

Electrodeposition of hybrid layers

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Hybrid sols based on TEOS–OCTMO (tetraethylorthosilicate–octyltrimethoxysilane) and TEOS–TEOT–OCTMO (tetraethylorthosilicate–tetraethylorthotitanate–octyltrimethoxysilane) were prepared by sol-gel method. The sols were electrodeposited on the steel substrates under different electric field strength. Microstructure of the layers was analysed by a scanning electron microscope and infrared spectroscopy methods. Impedance spectroscopy was applied to evaluate tightness of the layers.

Keywords: sol-gel, hybrids, electrodeposition.

1. Introduction

Hybrid materials are considered a promising candidate for corrosion protection of non-ferrous [1] as well as ferrous materials [2]. The main advantages of hybrids prepared by sol-gel technique are high scratch resistance, resistance to degradation impact of ultraviolet and high flexibility. Disadvantages of the hybrids as a corrosion protection layer are their high porosity, connected with nature of sol-gel prepared materials, and low adherence to the metal substrate usually observed. The adherence can be improved by proper chemical treatment of the metal surface, which leads to increasing adherence due to mechanical anchoring. Even better solution is to increase chemical reactivity of the gel towards substrate metal. Chemical bonding in connection with mechanical anchoring ensures the highest adherence. Hybrids containing titanium are proved to have better adherence to the steel substrate than pure TEOS based gels. Besides good adherence, the material for corrosion protection layer should exhibit some flexibility to prevent cracking due to thermal expansion matchless. One of the possible ways to make TEOS gel more flexible is to introduce linear polymer. Usually higher –C–C– chain leads to higher flexibility. Hybrids from the systems TEOS–OCTMO and TEOS–TEOT–OCTMO were selected as a corrosion protective layer material. The main goal of this work was to study structure and morphology of the layers prepared from the above hybrids and deposited on a steel substrate under electric field (electrodeposition). This method was proved to give good results in case of TEOS-phenyl trimethoxysilane on an aluminium substrate [3].

2. Experimental

All hybrid glasses were prepared from pure reagents: 98% TEOS and OCTMO (from Sigma-Aldrich), TEOT (from MERC), HCl and ethyl alcohol (from Polish Chemicals). Schematic structure of the precursors is shown in Fig. 1. Hybrids with two different compositions were prepared. The first one with titanium introduced in the form of TEOT with a molar ratio of TEOS:TEOT equal 1:0.2, while the second do not contain titanium. Molar ratio of TEOS:C₂H₅OH:H₂O:HCl was always 1:2:2.5:0.05. Ratio of TEOS to organic modifier (OCTMO) was kept constant 1:0.5. Hydrochloric acid

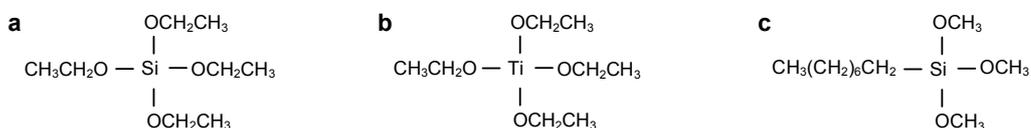


Fig. 1. Precursors used for synthesis: TEOS (a), TEOT (b), OCTMO (c).

was used as a catalyst. Sols of hybrids were prepared by mixing TEOS with TEOT or OCTMO during 30 min. Next, the solvent (ethyl alcohol) was added during continuous stirring and after additional 30 minutes the catalyst and water were added dropwise. After one-hour mixing formed sol was dissolved by addition of 5 ml of ethyl alcohol. So, prepared sol was used for electrodeposition which was carried out in the system shown schematically in Fig. 2. Stainless steel was used as the counter electrodes while a sample substrate was made from low carbon steel. Deposition was carried out under constant voltage. Current as a function of deposition time was registered by the computer. The thermal stability was studied by DTA analysis (Q1500, Hungary). Powdered samples were heated with a rate of 10°C/min in alumina crucible. FTIR analyses in a MIR region were carried out on BIO-RAD FTS-6000 spectrometer.

