Oxofluoride Complexes of Niobium(IV,V) in the Liquid Eutectic LiF–NaF–KF Melt at 700 °C with Varying Oxide-to-Niobium Molar Ratios

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Matthiesen, F., Jensen, P. T. and Østvold, T., 1998. Oxofluoride Complexes of Niobium(IV,V) in the Liquid Eutectic LiF–NaF–KF Melt at 700 °C with Varying Oxide-to-Niobium Molar Ratios. – Acta Chem. Scand. 52: 1000–1005. © Acta Chemica Scandinavica 1998.

The solubility of $Nb^{IV,V}$ as a function of the O^{2-} composition in the ternary eutectic LiF–NaF–KF (FLINAK) melt at 700 °C has been determined. Based on chemical analysis of melt samples suggestions related to the $Nb^{IV,V}$–O–F complex formation are given. When SrO was added to FLINAK containing 0.22 mol kg^{-1} K_2NbF_7, the following observations were recorded: (1) $n_O/n_{Nb} < 2$: all the Nb^V was dissolved; (2) $n_O/n_{Nb} > 2$; a solid of the type $AlkNbO_3$ was formed; (3) $n_O/n_{Nb} = 3$; a minimum of Nb^V and O^{2-} solubilities were observed; (4) $3 < n_O/n_{Nb} < 4$; the $AlkNbO_3(s)$ previously formed dissolved, and a complex ion of the type $NbO_4F_x^{(3+x)-}$ was most probably formed; (5) $n_O/n_{Nb} > 4$; no further dissolution of the Nb^V compound took place.

When Na_2O was added to a melt containing 0.25 and 0.14 mol kg^{-1} Nb^{IV} (prepared by equilibrating an Nb^V-containing melt with Nb metal), the following observations were recorded: (1) $n_O/n_{Nb} < 1$; all Nb^{IV} was dissolved; (2) $1 < n_O/n_{Nb} < 2.2$; the composition of Nb^{IV} was reduced but the O^{2-} composition was still increasing, indicating that the reaction, $3NbOF_5^{3-} + 2O^{2-} = NbOF_2(s) + 2NbO_2F_4^{4-} + 5F^-$, took place, (3) $2.2 < n_O/n_{Nb} < 3$; both Nb^{IV} and the O^{2-} compositions were decreasing, and a compound of the type Alk_2NbO_3 was precipitating; (4) $3 < n_O/n_{Nb} < 4$; the solid precipitate dissolved, and the dominating reaction was $Alk_2NbO_3(s) + xF^- + O^{2-} = NbO_4F_x^{(4+x)-} + 2Alk^+$; (5) at higher n_O/n_{Nb} ratios Na_2O dissolved as free O^{2-} ions. Up to $n_O/n_{Nb^{IV}} = 3$, the solidified melt samples were green and blue, at higher ratios white. The Nb^V samples were always white. Some preliminary Raman spectra were also recorded of some of the melt samples. The spectra indicated only Nb^V. This could be due to a decomposition of Nb^{IV} to Nb metal and Nb^V in the solid state, and the slow kinetics of the reverse reaction in the melt.

The 'solubility of Nb_2O_5' in FLINAK at 700 °C was measured to be ≈ 0.5 mol kg^{-1}, and the dissolution mechanism seems to be given by the reaction: $Alk^+ + Nb_2O_5(s) + xF^- = NbO_2F_x^{(1-x)-} + AlkNbO_3(s)$, with an equilibrium constant (molal) of 2.4.

During the last three decades a considerable amount of work devoted to the electrolytic deposition of niobium from molten salt solutions has been published. An important motivation for the above investigations has been the potential interest of making surface treatments with this metal due to its favourable corrosion properties in acidic media. A convenient solvent for the electrodeposition process is the LiF–NaF–KF eutectic melt, FLINAK. Also alkali chlorides and chloride fluoride mixtures have been suggested. Senderoff and Mellors[1–5]

were the first to demonstrate that it was possible to produce coherent coatings of niobium and other refractory metals by electroplating from a molten fluoride solvent. Since then the reduction mechanism of niobium has been the subject of many investigations, and many different mechanisms have been proposed. In a recent paper it was suggested that the reason for the discrepancy between the different mechanisms observed in the literature may be a lack of control of the oxide impurity level of the electrolytes used.[6] This is especially critical when niobium chloride compounds are used as a niobium source, owing to the very hygroscopic nature of such salts. The niobium fluoride complex, K_2NbF_7, has been frequently used and is less hygroscopic, but this compound must also be carefully purified to avoid oxides in

