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Phase separation in tellurite glass-forming systems containing B_2O_3, GeO_2, Fe_2O_3, MnO, CoO, NiO and CdO

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The boundaries between the regions of single-phase and two-phase glasses were established in tellurite glass-forming systems containing B_2O_3 and one of the following oxides: GeO_2, Fe_2O_3, CoO, NiO, MnO and CdO. The character of the microstructures inside and outside the regions of stable phase separation were determined by electron microscopy. It was shown that the existing microheterogeneities may either result from incomplete liquid immiscibility during melting and supercooling or be due to typical metastable separation.

1. Introduction

At present, there is a considerable interest in binary and multi-component glass-forming systems in which immiscibility takes place. The reviews by Charles [1], Uhlman and Kolbeck [2], James [3], Zarzycki [4], Andreev *et al.* [5] and Vogel [6] contain important generalizations dealing with the theoretical basis of this phenomenon. The relationship between liquid-phase separation and crystallization is discussed by Gutzow [7]. On the basis of general thermodynamic considerations he notes that liquid immiscibiltiy precedes crystallization. In addition to fundamental research, liquid-phase separation in glasses has a great significance in technological applications. In a review by Milyukov [8] the role played by metastable separation in the synthesis of photochromic, laser and optical glasses is discussed. This phenomenon is directly related to the formation of pseudo-fibre optical devices [9], glass ceramics [8, 10] and porous glasses for ultra-filters [11]. In this respect the investigation of the microheterogenous structure of the tellurite glasses is important for creating new optical materials transparent in the infra-red region [12, 13], as well as for the synthesis of oxide semiconducting [14, 15, 16] and magnetic [17] glasses for which TeO_2 is a glass-former.

The purpose of this paper is to determine the boundaries between the regions of single-phase and two-phase glasses in tellurite glass-forming systems containing B_2O_3 and one of the following oxides: GeO_2, Fe_2O_3, CoO, NiO, MnO and CdO. Special attention is paid to the morphology of the microheterogenous formations obtained when vitrifying the melts. Some compositions of these systems have been studied previously [18, 19].

Data in the literature on the immiscibility of tellurite glass-forming systems are quite sparce. The following systems have so far been investigated: TeO_2–B_2O_3 [20]; TeO_2–GeO_2 [21]; TeO_2–P_2O_5 [22], TeO_2–V_2O_5–GeO_2, TeO_2–V_2O_5–B_2O_3 and TeO_2–GeO_2–B_2O_3 [18, 19]. Vogel *et al.* [23] observed metastable phase separation in more complex tellurite systems.

2. Method of investigation

The batches were prepared of TeO_3 (Reachim, USSR), H_3BO_3 (Reachim, USSR) and oxides (labelled for analysis). The compositions were melted either in porcelain crucibles at temperatures between 600 and 1000° C or in quartz crucibles, when higher melting temperatures were required. After homogenization the melts were cooled in the crucibles to room temperature. Under such conditions of cooling it was possible for the processes of macro- and micro-separation to manifest themselves to a detectable degree.

The regions of immiscibility for the different systems were determined by visual observation of the samples after the crucibles were broken and

