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Effect of oxygen on structural properties of quenched Ge-Te melts

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By the deliberate addition of oxygen (up to 1.0 at. % in the form of GeO_2), its effect on the structure and properties of quenched Ge–Te glasses was studied. The glass-forming region of the water-quenched melts is narrowed by the addition of oxygen impurity. Replica electron micrographs of the glasses show apparent coarsening of the microstructure by such an oxygen addition, whereas the crystallization behaviour of the splat-cooled melts studied by DTA did not change significantly with this oxygen addition. Morphological features of GeTe crystallites in the glass + crystal portion observed in the oxygen-containing melts are described. However, in cases when either the melts were splat-cooled in an oxidizing atmosphere, or the DTA runs were made in air, a two-stage crystallization reaction was observed on DTA thermograms. Reactivity of the melts with SiO_2 glass vials is enhanced by the existence of the impurity oxygen.

1. Introduction

In the preparation of chalcogenide glasses it seems to be an almost permanently established procedure that the weighed mixtures are melted in sealed silica vials under vacuum to avoid the oxidation of the contained materials. Oxygen, however, remains the most important impurity in these glasses.

Although in the usual preparation procedures the SiO_2 vial itself may not react significantly with the glass batches, there is still some possibility of oxidation through procedures such as the following.

1. Water *on* SiO_2 glass. An instantaneous condensation of water vapour on the inside wall of the SiO_2 vial, when it is sealed *in vacuo*, say, 10^{-3} torr, is commonly observed by workers. (In a preliminary test of the present work, even after a thorough pretreatment of the SiO_2 vial by such procedures as soaking in 10% HF for 1 h, drying at 150°C for a week, baking by H_2 gas flame, and then cooling *in vacuo*, it was still observed.) This is because of the strong hygroscopic nature of the SiO_2 glass surface. Water of this kind may be minimized if the whole sample side portion of the vial is kept at least above 100°C when sealed off.
2. Water *in* SiO_2 glass. It has been reported that the water content of vitreous silica can be up to roughly 0.1 wt % (–OH) [1, 2]. Of this water in SiO_2 glass, the "% removable –OH" by vacuum degassing was shown to be highly temperature dependent [3] and most could not be removed until the temperature reached 980°C.
3. Spontaneous oxidation of materials. Some component elements of chalcogenide glasses, such as arsenic, are known to be oxidized in air at room temperature.

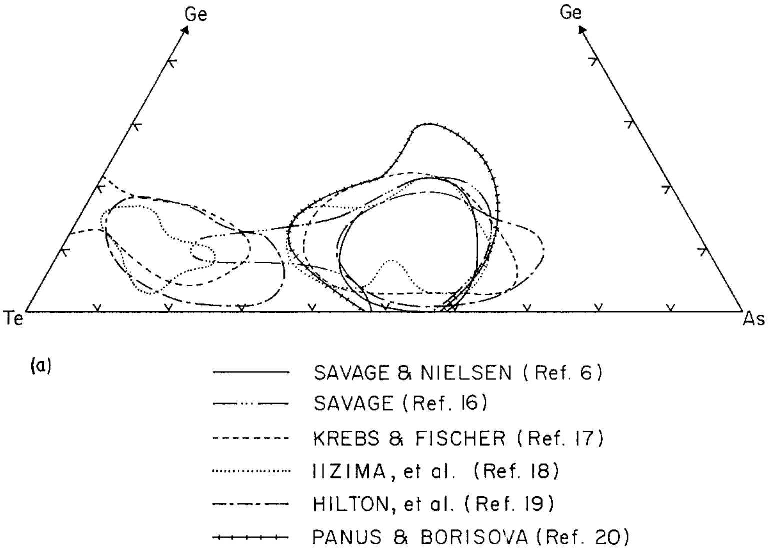
The effect of oxygen on the chalcogenide glasses in connection with the application to the infra-red transmission windows has been reported by several workers [4-10]. In contrast, numerous workers in the field of switching device glasses seem to have rarely taken precautions about its effect [11] in spite of the fact that in some cases the effect of oxygen impurity on the electrical conductivity of non-crystalline semiconductors has been emphasized [12].

