Chemistry of Niobium Chlorides in the CsCl–NaCl Eutectic Melt. 3. Solubility of Nb$_2$O$_5$ and SrO in the CsCl–NaCl Eutectic Melt with Additions of NbCl$_x$ (x=4, 5)

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The reactions between NbCl$_x$ (x = 4, 5) and Nb$_2$O$_5$(s) or SrO(s) have been studied in the eutectic NaCl–CsCl melt at 650°C. Samples were taken from melts containing NbCl$_x$ in equilibrium with these oxides and analysed for oxygen, niobium and, if present, strontium. The analysis indicated that NbCl$_5$ reacted with Nb$_2$O$_5$(s) according to the reactions $3NbCl_6^- + Nb_2O_5(s) + 7Cl^- = 5NbOCl_5^{2-}$ and $NbOCl_5^{2-} + Nb_2O_5(s) + (3x - 5)Cl^- = 3NbO_2Cl_x^{(x-1)-}$. The first reaction was completely shifted to the right. The equilibrium established for the second reaction had an equilibrium constant (pure component standard rate) $K = 5 \times 10^{-5}$.

NbCl$_4$ reacted with Nb$_2$O$_5$ according to the reaction $3NbCl_6^{2-} + Nb_2O_5(s) = 3NbOCl_x^{(x-2)-} + 2NbOCl_5^{2-} + (8 - 3x)Cl^-$. The NbOCl$_5^{2-}$ formed in this reaction reacted further with Nb$_2$O$_5$(s). In the presence of an excess of SrO(s), Nb(IV) and Nb(V) precipitated probably as NbO$_2$(s) and MNbO$_3$(s) (M = Na, Cs, $\frac{1}{2}$ Sr), respectively.

Previously, Raman spectroscopic studies[1] of the system CsCl–NbCl$_5$–NbOCl$_3$, absorption spectroscopic studies[2] of niobium chlorides and oxochlorides in molten alkali chloride melts, EMF measurements[3] of NbCl$_3$, and voltammetric studies[4] of niobium chlorides and oxochlorides in the CsCl–NaCl eutectic melt have been reported. In this paper we focus on the reactions between NbCl$_x$ (x = 4, 5) and Nb$_2$O$_5$ or SrO in the CsCl–NaCl eutectic at 650°C. Since NbCl$_2$ precipitates in the presence of oxides[2] and uncertainties are connected with the stability of NbCl$_3$ in alkali chloride melts at concentrations above 0.2 mol%,[3] these niobium chlorides have not been studied. In the early sixties Mellors and Senderoff[5] concluded that melts used for the electrodeposition of high-quality niobium should be free from oxides. Until recently, this conclusion has not been questioned. Christensen et al.[6] found that a small amount of oxide in LiF–NaF–KF eutectic melts containing niobium ions in equilibrium with niobium metal improved the current efficiency of the deposition reaction. Moreover, dense and coherent niobium metal deposits were obtained using the CsCl–NaCl eutectic melt[4] containing niobium chlorides and oxochlorides. The properties of dissolved niobium oxochlorides in melts used for electrolysis of niobium are therefore of interest. Picard and Bocage[7] have prepared a potential–

oxoacidity diagram describing the relation between the oxide activity and the reduction potentials for various niobium chlorides and oxides in the LiCl–KCl eutectic at 450°C. The diagram shows a strong influence of the oxide activity on the reduction potentials of the various niobium species. They have, however, not considered niobium oxochlorides in their work. Nb$_2$O$_5$ is an oxide with a very low solubility[7] in pure alkali chloride melts. SrO is considerably more basic than Nb$_2$O$_5$ and has a solubility of 10$^{-4.1}$ mol% in the NaCl–KCl eutectic at 700°C.[8] The solubility of Nb$_2$O$_5$ and SrO in alkali chloride melts containing Nb(V) and Nb(IV) chlorides will give information about the complex forming ability of these highly charged ions. The motivation for the present work is therefore to improve the understanding of the behaviour of niobium oxochlorides in molten alkali chlorides.

Experimental

The chemicals used and purification procedures are given in Table 1. To avoid moisture and oxygen from the atmosphere, the experiments and handling of the purified salts were carried out in a glove box with water content <1 ppm and oxygen content <5 ppm. A glassy carbon crucible (Carbone Lorraine V25, ∅ 40 mm) placed inside a fused silica tube served as melt container. The cell was

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Table 1. Producers and purification procedures of chemicals used.

