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The characterization of high-strength surface-crystallized glasses

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Controlled surface crystallization has become established as a method of significantly improving the mechanical strengths of glasses. Previous work has indicated that the surface state of the glass prior to crystallization can profoundly influence the microstructure of the surface-crystallized layer and thereby modify the mechanical strength of the material produced. The purpose of the present investigation was to study the effects of different surface-abrasion treatments, prior to crystallization, upon the microstructure of the surface-crystallized layer and the mechanical properties of two glasses. Indentation fracture was employed to characterize the glass surface and electron microscopy to investigate the microstructures that developed. For a calcium zinc aluminosilicate glass, although the microstructure of the surface-crystallized layer was dependent on the prior surface state of the glass, there was no clear cut relationship with the mechanical strength of the surface-crystallized glass. This was attributed to surface flow of the glass during heat-teatment. For a calcium aluminate composition, the microstructure of the crystallized layer was clearly dependent on the prior surface state of the glass and evidence was provided that flaws in the surface served to provide crystal nucleation sites. The mechanical strength of the surface-crystallized glass was markedly dependent on the microstructure and with a suitable surface treatment a mean modulus of rupture of 510 MN m^{-2} was achieved.

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1. Introduction

The process of controlled surface crystallization has now become well established as a means of increasing the strength of glass components [1–3]. For example, in the case of $ZnO–Al_2O_3–SiO_2$ glasses, an average bending strength of about 80 MN m^{-2} may be increased to 400–600 MN m^{-2} after suitable heat-treatment. Typically, a strength increase of this magnitude might be associated with a crystalline layer of about 100 μm.

Using a range of compositions within the calcium aluminate system, Partridge and McMillan [1] were able to identify a number of factors which influenced the development of surface crystalline layers. The condition of the glass surface prior to heat-treatment (the result of various abrasion processes, for example) together with environmental constraints during crystal nucleation were found to be important.

Two effects may contribute to the strengthening process associated with surface crystallization. One of these can be likened to that brought about by thermal toughening techniques. If the crystal phase developed in the surface layer has a significantly lower coefficient of thermal expansion than the residual glass phase in this layer, the net thermal expansion coefficient of the layer will be less than that of the underlying uncrystallized bulk glass. Therefore, during cooling after the crystallization heat-treatment, the composite glass–crystal outer layer will become stressed in compression. Thus this stress will have to be overcome by an externally applied tensile stress of a sufficient magnitude before fracture initiation can occur.

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Earlier work [1] has suggested, however, that prestressing resulting from thermal expansion mismatching is not a sufficient explanation for the strengthening effect resulting from surface crystallization. It appears that microstructural effects in the surface-crystallized layer also play an important role by limiting the severity of the microcracks present in the glass surface after heat-treatment.

There is also evidence that the microcracks present in the glass surface prior to heat-treatment provide nucleation sites for subsequent crystallization. If this is correct, the extent and nature of the surface damage present before heat-treatment will influence the ultimate microstructure of the surface-crystallized layer. On this view, the presence of a high density of small surface flaws, while leading to weakening of the original glass, would promote extensive nucleation of surface crystallization. This would favour the development of a fine-grained microstructure in the surface layer likely to result in enhancement of mechanical strength.

The purpose of the investigation reported here was to study the influence of different degrees of surface damage on the surface crystallization characteristics of two glasses. The effects upon crystal nucleation density and upon the mechanical strengths of the materials produced were of particular interest.

The investigation was designed according to the following schedule:

Surface crystallization
↓
Crystal nucleation studies
↓
Observation of crystalline layer development
↓
Strength testing.

Feasibility studies were carried out to assess the most suitable technique for effective surface characterization. Of these, the technique of surface decoration using gold deposition is dealt with elsewhere [4]. This non-destructive method, based upon the epitaxial growth of metallic thin films proved to be particularly successful for the decoration and identification of surface flaws in relatively highly finished samples. However, there was less success in the characterization of severely abraded surfaces as the decoration patterns were partially obscured by grinding marks and rifts. The results of these preliminary observations suggested that the decoration technique was not suitable for the characterization of the wide range of surface conditions which were of interest in the present study.

