

Physicochemical Properties of Melts Used for the Electrodeposition of Niobium

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Formation of oxyfluoroniobium compounds in the binary systems $\text{KF-Nb}_2\text{O}_5$ and $\text{K}_2\text{NbF}_7\text{-Nb}_2\text{O}_5$ and in the ternary system $\text{KF-K}_2\text{NbF}_7\text{-Nb}_2\text{O}_5$ has been expected. Therefore the phase equilibrium and surface tension of the above systems have been determined. The three systems have only been investigated up to 20 mol% Nb_2O_5 because of its limited solubility. The obtained results have confirmed the formation of oxyfluoroniobium compounds.

Key words: Phase Equilibrium; Surface Tension; Molten Salts; Refractory Metal; Oxyfluoroniobium Compounds.

1. Introduction

Niobium is a refractory metal which has wide industrial application. It is well known that its compounds can not be electrolytically reduced from their aqueous solution to the metal because of the low decomposition voltage of water. Electrodeposition of niobium from molten salts is an alternative method of manufacturing this refractory metal.

The electrodeposition of refractory metals has been investigated since the 60's of last century. Since that time the influence of impurities, the properties of the deposition, the mechanism of the electrodeposition and the physicochemical properties of melts used for the electrodeposition have been studied. Different results, depending on the composition of the studied systems (fluoride, chloride-fluoride or chloride systems, addition of oxide, etc.) have been obtained.

The present work deals with the investigation of $\text{KF-K}_2\text{NbF}_7\text{-Nb}_2\text{O}_5$, which is interesting from two points of view. From the theoretical point of view it is the formation of oxyfluoroniobate compounds, and from the practical point of view it is the possible utilization of the system (as part of a more complicated one) for the electrodeposition of niobium. The phase equilibrium and surface tension of $\text{KF-K}_2\text{NbF}_7\text{-Nb}_2\text{O}_5$ have only been determined up to 20 mol% of niobium

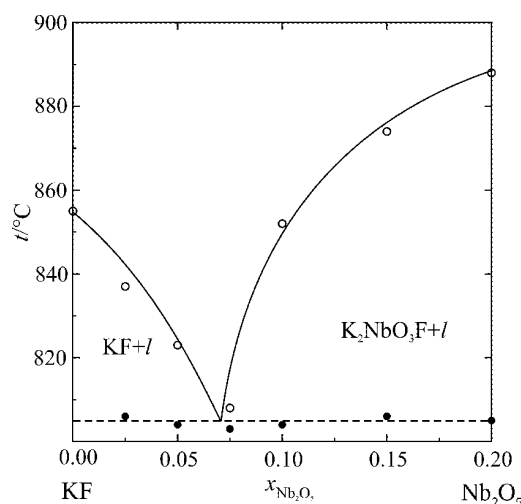


Fig. 1. The investigated part of the phase diagram of the $\text{KF-Nb}_2\text{O}_5$ system.

oxide because of the low solubility of oxide in the systems.

2. Experimental

The phase equilibrium of $\text{KF-K}_2\text{NbF}_7\text{-Nb}_2\text{O}_5$ has been studied by differential thermal analysis (DTA) and differential scanning calorimetry (DCS).

