

ELECTRODEPOSITION OF Nb AND Al FROM CHLOROALUMINATE MELT ON VITREOUS CARBON

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Abstract

Niobium and aluminium were electrodeposited at 200 °C under argon atmosphere onto vitreous carbon from inorganic chloroaluminate melts (AlCl₃+NaCl) with added niobium. Niobium was introduced into the electrolyte by anodic dissolution of metallic niobium or by chemical dissolution of Nb₂O₅ in a melt of equimolar AlCl₃+NaCl mixture. The processes of deposition/dissolution onto/from vitreous carbon were investigated by cyclic voltammetry and chronoamperometry. Characterization of the obtained deposits was done by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The only observed reduction processes on the working electrode in the potential window from 1.000 V to – 1.000 V vs. Al, were individual niobium deposition and codeposition of niobium and aluminium with Al-Nb alloys formation.

Electrodeposition of niobium from the chloroaluminate melt with added niobium (V) oxide seems to start at around – 0.100 V vs. Al and at about – 0.200 V vs. Al aluminium starts codepositing. During the codeposition Nb-Al alloys were formed. Niobium deposition starting potential from the electrolyte with niobium added by anodic dissolution starts at 0.100 V vs. Al, and aluminium codeposition starting potential was at around – 0.025 V vs. Al, followed by Nb/Al alloy formation.

Keywords: Electrochemical deposition, chloroaluminate melts, niobium, aluminium, Al-Nb alloys

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Introduction

Last 50 years have seen increasing demand for niobium and its alloys [1]. Niobium's specific characteristics like corrosion resistivity, superconductivity, thermostability and biocompatibility, make it very interesting basic or added component for alloys. Niobium alloys are successfully applied in electronic, automotive, nuclear and space industry, but also in medical aids and implants productions [1-3].

Metallurgical processes for production of niobium [4] and its alloys [5,6] are complicated (high or low pressures, high or low temperatures) and expensive [7]. Therefore, research and development efforts into niobium electrodeposition as a viable manufacturing alternative have intensified [8-11]. The melts made of chloride and fluoride salts were found to be suitable electrolytes for electrodeposition of niobium and some of its alloys [8-16]. However, these melts require operating temperatures well above 500 °C and produce toxic and corrosive fumes.

Relatively recently efforts have resulted in development of non-aqueous electrolytes-melts which can be stable at temperatures below 100 °C, so called ionic liquids [17,18]. Although ionic liquids seem to be suitable media for the application, the electrodeposition processes of niobium and its alloys from these electrolytes have not yet been extensively investigated.

In the relevant literature, there is evidence of attempts to electrodeposit niobium on graphite, vitreous carbon, diamond, steel, Ni, Mo, Mg, W, Nb, Pt, Fe, Cu, etc., from melts made of different combinations of Na, K, Li, Cs, Ca, Al chlorides and fluorides. Some of those works [12,19-24] describe alloys being formed from cathode substrate and Nb deposited. However, there are only a few works [11,22,23,25,26] describing Al and Nb co-deposition that results in Nb-Al alloy formation and those are on W, Cu and Nb cathodes, but not on vitreous carbon.

The aim of this work was to investigate the possibility of niobium deposition and aluminium–niobium codeposition on vitreous carbon from a low temperature melt made of equimolar $\text{AlCl}_3 + \text{NaCl}$ mixture with added niobium ions.

Experimental

All electrochemical experiments were performed in a three neck Pyrex glass cell, described elsewhere [27], under inert argon atmosphere at 200 °C. Central Teflon plug carried a vitreous carbon - working electrode with 0.5 cm² active surface; left plug held a shovel shaped anode of niobium (5 cm² 99.95% Nb) and argon inlet/outlet; right plug held a Luggin capillary with an aluminium reference electrode (cylindrical rod 3 mm in diameter, 99.999% Al) and a thermocouple connected to a thermostat of the thermo mantel. Experiments were performed in a hermetically sealed acrylic glove box. Electrochemical techniques were applied and results recorded by an EG&G PAR Potentiostat/Galvanostat Model 273A supplied with Power Suite software (Princeton Applied Research).

