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# The effect of sequence of sol-gel multilayer coatings deposition on corrosion behaviour of stainless steel 316L

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The possibility of producing protective coatings by the sol-gel process is discussed. Metaloorganic complexes open new possibilities for the syntheses of ceramic materials. The most important applications of Si alkoxides for the synthesis of inorganic-inorganic composites are presented. The $SiO_2$ protective coatings on surgical stainless steel 316L have been synthesized by the sol-gel techniques. The multi-layer coatings were deposited by the dip method using sols containing appropriate molar ratios of the precursor (tetraethoxysilan), anhydrous ethanol, nitric acid and acetic acid. Nanosilica with the surfactant didodecyldimethyl-ammonium bromide were added to the sols applied. Coatings were annealed from 200 °C to 300 °C. The electrochemical characterization by dc measurements of the protective coatings in Ringer's solutions is reported. The coatings performance has been compared using polarization characteristics. Two arbitrarily chosen values were taken: the current density at –750 mV and the potential corresponding to the current density of 2 $\mu A/cm^2$. The coatings were chosen and ranked with regard to additional parameters: the polarization resistance and the through-coating porosity. It has been established that the way of applying of the coatings had an influence on the protective properties. The best protective properties have the coatings obtained from sols consisting of three $SiO_2$ layers with nanosilica and three $SiO_2$ layers without nanosilica. The positive effect of nanosilica on the protective properties of the coatings was determinated. Small changes in the preparation process can often have disproportionate large effects on the quality of the coatings.

Key words: *sol-gel; nanosilica; potentiodynamic curves; surfactant; wet corrosion*

## 1. Introduction

Surface engineering techniques enable us to improve properties of metallic materials, raise their corrosion resistance, as well as reduce their 'wear and tear'. One of these techniques is the sol-gel process, which enables the synthesis of new ceramic materials. Coatings from sols can be obtained by dipping, spinning or spraying [1].

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Surface layers may be single- or multicomponent systems [2–5]. A major advantage of this method is that at no stage of the synthesis of ceramic material high temperatures are needed [6, 7]. The drawbacks inherent to the sol-gel method are shrinkage and porosity. The porosity of the coating can be reduced either by appropriate thermal treatment [6] or by increase of their thickness. However, inorganic coatings of the thicknesses smaller than 0.3–1.0 μm [8] are prone to cracks during drying or thermal treatment [9]. Higher thicknesses are obtained by decreasing the hydrolytic ratio $R_h$ [10] or by reducing the temperature of the thermal treatment [11].

Inorganic-inorganic composite coatings (where one of the components is an inorganic polymer obtained from the sol (the matrix), and the other inorganic component is a powder added to the sol) display lower porosity and shrinkage during drying and thermal treatment processes. In this way, so-called nanocomposites are obtained, i.e. composites of grain sizes (particle sizes) below 100 nm [12]. Experiments with stainless steel 316L [13, 14] using nanosilica and surfactants have revealed that the protective properties of the coatings obtained from modified sols are better than those prepared with sols containing no ceramic powders.

## 2. Experimental

The substrate investigated was stainless steel of the type 316L (surgical steel) of the chemical composition shown in Table 1. The steel samples were in the form of disks 14.8 mm in diameter and 1 mm thick. Prior to the deposition of the coatings, the surface of the steel was ground successively with abrasive papers of the grain-size distribution of 400, 600 and 800. The samples were then washed with distilled water, dried and degreased in a two-stage procedure using an ultrasonic bath (for 45 min in tetrachloroethylene ($C_2Cl_4$) and 15 min in anhydrous ethyl alcohol ($C_2H_5OH$)). The coatings were deposited on the steel samples.

