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MAGNESIUM OXIDE NANOWHISKERS ELECTROCHEMICALLY SYNTHETIZED FROM NITRATE MELTS

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Abstract

A novel formation of magnesium oxide/hydroxide nano whiskers synthesized by electrochemical magnesium deposition from magnesium nitrate melts is reported. It was found that reduction processes of nitrate, nitrite and water took part simultaneously with magnesium deposition and preceded magnesium hydroxide and magnesium oxide nano whiskers formation. Electrochemical techniques used were cyclic voltammetry and chronoamperometry. Obtained magnesium oxide and hydroxide deposits were analyzed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

Keywords: *magnesium oxide/hydroxide nano whiskers, electrochemical deposition, magnesium nitrate melts*

1. INTRODUCTION

In recent years, magnesium oxide (MgO) whiskers have been developed as an intensifier used in superconductive and spaceflight composite materials. This is primarily because the whiskers show some superior properties such as: high melting point, low density and high modulus of rupture [1,2]. Several studies on the preparation of MgO whiskers have been published [3-5]. For instance, the whiskers can be prepared by crystal growth in a melting salt system consisting of hydrous magnesium chloride and alkali metal chloride, where alkali metal chloride actually functions as a flux and hydrous magnesium chloride is hydrolyzed to produce magnesium oxide at a high temperature [4]. However, the major problem encountered in the direct melting dehydrochlorination of hydrous magnesium chloride at 800 °C is that the released hydrochloride would seriously corrode the reactor. Other authors [6] reported the whisker growth by vapor phase reactions between MgO and tungsten, hydrogen, and carbon. One of the disadvantages of this method was that the required growth conditions were too harsh. The conditions included relatively complicated apparatus and strict control of the growth process. There are reports [1] of a new method to obtain MgO whiskers, simply by heating a precursor, namely hydrous magnesium oxysulfate (MOS) whisker. In the literature [7] there are also reports on the preparation of MgO nanocrystals which include: sol-gel method, ion beam sputtering and electrostatic spray deposition [7].

Electrodeposition is one of the promising and relatively low cost methods for precise synthesis of various nanostructures. Electrochemical synthesis of magnesium hydroxide on metallic substrate from magnesium nitrate solution, combined with subsequent annealing of the synthesized layer, lead to a conclusion that higher applied voltage influenced crystal orientation and surface structure of the deposit [7].

In this work, we focus our attention on the electrochemical formation of magnesium oxide or oxi-hydroxide whiskers on glassy carbon substrate from magnesium nitrate melts during deposition of Mg at temperatures below 200 °C.

2. EXPERIMENTAL

All electrochemical experiments were performed in a three-electrode electrochemical cell made of Pyrex glass placed in a heating mantle, described elsewhere [8], under a purified argon atmosphere (99.99 % Ar), controlled by a Potentiostat/Galvanostat (Princeton Applied Research Corporation Model 273A). Working electrode was glassy carbon (P=0.8 cm^2), reference electrode was Mg wire (3 mm diameter 99.999 %) and anode was a curved rectangular Mg shovel (7.5 cm^2 active surface area, made of 99.999 % Mg). The melt used in this work was $Mg(NO_3)_2 \cdot 6H_2O$, which was prepared as follows: $Mg(NO_3)_2 \cdot 6H_2O$ was placed into the cell supplied with electrodes, argon supply was turned on and the system was heated gradually to the temperature of 100 °C.

Two electrochemical techniques were used in the experiments: linear sweep voltammetry (LSV) and chronoamperometry. The cyclic voltammetry experiments included one or more cycles where starting potential, E_S, was usually 50 to 100 mV more negative than the reversible potential of the glassy carbon working electrode, to a chosen final potential E_F and then returned back to E_S, all at scan rates 50 mVs^{-1}. The procedure for chronoamperometry included change of the working electrode potential from an initial potential, E_I, 50 to 100 mV more negative to glassy carbon reversible potential in the given melt, to a final chosen potential, E_X. E_X potential was held constant for 120 minutes, whereupon the cathode was retrieved from the cell under potential in order to preserve deposited material. Obtained deposit was washed with absolute ethanol and left on the electrode to dry in the air at room temperature.

Thus obtained samples were characterized by Scanning electron microscope (SEM) with an Energy dispersive spectroscopy (EDS) (SEM - "JEOL", model JSM-5800, Japan, EDS - "Oxford INCA 3.2", U.K.).

3. RESULTS AND DISCUSSION

Fig.1. and Fig.2. present SEM photographs and EDS analysis of magnesium oxide/hydroxide nanocrystals electrodeposited on vitreous carbon electrode from $Mg(NO_3)_2 \cdot 6H_2O$ melt at an overpotential of -500 mV vs. Mg and at an underpotential of 9mV vs. Mg. Magnesium oxide/hydroxide nanocrystals obtained on the working electrode after 30 cycles are presented in Fig.2.b).

In all cases, nanocrystals were of almost the same needle like shape – whiskers, different in length and thickness, contributing to highly developed surface of the deposit.

In the literature that describes magnesium hydroxide whiskers synthesis from water magnesium salt electrolysis [1-5,9], authors explain that at the beginning of deposition, the reduction of oxygen is dominant and leads to a porous structure until oxygen is consumed. Then, the reduction of water produces more hydroxides and a finer structure of the deposit should be formed. From a thermodynamic point of view, after the formation of a porous structure, the concentration of hydroxides, and consequently pH, increases locally between the pores of the structure which results in a higher rate of production of magnesium hydroxide. Sintering at high temperatures leads to oxidation of the substrate. Although a calcination reaction can be completed at temperatures lower than 500°C, the adherence of magnesium oxide to the coating is not effective enough at low sintering temperatures.