Indentation fracture methods [5] were investigated as a means of characterizing glass surfaces in terms of surface micro-strength and flaw density. The Hertzian fracture technique involves pressing a spherical indenter into a glass surface under controlled conditions until a ring crack is initiated. The interpretation of results relies upon the calculation of the radial stress field and the effective surface area 'sampled' by a given stress level. Preliminary experiments were encouraging and suggested that a wide range of surface conditions might be characterized in terms of mean critical stress and flaw number density.

A calcium–zinc–aluminosilicate composition (Glass 1) and a calcium aluminate (Glass 2) were investigated. Both glasses were known to exhibit significant increases in sample strength after surface crystallization.

2. Theory of Hertzian fracture

A direct method of data interpretation, which depends upon the calculation of the critical stress associated with a particular fracture, was considered appropriate for the present study [5]. The fracture stress is dependent upon P_F, the fracture load and the radial distance, y, defining the point of crack initiation. In the case of an ideal Hertzian field, the variation of stress with radial distance has the form,

$$\sigma = \frac{(1-2\nu)}{2\pi} \cdot \frac{P_\mathrm{F}}{y^2} \tag{1}$$

where ν is Poisson's ratio. Thus for a sufficiently large number of indentations a critical stress distribution may be calculated. Further, for a given stress level, σ, it is possible to define a number density function $u(\sigma)/A(\sigma)$ where

$$A(\sigma) = \pi \sum_{i=1}^{N} (y^2 - y_0^2). \tag{2}$$

In Equation 2, y_0 is the minimum value of y associated with a given stress level [5] and N is the number of indentations. Corrections to the radial stress field to incorporate the effect of elastic mismatch between indenter and specimen [6] were introduced into the analysis.

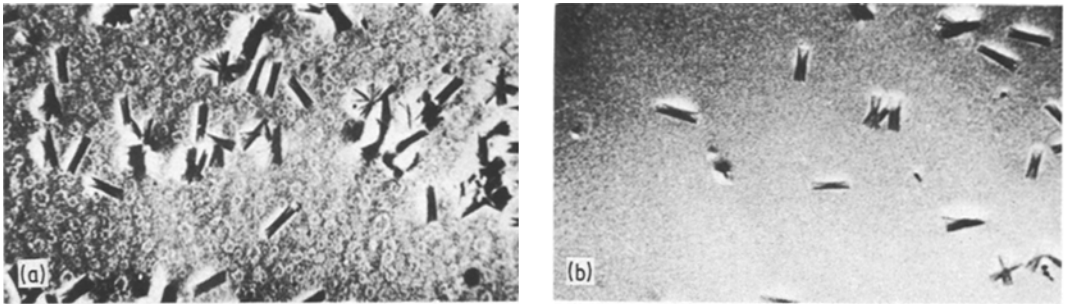

Figure 1 Surface microstructure of Glass 1 after heat-treatment at 835° C for 10 min. (a) 200 grit surface finish; (b) initial polish; (c) final polish.

3. Experimental procedure

The calcium–zinc–aluminosilicate composition (Glass 1) was as follows:

SiO_2 46.1; Al_2O_3 9.6; CaO 24.0; ZnO 20.3 (mol %)

Batches (200 g) were ball-milled for 1 h and melted at 1450° C for 12 h. After quenching, the glass was remelted for a further 8 h, cast into rectangular blocks and annealed for 1 h at 550° C. Specimens were cut into slices (4 mm thickness) using a diamond wheel and then received the appropriate surface treatment.

Samples of the calcium aluminate composition (Glass 2) in the form of annealed blocks (100 mm x 80 mm x 50 mm), were kindly supplied by G.E.C. Power Engineering Ltd, Stafford.

The test rig used for Hertzian fracture measurements was similar to that described in earlier papers [5, 7] comprising a hemispherical sapphire (8 mm diameter) and specimen support block connected to a compressed air supply. The applied load was controlled by a pressure regulator geared to a constant load rate of 13 kg sec^{-1}. The appearance of Newton's rings at the indenter/specimen interface allowed the variation of contact area with applied load to be measured. The fracture diameter was determined using a calibrated eyepiece.

Strength measurements were carried out using an Instron testing machine utilizing a 500 kg load cell and a loading rate of 1 kg sec^{-1}. Values of modulus of rupture (three-point bending test) were determined from the equation,

$$\sigma_c = \frac{3P_F l}{2bh^2} \tag{3}$$

where P_F is the load to failure and h, b and l are the specimen height, breadth and length, respectively. Specimens for strength testing were cut to a rectangular cross-section of 3.5 mm x 2.5 mm, the use of a 20 mm span width ensuring the minimization of shearing during fracture*.

