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Simulation studies on the nature of fractal dimensions of glass-ceramics at percolation threshold

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We simulate the fractal dimensions (*D*) of glass-ceramics resulting from different glass microstructures, at their percolation thresholds. We consider only crystallisation in glasses resulting from phase separation by nucleation. Phase separation may occur at a lower temperature or at the same temperature at which crystallisation takes place. We have studied both cases. The structure-property relationship of such glass-ceramics is dictated by the evolution of the structure of crystalline phase percolation cluster. At the percolation threshold the structure of the percolation path may be quantified by its fractal dimensionality (*D*). The value of *D* displays universal behaviour for a system in the thermodynamic limit. However, it deviates owing to finite size effects. Our simulations suggest that these deviations for a given system size depend on the nature of the glass microstructure. As the value of *D* reaches Euclidean dimension, the system attains more compact percolation cluster. This has invariably occurred in the present investigation for fine crystalline phase microstructure. © *2003 Kluwer Academic Publishers*

1. Introduction

Phase separation in glasses gives rise to two distinct types of glass microstructures. These pertain to (i) droplets of a different glass phase in the matrix of another glass phase and (ii) interconnected network like structures of the two glassy phases. The latter microstructures may result from phase separation by nucleation at higher second phase volume fraction owing to coalescence but normally are attributed to the characteristic features of phase separation by spinodal decomposition [1]. In contrast to the above, droplet microstructures result only due to phase separation by nucleation. The microstructural evolution of glass-ceramics is critically dependent on such glass microstructures since often only one of the phase will have a composition that is able to crystallise easily at given temperature. Besides this, if phase separation and crystallisation occur simultaneously then the kinetics of the former process and the consequent local compositional changes in the system will affect the latter [2]. If both glassy phases are spanning the three-dimensional microstructure of the glass then we can obtain an interpenetrating glass-ceramic composite with percolating crystalline and glassy phase(s) in the system. The bulk transport properties of glass-ceramics are dependent on the presence and structure of the spanning or percolating crystalline phase. The importance of such microstructure is enhanced when the glassy and the crystalline phase have significantly different properties since both phases span the three dimensional microstructure of the system. For instance, the glass might provide strengthening to the material while the crystalline phase the required transport property [3].

Properties of such systems are, therefore, dictated by the structure of the percolation cluster at and above x_c (the fraction of crystalline phase in the glass-ceramic at the percolation threshold). When it first appears the percolation path is extremely rarefied and stringy. This tenuous nature of the percolation cluster is characterised in the literature [4] by the fractal dimensionality (D). 'D' admits fractional value in contrast to the integral value of a Euclidean structure. Fractal objects are characterised by self similarity and fractional dimension D. Such objects possess similar morphology under a range of magnification indicating a hierarchical structure in the system. This is often termed as scale invariance property of a fractal object [5]. This remarkable characteristic of the growing percolating cluster at the percolation threshold may give rise to novel behaviour in the system. In the area of percolation theory [6], at percolation threshold x_c, D is computed using the

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relation

$$M(L) \propto L^{D} \quad (2)$$

where M is the number of sites in the infinite cluster with the system size given by L. For example, the total number of sites in a three dimensional system is given by $L \times L \times L$. The more D differs from the Euclidean dimension (d) the more rarefied is the structure. Hence, this quantity is of prime importance with regard to structure of the percolation cluster. In this paper, we present and discuss the results regarding the D values of glass-ceramics at their percolation thresholds found from our simulation studies of such systems from the perspective of percolation theory [7].

We consider crystallisation in glasses that are undergoing or have undergone phase separation by nucleation. Phase separation of oxide glasses gives rise to two glassy phases with network forming oxide rich (NFR) and the other network forming oxide lean (NFL) compositions. For prior phase-separated glasses we assume that the droplet phase has the NFL composition and crystallisation can only occur in this phase. In this case, if the droplet microstructure is very fine then crystal nucleation density is much higher compared to homogeneous glasses. Crystal growth occurs rapidly and is limited to within the boundaries of the droplets [8, 9]. Droplet regions of phase separation in glasses are known to be of relatively uniform size [10] and consequently uniform sizes of crystallites are obtained.

