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Influence of Oxide and Alloy Formation on the Electrochemistry of Ti Deposition from the NaCl-KCl-NaF-K₂TiF₆ Melt Reduced by Metallic Ti

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The redox reactions in KCl-NaCl-NaF-K₂TiF₆ melts reduced by titanium metal have been studied by cyclic voltammetry and chronopotentiometry. At platinum and nickel electrodes waves due to alloy formation were seen preceding the Ti(III) → Ti metal deposition wave. The presence of oxide species could be detected as waves on voltammograms performed with platinum electrodes. Deposits on nickel plates in general consisted of multiphase Ni-Ti layers. By varying the deposition potential outer layers with compositions ranging from pure titanium over NiTi to nickel-rich alloys such as Ni₃Ti could be obtained. Pulse plating produced the best titanium coating. With constant potential electrolyses it was also possible to deposit titanium diboride coatings of high quality from the mixed chloride-fluoride melts.

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Titanium and titanium alloys and compounds have recently attracted great interest because of their many uses, *e.g.*, in corrosion protection, as electrodes for metal production, and for medical purposes. The almost equimolar Ni-Ti alloy (nitinol) has memory shape properties, and it also seems to exhibit good biocompatibility^{1,2} thus being a promising candidate as an implant material. Another interesting titanium compound is TiB₂. In the last few years, because of a high corrosion resistance and electrical conductivity, electrodes coated with TiB₂ have proved to be useful as aluminum wettable cathodes.³

Due to its negative deposition potential titanium cannot be electrochemically deposited from aqueous media. In this respect fused salt electrolyses can be an interesting method for producing coatings of titanium metal as well as titanium alloys and compounds. Certainly the electrochemistry of titanium has been studied in a number of different molten salt media comprising all-chloride, all-fluoride, and mixed chloride-fluoride solvents.

Among the all-fluoride melts especially the LiF-NaF-KF eutectic (FLINAK) has often been used as a solvent in investigations on the electrochemistry and plating with titanium. In this melt a two-step reduction of Ti(IV) to titanium metal, Ti(IV) → Ti(III) → Ti is known to proceed.^{4,5} The electrochemistry in pure chloride melts, like LiCl-KCl or NaCl-KCl, is more complicated. Here the reduction of Ti(IV) typically takes place in three steps,⁶⁻⁸ Ti(IV) → Ti(III) → Ti(II) → Ti. When fluoride ions are added to chloride melts the higher oxidation states of the metals will often be stabilized due to formation of fluorocomplexes. In the case of titanium the same two-step reduction mechanism as in all fluoride melts was found in a KCl-NaCl molten salt bath,^{7,9,10} when sufficient fluoride were present (F/Ti molar ratio ≥ 6).

Concerning plating it has been possible to obtain titanium coatings of good quality on, *e.g.*, iron⁵ and steel¹¹ with FLINAK melts as the supporting liquid. At the temperatures applied (typically around 700°C) interdiffusion of titanium with the metallic substrates often plays an important role resulting in a good adherence of the titanium outer layer. Such an alloy formation has been observed when titanium was deposited from FLINAK on nickel⁵ and copper¹² substrates. The attempts to produce titanium surface layers from pure chloride melts have been less successful. Only in one case have coherent deposits of titanium been obtained from chloride melts; however the current efficiency was low and sludge formation occurred.⁸ The difficulties are probably largely related to the Ti(II)

oxidation state, *e.g.*, chemical disproportionation of Ti(II) to Ti(III) and powdery titanium metal is likely to happen.^{7,8} Thus although alkali chlorides are cheaper, less corrosive, and less toxic compared to alkali fluorides, electrodeposition of titanium from all-chloride melts seems troublesome. The use of mixed chloride-fluoride melts as supporting liquid offers an interesting alternative to the fluoride and chloride melts. They are in general less toxic and more soluble in water than the fluoride melts, which makes the dissolution of adherent solidified melt after electrolyses easier. Only a few works in the literature deal with deposition of titanium from such melts, *e.g.*, the KCl-NaCl-LiCl eutectic with K₂TiF₆ added has been applied to produce titanium coatings on steel.¹³ This substrate seems to be the only one which has been investigated in connection with mixed chloride-fluoride melts.

TiB₂ can be plated from fluoride melts, and we have previously¹⁰ attempted to make deposits from KCl-NaCl-NaF melts, however the resulting layer was poorly crystallized. Kaptay and Kuznetsov¹⁴ give references to most of the work done so far on TiB₂ deposition from molten salts in a recent review.

A major problem when depositing metallic surface layers from molten salts is the effects due to oxide impurities in the salt bath. The presence of oxide often results in deposits of poor quality ranging from modifications of the metallic crystal structure by interstitial oxygen to formation of metal oxides. It has been reported¹² that such oxide contamination caused porous surface layers and even formation of titanium oxides during deposition of titanium from FLINAK melts. Concerning investigations on the fundamental electrochemistry of titanium in alkali halide melts with oxide present only one paper⁹ mentions effects that may be caused by oxide contamination, and the knowledge about which species that form is also very scarce.

The aim of the present work is to explore the possibilities for applying KCl-NaCl-NaF melts to produce various coatings containing titanium, *e.g.*, titanium metal, nickel-titanium alloys, and TiB₂. Special attention is given to clarify which titanium-nickel alloys may be formed on nickel substrates by varying the deposition parameters. Further we want to investigate if the presence of oxide, possibly in the form of titanium oxofluoro species, can be detected electrochemically in the molten chloride-fluoride salt bath.

