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ALLOY FORMATION BY UNDERPOTENTIAL DEPOSITION OF Mg ON Al FROM NITRATE MELTS

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ABSTRACT

Magnesium has been underpotentially deposited on aluminium electrodes from magnesium nitrate and magnesium nitrate-ammonium nitrate melts at temperatures ranging from 85°C to 200°C. Electrochemical techniques used were cyclic voltammetry and potential step. Deposits were studied by electron microscopy, EDS and XRD. In the magnesium UPD region on Al the processes of nitrate, nitrite and water (when present) reductions take part simultaneously with magnesium UPD. The underpotential deposition of magnesium leads to Al₃Mg₂, Mg₂Al₃ i Al₁₂Mg₁₇ alloys formation.

INTRODUCTION

One of the ways to obtain a metal, and/or an alloy, under very controlled conditions is a direct isothermal electrochemical deposition (electrodeposition). Detailed investigations of the processes involved in electrodeposition of metals and alloys lead to recognition of electrodeposition of metals on foreign substrates at potentials more positive than the equilibrium potential of the depositing metal (the underpotential deposition – UPD) [2]. Most of the initial experimental work was done in aqueous electrolytes until 1980-ties when the same phenomena was observed with aluminium on gold, silver and copper from chloride melts at temperatures bellow 573K [1].

It was soon found that a metal electrodeposited at UPD from aqueous solution, nonaqueous solutions and melts at room temperature onto cathode of a different metal can diffuse into the substrate and make alloys.

However, literature is rather poor in articles describing electrodeposition of magnesium from nitrate melts or magnesium underpotential deposition and alloy formation from nitrate melts is practically nonexistent [3]. One of the main reasons must be the fact that it is impossible to remove water from

magnesium nitrate hexahydrate by heating, because it decomposes before it loses water and transforms into magnesium (II) oxide.

The aim of this work was to establish whether there was an underpotential deposition of magnesium onto aluminium from magnesium nitrate melts, and if there was one does it lead to magnesium/aluminium alloys formation.

EXPERIMENTAL

Experiments were done under 99,99% Ar atmosphere in a electrochemical cell made of Pyrex glass placed in a heating mantle with temperature controlled (electronic thermostat) between 363 and 463K \pm 2K. Working electrode was 3mm thick 99,999% pure Al cylinder; reference electrode was 3mm diameter 99,999% Mg wire in a glass Luggin capillary; and anode was 99,999% magnesium in the shape of a curved rectangular shovel (7,5 cm² active surface area). Temperature in the cell was controlled with a thermocouple (\pm 3K). Whole cell set up was placed into transparent plastic "glove box" in order to sustain a moisture free atmosphere around the cell.

The melts used for electrolytes were: Mg(NO₃)₂ x 6H₂O (at 340-400K), eutectic mixture Mg(NO₃)₂ x 6H₂O : NH₄NO₃ x XH₂O = 25 mas.% : 75 mas.% (at 380-450K), nonaqueous Mg(NO₃)₂ (at 440-500K), and nonaqueous eutectic mixture Mg(NO₃)₂ : NH₄NO₃ = 25 mas.% : 75 mas.% (at 390-500K). The procedure for water removal from magnesium nitrate hexahydrate consisted of two steps. First step: the mixture of 5g of magnesium nitrate hexahydrate and 15 cm³ of threemethylorthoformate was brought to boiling and kept for 90 minutes under reflux at 343K. Second step: after 90 minutes of previous treatment the mixture now consisting of an ethyl ester of formic acid, methanol and crystals of nonaqueous magnesium nitrate was submitted to vacuum distillation at 343K. Upon removal of the visible liquid the remaining crystals were vacuum dried for additional 60 minutes. Nonaqueous magnesium nitrate was kept in a closed glass container in a desiccator furnished with plenty of silicagel. Ammonium nitrate hexahydrate was dried for ten hours at 378K. Wanted amounts of magnesium nitrate alone, or mixtures with ammonium nitrate, were placed into the cell supplied with electrodes. Closed cell was then put into the heating mantel, argon supply was turned on and the system was heated gradually to the wanted temperature [4].

Electrochemical techniques used were: cyclic voltammetry and potential step. The potentials of working electrodes were measured in relation to the equilibrium potential of magnesium reference electrode in the melt used under given conditions.