As part of the series of structural studies on memory switching glasses at this laboratory [13], the present study was conducted on Ge–Te glasses with deliberate addition of oxygen impurities to study the latter's effect on their microstructure.

2. Literature

Savage and Nielsen [4-7] studied the effect of impurity oxygen on the infra-red transmission extensively. They attempted distillation of the glasses in hydrogen, as well as the usual outgassing of the vials and samples, to eliminate the oxygen impurity [5, 7]. Muir and Cashman [8] pretreated their Vycor vials in the study of a GeSeTe glass by applying a coating of pyrolytic carbon and baking. They also heat-treated the glass at 600° C in a stream of hydrogen and were able to purify it considerably. Hilton *et al* [9, 10] described the removal of the oxide impurity in glasses by either heating the molten glass under reduced pressure or by adding traces of gettering elements such as carbon or aluminium. Instead of those *post-melt* treatments mentioned above, Plumat [14] melted sulphide and selenide glasses in an atmosphere of $N_2 + 5\% H_2$ to avoid oxidation.

Deliberate addition of oxygen impurity to chalcogenide glasses has been attempted by Savage and Nielsen [4-6], who added up to 1.0 mol % oxide (in the form of As_2O_3, TeO_2 or GeO_2), and studied its effect on the infra-red transmission and glass formation. They observed that traces of oxide impurity assist glass formation in the selenide system [5], whereas a crystallizing tendency was enhanced in telluride glasses by the addition of oxide [6]. This result may suggest that the extreme scatter of "glass-forming regions" reported in the literature [15] for some chalcogenides may not only be due to the difference of the quenching rate depending on the workers but it could be due, in some cases, if not all, to the difference of the oxygen impurities in the different studies. Fig. 1a shows a collection of the glass-forming regions for the system Ge–Te–As as an example, and Fig. 1b indicates the possibility that every region shown in Fig. 1a could be a different section of the quaternary system Ge–Te–As–O (data from Refs. 16-20).



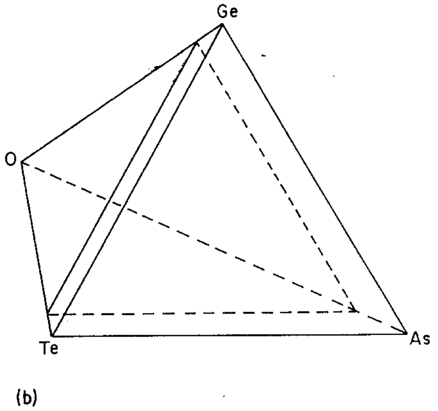


Figure 1 Large scatter of glass-forming regions data of air quenched melts in the system Ge–Te–As. (a) Collected data from the literature, and (b) a probable explanation for the scatter (see text). Different workers present data on planes with varying O_2 percentage.

Kolomiets and Shilo [21, 22] have conducted some exploratory work on the addition of larger amounts of oxygen into chacogenide glasses.

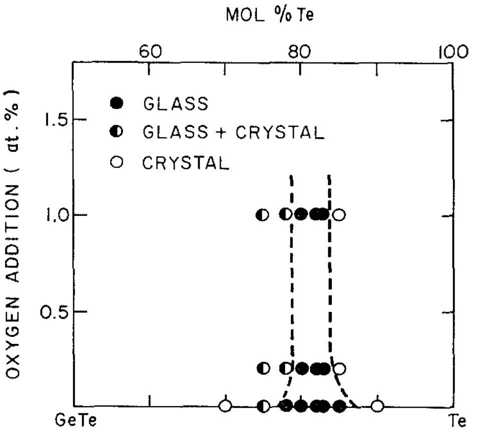


Figure 2 Glass-forming region of the water-quenched Ge–Te melts with respect to small oxygen addition.

