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A method of replicating glasses and glass ceramics at and near the sample surface

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A method for replicating glasses and glass-ceramics at and in close proximity to the surface is described. The replicas used are platinum–palladium pre-shadowed carbon replicas. The method consists of fracturing the sample and mounting it in such a manner that both the shadowing metals and the carbon substrate are deposited on the sample surface and cross-section simultaneously. Artefacts are discussed, and examples of the application of the method given.

1. Introduction

It is frequently of great interest to know the microstructure of a material at and very near to its surface. Yet it is somewhat difficult to characterize this near-surface region. In scanning electron microscopy the charging on non-conductors near an edge tends to obscure the fine details of the near-surface region of glasses and ceramics. Most specimen polishing methods tend to round over the sample edges at the very point of interest. For transmission electron microscopy a thin section extending from the surface into the sample would be highly desirable, but virtually impossible to prepare routinely. Thus, a replica technique is suggested. A replica of a cross-section of a sample extending up to the sample edge is difficult to prepare and to support in the microscope. The over-the-edge replica method described in this paper was developed to circumvent these problems. With it the specimen is replicated up to the edge and on to the specimen's original surface. Thus, it is possible not only to study the near-surface region, but also to examine the structures in three dimensions.

The over-the-edge replica has been used extensively in characterizing Corning's materials for a number of years. But, although the replicas are relatively simple to prepare, they do not appear to be in widespread use elsewhere. Nor is the over-the-edge technique described in the common books covering specimen preparation techniques for electron microscopy [1–3]. In our laboratory the method has been applied only to glasses and glass-ceramics, but it should be applicable to other brittle materials as well. In this paper the technique will be described, the source of artefacts explained and examples of its application shown.*

2. Technique for making the "over-the-edge" replica

A summary of the steps involved in making the replica is as follows:

(1) fracture the specimen;

(2) if desired, pre-etch the specimen;

(3) deposit first the pre-shadowing metal and then the carbon support substrate simultaneously on both the original surface and the fractured cross-section of the specimens;

(4) remove the replica simultaneously from both the original surface and the cross-section of the specimen;

(5) pick up the replica on a conventional specimen support grid.

Obtaining the proper configuration at the point where the fracture intersects the original specimen surface is critical. It has been our experience that the proper configuration is most readily obtained by partially scoring the surface of interest with a

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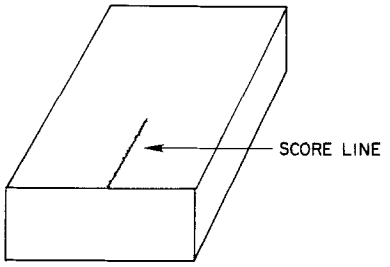

Figure 1 Sample scoring method.

wheel-type glass cutter as illustrated in Fig. 1, and then fracturing the specimen. The useful part of the specimen for the 'over-the-edge' replica is that portion which extends beyond the score line.

If depth measurements in the sample are to be determined from distance measurements along the replica of the cross-section, then it is important that the angle which the fracture makes with the surface be known. If the angle is 90° (and it usually is approximately that) then the depth in the sample and the distance along the replica of the cross-section are equal. However, for angles other than 90° the depth and distance are not equal, and it is not apparent from viewing the finished replica that this is the case. Therefore, that determination should be made using a light microscope prior to removal of the replica from the specimen.

If selective etching is required to delineate structures in the specimen, this is usally done after fracturing. However, if the original surface requires a more severe etch than does the cross-section, then the surface can be partially etched prior to fracturing. If it is desired to etch the cross-section but not the surface, then an adherent, protective coating must be applied to the specimen surface prior to fracturing, and removed prior to replication.

