

Behavior of Melts in the $\text{UO}_2\text{--SiO}_2$ System in the Liquid–Liquid Phase Separation Region

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Abstract—The behavior of melts in the uranium oxide–silicon dioxide system is experimentally investigated in air upon induction melting in a “cold crucible.” The existence of the two-phase liquid region in this system is confirmed. It is demonstrated that the melts absorb oxygen from air, which leads to crystallization of the $\text{UO}_{2.25}$ compound upon cooling. In the case of considerable internal heat release, sharp cooling of the melt surface results in the liberation of gas, which brings about bulging and, sometimes, melt ejection from the crucible.

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INTRODUCTION

The phase diagram of the $\text{UO}_2\text{--SiO}_2$ system was investigated in [1–5]. In [1–3], it was revealed that the system is characterized by the region of differentiation in the melt (liquid–liquid phase separation); however, this phenomenon was not found in [4, 5]. At present, preference in the scientific literature has been given to the variant proposed in [1] (see Fig. 1). The existence of binary compounds in the system under consideration was reported in none of the above works. However, the occurrence of the USiO_2 compound (the coffinite mineral [6, 7]) is described in the literature.

Nowadays, melts in the $\text{UO}_2\text{--SiO}_2$ system have attracted increased interest, because they allow one to simulate the genesis of the technogenic mineral chernobylite (new material in the form of high-uranium zircon $(\text{Zr,U})\text{SiO}_4$ characterizing mineralogy of fuel-containing lavas formed after the accident at the fourth unit of the Chernobyl nuclear power plant). According to the estimates [8, 9], this mineral is formed under the following conditions: the temperature T is equal to 1600°C , and the time of holding at this temperature is no shorter than three hours. The melting temperature of the lavalike mass containing chernobylite is higher than 1200°C . Moreover, it is necessary to clarify the problem as to the existence of the liquid–liquid phase separation region in the above system.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Silicon dioxide SiO_2 (the content of the main component is 99.9%) and uranium dioxide UO_2 depleted in ^{235}U (the content of the main component is 99%) were used as the initial materials. It is known that, upon heating in air, the uranium oxide absorbs oxygen and, at temperatures above 1300°C , has a composition corresponding to a mixture of oxides UO_{2+x} and U_3O_{8-z} [10].

Experiments with melts in the $\text{UO}_2\text{--SiO}_2$ system involve considerable problems associated with the following circumstances:

- (i) high melting temperatures of the components,
- (ii) a high risk of contamination of the melt by crucible materials, and
- (iii) the tendency of the components of the system toward the formation of suboxides, which upon evaporation form aerosols.

In this work, melts in the system under investigation were prepared for the first time by melting in a cold crucible. The experiments were performed on the COMETA facility (Nuclear Research Institute, Rez, Czech Republic) specially constructed for melting refractory oxide materials with melt temperatures of up to 3000°C in air. The facility was adapted for the operation with radioactive materials (in particular with UO_2) and intended for simulating real corium melts. The facility and the technique for performing meltings are described in more detail in our earlier work [11].

[†] Deceased.