Experimental

The solvent (NaCl, 60.5 mol %; KCl, 22.5 mol % and NaF, 17 mol %) was made from commercial pro analyses salts (Merck) dried in vacuum at 130°C. Before addition of the solutes the solvent was further purified in the electrochemical setup by heating up to 350°C under vacuum and subsequently under an argon atmosphere raising

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the temperature beyond the melting point. As previously¹⁰ the melt was pre-electrolyzed for 8 h with a carbon electrode ($I = 30$ mA) to remove oxide impurities and subsequently checked by cyclic voltammetry on gold and glassy carbon electrodes. After this treatment an oxide ion concentration of less than 0.1 mol % was found.

K_2TiF_6 (Johnson-Matthey) was recrystallized from hydrogen fluoride, added to the melt and reduced to Ti^{3+} by titanium granules (high purity, Johnson-Matthey) at approximately 700°C. The concentration of titanium in the melts (C_{Ti}) is given with respect to the amount after reduction with the titanium metal. Na_2CO_3 was used as the oxide source assuming that the salt disproportionated to Na_2O and CO_2 at the temperature of the melts (around 700°C). The molten salt samples were contained in glassy carbon crucibles placed inside a Hastelloy device with tight leads for the electrodes through a lid. The setup has been described in detail previously.¹⁵

The nickel and tungsten working electrodes were wires (Johnson-Matthey) with diameters of 2 and 1 mm, respectively. They were immersed 10 mm into the melt.

The electrochemical measurements were performed with a potentiostat (Tacussel PRT20-10) and a programmer (Tacussel GSTP4). The measurements were registered with an oscilloscope (Nicolet 310) and a X-Y recorder (Hewlett Packard).

The Pt^{2+} (1M)/Pt couple has been chosen as an internal reference system, and potentials refer to this redox couple unless otherwise stated.

The electroplated deposits were investigated using a Philips scanning electron microscope (SEM) 505 equipped with an energy dispersive X-ray analyser (EDAX). The X-ray diffraction analyses were carried out with a Philips PW 1050/1025 diffractometer. In all cases Cu $K\alpha$ radiation was applied.

Results and Discussion

Voltammetry.—It is important to be aware that signals due to alloy formation between titanium and the materials applied as working electrodes may occur at the voltammograms. In FLINAK melts such waves has been observed for copper,¹² platinum,⁴ glassy carbon,⁴ and nickel⁵ electrodes. It was previously shown that no alloy formation with titanium occurred, when tungsten working electrodes were applied.⁸⁻¹⁰ Thus in this case only the waves from the redox reactions of titanium are seen on the voltammograms. Figure 1A shows such a voltammogram performed on a K_2TiF_6 -NaCl-KCl-NaF melt reduced with titanium metal. Besides the signal due to oxidation of the tungsten electrode, two reduction waves that can be attributed to titanium species are seen. The most positive, R_1 at around -1.26 V, are due to reduction of a Ti(IV) species to Ti(III), the wave Ox_1 corresponds to the reverse reaction. The second one, R_2 near -2.73 V, can be related to deposition of titanium metal and is linked to the typical stripping wave Ox_2 . The standard potentials at 720°C for these reactions can be calculated to -1.104 and -2.324 V, respectively. These values agree well with those that we found previously.¹⁰

A voltammogram of the same melt at a nickel electrode is presented in Fig. 1B. In order to deduce which reduction and oxidation waves were coupled we also recorded voltammograms with other potential windows (not shown on Fig. 1B). At the positive limit the oxidation of the nickel electrode can be observed (-0.965 V). The Ti(III)/Ti(IV) oxidation wave can be seen as a shoulder on the nickel oxidation wave. Compared to voltammograms performed with tungsten electrodes (Fig. 1A), two new reduction waves can be seen, R_3 and R_4 at -2.21 and -2.61 V, respectively. Also during the reverse scan additional waves appear. The wave Ox_3 obviously corresponds to R_3 , whereas the two oxidation waves Ox_4 and Ox_4' both seem to be connected to R_4 . At approximately -2.75 V a weak wave, R_2 can be seen. The shoulder Ox_2 , which appears as the first oxidation signal on the reverse scan, corresponds to R_2 . We assign these waves to deposition/oxidation of titanium metal since R_2 occurs at a potential close to the one we found for reduction of Ti(III) to el-

