

Electrochemical corrosion behaviour of silica hybrid sol-gel coatings

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The aim of the present work is to produce hybrid inorganic-organic nanostructured sol-gel coatings and to study their structure and corrosion resistance. The coatings were synthesized by sol-gel technology at room temperature using vinyltrimethoxysilane (VTMS) as silicon precursor and methylmethacrylate (MMA) or hydroxyethylmethacrylate (HEMA) as organic materials in different proportions. The coatings were deposited on mill steel substrates and thermally treated at 25 and 200°C. The composition and the structure of the hybrids were characterized by FTIRS, XRD, BET-analysis, EDS, SEM and AFM. The presence of strong chemical bonds (Si–C, Si–O–C, Si–CH₃) between inorganic and organic parts of the hybrid materials, which are in amorphous state was proved. The size of nanounits and their aggregates as well as the surface roughness of the samples were also determined. The corrosion resistance of the coatings was studied using electrochemical potential-sweep technique and a model corrosive medium of 0.5 M Na₂SO₄ solution. It has been shown that the coating affects both partial corrosion reactions, but it decreases more strongly the anodic metal dissolution, thus decreasing the corrosion rate of the steel substrate more than an order of magnitude. The presence of a chemical bond of the coating with iron from the substrate is also established, which is in accordance with the good adhesion of this type of coating. The results of the present study suggest a possible application of the obtained hybrid materials as transparent coatings with good protective properties.

Key words: sol-gel, silica hybrids, nanostructure, corrosion resistant coatings.

INTRODUCTION

Over the last decades a great attention has been paid to the sol-gel chemistry, mainly because of its well-known advantages such as low synthesis temperature, high homogeneity and purity of obtained materials and proved possibility for producing new materials with appropriate physical and chemical properties [1–5].

H. Schmidt (Germany) and G. Weeks (USA) were the first published independently papers on creation of new family hybrid materials containing both organic and inorganic components [6, 7]. Because the hybrids are designed at a molecular and low molecular level, ranging from a few angstroms to a few nanometers in the structure is observed.

The sol-gel hybrid new materials were successfully prepared by intimately mixing of organic and inorganic components combining desirable properties of polymers (elasticity, hydrophobicity) with those of inorganic solids (hardness, thermal stability, chemical resistance). Furthermore, new unique properties coming in the hybrids from the synergy of both components are commonly observed [8–10].

Silica hybrid materials attracted much interest since they may be formed as nanocomposites and these materials were developed mainly by taking advantage of the mild chemical conditions of the sol-gel processes. The most popular precursors used for the synthesis of silicate hybrid nanocomposite materials assuring SiO₂ introduction are: TEOS, TMOS, ETMS, MTES, VTES, MTMS and THEOS. As an organic part oligomers or polymers, aggregates or particles as PEG, PEO, PVA, HEMA, PMMA, polystyrene, collagen and others could be used. One of the most interesting and important problems for studying hybrid nanocomposite materials is their structure analysis as well as the processes of aggregation and development of self-assembled structures [11–14]. Up to now the information about these structures and the processes occurring during their formation is largely missing. For synthesis of hybrid materials the choice of the type and quantity of precursors as well as of organic components is also of importance.

The sol-gel method provides a low-temperature route to preparation of environmentally friendly hybrid coatings, which are readily applied to most metallic substrates. The hybrid sol-gel coatings possess several advantages over the inorganic coatings in regard to their improved adhesion to

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metallic substrates, hydrophobicity, low permeability, elasticity and crack-free surface layers. The preparation of coatings by dipping of the substrates in the sol-gel solutions is one of the most simple and well-established methods to produce homogeneous coatings with uniform thickness. The interest in development of hybrid inorganic-organic coatings has greatly increased and the subject of investigations has been directed mostly to the structural chemistry and studies on their physical and chemical properties, and potential applications [15–19].

Nanostructured silica hybrid coatings based on self-assembled nanophase particles were synthesized and studied for long term protection of aircraft aluminum alloys against atmospheric corrosion [20–22]. The corrosion resistance of stainless steel, zinc-plated steel and aluminum alloys was greatly improved by using silica-PMMA hybrid coatings prepared at 200°C [23]. Silica hybrid coatings were obtained and investigated for corrosion protection of orthopedic metallic prostheses [24] and for conservation of art items [25].

The aim of the present work is to produce hybrid inorganic-organic nanostructured coatings by sol-gel technology and to study their electrochemical corrosion behaviour.

EXPERIMENTAL

Coating systems

The coating materials were synthesized by sol-gel technology at room temperature using vinyltrimetoxysilane (VTMS) as silicon precursor and methylmethacrylate (MMA) or hydroxyethylmethacrylate (HEMA) as organic materials in different proportions (5–20%). The coatings were deposited on mill steel substrates by dipping at controlled rate of 15 cm/min. The obtained layers were transparent, homogeneous with thickness 5–8 μm . Then they were dried at 25°C for 24 h and thermally treated at 50 and 200°C for 24 h in an electric furnace in air atmosphere.

