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Density of the System KF + K_2NbF_7 + Nb_2O_5

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The density of melts of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) up to 20 mol % Nb_2O_5 has been measured using the Archimedean method. On the basis of the measured density values, the molar volumes of the melts and partial molar volumes of Nb_2O_5 in different binaries were calculated. The density in the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) increases from KF through K_2NbF_7 to Nb_2O_5. In all three binary systems, some interactions have been determined.

Introduction

The molten system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) is interesting from both the theoretical and technological points of view. The melts of this system are promising electrolytes for the electrochemical deposition of smooth and adherent niobium layers on a metallic base.[1]

A crucial problem in niobium deposition in molten salts is the presence of oxygen in the electrolyte because it is extremely difficult to prepare a melt free of O^{2-} ions, especially for industrial applications. Formerly, it was assumed that the presence of O^{2-} ions may lower the quality of Nb coatings or even prevent the formation of Nb coatings. The influence of O^{2-} ions on the reduction mechanism of Nb and the formation of niobium−oxofluoride complexes in the melt has been studied elsewhere.[2−6]

Though electrolyte impurities, such as oxides, hydroxides, chlorides, bromides and iodides, were formerly considered to be undesirable,[7] later it was found that the presence of small amounts of oxides in the melt increases the current efficiency during electrolysis. Christensen et al.[4] obtained the highest current efficiency in melts with O/Nb molar ratios in the range of $1 < n_O/n_{Nb(V)} < 0.5$. The presence of oxide in the melt causes the formation of various oxofluoro complexes of niobium. It was shown that relatively pure Nb coatings can be obtained from FLINAK melts if $n_O/n_{Nb(V)}$ is less than 1. However, even a small number of O^{2-} ions can entirely change the mechanism of Nb deposition[2,3] depending on the types of niobium−oxofluorides formed in the melt.

The phase diagram[9−11] and the density[12] of the system KF(1) + K_2NbF_7(2) have been studied. The congruently melting compound K_3NbF_8 is formed in the system. Its melting temperature differs in the range of 760−770 °C.[9−11] The phase diagram of binary systems KF(1) + Nb_2O_5(3)[8,13,14] and K_2NbF_7(2) + Nb_2O_5(3)[14] and ternary system KF(1) + K_2NbF_7(2) + Nb_2O_5(3)[14] have been determined as well.

In the present work, the densities of binary systems K_2NbF_7(2) + Nb_2O_5(3) and KF(1) + Nb_2O_5(3) and ternary system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) have been measured. On the basis of the obtained data, we calculated the molar volumes of melts and partial molar volume of Nb_2O_5 in different binary systems. Results have been interpreted in terms of the interaction of components.

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Experimental Section

The density of the investigated melts was measured using the Archimedean method. A platinum vessel suspended on a platinum wire (in the leading tube) was used as the measuring body. After the sample melted, the measuring body was immersed in the melt, and the surface of the melt was always kept 2 mm over the top of the sphere. The depth of immersion was continuously monitored and controlled using the electrical contact. The dependence of the vessel volume on temperature was determined by calibration using molten NaCl and KF. For the measuring device control and the evaluation of experimental data, an on-line PC was used. A detailed description of the measuring device used is given elsewhere.[15]

For the preparation of the samples, the following chemicals were used: KF (Lachema, 99%), Nb_2O_5 (Aldrich, 99.9%), and K_2NbF_7 (prepared in Apatity, min. 99%). KF and K_2NbF_7 were dried in vacuum at 180 °C for 24 h. Handling of all salts was done in a glovebox under a dry, inert atmosphere.

The measurements were carried out in the temperature interval of approximately (100 to 150) °C. The samples were heated to ∼170 °C above the primary crystallization temperature. Then the first measurement in the cooling direction was performed until reaching a temperature of ∼20 °C above the temperature of primary crystallization. The second measurement was done in the heating direction, and the third measurement was done again in the cooling direction. The density results were automatically registered by the measuring device every 30 s for each melt. The densities were measured for each system up to 20 mol % of Nb_2O_5 because of the solubility of Nb_2O_5 in the temperature range interesting for technical applications.

