

## Electrochemical Behaviour of Niobium and Aluminium in Chloride Melts

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In the recent years there is growing interest towards studying of processes involving niobium and aluminium in chloride melts. Particular attention is attracted to the development of prospective method of electrorefining of niobium produced by reduction of the oxide with aluminium, and also to the preparation of Nb<sub>3</sub>Al intermetallides, which have relatively high temperature of transition to the superconducting state.

In the present work we investigated anodic dissolution of aluminium-niobium alloys in NaCl-KCl and NaCl-KCl-NbCl<sub>n</sub> melts, as well as cathodic reduction of niobium and aluminium from NaCl-KCl-NbCl<sub>n</sub>-AlCl<sub>3</sub> melts. The measurements were performed by galvanostatic, chronopotentiometric and potentiometric methods using an automatic electrochemical complex. Additionally, concentration of niobium, ω<sub>Nb</sub>, and its average oxidation state in the melt, n<sub>Nb</sub>, were also measured.

Studying the behaviour of Nb-Al alloy in NaCl-KCl melts by potentiostatic method showed that there is strong interaction between the components of the alloy. Polarization curves and chronopotentiograms recorded during anodic dissolution of the alloy include sections corresponding to the simultaneous dissolution of aluminium and niobium by three-electron reactions, oxidation Nb<sup>3+</sup>→Nb<sup>4+</sup>, niobium ionization by four-electron reaction, and the electrode passivation. After contacting the alloy with NaCl-KCl-NbCl<sub>n</sub> melt (ω<sub>Nb</sub>=7.0 wt.%, n<sub>Nb</sub>=3.7) at 710 °C we found that the surface layer of the alloy was depleted in aluminium content. The polarization of the electrode made of the alloy changes less upon increasing current density than the polarization of the electrode made of pure niobium (Fig. 1). This difference is likely arises due to preferential ionization of aluminium and thus comparatively small changes in niobium concentration in the melt layer near the electrode surface. At high current densities the potential changes of Nb-Al alloy and Nb electrodes have similar appearance.

We also studied the kinetics of electrochemical reduction of niobium and aluminium from NaCl-KCl-NbCl<sub>n</sub>-AlCl<sub>3</sub> melts containing 5.0 wt.% of Nb and 3.0 or 5.2 wt.% of Al at 730 °C, Fig. 2. A pure niobium cathode was used for this series of experiments. The polarization of glassy carbon cathode in NaCl-KCl-AlCl<sub>3</sub> (5.1 wt.% of Al) melt was measured at 720 °C in order to determine the potential of aluminum deposition. The appearance of "potential – current density" and "potential – time" dependencies were similar to these measured for niobium cathodic reduction from NaCl-KCl-NbCl<sub>n</sub> melts up to current densities of 1.5 A/cm<sup>2</sup>. At higher cathodic current densities there are regions of potential stabilization on the polarization curves, probably due to the formation of

niobium-aluminium alloys. Further increase of current density in all cases results in the deposition of aluminium as an individual phase at potentials around -2.0 V. The higher the concentration of niobium and aluminium in the melt, the more intense the formation of alloys of niobium and aluminium.

Using the obtained results we proposed possible process for electrochemical refining of niobium-aluminium alloys.

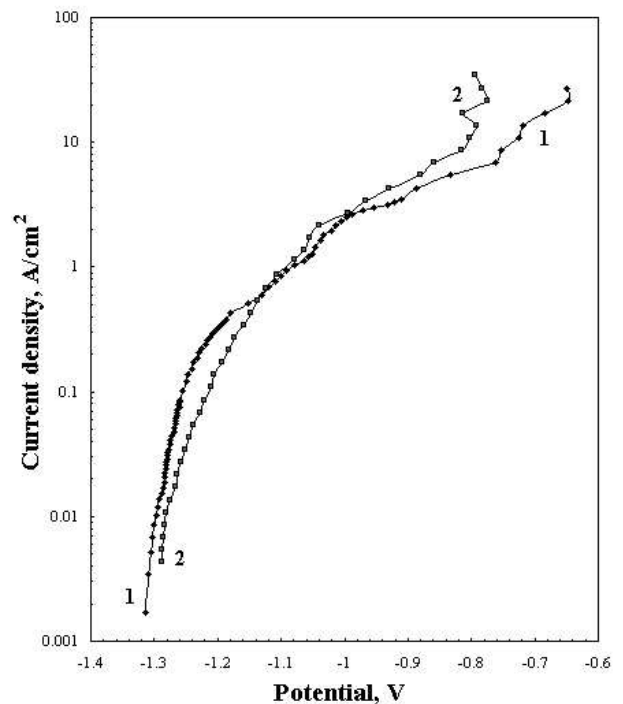


Fig. 1. Polarization curves recorded upon dissolution of Nb-Al alloy (1) and niobium (2) in NaCl-KCl-NbCl<sub>n</sub> melt (ω<sub>Nb</sub>=7.0 wt. %, n<sub>Nb</sub>=3.7) at 710 °C.

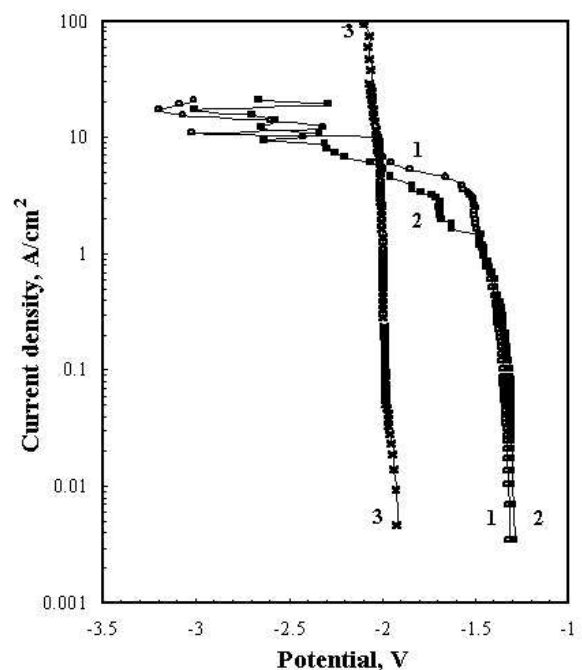


Fig. 2. Cathodic polarization of niobium (1, 2) and glassy carbon (3) electrodes in NaCl-KCl-NbCl<sub>n</sub>-AlCl<sub>3</sub> melt. ω<sub>Nb</sub>, wt. %: 1, 2 - 5.0; 3 - 0. ω<sub>Al</sub>, wt. %: 1 - 3.0; 2 - 5.2; 3 - 5.1.