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the melt. The solvent must also be dehydrolysed, which normally can be done by zone refining or by repeated recrystallization. Today it is known that the only stable oxidation states of niobium in FLINAK at 700 °C are $+4$ and $+5$.[6,7] This has been verified both by electrochemical[7] and gravimetric[6] techniques. Raman spectroscopy has verified the existence of the $NbF_7{}^{2-}$ ion in oxide-free FLINAK.[8] When Na_2O was added to the melt, new bands due to $NbOF_5{}^{3-}$ and $NbO_2F_4{}^{3-}$ and perhaps also $NbO_3F_3{}^{4-}$ species and polymeric structures consisting of distorted NbO_6 octahedrons appeared.[8] At $n_O/n_{Nb}=0.93$ the equilibrium

$$NbF_7{}^{2-} + O^{2-} = NbOF_5{}^{2-} + 2F^- \qquad (1)$$
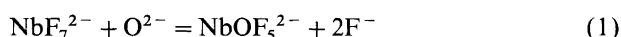
was suggested to explain the change in the Raman spectra with varying temperature.[8] It was also suggested by Matthiesen et al.[7] that reaction (1) could explain that the reduction wave due to the $NbF_7{}^{2-}$ complex did not vanish at $n_O/n_{Nb}=1$ because of a relatively small equilibrium constant. It is, however, most unlikely that the divalent oxide ion is not very strongly preferred as a first neighbour to Nb^{5+}. Another explanation may be that the oxide content of the melt at $n_O/n_{Nb}=0.93$ investigated by von Barner et al.[8] is not strictly correct. A slight change in composition due to evaporation may influence the n_O/n_{Nb} molar ratio, and therefore also the Raman spectrum. Furthermore they reported data at 'oxide saturation', which they indicate is at $n_O/n_{Nb}=3$. We have reasons to believe that the Na_2O solubility is very high in these melts. The solubility at $n_O/n_{Nb}=3$, however, is very small, as will be reported later. This means that the interpretations of the Raman data given by von Barner et al.[8] for the higher oxygen-to-niobium ratios may have to be reconsidered.

Data on Nb^{IV} in molten salts are scarce, and in fluoride melts very few data are available. Rosenkilde et al.[9] have, however, studied electrochemically both Nb^{IV} and Nb^V in FLINAK also with oxide added. Owing to a possible passivation of the glassy carbon electrode, attempts to measure the oxide composition in these melts as a function of oxide additions at given Nb contents failed. To obtain more information on the role of oxide in refractory metal halide melts, we therefore decided to study the composition of both the Nb^{IV}, Nb^V and the O^{2-} ions in FLINAK at 700 °C as a function of oxide additions at constant niobium compositions. Some Raman spectra were also recorded to verify the existence of the $NbO_4F_x{}^{(4-x)-}$ complex ion. The existence of this ion at high n_O/n_{Nb} ratios was indicated by chemical analysis of melt samples. Besides the fundamental aspect of the present work, this study is also motivated by the interest in these melts as reaction media for synthesis of new Nb–O compounds and as media for electroplating of niobium to improve surface properties of materials.

Experimental

All chemicals used were pre-treated. The alkali fluorides, p.a. quality from Merck, Germany, were recrystallized