The temperature dependence of the density was expressed in the form of the linear equation

$$\rho/\mathrm{g\cdot cm^{-3}} = a - bt/{}^{\circ}\mathrm{C} \qquad (1)$$

where ρ is the density and t is the temperature. For each measurement, one heating and two cooling curves were recorded. However, in some cases the last cooling run or last cooling and heating runs were useless. The reasons are quite unclear. The evaporation of the sample seems to

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Table 1. Regression Coefficients *a* and *b* and Standard Deviations of the Density of the Investigated System KF(1) + K_2NbF_7(2) + Nb_2O_5(3) and Mean Regression Coefficients *a* and *b* and the Standard Deviations Used for Equation 1[a]

x_1	x_2	x_3	a / $g \cdot cm^{-3}$	$\bar{a}$	$b \times 10^4$ / $g \cdot cm^{-3} \cdot {}^\circ C$	$\bar{b} \times 10^4$	SD × 10^4	SD × 10^4	t/°C
0.980	0.000	0.020	2.5497	2.5405	6.5028	6.3796	4.88	5.51	860−1000(c)
0.980	0.000	0.020	2.5397		6.3269		7.22		860−1000(h)
0.980	0.000	0.020	2.5320		6.3089		4.44		860−1000(c)
0.965	0.000	0.035	2.6484	2.6336	6.6194	6.4333	1.78	3.93	850−1000(c)
0.965	0.000	0.035	2.6291		6.3379		6.96		850−1000(h)
0.965	0.000	0.035	2.6233		6.3426		3.05		850−1000(c)
0.950	0.000	0.050	2.8731	2.8376	8.0579	7.4258	4.18	3.86	850−1000(c)
0.950	0.000	0.050	2.7693		6.5906		4.05		850−1000(h)
0.950	0.000	0.050	2.8704		7.6290		3.33		850−1000(c)
0.925	0.000	0.075	2.9855	2.9266	8.3204	7.5322	5.64	3.77	825−975(c)
0.925	0.000	0.075	2.8532		6.6795		2.42		825−975(h)
0.925	0.000	0.075	2.9412		7.5967		3.25		825−975(c)
0.900	0.000	0.100	2.9294	2.9762	6.8290	7.1219	3.50	3.10	870−1000(c)
0.900	0.000	0.100	3.0262		7.4996		3.65		870−1000(h)
0.900	0.000	0.100	2.9731		7.0372		2.16		870−1000(c)
0.850	0.000	0.150	3.2868	3.2323	8.2561	7.5758	10.10	8.73	900−1000(c)
0.850	0.000	0.150	3.2135		7.2916		11.20		900−1000(h)
0.850	0.000	0.150	3.1968		7.1796		4.88		900−1000(c)
0.800	0.000	0.200	3.6117	3.4699	9.3346	7.8652	6.55	4.89	910−1050(c)
0.800	0.000	0.200	3.3282		6.3957		3.22		910−1050(h)
0.000	0.950	0.050	3.2290	3.2238	10.7713	10.6473	3.66	3.66	730−870(c)
0.000	0.950	0.050	3.2186		10.5232		3.66		730−870(h)
0.000	0.900	0.100	3.2130	3.2215	10.8350	10.8606	3.24	3.24	770−650(c)
0.000	0.900	0.100	3.2301		10.8862		3.24		770−650(c)
0.000	0.850	0.150	3.1522	3.1755	10.3288	10.5402	8.95	8.95	680−720(c)
0.000	0.850	0.150	3.1988		10.7515		8.95		680−720(c)
0.000	0.800	0.200	3.2973	3.2973	12.1207	12.1207	25.30	25.30	550−620(c)
0.675	0.225	0.100	2.8248	2.7801	5.6944	5.2003	4.27	3.03	850−950(c)
0.675	0.225	0.100	2.8158		5.5466		1.64		890−930(h)
0.675	0.225	0.100	2.6998		4.3599		3.20		850−950(c)
0.450	0.450	0.100	3.0622	3.0464	7.6378	7.3821	4.96	4.61	760−910(c)
0.450	0.450	0.100	3.0307		7.1264		4.25		760−860(c)
0.225	0.675	0.100	3.0078	3.0234	7.0145	7.2772	5.54	5.07	730−830(c)
0.225	0.675	0.100	3.0390		7.5398		4.60		730−831(c)
0.600	0.200	0.200	3.1000	3.1000	5.6805	5.6805	8.01	8.01	850−960(c)
0.400	0.400	0.200	3.1861	3.1861	7.1274	7.1274	7.80	7.80	770−900(c)
0.200	0.600	0.200	3.9149	3.9149	17.4681	17.4681	14.10	14.10	745−760(c)