In depositing the replica materials (in our case platinum–palladium pre-shadowing [4] with a carbon substrate [5]) the line of intersection between the cross-sectional surface and the original surface, the shadowing metal source, and the carbon source, all lie in a plane. To aid in visualizing the arrangement, Fig. 2 is drawn from the viewpoint of the shadowing source. This source is usually positioned in the plane which bisects the angle between the two surfaces and is so located in that plane as to give the correct angles of incidence to both specimen surfaces. If differing amounts of shadowing are desired on the two surfaces, this may be accomplished by shifting the shadowing source slightly out of the above-

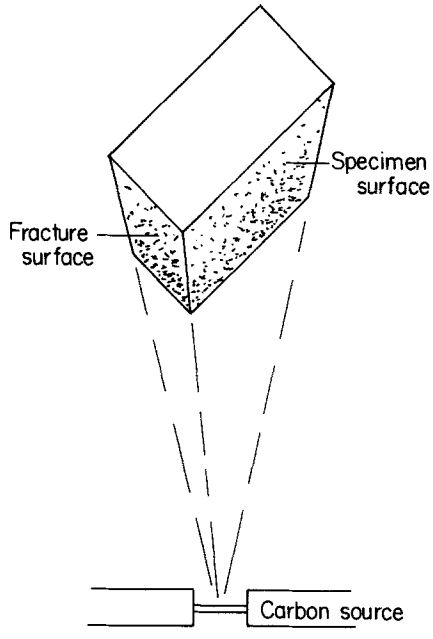

Figure 2 Replica deposition.

mentioned plane. The carbon source is so located in the plane normal to the line of intersection of the two specimen surfaces that identical angles of incidence are formed with these two surfaces. Appropriate increases in the amounts of both the shadowing metals and carbon are made to compensate for the abnormal positions of the two sources with respect to the specimen surfaces.

The replica is removed from the specimen by conventional techniques, using solvents appropriate for the material being replicated. However, at this point extreme care must be exercised to avoid tearing the replica at the line of intersection between the cross-section and original surfaces. Once released from the specimen the replica will flatten and float on the surface of the solvent. It may be left floating on the solvent surface for further cleaning if desired, and then transferred to water and picked up on a conventional specimen support grid.

3. Artefacts

Two types of artefacts have been encountered with "over-the-edge" replicas. One is seen only occasionally and results from failure of the replica to flatten sufficiently in the vicinity of the intersection of the two surfaces. The other is almost always present to some extent and is due to the fact that even if ideally flattened the replica would not be uniformly thick in the vicinity of the inter-

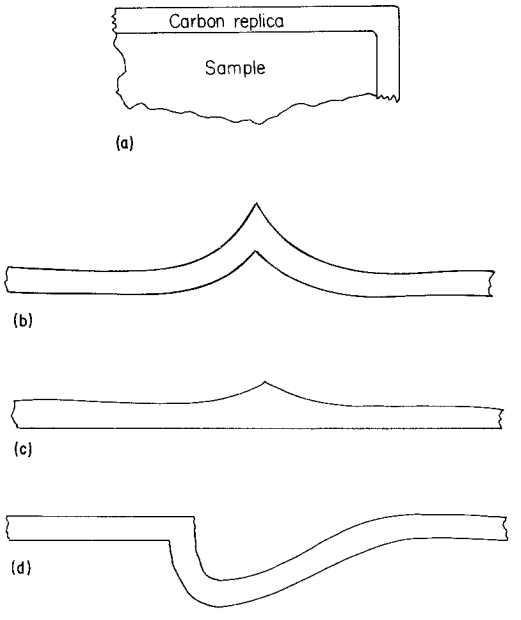

Figure 3 (a) Replica as-deposited on specimen. (b) "Flattened" replica. (c) Relative thickness of flattened replica as seen by electron beam. (d) Second "Flattened" replica.

section. However, this latter artefact is usually an asset in that it clearly defines the line of demarcation between the surface and the cross-section.

Fig. 3a depicts a typical deposited replica still attached to the specimen. Fig. 3b illustrates the most common configuration which a 'flattened' replica takes; and Fig. 3c shows the relative thickness of carbon which must be traversed by the electrons in passing through the replica shown in Fig. 3b. It will be noted that the effective carbon thickness is somewhat greater in the vicinity of the intersection of the two surfaces. In the attached negative prints, this appears as a relatively light line (Fig. 4, for example).

