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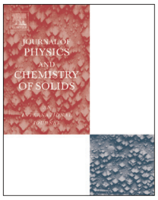

Topology and numerical simulation of phase separation in sodium silicate glasses

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ABSTRACT

Liquid/liquid phase separation in glasses may lead to heterogeneities in the nanometer scale. The droplet phase can be nucleated from a homogeneous liquid. The chemical composition of the nanoscale phase separation changes with temperature in contrast to the nanocrystallization. The understanding of topological changes in the glass networks is of importance for the changes in viscosity and the microscopic changes in the growth rate during the course of the phase separation process. This work considers a glass system in which one of the separated phases is much more rigid than the other and the formed new phase possesses a lower viscosity in comparison to the matrix phase. The chemical composition of the matrix changes only in a thin layer around the growing droplets. A shell with increased rigidity is formed which decelerates the growth by encapsulation.

1. Introduction

Heterogeneities in the nanometer scale embedded in a glassy matrix lead to new and challenging materials [1]. In principle there are two fairly different possibilities for such nanomaterials: liquid–liquid phase separation and nanocrystallization [2]. In the past few years, a number of papers have been published concerning nanomaterials prepared by nucleation of crystalline phases from a glass and subsequent crystal growth [3–6]. By contrast, only few papers are dedicated to the nucleation of a liquid droplet phase from a homogeneous liquid [7,8].

In principle, phase separation might occur above the liquidus temperature from a thermodynamically stable liquid. This yields two thermodynamically stable liquid phases with different chemical compositions. These phase separations occur for example in the systems SiO_2–MgO, SiO_2–CaO or SiO_2–La_2O_3 [9]. This type of phase separation usually leads to fairly coarse microstructures. The two liquid phases have different densities and hence due to the comparably low viscosities even sedimentation might occur. This is for example the case in a certain compositions range in the PbO–B_2O_3 system [10].

If below the liquidus temperature phase separation occurs, it is usually denoted as metastable phase separation. Here, the formed structures are much finer and sedimentation does not occur. Fundamental studies on phase separation are mainly restricted to the thermodynamics. Besides also experimental studies of the kinetics are reported. Hereby, Ostwald ripening and coarsening of a droplet structure plays an important part. In nearly all of these studies, the droplets consist of a phase which has a higher viscosity than the matrix phase. A typical example is the formation of SiO_2 rich droplets from a Na_2O–B_2O_3–SiO_2 glassy liquid [11]. Other examples are binary systems such as R_2O/SiO_2 (R=alkali), RO/SiO_2 (R=alkaline earth) or M_2O_3/SiO_2.

If nucleation of crystalline phases occurs in glass melts, the crystal phase has usually a constant composition which in simple cases does neither depend on time nor on temperature. The situation during binodal phase separation, which is characterized by a droplet nucleation and growth, is quite different. For all glassy liquids reported up to now in the literature, the immiscibility gap is closed at high temperature while it is open at low temperature. The binodal curve in metastable phase diagrams of systems that show phase separation stands for the compositions of the two liquid phases. While just below the critical temperature which is attributed to the maximum of the binodal curve, the compositions are not very different, the difference in the composition between the two liquid phases gets more pronounced while decreasing the temperature, i.e. increasing the undercooling. Hence, by contrast to the nanocrystallization, the chemical composition of the nanoscale phase separation is a function of temperature.

In general, most of the glasses build up continuous networks. Therefore, the rigidity of this network plays a key role in the understanding of the glass properties and is of particular importance for the viscosity. The kinetics of phase transition depends on

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structural changes in the network, hence it is very sensitive to viscosity changes. There is a reason to expect that if a stress field is created or the composition is locally changed, the transformation rate will be affected [2,4]. However, theoretical studies on crystallization of highly viscous melts are often restricted to isochemical systems, where the new phase formed has the same chemical composition as the ambient one [12–14]. On the other hand, systems which provide interesting materials properties are usually multicomponent (see e.g. [15,16]), and hence the composition of the glassy phase, especially near the new complexes, depends on time. This is the case for non isochemical crystallizing compositions as well as for all technically relevant systems which show phase separation.

In the past, a number of papers have been published concerning nucleation of crystalline phases from a glass and subsequent crystal growth. By contrast, only few papers are dedicated to the nucleation of a liquid droplet phase from a homogeneous liquid.

In this paper, an attempt is made which allow the description of the phase separation of glass taking into account not only thermodynamics but also changes of the glass network in terms of viscosity. This approach enables to consider microscopic changes in the properties, especially the growth rate during the course of the phase separation process.

2. The model

In the following, a glass is considered which shows a metastable immiscibility gap. That means the phase separation occurs at a temperature which is below the liquidus temperature. Two liquid phases of different compositions are formed. In the following, a special system is considered in which one of these phases is much more rigid than the other one (i.e. it exhibits much higher viscosity). This is for example the case in the Na_2O–SiO_2 system. Depending on the chemical composition, i.e. the Na_2O/SiO_2 ratio, Na_2O rich droplets, interpenetrating structures or SiO_2 rich droplets are formed [17].

