Original Paper

Viscous flow and surface crystallization caused by Vickers indentation

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Healing and nucleation activity of crack patterns caused by Vickers micro-indentations on the surface of diopside glass ($MgO \cdot CaO \cdot 2\ SiO_2$) were studied by optical and surface interference microscopy. Minimizing the glass surface during thermal treatments and healing of cracks result in funnel-like depressions symmetrically arranged around the Vickers indentation. Diopside surface crystals predominantly grow from previous crack edges. Thus, double chains of crystals reveal completely healed radial cracks while long range viscous flow at the formation of funnel-like depressions spreads off former double chains to form circular crystal chains.

1. Introduction

Glasses, glass-ceramics, and glass- or glass-ceramic matrix composites are promising candidates for new material applications in the field of electronics, biomaterials, multifunctional ceramics, and micro-system applications. Due to increased requirements of property tailoring, the extended variety of new, often crystallizing, glasses, the decreasing component dimensions, and the complex technology of manufacture more extensive knowledge of material properties and behavior is required particularly at high temperatures and with respect to the glass/air or glass/crystal interface.

Mechanical surface damaging and its influence on surface profile and surface-induced crystal nucleation during subsequent annealing or sintering are one interesting area within that context. Previous papers showed the technological importance of the differently prepared or treated glass powder surface for controlled sintering of crystallizing glass powders [1 and 2]. Recent studies [3 to 6] pointed out that sharp convex crack edges strongly trigger crystal nucleation activity before they disappear by thermal healing. The related basic mechanism is still under discussion.

In the present paper, large cracks at polished surfaces of diopside glass ($MgO \cdot CaO \cdot 2\ SiO_2$) were generated by Vickers micro-indentation to study the process of healing, the resulting surface roughness, and the nucleation efficiency of sharp crack edges.

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2. Experimental

2.1 Samples

The sample glass ($MgO \cdot CaO \cdot 2\ SiO_2$) was prepared from defined mixture of SiO_2 (Frechener Quarzsand MILLISIL W12, Sand- und Tonwerk Walbeck GmbH (Germany)), MgO, and $CaCO_3$ (pro analysis purity, Merck KGaA (Germany)) in normal laboratory condition. The batch was melted for 5 h at 1450 °C in a platinum crucible and cast onto steel plates. After cooling down, the glass plates were cut into stripes of (5 x 5) mm^2, polished with CeO_2, and finally cut into slices of ≈ (5 x 5 x 2) mm^3.

2.2 Sample preparation

The Vickers micro-indentation tests were made with indentation loads of 5 or 3 N on polished surfaces. Indented samples were subsequently annealed in an electric furnace at 820 °C for varied times of healing (20, 40, 80 and 160 min). A corundum tube (gas dense quality) furnace placed within a glove box was used for these experiments. The concentration of dust and relative air humidity during the thermal treatment was measured by the devices "Series 1.100" (GRIMM Labortechnik) and a "Series 2 MOISTURE IMAGE" (PANAMETRICS), respectively. Samples were automatically driven into the furnace chamber by

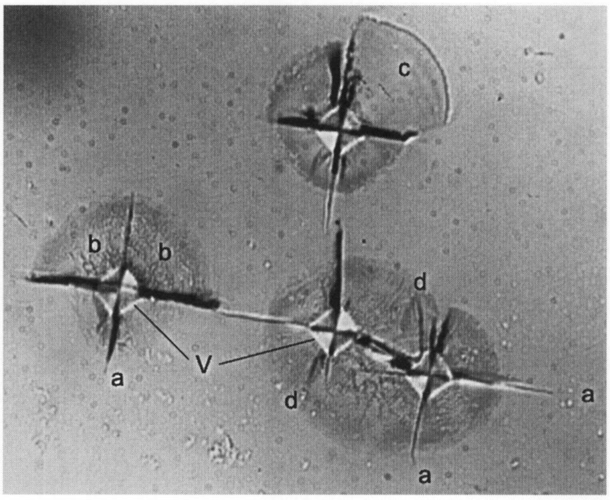


Figure 1. Transmitting light micrograph (top view) of typical crack patterns caused by Vickers indentation on polished surfaces of diopside glass (as received). V: pyramidal Vickers indentation, a: radial crack, b: lateral crack, c: shallow lateral crack, d: secondary radial crack (see figures 2a to d for schematical explanation).