The less common type of artefact is depicted in Fig. 3d and illustrated in Fig. 5 where the straight lines of the specimen are obviously distorted due to the curvature of the replica.

The severity of these artefacts may be reduced by keeping the thickness of the carbon substrates to a minimum. But this, in turn, also greatly increases the probability that the replica will separate at the intersection of the two surfaces.

4. Examples

The remainder of the paper will illustrate the application of the use of "over-the-edge" replicas. In all cases where micrographs from "over-the-edge" replicas are included the specimen surface is to the right and the cross-section to the left.

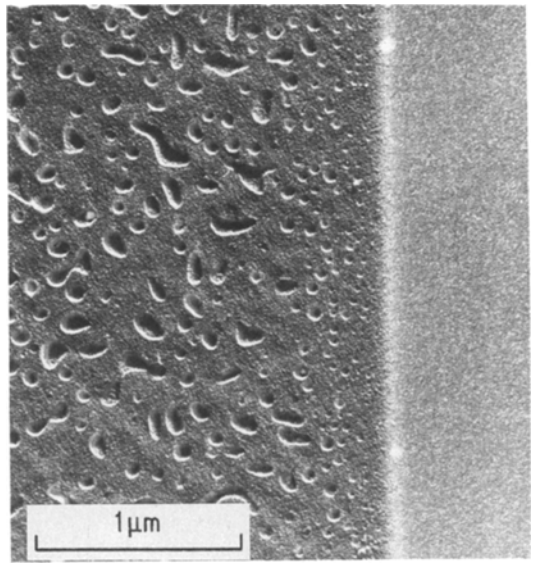

Figure 4 Sodium borosilicate opal glass.

Fig. 4 is a micrograph from a replica of an experimental sodium borosilicate opal glass. On cooling from the melt this particular composition phase separates into a sodium borate-rich glass and a silica-rich glass. The index of refraction mismatch between these two phases produces the opacity. As part of the testing of this composition, standard durability measurements in a strong dishwater detergent were run. In this test most glasses undergo a gradual degradation in appear-

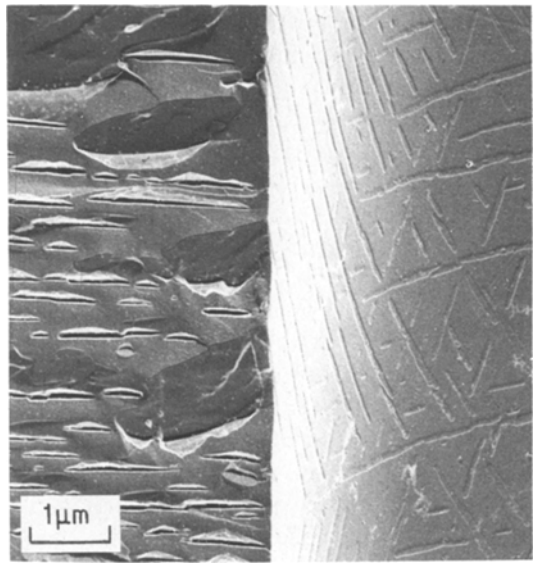

Figure 5 Replica illustrating one type of Artefact.

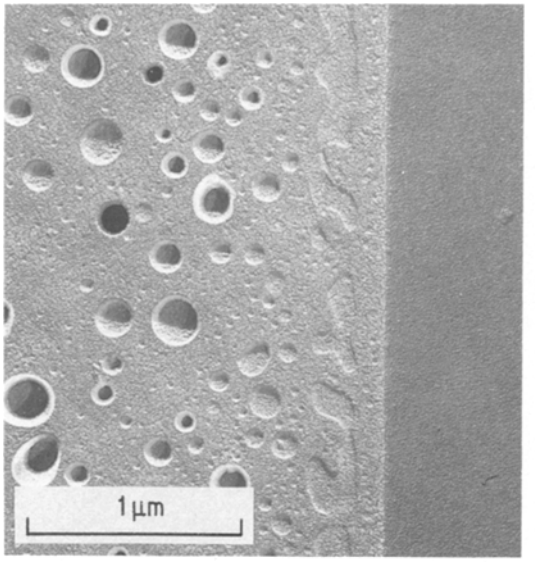

Figure 6 Irridescent opal glass.

