Electrochemical Behaviour of Aluminum Phosphate in Cryolite–Alumina Melts

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The present work deals with the electrochemical behaviour of aluminum phosphate in cryolite–alumina melts. In the process for electrowinning of aluminum, phosphorus acts as an impurity. It enters the system with raw materials (especially alumina), and leaves in the produced aluminum and the off-gases. The content of phosphorus in the electrolyte is in the order of hundreds of ppm, depending on the technology and the way of cell operation.

One of the important reasons for reduced current efficiency (CE) in the Hall – Heroult process is the presence of multivalent species in the bath, which are supposed to undergo cyclic electrochemical reduction and oxidation [1, 2]. Phosphorous is known to be the most deleterious impurity from the point of view of reduced CE, values around 0,8-1 % loss of CE per 100 ppm of P in the bath were reported both in industrial [3, 4] and laboratory cells [1, 2, 4]. The laboratory studies of effect of phosphorous on the CE [2, 4] indicated a change in its behaviour at high phosphorus contents; for more than 500 ppm of P in the bath the CE remains uneffected.

Experiments were carried out in a furnace under argon atmosphere at 1020 ºC. Alumina crucible served as container for the alumina saturated cryolite melt, and different amounts of dried $AlPO_4$ were added. Tungsten wires were used as working and counter electrodes, while aluminium was used as reference electrode.

Electrochemical reactions due to aluminium phosphate were studied by cyclic voltammetry in melts with different concentration of phosphorus from 50 to 1500 ppm. A tungsten working electrode in cryolite enables to study processes taking place from about 0.15 V to 1 V with respect to an aluminium reference electrode.

Fig. 1 shows two CVs recorded in molten cryolite-alumina at two different concentrations of phosphorous; 409 and 512 ppm. The CV for 409 ppm indicates a red/ox pair A/B. At around 0.25 V the alloying of aluminium with tungsten working electrode starts (G/H). In the second CV recorded with 512 ppm of P the peak couple C/D and waves E/F appear indicating a change in electrochemical behaviour with concentration, which could explain the CE dependence on P concentration in the bath.

Fig. 2 illustrates a CV obtained in a melt containing 813 ppm of phosphorus. One can see that a new peak I appears, occurring only in melts with concentration of P higher than about 800 ppm. It is probably due to slow formation of some reducible species, stable only in a certain narrow range of concentration.

References
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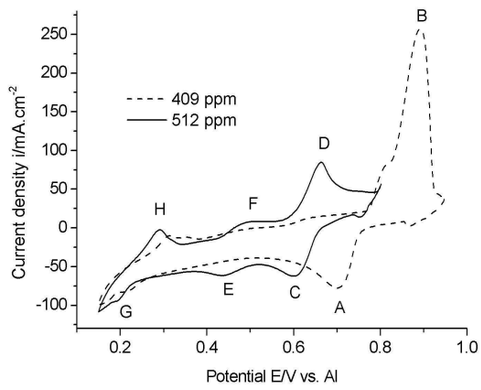

Fig.1. CV recorded in cryolite-alumina melt containing 409 and 512 ppm of phosphorus. Working electrode tungsten, reference electrode aluminum, sweep rate 0.1 $V.s^{-1}$.

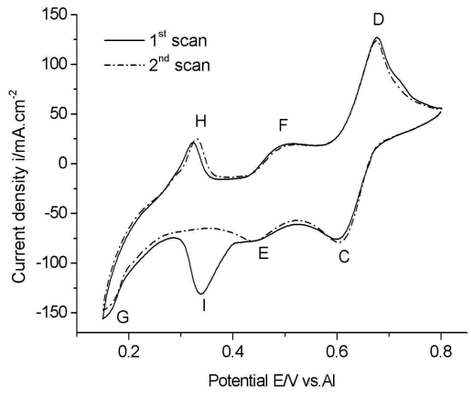

Fig. 2. Two scans recorded in a melt containing 813 ppm of phosphorus. Working electrode tungsten, reference electrode aluminum, sweep rate 0.2 $V.s^{-1}$.