under argon several times, and only transparent crystals were selected after each crystallization. K_2NbF_7 was prepared by fluorination of Nb_2O_5 (Alfa, 99.9%).[7] Na_2O was made by decomposing Na_2O_2 (p.a., Merck, Germany) under a vacuum of 10^{-3} mbar, at 600 °C for 12 h. Analysis by titration with HCl gave typically 98 mol% Na_2O. SrO was prepared by decomposing $SrCO_3$ (p.a., Merck, Germany) under vacuum, as above, at 900 °C for 36 h, and the SrO obtained contained typically 98 mol% SrO as measured by carbothermal reduction using an oxygen analyzer, Leco TC-436. In this technique 0.1 g of the sample is heated over a short time, 2–6 min, in a graphite crucible, sometimes with graphite powdered added, to temperatures sufficiently high for the carbothermal reduction of the oxide to occur. The CO formed is converted to CO_2 and analyzed quantitatively in an IR cell.[10] The Nb_2O_5 was dried at 150 °C for 24 h before use. Nb^{IV} was prepared by reducing K_2NbF_7 in FLINAK with Nb metal (Alfa, 99.9%). These metal pieces were rinsed in HF before use. The experiments and handling of purified salts were carried out in an argon-filled glovebox with water and oxygen contents less than 1 and 5 ppm, respectively. The furnace used to equilibrate the samples at 700 °C was mounted vertically under the box in such a way that the experimental cell could be handled from inside the box. The furnace and cell assembly are shown in Fig. 1. The cell assembly consisted of an outer silica envelope in which a glassy carbon crucible (V25, Carbone-Lorraine) was placed at the bottom. This crucible served as a melt container. A graphite lid was placed on the top of the crucible. This lid had holes for sample extraction and feeding of salts, stirring unit, electrodes and thermo-
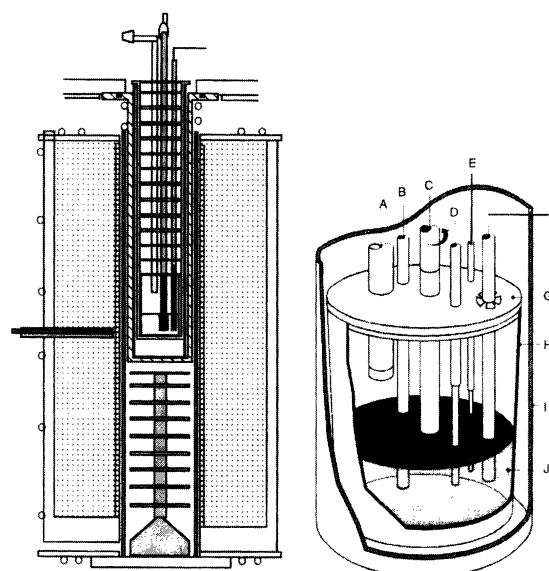

Fig. 1. Experimental cell and furnace mounted to glovebox: (A) quartz sampling tube; (B) graphite counter electrode; (C) stirrer; (D) glassy carbon indicator electrode; (E) platinum reference electrode; (F) thermocouple; (G) radiation shield; (H) glassy carbon crucible; (I) quartz container; (J) melt.

couple. Above this lid radiation shields were mounted to reduce the vertical temperature gradient over the experimental cell. The five lower ones were made of graphite, and the rest of sintered alumina. The liquid salt mixtures were in contact with glassy carbon and graphite materials only. Melt samples for chemical analysis were extracted from the melt using a graphite spoon, while stirring was performed with a graphite blade connected to an electric motor via a steel rod. Before use the glassy carbon crucible and the graphite parts in contact with the melt were heated under vacuum, 10^{-3} mbar, at 900 °C for 12 h. After melting, the weighed amount of FLINAK and K_2NbF_7, Na_2O or SrO was added to the melt. This mixture was equilibrated before a sample was taken. Then further additions of oxide were made and samples withdrawn at equilibrium conditions. These melt samples were always white. When Nb^{IV} was studied, the tetravalent niobium was first synthesized by adding Nb metal to the Nb^V containing mixture in such a way that the reaction

$$4\,Nb^V + Nb^0 = 5\,Nb^{IV} \tag{2}$$
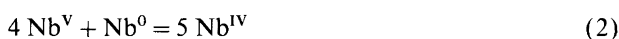
proceeded completely to the right. This was controlled by recording the weight change of the Nb metal which was withdrawn from the melt at given time intervals. Voltammograms recorded after the reduction process was completed did not reveal any Nb^V. The colours of the melt samples varied from blue/violet to turquoise up to $n_O/n_{Nb}=4$. At higher ratios the samples were white. Two solute compositions of 0.25 and 0.14 mol kg Nb^{IV} were studied, and identical results were obtained with respect to the composition behaviour of Nb and O with additions of Na_2O. Solubility studies of Nb_2O_5 in FLINAK at 700 °C were also performed by equilibrating the melt before sample extraction.

The oxide content of the extracted samples was determined by the carbothermal reduction method using Leco TC-436. To avoid contamination of our samples from moisture in the air, the samples were placed in tin capsules before they were removed from the glovebox and transferred to the oxide analyser. During the analysis the temperature of the samples in the graphite cell was increased linearly from 1000 to 2000 °C. The reaction between the graphite and our Nb-O-F complexes in the melt took place in a 'narrow temperature window' of 1000–1500 °C. Only one clearly defined reaction was observed. This allowed us to identify 'free' O^{2-} ions in the melt at n_O/n_{Nb} molar ratios larger than 4, as these ions gave rise to a new carbothermal reaction having a maximum rate at a lower temperature than the Nb-O-F complexes. Niobium analysis of extracted samples was performed by ICP, inductive coupled plasma emission spectroscopy, using a Jerryl Ash Atomscan 16 instrument. The samples, 0.2 g each, were dissolved in a mixture of 40% HF(10 ml) and 68% HNO_3(1 ml). In order to dissolve the samples completely, heating to 50 °C was necessary. It was also important to keep the solution

at 50 °C during analysis. Otherwise a colloidal precipitate was observed on the surface of the solutions.