Crystal morphology was examined using scanning electron microscopy and optical microscopy, the selection of a suitable technique being dependent upon the extent of crystal development. Crystal layer thickness measurements were made by examining specimen cross-sections following diamond wheel cutting, etching and polishing. A 30-sec etch in 5% HF allowed observation of crystalline layers in Glass 1. In contrast, the silica-free Glass 2 required a 20-min etch in order to obtain sufficient definition at the glass/crystal interface.

4. Results

4.1. Calcium–zinc–alumino–silicate (Glass 1)

X-ray diffraction studies indicated that heat-treatment within the temperature range 800–900° C resulted in the nucleation and growth of Willemite crystallites. Preliminary investigations showed that the size and number density were markedly dependent upon the surface condition prior to heat-treatment (see Fig. 1); the extension

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*Approximately 30 specimens were tested for each condition under investigation.

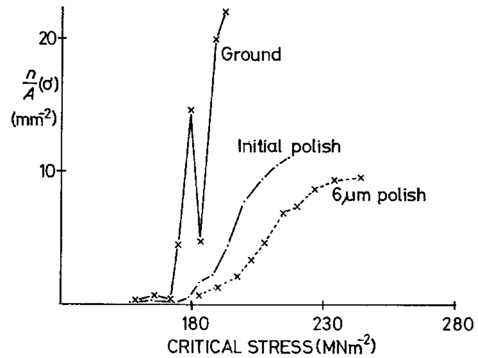

Figure 2 Indentation strength characteristics for Glass 1.

of heat-treatment times resulted in the development of surface crystalline layers.

The results of indentation fracture experiments for three surface conditions (~ 50 indentations per specimen) are shown in Fig. 2 and summarized in Table I. The transition from a heavily abraded surface (220 grit grinding) to a polished surface may be characterized in terms of both flaw severity (mean critical stress to failure) and number density: Fig. 2 indicates a displacement of the flaw function, $n(\sigma)/A(\sigma)$ towards higher values of critical stress. The range of σ_c values indicating flaw severity is also broadened as the surface finish is improved.

TABLE I Results for nucleation studies, indentation fracture measurements and modulus of rupture measurements for Glass 1

Nucleation studies (crystallite density) 840° C for 10 min	
(i) 220 grit grinding	3.2×10^{-2} μm^{-2}
(ii) Partial polish	3.5×10^{-3} μm^{-2}
(iii) Full polish (6 μm)	1.0×10^{-3} μm^{-2}
Indentation fracture	
(i) σ_c (ground)	178 MN m^{-2}
(ii) σ_c (partial polish)	187 MN m^{-2}
(iii) σ_f (full polish)	200 MN m^{-2}
Modulus of rupture	
(i) 200 grit abrasion	
820° C	1 h: 145 MN m^{-2} 2.5 h: 245 MN m^{-2} 4.3 h: 275 MN m^{-2}
840° C	1 h: 180 MN m^{-2} 1.6 h: 278 MN m^{-2} 2.5 h: 283 MN m^{-2}
(ii) Polished surface	
840° C for	2.5 h: 240 MN m^{-2}
(iii) Untreated glass (220 grit abrasion)	90 MN m^{-2}

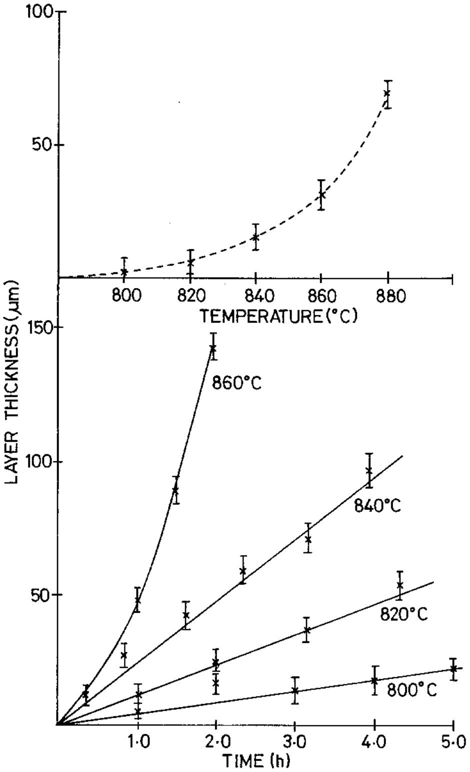

Figure 3 Surface crystallization characteristics for Glass 1.

