

W. SIMKA\*, D. MAJEWSKI\*\*, G. NAWRAT\*, A. KRZĄKAŁA\*, Ł. NIEUŻYŁA\*, J. MICHALSKA\*\*\*

## ELECTRODEPOSITION OF ZIRCONIUM FROM DMSO SOLUTION

### ELEKTROOSADZANIE CYRKONU Z ROZTWORU DMSO

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

W pracy przedstawiono badania woltamperometryczne procesu elektroosadzania cyrkonu z roztworu DMSO na różnych podłożach. Stwierdzono, że jest to proces wieloelektronowy zachodzący w kilku etapach. Ponadto otrzymano warstwy cyrkonu na tytanie, miedzi, stali kwasoodpornej i niklu. Wytworzony osad katodowy miał formę białego proszku, na skutek natychmiastowego utlenienia cyrkonu w kontakcie z powietrzem.

### 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 deposition describes mainly investigations of electrolysis of molten salts process [1-6]. While, widely described is deposition of zinc, cesium, aluminum, magnesium, cobalt, antimony, germanium, cadmium, Pt-Zn, Pd – Al alloys and silicon from ionic liquids

[7-19]. 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]  $Tf_2N$  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 from ionic liquid EMICl saturated with  $AlCl_3$ . Possibility of deposition lanthanum and Al-La alloy from ionic liquid was confirmed at the temperature equals 25°C.

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.

\* FACULTY OF CHEMISTRY, SILESIAN UNIVERSITY OF TECHNOLOGY, 6 B. KRZYWOSTEGO ST., 44-100 GLIWICE, POLAND

\*\* WELDING INSTITUTE, 16-18 BL. CZESŁAWA ST., 44-100 GLIWICE, POLAND

\*\*\* FACULTY OF MATERIALS SCIENCE AND METALLURGY, SILESIAN UNIVERSITY OF TECHNOLOGY, 8 KRASIŃSKIEGO ST., 40-019 KATOWICE, POLAND

## 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 methanolic solution was used, and the auxiliary electrode was platinum. Voltammetry investigations were carried out in dimethyl sulfoxide (DMSO) containing  $\text{LiClO}_4$  ( $0,4 \text{ mol/dm}^3$ ) with addition of  $10 \text{ g/dm}^3$  zirconium. Metal was added to electrolyte as adequate chloride:  $\text{ZrCl}_4$ . Temperature of investigations was equal  $40^\circ\text{C}$ . Voltammetry investigations were carried out in DMSO containing  $\text{LiClO}_4$  ( $0,4 \text{ mol/dm}^3$ ) with addition of  $10 \text{ g/dm}^3$  zirconium (as zirconium tetrachloride). Temperature of investigations was equal  $40^\circ\text{C}$ . Zirconium electrodeposition was investigated on: platinum (surface –  $s = 1,87 \text{ cm}^2$ ), nickel ( $s = 2,73 \text{ cm}^2$ ), copper ( $s = 2,72 \text{ cm}^2$ ), titanium ( $s = 2,78 \text{ cm}^2$ ), and stainless steel – SS ( $s = 2,76 \text{ cm}^2$ ).

### *Electrodeposition of zirconium form DMSO solution*

Investigations of zirconium electrodeposition were conducted with using DMSO solution with  $\text{LiClO}_4$  ( $0,4 \text{ mol/dm}^3$ ). To such prepared solution adequate amount of salt of deposited metal was added, the concentration of metal was  $10 \text{ g/dm}^3$ . Cathodic current density was equal  $4,4 \text{ mA/cm}^2$  at  $40^\circ\text{C}$ . 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%  $\text{HNO}_3$  (Cu), 18% HCl (Ni and SS), 1:1  $\text{HF}+\text{H}_2\text{SO}_4$  (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  $\text{LiClO}_4$ . 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-stages 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.  $\text{ZrCl}_4$  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  $\text{Zr}^{3+}$  converts to  $\text{Zr}^{4+}$  and hence  $\text{Zr}^{3+}$  could not be detected. Lorthioir et al. [31–32] reported that  $\text{ZrCl}_2$  was insoluble and is unstable above  $850^\circ\text{C}$ . 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  $\text{Zr}^{4+}$  to metallic Zr. Ryabov et al. [42] have reported that  $\text{Zr}^{4+}$  interacts with metallic Zr to form the dichloride. Sakakura [33–34] have reported the presence of  $\text{Zr}^{3+}$  in chloride melts. There exists large disagreement among the various studies with regard to the reduction mechanism of  $\text{Zr}^{4+}$  ions.