Working surface of the vitreous carbon electrode was mechanically polished on emery paper, and then on polishing cloth impregnated with Al_2O_3 powder. Finally, the electrode was washed in diluted HCl and rinsed in distilled and then deionised water. Aluminium electrodes surfaces were mechanically polished by emery paper and chemically etched in water solution of 50% HF + 15% H_2O_2 with intense stirring for 30 to 60 s, followed by 30 to 60 s of rest in the solution of cc. NH_4NO_3 + 5% H_2O_2 . Finally the electrodes were rinsed with distilled water, deionised water and absolute ethanol.

Niobium electrodes were mechanically polished by emery paper and etched in acid mixture of cc. HF : cc. HNO₃ = 3 : 1 in three intervals each of 10 s interrupted by rinsing in deionised water and finally washed with absolute ethanol.

The electrolyte used was a melt of equimolar AlCl₃+NaCl mixture enriched with Nb ions by chemically dissolved Nb₂O₅ or anodically dissolved Nb metal. Only fresh anhydrous AlCl₃ was used for each melt preparation. It was placed at the bottom of the cell and covered with NaCl which was previously dried for 10 hours at 550 °C. Mixture was then heated slowly to 200 °C until colourless liquid electrolyte was apparent. The liquid electrolyte was then subjected to pre-electrolysis (working electrode 99.999 Pt; counter and reference electrodes 99.999% Al) under argon atmosphere and current density of -0.2 mAcm^{-2} .

In the case of niobium being added by anodic dissolution of Nb metal, all the cell electrodes were niobium and working electrode was dissolved under argon atmosphere (the current density applied was 150 mAcm^{-2}) long enough to secure the wanted Nb concentration [23,25]. Typically dissolved Nb corresponded to about 0.4 to 1.2 mol% of NbCl₅ in the melt, which was recorded by weighting niobium anode.

Cyclic voltammetry experiments were performed by changing working electrode potential (measured versus Al reference electrode) at a chosen sweep rate (from 5 mVs^{-1} to 500 mVs^{-1}) from initial potential, E_i (usually 50 mV negative to equilibrium potential of vitreous carbon) to cathodic end potential, E_f , and back to E_i . Some of the cyclic voltammograms were obtained after the cathodic end potential, E_f , was held constant for some time before the reverse part of the cycle was performed. Potentiostatic experiments were carried out within the same potential windows by holding cathodic end potentials for 2-4 hours whereupon cathodes were withdrawn from the cell under applied potential. The surfaces of these electrodes were analyzed by scanning electron microscopy (SEM „JEOL”, model JSM-5800, Japan) and energy dispersive spectroscopy (EDS, „Oxford INCA 3.2”, U.K.).

Results and discussion

Cyclic voltammogram recorded with vitreous carbon electrode in the melt made of equimolar AlCl₃+NaCl mixture at 200 °C within chosen potential window is shown in Fig.1 and suggests start of aluminium deposition at around -0.025 V vs. Al. It displays only deposition and dissolution of aluminium.

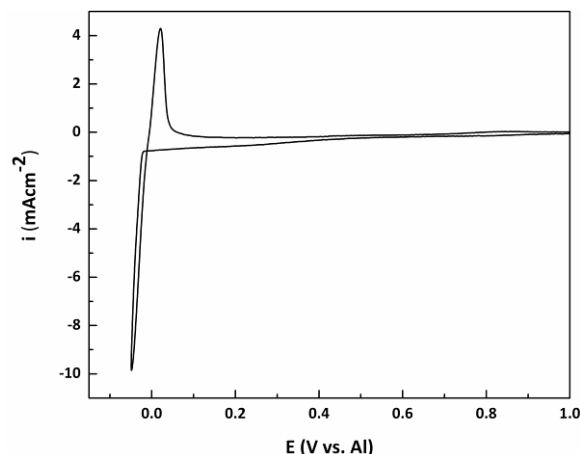


Fig.1. Voltammogram recorded with vitreous carbon electrode in $AlCl_3+NaCl$ melt, $v = 20$ mV/s; $E_i = 1.000$ V \leftrightarrow $E_f = -0.050$ V vs. Al; $T = 200$ °C.