Surface-layer growth characteristics are shown in Fig. 3. Heat-treatment at temperatures above 850° C resulted in rapid crystal growth and the formation of an unstable crystal layer (thickness > 150 μm); specimens tended to fragment on cooling. By reducing the heat-treatment temperatures to within the range 800–840° C, semi-transparent crystalline layers were grown to a depth of about 100 μm for heat-treatment times less than 5 h. Estimations of initial nucleation densities based on a short heat-treatment time (840° C for 10 min) are summarized in Table I.

Microscopic examination of surface layers indicated that considerable surface flow had occurred during the heat-treatment schedule. However, there was no evidence of significant specimen deformation. In order to establish the effect of time and temperature on any specimen strengthening, a range of modulus of rupture measurements was obtained for specimens heat-treated at temperatures less than 850° C (Fig. 4). These data, which were obtained for a coarsely ground surface (200 grit grinding), indicated that a maximum strength (~ 300 MN m^{-2}) corresponds to crystalline layer thickness of between 60 and 70 μm. No further strength increase was obtained by increasing either heat-treatment time or temperature.

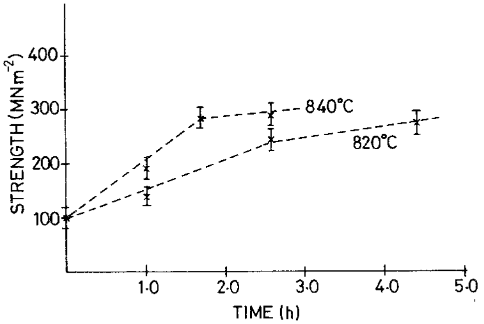

Figure 4 The effects of duration of heat-treatment on modulus of rupture of Glass 1.

The use of intermediate times (820° C for 2 h; 840° C for 1 h) resulted in a strength increase to approximately 200 MN m^{-2}. These data compare with a parent glass strength of 90 MN m^{-2}.

Modulus of rupture measurements obtained for polished specimens which have been heat-treated for 2.5 h at 840° C resulted in a mean breaking strength of 240 MN m^{-2} (Table I). This, and further tests using different heat-treatment schedules, suggested that no statistically significant differences in breaking strength could be obtained for the extreme range of surface conditions.

4.2. Calcium aluminate (Glass 2)

Preliminary work suggested that heat-treatment within the range 800–880° C would lead to the formation of stable surface crystalline layers of thickness less than 100 μm. Unlike Glass 1, no surface flow during heat-treatment was apparent; unfortunately the presence of grinding marks in the surface of abraded specimens obscured observation of initial nucleation. Therefore, the effects of temperature, time and surface condition were investigated by considering their influence upon macroscopic layer development, rather than upon nucleation density.

TABLE II Results for indentation fracture and modulus of rupture measurements for Glass 2

Indentation fracture	
(i) 6 μm polish (Surface B)	$\sigma_c = 336$ MN m^{-2}
(ii) 6 μm polish and free abrasion (Surface C)	$\sigma_c = 321$ MN m^{-2}
(iii) 6 μm polish and 800 grit grinding (Surface D)	$\sigma_c = 321$ MN m^{-2}
(iv) Ground – 200 grit (Surface E)	$\sigma_c = 286$ MN m^{-2}
Modulus of rupture	
(i) Surface A: Parent glass (220 grit abrasion)	120 MN m^{-2}
(ii) Surface B: 6 μm polish	314 MN m^{-2}
(iii) Surface C: 6 μm polish + free abrasion	388 MN m^{-2}
(iv) Surface D: 6 μm polish + 800 grit grinding	443 MN m^{-2}
(v) Surface E: 220 grit grinding	354 MN m^{-2}
(vi) Surface F: Diamond wheel cut	510 MN m^{-2}

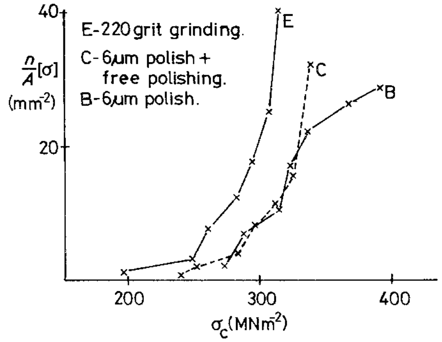

Figure 5 Indentation strength characteristics of Glass 2.