The potential step method included change of the working electrode potential from an initial potential E_f to a potential, E_x (50 to 100 mV more

positive to aluminum equilibrium potential in the given melt). E_x potential was held constant for 120 minutes, whereupon the cathode was retrieved from the cell under the reigning potential in order to preserve deposited material or possible alloys formed during UPD or OPD of aluminum. The electrodes were successively washed with deionized water or absolute ethyl alcohol until visible remains of melt were removed. The surfaces of such electrodes were analyzed by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray diffraction (XRD).

RESULTS AND DISCUSSION

SEM, EDS and XRD analysis of the Al working electrode surface exposed to linear sweep voltammetry as well as potential step regimes in the Mg UPD region (cathodically up to 50 mV vs. Mg) always showed presence of Mg, Al, oxygen and Al/Mg alloys irrespective of the moisture being present in the melt. Comparison of the EDS and XRD results obtained from

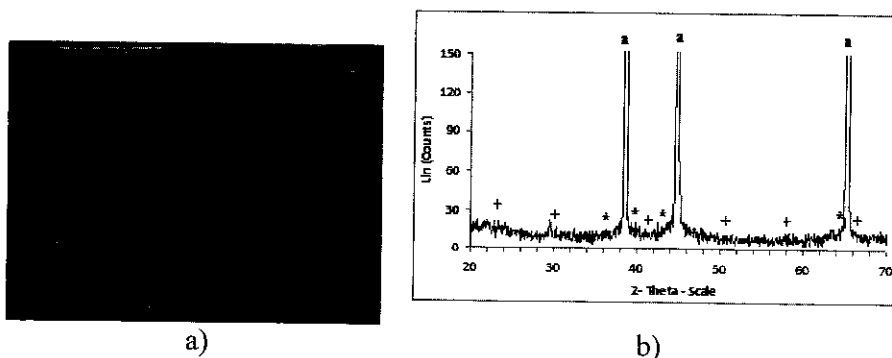


Figure 1. SEM and XRD data for the surface of the Al electrode after 120 minutes holding at the potential of $E_x = 0,050$ V vs. Mg in: a) $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ melt, $T = 370\text{K}$, mag. 5000x; b) in $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ melt, $T = 380\text{K}$; (a) - (p c k) aluminium; (*) - Centered cubic $\text{Al}_{12}\text{Mg}_{17}$; (+) monoclinic $\text{Mg}(\text{NO}_3)_2 \times (\text{H}_2\text{O})_2$ [4].

Al electrodes exposed to the potentials between Al reversible potential and 50 mV vs. Mg at temperatures bellow 500 K strongly suggest magnesium UPD accompanied by substrate alloying with deposited magnesium, Fig. 1. The alloys identified by XRD analysis formed at the Mg UPD on Al characteristic for each of the melts used are shown in Table 1.

Table 1. The alloys formed at the Mg UPD on Al from nitrate melts

Melt	Substrate	Alloy 1	Alloy 2
1. $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$	Al	$\text{Al}_{12}\text{Mg}_{17}$	
2. $\text{Mg}(\text{NO}_3)_2$	Al	$\text{Al}_{12}\text{Mg}_{17}$	Al_3Mg_2
3. $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3 \times \text{XH}_2\text{O}$	Al	Al_2Mg	Mg_2Al_3
4. $\text{Mg}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3$	Al	$\text{Al}_{12}\text{Mg}_{17}$	Mg_2Al_3

CONCLUSION

Kolb-Przasnyski-Gerischer [2] propose an magnesium underpotential deposition on aluminum at potentials close to 0,1 V vs.Mg, because the half work functions difference in the case of Al and Mg is 0,20 to 0,30 eV.

However, this rule does not predict whether there are going to be alloys formed between the substrate metal and underpotentially deposited metal. And yet, the most pronounced effects of the magnesium underpotential deposition from magnesium nitrate melts onto aluminium substrate found were three alloys formed with the substrate Al. All the alloys obtained were formed at the potentials 50 to 100 mV positive to Mg reversible potential and at the temperatures several hundred Kelvin degrees lower than the temperatures which are, according to the phase diagrams, needed for their formation thermally. The alloys formed were $\text{Al}_{12}\text{Mg}_{17}$, Al_2Mg and Mg_2Al_3 .

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