As a model corrosive medium 0.5 M Na_2SO_4 solution at 25°C was used.

Experimental techniques

The potential sweep technique (Princeton Corrosion Measurement System, PAR 263A potentiostat with Soft Corr III package) was applied for electrochemical and corrosion measurements. For investigation of the structure and surface morphology of the synthesized hybrids the following methods were used: FT-IR (IR- MATSON 7000 FTIR spectrometer), XRD (X-ray PW1730/10 diffractometer, in the 2θ range of 50–80°, Cu-K α radiation), BET

Analysis (Gemini 2370 V5.00), EDS (RONTEC EDS System) and AFM (NanoScope Tapping Mode TM).

RESULTS AND DISCUSSION

The results from the XRD-analysis (Fig. 1) prove that all hybrids obtained have basically an amorphous structure. The type of the XRD patterns, however, indicates that some processes of ordering have taken place. It is also established that the diffraction pattern intensity increases with increase in the organic component content.

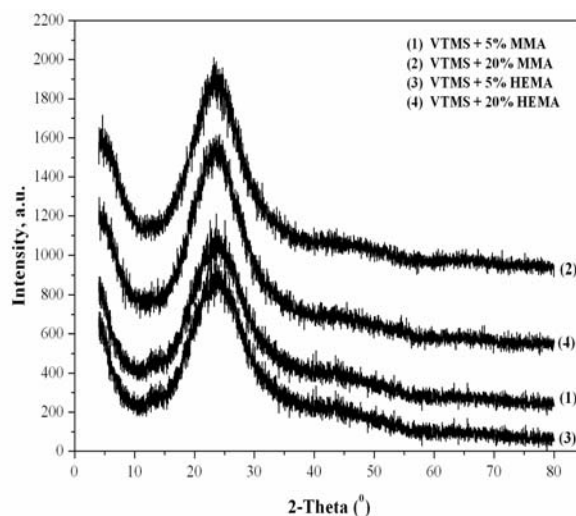


Fig. 1. XRD patterns of silica (VTMS) hybrids containing HEMA and MMA.

The FT-IR spectra of the synthesized inorganic-organic hybrids (Fig. 2) show that for all samples, bands at 1080, 790 and 480 cm^{-1} are observed, which are assigned to ν_{as} , ν_3 and δ of Si–O–Si vibrations. At the same time the band at 1080 cm^{-1} can be related to the presence of Si–O–C, C–O–C and Si–C bonds. The band at 960 cm^{-1} is due to stretching of Si–OH vibration. The band at 1439 cm^{-1} is assigned to C–O–H vibrations. The characteristic bands at around 3450 and 1620 cm^{-1} assigned to H–O–H vibration can also be detected. The absorption band at 2975, 1255, 880 and 694 cm^{-1} , due to the presence of Si–O–R (CH_3 and C_2H_5) and Si–C bonds, have been also observed. These facts directly prove the presence of strong chemical bonds between inorganic and organic parts of the hybrids. The EDS analysis proved the presence of Si, O and C elements in all hybrid samples studied.

From the data of BET analysis, it is established that the surface area is in the range from 327 to 340 m^2/g for the samples with 5% MMA or HEMA and from 64 to 71 m^2/g – for the samples with 20% MMA or HEMA. More detailed information on the nanostructure and surface morphology of the

matrices is obtained from the AFM studies. The presence of a heterogeneous structure with well-defined nano-units is observed. The average size of the nanoparticles on the sample surface is about 5–15 nm (Fig. 3a–d). The AFM micrographs show the topography of the synthesized hybrids with the height distribution profiles of the surface roughness. The latter depends obviously on the type and quantity of the organic components. With the increase in their content, the surface roughness decreases.

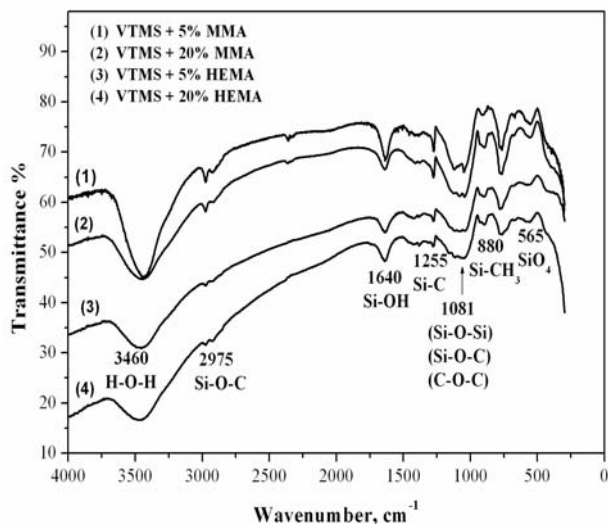


Fig. 2. FT-IR spectra of silica (VTMS) hybrids containing HEMA and MMA.