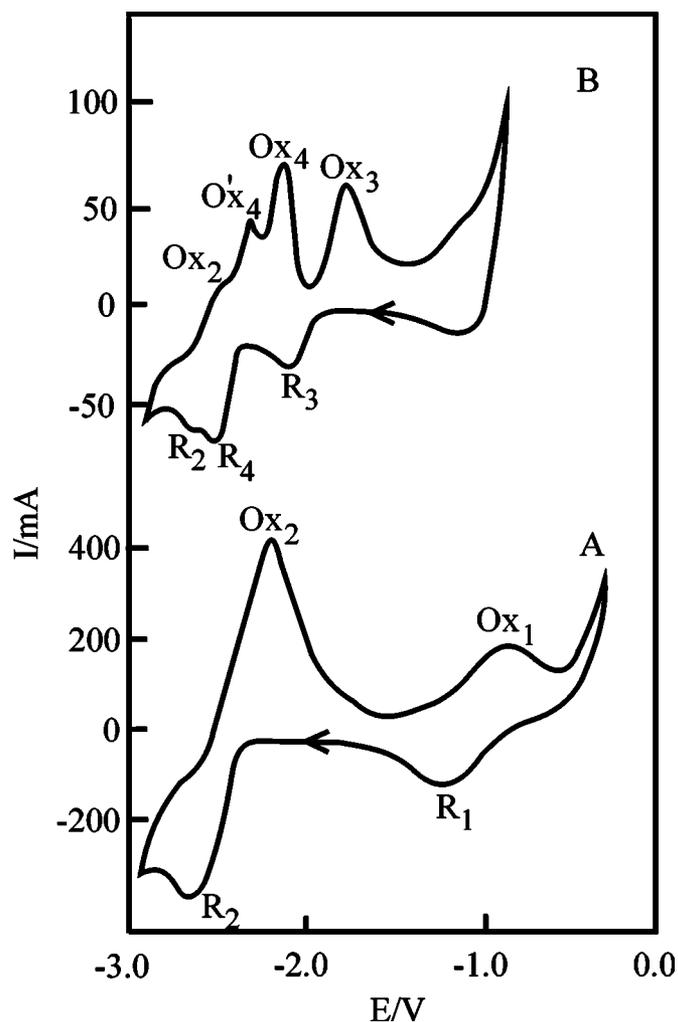


Figure 1. Cyclic voltammograms of a K_2TiF_6 -NaCl-KCl-NaF melt with titanium metal added. $C_{Ti} = 0.21$ mol/L; temperature 720°C and scan rate 1 V/s. (A) tungsten electrode, area = 0.61 cm², reverse potential -2.95 V (vs. Pt/Pt^{2+}) and (B) nickel electrode, area = 0.30 cm², reverse potential -2.93 V (vs. Pt/Pt^{2+}).

ementary titanium with a tungsten electrode (Fig. 1A). The picture with reduction waves preceding the wave for deposition of the pure metal is typical for alloy formation between the electrode and the deposited metal.

When the scan rate is decreased (Fig. 2) the reduction potentials remains almost the same but the waves appear more separated. It further seems that R_2 becomes more pronounced relative to R_3 and R_4 . This trend can also be observed on the oxidation waves, where Ox_2 grows relative to Ox_4 with decreasing scan rates. The change in the shape of the voltammograms is probably due to the change in the thickness of the alloy layers when the sweep rate is varied. At fast sweep rates only a few atomic layers are involved in the electrochemical reactions. It is known¹⁶ that under such circumstances the intermetallic diffusion at the surface proceeds faster than is the case in the bulk of the substrate. At slow sweep rates the accumulation process of titanium metal at the electrode surface becomes more significant than the diffusion into the substrate, thus it is expected that the peaks due to deposition/dissolution of the metal would grow with decreasing sweep rates.

According to the phase diagram of the Ni-Ti system¹⁷ the phases Ni_3Ti , $NiTi$, $NiTi_2$ exist. It seems reasonable to relate the peaks Ox_3 , Ox_4 , and Ox_4' to the oxidation of these compounds. Decreasing the sweep rate from 1 (Fig. 1B) to 0.1 V/s (Fig. 2A) makes the

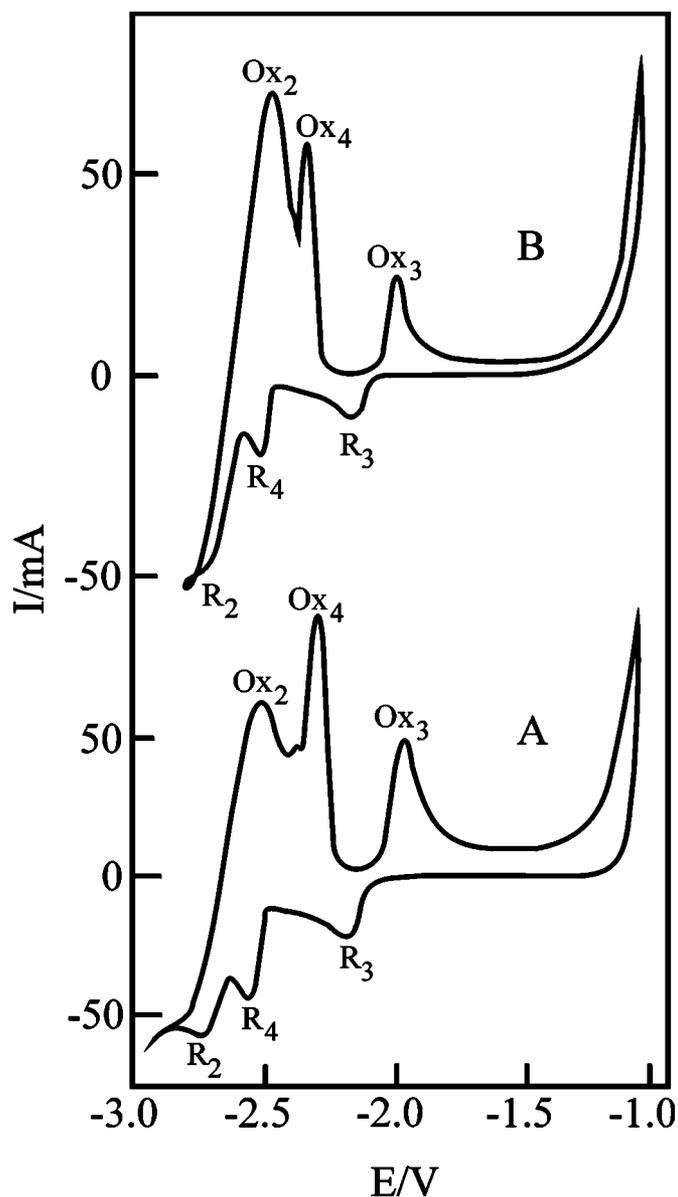


Figure 2. Cyclic voltammograms at different scan rates of a $\text{K}_2\text{TiF}_6\text{-NaCl-KCl-NaF}$ melt reduced with titanium metal. Nickel working electrode (area = 0.30 cm^2), temperature, 720°C ; $C_{\text{Ti}} = 0.21 \text{ mol/L}$. Scan rates: (A) 0.1 and (B) 0.02 V/s.