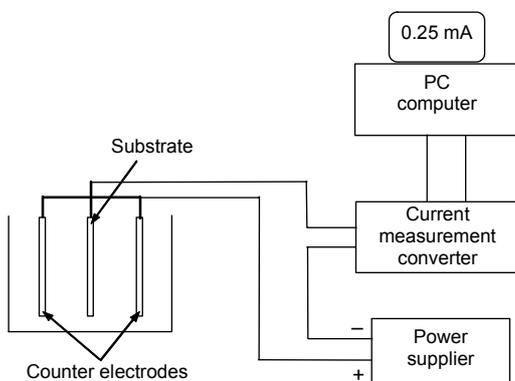


Fig. 2. Schematic diagram of assembly used for electrodeposition.

Absorption spectra were measured from 400 to 4000 cm^{-1} using KBr pellet techniques. The resolution was 4 cm^{-1} . Impedance spectroscopy was carried out on HIOKI 3532 RLC meter.

3. Results and discussion

The results of DTA analyses are shown in Fig. 3. Both hybrids exhibit similar thermal behaviour. Generally two exothermal effects are observed. Thermal decomposition starts at $\sim 180^\circ\text{C}$ and is connected with the removal of residual solvent, decomposition and combustion of ethylene groups. The next effect is due to the removal of catalyst and methylene groups.

Electrodeposition was carried out under different voltage from 0.5 to 30 V. Current characteristic as a function of deposition time is shown in Fig. 4. Current dropped rapidly after the voltage was switched on and decreased further during the whole

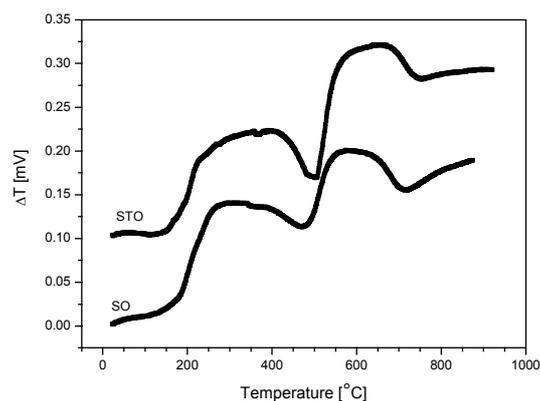


Fig. 3. DTA curves of titanium containing hybrid – STO, and hybrid without titanium – SO.

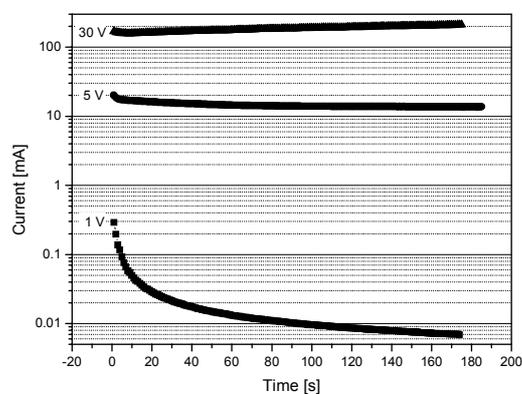


Fig. 4. Current as a function of deposition time for selected voltages (1, 5, 30 V).

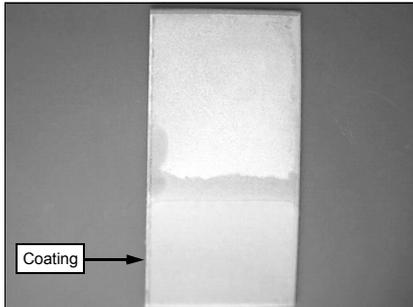


Fig. 5. Picture of the sample deposited under 1 V during 3 min.