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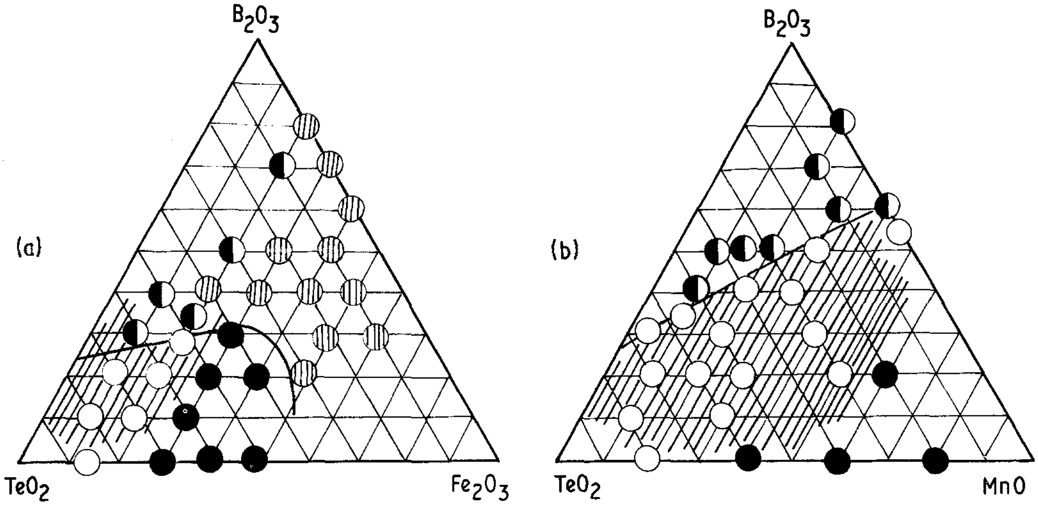


Figure 1 Liquid-phase separation and glass-formation regions in (a) the TeO_2–B_2O_3–Fe_2O_3 system and (b) the TeO_2–B_2O_3–MnO system. ○: glass; ●: crystallization; ◐: liquid–liquid phase separation; ◍: crystallization and liquid–liquid phase separation.

they are graphically represented on the Gibbs triangle. The regions of glass formation depend on the cooling rate and that is why they can only be roughly shown by lines (Figs 1, 4 and 8). According to data from X-ray micro-analysis [18, 19], the differences between the initial batch compositions prepared by us and the analytical compositions of the melts were less than 5 wt %.

The character of the microstructure was determined by electron microscopy through application of the carbon–platinum replica technique. The replicas were obtained from a freshly fractured surface of the specimen, and on certain occasions the surface was chemically etched with 2% HF acid. The observations were made on an EM–301 Philips electron microscope. A JEOL X50A X-ray

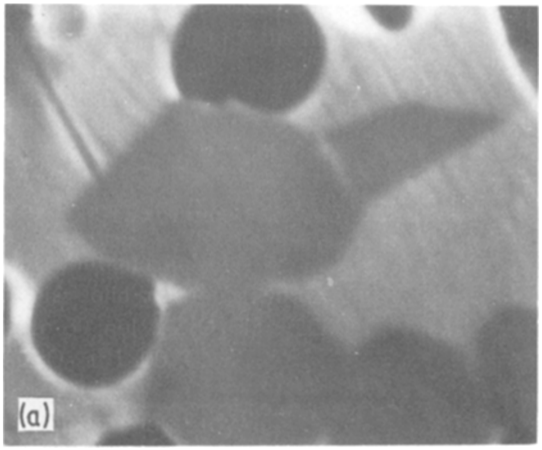
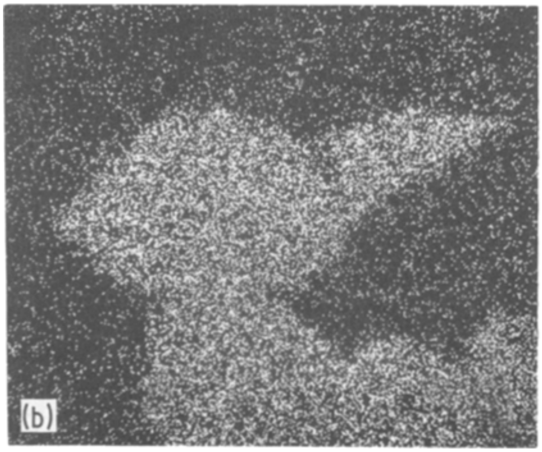
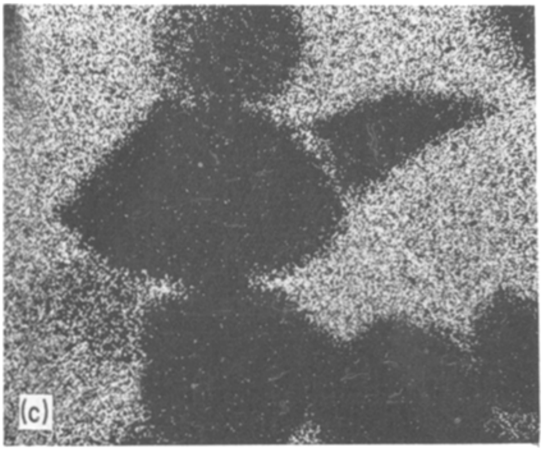