peak Ox_4' less intensive and with a sweep rate at 0.02 V/s (Fig. 2B) it becomes hardly visible. This behavior seems to be in agreement with the fact that we never obtained a definite layer of NiTi_2 during our deposition experiments at fixed potentials, whatever potential we applied. This suggests that NiTi_2 is only a transition state during the electrochemical deposition. This is interesting to compare with previous results by Robin *et al.*⁵ obtained at nickel electrodes on Ti(III) dissolved in FLINAK melts with a scan rate of 0.1 V/s (*i.e.*, the same as in Fig. 2A). On the oxidation part of their voltammogram the pattern with three oxidation waves seems to be similar to what we find, however, the reduction part differs since they⁵ only assign one wave due to alloy formation.

Chronopotentiometry and thermodynamic estimations.—Chronopotentiometry can often supply useful information about the alloy formation at the surface of an electrode. In Fig. 3 we present a current reversal chronopotentiogram at a nickel electrode. In addi-

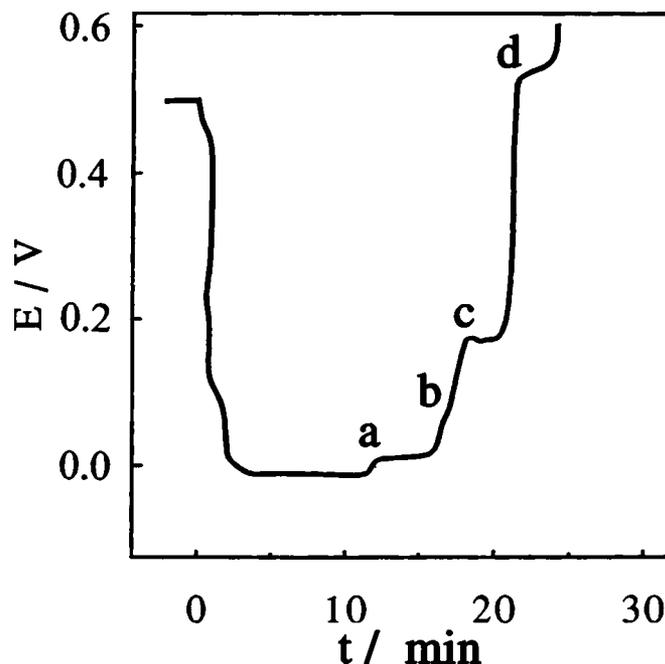
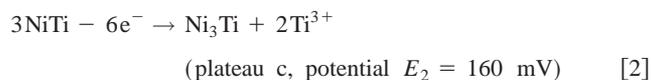
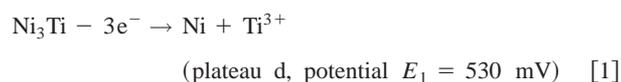


Figure 3. Current reversal chronopotentiogram at a nickel electrode in a $\text{K}_2\text{TiF}_6\text{-NaCl-KCl-NaF}$ melt at 720°C . $C_{\text{Ti}} = 0.1 \text{ mol/L}$. Electrode area: 0.32 cm^2 . Current -4 mA (12 min) and $+4 \text{ mA}$. Potentials given vs. Ti/Ti^{3+} .

tion to the plateau a, which corresponds to dissolution of the pure titanium, two plateaus are clearly seen at 530 and 160 mV vs. Ti/Ti^{3+} . We may suggest that these are connected to the equilibrium reactions



Further, a shoulder (marked b at Fig. 3) is seen at a potential $E_3 = 70 \text{ mV}$, which could have the same origin as Ox_4' (Fig. 1 and 2). It may be related to the equilibrium



In a recent paper Robin¹⁸ also observed three steps connected to the dissolution of titanium-nickel alloys deposited from an all fluoride melt (FLINAK). The potential corresponding to the dissolution of Ni_3Ti is in a good agreement with our value. For the other two potentials the values obtained by Robin are somewhat higher than ours.

The potential values are correlated to the thermodynamic properties of the alloys. According to the Reactions 1-3 the Gibbs energies of formation of the three alloys are linked to the E values through the equations

$$\begin{aligned} \Delta G_{\text{Ni}_3\text{Ti}} &= -3FE_1 \\ \Delta G_{\text{NiTi}} &= (-6FE_2 + \Delta G_{\text{Ni}_3\text{Ti}})/3 \\ \Delta G_{\text{NiTi}_2} &= -3FE_3 + \Delta G_{\text{NiTi}} \end{aligned}$$

Applying the measured potentials the following values are obtained

$$\begin{aligned} \Delta G_{\text{Ni}_3\text{Ti}} &= -154 \text{ kJ mol}^{-1} \\ \Delta G_{\text{NiTi}} &= -82 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta G_{\text{NiTi}_2} = -102 \text{ kJ mol}^{-1}$$