Chemical producer and purification	
CsCl	Fluka > 99.9%, dried with HCl and recrystallised.
NaCl	Merck p.a., recrystallised.
NbCl$_5$	Alfa grade 1, resublimed under vacuum.
NbCl$_4$	Made from sublimed NbCl$_5$ (Alfa grade 1) and Nb (Alfa > 99.9%) according to Schäfer and Dohman.[10] The purity of the NbCl$_4$ made was > 98%.
Nb$_2$O$_5$	Alfa 88291 > 99.9%, dried under vacuum.
SrO	Made from SrCO$_3$ (Alfa > 99.9%) by heating to 900°C under vacuum. The purity of the SrO made was > 99%.

placed in a Kanthal-wound vertical and tubular furnace controlled with an Eurotherm controller. The furnace was mounted under the glove box in such a way that the experimental cell could be handled from inside the box. The temperature in the melt was measured with a calibrated thermocouple (Pt/Pt, 10% Rh), and the temperature in the cell was stable within ± 2°C. Since Nb(V) chloride melts are able to oxidise gold,[9] and therefore probably also platinum, the wires of the thermocouple were only immersed into the melt for times necessary to read the temperature and lifted well above the melt between measurements. Radiation shields made of alsint discs were placed above the crucible to ensure low-temperature gradients around the crucible. The alsint discs had two holes, one for the thermocouple and one for fused silica tubes to allow addition of salts and removal of melt samples. The fused silica tubes for melt sampling were fitted with a quartz sinter (pore size 15–90 μm) at the bottom to avoid solid particles from entering the sampling tube. The tube was only immersed in the melt during extraction of samples (1–2 min).

The vapour pressure of pure NbCl$_5$ at 650°C is several atmospheres. To avoid losses of NbCl$_5$ by evaporation during addition of the salt to the melt, CsNbCl$_6$ was prepared in a sealed quartz cell by carefully melting and mixing CsCl and NbCl$_5$. This salt was then added to the melt to change the melt composition.

A total of four experiments were run. Each experiment started with 30–40 g of the pure NaCl–CsCl eutectic. In experiments with melts saturated with Nb$_2$O$_5$(s) or SrO(s), excess oxide was added to the eutectic. 24 h after addition, samples were extracted and analysed to check the solubility of the oxides in the eutectic. Then carefully weighed amounts of NbCl$_4$ or CsNbCl$_6$ were added. NbCl$_4$ and SrO(s) were added simultaneously in the experiment when a 1:1 molar ratio between SrO and NbCl$_4$ was studied. When the melt had equilibrated (about 24 h after addition), a sample of typically 2 g was extracted from the melt and weighed. The addition and sampling procedure was repeated until about 10 mol% niobium chloride had been added. For each experiment the pure CsCl–NaCl eutectic was analysed as previously de-

scribed.[3] The oxide content in the eutectic was below 10^{-4} mol%. The oxide content in the other samples was analysed with a LECO TC-436 oxide analyser equipped with EF-500 furnace unit. The LECO oxide analysis is done by heating the sample with carbon up to 2800°C for a short time period. The oxide reacts to CO(g), which is then catalytically converted into CO$_2$(g). The CO$_2$ is analysed using IR spectroscopy. The samples were weighed in the glove box, sealed in tin capsules and transferred to the LECO analyser. Thus, the samples were isolated from moisture and oxygen. Niobium and strontium analyses were carried out on an ICP atomic emission spectrophotometer (Jerryl Ash Atomscan 16).

Results

The concentrations of oxygen and niobium in the melts in the four series of experiments are given in Table 2. Figure 1 shows a plot of the mole fraction of niobium versus the mole fraction of oxide in a melt containing excess Nb$_2$O$_5$ to which CsNbCl$_6$ was added. The oxide content in the melt increased linearly with the amount of Nb(V) chloride in the melt. The oxide to niobium ratios, x_O/x_{Nb}, in all samples were 1.19. The molten samples showed the transparent yellow colour of NbOCl$_3$ in CsCl.[1] Figure 2 shows a plot of the mole fraction of niobium added versus the mole fraction of oxide when CsNbCl$_6$ was added to a melt containing an excess of SrO. The oxide content in the melt was much lower than, and almost independent of, the amount of CsNbCl$_6$ added. The molten samples were colourless and transparent, and the amounts of niobium in the melt samples were below in the detection limit of the analysis (0.0001 mol%). The oxide to niobium ratio in a melt containing an excess of Nb$_2$O$_5$ to which NbCl$_4$ was added was also slightly higher than one, as shown in Fig. 3. The oxide content increased linearly with the amount of niobium in the melt. The molten samples had a strong, green colour. Figure 4 shows a plot of the mole fraction of niobium versus the mole fraction of oxide in a melt to which NbCl$_4$ and SrO were added in a 1:1 molar ratio. The regression line in the figure has a slope of 1. The colour of this melt was also green. An excess amount of SrO was added to the strongly green-coloured melt containing almost 6 mol% niobium. After 24 h a colourless and transparent sample of the melt was taken, and the niobium content in the sample was below the detection limit of the analysis.