3. Experimental

The SiO_2 vials were pretreated by soaking at 980°C for 5 to 6 h in a gas mixture (99.8% N_2 + 0.2% H_2) and cooled in the same gas flow. Weighed mixtures of metallic germanium and tellurium, both with the nominal purity of better than 99.9%, were sealed into the pretreated SiO_2 vials under 10^{-4} torr, heated at 800°C for 1.5 h, with frequent rocking, and quenched into cold water. The sample size was similar to that in the previous work [13]. To study the effect of oxygen impurity, a little GeO_2 was added to the batch mixture in such an amount that the calculated amount of oxygen in the melt would be either 0.2 or 1.0 at.% of the total amount of the oxygen-free batch.

Glass formation was determined by visual inspection, X-ray diffraction, and scanning electron microscopy. The microstructure of the glasses obtained was studied by replica electron microscopy. The two-stage replica (acetate and Pt shadowed carbon) of fractured surfaces etched with an acid mixture ($HF + HNO_3 + 4H_2O$) for 1.5 min was examined in a Zeiss EM 9S electron microscope. Some part of the water-quenched melts, whether glassy or crystalline, were then further splat-cooled [13] and subjected to DTA to find any change of crystallization behaviour after the oxygen addition.

4. Results and discussions

4.1. Glass-forming region

As has been described previously [13], when Ge–Te compositions melted in SiO_2 vials are subjected to water quenching, two or three different layers are generally formed because of the considerable gradient in quenching rate from the outer to the inner portion of the melt, e.g., inner portion: GeTe crystal + Te crystal; middle portion: glass + GeTe crystal; outermost portion: glassy. The glass formation region in Fig. 2 is determined by optical microscopic observations and X-ray diffraction. It can be seen that additions of oxygen impurity as small as 0.2 at.% apparently narrow the glass-forming region as shown in this figure, which is consistent with the observations on other telluride glasses by Savage and Nielsen [6].

4.2. Microstructure

Fig. 3a shows the electron microscopic features of fractured and etched surfaces of the $Ge_{20}Te_{80}$

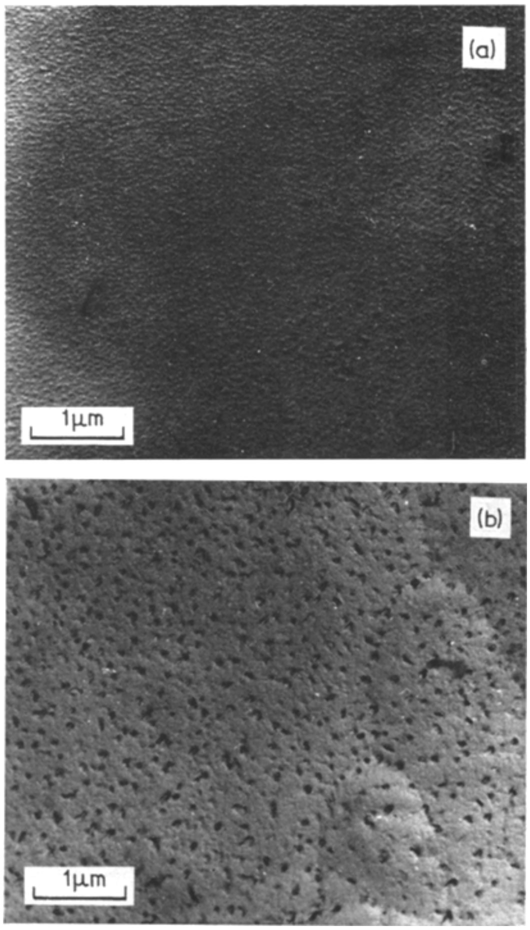


Figure 3 Replica electron micrographs of the fractured and etched (by acid mixture for 1.5 min) surfaces of of (a) the $Ge_{20}Te_{80}$ glass, and (b) the $Ge_{20}Te_{80}O_{1.0}$ glass.

glass. Fig. 3b shows a similar micrograph of the $Ge_{20}Te_{80}O_{1\cdot0}$ composition, indicating that 1.0 at. % addition of oxygen definitely coarsens the microstructure of the inhomogeneity, indeed a clear phase separation seems to result as a function of oxygen content. Fig. 4a shows the micrograph of $G_{18}Te_{82}$ glass. The anisotropic feature in the figure is believed to be due to the thermal stress in the glass, because the glassy outer layer obtained in the quenched melt was particularly thick in this case compared to the other cases. Fig. 4b is the micrograph of the $Ge_{18}Te_{82}O_{1\cdot0}$ glass, showing again the coarsening of the "unmixed" microstructure by 1.0 at. % addition of oxygen.