Voltammograms obtained with vitreous carbon from the melt with niobium added by chemical dissolution of Nb_2O_5 are shown in Fig.2. a) and b). Those presented in Fig.2. a) show: one reduction and one oxidation peak (I and I_a) in the potential window from 1.000 V vs. Al to 0.100 V vs. Al; two reduction and two oxidation peaks (I, II and I_a , II_a) in the potential window from 1.000 V vs. Al to -0.250 V vs. Al; two reduction peaks (I, II) and one reduction current increase (III); and two oxidation peaks (I_a , II_a+III_a) in the potential window from 1.000 V vs. Al to -0.500 V vs. Al. Fig.2. b) shows voltammograms recorded in the potential window from 1.000 V vs. Al to -1.000 V vs. Al scanned at different scan rates. Comparison of voltammograms of Fig.2 with the voltammogram from Fig.1 allows for assumptions that the first two reduction peaks (I and II) and their anodic counterparts (I_a and II_a) reflect niobium reduction and oxidation in two steps [12,13,21]. First step of Nb(V) into Nb(IV) appears at around 0.375 V vs. Al, and second Nb(IV) into Nb at around -0.100 V vs. Al. The $i_{peak} = v^{1/2}$ analysis (i_{peak} – maximum peak current, v – sweep rate) for the second peaks (II and II_a) of the voltammograms presented in Fig. 2.b) revealed a linear function, which suggests diffusion controlled rate of the second step, i.e. Nb(IV) into Nb [28]. This would mean that niobium deposition, in the electrolyte used, proceeds under diffusion control at potentials more cathodic than -0.100 V vs. Al, all the way to -0.200 V vs. Al where aluminium deposition is observed as well. This was expected, because niobium concentration in the electrolyte was relatively small. It appears that aluminium and niobium codeposit at potentials more negative than -0.250 V vs. Al. In fact, with increasing cathodic overpotential from -0.200 V vs. Al onwards, Nb continues to deposit with diffusion limited current and aluminium with ever increasing rate. Anodic peaks (II_a and II_a+III_a) support the above assumptions. Two anodic peaks situated at most negative potentials in Fig 2. b) reflect: smaller one (III_b) - a dissolution of deposited Al which did not enter Nb-Al alloy; larger one (II_a+III_a) - a dissolution of codeposited Al and Nb, most probably Nb-Al alloy with different Nb participation.