These values are systematically greater (about 40%), than the values given in Barin's handbook.¹⁹ To explain that divergence the presence of divalent titanium ions could be suggested in the mixed chloride-fluoride melts. Indeed, it is well known^{7,20} that, in pure alkali chloride melts, titanium ions in equilibrium with titanium metal exist mainly in the divalent form, Ti^{2+} . However, this hypothesis is not likely to apply to our melts. Introducing alkali fluorides into the bath stabilizes the higher oxidation state.^{7,21} It has been shown⁷ that the amount of Ti^{2+} becomes very small for a molar ratio $\text{F}^-/\text{Ti}_{\text{ion}}$ greater than 6. In the present electrolyte the ratio is around 50 which excludes the possibility of significant amount of Ti^{2+} . This conclusion is confirmed by the recent work of Polyakova *et al.*,⁹ who studied the reduction of titanium ions in nearly the same solvent as we apply. For the Ni_3Ti alloy our result for the Gibbs energy of formation is in good agreement with the value measured by Gachon *et al.*²² It should be pointed out that the thermochemical measurement reported in the literature seems to disagree quite considerably.²³

Oxide additions.—The obvious choice for a working electrode to investigate the influence of oxide would be tungsten. Unfortunately the waves on the cyclic voltammograms performed with tungsten electrodes merged to such an extent that made it impossible to distinguish any effect from the oxide additions. Consequently we have applied platinum indicator electrodes for our investigations. This offered the advantage of a large potential window but also a risk of perturbation from titanium-platinum alloy formation. The result can be seen in Fig. 4, that shows voltammograms recorded with platinum electrodes on melts with various oxides to titanium molar ratios. On the voltammogram with no oxide added (Fig. 4A) the waves R_1 (-1.25 V) and Ox_1 occur at potentials very similar to what we found with tungsten electrodes (Fig. 1A). They are certainly due to the Ti(III)/Ti(IV) redox couple. We also recognize the reduction wave R_2 (-2.75 V), which we have previously related to deposition of titanium metal. Indeed the corresponding oxidation wave, Ox_2 , has the typical shape of a stripping wave. Similar to the case with nickel electrodes, a reduction wave, R_3 (-2.00 V), preceding the metal deposition wave can be observed. From experiments performed with different cathodic switching potentials it appears that the oxidation waves Ox_3 and Ox'_3 are connected to R_3 . These waves can be explained as due to deposition and dissolution of Ti-Pt alloys. It is known from the phase diagram,²⁴ that titanium and platinum form several intermetallic compounds, *e.g.*, Ti_3Pt and TiPt . Polyakova *et al.*⁹ found reductions, similar to our R_1 and R_3 waves. They also observed several oxidation waves, which were assigned to the dissolution of titanium-platinum alloys.

In Fig. 4B is a voltammogram of a melt with oxide added (O/Ti molar ratio equal 0.44). Clearly a new reduction wave $\text{R}_{\text{O}1}$ (-1.81 V) appears at a potential more positive than the one for alloy formation (R_3). It also seems that R_1 is disappearing. On the oxidation side the wave due to dissolution of metallic titanium (Ox_2) has obviously decreased upon oxide addition, and a wave Ox' , which appear at a potential near Ox'_3 (Fig. 4A) has grown. The voltammogram on Fig. 4B with the less negative reverse potential could suggest that Ox' to some extent is associated with $\text{R}_{\text{O}1}$. With tungsten electrodes a small anodic peak, which may compare to our Ox' peak, has been related to the presence of oxide in $\text{K}_2\text{TiF}_6\text{-NaCl-KCl-NaF}$ melts.⁹ However no cathodic wave due to oxide as clear as $\text{R}_{\text{O}1}$ has been observed previously.

The voltammogram of a sample with even more oxide added (O/Ti = 1.5) can be seen at Fig. 4C. Some interesting changes can be observed when we compare it to the voltammogram with less oxide added (Fig. 4B). It is obvious that the current due to titanium deposition (the R_2 wave) decreases considerably when more oxide is added. Second, a new reduction wave $\text{R}_{\text{O}2}$ appears at -1.50 V. The shape of this wave is not what would be expected for a deposition