Although no dramatic change in microstructure of the glassy portions of the melts was observed by changing the composition from 20 to 18 at. % Ge as shown in Figs. 3 and 4, the features of the glass + crystal portions (next to the glassy outermost layer), which represent the nature of the crystal precipitation during quenching, revealed some differences. Fig. 5 shows a scanning electron micrograph of the array of GeTe crystals embedded in the glassy matrix observed in the water-quenched melt of $Ge_{20}Te_{80}O_{1\cdot0}$ composition. Such an intermediate layer consisting of glassy and crystalline phases as shown in this figure was not obtained in the melt of $Ge_{20}Te_{80}$ with no oxygen addition. As is apparent in the figure, the array is typical of dendrites, interconnected with each other. This dendritic feature was not observed in the case of the $Ge_{18}Te_{82}O_{1\cdot0}$ composition as shown in Fig. 6, in which the replica electron micrographs of the crystallites appearing in the intermediate layers of the $Ge_{20}Te_{80}O_{1\cdot0}$ melt (Fig. 6a) and the $Ge_{18}Te_{82}O_{1\cdot0}$ melt (Fig. 6b) are compared at the same magnification. The tiny crystals in the latter are not interconnected with each other apparently, indicating that every crystallite precipitated out of the melt independently.

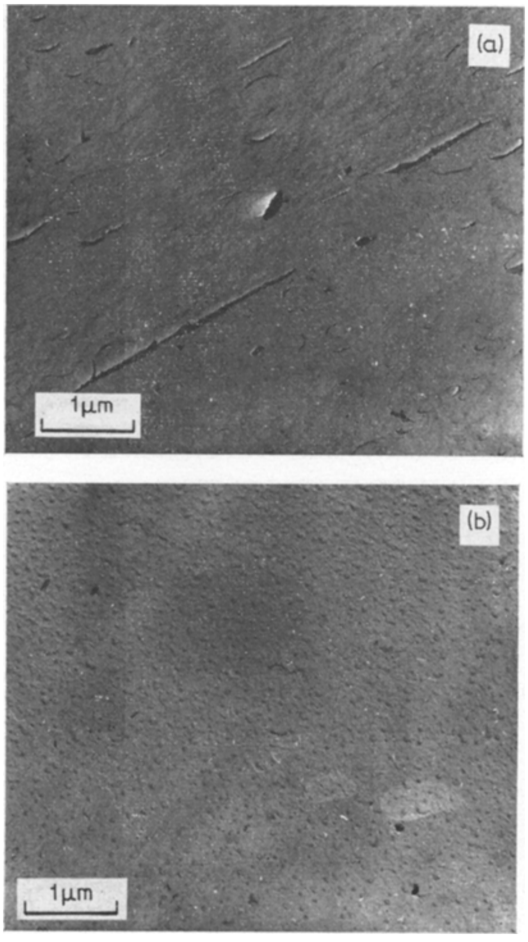


Figure 4 Replica electron micrographs of the fractured and etched (by acid mixture for 1.5 min) surface of (a) the $Ge_{18}Te_{82}$ glass, and (b) the $Ge_{18}Te_{82}O_{1\cdot0}$ glass.

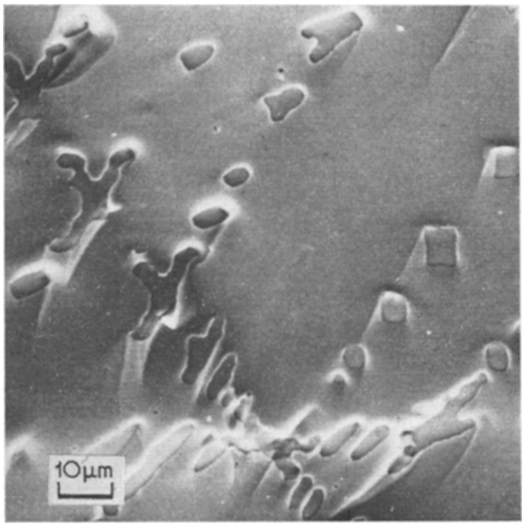


Figure 5 Scanning electron micrograph of GeTe dendrites embedded in $Ge_{20}Te_{80}O_{1\cdot0}$ glass. Etched by acid mixture for 1.5 min.