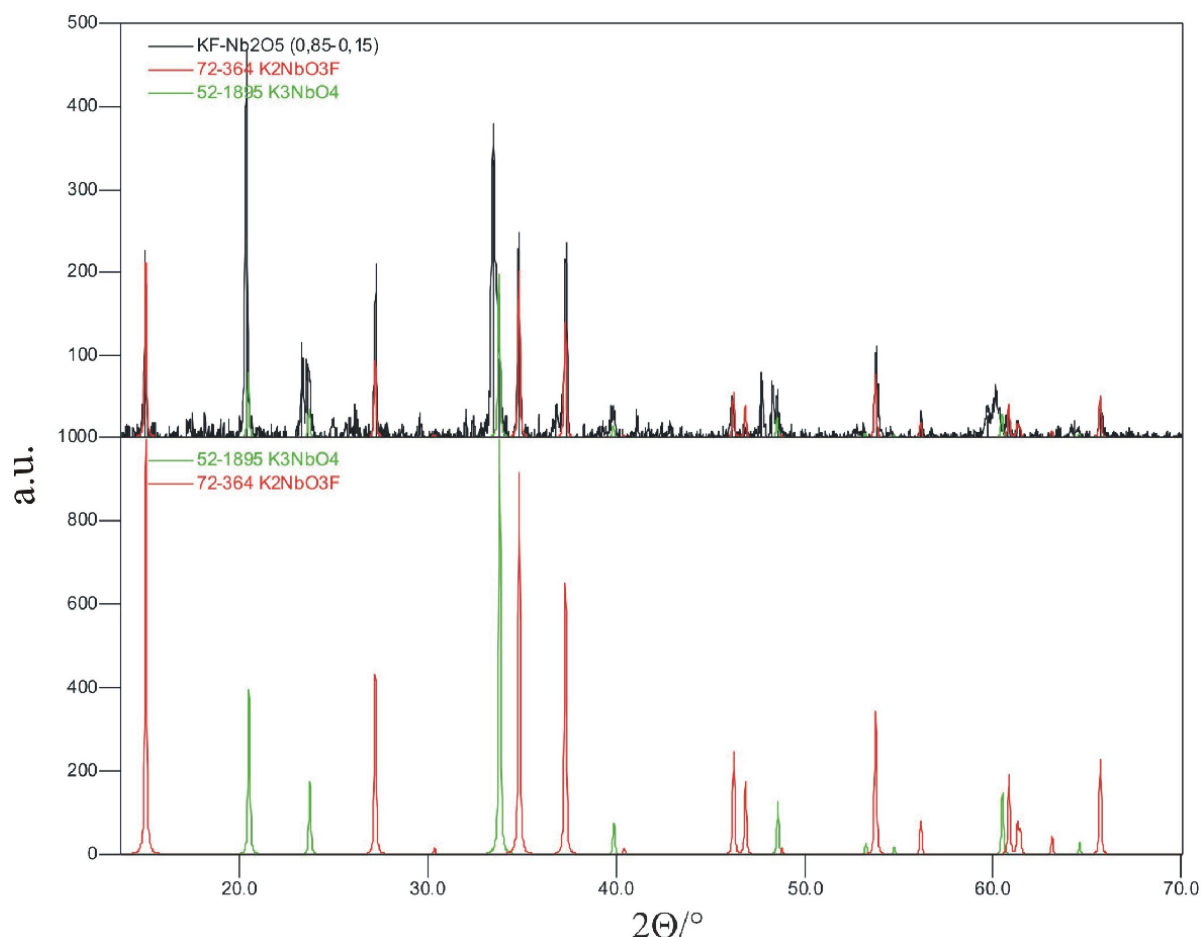


Fig. 2. X-Ray diffraction pattern of the binary mixture $\text{KF-Nb}_2\text{O}_5$ ($x_{\text{Nb}_2\text{O}_5} = 0.150$).

A water-cooled electrical furnace provided with an argon atmosphere and adjustable heating/cooling rate was employed for the DTA experiments. The temperature control and data processing were performed using a computerized measuring device. Each sample, 10 g in weight, was placed in a platinum crucible. The corresponding heating and cooling curves were recorded at 1–5 °C/min. The temperature was measured with a Pt-Pt10Rh thermocouple, calibrated with NaCl, KCl, and Na_2SO_4 . The measured transition temperatures were reproducible within ± 2 °C.

The DSC investigations were performed using the Setaram DSC 111 experimental device. Each sample, approximately 0.2 g, was placed in a specially designed sealed platinum crucible with 6.2 mm outer diameter. Temperature monitoring and data processing were computer-operated.

The surface tension of the $\text{KF-K}_2\text{NbF}_7\text{-Nb}_2\text{O}_5$ melts was investigated using the maximum bubble pressure method. The measuring device consisted of a resistance furnace provided with an adjustable head fixing the position of the capillary (Pt20Rh), the Pt-Pt10Rh thermocouple and a platinum wire, which served as electrical contact to adjust the exact touch of the capillary with the liquid surface. A detail information about the experimental device and method has been described in [1, 2].

For the preparation of samples, the following chemicals were used: KF (Lachema, 99%), Nb_2O_5 (Aldrich, 99.9%) and K_2NbF_7 (prepared in the Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Science Center of RAS, Apatity, min. 99%). KF and K_2NbF_7 were dried in vacuum at 180 °C for 24 h. The samples were prepared in

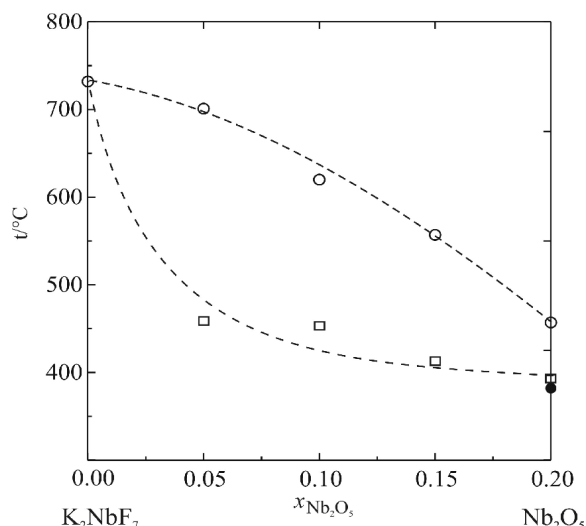


Fig. 3. The investigated part of the phase diagram of the K_2NbF_7 - Nb_2O_5 system.

a glove box under a dry inert atmosphere by mixing the pure compounds and placing them into Pt crucibles.

