Surface Tension of Melts of the System KF + K_2NbF_7 + Nb_2O_5

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The surface tension of the molten system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) up to $x_3 = 0.2$ has been investigated using the maximum bubble pressure method over the temperature range from 1133 K to 1233 K. The uncertainty of the surface tension measurement was estimated to be ±1.5%. On the basis of the data presented, the composition dependence of the surface tension and the surface tension excess were calculated.

Introduction

Niobium belongs to the refractory metals with wide industrial applications.[1] The system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) seems to be a part of a more complicated, promising system for electrochemical deposition of smooth and adherent niobium layers on metallic surfaces. Surface tension is also interesting from a theoretical point of view because a knowledge of this physicochemical property may contribute to the clarification of the structure of these melts.

The phase diagram of the system KF(1) + K_2NbF_7(2) has been studied in the past.[2−4] In this system, a congruently melting compound K_3NbF_8 whose melting point is in the temperature range from 1033 K to 1043 K is formed. This intermediate compound divides the system into two simple eutectic systems. The coordinates of the eutectic points according to different authors are in the range of $x_{2e'} = 0.265$, $T_{e'} = 992$ K and $x_{2e''} = 0.81$, $T_{e''} = 976$ K according to Kamenskaya et al.[2] McCawley et al.[3] reported $x_{2e'} = 0.25$, $T_{e'} = 997$ K, and for the second eutectic point, $x_{2e''} = 0.8$, $T_{e''} = 981$ K. The coordinates of eutectic points according to Mukhard et al.[4] are $x_{2e'} = 0.23$, $T_{e'} = 996$ K and $x_{2e''} = 0.8$, $T_{e''} = 979$ K.

In the present work, the surface tension of the ternary system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) up to $x_3 = 0.2$ has been measured, which is the experimentally attainable region of the system. The surface tension of this system could not be found in the literature. The results have been interpreted in terms of interactions of components leading to the formation of fluorooxoniobate complexes.

Experimental Section

The surface tension of the KF(1) + K_2NbF_7(2) + Nb_2O_5(3) 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 that served as an electrical contact to adjust the exact touch of the capillary with the liquid surface.

A Micromega ICN 77343C2 temperature controller was used to adjust the experimental temperature of the furnace using an additional Pt-Pt10Rh control thermocouple placed in the working shaft of the furnace. An MT-100 voltmeter was used for temperature measurements.

A platinum capillary with an outer diameter of 3 mm was used. To obtain precise results, the capillary tip was carefully machined. The orifice had to be as circular as possible, with a sharp conical edge. A precise inner diameter of the capillary is very important if accurate measurements are required. The actual capillary radius was calculated with respect to the actual experimental temperature in the furnace.

A special water-cooled furnace lid was used for the capillary support. A micrometric screw, fixed on the lid, determined the position for the exact touch of the capillary with the liquid surface and indicated the desired immersion depth with a standard uncertainty of $u_r = 0.01$ mm.

A Commet LB 1000 digital micromanometer with two measuring ranges, 200 Pa and 1000 Pa, was used for pressure determinations. This enabled us to measure the pressure with an uncertainty of $u_p = 1$ Pa. Nitrogen was used to form the bubbles and to maintain an inert atmosphere over the sample. The gas was slowly fed through the capillary during the experiment to avoid condensation in the upper part of the capillary. The nitrogen flow was adjusted using a fine needle valve. The rate of bubble formation was approximately 1 bubble in (20 to 30) s.

For the preparation of mixtures, the following chemicals were used: KF (Fluka), K_2NbF_7 (prepared in Apatity), and Nb_2O_5 (Aldrich), all of analytical-grade purity. KF was dried at 873 K for 2 h. K_2NbF_7 was dried in vacuum at 403 K for 1 day. All salt handling was done under a dry inert atmosphere in a glovebox, where the samples (the volume of one mixture was approximately 15 mL) were weighted in equivalent ratios of the particular components and subsequently mixed. The standard uncertainty in composition was $u_{xi} = 0.005$.

