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ALLOY FORMATION BY Al AND Nb ELECTRODEPOSITION FROM CHLOROALUMINATE LOW TEMPERATURE MELT

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Abstract

Electrodeposition of Nb and Al onto platinum from equimolar AlCl₃+NaCl melt enriched with niobium ions was studied at 200 °C. Nb was introduced into the melt by anodic dissolution of Nb anode. Experimental techniques used for deposition and dissolution processes were cyclic voltammetry and potential step, and for analysis of the deposits obtained, scanning electron microscopy-SEM, X-ray diffraction-XRD and energy dispersive spectrometry-EDS. Niobium was deposited at overpotential individually and co-deposited with aluminium at aluminium overpotentials. It was found that Nb/Al, Nb/Pt, Al/Pt alloys were formed and Al and Nb deposited, depending on the potential applied.

Keywords: niobium, aluminium, Al-Nb alloy, Nb-Pt alloy, chloroaluminate melts

1. INTRODUCTION

Aluminium and niobium are metals which cannot be electrodeposited from electrolytes containing water or moisture. Their reversible potentials are significantly more negative than the reversible potential of hydrogen. Therefore, they have to be electrodeposited from melts or ionic liquids. Elevated temperatures needed to maintain a melt liquid and conductive sometimes lead to alloy formation between deposited metal and the cathode material used [1]. Electrochemical codeposition of two or more metals, on the other hand, offers an easy controlled and useful method for alloy formation. It is particularly useful in recycling processes which include Al, Nb and similar metals, because instead of obtaining individual metals which have to be subsequently processed into alloys, wanted alloys can be obtained directly.

Electrodeposition of niobium and its codeposition with aluminium from melts or ionic liquids have been a subject of very few reports [2-6] and those were devoted mainly to the mechanism of niobium ion reduction in the deposition process. Meanwhile, it was suggested that Nb/Al and Nb₃Pt alloys are good candidates for the next generation of superconductors [5,7,8].

In this work, the aims were to deposit niobium individually and, if possible, codeposit it with aluminium onto platinum (as neutral substrate) from a chloroaluminate melt enriched with niobium ions.

2. EXPERIMENTAL

All electrochemical experiments were performed in a three neck Pyrex glass cell, described elsewhere [9] under argon atmosphere (99.99 % Ar), at 200 °C. Cyclic voltammetry and constant potential electrolysis were carried out using a EG&G PAR Potentiostat/Galvanostat Model 273A (controlled with Power Suite software, Princeton Applied Research Corporation). Working electrode was a platinum rectangular plate (P=0.5cm², 99.999% Pt, Johnson, Matthey & Co. Ltd. Chemical division), reference electrode was an aluminium cylindrical rod (3mm in diameter, 99.999% Al, LTS Chemical Inc.) placed in a Luggin capillary, while the anode was shovel shaped and made from niobium (5cm² 99.95% Nb, HLMET Co, Ltd.). The electrolyte used in this work was a melt made of an AlCl₃+NaCl equimolar mixture with anodically

dissolved Nb [9]. Anodic dissolution of metallic niobium into the melt was carried out at current density of 150 mA cm^{-2} , long enough to secure the wanted Nb concentration [5,6] (all the cell electrodes were made from niobium during this procedure). Typically dissolved quantity of Nb corresponded to 0.4 to 1,2 mol% of NbCl_5 in the melt.

Electrochemical techniques used in the experiments were linear sweep voltammetry (LSV) and chronoamperometry. Some of the cyclic voltammograms were obtained by holding the final potential E_f constant for a specific time before the reverse segment of the cycle was performed. The chronoamperometry procedure involved a change of the working electrode potential from a starting potential, E_i , to a final potential, E_f , in the Al overpotential region and held constant at this potential for 120 minutes. The cathode was then retrieved from the cell under potential in order to preserve the deposited material. Samples were then washed with absolute ethanol and distilled water to remove the residual melt and left to dry in the air at room temperature.