means of a stepper motor. This experimental technique ensures several advantages. A very low concentration of dust is necessary for low nucleation density on the polished glass surface. The scatter of crystal growth rate data was minimized by the controlled drying process of atmosphere in the glove box due to the influence of water vapor on the crystal growth rate. Finally, small furnace dimensions and the use of a stepper motor allow high precision of the annealing procedure.

2.3 Measurements

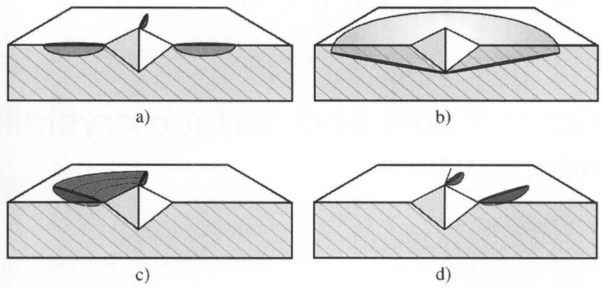
Each sample was characterized before and after Vickers micro-indentation as well as after each annealing step. The glass surface and micro-indentations were observed by optical and surface interference microscopy (Jenapol, Carl Zeiss Jena and microscope interferometer Maxim GP, Zygo, respectively). Pictures of patterns were obtained by a CCD camera HITACHI KP161 and were processed by the software ImageC® (Imtronic).

3. Results

3.1 Crack patterns

Figure 1 shows typical crack patterns caused by Vickers indentation on polished surfaces of diopside glass. A schematic representation of the mentioned crack types is given in figures 2a to d according to [7].

The crack pattern surrounding the Vickers imprints (figure 1 (V)) was most frequently dominated by radial cracks (figure 1 (a) and figure 2a) that follow the diagonals of the Vickers indentations. Radial cracks are nucleated by flaws at plastic deformation zone boundary and are driven by the elastic stress field arising from the strain mismatch of the plastically deformed zone embedded in the surrounding elastically restraining matrix. In the present study, the time of radial crack generation was not measured. However, according to [7], it is reasonable to assume that radial cracks occur on loading in the present case. Although radial cracks may occur both on loading and unloading [7], radial crack generation during loading was found to be accompanied by secondary radial cracks (figure 1 (d) and figure 2d). Such cracks which slightly deviate from the diagonal direction appear in the present study. The conspicuous darkly shadowed radial cracks are in nonperpendicular orientation to the glass surface.



Figures 2a to d. Scheme of basic crack types caused by Vickers indentations according to [7]. Crack types: a) radial, b) lateral, c) shallow lateral, d) secondary radial.

During unloading, the elastic deformation induces slight reverse shift of imprint surface. This shift can cause lateral cracks beneath the sample surface indicated by smoothly darkened areas within most of the quadrants formed by radial cracks (figure 1 (b) and (c)). Such cracks were described in [7] as entirely occurring during late stages of unloading. After their generation at the tip or the edge of the contact impression they grow rapidly almost parallel and close to the surface. Thus, they are frequently truncated by radial or secondary radial cracks into quarter-plate geometry. As similar type of cracks, lateral shallow cracks (figure 2c) frequently occur. Such crack creation can result in flat conchoidally shaped glass chips or floes which are almost entirely fractured from the sample. These floes can slightly stand out of the surface. This displacement was confirmed by microscope observation of Newton optical interference stripes localized in the crack field.

The probability of occurrence of different basic crack types was slightly influenced by the experimental condition. Only a small effect of the axial orientation of micro-indentation with respect to the orientation of previous polishing of the glass surface was evident. The length of the radial cracks increased with increasing load.