Some supplemental observations on the dendritic crystallites of GeTe are worth mentioning. As can be seen in Fig. 6a, small steps on the surface of the dendrites were observed in most electron micrographs. Since the acid mixture mentioned above dissolved the crystalline portions preferentially, the fractured surface of the melt similar to that in Fig. 6a was subjected to

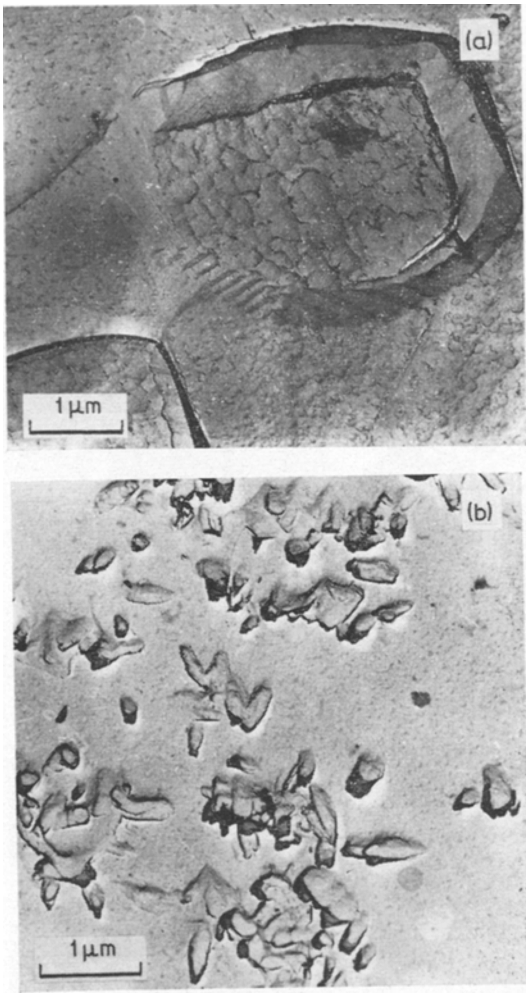


Figure 6 Replica electron micrographs of GeTe crystals in glass and crystal portion of (a) $Ge_{20}Te_{80}O_{1\cdot0}$ melt, and (b) $Ge_{18}Te_{82}O_{1\cdot0}$ melt. Etched by acid mixture for 1.5 min.

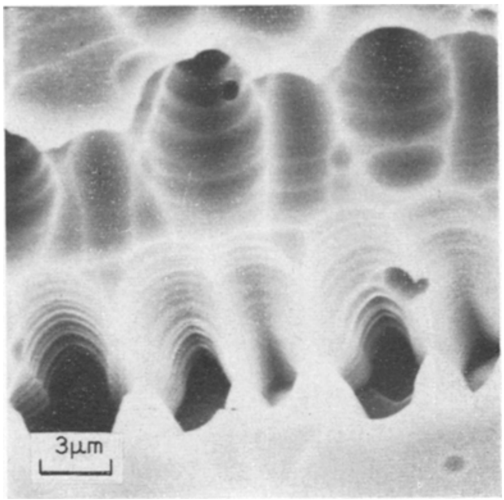


Figure 7 Scanning electron micrograph of deeply etched surface of fractured glass + crystal portion of $Ge_{20}Te_{80}O_{1\cdot0}$ melt. Etched by acid mixture for 15 min.