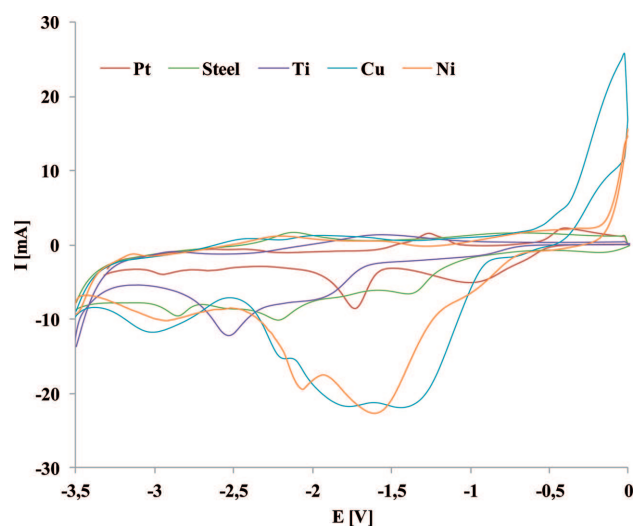


Fig. 1. Cyclic voltammogram at various substrates

In Figs. 2–5 SEM and EDX analysis of obtained coatings are shown. When titanium electrode was used as the substrate fine and adherent coating was obtained (Fig. 2). Small crystallites of zirconia are seen and coating is compact. EDX analysis shows presence of zirconium and substrate elements. Also peaks of S and Cl as the result of decomposition of electrolyte are seen, Cu peak whereas is the effect of contamination. In case of stainless steel (Fig. 3) compact coating was obtained with single scratches. Generally coating was compact and well adherent to steel substrate. Zirconium peak on EDX analysis is distinct and also peaks of substrate are seen e.g. Fe, Cr, Ni. Here, also as mentioned above some peaks, as a result of contamination, are present: Cl and S – result of decomposition of electrolyte and also Mg – residue after drying  $\text{ZrCl}_4$ , where  $\text{MgSO}_4$  was used. On the copper substrate (Fig. 4) homogeneous (uniform) coating of high surface area was obtained. Here, large crystallites of  $\text{ZrO}_2$  are seen. EDX analysis confirmed presence of zirconium and similarly like above contaminations from electrolyte and drying process are

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.

