Title
ON THE LOCATION OF METASTABLE IMMISC-IBILITY IN THE SiO2-Al2O3 SYSTEM

Author
Risbud, S.H.

Publication Date
1978-10-01

Submitted to the American Ceramic Society

LBL-8354 c.2
Preprint

ON THE LOCATION OF METASTABLE IMMISCIBILITY IN THE SiO_2-Al_2O_3 SYSTEM

Subhash H. Risbud and Joseph A. Pask

October 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

ON THE LOCATION OF METASTABLE IMMISCIBILITY IN THE SiO_2-Al_2O_3 SYSTEM

Subhash H. Risbud* and Joseph A. Pask

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California,
Berkeley, California

Jantzen and Herman[1] have raised questions regarding thermodynamic calculations and experimental results[2,3] related to metastable immiscibility and crystallization of <u>bulk</u> melts and glasses in the SiO_2-Al_2O_3 system. This discussion is presented to show how differences in considering concepts of glass transition, effects of experimental cooling rates, cooling rates influenced by sample thickness, and thermal history can be problematic in the experimental attempts to locate the boundaries of the much anticipated liquid immiscibility in alumino silicate glasses. We also cite the experimental evidence from several investigations, including our own, to show that the miscibility gap proposed by Jantzen and Herman[1] is a result of the much faster cooling rate to which their glass specimens were exposed.

The decomposition behavior and structure of glasses examined by Jantzen and Herman[1] can be expected to be different from the behavior of melts and glasses we examined because of the different glass preparation procedures. While we prepared glasses[2] in <u>bulk form</u> in sealed molybdenum crucibles (≈3.75 x 2.5 cms) by quench cooling homogenized melts in helium at a rate of ≈15°K/sec, the glasses studied by Jantzen and Herman[1] were

---

[*] Now at Department of Metallurgy and Material Engineering and Materials Research Center, Lehigh University, Bethlehem, PA 18015.

prepared in the form of thin ribbons at cooling rates of $\approx 10^6$°K/sec. The estimated curve of glass transition temperatures (corresponding to a viscosity of $\approx 10^{14.6}$ poises) versus composition shown in our work[2] represents the equilibrium glass transition ($Tg_{(eq)}$ for a metastable state achieved under conditions approaching an infinitely slowly cooled glassy liquid. On the other hand, the rapidly cooled glasses examined by Jantzen and Herman will show a higher glass transition temperature as shown schematically in Fig. 1. On reheating the rapidly cooled glass, decomposition to cause phase separation can occur at a much lower temperature than $Tg_{(eq)}$ because of a higher free energy driving force and the existence of high mobility molecular species frozen-in during the rapid quench. The rapidly cooled glass is thus likely to exhibit thermal instability at a lower temperature than one would expect for a slowly cooled glass, i.e. below Tg. As illustrated in Fig. 1 this temperature would be lower, the higher the frozen in Tg.

Further, as demonstrated in the work of Neilsen,[4] the initial state of the glass can also have a remarkable effect on the mechanism (spinodal or nucleation-growth) by which the glass phase separates upon reheating. An example of this quenching history dependence can be readily seen in the work of MacDowell and Beall[5] where structures ranging from the droplet type to interconnected type were observed in the same sample because of cooling rate differences between the center and edges of the sample. Also, while MacDowell and Beall[5] and Jantzen and Herman[1] both report an interconnectivity characteristic of spinodal decomposition in the as-quenched 20 mole% Al_2O_3 glass, Takamori and Roy[6] found only "inhomogeneities of the order of $\leqslant 100$Å" and no evidence of interconnectivity in their splat cooled glass of the same composition even upon reheating up to the crystallization temperature.[6]

The miscibility gap proposed by Jantzen and Herman[1] has an upper consolute temperature of ~650-700°C at ~28 mole% Al_2O_3 with composition limits of ~12 and 41 mole% Al_2O_3 at ambient temperatures. The existing experimental data in the literature, which can also be presumed to be correct, but show different composition and temperature limits. On the silica-rich end, immiscibility in a glass containing 6.44 mole% Al_2O_3 was reported by Nassau et al.[7] using light scattering of a laser beam. MacDowell and Beall[5] also report phase separation in a 10 mole% Al_2O_3 composition. Similarly, on the alumina-rich end phase separation of a 50 mole% Al_2O_3 composition was found by MacDowell and Beall.[5] Further, Takamori and Roy[6] observed fine structures in splat cooled glasses up to ≈54 mole% Al_2O_3 compositions. Different consolute temperatures were again indicated by the experimental data of Nassau et al.[7] and the observation of phase separation. Galakhov et al.[8] after annealing glass compositions in the range 15 to 30 mole% Al_2O_3 at temperatures of ≈1225 to 1275°C. Similarly, we consistently observed glass compositions of ≈11 to 12 mole% Al_2O_3 in metastable equilibrium with mullite in our study of the 47 mole% Al_2O_3 (60 wt%) melts.[3] Assuming prior phase separation this glass composition closely follows the silica rich boundary of the miscibility gap we calculated.[2]