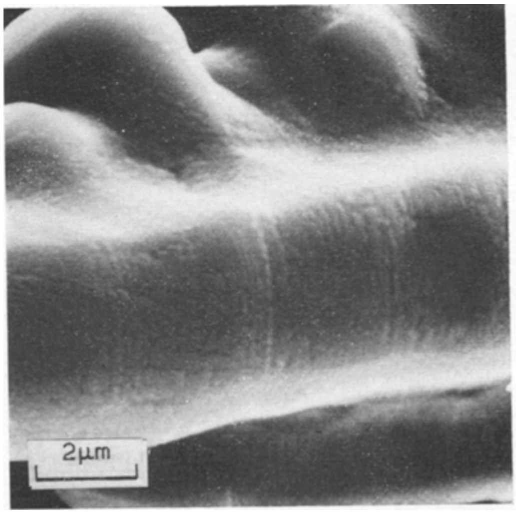


Figure 8 Scanning electron micrograph of a typical GeTe dendrite appearing in crystalline portion of $Ge_{22}Te_{78}O_{0\cdot2}$ melt, revealing steps perpendicular to the axis.

deep etching and then examined by a scanning electron microscope. As shown in Fig. 7, holes on the surface, resulting from etching out the dendritic crystals from the glassy matrix, show that the dendrites had many fine striations, which appear perpendicular to the axes of dendritic crystals and parallel with each other. That these striations are the negative replica of the steps observed in Fig. 6a and that they are not merely an artifact of the etching reagent is supported by the careful observation of GeTe dendrites that appeared in the crystalline innermost portion of $Ge_{22}Te_{78}O_{0\cdot2}$ melt as in Fig. 8. In this figure apparently similar but positive striations perpendicular to the axes can be noticed. Cyclic variations in flux-grown crystals such as striations or growth steps have been attributed to temperature fluctuation, compositional fluctuation, etc. [23]. Whether or not this applies to the steps of the crystals appearing in the water-quenched melt is not clear. The observation that the steps are always perpendicular to the axes of dendrites, however, could be attributed indirectly to some level of submicroscopic nonuniformity [24] of the melt.

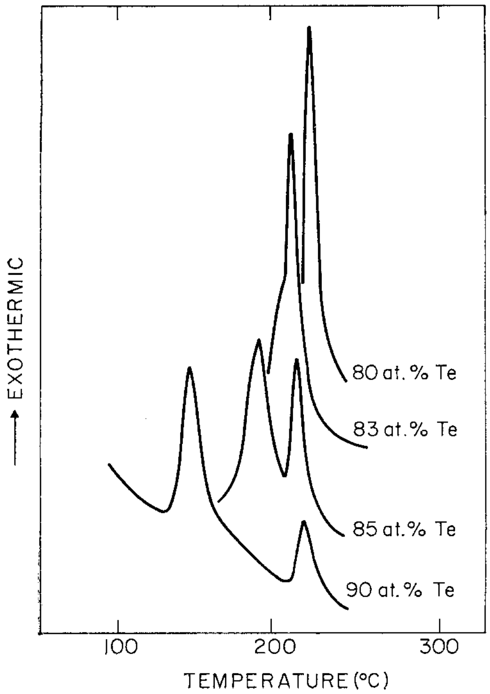
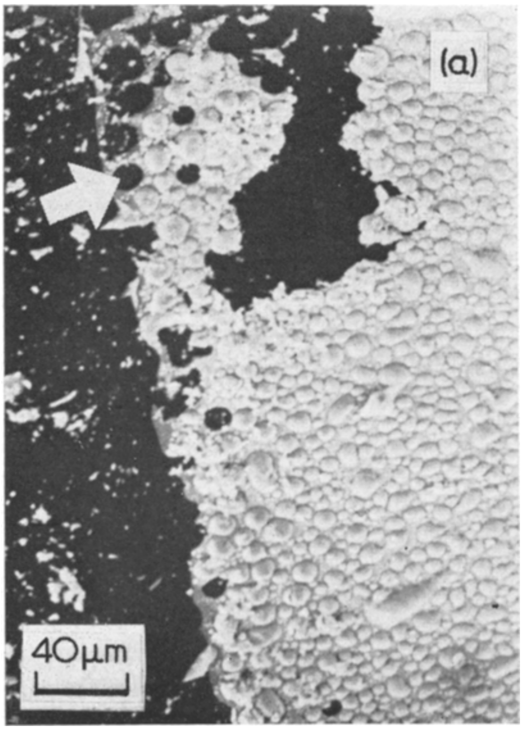


Figure 9 DTA thermograms of crystallization reaction of Ge–Te glasses splat-cooled in oxidizing atmosphere. Heating rate was 10°C min^{-1}. When the glasses are splat-cooled in inert atmospheres, the second peaks at higher temperatures do not appear [13].