3. Results and Discussion

The phase diagram of KF - Nb_2O_5 consists of two crystallization fields in the investigated region (Fig. 1). One of them belongs to the crystallization of pure KF .

Based on X-ray diffraction analysis (Fig. 2), the second one was assigned to K_2NbO_3F . This compound may form according to the reaction



The formation of K_2NbO_3F in this binary system was for the first time published by Budova and Voskresenskaja [3]. The exact composition at the eutectic point was not calculated but estimated, based on the temperature difference between the eutectic temperature and the temperature of the liquid 1. The coordinates of the eutectic point lie close to $x_{Nb_2O_5} = 0.075$ and $t_e = 805$ °C. These values are not the same as those reported in [3–5]. This could be caused by the different experimental techniques used for the investigation of the system.

The cooling curves of K_2NbF_7 - Nb_2O_5 mixtures were characterized by the presence of two or three thermal effects. The phase diagram is shown on the Figure 3.

The temperature of the highest thermal effect can be attributed to the temperature of primary crystallization. The temperature of the second thermal effect lies in a wide temperature range. Therefore it can not be assigned to the eutectic temperature or the temperature of phase transition, but a solid solution could be expected in the studied concentration range. Konstantinov [6] has

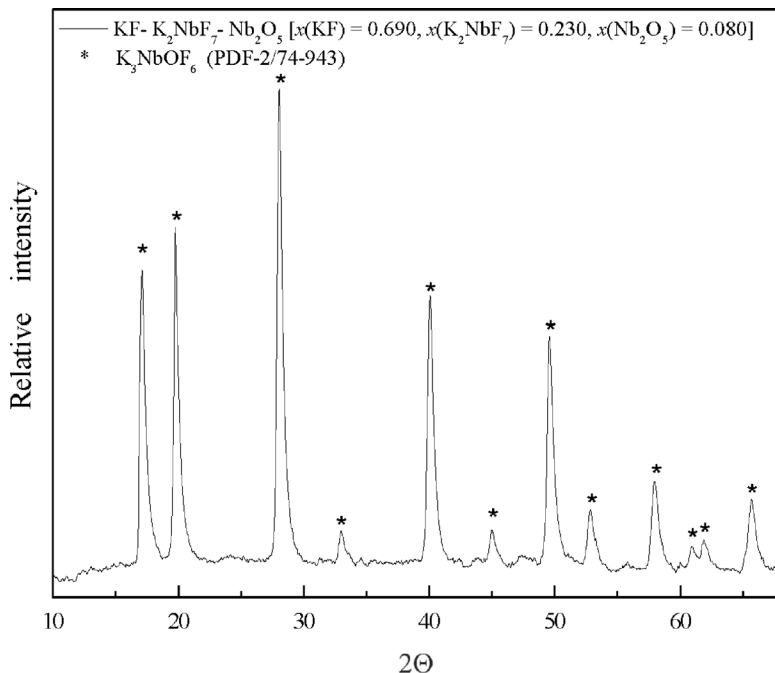


Fig. 4. X-Ray diffraction pattern of the ternary system KF - K_2NbF_7 - Nb_2O_5 .

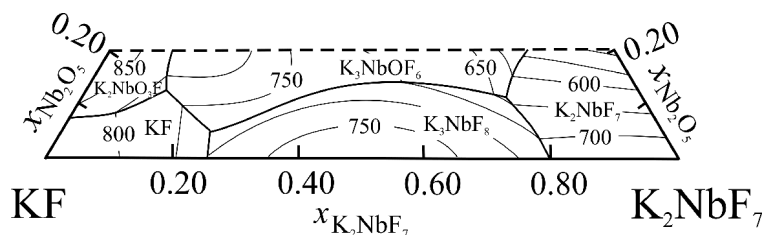


Fig. 5. The investigated part of the phase diagram of the KF-K₂NbF₇-Nb₂O₅ system. The isotherms are in °C.

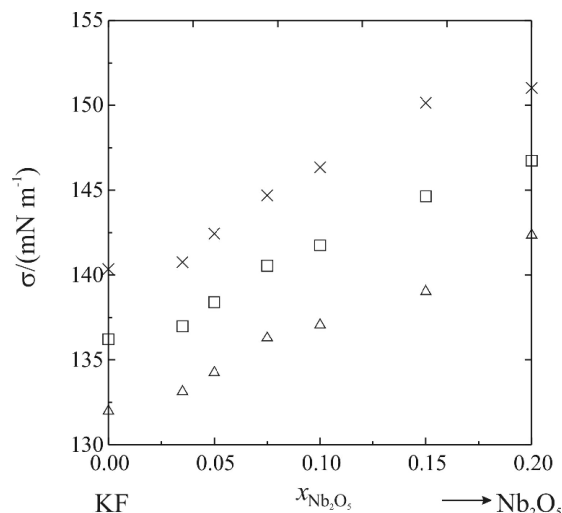


Fig. 6. Surface tension in the KF-Nb₂O₅ system. × - 860 °C; □ - 910 °C; △ - 960 °C.