Some preliminary Raman spectra were recorded using windowless graphite cells. This technique was developed by Gilbert and coworkers.[11]

Results and discussion

In Figs. 2–5 standard deviations in the composition determinations are given as error bars.

The Nb_2O_5 solubility data are shown in Fig. 2. The n_O/n_{Nb} molar ratio and the compositions of Nb^{5+} and O^{2-} in mol kg^{-1} versus *mol kg^{-1} O^{2-}* added are presented. The amount of oxygen removed during sampling is corrected for in the data. A decrease in the n_O/n_{Nb} molar ratio in the melt from the theoretical value of 2.5 is observed initially indicating a very low Nb_2O_5 solubility. An average ratio of ≈ 2 is reached when there is no further increase of niobium and oxygen in the melt. This indicates that the reaction

$$Alk^+ + Nb_2O_5 + xF^- = NbO_2F_x^{(1-x)-} + AlkNbO_3(s) \tag{3}$$
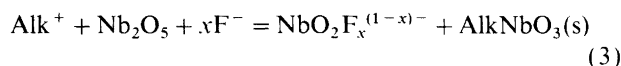
takes place during Nb_2O_5 dissolution. If we assume that the equilibrium constant for reaction (3) on a molal basis, $K_1 = 2.4$, the calculated lines in Fig. 2 occur. Since
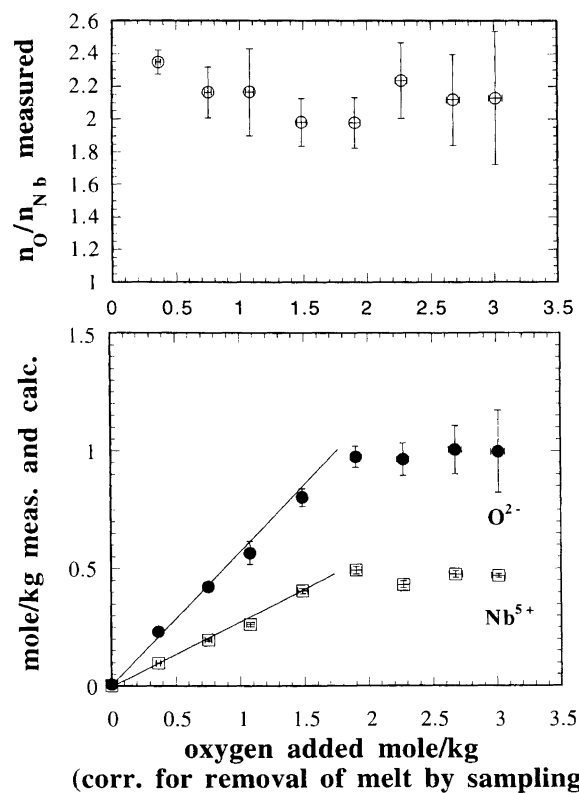

Fig. 2. Nb_2O_5 solubility and the molar ratio of O^{2-} and Nb^{5+} in the liquid LiF–NaF–KF eutectic at 700 °C. □, Nb^V; ●, O^{2-}. Error bars of the n_O/n_{Nb} ratios are calculated from the errors in the O^{2-} and Nb^{5+} composition determinations.

these lines fit well with the measured data, it is reasonable to assume that the $NbO_2F_x^{(1-x)-}$ complex is responsible for the Nb_2O_5 solubility.

The influence of SrO in K_2NbF_7 containing FLINAK melts at 700 °C was studied as a function of the n_{SrO}/n_{Nb^V} molar ratio. From a previous study[12] we had reasons to believe that reactions of the type

$$y\,O^{2-} + NbF_7^{2-}\ (\text{in FLINAK})$$
$$= NbO_yF_x^{(2y+x-5)-} + (x-7)F^- \qquad (4)$$
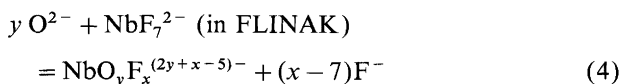
would be strongly shifted to the right. SrO was therefore chosen as an oxide source, since it is much easier to handle than Na_2O. It turned out, however, that the above assumption was only partly true. In Fig. 3 the oxide and Nb^V compositions in the melt are plotted versus the n_{SrO}/n_{Nb^V} molar ratio. The oxide and niobium contents in both the melt and in the possible solid Nb–O-containing compounds are included in this ratio. It is possible to give an evaluation of the stoichiometry of precipitating species as well as the complexes formed in the melt from the observations below.