The electrodeposits were examined by scanning electron microscope with an energy dispersive spectroscopy (EDS) (SEM - "JEOL", model JSM-5800, Japan, EDS - "Oxford INCA 3.2", U.K.) and X-ray diffraction (XRD, Enraf Nonius powder diffractometer).

3. RESULTS AND DISCUSSION

Typical examples of voltammograms obtained with a platinum working electrode in the melt of equimolar $\text{AlCl}_3 + \text{NaCl}$ mixture enriched with anodically dissolved niobium are presented in Fig. 1.a) and b). Fig. 1.a) displays a voltammogram obtained with the cathodic end potential stopped at 0,000 V vs. Al. The graph shows one cathodic peak and one anodic counterpart. The voltammogram in Fig. 1.b) obtained with cathodic end potentials in the region of aluminium overpotential values, displays two deposition and two (sometimes three) dissolution peaks. When the cathodic end potential exceeds the aluminium reversible potential in the used melt, the area under the curve for the three anodic peaks increases with increased deposition time, which is also true for the one dissolution peak when the cathodic potential is held at values positive to the aluminium reversible potential, Table 1.

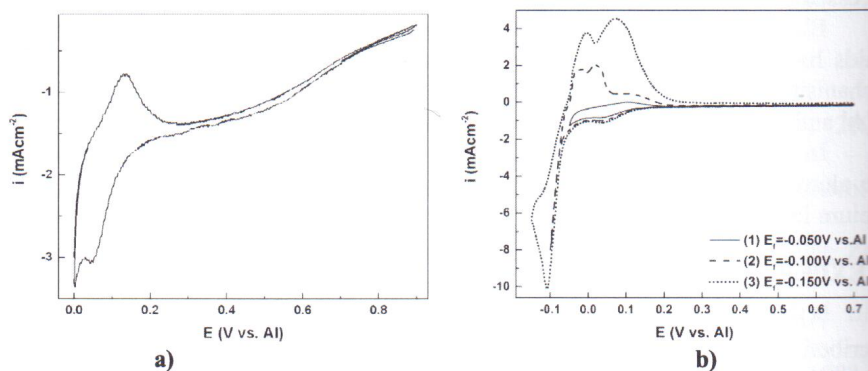


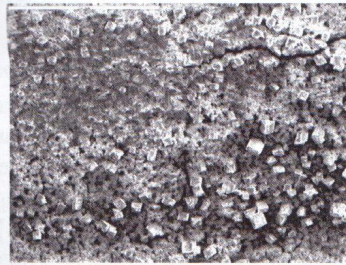
Figure 1 - Linear sweep voltammograms obtained on platinum electrodes from equimolar $\text{AlCl}_3 + \text{NaCl}$ melts with anodically dissolved Nb obtained at 200°C ; $v = 20 \text{ mV/s}$; a) $E_i = 0.900 \text{ V} \leftrightarrow E_f = 0.000 \text{ V vs. Al}$; b) $E_i = 0.700 \text{ V} \leftrightarrow E_f = -0.050 \text{ V vs Al}$ (solid line); $E_f = -0.100 \text{ V vs. Al}$ (dashed line); $E_f = -0.150 \text{ V vs. Al}$ (dotted line).

Results of SEM, EDS and XRD analysis obtained from platinum electrode in the used electrolyte exposed for 2 hours to a - 0.070 V overpotential vs. Al are presented in Fig. 2.a), b) and c). SEM photograph, Fig.2.a) reveals a rather coarse electrode surface showing a thick deposit being

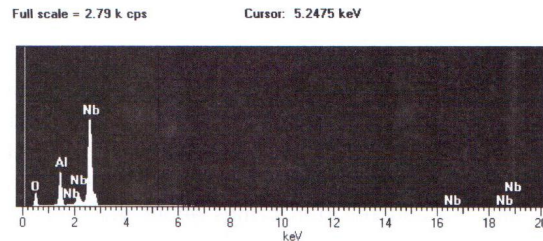
formed predominantly in the shape of boulders. EDS analysis of the deposit in Fig.2.b). shows presence of niobium, aluminium and oxygen. XRD spectra of the same deposit in Fig.2.c) suggest that beside metallic Nb and Al some Nb/Al, Nb/Pt and Al/Pt alloys are being formed as well.