Surface characterization using indentation fracture was attempted on the five surface conditions summarized in Table II. Flaw number density functions are shown in Fig. 5. Results obtained for surface conditions B and D (6 μm polish; 6 μm polish followed by 800 grit light abrasion) were identical. Differences between surface conditions B and C were also only apparent for $\sigma_c > 320$ MN m^{-2}. Using the smallest indenter available no meaningful data could be obtained for a diamond cut surface; this suggests a very high surface strength above that associated with a polished surface.

Data presented in Fig. 5 indicate that, in general, there is an increase in σ_c associated with an improvement in surface finish.

The influence of heat-treatment time and temperature is indicated in Fig. 6 which shows that heat-treatment temperatures of 850 and 875° C led to crystalline layer thicknesses of approximately 90 μm for times of 5 h and 3 h, respectively.

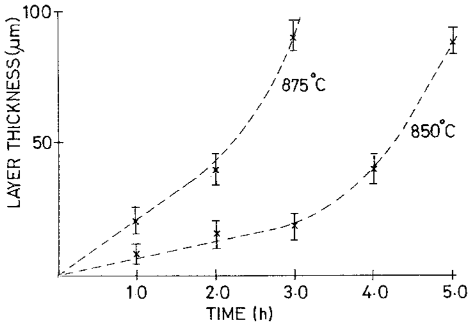

Figure 6 Surface crystallization characteristics of Glass 2.

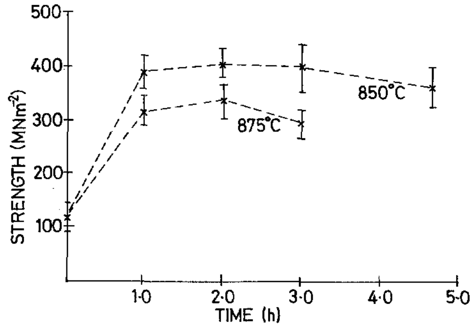

Figure 7 The effects of duration of heat-treatment on modulus of rupture of Glass 2.

Fig. 7 shows the strength characteristics of Glass 2. Within these experiments the maximum strength increase (to ~ 400 MN m^{-2}) was obtained at a temperature of 850° C, any further increase in temperature to 875° C leading to a reduction in modulus of rupture. In both cases, however, there is a significant increase in strength compared with the parent glass (120 MN m^{-2}). Further, the extension of heat-treatment times eventually results in a strength reduction; this coincides with layer thicknesses greater than about 100 μm. It is also of interest that for a given temperature, maximum strength is achieved after very short heat-treatment times (layer thickness of 15–25 μm). This contrasts with equivalent data obtained for Glass 1.

Fig. 8 indicates that for the two extreme cases of 200 grit grinding and 6 μm polish, there are considerable differences in crystal morphology. Microscopic examination suggested that for a polished surface two levels of crystallization are present, large scale structures (~ 50 μm) are superimposed upon a matrix of much smaller fibrils (1 μm diameter). These fibrils tend to radiate from a central point within the larger formations. In contrast, heat-treatment of a heavily abraded sample results in no large scale structures, the smaller fibrils extending into the bulk glass in a direction perpendicular to the surface. In this case the resultant glass/crystal boundary is more uniform in form.

The effect of lightly abrading a polished surface was also investigated. Polished specimens received "free abrasion" using a fluidized bed containing 30 mesh silicon carbide particles. This reduced the dimensions of the large-scale structures to approximately 25 μm. Further, light grinding with 800 grit paper resulted in crystal formation similar to that obtained for 200 grit abrasion. Similarly, an "as-received" diamond-cut surface showed no large-scale crystal formations.

Strength measurements were obtained for crystallized specimens which had received surface treatments summarized in Table II and Fig. 9. Specimens were heat-treated at 850° C for 3 h. The lowest value of modulus of rupture (314 MN m^{-2}) was obtained by crystallizing a polished surface. Coarse grinding (220 grit) as a pre-treatment procedure resulted in a similar strength of 354 MN m^{-2}. These data compare with a parent glass fracture stress of 120 MN m^{-2} (non-crystallized, diamond wheel cut). This may be viewed in terms of an increase in the density of nucleating sites. However, further increases were obtained by light abrasion of 6 μm polished surfaces prior to heat-treatment. Free abrasion of a polished surface led to an increase to 388 MN m^{-2} while similar treatment with 800 grit paper resulted in a strength of 443 MN m^{-2}. The maximum specimen strength (510 MN m^{-2}) was obtained by crystallizing a surface which had been cut with a diamond wheel and received no further treatment.