Discussion

The reaction

$$3NbCl_6^- + Nb_2O_5(s) + 7Cl^- = 5NbOCl_5^{2-} \qquad (1)$$
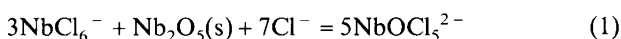
has been shown to take place in molten CsCl when NbCl$_5$ is dilute.[1] The Gibb's free energy change for the reaction

Table 2. Concentrations of oxygen and niobium in the various CsCl–NaCl eutectic melts containing $NbCl_x$ (x=4, 5) and Nb_2O_5(s) or SrO(s) equilibrated at 650°C.

Experiment	Sample/(mol% O/mol% Nb)[a]									
	1[b]	2[c]	3	4	5	6	7	8	9	10
CsNbCl₆–Nb₂O₅(satd.)	$<10^{-4}$/0	$<10^{-3}/<10^{-3}$	0.75/0.63	2.19/1.84	5.07/4.27	7.87/6.63	10.64/8.96			
CsNbCl₆–SrO(satd.)	$<10^{-4}$/0	0.41/0	0.40/0.34	0.38/1.03	0.06/2.30	0.10/3.55	0.20/4.76	0.20/5.93	0.22/7.15	0.11/8.50
NbCl₄–Nb₂O₅(satd.)	$<10^{-4}$/0	$<10^{-3}/<10^{-3}$	0.83/0.65	2.20/1.88	4.94/4.48	4.90/4.59	6.12/5.75	6.93/6.67	8.08/7.48	8.85/8.25
NbCl₄–SrO 1:1	$<10^{-4}$/0		0.50/0.51	1.01/0.95	1.95/2.00	3.89/3.95	5.56/5.54	8.54/8.58		

[a] The appendix explains how these data were obtained from chemical analysis. [b] Pure CsCl–NaCl eutectic. [c] CsCl–NaCl eutectic containing Nb₂O₅(s) or SrO(s) (no niobium chloride added).
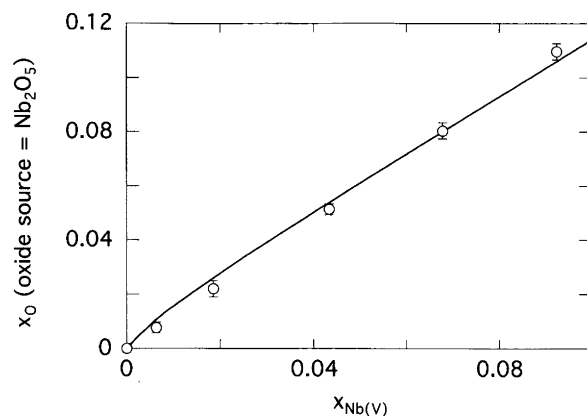
Fig. 1. Mole fraction of oxide plotted versus mole fraction of niobium in a NaCl–CsCl eutectic melt saturated with Nb₂O₅(s) at 650°C. To change the Nb(V) concentration CsNbCl₆ was added. The error bars are based on the standard deviation of the oxide analysis data. The full line represents x_O/x_{Nb} assuming that the stoichiometric equilibrium constant of reaction (3) $K' = 5 \times 10^{-5}$ and $x_O/x_{Nb} = (x_{NbOCl_5^{2-}} + 2x_{NbO_2Cl_x^{(x-1)-}})/(x_{NbOCl_5^{2-}} + x_{NbO_2Cl_x^{(x-1)-}})$.
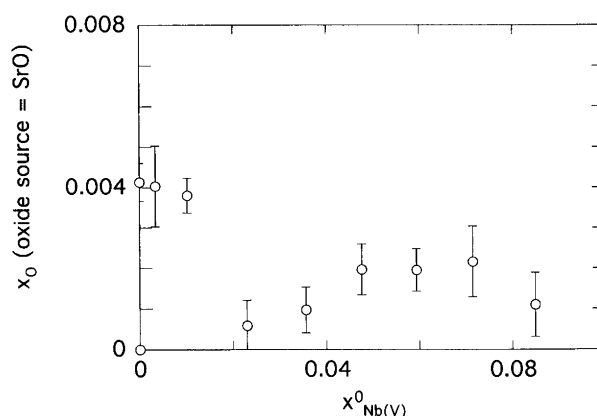