Figure 2 Distribution of TeO_2 and Fe_2O_3 in the lower layer of a two-phase glass having the composition 30 mol% TeO_2–40 mol% B_2O_3–30 mol% Fe_2O_3. (a) compo × 4500; (b) Fe-K × 4500; (c) Te-K × 4500.





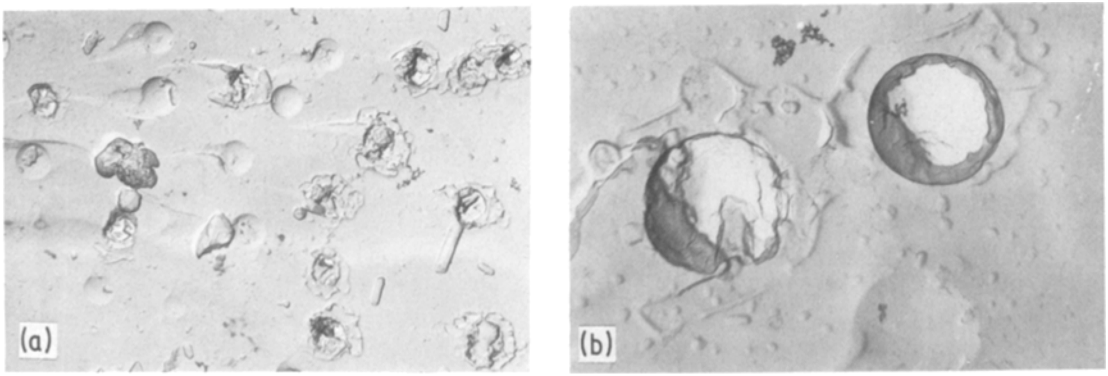


Figure 3 Metastable phase-separation and corrosion of the droplets with a transitional zone in a glass of composition. 40 mol% TeO_2–20 mol% B_2O_3–40 mol% Fe_2O_3. (a) × 6500, (b) × 28000.

microanalyser was used to determine the distribution of the components in the droplets and the matrix.

3. Experimental results

The glass-formation area in the TeO_2–B_2O_3 Fe_2O_3 system is relatively small, while the liquid-phase separation includes many compositions rich in TeO_2 (see Fig. 1a). This is because there is a liquid-phase separation in the TeO_2–B_2O_3 system [20] but such a separation is missing in the TeO_2–Fe_2O_3 system [24]. The hydration is typical for compositions having a high B_2O_3 concentration. The picture is further complicated when, along with micro-separation, crystallization is observed in certain two-phase compositions. Liquid immiscibility and crystallization take place independently of each other in the TeO_2–B_2O_3–Fe_2O_3 system. As indicated by the data of the X-ray microanalysis (see Fig. 2a, b and c), iron is detected mainly in the crystals and this makes it possible to assert that these are of Fe_2O_3. For a large number of compositions, this compound crystallizes more easily in non-equilibrium conditions than do the other compounds. TeO_2 and B_2O_3 are distributed both in the droplets and in the amorphous matrix. In compositions located outside the macro-separation area, droplet-like formations are found. The higher corrosion rate of the droplets, as well as of the transitional zone between them and the matrix, may be accepted as an indication of high B_2O_3 concentration both in the droplets and in the transitional zone (see Fig. 3a and b).