$0 < n_{SrO}/n_{Nb^V} < 2$: The Nb composition in the melt is constant and all the oxide added goes in solution. This is consistent with reaction (4), and the formation of $NbOF_5^{2-}$ and $NbO_2F_4^{3-}$ complexes in the melt as suggested by von Barner et al.[8]

$2 < n_{SrO}/n_{Nb^V} < 3$: Precipitation of a compound, AlkNbO$_3$, occurs. The solubility of KNbO$_3$ in FLINAK at 700 °C was determined by Rosenkilde et al.[9] to be 0.032 mol kg^{-1} in reasonable agreement with the above data at $n_{SrO}/n_{Nb^V} = 3$. The slopes of the lines showing the decreasing Nb^V and O^{2-} compositions in the melt are
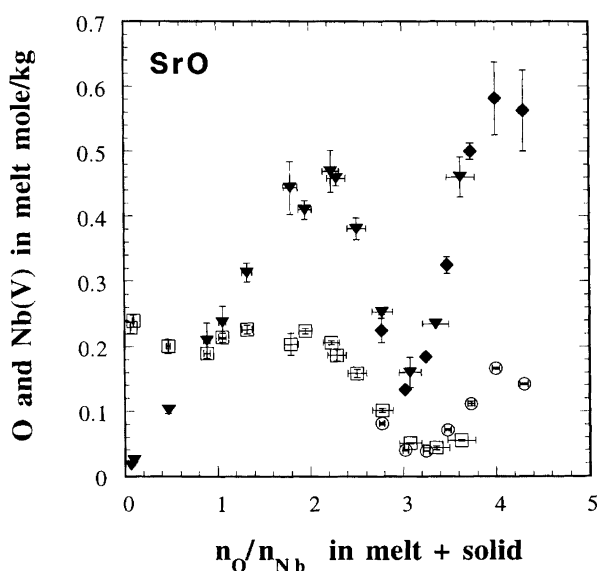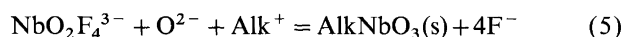

Fig. 3. Oxide (SrO) and Nb^V compositions in the liquid LiF–NaF–KF eutectic at 700 °C versus the molar ratio of the total amount of oxide and niobium in the melt and in the solid phases. The total composition of Nb^V was 0.22 mol kg^{-1} in two different runs. □ and ○, Nb^V; ▼ and ◆, O^{2-}.

close to -1 and -2, respectively, indicating that reaction (5)

$$NbO_2F_4^{3-} + O^{2-} + Alk^+ = AlkNbO_3(s) + 4F^- \qquad (5)$$

took place in the melt.

$3 < n_{SrO}/n_{Nb^V} < 4$: Dissolution of the AlkNbO$_3$ compound occurs. The slope of the increase in oxygen composition versus oxygen added is close to 4, and the similar slope for niobium is close to 1. The data show that the basicity of these melts is too high for SrO to dissolve completely, but indicate the formation of $NbO_yF_x^{(2y+x-5)-}$ complexes, probably with $y=4$. Na_2O is used as an oxide source in an ongoing work to study the effect of this very basic additive on the dissolution process of the AlkNbO$_3$ solid in FLINAK.

A preliminary Raman spectrum of the above melt at $n_{SrO}/n_{Nb^V} = 4.1$ showed a very weak polarized band around 820 cm^{-1}. This band is most probably due to the Nb=O stretching frequency in a $NbO_4F_x^{(3+x)-}$ type complex. Von Barner et al. contributed this band to Nb=O symmetric stretching frequency of the $NbO_3F_x^{(1+x)-}$ ion at 'Na$_2$O saturation'. This information should probably be reconsidered in view of the above solubility data.