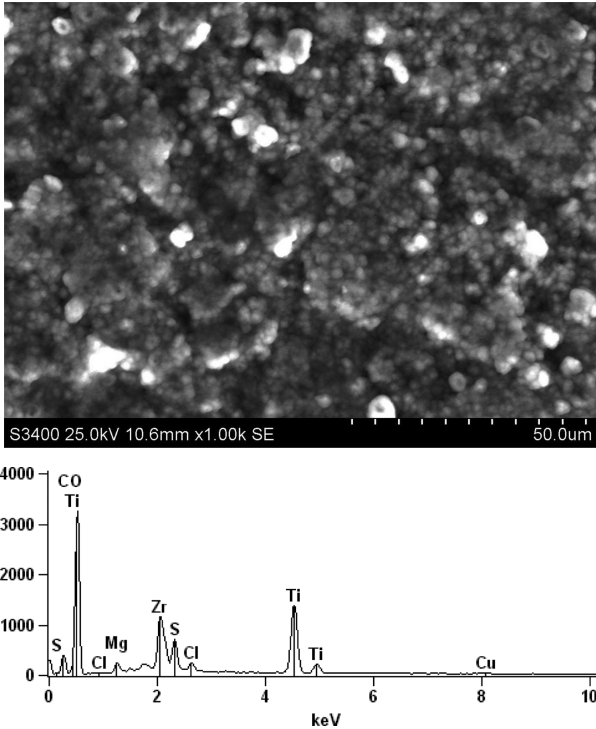


Fig. 2. SEM image and EDX spectrum of zirconium deposited on Ti substrate

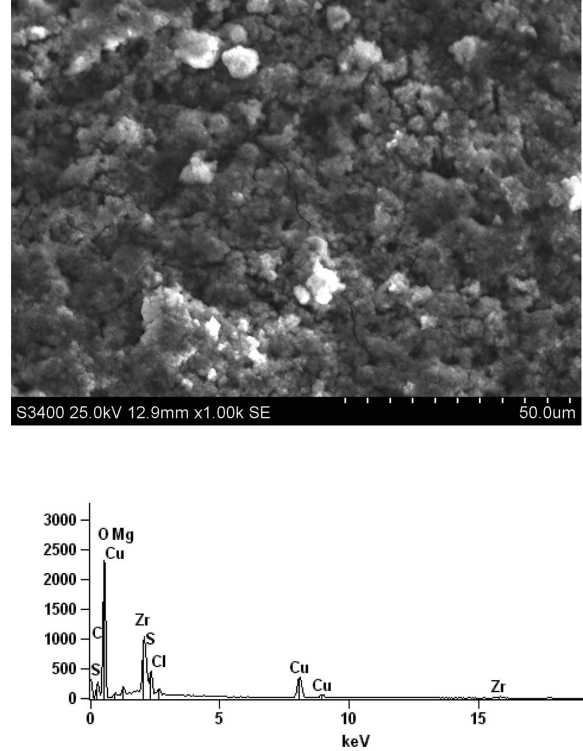


Fig. 4. SEM image and EDX spectrum of zirconium deposited on copper substrate

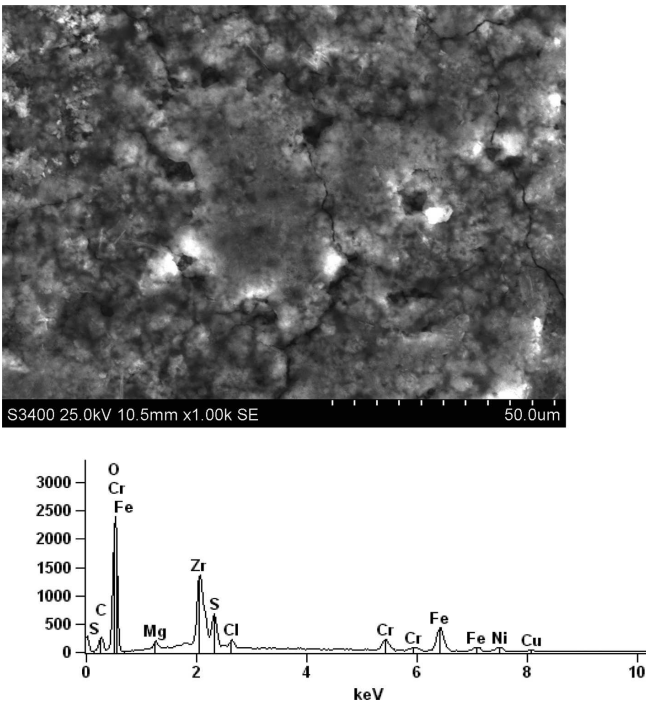


Fig. 3. SEM image and EDX spectrum of zirconium deposited on SS substrate

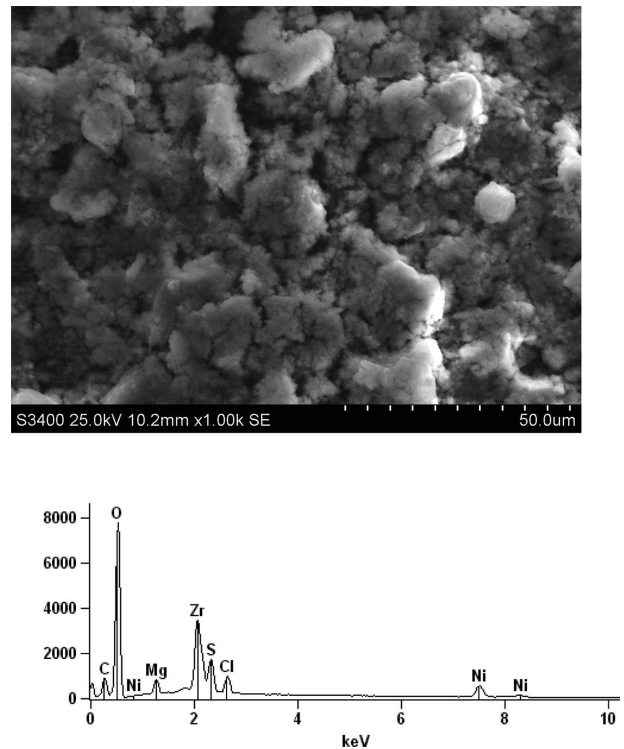


Fig. 5. SEM image and EDX spectrum of zirconium deposited on nickel substrate

#### 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

- [1] M. Long, H.J. Rack, *Biomaterials* **19**, (1998) 1621.
- [2] G.W. Mellors S. Senderoff, *Journal of Electrochemical Society* **113**, 60 (1966).
- [3] F. Basile, E. Chassaing, G. Lorthioir, *Journal of Applied Electrochemistry* **11**, 645 (1981).
- [4] S. Yoshiharu, *Journal of Electrochemical Society* **151**, C187 (2004).
- [5] Z. Chen, Y.J. Li, S.J. Li, *Journal of Alloys and Compounds* **509**, 5958 (2011).
- [6] S. Ghosh, S. Vandarkuzhali, P. Venkatesh, G. Seemivasan, T. Subbramanian, R.B. Prabhakara, K. Nagarajan, *Journal of Electroanalytical Chemistry* **627**, 15 (2009).
- [7] H. Groult, A. Barhoun, E. Briot, F. Lantelme, C.M. Julien, *Journal of Fluorine Chemistry* **132**, 1122 (2011).
- [8] M. Galiński, A. Lewandowski, I. Stępnia, *Electrochimica Acta* **51**, 5567 (2006).
- [9] P. Walden, *Bulletin de l'Academie Imperiale des Sciences* **8**, 405 (1914).
- [10] H.L. Chum, V.R. Koch, L.L. Miller, R.A. Osteryoung, *Journal of American Chemical Society* **97**, 3265 (1975).
- [11] J. Gate, B. Gilbrt, R.A. Osteryoung, *Inorganic Chemistry* **17**, 2728 (1978).
- [12] J. Robinson, R.A. Osteryoung, *Journal of American Chemical Society* **11**, 323 (1979).
- [13] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, *Inorganic Chemistry* **21**, 1263 (1982).
- [14] T.B. Scheffer, C.L. Hussey, K.R. Seddon, C.M. Kear, Armitage, *Inorganic Chemistry* **22**, 2099 (1983).
- [15] T.M. Laher, C.L. Hussey, *Inorganic Chemistry* **22**, 3247 (1983).
- [16] T.B. Scheffler, C.L. Hussey, *Inorganic Chemistry* **23**, 1926 (1984).
- [17] J.S. Wilkes, M.J. Zaworotko, *Journal of Chemical Society, Chemical Communications* **0**, 965 (1992).
- [18] S. Zein El Abedin, F. Endres, *ChemPhysChem* **7**, 58 (2006).