3.2 Crack healing

Different stages of crack healing were studied for various Vickers indentations by means of optical and interference microscopy. A series of optical micrographs is shown in figures 3a to e (top). The as received crack pattern (figure 3a (top)) consists of four symmetrically arranged radial cracks (sharp black lines) backed by a large circumpolar lateral crack beneath the sample surface (spherically shadowed area).

The surface profile of this Vickers indentation, measured by interference microscopy before thermal treatment, is shown in figure 3a (bottom) revealing an almost conical surface elevation of ≈ 0.6 µm in height with nearly planar slopes surrounding the Vickers indentation.

The gradual evolution of crack healing is illustrated in figures 3b to e. After 20 min of annealing at 820 °C (figure 3b) former radial cracks are almost healed. Bright lines indicate their former position. Previous measurements by atomic force microscopy [8] suggest that light refraction at flat surface notches causes these lines.

More conspicuously, four dark ovals appear in the middle part of former radial cracks in figure 3b (top). Interference microscopic studies reveal them as deep "funnel-like depressions" (figure 3b (bottom)). During subsequent annealing (figure 3c) these depressions were further broadened. In late healing stages ($t > 80$ min), the funnel-like depressions almost disappear leaving behind weak shallow depressions after 160 min. The described funnel-like depressions usually occur during healing of Vickers indentations made with loads $F > 1$ N. For $F < 1$ N, radial cracks healed without causing any significant funnel-like depression. The depression size (depth and width) correlates to the length of radial cracks that increases with increasing Vickers indentation load. Although depression centers are arranged in radial symmetry, they can differ in size. In most cases, depressions arranged in opposite position show the same size.

Placed between the four funnel-like depressions, smoothly shadowed regions appear in transmitting micrographs (best pronounced in figures 3c and d). Surface profiling measurements reveal them as "slight elevations" with a maximum of ≈ 6 µm in height at $t = 40$ min. Their peaks are centered in the four quadrants. Their height considerably exceeds that of the "crater wall" (up to ≈ 0.6 µm in height) limiting the Vickers imprints. The height of the "crater wall" does not rise during later healing. In contrast to that, the heights of slight elevations lightly increase during the medium stages of healing. Interference microscope line scans give clear evidence that both elevation types occur independently and simultaneously. In figure 3b radial regions in the outer parts of each of the four quadrants are observable, which are clearly contrasted because of refraction effects. In all probability, these refraction effects are caused by sharp edges of shallow glass pieces fractured during the early annealing treatment.

3.3 Surface crystallization

In figure 4 the distribution pattern of diopside surface crystals grown from a Vickers crack pattern is shown. Apart from a few randomly distributed crystals, most of them are regularly arranged. Many crystals are scattered along the squared edges of the previous pyramidal Vickers imprint (in the center of figure 4). Double chains of crystals appear along the outer part of the former radial cracks shown in vertical orientation in figure 4. In the middle section, that double chain spreads off to oval rings of single crystal chains. Within these oval rings dark median lines reveal the former radial crack. Along those lines, attributed to surface notches by means of interference and atomic force microscopy [8], crystals do not frequently occur. The oval rings appear differently pronounced for differently oriented radial cracks as illustrated in figure 4 by comparing the radial cracks in vertical and horizontal orientation. In many cases, one oval is completely surrounded by the crystal chain while the opposite one is not, like the right oval ring in figure 4 which is still open. In this case, some crystals appear along the horizontal median line. The two diagonally arranged black dots (in the upper left and lower right quadrants) were checked by interference microscope to be small funnel-like hollows.