Unfortunately, Jantzen and Herman[1] have misinterpreted our reported quenching experiments on the 47 mole% Al_2O_3 composition. The quenching experiments were designed to show that melts homogenized at 2090°C were easily supercooled to about 1325°C at which point mullite crystallization occurred. This temperature approximately corresponded to the boundary of a previously calculated liquid miscibility gap.[2] Thus, quenching directly to room temperature or 600°C (which is below $Tg_{(eq)}$), or delaying the cooling at any temperature above 1325°C or cooling to 1500°C and then reheating to 1725°C prior to quenching always produced mullite crystals of the same composition or morphology. Supercooling into the range of 1325 to 730°C and holding prior to quenching resulted in mullite with lower Al_2O_3 contents indicating that mullite had crystallized and exsolved some Al_2O_3 during the holding period. These experiments indicated that mullite crystallized in the melt at about 1325°C at our experimental cooling rate. Consequently, raising the temperature to 1725°C after first cooling to 925°C resulted in recrystallization, or reversion, of the mullite that was precipitated at 925°C. The close association of these experimental data (for the 47 mole% Al_2O_3 melts) with the position of the calculated miscibility gap leads us to believe that in this case liquid immiscibility occurs as a precursor to the observed metastable mullite crystallization. This point was discussed in the paper.[3]

In summary, we believe that the miscibility gap calculated by us from the phase diagram liquidii represents a metastable equilibrium condition between the separated glassy phases.[2] It is possible to circumvent this metastable equilibrium by kinetic phenomenon when rapid cooling techniques are employed. Thus, rapid quenching can suppress the miscibility gap. Furthermore, because of the resulting highly energetic state of the glass, subsequent heating can cause decomposition reactions at temperatures below $Tg_{(eq)}$. Our experimental quench cooling rates were slow enough to provide essentially metastable equilibrium conditions. The cooling rate employed by Jantzen and Herman[1] considerably suppressed the miscibility gap. Their questions have once again pointed to the importance of considering metastable transformations[9] in the development of ceramic microstructures and have re-emphasized[2] the difficulties associated with experimentally defining the detailed miscibility gap in the SiO_2-Al_2O_3 system.

ACKNOWLEDGMENT

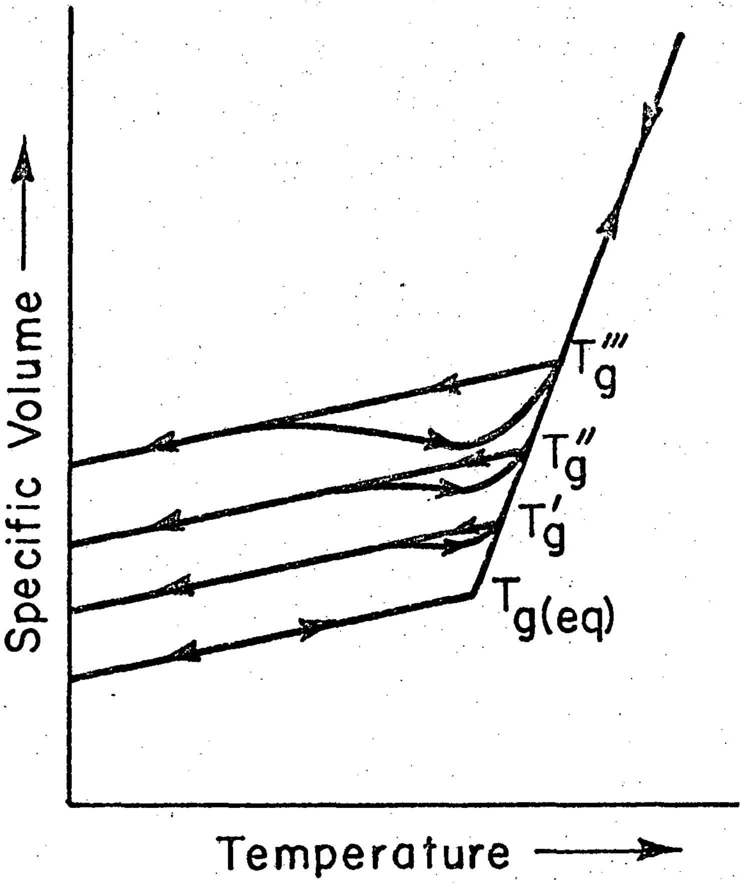
This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

REFERENCES

1. C. M. Jantzen and H. Herman, "Phase Equilibria in the SiO_2-Al_2O_3 System," J. Amer. Ceramic Soc.,
2. S. H. Risbud and J. A. Pask, "Calculated Thermodynamic Data and Metastability Immiscibility in the System SiO_2-Al_2O_3," ibid, 60, 418-24 (1977).
3. S. H. Risbud and J. A. Pask, "Mullite Crystallization from SiO_2-Al_2O_3 Melts," ibid, 61, 63-67 (1978).
4. G. F. Neilsen, "Spinodal Decomposition in Soda-Silica Glass," Phys. Chem. Glasses, 10 [2] 54-62 (1969).
5. J. F. MacDowell and G. H. Beall, "Immiscibility and Crystallization in Al_2O_3-SiO_2 Glasses," J. Amer. Ceramic Soc., 52 [1] 17-25 (1969).
6. T. Takamori and R. Roy, "Rapid Crystallization of SiO_2-Al_2O_3 Glasses," ibid, 56 [12] 639-44 (1973).
7. K. Nassau, J. W. Shiever and J. T. Krause, "Preparation and Properties of Fused Silica Containing Alumina," ibid, 58 [9-10] 461 (1975).
8. F. Ya. Galakhov, V. I. Aver'yanov, V. T. Vavilonova, and M. P. Areshev, Soviet Journal of Glass Phys. & Chem. (English Translation) 2 [2] 127-32 (1976).
9. S. H. Risbud and J. A. Pask, "SiO_2-Al_2O_3 Metastable Phase Equilibrium Diagram without Mullite," J. Materials Science, 13, 2449-2454 (1978).

FIGURE CAPTION

Schematic of specific volume vs. temperature for melts cooled at increasing rates from $Tg_{(eq)}$ to Tg''' and subsequently heated.



XBL 7810-6017

Fig. 1.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720