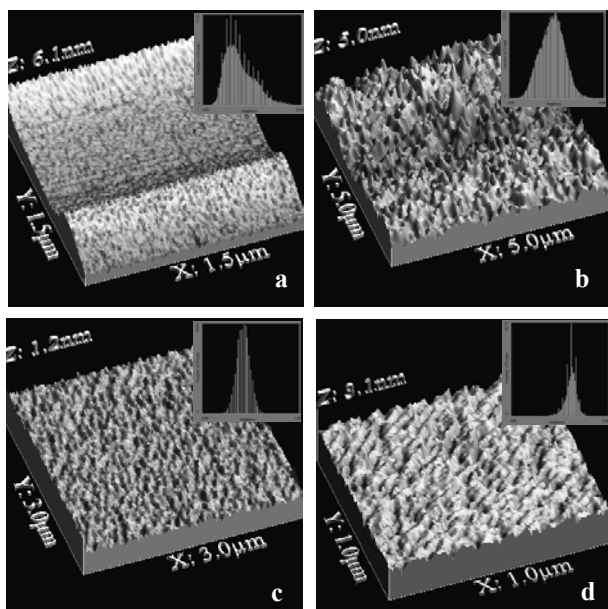


Fig. 3. AFM images height distribution profile of surface roughness of silica (VTMS) hybrids containing: (a) 5% HEMA; (b) 20% HEMA; (c) 5% MMA; (d) 20% MMA.

The electrochemical measurements show that the silica hybrid coatings with both organic materials (MMA or MA) affect both partial corrosion reactions, but it decreases more strongly the anodic metal dissolution reaction, thus shifting the

corrosion potential in positive direction and decreasing the corrosion rate of the steel substrate more than an order of magnitude (Figs. 4 and 5). Those effects, however, are more strongly expressed for coatings containing MMA as organic material (Fig. 5). It is established that the temperature of thermal treatment of the coated samples affects the corrosion resistance of the coatings, obviously due to additional densification of the hybrid structure, but the effect is rather mild (cf. Table 1 and Fig. 6).

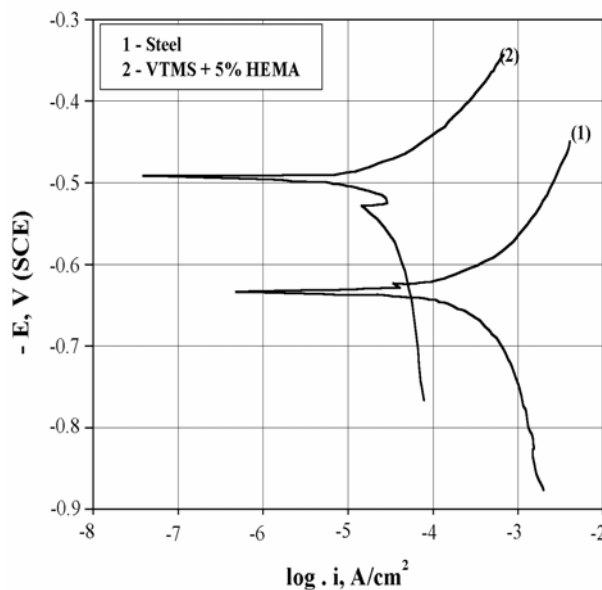


Fig. 4. Potentiodynamic polarization curves of mild steel substrate (1) and steel with hybrid coatings containing VTMS + 5% HEMA (2) treated at 50°C/24 h, in 0.5 M Na₂SO₄.

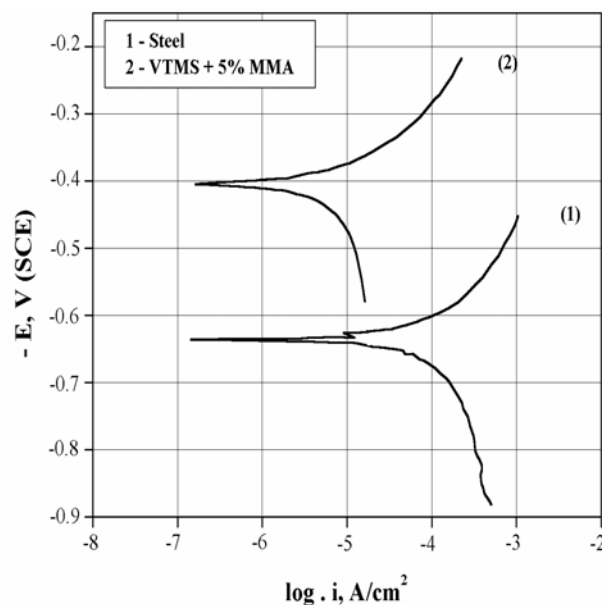


Fig. 5. Potentiodynamic polarization curves of mild steel substrate (1) and steel with hybrid coatings containing VTMS + 5% MMA (2) treated at 50°C/24 h, in 0.5 M Na₂SO₄.