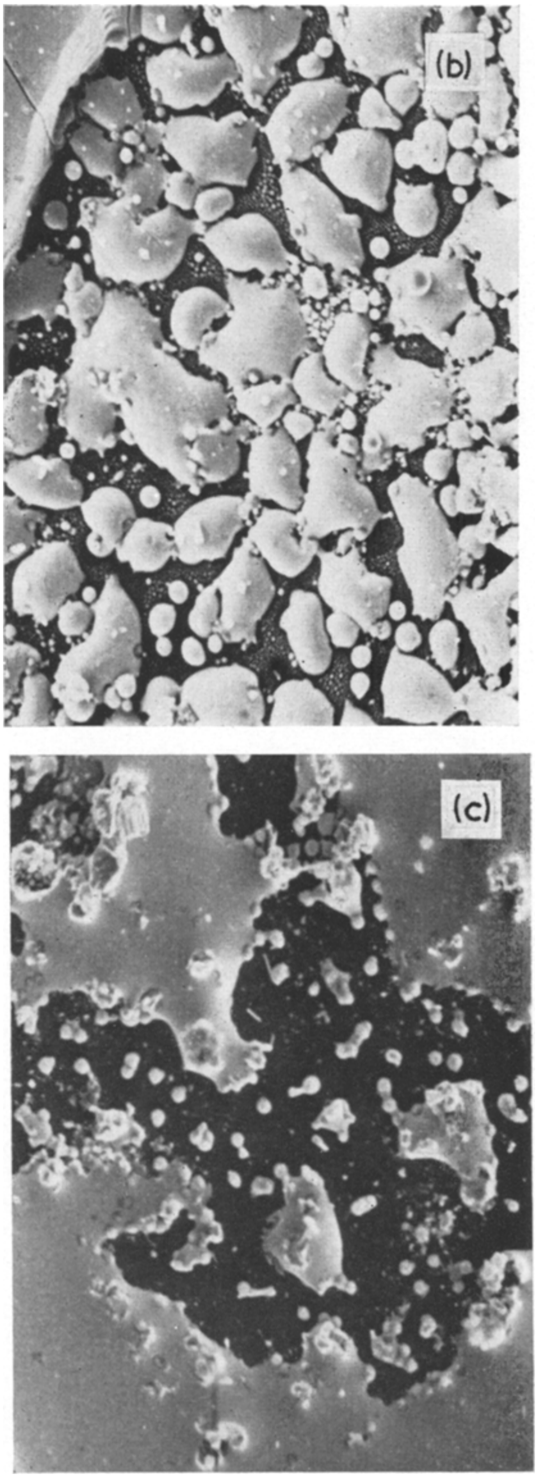


Figure 10 Change of wettability of Ge–Te melts to SiO_2 glass by oxygen addition. (a) $Ge_{20}Te_{80}$, (b) $Ge_{20}Te_{80}O_{0.2}$, and (c) $Ge_{20}Te_{80}O_{1.0}$.

4.3. Crystallization behaviour

When the melt was splat-cooled, it was possible to obtain X-ray amorphous materials of the composition up to 90 at.% Te, whether or not the melt contained the oxygen additive. The splat-cooled glasses were studied by DTA to find any change of crystallization behaviour by these oxygen additions. Both the splat-cooling and DTA were conducted in an inert atmosphere (either N_2 or Ar). In spite of the fact that there was an apparent change in microstructure as described in the previous section, all the DTA thermograms of the glasses with oxygen impurity were similar to those without oxygen addition and the same as those reported already [13]. An additional peak appears on the thermogram, at a slightly higher temperature (see Fig. 9) only when an oxidizing atmosphere ($P_{O_2} < 0.21$ atm) is used either for the DTA run or for splat cooling high Te-content melts. Although the oxygen content in such cases was not determined and the shiny black appearance of the sample was much the same with those prepared in an inert atmosphere, at least the local content of oxygen is likely to be much higher than 1.0 at. %. The relative peak heights on the thermograms varied a little, depending on the oxidizing atmosphere, whereas the peak positions, (i.e., the reaction temperatures) were quite reproducible in all cases examined. After the DTA run, the sample was subjected to X-ray diffraction. No extra peaks (of any oxides) other than GeTe and Te were found on the diffractogram. The role of the oxygen in this case is not clear, but the result suggests the importance of the atmosphere in the melting stage as well as during switching operations.