Table 1. Chemical composition of stainless steel 316L (wt. %)

| C | Cr | Ni | Mo | Mn | Si | Cu | V | S | P |
|---|---|---|---|---|---|---|---|---|---|
| 0.03 | 17.28 | 14.80 | 2.8 | 1.96 | 0.19 | 0.07 | 0.035 | 0.03 | 0.024 |

For the preparation of the $SiO_2$ coatings, tetraethoxysilane ($Si(OC_2H_5)_4$; TEOS) was used. TEOS was diluted with anhydrous ethyl alcohol and homogenized in an ultrasonic bath for 75 min. Then, the remaining components were added to the solution and homogenization was carried out for 85 min. The starting sols (referred to as A and B, Table 2) obtained in this way were applied to the preparation of the sols used for the deposition of the coatings. A certain amount of nanosilica in the presence of an appropriate surfactant was added to the sol B, and the mixture was then stirred in an ultrasonic bath for 60 min at a constant temperature ($T = 20$ °C). The surfactant, DoDAB (didodecyldimethylammonium bromide, $(C_{12}H_{25})_2N(CH_3)_2Br$)) was used to reduce agglomeration of nanosilica with the particle size from 5 to 32 nm. Table 3 shows the composition of the sol K, which was used for preparation of the coatings.

Table 2. Chemical composition of the sols A and B

| Sol | Composition | | | |
|---|---|---|---|---|
| | TEOS [g] | $C_2H_5OH$ [g] | $HNO_3$ [g] | $CH_3COOH$ [g] |
| A | 18.660 (20 ml) | 15.800 (20 ml) | – | 4.202 (4 ml) |
| B | 26.050 | 43.043 | 0.0062 | 0.0068 |

Table 3. Chemical composition of the sol K

| Sol | Composition | | | |
|---|---|---|---|---|
| | Sol B [ml] | Sol A [ml] | Nanosilica [g] | DoDAB [g] |
| K | 15.0 | – | 0.0065 | 0.0105 |

The coatings were deposited on the substrate by dip-coating. The samples were dipped in the sol for 2 min in order to establish equilibrium at the substrate–solution phase boundary. The dipping and withdrawing of samples was performed at a constant rate of 1.0 mm/s. The samples were subsequently dried in the cool air for 24 h, and fired in an electrical furnace which was heated to the ultimate temperature at a rate of 2.0 °C/min. The samples were sintered for 60 min. In this way, six-layer coatings were obtained. The coatings have been assigned the following symbols: capital letter K followed by a number (from 0 to 7). The compositions of particular layers of the coatings and the sintering temperatures are shown in Table 4.

Table 4. Preparation of the coatings

| Layer | Sample | | | | | | | | Sintering [°C] |
|---|---|---|---|---|---|---|---|---|---|
| | K0 | K1 | K2 | K3 | K4 | K5 | K6 | K7 | |
| 1 | A | B | K | K | B | A | A | K | 300 |
| 2 | A | B | B | A | K | K | K | A | 280 |
| 3 | A | B | K | K | A | B | A | K | 260 |
| 4 | A | B | A | B | K | K | K | A | 240 |
| 5 | A | B | K | K | B | A | A | K | 220 |
| 6 | A | B | B | A | K | K | K | A | 200 |

The dc measurements designed for the assessment of corrosion resistance involved recordings of polarization curves in a conventional three-electrode system. The measuring set (fully automatic) consisted of a measuring vessel, an SI 1286 potentiostate and a computer. Prior to the measurements, the samples were soaked in the Ringer solution (NaCl, 8.60 g/dm$^3$; KCl, 0.30 g/dm$^3$; $CaCl_2$, 0.48 g/dm$^3$) for 10 min and then polarized in the same solution in the anodic direction at the rate of 1 mV/s, starting with the potential of –1000 mV (the electrochemical potential is related to the saturated calomel electrode (SCE) in all cases presented).

## 3. Results and discussion

Figure 1 shows the values of the corrosion potential (*E′*) measured after 10-min exposures of the samples of stainless steel 316L (both coated and uncoated) to the Ringer solution. The appropriate thermal treatment, as well as addition of nanosilica as a filling material, accounts for the 'refining' of the surface. The comparison of the measured *E′* values suggests that the sequence of film deposition and thermal treatment could decrease the number of cracks in the coatings. It is well known that reducing the ratio of cathode area to anode area results in a decrease of the corrosion potential [15]. From the results reported in our previous papers [16,17] it can be inferred that when the number of layers in coating increases so does the *E′* potential.