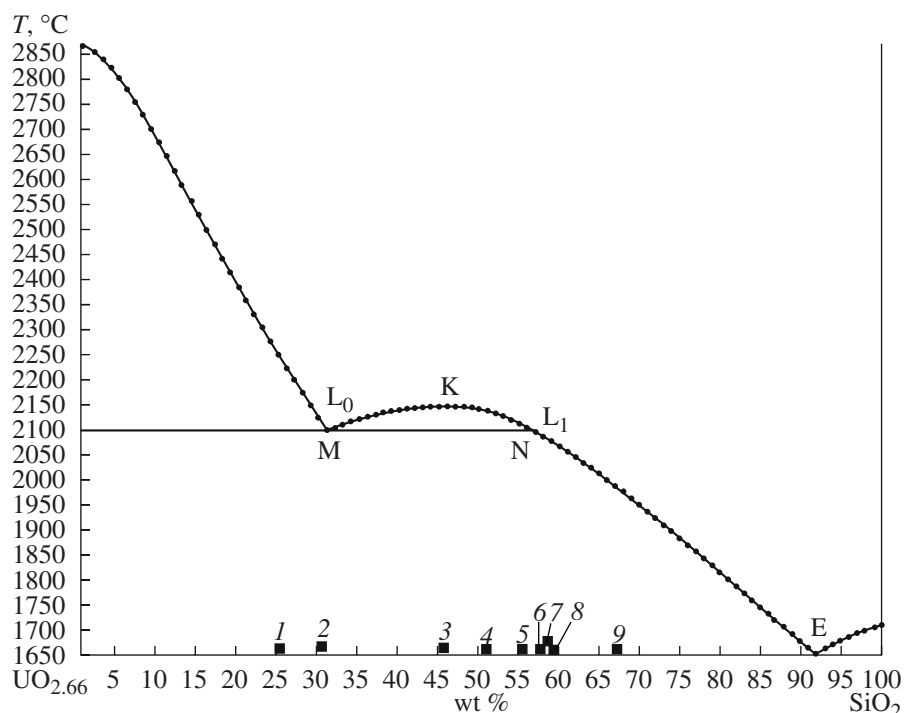


Fig. 1. Phase diagram of the $\text{UO}_2\text{-SiO}_2$ system in air according to the data taken from [1]. The compositions of the points of the analysis of the quenched samples in our experiments (Table 1) are shown. Designations: M is the monotectic point, N is the point bounding the liquid-liquid phase separation region, K is the consolute point, L_0 is the point corresponding to the limiting composition of the liquid enriched in the uranium oxide (MK line), and L_1 is the point corresponding to the limiting composition of the liquid enriched in silica (NK line).

Quenched samples and ingots were studied on a Philips PW 1800 (the Netherlands) diffractometer ($\text{CoK}\alpha$ radiation). The X-ray diffraction patterns were identified with the PDWin program package (developed at the NPO Burevestnik). Energy-dispersive X-ray analysis of polished sections was performed on a Philips SEM XL 30 CP scanning electron microscope (SEM) equipped with a ROBINSON detector. The residual pressure in the SEM chamber was equal to 0.5 mbar, and the voltage used for energy-dispersive X-ray analysis was 30 kV. The oxygen concentration in oxide phases was determined from the difference upon normalization of the total composition to 100%. The accuracy in the determination of the concentrations of the main elements amounted to $\pm 3\text{--}5\%$.

EXPERIMENTAL RESULTS

In this series of experiments, we carried out two meltings: (1) the final composition of the melt bath with respect to the initial oxides in the first experiment was $\text{UO}_2/\text{SiO}_2 = 70/30$ (wt %), and (2) the final composition of the melt bath with respect to the initial oxides in the second experiment was $\text{UO}_2/\text{SiO}_2 = 50/50$ (wt %). Since it was always difficult to start the melting and to maintain the melt with a high SiO_2 content due to the high electrical resistivity of the melt, the batch materials (SiO_2 powder, pieces of fused UO_2 , mixture of UO_2

+ SiO_2 powders) were placed in the crucibles in layers so that the UO_2 oxide initially melted, then the SiO_2 oxide dissolved in the UO_2 melt, and the powder mixture melted finally. Therefore, the SiO_2 oxide and the powder mixture started to melt in the UO_2 melt with a temperature of higher than 2800°C , which determined the high overheating of the melt with the SiO_2 oxide. The overheating was responsible for the appearance of dense aerosols above the melt. This complicated the visual control over the melting and the measurement of the temperature. The visual image of the melt surface (in the first experiment) at this instant of time is displayed in Fig. 2. When taking the melt samples with the use of the copper sampler, the viscous melt streams out behind it in the form of fibers (Fig. 3). The first experiment was successfully completed, and we obtained the rod samples and the vitreous ingot.

In the second experiment, in order to decrease the yield of aerosols, the generator voltage and, hence, the heating power was reduced in three stages (Table 1). This led to a decrease in the density of aerosols. However, a decrease in the power at the fourth stage of the experiment resulted in crystallization at the bath surface, which blocked the release of gases from inner layers of the bath. More recently, we revealed that the dark layer at the surface of the melt mirror and, hence, the solid crust represent a glass or a glass-ceramic material. Then, the voltage across the inductor was increased to