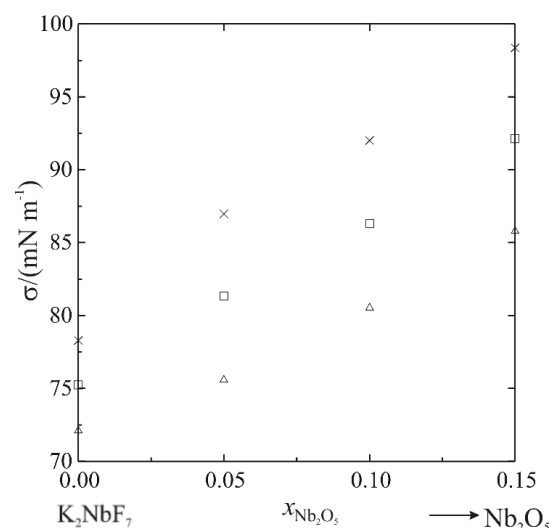
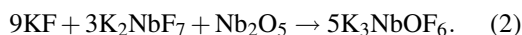


Fig. 7. Surface tension in the K₂NbF₇-Nb₂O₅ system. × - 860 °C; □ - 910 °C; △ - 960 °C.

reported the eutectic temperature $t_e = 380$ °C. However, according to our results this value was recorded only for the sample with $x_{\text{Nb}_2\text{O}_5} = 0.20$.

In the KF-K₂NbF₇-Nb₂O₅ ternary system another oxyfluoroniohium compound was found. K₃NbOF₆ may form in the ternary system according to the reaction



The X-ray diffraction pattern of the ternary sample with $x_{\text{KF}} = 0.69$, $x_{\text{K}_2\text{NbF}_7} = 0.23$, $x_{\text{Nb}_2\text{O}_5} = 0.08$ is shown in Figure 4.

The phase diagram of the KF-K₂NbF₇-Nb₂O₅ system consists of five crystallization fields in the investigated region (Fig. 5), where corresponding compounds crystallize.

More information about the phase equilibrium of KF-K₂NbF₇-Nb₂O₅ has been published in [7].

The surface tension of KF-Nb₂O₅ and K₂NbF₇-Nb₂O₅ increases with the increasing content of Nb₂O₅ (Figs. 6 and 7). The maximum values of the surface

tensions were obtained at 860 °C in both systems. Nb₂O₅ is not a surface active species in these molten salts, because its addition to the melt caused a decrease of the surface tension.

The surface tension of KF-K₂NbF₇-Nb₂O₅ was calculated using the multiple linear regression analysis, and the dependence of the surface tension on the composition at the temperature 910 °C is shown in Figure 8. It is obvious that the surface tension decreases from K₂NbF₇ through KF to Nb₂O₅.

Detail information about the surface tension of the KF-K₂NbF₇-Nb₂O₅ system can be found in [8].

4. Conclusion

The phase equilibria and surface tension of the system KF-K₂NbF₇-Nb₂O₅ have been investigated.

In the KF-Nb₂O₅ binary system as well as the KF-K₂NbF₇-Nb₂O₅ ternary system the formation of oxyfluoroniohium compounds has been observed. Their presence in the phase diagram has been expressed as a new field of crystallization. X-Ray diffrac-

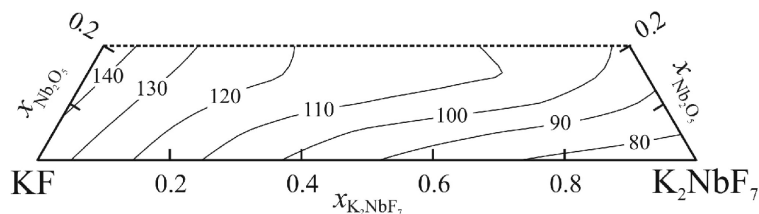


Fig. 8. Surface tension of the KF-K₂NbF₇-Nb₂O₅ system at 910 °C. Values are in mN m⁻¹.

tion analysis was used for the identification of the samples.

The surface tension investigations showed that Nb₂O₅ is not a surface active species in the KF-Nb₂O₅ and K₂NbF₇-Nb₂O₅ melts. Its addition to these melts increases the surface tension.

For possible industrial application it is better to use melts with the lower Nb₂O₅ content. In this case the

surface tension is lower. These results agree well with the viscosity investigation of this system [9].

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