ELECTRODEPOSITION OF ZIRCONIUM FROM DMSO SOLUTION

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Investigations of voltammetry zirconium deposition from DMSO solution on different substrates were taken. It was found that this is multi-electron process proceeding in a few stages. Moreover, zirconium layers were obtained on titanium, copper stainless steel and nickel. Obtained deposit was in form of white powder, which immediately was oxidized to ZrO\(_2\) in the presence of air.

Keywords: zirconium; DMSO; electrodeposition; voltammetry

In this work preliminary investigations of zirconium electrodeposition from dimethyl sulfoxide (DMSO) solution on different substrates are presented. The aim of this study was determination possibility of zirconium deposition by electrochemical method from DMSO solution on platinum, steel, copper, nickel and titanium.

1. Introduction

Zirconium and zirconium alloys are widely used in industry, due to their resistance to corrosion and tolerance of high temperatures. For instance, zirconium alloys are used in the aviation industry, particularly in jet engines. When included in magnesium alloys, zirconium acts as a potent grain refiner, which has led to rapid development of the use of these alloys. Metallic zirconium is also used in nuclear reactors due its small neutron cross section, which increases the efficiency of atomic energy generation. Zirconium has further applications in other fields, such as the chemical industry.

Nowadays zirconium coatings can be obtained only with PVD method or by molten salt electrolysis. Electrochemical process of layering zirconium from non-aqueous solution requires very complicated apparatus and is very energy-consuming. The reason of this situation is fact that zirconium layers cannot be obtained from aqueous solutions because discharge potential of zirconium is much lower than hydrogen deposition potential and overpotential of hydrogen evolution on zirconium is relatively low. Applying organic solvent in this process could be good solution to mentioned above disadvantages. Literature concerning zirconium electrodeposition describes mainly investigations of electrolysis of molten salts process [1-6]. Investigations of electrodeposition of titanium, tantalum and lanthanum from organic solutions is reported only in a few papers [20-23]. There is a lack of investigations concerning zirconium [24]. Paper [20] refers to investigations of electrodeposition titanium on gold from ionic liquid [BMIm]BTA. It was found that it is two-stages process. First proceeds reduction of TiCl\(_4\) to TiCl\(_2\), the second stage encloses reduction of TiCl\(_2\) to metallic titanium. During anodic digestion titanium layer also digestion of substrate (gold) was observed, and formation of Au-Ti alloy was possible. Investigations of electrodeposition of tantalum from ionic liquid [BMP]Tf\(_2\)N on NiTi alloy were presented in [21]. Process was conducted at temperature 200°C using LiF as electrolyte enlarging conductivity of the solution. Dense layers of a good adhesion were obtained. It was found that covering NiTi alloy with tantalum layer distinctly increases corrosion resistance of alloy. Papers [22-23] present investigations of electrodeposition of lanthanum and Al-La alloy form ionic liquid EMICl saturated with AlCl\(_3\). Possibility of deposition lanthanum and Al-La alloy form ionic liquid EMICl saturated with AlCl\(_3\). Possibility of deposition lanthanum and Al-La alloy form ionic liquid was confirmed at the temperature equals 25°C.

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2. Experimental

Voltammetry investigations of Zr deposition from DMSO solution

Investigations were carried out in the range of potential from 0 V to -3.5 V with the step 200 mV/s. Potentiostat Autolab PGSTAT30, with thermostat Funge Medigen E1 and standard three – electrode cell were used. As reference electrode Ag/AgCl in 5% LiCl absolute methanol solution was used, and the auxiliary electrode was platinum. Voltammetry investigations were carried out in dimethyl sulfoxide (DMSO) containing LiClO₄ (0.4 mol/dm³) with addition of 10 g/dm³ zirconium. Metal was added to electrolyte as adequate chloride: ZrCl₄. Temperature of investigations was equal 40°C. Voltammetry investigations were carried out in DMSO containing LiClO₄ (0.4 mol/dm³) with addition of 10 g/dm³ zirconium (as zirconium tetrachloride). Temperature of investigations was equal 40°C. Zirconium electrodeposition was investigated on: platinum (surface - s = 1.87 cm²), nickel (s = 2.73 cm²), copper (s = 2.72 cm²), titanium (s = 2.78 cm²), and stainless steel – SS (s = 2.76 cm²).