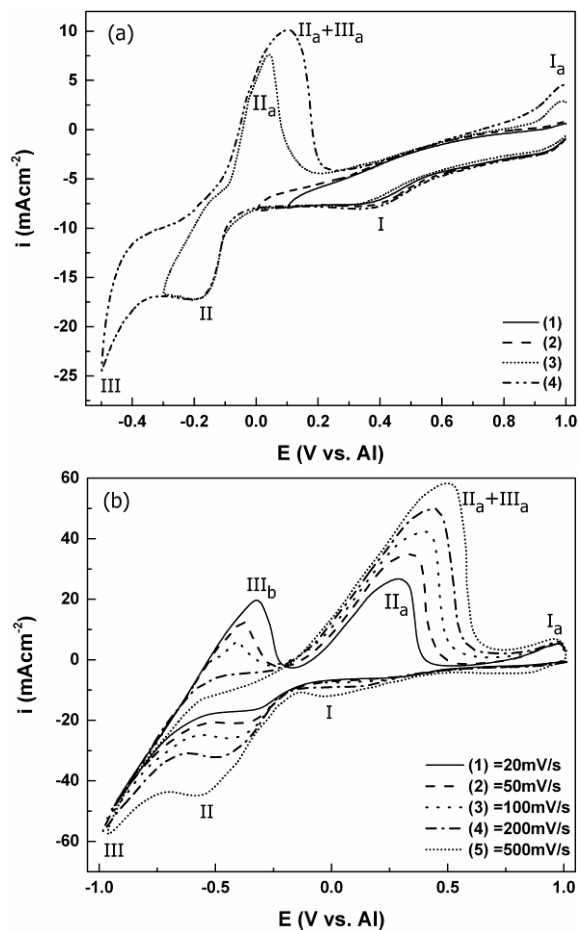


Fig. 2. Voltammograms recorded with vitreous carbon electrode in $\text{AlCl}_3+\text{NaCl}$ melt with Nb_2O_5 added, $T = 200\text{ }^\circ\text{C}$; **a**) $E_i = 1.000\text{ V} \leftrightarrow E_{f(1)} = 0.100\text{ V}$; $E_{f(2)} = 0.000\text{ V}$; $E_{f(3)} = -0.300\text{ V}$; $E_{f(4)} = -0.500\text{ V}$ vs. Al; $v = 20\text{ mV/s}$, **b**) $E_i = 1.000\text{ V} \leftrightarrow E_f = -1.000\text{ V}$ vs. Al.

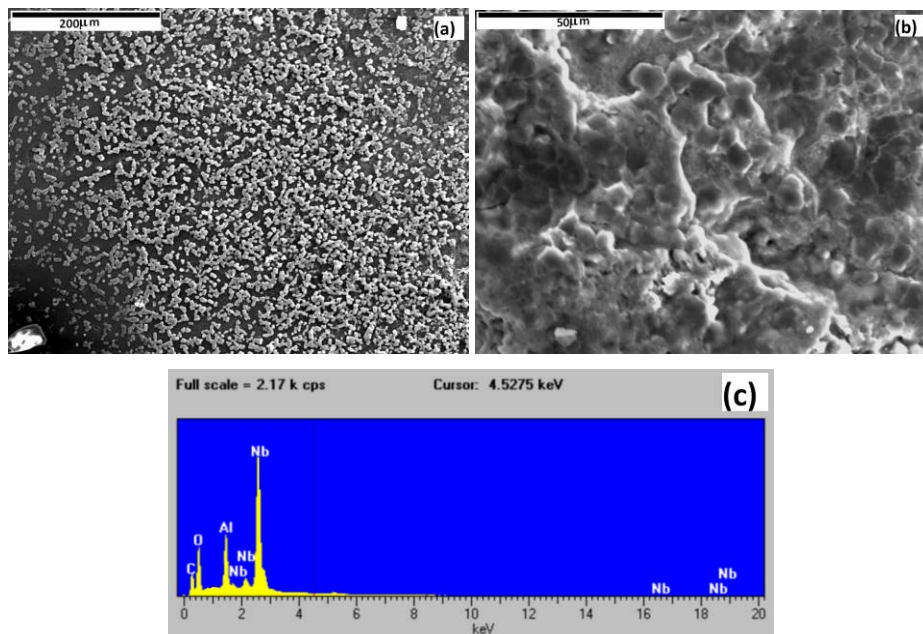


Fig. 3. SEM photograph of a vitreous carbon electrode surface recorded after 2 hours of potentiostatic pulse of -0.450 V vs. Al cathodic overpotential applied in $\text{AlCl}_3+\text{NaCl}$ melt with added Nb_2O_5 , $T = 200\text{ }^\circ\text{C}$: a) magnification 200x; b) magnification 1000x; c) EDS analysis of the sample given as a) and b).

Results of SEM and EDS analysis obtained from vitreous carbon electrode, in the electrolyte used with the niobium added by Nb_2O_5 dissolution, exposed for 2 hours to a potential step reaching into aluminium overpotential region are presented in Fig.3. The deposit shown in Fig.3. a) and b) was identified in Fig.3.c) as Nb and Al. These findings support the assumptions made earlier that niobium and aluminium have been deposited and codeposited. A trace of oxygen was impossible to avoid because the samples had to be exposed to the air during handling.

Typical examples of voltammograms recorded with vitreous carbon electrode in the electrolyte made of equimolar $\text{AlCl}_3+\text{NaCl}$ mixture with niobium added by anodic dissolution of Nb metal, are presented in Fig.4. a), b) and c).