A smaller two-phase area in the liquid state is

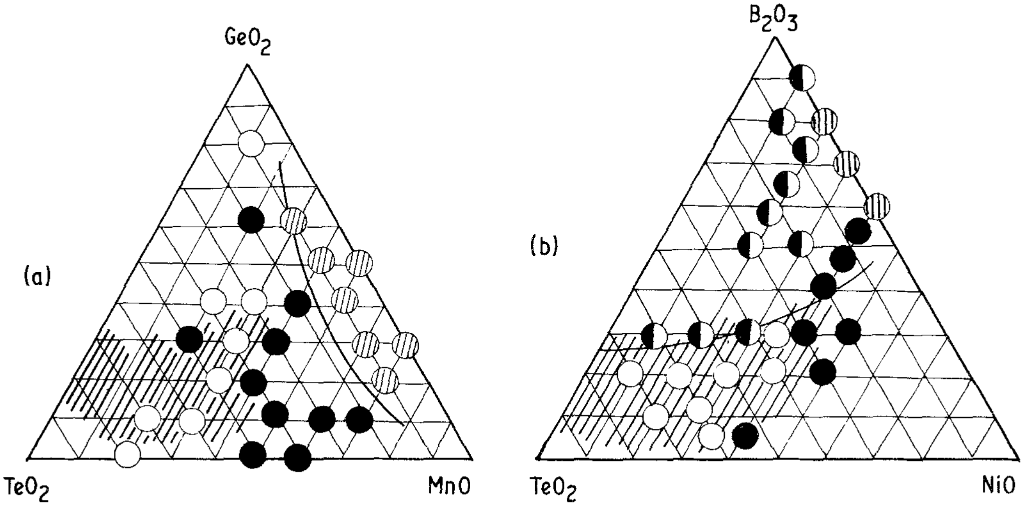


Figure 4 Liquid-phase separation and glass-formation regions in (a) TeO_2–GeO_2–MnO system, and (b) the TeO_2–B_2O_3–NiO.

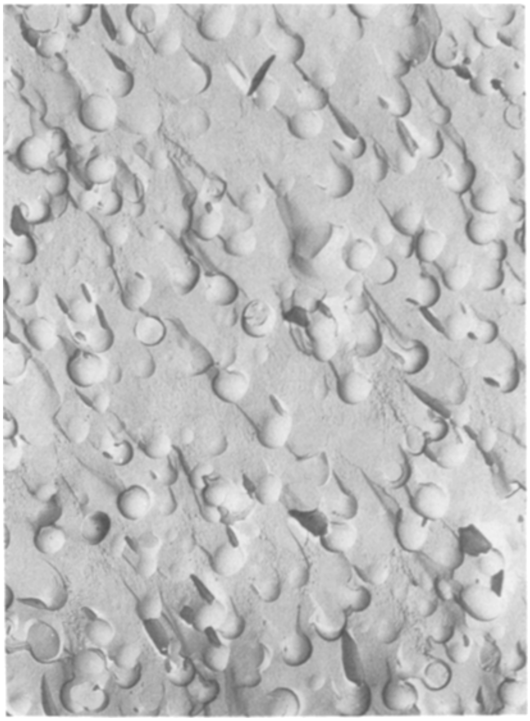


Figure 5 Metastable phase-separation of a glass with a composition 50 mol% TeO_2–10 mol% GeO_2–40 mol% MnO, × 5500.

observed in the TeO_2–B_2O_3–MnO system (Fig. 1b), while the region of single-phase glass-formation is wider. Moreover, we assume that the dissociation of the initial MnO_2 is completed and only MnO remains in the melts. This assumption is very conditional, because, in actuality, there exist differently valent forms (Mn^{2+}, Mn^{3+}) which are typical for many of the transitional ions contained in oxide glasses.

Both the region of macro-separation and the region of glass-formation include a small number of compositions in the TeO_2–GeO_2–MnO system (see Fig. 4a). Obviously, GeO_2 does not stimulate glass-formation to the same degree as B_2O_3 does. Since in the GeO_2–MnO system [25] liquid-phase separation occurs, and, since, in the TeO_2–GeO_2 system there are only microheterogenous formations, metastable immiscibility to the GeO_2–TeO_2 side is observed when varying the compositions in the three-component TeO_2–GeO_2–MnO system.

