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Morphological Changes produced by Amorphous Phase Decomposition in the Na_2O-SiO_2 System

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The Na_2O-SiO_2 system was used as an experimental model for a study of immiscibility which occurs metastably from approximately 0 to 20 mol % soda in this system. The time and temperature of heat treatment of glass samples was varied in order to observe the progressive development of metastable and unstable types of morphologies by electron microscopic techniques. The development of the morphologies is explained on the basis of hypothetical free-energy curves.

1. Introduction

Amorphous phase immiscibility has been of interest to glass technologists for many years. The mechanisms of amorphous phase decomposition were poorly understood because analytical techniques available could not always resolve the phases formed by the decomposition. The decomposed phases can be resolved by electron microscopic techniques which have been applied in the study of immiscibility in oxide and metallic systems. As a result of these experimental studies and consequent theoretical development, principally by Cahn [1], interest in phase immiscibility has been greatly stimulated.

This study examines the dependence of the microstructures resulting from amorphous decomposition on the time and temperature of heat treatment and relates volume fraction changes to hypothetical free-energy curves. The Na_2O-SiO_2 system was chosen for the study because of the availability of information on this system in the literature, and because the phases in the system appeared to be amenable to the experimental techniques.

2. Experimental

A glass containing 87.4 mol % SiO_2 and 12.6 mol % Na_2O was prepared by melting a mixture of sodium-carbonate and AMERSIL® quartz to make the desired theoretical composition. The glass was melted in platinum in a gas-fired furnace at 1510°C for approximately 50 h, poured out on steel plates, and annealed. One slab of glass was selected for the study of morphological changes during heat treatment. The slab, approximately 6 × 18 by $\frac{1}{2}$ in., (15.2 × 45.7 × 1.3 cm) poured from the 10-lb (4.5 kg) melt, was divided into appropriate sample sizes. Three representative samples from the slab were submitted for chemical analysis and electron microscopy to test its chemical and morphological homogeneity. No apparent variations were observed in the chemical composition or the morphology. The relative phase volume differences determined by point-count analysis showed ± 5% variation. Fig. 1 is an electron micrograph showing the morphology of the starting material. Subsequent heat treatments represent rearrangements of this starting material.

Samples approximately $\frac{1}{4} \times \frac{1}{4} \times \frac{1}{2}$ in. (0.6 × 0.6 × 1.3 cm) were cut from the glass and heat treated in tubular electric muffle furnaces accurately maintained to ± 1°C of the desired heat treatment temperature. The samples were rapidly inserted into furnaces maintained at the desired temperature and quenched to room temperature. They were then fractured and etched for 15 sec in a 2% HF solution in water. The etched samples were carefully cleaned ultrasonically in order to remove residual colloidal silica. It was found that atmospheric attack on the glasses, after fracturing or etching, produced crystals on the surface. This contamination was avoided by minimising the time from the fracturing to the preparation of replicas. The fractured and etched surfaces were shadowed

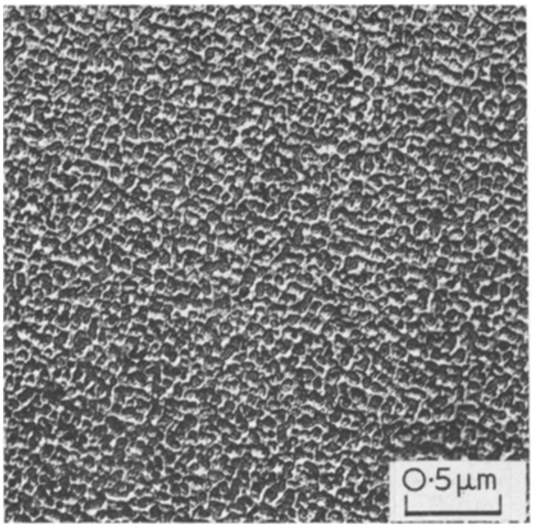


Figure 1 Electron micrograph of annealed glass illustrating morphology of starting material.

with platinum evaporated at an inclined angle of approximately 20° and reinforced with evaporated carbon. The etching and replication technique produced sufficient contrast to distinguish the phases adequately in all samples for the decomposition study.

3. Results

The glass composition used in this study was selected from the data given by Tomozawa, Herman, and MacCrone [2] and Charles [3] This composition decomposes metastably at temperatures from 750 to 820°C and unstably below 750°C. Charles [4] has calculated free energy values as a function of composition in the region of unmixing temperatures. The results of this study will be discussed in relation to the above work.

3.1. Metastable Region

The morphology developed in the metastable immiscibility region is characterised by discrete spherical particles of a silica-rich composition distributed randomly throughout a continuous matrix. The matrix phase is homogeneous at the heat treatment temperature and further phase separation occurs in the matrix phase during quenching.