4.4. Reactivity with SiO_2 glass

The possible reaction of chalcogenide melts with SiO_2 vials is often considered to be a potential source of oxygen impurity. Observations in the course of the present work do not seem to support this idea. Fig. 10 shows scanning electron micrographs of the feature of wetting by a $Ge_{20}Te_{80}$ melt on the wall of SiO_2 glass vials by small additions of oxygen. It is observed that the $Ge_{20}Te_{80}$ without oxygen addition wets the wall very poorly and often droplets fall off easily (arrow in the figure). By the addition of oxygen their wettability to the SiO_2 wall is improved. When the $Ge_{20}Te_{80}O_{1.0}$ composition was melted at 800°C for 45 h, apparent reaction between SiO_2 glass and the melt was observed as shown in Fig. 11. Fig. 11a shows that the $Ge_{20}Te_{80}O_{1.0}$ glass remains sticking to SiO_2 glass wall when the SiO_2 vial is fractured, showing strong bonding between the glass and the SiO_2 vial, which is not observed on the glass with no oxygen addition. Fig. 11b shows the fractured section of the SiO_2 glass wall which is apparently corroded by the melt. The observations in Figs. 10 and 11 indicate that the reactivity of the Ge–Te melt with the SiO_2 vial becomes significant (so that it can be a source of the additional oxygen impurity) only when some oxygen impurity is provided by any other sources beforehand.

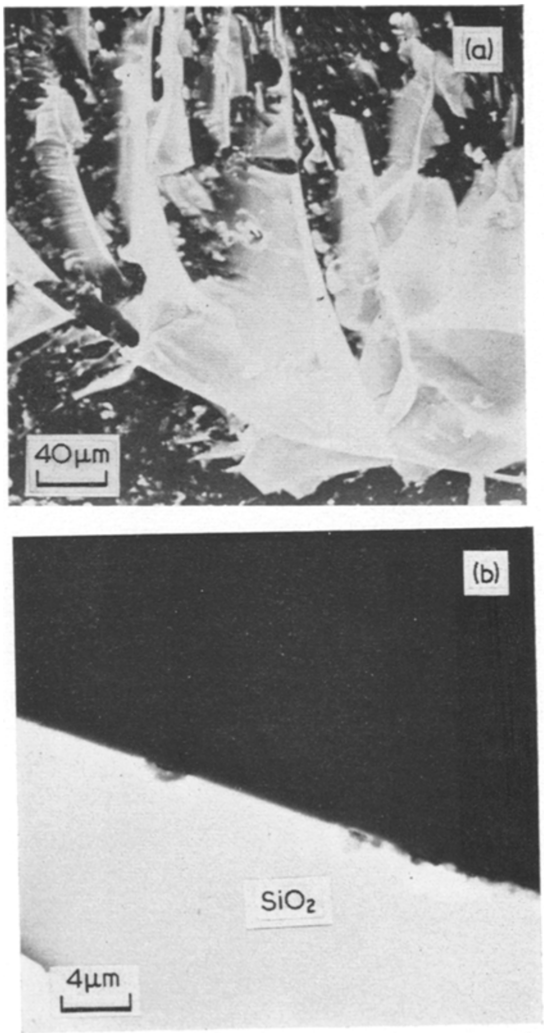


Figure 11 Apparent reaction of $Ge_{20}Te_{80}O_{1.0}$ melt with SiO_2 vial. (a) Strong bonding of the melt (white portion) to the SiO_2 glass wall (black portion) after breaking the vial is due to (b) the corrosive reaction of the melt with SiO_2 glass.

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