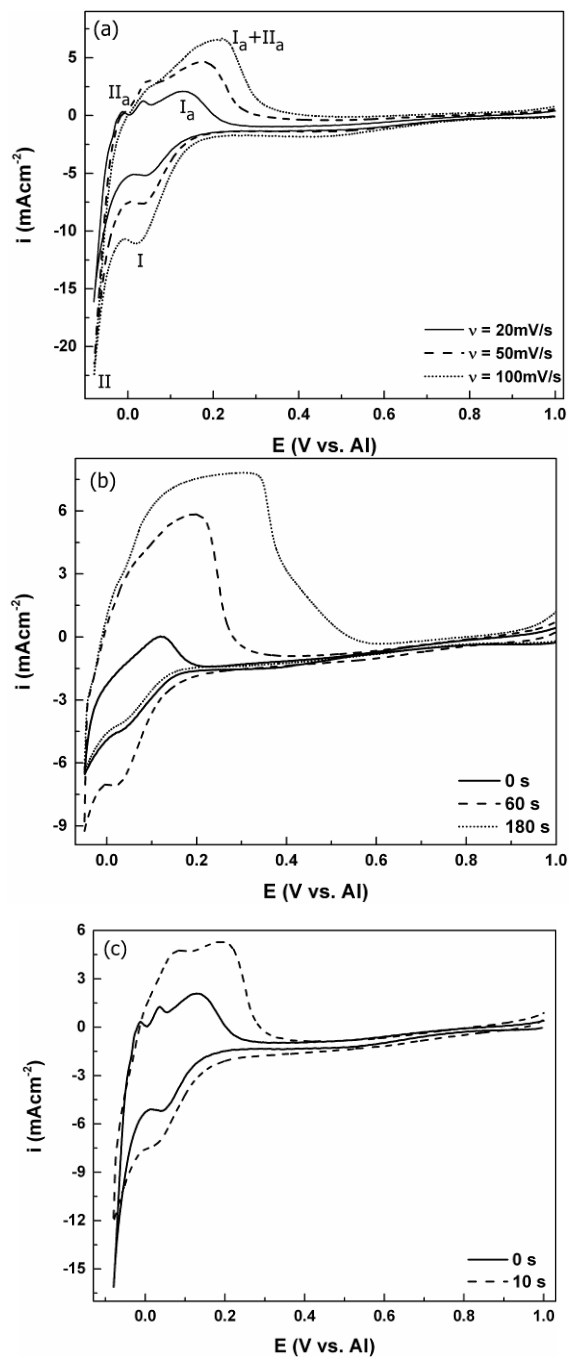


Fig. 4. Voltammograms recorded on vitreous carbon electrode in AlCl₃+NaCl melt with Nb added by anodic dissolution of Nb: **a)** different sweep rates applied; **b)** and **c)** cathodic end potential, E_f , being held for different time, $v = 10$ mV/s; $T = 200$ °C.

Some differences between the voltammograms shown in Fig.2. a) and b) recorded in the melt with niobium added by Nb_2O_5 dissolution and these ones shown in Fig.4. a), b) and c) are obvious. First, the number of reduction and oxidation peaks is different and second, the starting potentials of the recorded peaks are different.

In Fig.4 a), b) and c) there is one reduction peak and one reduction current increase: the first (situated at more positive potentials (I) starting at around 0.100 V vs. Al) reflects niobium deposition, and the second (situated at more negative potentials (II) starting at around -0.025 V vs. Al) reflects aluminium deposition and codeposition with Nb. Analysis of the niobium deposition peaks obtained with different sweep rates (e.g. Fig. 4.a) according to relation $i_{\text{peak}} = v^{1/2}$ resulted in a straight line, suggesting diffusion controlled niobium deposition. This has been expected, because niobium concentration in the electrolyte was relatively small. The dissolution of the niobium electrodeposited (the first reduction peak I) is reflected in the oxidation peak positioned at the most positive potentials (I_a). However, dissolution of the aluminium deposited and codeposited with niobium is reflected partly by already mentioned oxidation peak (I_a) and by the other two positioned at more negative potentials (II_a and I_a+II_a). At potentials from 0.700 V vs. Al to 0.300 V vs. Al, sometimes traces of a reduction peak (with no oxidation counterpart) can be noticed. This might be reflection of a very small concentration of Nb(V) ions, product of anodic niobium dissolution, being reduced to some lower oxidation state [12,13,21].