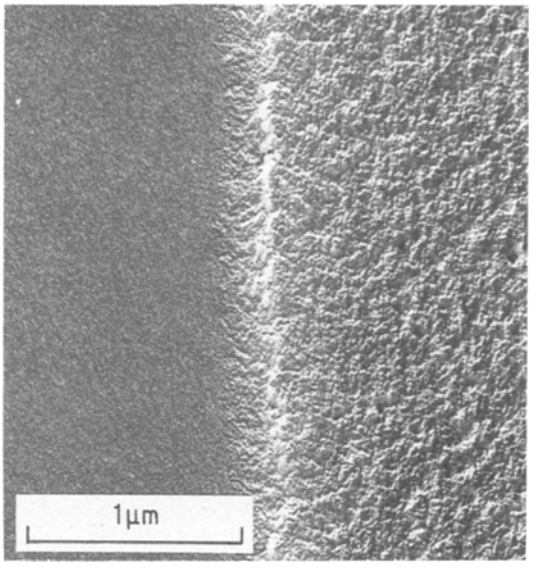

Figure 7 Leached borosilicate glass.

ance due to a loss of gloss. The initial durability of this sodium borosilicate composition was quite good, but after a certain period of time the appearance of the ware quickly deteriorated. In Fig. 4 it is observed that at the surface there are none of the relatively soluble sodium borate-rich droplets. Slightly below the surface the droplets are present, but are in the form of relatively small spheres. As the glass in these layers was slowly removed by the detergent solution, the surface remained relatively smooth. However, at approximately 0.5 μm below the surface the soluble sodium borate-rich phase is observed to be relatively large and irregularly shaped. When the detergent solution reached this depth, relatively deep pits were etched into the surface. These pits are both large enough to scatter light, and to trap dirt, and were thus responsible for the unsatisfactory appearance of the ware.

Fig. 6 is from a related composition. When experimental dinner plates were pressed from this glass, they were found to be irridescent in some areas. The reason for the irridescence was not understood. In this micrograph it will be noted that approximately 1500 Å below the "as-formed" surface the sodium borate-rich phase was formed as a layer of elongated droplets. It was apparent that the droplets had formed in the glass prior to the pressing operation. During the pressing as the glass moved outward along the plunger surface these droplets were elongated parallel to and at nearly a fixed distance from the glass surface. Thus, there was nearly a continuous layer of glass just below the plate surface which had an index of refraction different from that of the matrix glass above. Furthermore, the distances were such that light reflected from the plate surface and from the elongated droplet surface interfered, producing the irridescence.

Although undesirable in the above case, interference effects can be useful. Fig. 7 is a micrograph from a leached borosilicate glass. The object here was to produce an antireflection layer on the glass by changing the index of refraction of a suitably thick surface layer through leaching.

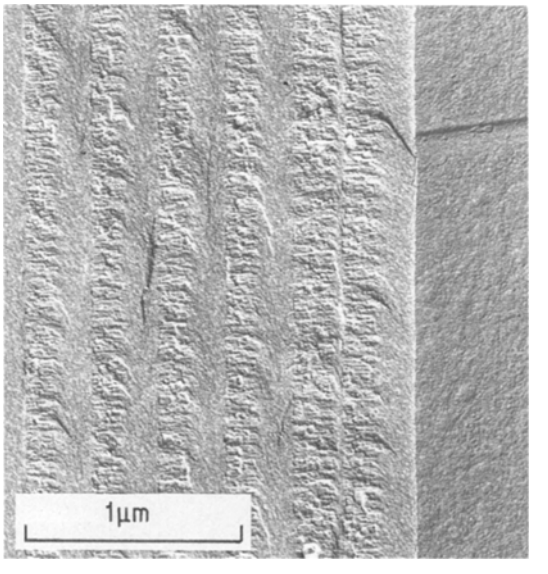

Figure 8 Multi-layered anti-reflection coating.