One typical structure is shown in Fig. 5. It possesses a high concentration of uniformly distributed small, 1 μm diameter droplets.

The stable glasses are located close to the TeO_2 angle in the TeO_2–B_2O_3–NiO system (see Fig. 4b). Two immiscible phases are obtained in supercooled melts in the direction of the B_2O_3 angle. The upper layer hydrates easily in air and the observation of its structure with an electron microscope is difficult. In this case the appearance of the microheterogenous distribution of tellurium in the upper layer is established by X-ray microanalysis (see Fig. 6a) of the sample with initial composition of 30 mol% TeO_2–50 mol% B_2O_3–20 mol% NiO. In the lower layer the amount of B_2O_3 is small and that of TeO_2 is considerable (Fig. 6b). NiO is distributed mainly in the lower layer. The rest of the transitional ions studied also dissolve in the layer enriched in TeO_2. The micro-immiscibility in the region with high B_2O_3

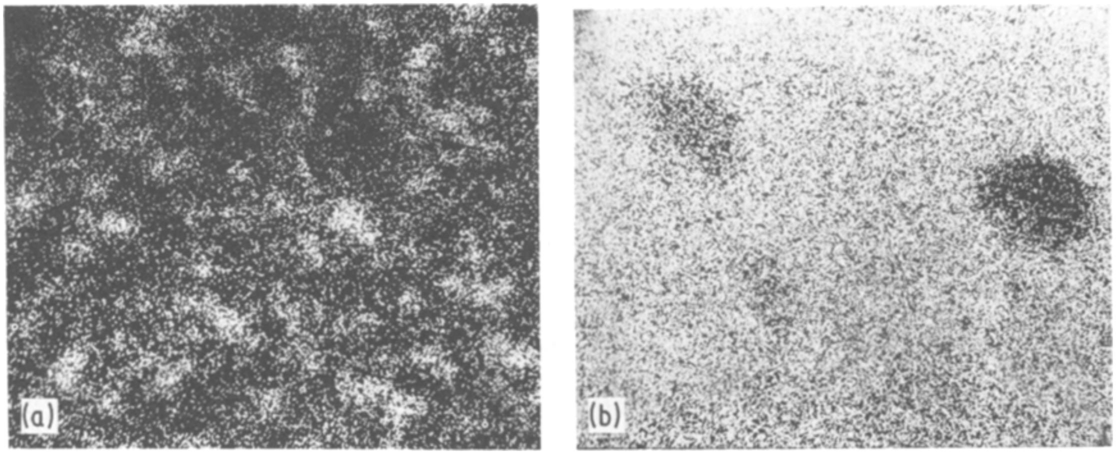


Figure 6 Distribution of TeO_2 in a two-phase glass with a composition 30 mol% TeO_2–50 mol% B_2O_3–20 mol% NiO composition. (a) lower layer, × 4500; (b) upper layer, × 4500.