The influence of Na_2O on K_2NbF_6 dissolved in FLINAK at 700 °C was studied as a function of the $n_O/n_{Nb^{IV}}$ molar ratio for two Nb^{IV} compositions, 0.252 and 0.136 mol kg^{-1} respectively. In Figs. 4 and 5 the oxide and Nb^{IV} compositions in these melts are plotted versus the $n_O/n_{Nb^{IV}}$ molar ratio. The oxide and niobium contents in both the melt and in the possible solid Nb–O-containing compounds are again included in the ratio. From these data it was possible to get some insight into the stoichiometry of precipitating species and the complex ions in the melt in the same way as described above. The same trend in the data is observed for both the total Nb^{IV} compositions used, indicating reproducible results.

$0 < n_O/n_{Nb^{IV}} < 1$: The Nb composition in the melt is close to constant and all the oxide added goes into melt. This is consistent with reaction (6)

$$NbF_6^{2-} + O^{2-} + (x-6)F^- = NbOF_x^{(x-2)-} \qquad (6)$$
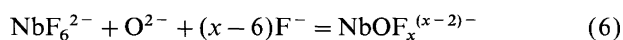
and the formation of the $NbOF_5^{3-}$ complexes in the melt, by analogy with the $NbOF_5^{2-}$ formed when Nb^V is dissolved in FLINAK at this oxide to niobium molar ratio.

$1 < n_O/n_{Nb^{IV}} < 2.2$: Precipitation of a compound NbOF$_2$ or AlkNbOF$_3$ and a formation of the $NbO_2F_x^{x-}$ complex ion occur. The slopes of the lines describing the changes in the Nb^{IV} and O^{2-} compositions are on the average -0.3 and $+0.5$ for the two data sets, respectively, indicating a reaction of the type

$$2O^{2-} + 3NbOF_5^{3-} = 2NbO_2F_4^{4-} + 5F^- + NbOF_2(s) \qquad (7)$$
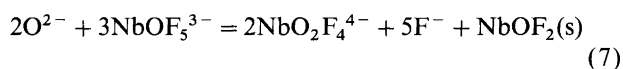
The reason why the O^{2-} composition increases beyond $n_O/n_{Nb^{IV}} = 2$, may be some solubility of the NbOF$_2$ or
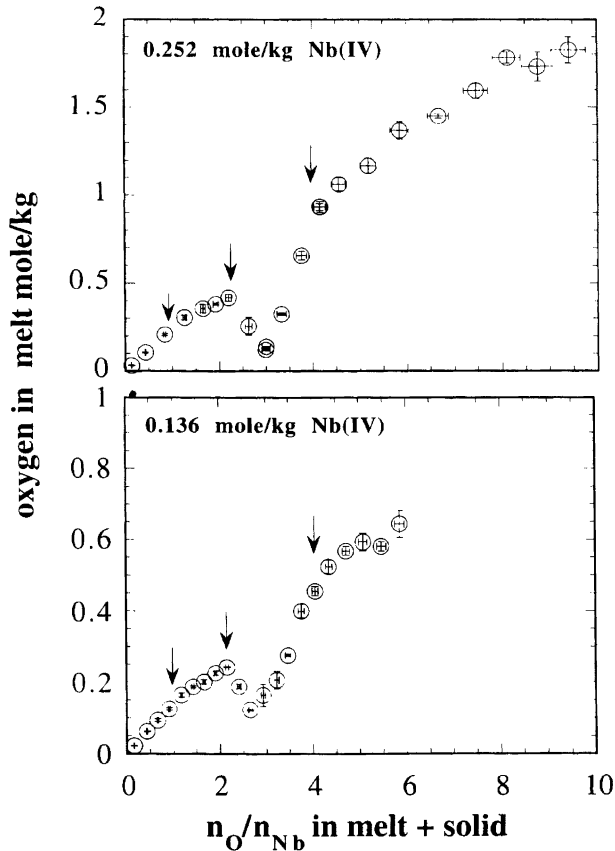
Fig. 4. Oxide (Na$_2$O) compositions in the liquid LiF–NaF–KF eutectic at 700 °C containing Nb^{IV} versus the molar ratio of oxide and niobium in the melt and in the solid phase. Arrows indicate where changes in slopes occur.