Fig. 2. Mole fraction of dissolved oxide plotted versus mole fraction of added niobium in a NaCl–CsCl eutectic melt saturated with SrO(s) at 650°C. To change the Nb(V) concentration CsNbCl₆ was added. The error bars are based on the standard deviation of the oxide analysis data.

$$3NbCl_5(g) + Nb_2O_5(s) = 5NbOCl_3(g) \tag{2}$$

at 650°C is -142 kJ mol⁻¹.[11] It is therefore reasonable to believe that reaction (1) probably also takes place in the molten CsCl–NaCl eutectic at 650°C. Since the molar ratio x_O/x_{Nb} always was 1.19 when Nb(V) was added to the CsCl–NaCl eutectic containing excess Nb₂O₅(s), more than the stoichiometric amount of Nb₂O₅ according to reaction (1) is dissolved. von Barner et al.[12] have shown that niobium oxofluoride ions of the type $NbO_2F_x^{(x-1)-}$ exist in the molten LiF–NaF–KF eutectic when the oxide to niobium molar ratio is larger than one. Moreover, voltammograms of a CsCl–NaCl eutectic containing $NbOCl_5^{2-}$ saturated with Nb₂O₅(s) showed peaks belonging to a product from the reaction between
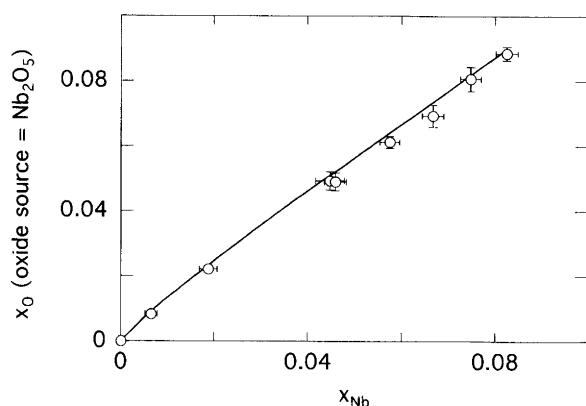
Fig. 3. Mole fraction of oxide plotted versus mole fraction of niobium in a NaCl–CsCl eutectic melt saturated with $Nb_2O_5(s)$ at 650°C to which $NbCl_4$ was added. The error bars are based on the standard deviations in the analysis of oxide and niobium. The full line represents x_O/x_{Nb} assuming that the stoichiometric equilibrium constant of reaction (3) $K' = 5 \times 10^{-5}$ and $x_O/x_{Nb} = (x_{NbOCl_x^{(x-2)-}} + x_{NbOCl_5^{2-}} + 2x_{NbO_2Cl_x^{(x-1)-}})/(x_{NbOCl_x^{(x-2)-}} + x_{NbOCl_5^{2-}} + x_{NbO_2Cl_x^{(x-1)-}})$.
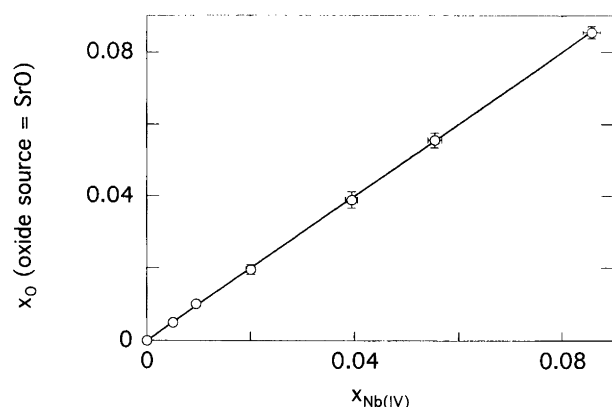
Fig. 4. Mole fraction of oxide plotted versus mole fraction of niobium in a NaCl–CsCl eutectic melt at 650°C where $NbCl_4$ and SrO were added in a 1:1 mole ratio. The error bars are based on the standard deviations in the analysis of oxide and niobium. A line with slope 1 is included in the plot.