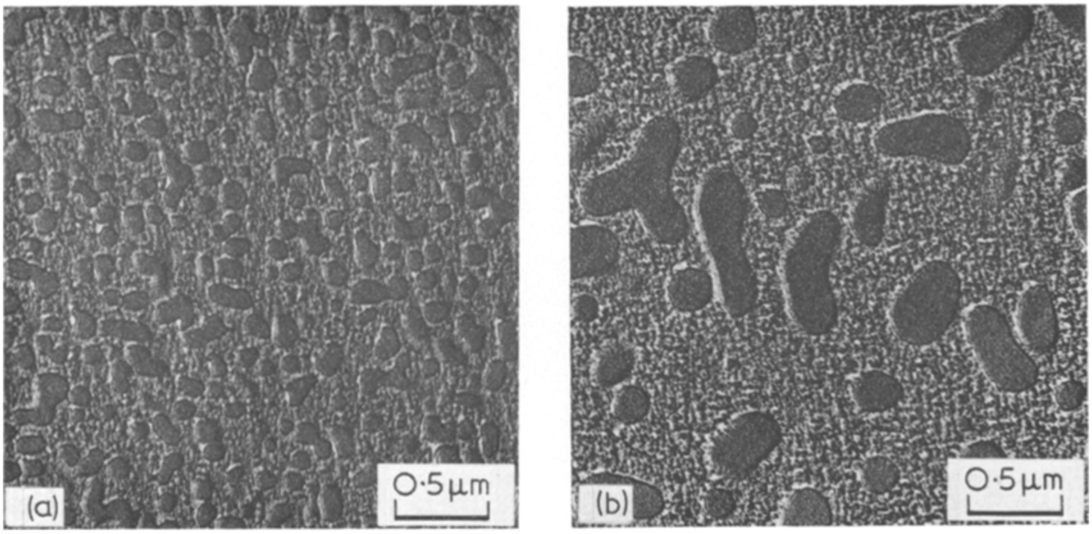
Figs. 2a, b and c are electron micrographs of samples heat treated for $\frac{1}{4}$ to 8 h at 770°C, which is in the metastable decomposition zone. Microstructure analysis by point-count techniques indicated a rapid change from the volume fraction of the starting material to a volume fraction which remained constant in time throughout the series as shown in fig. 3. The free energy of mixing is minimised after the volume fraction becomes constant and the rest of the morphological changes are caused by reduction of surface energy. The decomposition process in the metastable region has been described as classical nucleation and growth which is characterised by an increase in number and size of particles with time. It may be readily seen from the rapid decrease in the number of particles of the second phase, that this is not the case with the rearrangement of the starting material which had decomposed during the initial quench and annealing. This decrease in number and increase in size is analogous to the Ostwald ripening observed in metallic systems discussed by Oriani [5]. The ripening continued until the process was stopped by crystallisation. The number of particles per unit volume determined from the micrographs indicates inverse proportionality to time ($N \propto t^{-1}$) and was found to be insensitive to temperature of heat treatment.

3.2. Unstable Region

The morphological development in the unstable region is similar initially to that observed in the metastable region. As the process continues, however, discrete particles do not form, but the grains of each phase rearrange to give a vermiform phase distribution characterised by continuity of both phases. A typical morphological development sequence of the unstable region is shown in figs. 4a, b and c which are electron micrographs of samples heat treated at 600°C. Relative phase volumes, determined by point-count analysis, show a decrease in the volume of the high-silica phase to a minimum and then a gradual increase to a constant volume fraction. Observed values for the 600°C isotherm are shown in fig. 3. A trend of this type was observed in several other isothermal series in the unstable area. The rate at which the minimum is reached is quite temperature sensitive and yields an approximate apparent activation energy of 35 kcal/mol.

4. Discussion

The process of amorphous decomposition by either metastable or unstable mechanisms is driven by the minimisation of the Gibbs Free



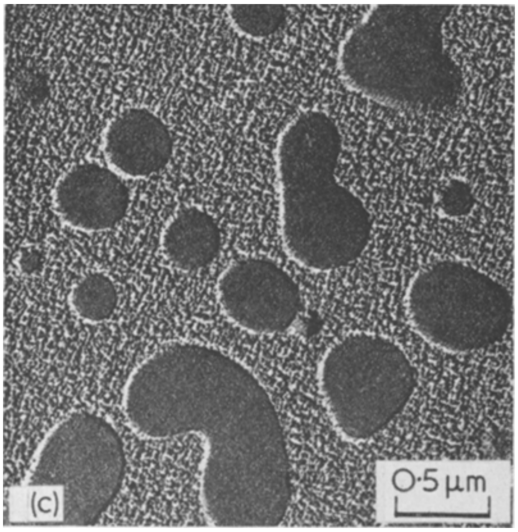


Figure 2 Electron micrographs demonstrating morphological changes in the metastable region: (a) 770° C, ¼ h, (b) 770° C, 2 h, (c) 770° C, 8 h.