For simultaneous phase separation and crystallisation we only consider the case in which crystallisation occurs in the matrix. As the former process progresses with time, more and more droplets of NFR phase are formed and the matrix composition tends towards the NFL composition. With change in the matrix composition towards the NFL composition the crystal nucleation rate increases with time and later attains a constant value when the matrix phase reaches its equilibrium NFL composition [2]. As the initial glass composition is shifted away from NFL composition the time required to achieve constant nucleation rate (induction time) is found to increase. Thus, induction time indicates time required by the system to go into the steady state regime of nucleation from the transient one during the process of crystallisation. We now present the salient features of the cases modelled. The details of the models, their crystallisation behaviour and the other aspects of percolation behaviour are given elsewhere [7, 11]. The results of these models are in conformity with the experimental observations [12–14].

2. The model

All systems in these cases are three-dimensional ($3D$) cubic array of $L \times L \times L$ sites. We start with a model system (called system 1 and constructed using the static Monte Carlo technique) with isothermal crystallisation kinetics, which qualitatively resembles that of a homogeneous oxide glass [6]. The salient features of this system relate to homogeneous nucleation and polymorphic crystallisation. The system is comprised of sites and these sites are assigned values between 0 and 1. The spatial distribution of numbers assigned to sites around each site, in the present study, is also near to a Gaussian. We conceive a probability p that is zero initially and then incremented by 0.00001 in each step. During each such step we compare the site values with p and if the former is less than the latter then the site is defined to be crystalline. Crystallisation occurs as p is increased from its initial value of 0. Thus for a given p, every site is supposed to possess a cluster of size $[1-(\text{site value}-p)]r^{*}$, where r^{*} is the critical size of the nucleus. The p value at which a crystalline cluster connecting two opposite ends of system is first observed is defined as the percolation threshold (p_{c}). The probability of a site being crystalline at any p is given by the fraction of crystalline phase (x) formed at the value. The fraction of crystalline phase at p_{c} is x_{c}.

We extend this model to include the simulation of crystallisation of phase-separated glasses. To model such systems we assume that the systems consist of two types of sites: NFL and NFR. We assume that under the given conditions crystallisation can only occur in the NFL phase. For systems with different compositions we assume different relative fractions of NFL and NFR phases. Since crystallisation can occur only in NFL phase therefore, we assume sites belonging to this phase to possess values according to the system 1 distribution. Rest of the sites (belonging to NFR phase) does not crystallise during the isothermal crystallisation (IC) process and therefore are assigned value 1. As mentioned earlier that for any values of p (between 0 to 1), the corresponding r of these sites (belonging to NFR) will be less than r^{*}. Hence possibility of crystallisation on such sites is a priori ruled out.

However, for simultaneous phase separation and crystallisation the nature of a site (whether it is NFL or NFR) is not defined prior to crystallisation. A finite probability exists for a site to belong to either of the compositions [7, 11]. Now according to the glass composition and the droplet microstructure and further whether phase separation and crystallisation occur simultaneously or not we conceive of three cases. For all cases, we assume the droplet size to be constant in a system akin to those observed in actual experiment [10]. The three cases of phase-separated glasses that we deal with are labelled as 2, 3, and 4. To understand the effect of different fractions of droplet phase on IC we select two different compositions with different fractions of NFL phase in each case. The details of the systems we model in each case are given in Table I. As mentioned before the IC behaviour of such systems has been reported elsewhere [11] and is in qualitative agreement with experimental observations [12–14].

Now systems 2a, 2b, 3a, 3b, 4a, and 4b are subjected to IC and the percolation characteristics of the systems studied. In the next two sections we present and discuss the percolation characteristics (viz. the fractal dimensionality, the percolation threshold and the strength of the percolation cluster) at the percolation threshold.

TABLE I Characteristics of various systems modelled in the present investigation

			Nature of glassy phase(s)	
Case	System	Fraction of NFL phase	NFL	NFR
1[h]	1	1	Homogeneous	
2[pps]	2a	0.2	Droplet (a cube of sites)	Matrix
	2b	0.3	-do-	-do-
3[pps]	3a	0.2	Droplet—size of one site	Matrix
	3b	0.3	-do-	-do-
4[spsc]	4a	0.9 (at the end of crystallisation process)	Matrix	Droplet—size same as 2a & 2b
	4b	0.8 (at the end of the crystallisation process)	-do-	-do-

[h] Homogeneous glass.
[pps] prior phase-separated.
[spsc] simultaneous phase separation and crystallisation.