Fig. 5. Niobium compositions in the liquid LiF–NaF–KF eutectic at 700 °C containing Nb^{IV} versus the molar ratio of oxide and niobium in the melt and in the solid phase. Arrows indicate where changes in slopes occur.
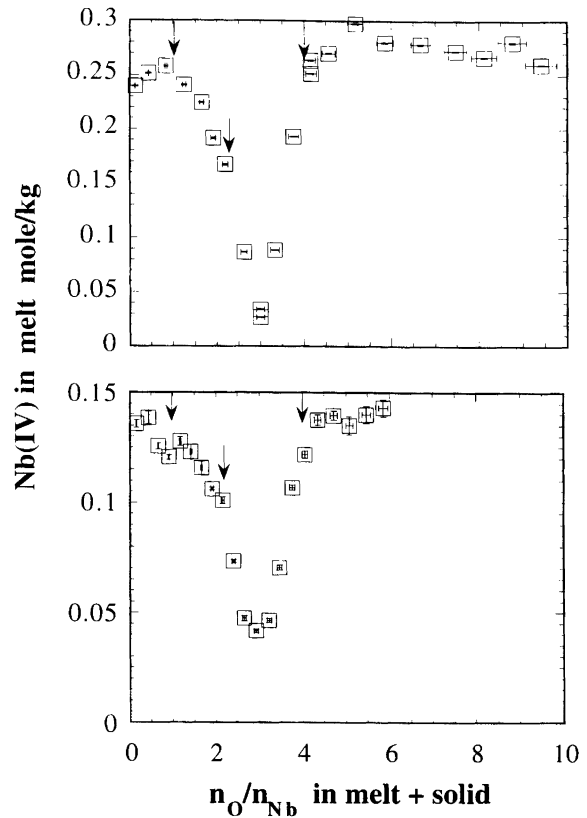
AlkNbOF$_3$ solids. We may also have a small amount of NbO$_3$F$_x^{(x+1)-}$ containing complexes in the melt.

$2.2 < n_O/n_{Nb^{IV}} < 3$: Precipitation of a compound, Alk$_2$NbO$_3$, probably occurs. The slopes of the lines showing the decreasing Nb^{IV} and O^{2-} compositions in the melt are close to -0.75 and -1.8, respectively, indicating that a reaction of the type

$$NbO_2F_4^{4-} + O^{2-} + 2\,Alk^+ = Alk_2NbO_3(s) + 4F^- \qquad (8)$$
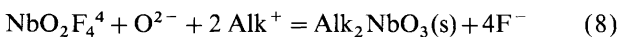
takes place. There is probably some solubility of Alk$_2$NbO$_3$, and this may account for the deviation in the slopes from -1 and -2, respectively.

$3 < n_O/n_{Nb^{IV}} < 4$: Dissolution of the newly precipitated solid occurs. The data show that O^{2-} increases by slightly less than 4 and Nb^{IV} by slightly less than 1 for each O^{2-} added. This is consistent with the reaction

$$Alk_2NbO_3(s) + O^{2-} = NbO_4^{4-} + 2Alk^+ \qquad (9)$$
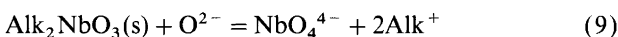
$n_O/n_{Nb^{IV}} > 4$: The added Na$_2$O now dissolves in our opinion as 'free' O^{2-} and Na$^+$ ions. Higher O^{2-} coordinations than 4 around the Nb^{IV} ion are not very likely due to the high negative charge of the NbO$_4^{4-}$ ion. At these high $n_O/n_{Nb^{IV}}$ ratios a new feature is observed in the data from the Leco analysis of the oxide in the samples. Figure 6 shows the results of two Leco runs. One at $n_O/n_{Nb^{IV}} = 3.86$ and one at $n_O/n_{Nb^{IV}} = 5.71$. The new reaction peak, which only was observed when $n_O/n_{Nb^{IV}} > 4$, is evident. The 'free' oxide reacts easier with carbon and the reaction therefore occurs at a lower temperature.

Some data were also obtained with SrO as an oxide source instead of Na$_2$O. Measurements were carried out for $0 < n_O/n_{Nb^{IV}} < 4$, but only the oxide content of the melt samples was determined. Almost the same trend in the oxide composition as the one given in Fig. 4 was found. In the region $1 < n_O/n_{Nb^{IV}} < 2.5$, the oxide composition versus $n_O/n_{Nb^{IV}}$ showed a gradual change in slope from being positive at low oxide to niobium molar ratios to become negative at the higher values. This again indicates the more acid character of SrO relative to Na$_2$O.

