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Abstract

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ON THE QUESTION OF LIQUATION PHENOMENA IN SILICATE MELTS

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In connection with the study of the glassy state, on the one hand, and of the processes of formation of finely crystalline materials that have been given the name sitalls, on the other, the attention of researchers has been attracted by liquation phenomena, which lead to the formation of two amorphous phases existing as regions or droplets of very small size. To clarify certain details of such liquation processes, we investigated the behavior of melts in the systems $CaO-SiO_2$ and $SrO-SiO_2$, in which liquation regions had previously been established ([1], [2]), as well as in the system $BaO-SiO_2$, in which there is only a tendency toward liquation.

For the preparation of samples, silica in the form of a fine powder of rock crystal (99.90% SiO_2) and chemically pure alkaline-earth carbonates were used. Thoroughly mixed batches were shaped and melted in an electric arc. The samples prepared in this way were held in a microfurnace ([3]) at temperatures exceeding the liquidus by up to 200° for periods from 30 seconds to 3 minutes and were subjected to rapid cooling—quenching. Polished sections were prepared from the quenched samples. After very brief etching in dilute hydrofluoric acid, their structure was determined at maximum magnifications in a light microscope and with the aid of an electron microscope, for which carbon-platinum replicas were prepared.

It is known that in systems in which liquation occurs, as the liquation region is approached the melts begin to lose the ability to be quenched into transparent glass.

A comparison of the behavior of melts upon quenching in the binary systems of silica with CaO, SrO, and BaO with the corresponding phase diagrams showed that, with increasing silica content up to the composition at the eutectic between silica and the silicate closest to it, the melts are quenched to glass. At higher silica contents they begin to opalesce and become turbid. The region of melts that opalesce and become turbid upon quenching, called the preliquation region, occupies on the phase diagrams the interval from the indicated eutectic to the binodal curve that bounds the region of macroliquation. In the system $BaO-SiO_2$ the corresponding region extends to compositions containing approximately 95% silica, since macroliquation is absent in it. The structure of

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

a sample from the preliquation region of the $CaO{-}SiO_2$ system, quenched from temperatures above the liquidus, is shown in Fig. 1, where a part of the phase diagram indicates the composition and temperature from which quenching was carried out, and also gives a photograph of a sample quenched into transparent glass. The structure of a sample from the preliquation region, observed in the photograph, is repeated also in samples from analogous regions of the two other systems. The droplet-like appearance of the heterogeneities leaves no doubt as to their liquation nature. However, the "microliquation" observed here differs substantially from ordinary, or macroliquation, in that the very small droplets that have arisen cannot by any means be suc–

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Fig. 1. Electron-microscope photographs of quenched samples, indicating the corresponding figurative points on the phase diagram of the $CaO{-}SiO_2$ system with stitching: *a* –from the region of compositions quenching to transparent glass; *b* –from the preliquation region

Fig. 2. Microphotographs of a quenched sample from the region of macroliquation. *a* –macroliquation, general view of the polished section, 300×; *b* –microliquation, photograph only of the less silica-rich glass (the polished section is the same). 3195×

can coarsen and produce a structure with large regions of one amorphous phase within another. A characteristic example in this respect is found in the work of Argyle and Hummel (^{4}) on the system $BaO{-}SiO_2$, in which liquation phenomena were likewise detected. The sizes of the regions of one liquid in the other do not exceed approximately 0.25 μ, although the heating time at temperatures above the liquidus reached 20 hours. It is precisely because of the sharp distinction between micro- and macroliquation that it is possible to establish accurately the boundaries of the macroliquation region recorded on many phase diagrams of silicate systems.

The facts presented make it possible to conclude that there exist two different kinds of liquation phenomena: microliquation and macroliquation. Their cause is probably one and the same and, according to current views, is associated with the struggle for oxygen between the cations of the glass former and the modifier. However, the influence of the quantitative ratio of the components on the composition, structure, and physical properties of the products of its decomposition in the process of liquation leads to a substantially different final state.

In studying polished sections in which macroliquation is observed, it was found that their phase composition and structure differ from those presented in previous investigations ([1], [2]). According to those investigations, the indicated polished sections consist of two glasses, and one of them, the less siliceous one, should contain crystals of cristobalite, allegedly separating out during quenching as a consequence of the high crystallization capacity of this liquid. In reality, as the present investigation has established by X-ray and microscopic methods, the less siliceous glass contains no crystalline phase, but has a heterogeneous structure similar to the structure of specimens with a microliquation structure. The microphotograph in Fig. 2a shows the general appearance of a polished section with the characteristic picture of macrostratification. Already here the heterogeneous character of the surface of the less siliceous glass is noticeable. Photograph 2b was taken from the same polished section at higher magnification. Here a region with the less siliceous glass is photographed, and its microliquation structure is clearly visible, without separations of any crystals, very similar to the structure of the specimen from the preliquation region in Fig. 1b. This new and interesting fact prompted a study of the structure of specimens with macroliquation not only in binary systems of silica with alkaline-earth oxides, but also in a number of other systems. Polished sections were prepared and examined in the systems TiO_2-SiO_2, $Gd_2O_3-SiO_2$, $Dy_2O_3-SiO_2$, $Er_2O_3-SiO_2$, and everywhere the picture proved to be the same: the less siliceous glass always had a microliquation structure and contained no silica crystals. It should be noted that after Greig' s work on the study of macroliquation in a number of binary silicate systems ([1]), who evidently took the microliquation decomposition of the less siliceous melt for crystallization of cristobalite, all other investigators (including one of the authors of the present communication) adhered to the same opinion regarding the character of the heterogeneous structure of one of the coexisting glasses. For example, in the works of DeVries, Roy, and Osborn ([5], [6]) on the systems TiO_2-SiO_2 and $CaO-TiO_2-SiO_2$, it is stated that in macroliquation a silica-rich melt and a melt enriched in TiO_2 coexist; the latter cannot be quenched to glass and, on solidifying, devitrifies and gives a gray-blue mass. However, the devitrification product was not identified either by X-ray or by other methods. There is now reason to believe that in all cases of macroliquation of silicate melts, the turbidity and opalescence of one of the coexisting glasses are caused predominantly by the phenomenon of microliquation. At the same time, of course, the possibility of its simultaneous crystallization is not excluded.

The discovered microliquation of the less siliceous liquid, accompanying macroliquation, can be explained by the fact that this liquid is the limiting one in a series of melts lying in the preliquation region and possessing the capacity for microliquation.

In our work on the system Al_2O_3—SiO_2 ([7]) the supposition was expressed that, in microliquation, the coexisting phases differ little in composition. The fact established in the present investigation—the joint independent existence in one and the same sample of macro- and microliquation—indirectly confirms this supposition. Indeed, the coexistence of three liquid phases in a binary system is possible only under the condition that their compositions differ; and if the compositions of the liquids arising as a result of macroliquation differ strongly from one another, then the difference in composition of the liquids coexisting metastably during microliquation must be considerably smaller.

The facts obtained are of substantial importance for the development of ideas about liquation phenomena; they touch upon certain questions in the theory of heterogeneous equilibria, the structure of glasses, and their crystallization.

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