Table 1- Impact of change in cathodic end potential and holding times on the amount of dissolved anodic charge.

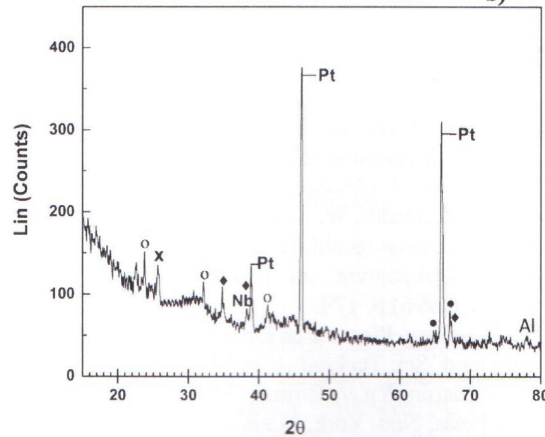
<i>Cathodic potential [mV vs. Al]</i>	<i>Holding time [s]</i>	<i>Anodic charge [mAs cm⁻²]</i>
5	300	15,13
-50	60	33,54
-50	180	58,82
120	60	265



a)



b)



c)

Figure 2 - a) SEM photo of the Pt surface after 2h being hold at $E_f = -0.070V$ vs. Al in the melt of equimolar mixture $AlCl_3+NaCl$ with anodically dissolved Nb at 200 °C (magnification 110x); b) EDS analysis of the same sample; c) XRD analysis of the same sample given in a): (Pt)-Pt[10]; (Nb)- Nb[11]; (●)- $AlNb_3$ [12]; (○)- Al_3Pt_5 [13]; (◆)- Nb_3Pt [14]; (x)- NbO_2 [15]; (Al)-Al[16].

It should be added that the EDS analysis of the samples obtained with potentials applied in the region somewhat cathodic to the maximum current of the first peak and still well anodic to the aluminium reversible potential identified only niobium and platinum, and the unavoidable oxygen, of course. The XRD results of the same samples besides metallic Nb and Pt substrate identified Nb/Pt alloy alike the system of Nb onto Au in the same melt [17].

The above presented findings propose the following picture:

- at potentials negative to the maximum of the first cathodic peak of the voltammograms, but still positive to the maximum of the second cathodic peak, there is evidence of metallic Nb and Nb₃Pt alloy being formed. Therefore, the potential close to the maximum of the first cathodic peak should be considered as the Nb reversible potential in the system used. Dissolution of the deposited Nb is represented by a well pronounced anodic peak;
- at potentials slightly negative to the maximum of the second peak, of the voltammogram, there is evidence of metallic Nb, metallic Al, Nb/Pt and Al/Pt alloys in the deposit obtained. This situation in the anodic part of the voltammogram is depicted by at least two anodic peaks (the one at more negative potentials reflects Al dissolution, the one at more positive potentials reflects Al/Nb alloys and Nb dissolution) often followed by the third one fading away reflecting Nb dissolution.
- at higher aluminium overpotentials all cathodic and anodic peaks increase in height and area except for the Nb deposition peak which soon reaches diffusion controlled deposition current density.

4. CONCLUSION

It was found that niobium can be electrodeposited and codeposited with aluminium onto a platinum electrode from a melt of an equimolar mixture of AlCl₃+NaCl with anodically dissolved niobium at 200 °C. It was recorded that the reversible potential of Nb present in the used small concentration was 0.050 to 0.100 V positive to the Al reversible potential in the melt. Al and Nb codeposition brings about the formation of an AlNb₃ alloy while Al [18] and Nb underpotential deposition produces Al₃Pt₅ and Nb₃Pt alloys by an interdiffusion interaction with the Pt substrate.

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