Raman spectra of some of the FLINAK–Nb^{IV}–O samples were recorded at ICE/HT, FORTH, Patras, Greece in the laboratory of G. N. Papatheodorou[16] a year after the solubility measurements were completed. The spectra were obtained at 700 °C, and indicated that only Nb^V was present in melts rich in oxide. The reason for this observation may be a decomposition of Nb^{IV} to Nb metal and Nb^V in the solid state, and the slow kinetics
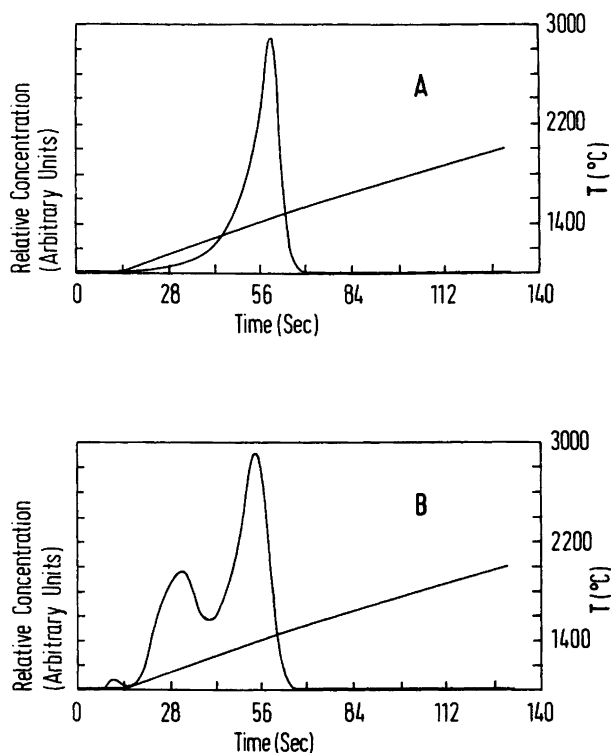
Fig. 6. Oxide analysis curves as obtained by the Leco method at different $n_O/n_{Nb^{IV}}$ molar ratios. (A) $n_O/n_{Nb^{IV}} = 3.68$; (B) 5.71.

for the reverse reaction in the melt. However, this decomposition will not influence the ICP analysis of Nb reported earlier in the present communication. We intend to repeat the Raman investigation of the present melt systems using a windowless cell of Ag or Nb wire in the graphite cell. These metals will reduce Nb^V to Nb^{IV} before the spectra are recorded.[17]

The solubility and Raman data obtained so far of melts with $n_{SrO}/n_{Nb^V} = 4$ and '$n_{Na_2O}/n_{Nb^{IV}}' = 4$ and 5, however, indicate that a complex of the form $NbO_4F^{(3+x)-}$ is formed with a Nb=O stretching frequency at 825 cm^{-1}. Similarities are observed in the frequencies published by von Barner et al.[8] and those observed at ICE/HT, FORTH for oxide to niobium molar ratios larger than 1. This indicates that niobium was in the same valence state in both melts. The spectrum recorded by von Barner et al.[8] for Na$_2$O 'saturated melts' was very similar to the data recorded at ICE/HT, FORTH for $n_{SrO}/n_{Nb^V} = 4$ and '$n_{Na_2O}/n_{Nb^{IV}}' = 4$ and 5. It is, however, quite clear that the 'saturated' melts investigated by von Barner et al. probably had an unknown composition which may be approximated by $n_O/n_{Nb^V} > 4$. The frequencies observed at the high n_O/n_{Nb^V} ratio may therefore not be due to the suggested $NbO_3F_x^{(6+x-5)-}$ ion.

From the above discussion, we may conclude that new and improved Raman spectra should be obtained for both Nb^{IV} and Nb^V in FLINAK. Work is in progress to obtain such data.

Conclusions

When Nb$_2$O$_5$ is added to FLINAK the NbO$_2$F$_4^{4-}$ ion and AlkNbO$_3$(s) are formed. The reaction between Nb$_2$O$_5$ and FLINAK is not complete at low 'Nb$_2$O$_5$' compositions.

Additions of Na$_2$O to FLINAK containing Nb^{IV} and SrO to FLINAK containing Nb^V show that such melts have an oxide solubility minimum at $n_O/n_{Nb} = 3$. In Nb^{IV} containing melts NbOF$_2$ and Alk$_2$NbO$_3$ seem to precipitate at given oxide to niobium molar ratios, while only AlkNbO$_3$ is formed in Nb^V melts. Preliminary Raman spectra together with solubility data indicate the formation of NbOF$_5^{3-}$, NbO$_2$F$_4^{4-}$ and NbO$_4$F$_x^{(4+x)-}$ ions in Nb^{IV} containing FLINAK melts.

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