The surface tension γ may be calculated according to the equation[5]

$$\gamma = \frac{r}{2}(P_{\max} - gh\rho) \qquad (1)$$

where r is the capillary radius, $P_{\max}$ is the maximum bubble pressure when the bubble is a hemisphere with the radius equal to the radius of the capillary, g is the acceleration

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Table 1. Regression Coefficients *a* and *b* of the Temperature Dependence of the Surface Tension and Standard Deviation of Approximation (SD) of Individual Melts of the System KF(1) + K_2NbF_7(2) + Nb_2O_5(3)

x_1	x_2	x_3	*a*/ mN·m^{-1}	*b*/ mN·m^{-1}·K^{-1}	SD/ mN·m^{-1}	*T*/K
1.000	0.000	0.000	233.93	0.083	0.28	1152−1230
0.980	0.000	0.020	222.91	0.074	0.43	1137−1327
0.965	0.000	0.035	225.95	0.075	0.43	1133−1308
0.950	0.000	0.050	234.22	0.081	0.47	1125−1300
0.925	0.000	0.075	238.73	0.083	0.58	1107−1308
0.900	0.000	0.100	250.23	0.092	0.79	1145−1296
0.850	0.000	0.150	275.00	0.110	0.69	1181−1305
0.800	0.000	0.200	248.00	0.086	0.69	1181−1318
0.000	1.000	0.000	147.40	0.061	0.28	1031−1134
0.000	0.950	0.050	215.00	0.113	3.36	1070−1150
0.000	0.900	0.100	221.05	0.114	0.70	918−1066
0.000	0.850	0.150	240.00	0.125	1.74	948−1046
0.675	0.225	0.100	219.20	0.084	3.56	1155−1211
0.450	0.450	0.100	275.74	0.141	1.66	1149−1238
0.225	0.675	0.100	247.00	0.123	0.10	1081−1132
0.600	0.200	0.200	189.03	0.055	0.15	1122−1178
0.400	0.400	0.200	187.00	0.059	0.53	1118−1166
0.200	0.600	0.200	206.00	0.083	1.25	1105−1223

due to gravity, h is the depth of immersion of the capillary, and ρ is the density of the melt. However, there is also the possibility of calculating the surface tension of the liquid without the knowledge of the density of the melt. Eliminating the density, ρ, from eq 1 for two different immersion depths, we obtain the equation

$$\gamma = \frac{r}{2}\,\frac{P_{\max,1}h_2 - P_{\max,2}h_1}{h_2 - h_1} \qquad (2)$$

where $P_{\max,i}$ is the maximum bubble pressure at immersion depth h_i. Although the density data for the investigated melts were known, eq 2 was preferably used.

The measurement was carried out in the temperature interval of approximately (80 to 100) K starting 20 K above the temperature of primary crystallization. The surface tension measurement was performed at four different depths of immersion {usually (2, 3, 4, and 5) mm}, yielding six surface tension values for each temperature.

For measurement in the ternary system KF(1) + K_2NbF_7(2) + Nb_2O_5(3), cross sections with a constant content of niobium pentoxide (x_3 = 0.1 and 0.2) were chosen. In the boundary binary system KF(1) + Nb_2O_5(3), the figurative points with contents of x_3 = 2, 3.5, 5, 7.5, 10, 15, and 20 were selected. In the binary system K_2NbF_7(2) + Nb_2O_5(3), figurative points with contents of x_3 = 0.02, 0.035, 0.05, 0.075, 0.1, 0.15, and 0.2 were selected. The surface tension of the binary system KF + K_2NbF_7 has been already measured.[6]

In the surface tension measurements using the maximum bubble pressure method, several sources of errors may occur. As mentioned above, the exact machining of the capillary orifice is important. A deviation from the circular shape caused in our case an uncertainty of 0.5 mm. The determination of the immersion depth had an uncertainty of u_l = 0.01 mm. The standard uncertainty of the pressure measurement was u_p = 1 Pa. The standard deviations of the experimental data, based on the least-squares statistical analysis, were in the range of (0.28 to 3.56) mN·m^{-1}.

The experimental setup was checked by measuring the surface tension of pure molten sodium chloride. The comparison of the obtained data with those given by Janz et al.[7,8] is the following: for T = 1109 K, it is 111.43 mN·m^{-1}, compared with 111.3 mN·m^{-1} for T = 1110 K given in the literature.[8]

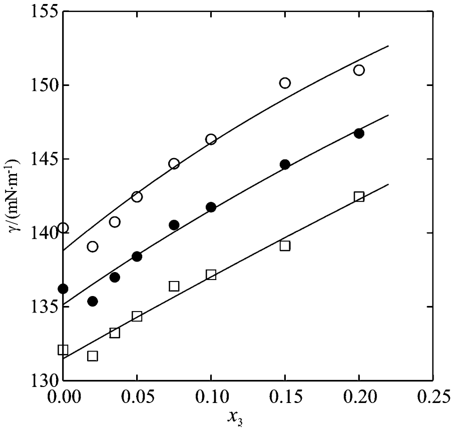

Figure 1. Surface tension in the system KF(1) + Nb_2O_5(3). ○, 1133 K; ●, 1183 K; □, 1233 K.