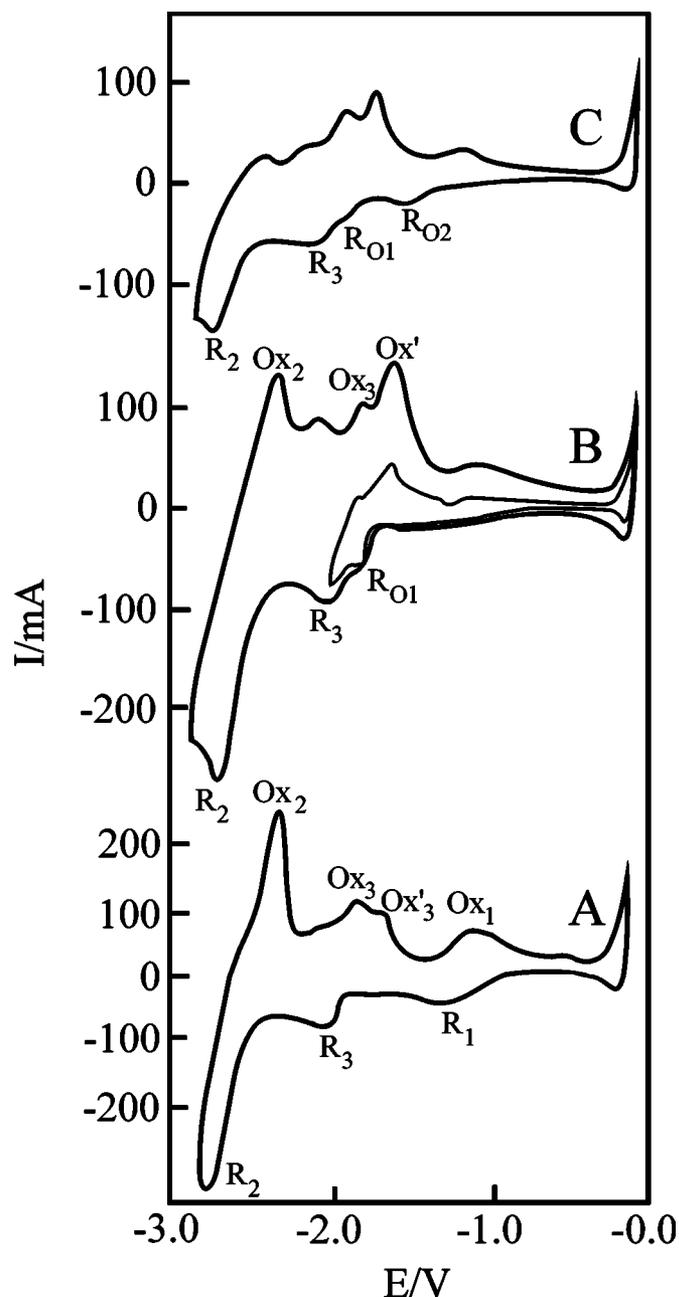


Figure 4. Cyclic voltammograms of $\text{K}_2\text{TiF}_6\text{-NaCl-KCl-NaF}$ melts at 720°C with and without added oxide. Platinum working electrodes (area = 0.31 cm^2), scan rate 1 V/s . (A) $C_{\text{Ti}} = 0.18 \text{ mol/L}$, no oxide added; (B) $C_{\text{Ti}} = 0.18 \text{ mol/L}$ with 0.080 mol/L oxide added; (C) $C_{\text{Ti}} = 0.104 \text{ mol/L}$ with 0.156 mol/L oxide added.

process; it rather resembles one of the homogeneous reactions in solution for the Ti(IV)/Ti(III) system. However it is not likely that it is due to reduction of a titanium(IV)-fluorocomplex since it appears at a potential different from R_1 in the melt without oxide added (Fig. 4A).

An explanation for these changes could be that the $\text{R}_{\text{O}1}$ and $\text{R}_{\text{O}2}$ waves arise from the reduction of two oxofluorotitanate complexes. It has recently been shown by vibrational spectroscopy that TiF_6^{2-} and TiOF_5^{3-} complexes are formed in FLINAK melts.²⁵ Concerning NaCl-KCl-NaF melts our preliminary Raman results indicate, that TiF_6^{2-} also exists in the mixed fluoride-chloride medium (bands at 613 and 290 cm^{-1}) and that oxofluoro complexes of the $\text{TiOF}_n^{(n-2)-}$

type are formed when oxide is present (bands around 910 cm^{-1}). In the FLINAK solvent we have observed two distinct vibrational bands in the $900\text{ to }1000\text{ cm}^{-1}$ region for melts with an O/Ti molar ratio of 1.5 (*i.e.*, similar oxide contents as the melt in Fig. 4C). This certainly suggests that more oxofluoro complexes may be involved. However to determine exactly which complexes we are dealing with more spectroscopic measurements will be needed.

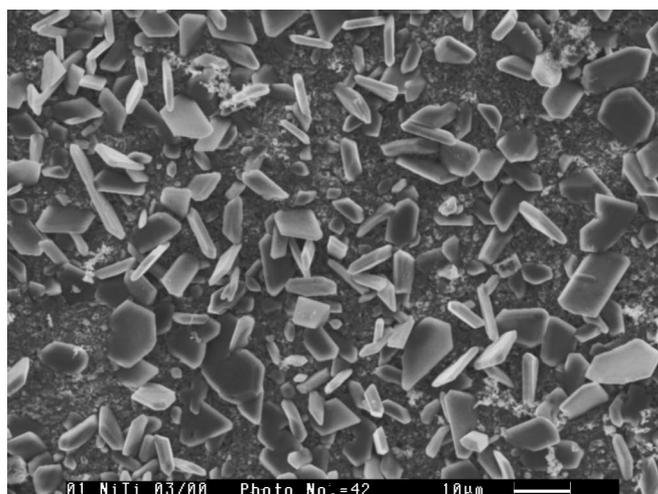
Depositions.—The amount of materials involved in the electrochemical reaction in the transient technique investigations remain very small, around a few micromoles and the thickness of the deposit does not exceed a few atomic layers. To obtain thicker layers which could be analyzed by EDX and X-ray diffraction longer electrolysis must be performed. The nature and morphology of the deposits was also investigated in order to examine the ability of alloyed layers to form protecting coatings. Deposition on nickel substrates were performed at different constant potentials, constant currents, and with pulse current.

Figure 5A shows a SEM photograph of the surface of a constant potential deposit on a nickel plate maintained at -2.06 V (*vs.* Pt/Pt²⁺) during 70 mins in a Ti(III)-NaCl-KCl-NaF melt at 700°C . The deposit consists of titanium crystals (according to EDX analysis) on top of the pure nickel substrate. The crystal adherence is poor and the cross-sectional analysis indicated that no intermediate alloy layers existed between the nickel substrate and the titanium crystals.