[a] c − cooling; h − heating.

be one of the reasons. Even a small amount of condensed vapor can result in friction between the platinum wire (on which the measuring body was suspended) and leading tube. For each errorless curve, coefficients *a* and *b* were obtained. The values of constants *a* and *b* together with the standard deviations of approximations, obtained by the linear regression analysis of the experimentally obtained data, are given in Table 1. The results of measurements at 850 °C, 900 °C, and 950 °C are summarized in Table 2.

Results and Discussion

System KF(1) + Nb_2O_5(3). The density of the system KF(1) + Nb_2O_5(3) is shown in Figure 1. The density increases with increasing content of Nb_2O_5. All three values of the density were averaged for each composition. The concentration dependence of the molar volume of this system at 900 °C can be described by the equation

$$V/\mathrm{cm^3 \cdot mol^{-1}} = (30.95 + 27.15x_3)$$

$$\mathrm{SD} = 0.13\ \mathrm{cm^3 \cdot mol^{-1}} \quad (2)$$

By differentiating eq 2 according to x_3 and introducing the result into the equation

$$\bar{V}_3 = V + x_1\left(\frac{\partial V}{\partial x_3}\right) \quad (3)$$

we can obtain the partial molar volume of Nb_2O_5 in the form

$$\bar{V}_3/\mathrm{cm^3 \cdot mol^{-1}} = 58.08 \pm 0.10 \quad (4)$$

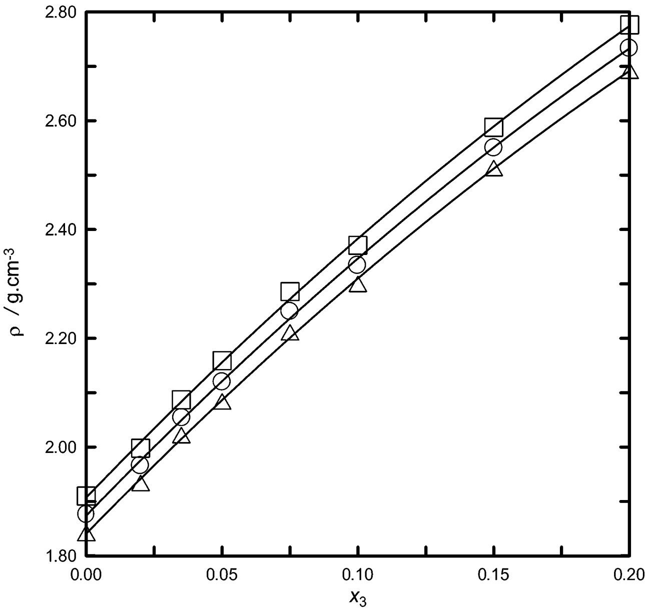

Figure 1. Density, ρ, of the system KF(1) + Nb_2O_5(3). □, 850 °C; ○, 900 °C; △, 950 °C.

Table 2. Calculated Data for the Density of the Molten System KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at 850 °C, 900 °C, and 950 °C

			ρ/g·cm^{-3}		
x_1	x_2	x_3	850 °C	900 °C	950 °C
0.980	0.000	0.020	1.9969	1.9663	1.9344
0.965	0.000	0.035	2.0857	2.0546	2.0224
0.950	0.000	0.050	2.1882	2.1693	2.1321
0.925	0.000	0.075	2.2783	2.2487	2.2111
0.900	0.000	0.100	2.3490	2.3352	2.2996
0.850	0.000	0.150	2.5850	2.5505	2.5126
0.800	0.000	0.200	2.8182	2.7620	2.7227
0.000	0.950	0.050	2.3135	2.2656	2.2123
0.000	0.900	0.100	2.2920	2.2441	2.1898
0.000	0.850	0.150	2.2743	2.2269	2.1742
0.000	0.800	0.200	2.2671	2.2671	2.2671
0.675	0.225	0.100	2.3408	2.3121	2.2861
0.450	0.450	0.100	2.4130	2.3820	2.3451
0.225	0.675	0.100	2.4116	2.3685	2.3321
0.600	0.200	0.200	2.6172	2.6172	2.6172
0.400	0.400	0.200	2.5802	2.5802	2.5802
0.200	0.600	0.200	2.4301	2.4301	2.4301