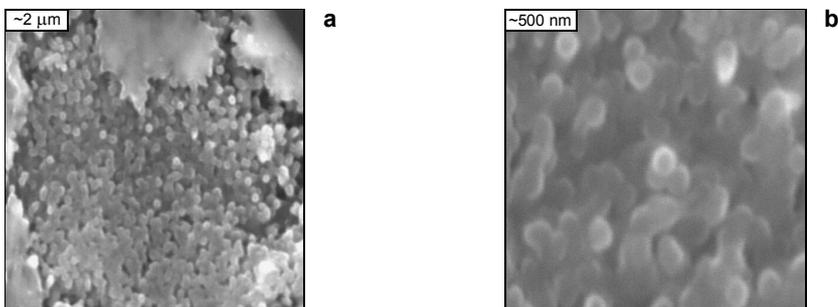


Fig. 6. SEM picture of the TEOS–OCTMO coating obtained under 1 V, 3 min.

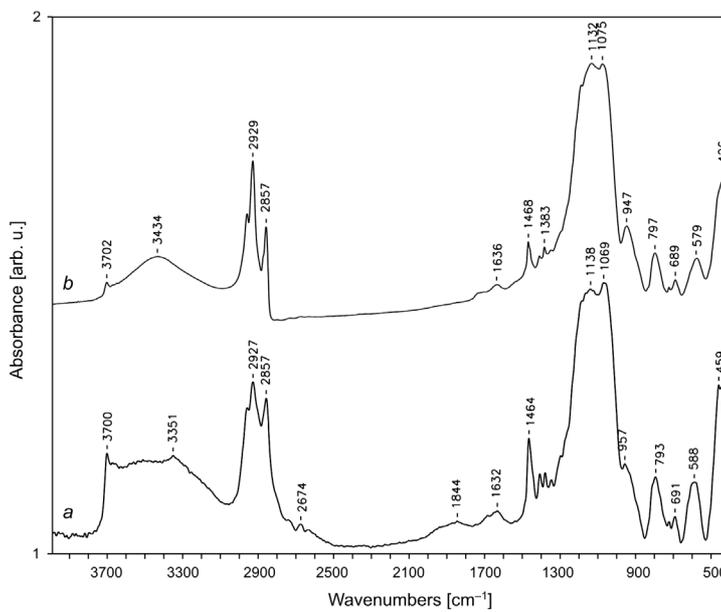


Fig. 7. MIR spectra of TEOS–OCTMO in the form of conventional gel (a), and as an electrodeposited layer (b).

deposition time, but only when the voltage did not exceed 1.5 V. The initial sudden drop is connected with polarisation of the electrode, while the following decrease is due to the deposition of non-conductive particles leading to lowering of the active surface of the electrode. When the applied voltage is higher (above 1.5 V), current starts to increase after the initial drop. A current increase is a result of the dissolution of the electrode material.

An example of the sample with the layer deposited under 1 V is shown in Fig. 5. Deposited coating is smooth and uniform with milky-like colour. Very similar results were obtained in case of both hybrids. The best results were obtained when the deposition was done under 1 V. Higher voltage leads to much thinner layer. While voltage was lower than 1 V, the coating was thicker but much more porous.

Scanning electron microscopy was applied to study morphology of the coatings. Some examples are shown in Fig. 6. The coating is built with round and uniform SiO_2 particles. The diameter of the particle is in the range of nanometers ~ 200 nm – see Fig. 6b.

The material of the coating was analysed by the IR and compared with the hybrid obtained in the conventional way. The results are shown in Fig. 7. The main difference between spectra is exhibited in the intensity of 1468 cm^{-1} band. This band is connected with $\text{O}-\text{C}(\text{H}_3)$ stretching vibration in methoxy groups [4]. The layer material obtained by electrodeposition contains much less methoxy groups so is more polymerised (three-dimensional $\text{Si}-\text{O}-\text{Si}$ network is formed).