In the case of the formation of SiO_2 rich droplets, the matrix phase has to be enriched in Na_2O, which leads to a decrease in the rigidity of the network and hence to a decrease in the viscosity. This should lead to a rapid growth of the droplets and to subsequent Ostwald ripening which leads to coarse droplets. This case is most frequently observed.

The opposite case from a certain point of view is more interesting and the matter of interest in the present study. Here, droplets enriched in Na_2O are formed. In analogy to previous papers on glass crystallization, it was assumed that phase separation is a similar process and the formation of the nuclei takes place in the floppy regions of the glass network. Then, the droplets start to grow. In the following these droplets are denoted as phase A. The matrix phase (phase B) is enriched in SiO_2. It is now considered that it will take a distinct time until the macroscopic (metastable) equilibrium between the two phases A and B according to the metastable phase diagram is reached. In a macroscopic scale, the chemical composition of the matrix changes steadily until the compositions equal to the metastable equilibrium are obtained. As shown in Fig. 1, at a temperature of T_1, liquid phases with the compositions A_1 and B_1 are formed. The novel point of view takes into account that the enrichment of SiO_2 takes place at first in a microscopic scale near the formed droplets. The chemical composition of the matrix changes only in a thin layer around the droplets. This should lead to a shell which has a higher rigidity and hence an increased viscosity.

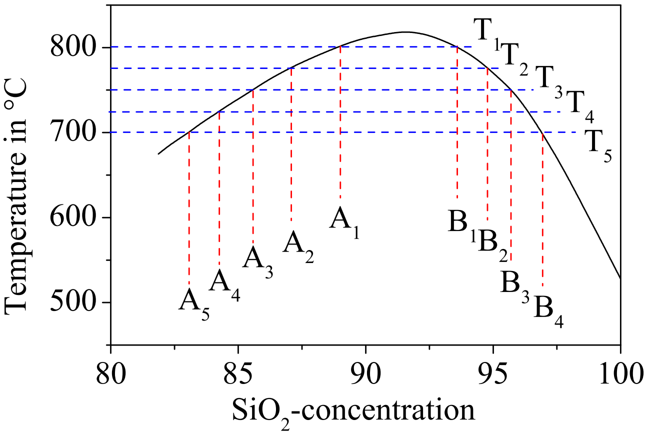

Fig. 1. Binodal metastable phase diagram in the system Na_2O–SiO_2. At the temperature T_1, liquid phases with the compositions A_1 and B_1 are formed.

3. Calculations

In the following, a process is considered in which the homogeneous glassy phase has the binary composition $(Na_2O)_{x_{in}}(SiO_2)_{1-x_{in}}$ (x_{in}=initial value) at temperatures above the critical temperature, i.e. the maximum of the binodal curve. Below this temperature, phase separation may occur. When cooled to a temperature T_1, liquid–liquid phase separation occurs and as shown in Fig. 1, the two phases with the compositions A_1 and B_1 are formed. At this temperature, the droplets contain fraction of x_A Na_2O and the matrix phase contains the fraction of x_B Na_2O. In general, the fraction of x can be regarded as the fraction of those components that modify the glass network, i.e. leading to lower viscosities.

In the chosen example, two phases are formed according to the following reaction:

$$(Na_2O)_x(SiO_2)_{1-x} \rightarrow y(Na_2O)_{x_A}(SiO_2)_{1-x_A} + (1-y)(Na_2O)_{x_B}(SiO_2)_{1-x_B} \tag{1}$$

At the time where the droplet with the Na_2O fraction of x_A is formed, a certain quantity y is shoved away i.e. is "repulsed" from the droplets and is given by

$$y = \frac{x - x_B}{x_A - x_B} \tag{2}$$

A nucleus with the size r is formed immediately and marks the beginning of the process. Then it starts to grow. The chemical composition of the matrix changes steadily until the compositions according to the binodal curve are obtained at infinitely long times. Taking into account the microscopic scale, the situation is somewhat different.

In the following, a half-line domain $0<z<\infty$ is considered. The framework is moving with the growing new droplet, so that at any time, t, the point $z=0$ remains at the interface. This model is illustrated in Fig. 2 for an arbitrary area represented by the square which contains only one liquid droplet after the phase separation. It can be seen that the composition around the droplet x is a function of time and z.

In the following, the dependence of the concentrations, $x(z,t)$, in the ambient melt at the distance z and time t is considered to change according to Fick's law

$$\frac{\partial x}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial x}{\partial z}\right) \tag{3}$$

According to the initial condition at time $t=0$ the concentration is $x=x_{in}$. The boundary condition reflects that at the surface of the droplet there is an additional consummation flux $-(dr/dt)(x-x_A)$.