As can be seen, no dependence on KF was obtained, and the partial molar volume of Nb_2O_5 represents the molar volume of Nb_2O_5, which means that the volume properties of the above binary behave ideally in the composition range up to 20 mol % Nb_2O_5. However, it does not mean that any reactions take place in this system.

System K_2NbF_7(2) + Nb_2O_5(3). The density of the system K_2NbF_7(2) + Nb_2O_5(3) is shown in Figure 2. The molar volumes have been calculated from the first cooling values of the densities because after the second heating of the sample slight evaporation was detected. The density of the system K_2NbF_7(2) + Nb_2O_5(3) decreases with increasing content of Nb_2O_5. The concentration dependence of the molar volume at 900 °C can be described by the equation

$$V/\text{cm}^3\cdot\text{mol}^{-1} = (132.56 + 23.88x_3 - 76.75{x_3}^2) \qquad \text{SD} = 0.20\ \text{cm}^3\cdot\text{mol}^{-1} \tag{5}$$

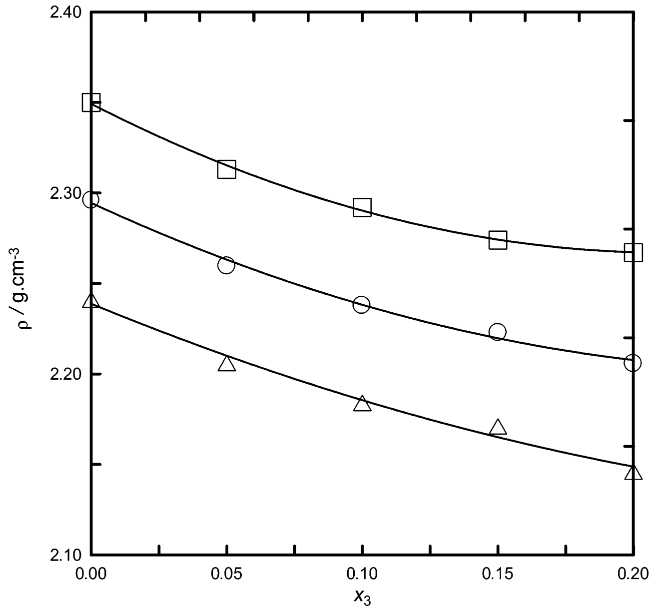

Figure 2. Density, ρ, of the system K_2NbF_7(2) + Nb_2O_5(3). □, 850 °C; ○, 900 °C; △, 950 °C.

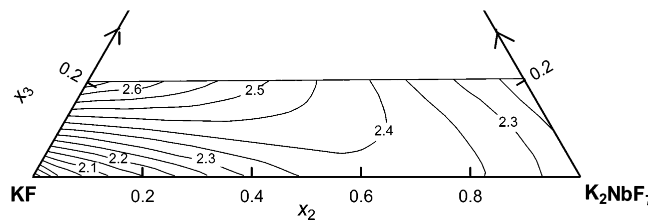

Figure 3. Density, ρ, of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at 900 °C. Values are in g·cm^{-3}.

The partial molar volume of Nb_2O_5 can be described by the equation

$$\bar{V}_3/\text{cm}^3\cdot\text{mol}^{-1} = (79.68 + 76.75{x_2}^2) \tag{6}$$

and for $x_2 \rightarrow 1$ the partial molar volume of Nb_2O_5 has the value of $\bar{V}_3$ = (156.43 ± 0.22) cm^3·mol^{-1}. In this binary system, the value of the partial molar volume of Nb_2O_5 is considerably higher than in the previous system. Moreover, the ideal behavior of the volume properties can be excluded here, probably because of the formation of more voluminous species.