However, magnesium oxide/hydroxide whiskers synthesis by magnesium electrodeposition from nitrate melts proceeds differently. According to the literature [8-11], anion reduction processes taking place in the magnesium nitrate melts generate active oxygen species:

$$NO_3^- + 2e^- \rightarrow NO_2^- + O^{2-}, \quad (1)$$

$$2\,NO_3^- + 2e^- \rightarrow 2\,NO_2^- + O_2^{2-}, \quad (2)$$

$$NO_3^- + 3e^- \rightarrow NO + 2\,O^{2-}. \quad (3)$$

which with magnesium ions, present in the electrochemical double layer, produce oxides:

$$Mg^{2+} + O^{2-} \rightarrow MgO \quad (4)$$

The model consistent with with the above is presented in Fig.3.

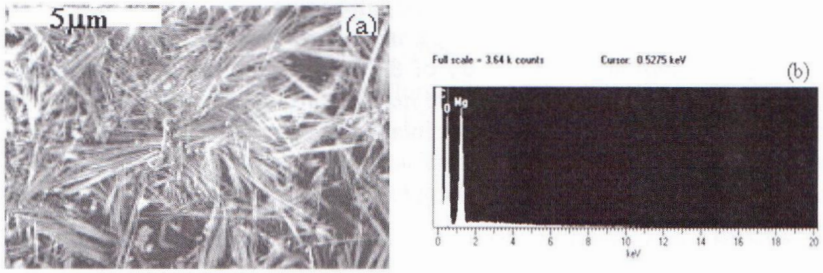

Figure 1 - (a) SEM image of magnesium oxide/hydroxide whiskers obtained at constant overpotential of -500mV vs. Mg for 2 hours at T=100°C from $Mg(NO_3)_2 \cdot 6H_2O$ melt, magnification 500x; (b) EDS spectrum of the whiskers presented in a).

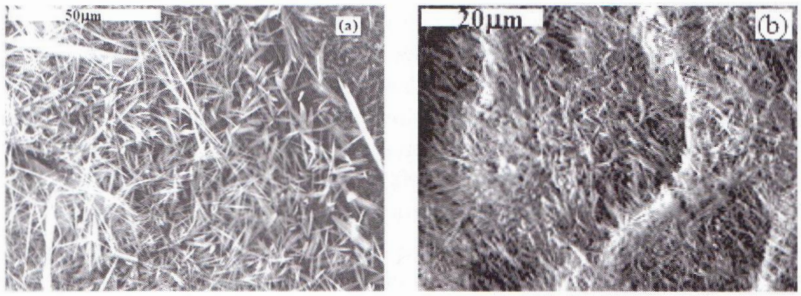

Figure 2 - (a) and (b) SEM images of $MgO/Mg(OH)_2$ whiskers obtained at T=100°C from $Mg(NO_3)_2 \cdot 6H_2O$ melt, at: (a) constant underpotential of 9 mV vs. Mg for 2 hours, magnification 1000x; (b) after 30 cycles in the potential span from E_S= +1.2 to $E_{F=}$ -0.8 V vs. Mg, scan rate 50mV/s, magnification 2000x.

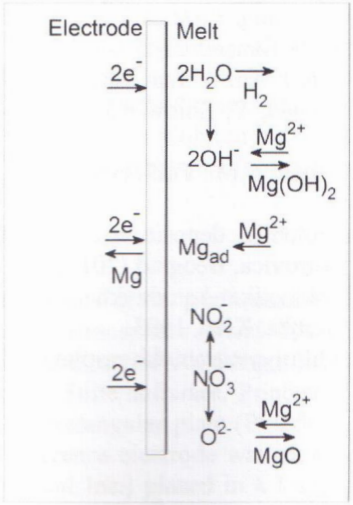

Figure 3 - Processes occurring in/on the surface of working electrode leading to magnesium oxide whiskers formation

When moisture is present in the melt, magnesium hydroxides are also formed [9-11]:

$$Mg^{2+} + NO_3^- + H_2O + 2e^- \rightarrow Mg(OH)_2 + NO_2^- \quad (5)$$

However, these magnesium hydroxides are transformed into oxides only during oxidation processes at temperatures above 300°C according to

$$Mg(OH)_2 \leftrightarrow MgO + H_2O \quad (6)$$

and depending on the value of the thermal decomposition constant.

It was found that in the melts used it is not only deposition time, but also applied voltage that can greatly change the morphology of the magnesium oxide/hydroxide coating. Whiskers are formed in constant potential regime in magnesium underpotential and overpotential regions but their size and number increase with increasing negative potential and time of deposition. However, magnesium oxide/hydroxide whiskers can be formed also by cycling potential of the working electrode from magnesium underpotential to magnesium overpotential region and back.

4. CONCLUSION

Magnesium oxide and hydroxide nano size whiskers can be electrochemically synthetized, namely by magnesium overpotential and underpotential deposition from magnesium nitrate melt at 100°C. It has been found that by adjusting parameters of electrodeposition such as applied potential it is possible to control the morphology and the structure of deposits. The size and the number of the whiskers formed depend on the value and the duration of the constant potential applied. It was found that MgO whiskers can be formed by cyclic potentials as well.

It was proven that a carefully planned magnesium electrodeposition from magnesium nitrate melt at the temperatures below 200°C can be an easy and a low cost method for the synthesis of new and interesting morphologies of magnesium oxide/hydroxide nanocrystals including magnesium oxide whiskers.

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