EXPERIENCE ON CENTRIFUGATION OF FLUORIDE-ALUMINA-SILICA MELTS

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Liquation in fluoride-alumina-silica melts is accompanied by the melt separation into alumina-silica and fluoride components. Considering high crystallization ability of fluoride phase it's quite complicated to perform diagnostics of liquation in such systems by cooling method that is usually used in such cases. Really, for a researcher the cooling samples 2 & 3 (fig. 1) look identical in the situation when there is no separation into two layers and they have drop-emulsive form.

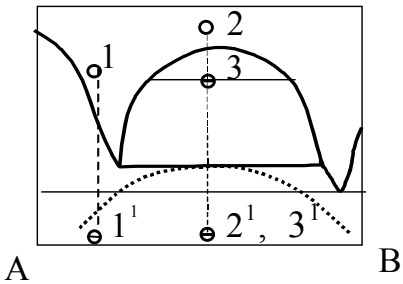

Fig.1. Liquation structure: 1, 2 - Out of liquation field; 3- Liquation; 1^1, 2^1,3^1 - Products of cooling.

As a rule, near the borders of boundary curve, the liquation systems are presented by thin emulsion of one-in-another melt. In this case liquation also does not differ from simple crystallization of fluorides from homogeneous melts. Similar situation happens upon metastable liquation (point 1, fig. 1). Therefore exact setting of liquation borders is speculative often. Determination of chemical composition of liquating phases is also complicated due to secondary decomposition during the cooling process and small size of the phases.

Centrifugation of melts at high temperatures allows avoiding these difficulties as the method is based on separation of the phases in accordance with their density. In this case the phases are fluoride and alumina-silica melts. First high-temperature centrifugation of fluoride-alumina-silica melts was used for determination of areas of so-called "microliquation" in the nepheline-sodium fluoride system (fig. 2). Absence of the melt separation was interpreted as a proof of monophase structure of "microliquation" interval.

We used centrifuge for the area of stable liquation of the above-mentioned diagram in order to discover complete phases separation for further chemical analysis. The experiments have been performed on a high-temperature centrifuge in Munich University, in the Institute of mineralogy, petrology & geochemistry. The basis of the device is a standard laboratory centrifuge (Cryofuge 8500i) with maximum speed of rotation 4000 min-1. Accuracy of speed measurement is 10 min-1. Acceleration of 2600 g. is reached upon rotation radius of 260mm. The centrifuge is equipped with rotating contact system of 12 sliding electrical pairs produced by RIE-TECH for transfer of voltage from thermocouples to thermoreguler and supply of electricity to the heaters of the furnace. Usually, upon the centrifuge work, temperature of inner room of the centrifuge may exceed 100°C due to rubbing of rotating parts against air and furnace heating. The advantage of the centrifuge is a high-capacity refrigerator that allows to maintain a stable temperature in hermetically sealed inner room within the range of +40 to ¬20°C. It provides the possibility to keep the contact system at 0°C and, thus, to avoid signal distortion of thermocouple upon long rotation.

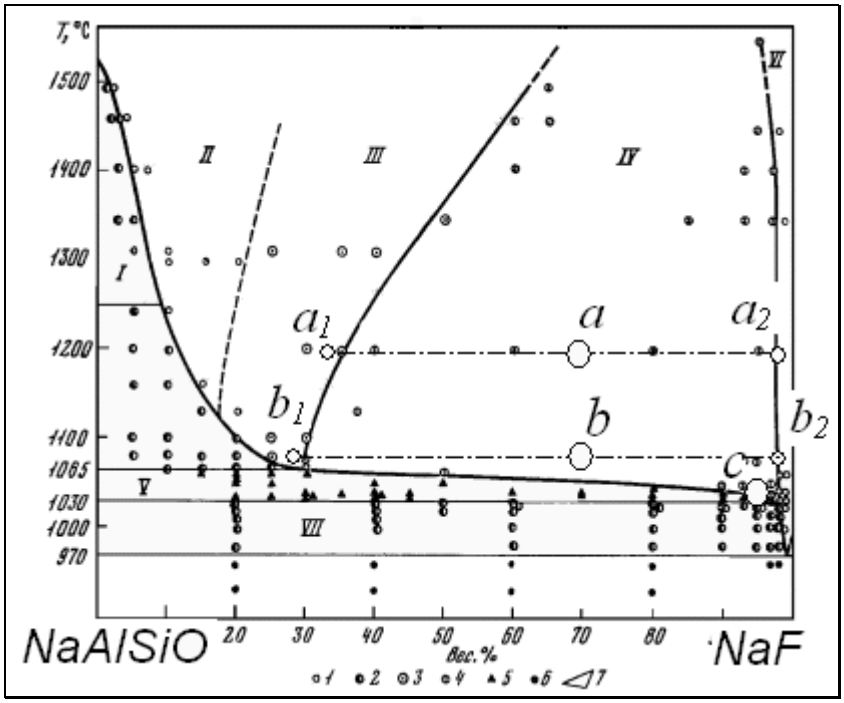

Fig. 2. Phase diagram of Ne-NaF system. I –carneguite (below 1248°-nepheline)+ liquid; II–one liquid; III-"microliquation"; V–two liquids; V-nepheline+two liquids; VI-fluoride liquid; VII-nepheline+fluoride liquid; ***a,b,c***,– experimental mixtures.