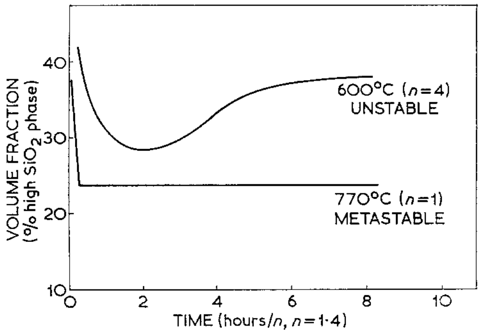
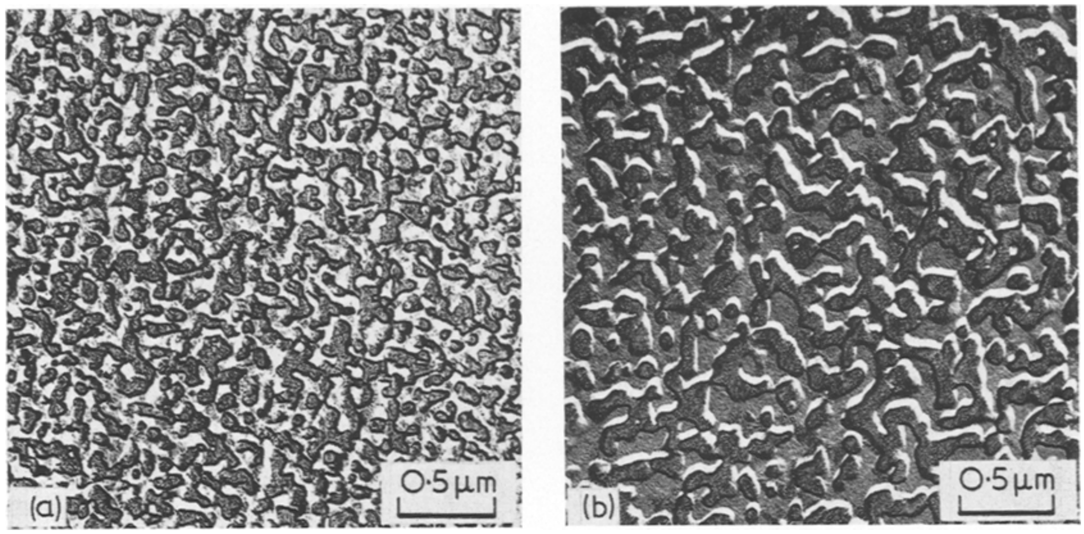


Figure 3 Phase volume change as a function of heat treatment time.

Energy of Mixing. Any small compositional fluctuations which locally increase the free energy are unstable and will decay spontaneously. Local compositional fluctuations which decrease the free energy are stable and will grow. An inspection of the free energy of mixing curves indicates whether local fluctuations in composition raise or lower the total free energy. When the free energy curve is concave upwards (as in continuous solutions or outside the spinodes), local fluctuations increase the free energy; when it is concave downwards (inside the spinodes), local fluctuations decrease the free energy. In either case, the normal diffusion process prevails and is characterised by migration of atoms from areas of high concentration to areas of low concentration.

Fig. 5 is a plot of hypothetical free energy of mixing versus composition for two temperatures. The points of inflection were determined from the data published by Tomozawa [2] and Charles [3]. The following discussion depends on the points of inflection and not the magnitude of the free energy of mixing.

As shown in fig. 5, 770° C isotherm, a homogeneous glass of the composition studied will decompose by nucleation and growth of particles of a high-silica phase with a free energy E_2. Compositional fluctuations about the initial composition are unstable and will decay because



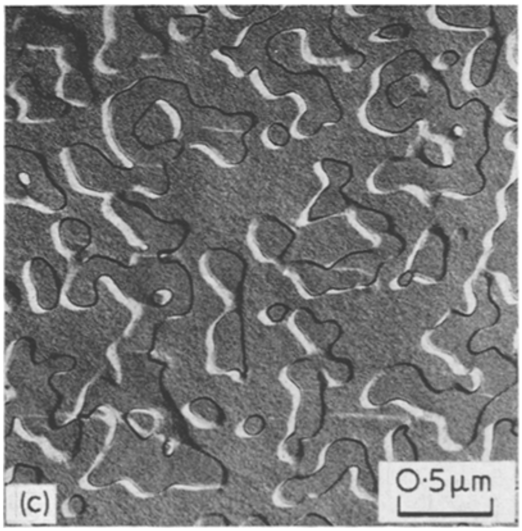


Figure 4 Electron micrographs demonstrating morphological changes in the unstable region: (a) 600° C, 2 h, (b) 600° C, 8 h, (c) 600° C, 32 h.

the free energy curve is concave upwards. The formation of the high-silica phase causes a gradual change in the composition of the matrix from the original to the most stable high-soda phase for this isotherm which is that with the free energy of E_1. Application of the lever rule on the tie line from E_1 to E_2 will indicate the relative volume fractions. The change in the volume fractions of this type would show a continual increase in the volume fraction of the high-silica phase.