$NbOCl_5^{2-}$ and $Nb_2O_5(s)$.[4] Together with the present results it seems reasonable to assume that oxochloride ions of the type $NbO_2Cl_x^{(x-1)-}$ exist in the molten CsCl–NaCl eutectic, and that the equilibrium

$$NbOCl_5^{2-} + Nb_2O_5(s) + (3x-5)Cl^- = 3NbO_2Cl_x^{(x-1)-} \quad (3)$$
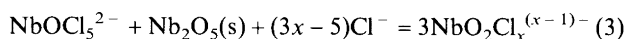
is established. The equilibrium constant for reaction (3) is given as

$$K = \frac{a_{NbO_2Cl_x^{(x-1)-}}^3}{a_{NbOCl_5^{2-}} \cdot a_{Cl^-}^{(3x-5)}} = \frac{x_{NbO_2Cl_x^{(x-1)-}}^3}{x_{NbOCl_5^{2-}} \cdot \gamma_{Cl^-}^{(3x-5)}} \times \frac{\gamma_{NbO_2Cl_x^{(x-1)-}}^3}{\gamma_{NbOCl_5^{2-}} \cdot \gamma_{Cl^-}^{(3x-5)}} = K' K^\gamma \quad (4)$$

where K' is the stoichiometric equilibrium constant and K^γ is a correction term containing the activity coefficients. Our data allow us to calculate the mole fractions of $NbOCl_5^{2-}$ and $NbO_2Cl_x^{(x-1)-}$ from the oxygen to niobium ratio, x_O/x_{Nb}, in the melt if we assume that $NbOCl_5^{2-}$ and $NbO_2Cl_x^{(x-1)-}$ are the only oxospecies. Using this procedure and $x = 3$ for the number of Cl^- ions in the $NbO_2Cl_x^{(x-1)-}$ complex, the equilibrium can be fitted to the experimental data. Since x_{Cl^-} is close to one in these melts, K' is not very sensitive with respect to x, and changing the value of x will not change K' much. Using a Raoultian standard state for the Cl^- activity and a Henrian standard state for the activities of the niobium complexes, $K \approx K'$, since $x_{Cl^-} \approx 1$ and the mole fractions of the niobium complexes are small. Included in Fig. 1 is a line showing x_O/x_{Nb} when $K' = 5 \times 10^{-5}$. The modelled line agrees reasonably well with the experimental data. An even more convincing agreement between modelled and experimental data would be obtained if ions of the form $Nb_2O_4Cl_x^{(x-2)-}$ or $Nb_3O_6Cl_x^{(x-3)-}$ were the products of reaction (3), but these or similar ions have not been reported in the literature, and we therefore believe that $NbO_2Cl_x^{(x-1)-}$ is the most probable product.

The interpretation of the data from the experiment where $NbCl_4$ and SrO were added in equal amounts is fairly straightforward. A molar ratio $x_O/x_{Nb} = 1$ indicates that the reaction

$$NbCl_6^{2-} + SrO(s) = NbOCl_x^{(x-2)-}$$
$$+ SrCl_2(in\ (Na,\ Cs)Cl_{eut}) + (4-x)Cl^- \quad (5)$$
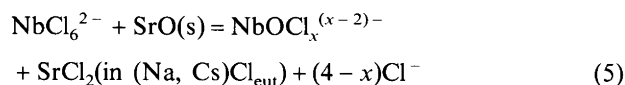
takes place in the melt. A further support for this argument is the large negative Gibb's free energy change $(\Delta_r G°_{923} = -307\ kJ\ mol^{-1})$[11] for the reaction

$$NbCl_4(g) + SrO(s) = NbOCl_2(s) + SrCl_2(s) \quad (6)$$
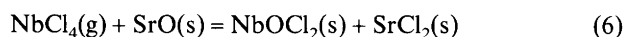
In the experiment where $NbCl_4$ was added to a melt saturated with $Nb_2O_5(s)$ it is reasonable to assume that dissolved $NbCl_4$ reacted with $Nb_2O_5(s)$ according to the reaction