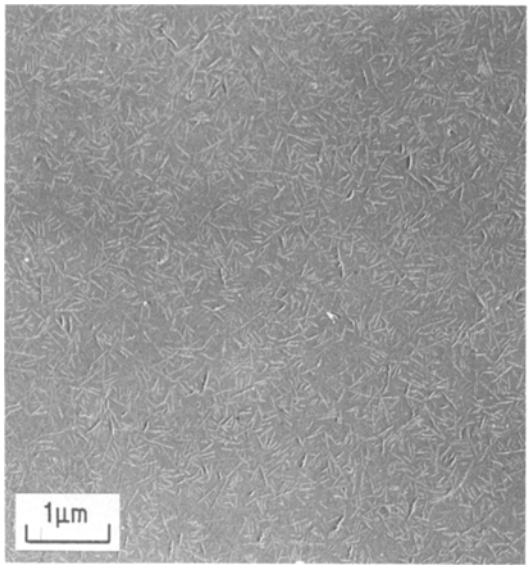

Figure 9 Conventionally treated Fotoform® brand glass.

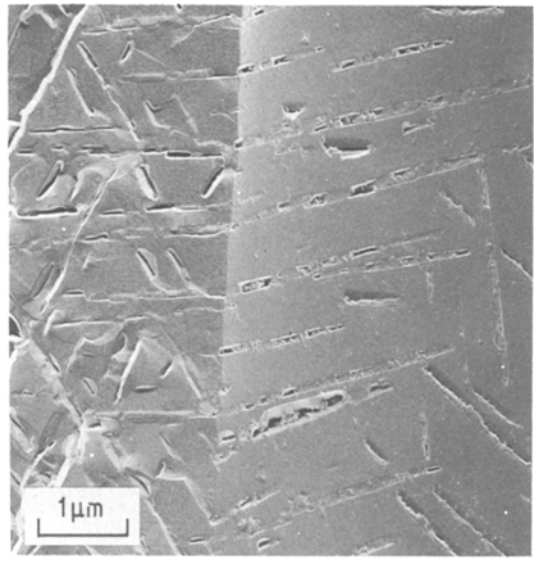

Figure 10 Over-the-edge replica of specially-treated Fotoform® brand glass.

Another approach to the reduction of light losses at glass interfaces is to deposit layers of the proper thicknesses and of differing indices of refraction on the glass. Fig. 8 illustrates a multi-layer silica/titania anti-reflection coating on a glass substrate.

Fig. 9 is from a conventional replica of a polished and etched surface of Corning's lithium metasilicate-containing chemically machinable glass marketed under the Fotoform® trademark. This micrograph is typical of what would be observed regardless of the orientation of the polished section within the sample. Because of the unique solubility characteristics of this glass, it was of interest to know the three-dimensional shape of the lithium metasilicate crystals. But this was difficult to deduce with certainty from the two-dimensional replicas. Both the number and size of the lithium metasilicate crystals may be varied by altering the ultraviolet exposure and/or heat treatment. A sample was prepared so as to contain larger lithium metasilicate crystals, and a micrograph from an over-the-edge replica of it is shown in Fig. 10. Here it is observed that the two-dimensional dendritic branches observed in Fig. 9 are, in reality, sheets. From a number of such micrographs it was then possible to construct a three-dimensional model of the lithium metasilicate crystals in this glass.

5. Conclusion

A method for preparing "over-the-edge" replicas from glasses and glass-ceramics has been described. These replicas have proved to be very useful in studying the microstructure of selected materials in close proximity to the surface.

Acknowledgments

I would like to acknowledge the capable assitance of Mr R. F. Heitzenrater and Mrs C. D. Smith, who contributed to the development of the "over-the-edge" replica technique and prepared the replicas from which the micrographs in this paper were taken.

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