5. Discussion

In order to assign some meaning to the results of the experiments presented in this paper it is useful to distinguish between two separate roles of surface flaws:

(i) the action of flaws as stress concentrators which are present prior to crystallization and which may or may not be modified during the heat-treatment process;

(ii) the action of flaws as nucleation sites for surface crystallization.

Using indentation fracture, it has been established that a wide range of surface flaws exist for various surface conditions and that these may be characterized in terms of σ_c, mean critical stress to failure; it should not necessarily be assumed that the type of flaw acting as a crystal nucleation site assumes an important role as a stress concentrator.

The surface ctystallization behaviour of the calcium aluminate composition (Glass 2) is complex. However, it is clear that the strength of the surface-crystallized materials produced is strongly dependent on the surface state of the parent glass. The results may be classified as in the following sections.

5.1. Light abrasion (Surfaces C and D)

These treatments resulted in significantly higher mean strengths (388 and 443 MN m^{-2}, respectively) than the value obtained for the material

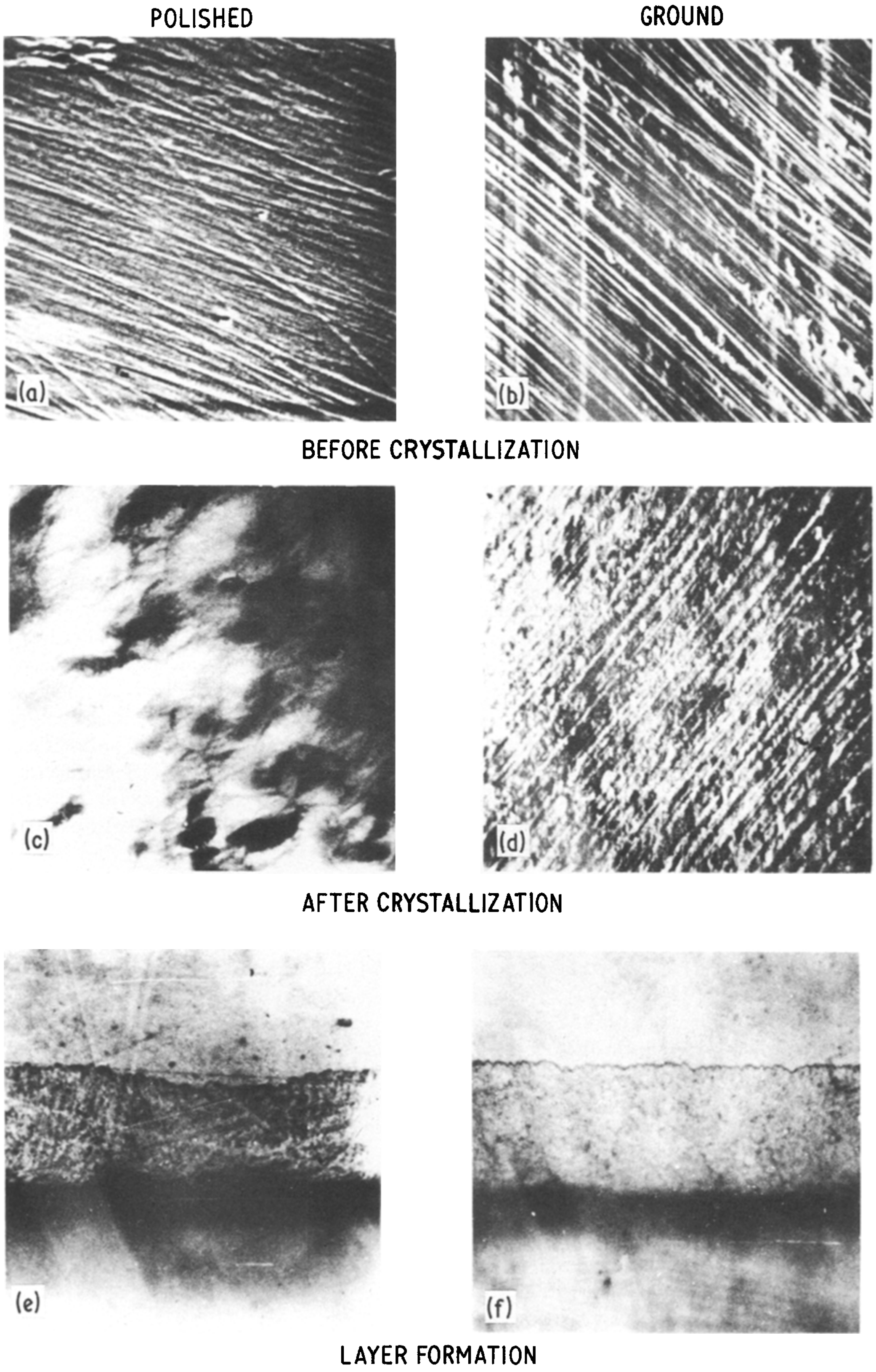

Figure 8 Surface microstructure of Glass 2. (a) × 2400, (b) × 2370, (c) × 500, (d) × 280, (e) × 1000, (f) × 1000.

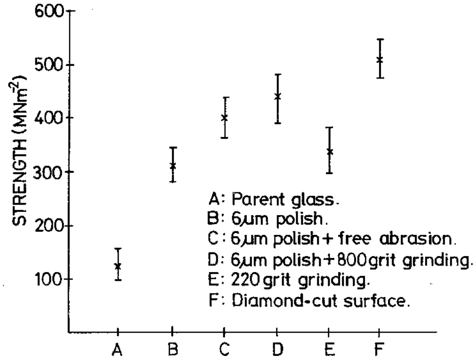

Figure 9 The effects of prior surface treatment upon moduli of rupture of surface-crystallized Glass 2 (heat-treatment 850° C for 3 h).

which had received only the 6 μm diamond polish (Surface B: mean strength 314 MN m^{-1}). The higher strengths are attributed to the development of finer-grained microstructures in the surface-crystallized layer resulting from higher crystal nucleation densities. The findings support the belief that flaws introduced by abrading processes act as sites for nucleation of surface crystallization.

5.2. Coarse abrasion (Surface E)

The material processed in this way had a mean strength (354 MN m^{-2}) which was not greatly different from that of surface crystallized glass which had simply been polished (Surface B). It was noted, however, that the scale of the microstructure of the surface-crystallized layer was significantly finer for the coarsely abraded glass. This might have been expected to favour the development of a higher mechanical strength. It is believed that the explanation of this discrepancy is that the coarse abrasion, while promoting a higher crystal nucleation density, introduced severe flaws which were not sufficiently modified during the crystallization heat-treatment. Thus the effect of these flaws would be to weaken the surface-crystallized glass.

