-treated in the same way did not reveal any significant difference. On this evidence, it seems



(a) (b) (c) (d) (e) (f)

Figure 4 Electron micrographs showing the effect on the surface structure of Glass 70P of heat-treatment at 525° C for various times.

unlikely that the surface crystalline layer can have an expansion coefficient less than that of the uncrystallised core and therefore the strengthening effect cannot be attributed to pre-stressing arising as a result of differential contraction.

Another possible explanation of the strengthening effect is that the development of lithium disilicate crystals on the glass surface affects the size and distribution of the microcracks. Any process which results in reduction of the lengths of the microcracks would be expected to result in a higher mechanical strength. Attempts have been made to determine whether a relationship exists between the mechanical strengths of the specimens and the lengths of the microcracks that could be present, assuming that the crystals act as "flaw limiters". This has been done for specimens of Glass 70 in the quenched state and after heat-treatment at 525° C for times of 0.5 and 0.75 h. These heat-treatments result in significant increases in the strength of the glass and in the presence of discrete crystals at the surface of the specimens. It was found that as the strength of the glass increased during heat-treatment at 525° C the average distance between the crystals increased. This result is the reverse of what might have been expected and in this case it does not appear that the development of surface crystallisation increases the mechanical strength of the glasses by limiting the size of the flaws.

An alternative explanation of the strengthening effect may be that, during heat-treatment of the glasses, viscous flow occurs, which reduces the severity of the flaws on the surface. To examine this, the strengths of abraded and etched rods of soda-lime-silica glass were measured before and after heat-treatment at 525° C for 4 h. It can be seen from table III that significant strengthening of the abraded rods did not occur and also a large reduction in the strength of the etched rods was observed. Since heat-treatment of both Glass 70 and the soda-lime-silica glass was carried out at a temperature corresponding to similar glass viscosities, the strengthening in the former case is unlikely to be due to the reduction in the severity of the flaws resulting from viscous flow of the glass during heat-treatment.

TABLE III The effect of heat-treatment at 525° C for 4 h on the moduli of rupture of a soda-lime-silica glass and Glass 70.

Condition	Mean modulus of rupture kg/cm^2	
	soda-lime-silica glass	glass 70
As-received	—	1850
Heat-treated	—	3865
Abraded	930	944
Abraded, then heat-treated	1085	2159
Etched	4810	6645
Etched, then heat-treated	1734	4141

A further possibility is that the strengthening effect occurs because the crystals form preferentially around the microcracks or around the ends of microcracks and in this way the stress raising ability of the microcracks is reduced or even eliminated. The ability of microcracks to nucleate crystallisation at the surface of the glass has been previously reported by Ernsberger [3]. This was shown by drawing a clean fire-polished glass fibre lightly across the pristine surface of plate glass to produce a line of microcracks. By subsequent heat-treatment of the glass it was possible to show that each microcrack became a nucleus for crystallisation so that a long straight chain of crystals was produced on the surface.

Although no experiments have been carried out on specimens artificially flawed in this way, some studies of the effect of the surface condition of the glasses prior to heat-treatment have been made (table III).

Abraded rods of Glass 70 heat-treated at 525°C for 4 h showed a marked increase in strength and this can be attributed to the effects of surface crystallisation in reducing the severity of surface flaws. The reduction in strength of the etched specimens as a result of the same heat-treatment may appear surprising since this implies that the flaws present after heat-treatment are more severe than those initially present. However it is possible that during heat-treatment two processes occur which affect the state of the surface. One of these processes leads to the production of flaws, while the other process (crystallisation) limits the severity of the flaws which can develop. If this is so, the final strength will be more characteristic of the size and distribution of the crystals rather than of the initial state of the glass surface. The observation that the strengths of the specimens which were heat-treated in the etched condition were not significantly different from those heat-treated in the "as-received" condition lends some support to this idea.

5. Conclusion

It has been shown that significant strength increases occur for binary lithium silicate glasses as a result of heat-treatment at temperatures in the range 500 to 600° C. These increases are attributed to the formation of a partially crystallised layer on the surface. The presence of P_2O_5 in the glass reduces the extent of the strength increase and this is attributed to the inhibiting effect of this oxide on the development of lithium disilicate crystals.

With regard to the mechanism of the strengthening action, it has been shown that this does not arise from pre-stressing of the glass surface as a result of the formation of crystals. There is some evidence to suggest that the development of crystals reduces the severity of the flaws, possibly as a result of the microcracks themselves acting as nucleation sites for crystallisation. This explanation is, however, only tentative.

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