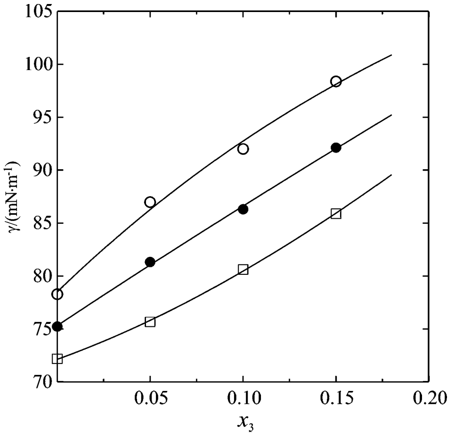

Figure 2. Surface tension in the system K_2NbF_7(2) + Nb_2O_5(3). ○, 1133 K; ●, 1183 K; □, 1233 K.

The temperature dependence of the surface tension was expressed by the linear equation

$$\gamma = a - bT \qquad (3)$$

where γ is the surface tension and T is the temperature. The values of constants a and b in eq 3, obtained from the linear regression analysis, together with the values of the standard deviations of approximation for the investigated KF(1) + K_2NbF_7(2) + Nb_2O_5(3) melts are given in Table 1. The experimental data for the system KF(1) + K_2NbF_7(2) were taken from previous work.[6] The original data is available as Supporting Information.

Results and Discussion

The concentration dependence of the surface tension of the binary systems KF(1) + Nb_2O_5(3) and K_2NbF_7(2) + Nb_2O_5(3) at temperatures of 1133 K, 1183 K, and 1233 K are shown in Figures 1 and 2, respectively. In both systems, the surface tension increases with increasing content of Nb_2O_5. The experimental data of the surface tension for both binaries were described by a polynomial fit curve.

To get some information on the structure of the melt, it is very important to define the course of the surface tension in the ideal solution. A general approach used for the variation of surface tension with composition was given by Guggenheim,[9] who stated that the surface tension of an ideal solution should follow the simple additivity law. For

Table 2. Surface Tension of Some Oxides Found in the Literature

oxide	T/K	γ/mN·m^{-1}	comment	ref
MgO	1573	620	extrapolated	Vadasz et al.[10]
ZnO	1573	748	extrapolated	Vadasz et al.[11]
CaO	1573	656	extrapolated	Vadasz et al.[11]
FeO_n	1673	584	wüstite	Boni and Derge[12]
FeO	1673	590	addition of Fe_2O_3	Okunev and Galimov[13]
FeO	1693	585		Janz[14]
FeO	1573	586	extrapolated	Vadasz et al.[11]
Al_2O_3	1573	400	extrapolated	Vadasz et al.[10]
Al_2O_3	2050	690	extrapolated	Kingery[15]
Fe_2O_3	1573	374	extrapolated	Vadasz et al.[11]
SiO_2	2073	307	extrapolated	Kingery[15]
SiO_2	1773	298		Janz[14]
SiO_2	1573	280	extrapolated	Vadasz et al.[10]
GeO_2	1473	253		Janz[14]
V_2O_5	1133	87		Janz[14]
P_2O_5	473	58		Janz[14]

the surface tension of the real ternary system, it can then be written

$$\gamma = \sum_{i=1}^{3}\gamma_i x_i + \sum_{\substack{i=1\\ i\neq j}}^{3}(x_i x_j \sum_{n=0}^{s} A_{nij} x_j^n) + x_1 x_2 x_3 \sum_{p,q=0}^{2} B_{pq} x_2^p\, x_3^q \qquad (4)$$

In eq 4, the γ_i's are the surface tensions of pure components, and the x_i's are their mole fractions in the mixture. Coefficients p and q are integers in the range of 0 to 2. The first term represents the contribution of pure compounds, the second one, the interactions in the binary systems, and the third one, the interactions of all three components.

The calculation of coefficients A_{nij} and B_{pq} for the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) was performed using multiple linear regression analysis, omitting the statistically nonimportant terms at the 0.99 confidence level. To calculate the surface tension and especially the surface tension excess of the ternary system, the values of the surface tension of the under-cooled liquid Nb_2O_5 at temperatures of 1133 K, 1183 K, and 1233 K have to be known. Unfortunately, the surface tension of Nb_2O_5 could not be found in the literature, thus it has to be estimated. Without introducing the surface tension values for Nb_2O_5, nonphysical and even negative values for the surface tension of Nb_2O_5 could be obtained.