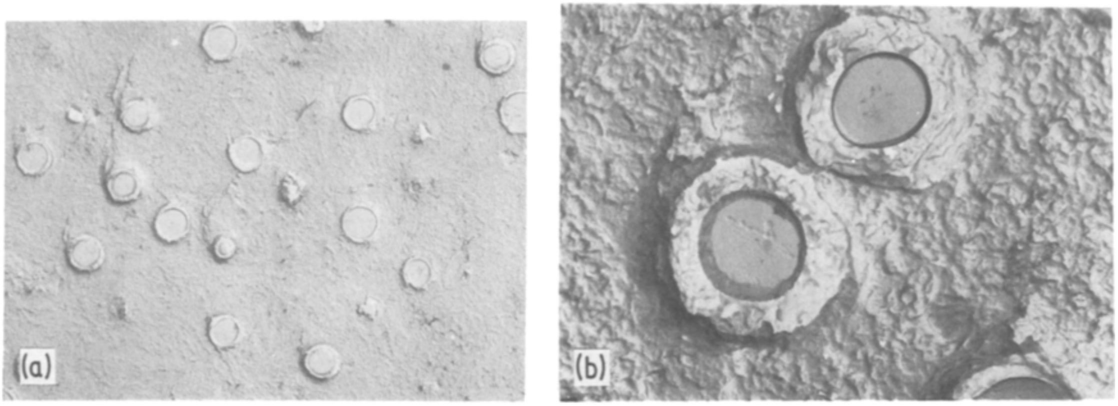


Figure 7 Micro-separation in a glass with a composition 5 mol% TeO_2–90 mol% B_2O_3–5 mol% NiO. (a) × 2000 and (b) × 15000.

concentration is characterized by droplet-like formations (see Fig. 7a), usually with a transitional zone (see Fig. 7b) in a corroded matrix.

There exist wide regions of stable glasses and liquid separation in the TeO_2–B_2O_3–CoO system (see Fig. 8a). According to [26], the immiscibility in liquid state in the B_2O_3–CoO system is of sintectic type. Visual observations for this system show that, after the samples are quenched, the upper layer comprises an opaque amorphous mass while the lower layer consists of a black glass in which lilac-coloured crystals may appear upon slow cooling. Micro-separation is detected in the bright-coloured borate phase as amorphous droplets dispersed in the corroded matrix (see Fig. 9a). The same picture for the upper layer is observed for the three-component compositions of the two-phase glasses. Moreover, well-shaped droplets exist in the lower layer of some compositions (Fig. 9b).

The region of liquid-phase separation for the TeO_2–B_2O_3–CdO system is similar to that for the TeO_2–B_2O_3–CoO system: it spreads from the TeO_2–B_2O_3 side to the CdO–B_2O_3 side (see Fig. 8b). The reason for this is that in the two binary-phase diagrams there exist regions of compositions containing two immiscible liquids [20, 27]. However, in the third TeO_2–CdO system [28] no liquid separation is established.

4. Discussion

In view of the procedures used for synthesis, the regions of liquid-phase immiscibility obtained cannot be interpreted as equilibrium ones. However,

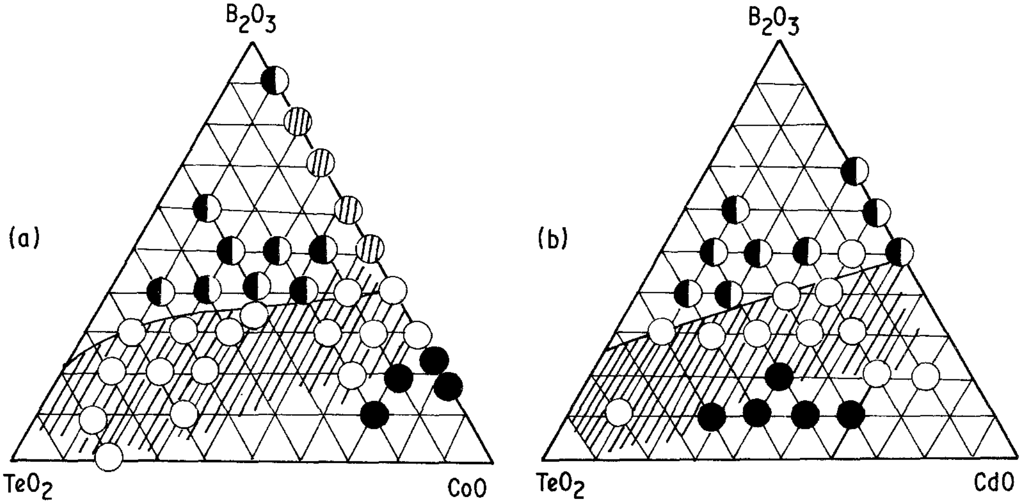


Figure 8 Liquid-phase separation and glass-formation regions in the systems (a) TeO_2–B_2O_3–CoO; and (b) TeO_2 B_2O_3–CdO.