As the layers were intended to be used as an corrosion protection layer on a steel substrate, a preliminary study of chemical resistance to corrosion environment was performed using impedance spectroscopy (IS) and corrosion tests. Electric characteristic of the layers was measured in air and after immersion of the sample in 5% salt (NaCl) solution during 1 hour. Selected results are shown in Fig. 8. In case of penetration of the salt through the layer or delamination of the coating, corrosion process should be seen in the IS spectra as an additional dielectric loss peak. The only effect observed is lowering of the resistance of the sample immersed in the salt, as compared to the sample

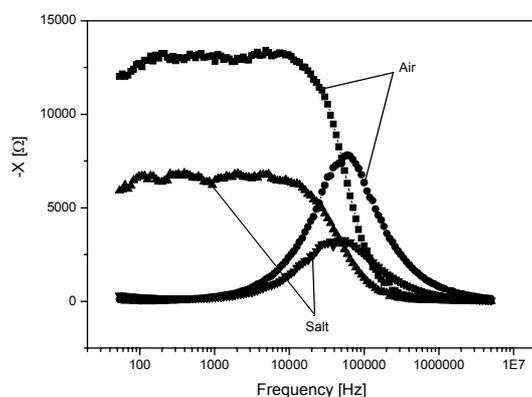


Fig. 8. IS spectra obtained on the dry sample and after immersion in NaCl solution.

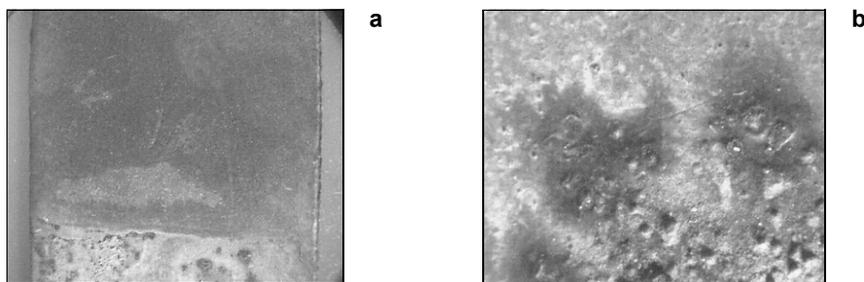


Fig. 9. Results of a corrosion test in natural open-air environment: sample with protected layer (a), scale of corrosion seen on uncovered part of the sample (b).

measured in the air – see Fig. 8. It is due to natural porosity of the sample, causing water to penetrate through the layer, though salt solution does not react with the steel substrate.

To verify obtained layers in the natural corrosion conditions, the samples were tested during two months (July–August). Picture of the sample after corrosion in open-air conditions is shown in Fig. 9. While non-covered metal is highly corroded, the surface under coating is almost untouched by this process.

4. Conclusions

Hybrid layers based on TEOS–OCTMO and TEOS–TEOT–OCTMO sols and obtained by cathode electrodeposition method are built with highly polymerised SiO_2 particles. The particle size is in the range 100–300 nm. In spite of observed porosity, the layers create good corrosion protection against atmospheric environment.

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References

- [1] MESSADDEQ S.H., PULCINELLI S.H., SANTILLI C.V., GUASTALDI A.C., MESSADDEQ Y., *Microstructure and corrosion resistance of inorganic-organic (ZrO_2 -PMMA) hybrid coating on stainless steel*, *Journal of Non Crystalline Solids* **247**, 1999, pp. 164–70.
- [2] WAGNER G.W., SEPEUR S., KASEMANN R., SCHMIDT H., *Novel corrosion resistant hard-coatings for metal surfaces*, *Key Engineering Materials* **150**, 1998, pp. 193–8.
- [3] SHEFFER M., GROYSMAN A., MANDLER D., *Electrodeposition of sol-gel films on Al for corrosion protection*, *Corrosion Science* **45**(12), 2003, pp. 2893–904.
- [4] BRINKER C.J., SCHERER G.W., *Sol-Gel Science*, Academic Press, New York 1990.

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