- [19] M.C. Buzzeo, R.G. Evans, R.G. Compton, *ChemPhysChem* **5**, 1106 (2004).
- [20] Y. Ito, T. Nohira, *Electrochimica Acta* **45**, 2611 (2000).
- [21] J. Uhlíř, *Journal of Nuclear Materials* **360**, 6 (2007).
- [22] S. Pandey, *Analytica Chimica Acta* **45**, 38 (2006).
- [23] F. Endres, M. Bukowski, R. Hempelmann, H. Natter, *Angewandte Chemie International Edition* **42**, 3428 (2003).
- [24] P. Yu, J. Yan, J. Zhang, L. Mao, *Electrochemistry Communications* **9**, 1139 (2007).
- [25] W. Simka, D. Puszczczyk, G. Nawrat, *Electrochimica Acta* **54**, 5307 (2009).
- [26] I. Valov, D. Stoychev, T. Marinova, *Electrochimica Acta* **47**, 4419 (2002).
- [27] S. Zein El Abedin, U. Welz-Biermann, F. Endres, *Electrochemistry Communications* **7**, 941 (2005).
- [28] L. Yang, R.G. Hudson, *Trans Met Soc AIME* **215**, 589 (1959).
- [29] D. Inman, G.J. Hills, L. Young, J.O'M. Bockris, *Annals of the New York Academy of Sciences* **79**, 803 (1960).
- [30] R. Baboain, D.L. Hill, R.A. Bailey, *Journal of Electrochemical Society* **112**, 1221 (1965).
- [31] E.M. Larsen, J.J. Ledy, *Journal of American Chemical Society* **78**, 5983 (1956).
- [32] F. Basile, E. Chassaing, G. Lorthioir, *Journal of Applied Electrochemistry* **11**, 187 (1981).
- [33] F. Basile, E. Chassaing, G. Lorthioir, *Journal of Applied Electrochemistry* **14**, 731 (1984).
- [34] T. Sakakura, *Denki Kagaku* **34**, 780 (1966).
- [35] T. Sakakura, *Denki Kagaku* **38**, 423 (1970).
- [36] Y. Sakamura, *Journal of Electrochemical Society* **151**, (2004) C187
- [37] T.N. Grechina, U.T. Barchuk, *Ukrainian Khemikal Zhurnal* **29**, 722 (1963).
- [38] A.N. Baraboshkin, M.V. Smirnov, N.A. Saltykova, *Proceedings of the All Union Conference on Physical Chemistry of Molten Salts and Slags, Aec-Tr-5948*, 370, November 1960.
- [39] T.N. Grechina, V.T. Barchuk, I.N. Sheiko, *Ukrainian Khemikal Zhurnal* **39**, 501 (1973).
- [40] M.V. Smirnov, A.N. Baraboshkin, V.E. Komarov, *Journal of Chemical Physics* **37**, 1669 (1963).
- [41] B. Swaroop, S.N. Flengas, *Canadian Journal of Chemistry* **44**, 199 (1966).
- [42] G.J. Kipouros, S.N. Flengas, *Journal of Electrochemical Society* **132**, 1087 (1985).
- [43] S.V. Aleksandrovskii, A.N. Naumchik, R.A. Sandler, O.A. Dubovikov, E. Ryabov, *Atomic Energy* **38**, 204 (1975).