Table 1. Electrochemical corrosion parameters: corrosion potential (E_{corr}) and corrosion current density of the steel and steel samples with hybrid coatings.

Samples	Temperature of treatment	E_{corr} V, SCE	i_{corr} $\mu\text{A}/\text{cm}^2$
steel	-	-0.615	250
Steel/VTMS+5%HEMA	50°C	-0.480	45
Steel/VTMS+5%HEMA	200°C	-0.370	15
Steel/VTMS+5%MMA	50°C	-0.415	35

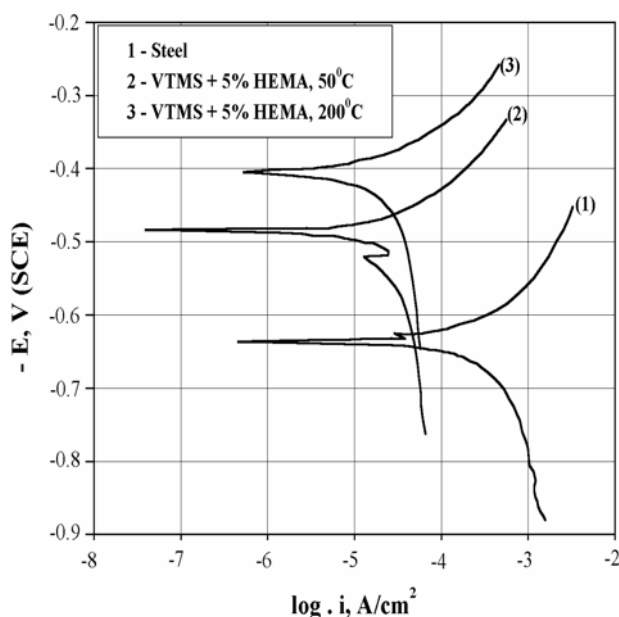


Fig. 6. Potentiodynamic polarization curves of mild steel substrate (1) and steel with hybrid coatings containing VTMS + 5% HEMA treated at 50°C/24 h (2) and 200°C/24 h (3), in 0.5 M Na_2SO_4 .

The presence of a chemical bond of the hybrid coating with the iron from the substrate is also established, which is in accordance with the good adhesion and properties of the coating.

CONCLUSION

Silica hybrid inorganic-organic nanostructured coatings were obtained by sol-gel technology using vinyltrimethoxysilane (VTMS) as silicon precursor and methylmethacrylate (MMA) or hydroxyethyl-methacrylate (HEMA) as organic materials. The composition and structure of the hybrid coatings were characterized and their corrosion resistance investigated. The results from the present study suggest possible application of the obtained hybrid materials as transparent coatings with good adhesion and protective properties.

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КОРОЗИОННО-ЕЛЕКТРОХИМИЧНИ ОТНАСЯНИЯ НА ЗОЛ-ГЕЛНИ ХИБРИДНИ ПОКРИТИЯ

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(Резюме)

Целта на настоящата работа е да се получат хибридни неорганично-органични наноструктурирани покрития и да се изследва тяхната структура и корозионна устойчивост. Покритията бяха синтезирани чрез зол-гелна технология при стайна температура, използвайки винилтриметоксисилан (VTMS) като силициев прекурсор и метилметакрилат (ММА) като органичен материал в различни съотношения. Покритията бяха отложени върху образци от нисковъглеродна стомана и термично третираны при 25 и 200°C. Съставът и структурата на покритията бяха охарактеризирани с помощта на FTIRS, XRD, BET, EDS, SEM, AFM и други методи. Потвърдено бе наличието на силни химически връзки (Si-C, Si-O-C) между органичната и неорганична част на хибридният материал, който е в аморфно състояние. Размерът на наночастиците и на техните агрегати, както и повърхностната грапавост на различните хибридни покрития са също оценени.

Корозионната устойчивост на покритията бе изследвана с помощта на потенциодинамична поляризационна техника и моделна корозионна среда от 0.5 M Na₂SO₄. Показано бе, че покритието оказва влияние и на двете парциални корозионни реакции, но понижава значително по-силно скоростта на анодната реакция на разтваряне на метал, при което скоростта на корозия на стоманената основа намалява над един порядък. Установено е наличието на химическа връзка между покритието и желязото от основата, което е в съгласие с добрата адхезия на покритията. Резултати от настоящото изследване са указание за възможно приложение на получените хибридни материали като прозрачни защитни покрития.