4. Discussion

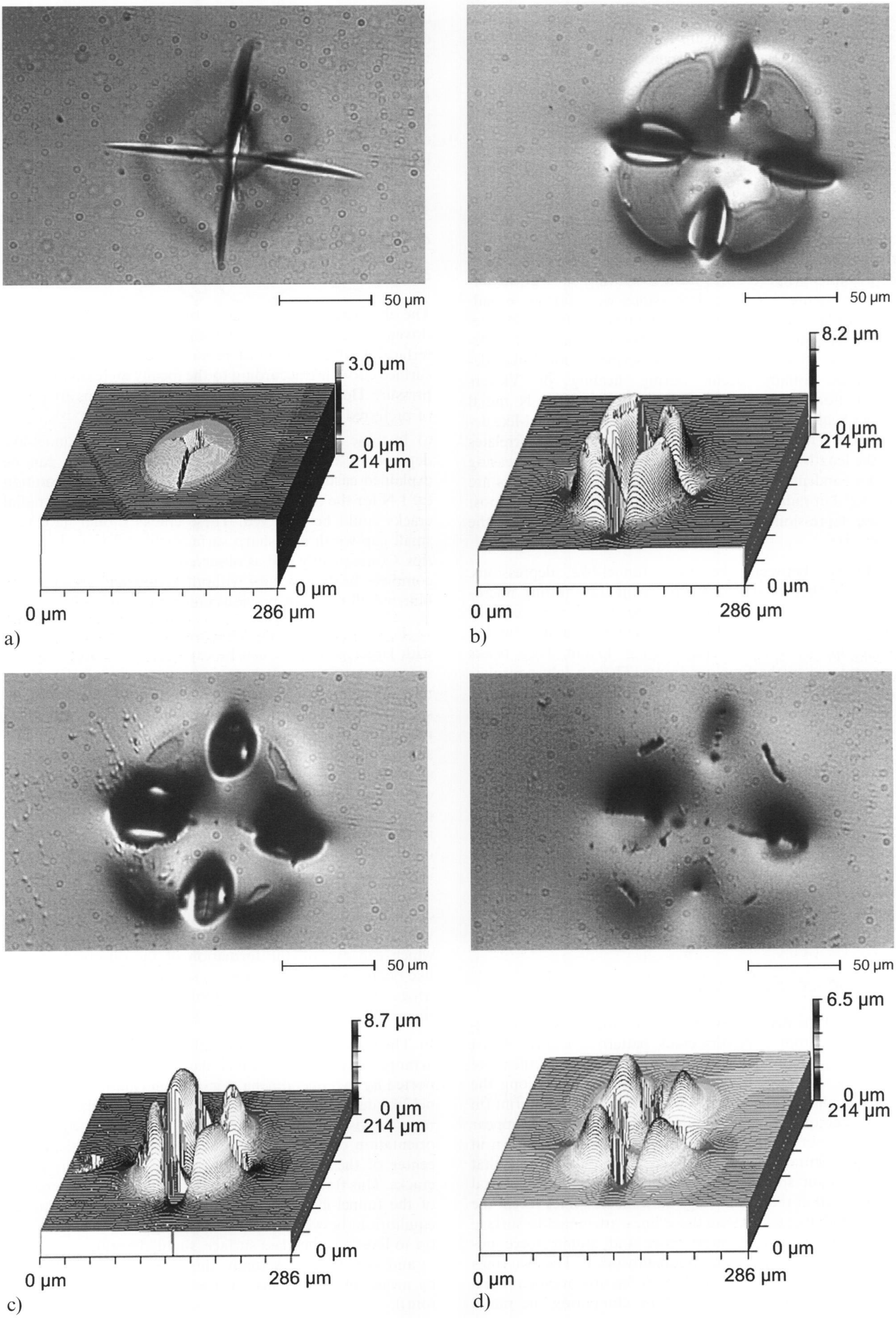
4.1 Healing

The observed gradual evolution of crack healing is probably driven by local viscous flow minimizing the glass/air interface. That flow is most pronounced at points of sharp surface curvature according to the locally increased Laplace pressure. Hence, both the crack edges and the tips are points of preferred healing activity by viscous flow.

a) In these terms, the occurrence and shape of funnel-like depressions during the healing of radial cracks can be explained easily. For small load of the Vickers indentation (≤ 1 N for the diopside glass under study) only small radial cracks could be observed. These cracks should have very small gap width and sharp surface curvatures at the crack tips. Consequently and as observed experimentally, fast and complete healing occurs without significant viscous flow blurring all traces of previous crack patterns.