System KF(1) + K_2NbF_7(2) + Nb_2O_5(3). The density of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) is shown in Figure 3. The density in the system increases from KF through K_2NbF_7 to Nb_2O_5. Generally, the dependence of the molar volume of the ternary system on composition at constant temperature can be described by the Redlich–Kister-type equation

$$V = \sum_{i=1}^{3} x_i V_i + \sum_{i \neq j}^{3} x_i x_j \sum_{n=0}^{k} A_{nij} x_j^n + B x_1^p x_2^q x_3^r \tag{7}$$

where p, q, r, and n are adjustable integers. The first term represents ideal behavior, the second one describes the binary interactions, and the third one represents the interaction of all three components.

In our case, constants V_i, A_{nij}, and B in eq 7 were calculated using multiple linear regression analysis omit-

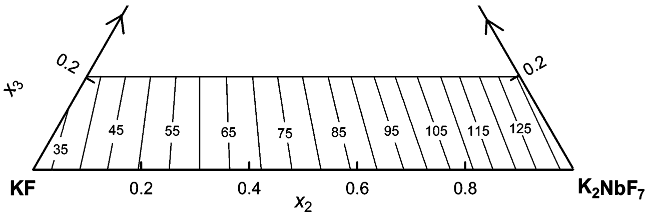

Figure 4. Molar volume, V_m, of KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at 900 °C. Values are in $cm^3 \cdot mol^{-1}$.

Table 3. Calculated Coefficients V_i and A_{nij} and the Standard Deviations of the Density of the System KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at Different Temperatures

coefficient	t/°C		
g·mol^{-3}	850	900	950
V_1	30.69 ± 0.34	31.25 ± 0.38	31.83 ± 0.43
V_2	131.73 ± 1.69	134.80 ± 1.88	138.01 ± 2.16
V_3	110.30 ± 2.12	116.17 ± 2.43	120.79 ± 2.84
A_{112}	−47.73 ± 9.28	−53.64 ± 10.28	−60.06 ± 11.82
A_{023}	8.30 ± 2.10	6.75 ± 2.31	6.93 ± 2.58
A_{013}	−65.20 ± 4.67	−72.33 ± 5.21	−77.86 ± 6.00
SD	0.93	1.03	1.18

ting the statistically nonimportant terms on the 0.99 confidence level. The following final equation was obtained:

$$V/\text{cm}^3\cdot\text{mol}^{-1} = x_1V_1 + x_2V_2 + x_3V_3 + A_{112}x_1x_2^2 + A_{023}x_2x_3 + A_{013}x_1x_3 \quad (8)$$

The values of constants V_i and A_{nij} in eq 8 as well as the standard deviations of approximation for temperatures 850 °C, 900 °C, and 950 °C are given in Table 3.

The molar volume of the system KF(1) + K_2NbF_7(2) + Nb_2O_5(3) at the temperature of 900 °C is shown in Figure 4.

From the parameters of eq 8, the molar volumes of the system (1/1) KF/K_2NbF_7 + Nb_2O_5 were calculated at 900 °C up to 20 mol % Nb_2O_5 with a step of 1 mol %. Let us define the system (1/1) KF/K_2NbF_7 to be K_3NbF_8(4) and its molar fraction to be x_4. Then the equation representing the dependence of the molar volume on the composition of Nb_2O_5 in the system K_3NbF_8(4) + Nb_2O_5(3) was calculated:

$$V/\text{cm}^3\cdot\text{mol}^{-1} = (74.48 + 22.16x_3 + 14.69x_3^2)$$
$$\text{SD}/\text{cm}^3\cdot\text{mol}^{-1} = 1.25 \times 10^{-3} \quad (9)$$

Then the partial molar volume of Nb_2O_5 can be described by the equation

$$\bar{V}_3/\text{cm}^3\cdot\text{mol}^{-1} = (111.33 - 14.69x_4^2) \quad (10)$$

and for $x_4 \rightarrow 1$ the partial molar volume of Nb_2O_5 has the value of $\bar{V}_3 = 96.64$ $cm^3 \cdot mol^{-1}$. In this binary system, the value of the partial molar volume of Nb_2O_5 is considerably higher than in the first one but lower as in the second one. It can be said that the partial molar volume increase in the series KF(1) + Nb_2O_5(3) < K_3NbF_8(4) + Nb_2O_5(3) < K_2NbF_7(2) + Nb_2O_5(3).

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