3. Results and discussion

The percolation threshold is found in terms of fraction of crystalline phase (x) in the system. As mentioned before, this (x) is interpreted as the probability of any site in the system being crystalline. The value of the percolation threshold of a system is unique only for an infinite system. Such a characteristic value is termed as universal value of a system in thermodynamic limit. Therefore, for a finite system, we determine D only at an effective percolation threshold $x_c(L)$. This is the most probable value of x for the system at the percolation threshold found from a large number of Monte Carlo (MC) simulations [6, 11]. We used 500 such MC simulations of 3D cubic arrays of size corresponding to $L = 180$ to find $x_c(L)$ for each system. The slope of the plot of log M versus log L gives D for the system considered. The data points required for such plots are the average values of 500 MC simulations for systems of size $L \times L \times L$. The different system sizes used for this purpose are those corresponding to $L = 140$, 150, 160, 170 and 180. The value of D (in column 2) and x_c (in column 3) for each system modelled is given in Table II. For the sake of comparison we have also given the universal value of D of percolation cluster at the threshold for 3d systems.

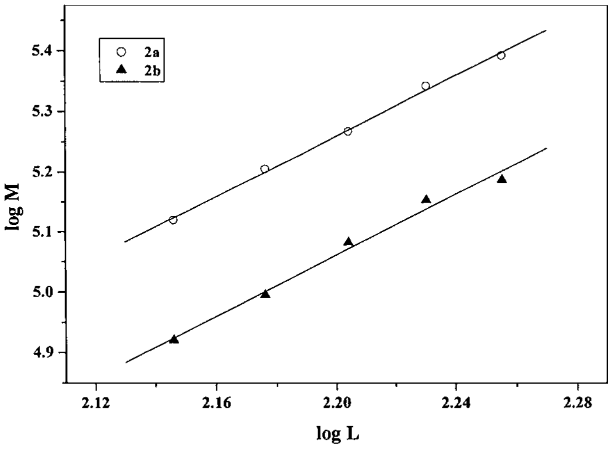

Figure 1 Log M versus log L plots for systems 2a and 2b.

We treat the value of D for system 1 as the standard for the given system size since all other systems are extensions of this model. As expected the D value of system 1 is almost the same as the universal value. Further, from the results given in Table II it is apparent that the fractal dimensions of systems 2a, 2b, and 4a are same or near to the universal value. Fig. 1 shows the log M versus log L plots for systems 2a and 2b and, as expected, the plots are straight-line fits. Fig. 2 shows the log M versus log L plots for systems 3a and 3b. Fig. 3 depicts the log M versus log L plots for systems 4a and 4b. The plots in Fig 3 are straight-line fits.

TABLE II System characteristics at x_c

System	D	$x_c(L)$
Universal value[a]	2.53	–*
1	2.51	0.0969
2a	2.51	0.1429
2b	2.53	0.1055
3a	2.62	0.0952
3b	2.58	0.0941
4a	2.50	0.0965
4b	2.68	0.1049

[a] Reference [5].
*System specific.

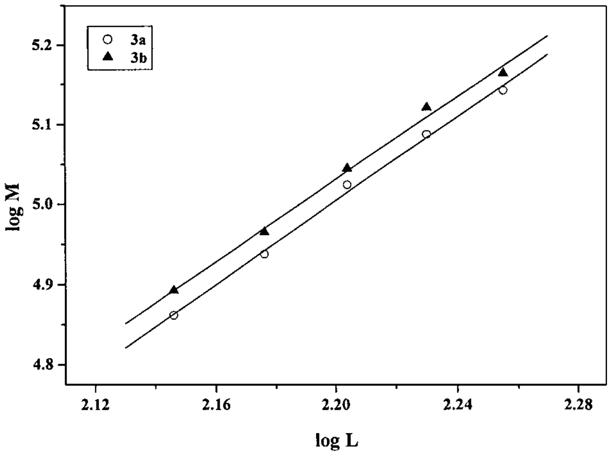

Figure 2 Log M versus log L plots for systems 3a and 3b.