For large loads of the Vickers indentation (> 1 N) cracks with larger gap width can be expected. Assuming that the inner part of the radial crack (near to the plastic deformation zone) are pressed together due to the elastic response of the glass on unloading or due to later structural relaxation, the largest crack width will remain in the middle section of radial cracks. Thus, crack healing simultaneously starts at all parts of the elliptical periphery crack tip (see e.g. figure 2a), including the part close to the Vickers imprint. This section is shown as the inner end of radial cracks in the two-dimensional micrographs. For sufficiently large crack width, healing of crack tips can lower the (concave) surface curvature considerably. For this case, the (convex) surface curvature at the almost rectangular edges (were crack flanks cross the glass surface) can reach comparable values. This latter effect should spread off the crack width, which can explain the formation of the observed funnel-like depressions. This process is similar to the shrinkage of irregularly shaped cavities to residual spherical pores during the sintering of powder compacts.

b) The typical occurrence of slight elevations symmetrically arranged between the funnel-like depressions can be supported by two phenomena. First, the formation of the funnel-like depression, driven by minimizing the glass surface, requires viscous flow of material perpendicularly to the orientation of the radial crack. Thus, glass flows into the center of the four quadrants split up by the four radial cracks. This flow continuously goes on during the formation of the funnel-like depression. As a result of the dynamic equilibrium between that process and the viscous flow that try to level out the glass surface, slight elevations can occur – and later vanish. Actually, this effect could be observed by means of interference microscopy (figure 3b to e (bottom)).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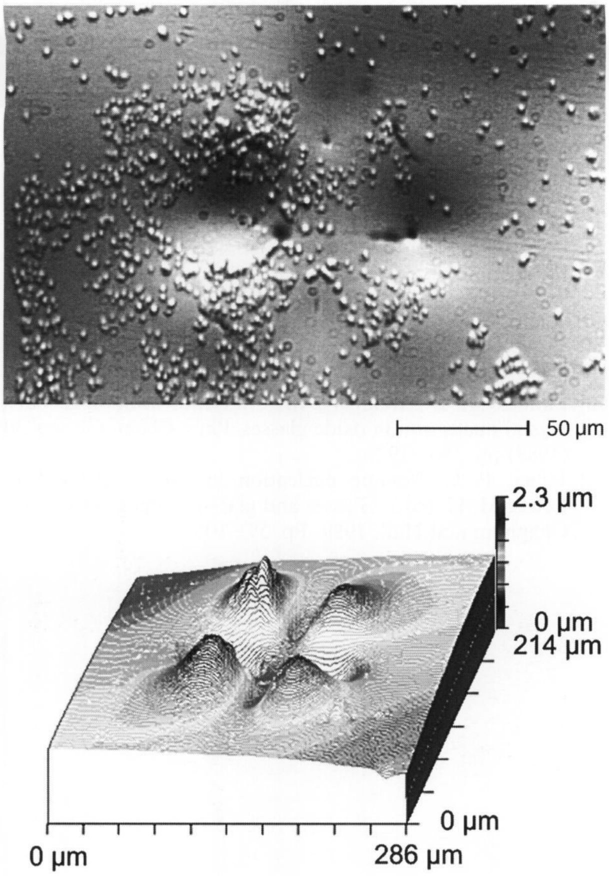

e)

Figures 3a to e. Transmitting light micrographs, top view (top) and surface profiles measured by interference microscopy (bottom) of a) as received crack pattern caused by Vickers indentation with 5 N in polished diopside glass, b) crack pattern out of figure 3a shown after 20 min of annealing at 820 °C, c) crack pattern out of figure 3a shown after 40 min of annealing at 820 °C, d) crack pattern out of figure 3a shown after 40 min of annealing at 820 °C, e) crack pattern out of figure 3a shown after 40 min of annealing at 820 °C.