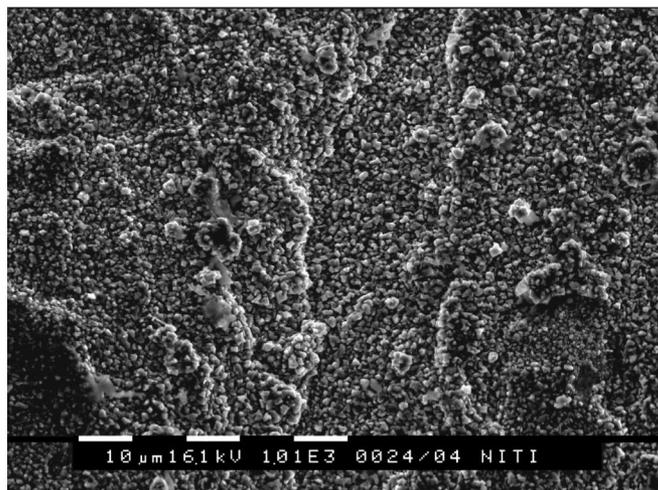
In Fig. 5 is further shown SEM photographs of the surface and cross section of a deposit on a nickel plate performed at a constant potential of -1.635 V for 70 min. From Fig. 5B it can be seen that the surface consists of a coherent layer of small ($\sim 1\text{ }\mu\text{m}$) crystals. The SEM picture of the cross section (Fig. 5C) reveals that the deposit consists of two layers. Both the inner and the outer layer have a thickness of approximately $2\text{ }\mu\text{m}$. The outer layer seems homogeneous and of uniform thickness. Between the inner layer and the substrate a Kirkendall layer appears. EDX analyses showed that the outer layer is composed of almost equal amounts (atom %) of titanium and nickel, whereas the inner layer has a nickel-to-titanium atomic ratio near three. The X-ray diffractogram of the plate has lines, which can be assigned to NiTi (d values of 2.18 and 2.02 \AA) and Ni₃Ti (d values of 1.95 , 2.08 , and 2.13 \AA , *i.e.*, the three strongest lines). Since we deal with a rather thin deposit it is not surprising, that the strongest line due to nickel (from the substrate) was also observed. We have further performed deposition experiments with pulse current. Figure 6 shows SEM micrographs of such a deposit. The surface (Fig. 6A) consists of a coherent and well-crystallized layer. EDX analysis showed that this layer was pure titanium metal. From the SEM photograph of the cross section (Fig. 6B) it appears that the coating is built up of three layers with a total thickness around $30\text{ }\mu\text{m}$. Between the substrate and the inner layer a Kirkendall interface has formed. EDX analysis of the cross section indicated the presence of titanium metal (outer layer) and NiTi (middle layer). It was difficult to make an exact analysis of the rather thin inner layer; but the nickel contents increased when the substrate was approached. The X-ray diffractogram showed lines due to titanium metal and NiTi.

A deposition at constant current (-38 mA) performed during 65 min in a melt with oxide added (O/Ti ≈ 1.5) resulted in the formation of a rather thin layer ($\approx 1\text{ }\mu\text{m}$) with a few crystals on the top. EDX analysis of both the surface and cross section showed that the layer consisted of Ni and Ti in the proportion of 3:1. The crystals were pure titanium metal. A X-ray diffractogram confirmed that the layer was made of Ni₃Ti; the three strongest lines for this compound (d values of 1.95 , 2.08 , and 2.14 \AA) were all observed. It seemed that no lines due to oxygenated species could be detected.

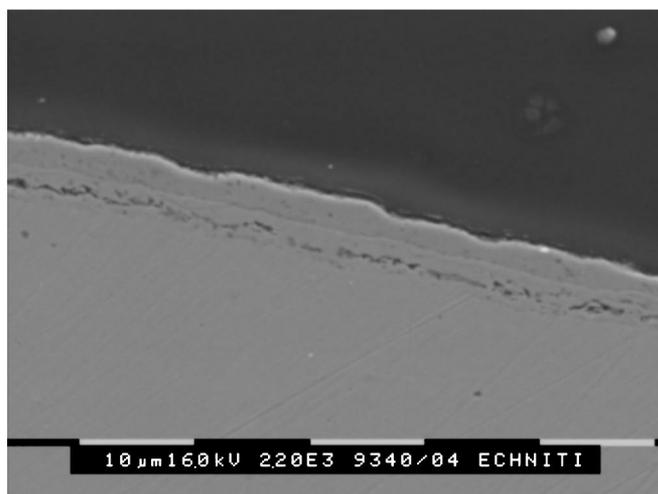
Our attempts to deposit TiB₂ were more successful than previously.¹⁰ When depositions were performed at constant potential just after the addition of KBF₄ to the K₂TiF₆-chloride-fluoride melt a well-crystallized and uniform surface layer could be obtained (Fig. 7). X-ray analyses showed that the layer consisted of pure TiB₂ (d values of 1.37 , 1.51 , 2.04 , and 2.62 \AA). Compared to our previous¹⁰



(A)

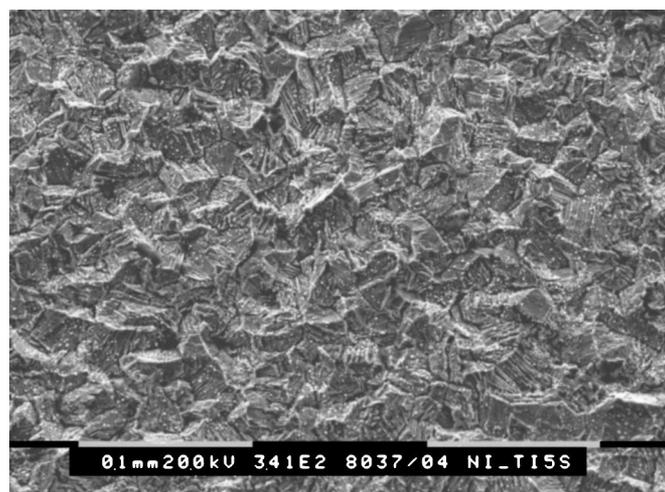


(B)