Surface tension values of some oxides are given in Table 2. As can be seen from the Table, the surface tension of oxides decreases from approximately 600 mN·m^{-1} for divalent oxides to less than 100 mN·m^{-1} for pentavalent oxides. However, V_2O_5 and P_2O_5 do not belong to the refractory oxides, and for the surface tension of Nb_2O_5, values around 200 mN·m^{-1} could be expected. Therefore, values of 200, 190, and 180 mN·m^{-1} were chosen at temperatures of 1133, 1183, and 1233.15 K, respectively.

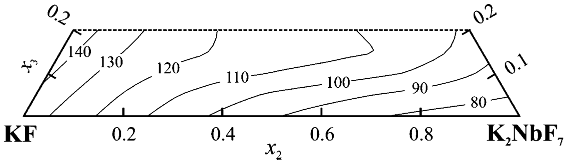

Figure 3. Surface tension of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at a temperature of 1183 K. Values are in mN·m^{-1}.

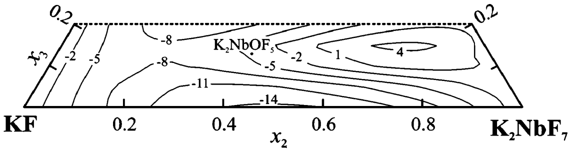

Figure 4. Surface tension excess of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at a temperature of 1183 K. Values are in mN·m^{-1}.

For the concentration dependence of the surface tension of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3), the following final equation was then obtained:

$$\gamma = \gamma_1 x_1 + \gamma_2 x_2 + \gamma_3 x_3 + x_1 x_2 A_{012} + x_1 x_2 x_3 B_{00} + x_1 {x_2}^2 {x_3}^2 B_{01} + x_1 {x_2}^2 {x_3}^3 B_{12} \qquad (5)$$

The calculated values of the surface tension of pure components, γ_i, coefficients A_{nij} and B_{pq}, and the standard deviations of approximation, SD, for three chosen temperatures 1133 K, 1183 K, and 1233 K are given in Table 3.

In eq 5, the statistically important binary interaction was found only in the subsystem KF + K_2NbF_7. This interaction obviously corresponds to the formation of the complex anion $[NbF_8]^{3-}$, which is in agreement with the phase equilibrium investigation of this system.[2-4]

The surface tension of the ternary system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at a temperature of 1183 K is shown in Figure 3. It is obvious that the surface tension decreases from KF through K_2NbF_7 to Nb_2O_5. Statistically important ternary interactions found in the ternary system (cf. the last three terms on the right side of eq 5) probably refer to the formation of fluorooxo complex species in the system.

The surface tension excess of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) is shown in Figure 4. There is a broad area of negative surface tension excess, whose minimum is located near the figurative point of the fluorooxo complex compound K_2NbOF_5. Negative surface excess indicates the surface adsorption of species that are more covalent in character, which are concentrated on the melt surface and become surface-active. Therefore, the strongest covalent species will influence the composition dependence of the surface tension. Such a species is probably the fluorooxo complex species $[NbOF_5]^{2-}$, whose presence in the LiF + KF + K_2NbF_7 + K_2O melts was suggested by Van et al.[16] on the basis of voltammetric, chronopotentiometric, and IR spectroscopic studies.

Table 3. Calculated Values of the Surface Tension of Pure Components γ_i and Coefficients A_{nij} and B_{pq} and Standard Deviations of the Fit, SD, for the System KF(1) + K_2NbF_7(2) + Nb_2O_5(3)

	temperature		
coefficient	1133.15 K	1183.15 K	1233.15 K
γ_1/mN·m^{-1}	139.5 ± 0.5	135.8 ± 0.4	132.0 ± 0.5
γ_2/mN·m^{-1}	79.7 ± 0.6	75.0 ± 0.5	70.4 ± 0.7
γ_3/mN·m^{-1}	200.2 ± 1.1	190.1 ± 0.9	179.7 ± 1.2
A_{012}/mN·m^{-1}	−49.3 ± 3.7	−56.6 ± 2.9	−65.9 ± 3.8
B_{00}/mN·m^{-1}	−(4.07 ± 0.68) × 10^{2}	−(2.65 ± 0.53) × 10^{2}	
B_{01}/mN·m^{-1}	(2.90 ± 0.25)1 × 10^{4}	(2.37 ± 0.20) × 10^{4}	(1.54 ± 0.21) × 10^{4}
B_{12}/mN·m^{-1}	−(1.23 ± 0.11) × 10^{5}	−(9.75 ± 0.84) × 10^{4}	−(6.43 ± 1.06) × 10^{4}
SD/mN·m^{-1}	1.2	0.9	1.3

Supporting Information Available:

Original data for the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3). This material is available free of charge via the Internet at http://pubs.acs.org.

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