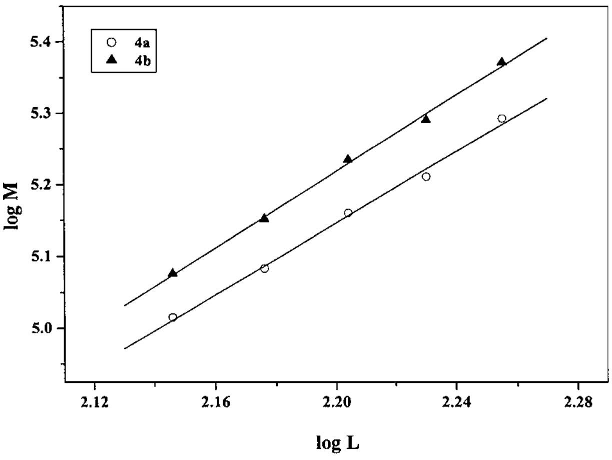

Figure 3 Log M versus log L plots for systems 4a and 4b.

However, the D values of systems 3a and 3b show 2–3% deviation and 4b shows significant deviation (about 6%) from the universal value. It is important to analyse and understand particular features of systems leading to different finite size effects since real systems are always finite. The primary difference between cases considered pertains to the microstructural features of the glasses. In this sense, we compare the D values of different systems with respect to the crystallisation characteristics of different systems owing to different glass microstructures. We first compare systems 2a, 2b, 3a, and 3b since these systems are crystallisation models of prior phase-separated glasses and then discuss the results pertaining to systems related to simultaneous phase separation and crystallisation (4a and 4b).

Systems 2a, 2b, 3a and 3b are similar since crystallisation occurs in the droplets in prior phase-separated systems. However, the droplet size in systems 3a and 3b is much smaller than in 2a and 2b. For systems in case 2 each droplet consists of 27 sites with an edge consisting of three site each (i.e., the length of an edge is 3 arbitrary units). Further, such droplets may have common sites (that is, two overlapping droplets with some common space) thus forming connected clusters of droplets, while in systems 3a and 3b a droplet consists of one site of the system only and therefore little or no growth is possible. Owing to this the crystal nucleation density of system 3a and 3b are higher compared to 2a and 2b. However, growth may be possible if several droplets are neighbours, i.e., droplets have common sides/faces. Consequently system 3b has a lower crystal nucleation density than 3a since more growth is possible.

As mentioned before D is a universal exponent. Therefore the deviation in D values of systems 3a and 3b indicate that the finite size effects owing to their glass microstructural features lead to slower convergence to the universal value compared to other systems. Further, compared to other systems the high D values of systems 3a and 3b indicate that the average density is nearer to the Euclidean density. This indicates that the structure is more compact when the droplet size is finer and consequently crystal nucleation density is higher.

Next we observe systems 4a and 4b have very different D values. Here crystallisation is occurring during phase separation. Thus the composition of the systems changes during the process. Consequently the results of our modelling show that the induction periods for crystal nucleation and growth are different. This means growth can only occur when the region surrounding the crystal nucleus has acquired NFL composition. With increase in difference of the initial glass composition from the NFL composition then the difference between induction periods for crystal nucleation and growth increases. Owing to this impeded growth, crystal nucleation density in system 4b is higher than that of system 4a in the intermediate and later stages of transformation [7, 11]. As has been found for systems 3a and 3b, a higher crystal nucleation density leads to a more compact structure at the percolation threshold. That the effect is quite severe for system 4b is brought out by the magnitude of the deviation of D from the universal value.

4. Conclusions

We have determined the fractal dimensionality of various models of glass-ceramics resulting from glasses that are prior phase-separated and those that are undergoing crystallisation during phase separation. We have found that for finite systems the fractal dimensionality increases with increase in fineness of the glass-ceramic microstructures. That is, with increases in crystal nucleation density the structure of the percolation cluster becomes more compact since the deviation from universal fractal dimensionality is towards the Euclidean one.

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