Electrodeposition of zirconium form DMSO solution

Investigations of zirconium electrodeposition were conducted with using DMSO solution with LiClO₄ (0.4 mol/dm³). To such prepared solution adequate amount of salt of deposited metal was added, the concentration of metal was 10 g/dm³. Cathodic current density was equal 4,4 mA/cm² at 40°C. Electrodeposition of zirconium was carried out on copper, nickel, titanium, and SS substrates. Samples of the diameter 3 mm and length 3 cm were grinded with abrasive paper 600, degreasing with isopropanol and etched in 33% HNO₃ (Cu), 18% HCl (Ni and SS), 1:1 HF+H₂SO₄ (Ti).

After electrodeposition microstructure of examined samples was evaluated on the base of SEM images (Hitachi S-3400N) and also the chemical composition of obtained layers was analysed by EDX method (Thermo Noran).

3. Results and discussion

In Fig. 1 voltammetric curves registered during investigations of electrochemical zirconium deposition are presented. Each diagram presents also curve in the range of 0 – -3,5 V registered for DMSO solution containing only LiClO₄. In this case any peaks occurs what indicates that any electrochemical reactions take place in examined range of potential. Voltammetry investigations shows that zirconium deposition on examined substrates is possible (Fig. 1). Depending on used substrates different shapes of voltammetric curves is observed. On platinum electrode are observed four peaks at the potential -1,0; -1,75; -2,6; -3V (Fig. 1). It allows to claim that electrodeposition is multi-sages process and each peak corresponds to adequate stages of reduction of zirconium ions. Here, it is clearly seen this electroreduction is reversible process on platinum electrode. In case of the other metal substrates cathodic peaks are not so distinct and there is difficult to fit anodic peaks to them what could indicate that same reduction reactions of zirconium ions are not reversible. Those differences depend on different conditions of adsorption upon different metals and on the different behaviours of the metals in the electrolyte [25]. Zirconium has been reported by several investigators to exist in many oxidation states in molten alkali halides. ZrCl₄ in LiCl–KCl has been studied by Yang and Hudson [27], Inman et al. [28], Bailey et al. [29], Larsen and Leddy [30] and Lorthioir et al. [31-32], Sakakura [33-34] and Sakamura [35]. Larsen and Leddy [30] have reported that Zr⁴⁺ converts to Zr³⁺ and hence Zr⁵⁺ could not be detected. Lorthioir et al. [31-32] reported that ZrCl₂ was insoluble and is unstable above 850°C. Studies on the Zr behaviour in NaCl–KCl melts have been reported by Barchuk et al. [36], Smirnov et al. [37] Baraboshkin et al. [37] Sheiko et al. [38] Komarov et al. [39], Flengas and co-workers [40-41], Lorthioir et al. [32] and Ryabov et al. [42]. Many different mechanisms have been reported for the reduction of Zr⁴⁺ to metallic Zr. Ryabov et al. [42] have reported that Zr⁴⁺ interacts with metallic Zr to form the dichloride. Sakakura [33-34] have reported the presence of Zr⁵⁺ in chloride melts. There exists large disagreement among the various studies with regard to the reduction mechanism of Zr⁴⁺ ions.
also present. Application of nickel as a substrate (Fig. 5) in electrodeposition of zirconium results in receiving high surface area of the coating with large crystallites but adhesive to the substrate. EDX analysis shows as above presence of zirconium, copper and the same contamination but the oxygen peak is much higher than in other cases, what indicates on higher degree of zirconium oxidation.

All obtained Zr coatings were oxidized after the process and white powder deposit on the coating was observed as a result of exposure to air and water, after relatively short time [26]. This is the result of fact that zirconium is active metal which is immediately covered with oxide layer in the presence of oxygen, and cathodic deposit could be in the form of powder of relatively high surface area.
4. Conclusion

In this study preliminary investigations of electrochemical deposition of zirconium from DMSO solution were presented. It was found that this process is multi-stages and can proceed on different metallic substrates. The cathodic deposit in form of powder is obtained which immediately oxidizes to zirconia in contact with air. Obtained results are perspective, but further study are needed to form the compact zirconium layers.

REFERENCES