Second, the slight elevations may be related to the well-pronounced shallow lateral cracks (see figure 2c), which can cause almost isolated pieces of glass. During later healing, these pieces of glass tend to round their sharp surface. Again, the related viscous flow is directed to the centers of the four quadrants split by the radial cracks, which also can explain the observed slight surface elevations.

4.2 Surface crystallization

The arrangement of crystals is closely correlated to the shape of crack pattern caused by Vickers indentation. This finding confirms previous studies showing that locally damaged glass surface catalyzes devitrification and that surface crystals preferentially nucleate from sharp convex surface edges, corners or tips (see e. g. [5, 6 and 9]). Thus, in our case, the majority of surface crystals arise from the former edges of the Vickers indentation imprint and the induced radial cracks. The observed double chain of crystals along the trace of healed radial cracks can be attributed to the former two opposite crack edges. In some cases, crystals

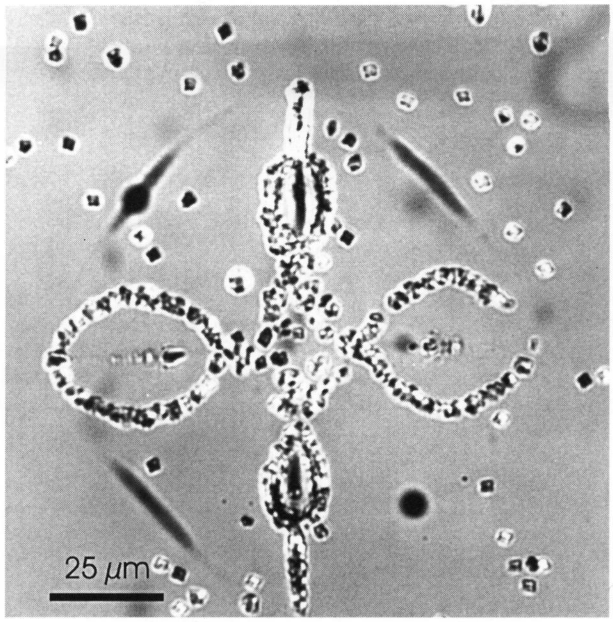

Figure 4. Transmitting light micrograph (top view) of diopside surface crystals caused by previous Vickers indentation with 5 N and subsequent annealing at 810 °C for 330 min.

could be found along the cross-line of flat lateral cracks and the glass surface.

As illustrated in figures 3a to e, all cracks completely heal (rounding all points of sharp surface curvature) before surface crystals can grow up to detectable size. Thus, the existence of crystal chains along previous radial cracks indicates that crystal nucleation proceeds early — before crack healing could cause significant rounding of crack edges. This is possible because the maximum temperature of nucleation, T_{max}, does not significantly exceed the glass transition temperature, T_g (see e.g. [10]). Although undetectable, supercritical crystal nuclei (usually of some nm in size, see e.g. [11]) can survive and grow to detectable size notwithstanding any viscous flow of the parent glass phase during the crack healing.

Thus, the comparison of the probable position of nucleation and the later position of detectable crystals can reveal spatial patterns of viscous flow during crack healing. In that sense, the surface crystal arrangement shown in figure 4 can additionally support the explanation for the formation of funnel-like depressions given in section 4.1. Along the vertically oriented traces of former radial cracks, diopside crystals are partially arranged as double chains. These chains spread off to oval rings in the inner part of the former radial cracks. The darkly shadowed areas in their center indicate the deepest parts of the funnel-like depression.

5. Conclusion

Surface crystal patterns are initiated by surface changes induced by Vickers micro-indentation. Development of surface crystal patterns is probably supported by gradual surface-viscous-flow changes during thermal treatment caused by the endeavor of the sample to minimize its surface. Observation of these surface crystal patterns and their development could help to find the mechanism of surface nucleation of glasses.

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6. References

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