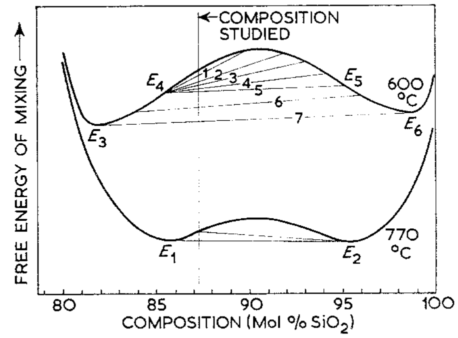


Figure 5 Free energy of mixing versus composition.

The material used in this study was decomposed prior to heat treatment to mixtures of phases which were produced by decomposition during quenching and annealing. These mixtures may be represented by a range of compositions and associated free energies. Theoretically, isothermal heat treatment of this material yields the same phases and the same final volume fractions as the decomposition of a homogeneous system of the same total composition. The rearrangement process does not require nucleation because phase separation occurred during the initial decomposition. The volume fraction of the high-silica phase may decrease, as observed experimentally and shown in fig. 3, if the initial volume fraction of the high-silica phase is higher than the final metastable volume fraction. The predominant morphological change in the metastable region is the coarsening or

Ostwald ripening resulting from a minimisation of surface energy by reduction in surface area.

When heat treated at 600°C the glass decomposes by an unstable or spinodal process which does not require nucleation. Compositional fluctuations which are formed, grow because the free energy of mixing is lowered by the unmixing. (Free energy curve concave downward.) The observed progression of change in the volume fraction of the high-silica phase as shown in fig. 3 may be explained by the tie lines 1 to 5 below the 600°C free energy curve of fig. 5. The free energy of mixing of the phase assemblages represented by each tie line is progressively lowered. The high-soda phase cannot extend beyond the spinode at point E_4 because further decomposition would produce a local increase in free energy which would be spontaneously homogenised. When the composition of the high-silica phase reaches the spinode on the other side of the plot at point E_5, local compositional fluctuations of both end-member phases raise the free energy and are homogenised. The further reduction in total energy is produced by diffusion through preformed phase boundaries rather than by local fluctuations as illustrated by tie lines 6 and 7. The bulk diffusional adjustment of the phase assemblages is completed when the minimum energies are reached at points E_3 and E_6 which are the end-member compositions of the miscibility gap and represent the lowest total free energy at this temperature.

Experimentally observed volume fraction changes are compared with those computed, applying the lever rule, from the hypothetical free energy of mixing curves in table I. The data agree with the accuracy to be expected by the calculations and point-count techniques ($\sim \pm 5\%$).

TABLE I Comparison of observed and calculated volume fraction changes for isothermal decomposition (600°C).

Observed		Calculated from fig. 9	
(Hours)	Volume fraction (High-silica phase)	Tie line	Volume fraction (High-silica phase)
$\frac{1}{4}$	0.47	1	0.45
$\frac{1}{2}$	0.41	2	0.34
1	0.41	3	0.28
2	0.37	4	0.24
4	0.30	5	0.21
8	0.31	6	0.26
16	0.34	7	0.34
32	0.38		

5. Conclusions

It is possible to produce two characteristic types of morphologies of amorphous phases in this system. These are: 1. discrete particles of one phase dispersed in a continuous matrix phase formed in the metastable region and 2. highly interconnected phases (vermicular) formed in the unstable region. The microstructures continue to coarsen with continued heat treatment until the ripening process is interrupted by crystallisation.

Both processes are driven by the minimisation of the Gibbs Free Energy of Mixing. The mechanism of minimising this energy is different. In the metastable region, the mechanism of classical nucleation and growth produces a continuous volume increase of a dispersed phase of constant composition in a matrix of decreasing volume and changing composition. The mechanism of decomposition in the unstable region, referred to as spinodal decomposition, may produce a reversal in phase volume changes while continuous compositional changes occur in both phases during isothermal heat treatment. The volume fraction of the phase with the greater departure from the original composition decreases to a minimum when both compositions are at the spinodes. Further compositional adjustment is accomplished by diffusion between preformed phase volumes rather than by local fluctuation. The final metastable volume fraction is attained when both phases reach the minimum free energy compositions for the isotherm. Further adjustment of the morphology is accomplished without change in volume fraction by a ripening or coarsening process driven by the minimisation of surface energy.

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