5.3. Diamond-cut surface (F)

The surface crystallization of glass prepared in this way resulted in the highest mean strength indicating that this cutting process introduces a high density of comparatively mild flaws. These provide a high density of nucleation sites favouring a fine-grained surface microstructure but at the same time the severity of these flaws as stress raisers is probably favourably modified during the crystallization process. The combined effect of these two factors is to generate a surface-crystallized layer having characteristics favouring high mechanical strengths.

The results obtained for the calcium zinc aluminosilicate composition, differ from those for Glass 2 and it is considered significant that considerable surface flow occurred during the heat-treatment process. Although there were differences in nucleation density associated with the two extreme surface conditions, no distinct types of crystal morphology were apparent. It is evident for this glass that no well-defined correlation exists between surface condition and final sample strength for the surface conditions under investigation.

6. Conclusions

Investigation of the surface crystallization behaviour of two glasses allows the following conclusions to be drawn.

(1) The microstructures of the surface crystalline layers are dependent upon the surface state of the glasses before the crystallization heat-treatment and a valuable technique for characterizing such surface states is indentation fracture.

(2) In the case of a calcium zinc aluminosilicate composition, the occurrence of surface flow during heat-treatment exerted a major influence upon the mechanical strength of the surface-crystallized glass. For this material, the highest mean strength achieved was 282 MN m^{-2}.

(3) For a calcium aluminate glass, the microstructure of the surface-crystallized layer was clearly dependent on the surface state of the parent glass and this provided evidence that microcracks served to provide crystal nucleation sites. The application of a suitable surface treatment (diamond wheel cutting) enabled a mean strength of 510 MN m^{-2} to be achieved.

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