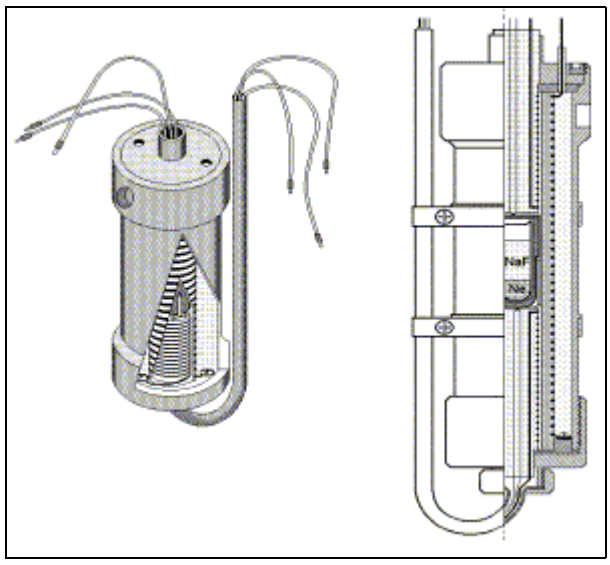

Fig.3. Structure of centrifuge furnace with 3-section heater, T=1300°C, a=2600g.

The centrifuge is equipped with high-temperature electric furnace (up to 1300°C) and can generate acceleration of gravity up to 2600 g upon normal pressure. It's also possible to use autoclave with heating up to 1200°C, upon pressure up to 1000bars and acceleration of gravity up to 1000g.

In this work a rotating furnace was used, upon a normal pressure. It has a 3-section heater and 3 Pt-PtRh thermocouples that maintain temperature with accuracy to within 1oC along the whole sample 22 mm long and 8mm. diameter. (fig. 3). Temperature regulation was performed by 3 "Eurotherm 814" units.

The mixtures prepared from synthetic nepheline and sodium fluoride were used as initial materials. Melted in advance in the electric furnace in welded platinum capsules samples were placed, without breaking the capsule containment, in a centrifuge where they were melted and separated at the fixed temperature during 60 min. with 1000g. acceleration.

Experiments in the range of NaF 70-95% mass (the rest is nepheline) showed that complete separation of the melts into two layers (fig. 4) takes place. Visible traces of mutual penetration of liquid phases exceeding 0,001mm were not found. EMP analysis of the phases showed that mixtures of the layers at the separation border and periphery are identical. The solution of alumina-silica component in the fluoride melt is not more than 1% mass. Vice versa, the solution of sodium fluoride in nepheline melt is considerably higher and amounts to 10-20% mass., that is much higher than the solution of sodium fluoride in silicate glass with similar mixture (1,5-3%). Position of the connode, estimated basing on the volume ratio resulted from experiments and data of phases density, is shown in the fig. 2 (a1-a2, b1-b2).

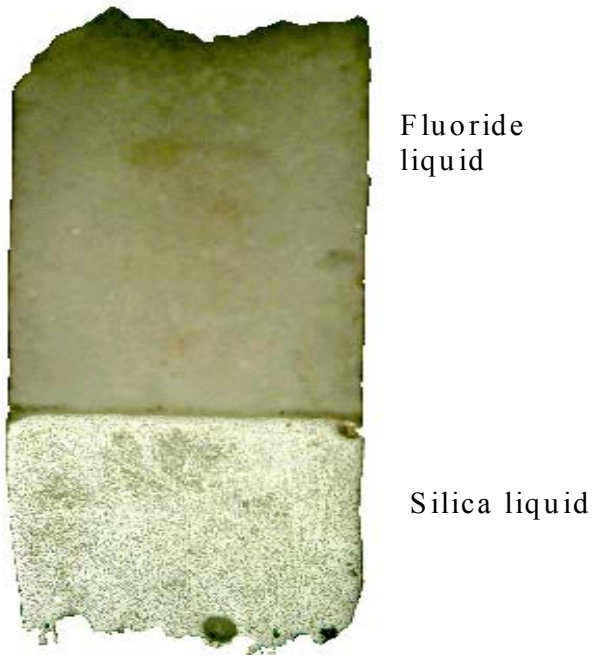

Fig.4. View of the sample after centrifugation

Thus, the performed experiments showed effectivity of high-temperature centrifugation usage for research of the processes related to liquation separation of melts.

References

Kogarko L.N., Kriegman L.D. (1970). Phase balance in the system nepheline – sodium fluoride // Geochemistry. N2.