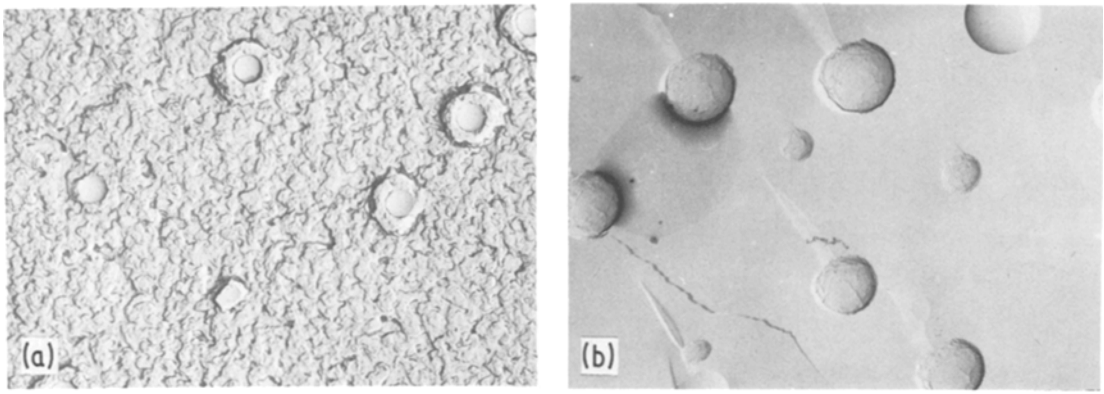


Figure 9 Micro-separation of glasses with composition (a) 80 mol% B_2O_3–20 mol% CoO, × 4000; (b) 20 mol% TeO_2–50 mol% B_2O_3–30 mol% CoO, × 5500.

under other experimental conditions they would be practically the same, as it is known that macro-separation occurs at a very high rate and cannot be averted at cooling. Only some variation of the relative amount of the two co-existing liquids and their composition is possible.

The occurrence of metastable separation outside the region of two liquids may be explained by the concept of Roy [29] applied to a ternary system. The continuation of the surface of immiscibility dome gives the compositions of the supercooled liquids which could be in metastable equilibrium. Probably, the microstructure shown in Fig. 5 has such an origin.

All compositions which are located in the regions of macro-immiscibility possess, in addition, micro-separation in one, or sometimes both, of the layers (see Fig. 6a). The main reason for that is the occurrence of metastable aggregation of amorphous droplets in supercooled melts instead of crystallization. Such a phenomenon has been observed in the upper layer of the two-phase glasses of the TeO_2–B_2O_3 system [20].

Another kind of micro-separation may be obtained as a result of the process not being terminated during the melting. For example, close to and on both sides of the boundary of separation of the two immiscible melts there remain spherical droplets. As these droplets have not been able to reach the boundary surface and join their own melt, they remain frozen in the amorphous matrix. Their number will be particularly high in a melt of higher viscosity. The micro-separation of the sample shown in Fig. 9a and b has such an origin.

If the composition is located close to the binodal surface, the amount of one of the liquids is much smaller than that of the other. Then, instead of macro-separation of the two liquids, the formation of a certain number of droplets of the one liquid immersed in the other liquid is possible. It is obvious that, although these droplets are by origin due to stable liquid-phase macro-separation, they are morphologically manifested as micro-separation. The droplets in a specimen of compositions 90 mol% B_2O_3–5 mol% TeO_2–5 mol% NiO (Fig. 7a and b) have a similar origin. From the above discussion it is clear that two-phase glasses may actually possess a complex morphology.

5. Conclusion

It is established that with the addition of Fe_2O_3, CoO, NiO or CdO to the TeO_2–B_2O_3 binary glass-forming system the regions of liquid immiscibility are preserved. Stable glasses are obtained with the participation of MnO, CoO and CdO and it is found that Fe_2O_3 enhances the crystallization capacity. The transitional oxides dissolve in phases enriched in TeO_2. Macro-immiscibility is accompanied by micro-separation both inside and outside the dome of immiscibility. This complex picture may result either from incomplete separation during melting and quenching or from typical metastable separation.

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