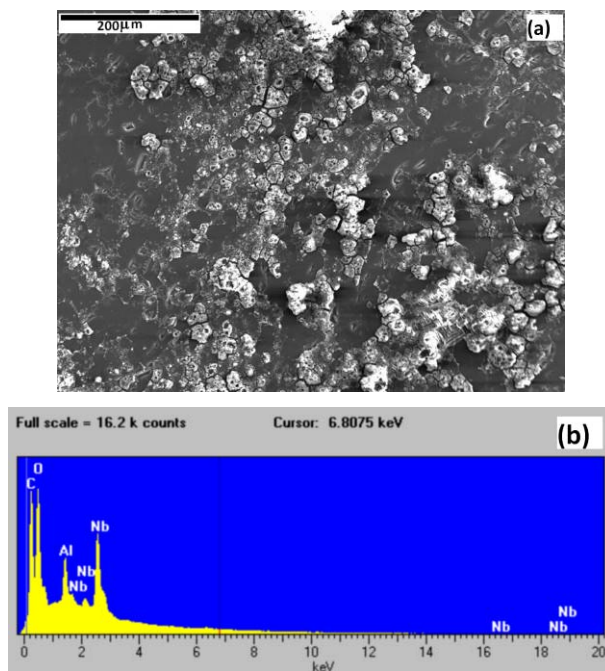


Fig. 5. **a)** SEM photograph of the vitreous carbon electrode surface recorded after 4 hours of -0.030 V vs. Al cathodic overpotential applied as potentiostatic pulse in $\text{AlCl}_3+\text{NaCl}$ melt with Nb added by anodic dissolution, magnification 170 x; **b)** EDS analysis of the sample given as a); $T = 200$ °C.

The results obtained with cyclic voltammetry in the electrolyte with niobium added by anodic dissolution on working electrode held for some time at the cathodic end potential, E_f , entering both Nb and Al overpotential region, are shown in Fig. 4.b) and c) and support the general picture of niobium deposition and Al-Nb codeposition and alloy formation on vitreous carbon from used melt. Further confirmation was found in SEM and EDS analyses of the vitreous carbon surfaces being exposed for some time to potential step into aluminium overpotential region, Fig.5. a) and b). Clear evidence of Nb and Al being present in the grains of deposit from Fig.5.a) is shown in Fig.5.b).

Conclusions

Niobium was electrodeposited individually and codeposited with aluminium onto vitreous carbon from the melts made of $\text{AlCl}_3+\text{NaCl}$ equimolar mixture enriched with niobium at temperature $T = 200\text{ }^\circ\text{C}$.

From the electrolyte made of equimolar $\text{AlCl}_3+\text{NaCl}$ mixture with Nb added by Nb_2O_5 niobium deposition starts at about -0.100 V vs. Al and aluminium codeposition at around -0.200 V vs. Al, while from the electrolyte with niobium added by anodic dissolution of niobium, deposition starts at about 0.100 V vs. Al and aluminium codeposition at around -0.025 V vs. Al.

Codeposition of niobium and aluminium enables formation of Nb-Al alloy in a very controlled way by applying appropriate potential of electrodeposition at temperatures much lower than the temperatures used in conventional metallurgy. At aluminium overpotentials higher than -0.200 V vs. Al (in the melt with dissolved Nb_2O_5) and -0.025 V vs. Al (in the melt with anodically dissolved Nb), Nb-Al alloys with comparable content of both components are formed. For a given time of deposition, presence of Nb in a deposited alloy is controlled by Nb concentration in the electrolyte used and Al content is decided by the aluminium overpotential (current density) applied.

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