$$3NbCl_6^{2-} + Nb_2O_5(s) = 3NbOCl_x^{(x-2)-} + 2NbOCl_5^{2-}$$
$$+ (8-3x)Cl^- \quad (7)$$
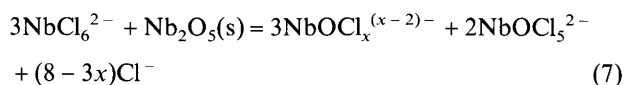
for three reasons: (1) The large negative value of the Gibb's free energy change $(\Delta_r G°_{923} = -166\ kJ\ mol^{-1})$[11] for the reaction

$$3NbCl_4(g) + Nb_2O_5(s) = 3NbOCl_2(s) + 2NbOCl_3(g). \quad (8)$$
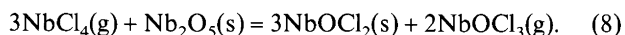
(2) The measured x_O/x_{Nb} ratio is slightly larger than one. (3) Some $NbOCl_5^{2-}$ is formed according to reaction (7), and since $Nb_2O_5(s)$ is present in excess, some $NbO_2Cl_x^{(x-1)-}$ will also form according to reaction (3). Using $K' = 5 \times 10^{-5}$ to calculate the amounts of $NbOCl_5^{2-}$ and $NbO_2Cl_x^{(x-1)-}$, a molar ratio x_O/x_{Nb} represented by the line in Fig. 3, which compares well with the experimental data, is obtained.

In the experiment where $CsNbCl_6$ was added to a melt containing an excess of $SrO(s)$, colourless melt samples practically free from niobium were obtained. The amount of strontium in all samples was about three times the amount of $CsNbCl_6$ added to the melt, i.e., $n_{Sr}/n_{Nb} \approx 3$. Picard and Bocage[7] claim that $LiNbO_3(s)$ is stable at O^{2-} concentrations higher than 5.5×10^{-5} mol% in LiCl–KCl eutectic melts at $450°C$. The solubility of SrO in the NaCl–KCl eutectic is $10^{-4.1}$ mol% at $700°C$,[8] and it therefore seems reasonable to assume that all the niobium added to the melt precipitated as $MNbO_3(s)$ (M = Na, Cs, $\frac{1}{2}$Sr) according to the reaction

$$NbCl_6{}^- + 3SrO(s) + MCl = MNbO_3(s) + 3SrCl_2 + Cl^- \quad (9)$$
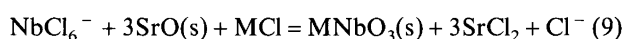
The oxide found in the melt was due to the solubility of $SrO(s)$ in the eutectic alone. Also, the melt containing about 6 mol% Nb(IV) saturated with $SrO(s)$ was colourless, with a very low niobium concentration (≤ 0.0001 mol%). According to Picard and Bocage,[7] Nb(IV) precipitates as $NbO_2(s)$ in LiCl–KCl eutectic melts at $450°C$ when the O^{2-} concentration is above 5.5×10^{-14} mol%. It is therefore likely that Nb(IV) oxochlorides present in our melt precipitated as $NbO_2(s)$ when excess $SrO(s)$ was added. This conclusion is supported by strontium analysis of the melt after addition of excess $SrO(s)$. The analysis showed that the molar ratio between strontium in the melt and $NbCl_4$ added to the melt was close to two.

Conclusion

In the Nb(V)-containing NaCl–CsCl eutectic melt at $650°C$, Nb_2O_5 dissolves as $NbOCl_5{}^{2-}$ and $NbO_2Cl_x{}^{(x-1)-}$. When $NbCl_4$ is added to a NaCl–CsCl eutectic melt containing $Nb_2O_5(s)$ at $650°C$, Nb_2O_5 dissolves as $NbOCl_x{}^{(x-2)-}$, $NbOCl_5{}^{2-}$ and $NbO_2Cl_x{}^{(x-1)-}$. In the eutectic NaCl–CsCl melt saturated with $SrO(s)$ at $650°C$, Nb(V) and Nb(IV) form the oxide compounds $MNbO_3(s)$ (M = Na, Cs, $\frac{1}{2}$Sr) and $NbO_2(s)$, respectively, with very low solubility.

Appendix

Melt samples from the experiment where $CsNbCl_6$ was added to a melt containing an excess amount of $Nb_2O_5(s)$ were analysed for oxygen only. Other samples were analy-

sed for oxygen, niobium and, if present, strontium. The mole fractions of niobium and oxygen in the various samples were calculated from the analyses results as given below.