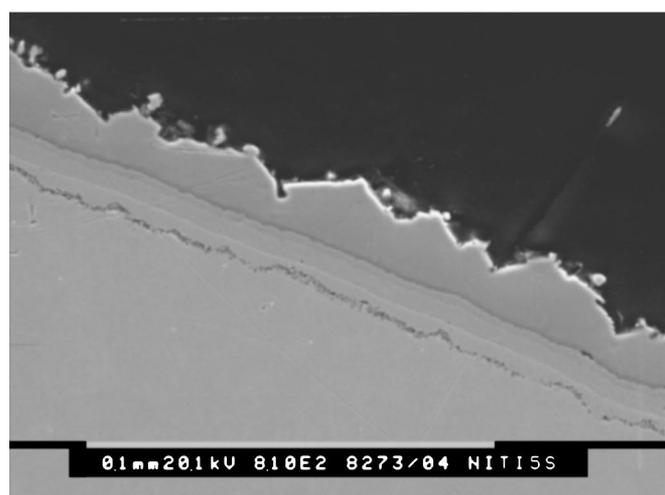


(C)

Figure 5. SEM micrographs of constant potential deposits on nickel plates from a NaCl-KCl-NaF-K₂TiF₆ melt with titanium metal added. $C_{\text{Ti}} = 0.30\text{ mol/L}$, temperature, 700°C . (A) Fixed potential $-2.06\text{ V vs. Pt/Pt}^{2+}$ for 1 h 10 min, surface (B) and (C). Fixed potential $-1.635\text{ V vs. Pt/Pt}^{2+}$ for 1 h 15 min; (B) surface and (C) cross section.

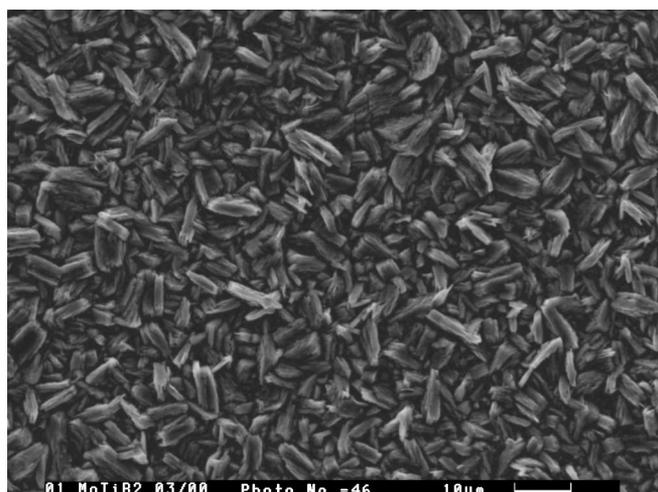


(A)

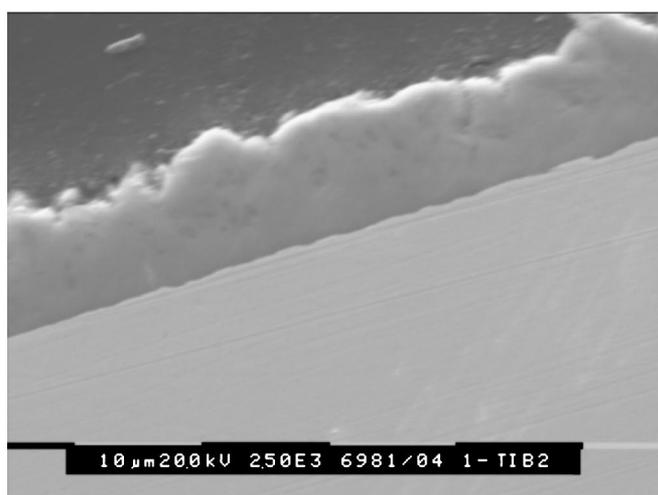


(B)

Figure 6. SEM micrographs of a pulse deposit on a nickel plate from a NaCl-KCl-NaF-K₂TiF₆ melt reduced with titanium metal. Temperature: 720°C. $C_{Ti} = 0.21$ mol/L. Pulse conditions: -3 mA in 22 ms and -70 mA in 2 ms, for 2 h, 40 min total. (A) Surface and (B) cross section.



(A)



(B)

Figure 7. SEM micrographs of a constant potential deposit from a NaCl-KCl-NaF-K₂TiF₆-KBF₄ melt with titanium metal added on a molybdenum plate at 700°C. $C_{Ti} = 0.30$ mol/L and $C_B = 0.600$ mol/L. Deposition for 1 h, 30 min, at -1.95 V (vs. Pt/Pt²⁺). (A) Surface and (B) cross sections.

plating experiments to obtain TiB₂ the concentrations of titanium and boron solutes were doubled, and the deposition potential was also somewhat changed (from -2.2 to -1.95 V vs. Pt/Pt²⁺). After some hours the melt seemed to be depleted in boron (due to the evaporation of approximately 10%/h at 700°C), and it was no longer possible to get good deposits.

Conclusions

The presence of oxide (in form of titanium oxofluoro species) can be detected as waves on the cyclic voltammograms. In general the use of a mixed fluoride-chloride melt as the supporting liquid seems to be a promising alternative to the all-fluoride melts for deposition processes involving titanium alloys and compounds. By electrolysis at various constant potentials surface layers of different Ni-Ti alloys, e.g., NiTi (nitinol), could be deposited on nickel substrates. With pulse plating coherent nickel titanium multilayers with titanium metal as the outer layer were obtained from mixed chloride-fluoride melts. Also deposition of high quality TiB₂ layers was possible from such melts. With the oxide present, only thin surface layers of Ni₃Ti could be deposited.

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