In the $CsNbCl_6$–Nb_2O_5(satd.) experiment the amount of Nb(V) in the melt was calculated as the sum of the amount of $CsNbCl_6$ added and the amount of oxide was determined by analysis multiplied by 2/5 (the niobium to oxide ratio in Nb_2O_5). The total mass of the melt at any time was calculated as the sum of the eutectic, the added $CsNbCl_6$ and the dissolved Nb_2O_5. The mass of each sample extracted was subtracted from this sum. Knowing the total mass, the amount of niobium and oxygen in the melt, and the mass of an extracted sample, the number of moles of niobium and oxide in this sample, n_{Nb} and n_O, could be calculated. Assuming that the species (Na, $Cs)_2NbOCl_5$, (Na, $Cs)_2NbO_2Cl_3$ and (Cs, Na)Cl were present in the melt [reactions (1) and (3)], the number of moles of (Na, $Cs)_2NbOCl_5$ and (Na, $Cs)_2NbO_2Cl_3$ in the samples would be given by $n_{Nb} - (n_O - n_{Nb}) = 2n_{Nb} - n_O$ and $n_O - n_{Nb}$, respectively. Knowing the number of moles of niobium and oxygen and the mass of the extracted sample, m_{sample}, the total number of moles in the sample, n_{sample}, were calculated using the equation:

$$n_{sample} =$$

$$n_{Nb} + [m_{sample} - (2n_{Nb} - n_O)(M_{NbOCl_3} + 2M_{(Cs,Na)Cl}) -$$

$$(n_O - n_{Nb})(M_{NbO_2Cl} + 2M_{(Cs,Na)Cl})]/M_{(Cs,Na)Cl}$$

where $M_{(Cs, Na)Cl} = 0.35 \, M_{NaCl} + 0.65 \, M_{CsCl}$ (the molar mass of the eutectic).

For the $CsNbCl_6$–SrO(satd.) experiment, the only species present in the melt in significant amounts were $SrCl_2$ and (Cs, Na)Cl [reaction (9)]. Thus the total number of moles present in a sample extracted for analysis were calculated as

$$n_{sample} = n_{Sr} + (m_{sample} - n_{Sr}M_{SrCl_2})/M_{(Cs, Na)Cl}.$$

For the $NbCl_4$–Nb_2O_5(satd.) experiment the species (Na, $Cs)_2NbOCl_4$, (Na, $Cs)_2NbOCl_5$, (Na, $Cs)_2NbO_2Cl_3$ and (Cs, Na)Cl were assumed to be present [reactions (3) and (7)]. The number of moles of (Na, $Cs)_2NbOCl_4$, $[\frac{3}{5}(2n_{Nb} - n_O)]$, and (Na, $Cs)_2NbOCl_5$, $[\frac{3}{5}(2n_O - n_{Nb})]$, are given by reaction (7) and the number of moles of niobium and oxygen in these samples. The total amount of moles present in the samples was calculated using the equation

$$n_{sample} = n_{Nb} + \frac{m_{sample}}{M_{(Cs,Na)Cl}} - [(2n_{Nb} - n_O)(\frac{2}{5}M_{NbOCl_3}$$

$$+ \frac{3}{5}M_{NbOCl_2} + 2M_{(Cs,Na)Cl}) - (n_O - n_{Nb})(M_{NbO_2Cl}$$

$$+ 2M_{(Cs,Na)Cl})]/M_{(Cs,Na)Cl}$$

For the $NbCl_4$–SrO 1:1 experiment the species $SrCl_2$, (Na, $Cs)_2NbOCl_4$ and (Cs, Na)Cl were assumed to be

present [reaction (5)]. The total amount of moles present in each sample were calculated according to the equation

$$n_{sample} = n_{Nb} + n_{Sr}$$

$$+ \frac{m_{sample} - n_{Nb}(M_{NbOCl_2} + 2M_{(Cs,Na)Cl}) - n_{Sr}M_{SrCl_2}}{M_{(Cs,Na)Cl}}$$

The mole fractions of niobium and oxygen in the melt at any time were calculated as n_{Nb}/n_{sample} and n_O/n_{sample}.

If the numbers of Cl^- ions assumed in the complexes in the above equations are wrong, the molar masses of the complexes will be somewhat in error. However, only minor errors will be introduced in the mole fractions of niobium and oxygen, since all melts were concentrated in NaCl and CsCl.

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