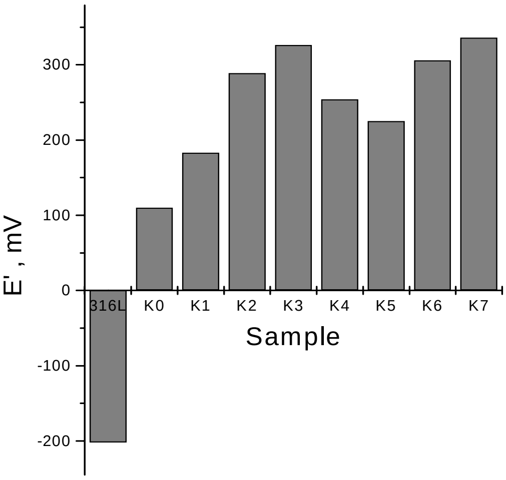

Fig. 1. Corrosion potential values *E′* for coated and uncoated stainless steel 316L measured after 10 min exposure to the Ringer's solution

Figure 2 presents the polarization curves of stainless steel 316L with the coatings deposited from the sols. The values of the cathode and anode current densities are much lower for the coated samples as compared to the uncoated stainless steel 316L samples. Low anode current values up to the potential slightly exceeding 1000 mV were determined for the sample K5.

The polarization curves for the bare and coated steel samples are plotted in Figs. 3–5. As shown in the figures, the coatings with their first layers obtained from the sols with no nanosilica additives display lower cathode current densities than those prepared from the sols with nanosilica additions (Figs. 3 and 4). The value of the pitting potential ($E_{2\mu A/cm^2}$), however, is influenced by the last (6th) deposited layer. Thus, when this layer is deposited from the sol with the silica additive, the pitting potential reaches higher values than when it is deposited from the sol with no additive (Figs. 3 and 4).

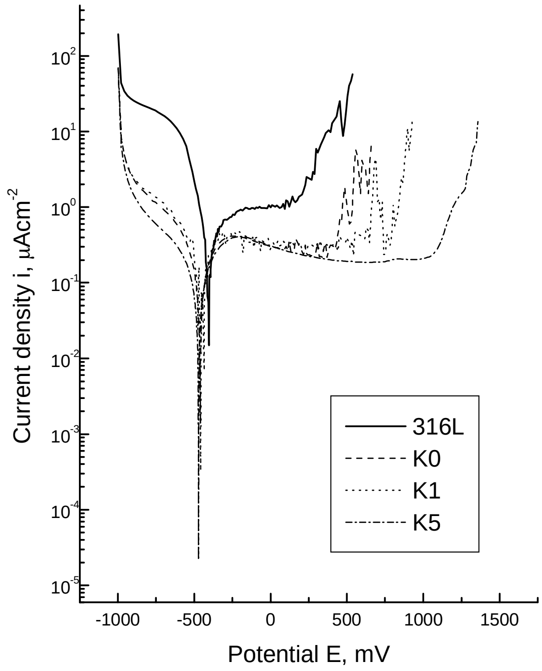

Fig. 2. Polarization curves for sol-gel coated stainless steel 316L

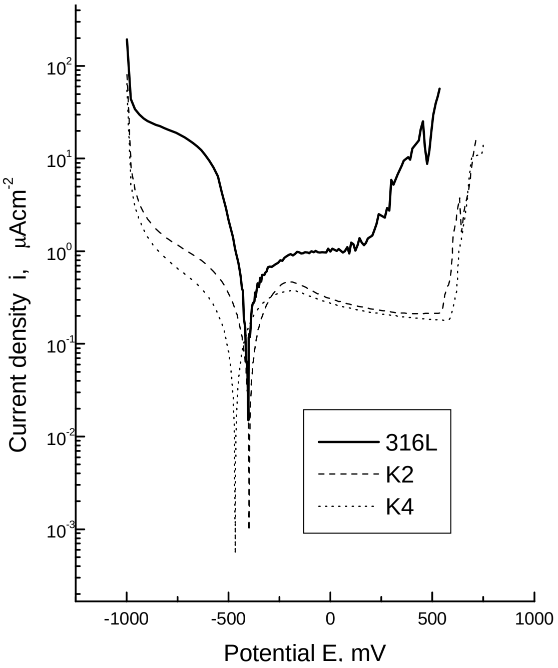

Fig. 3. Polarization curves for sol-gel coated stainless steel 316L

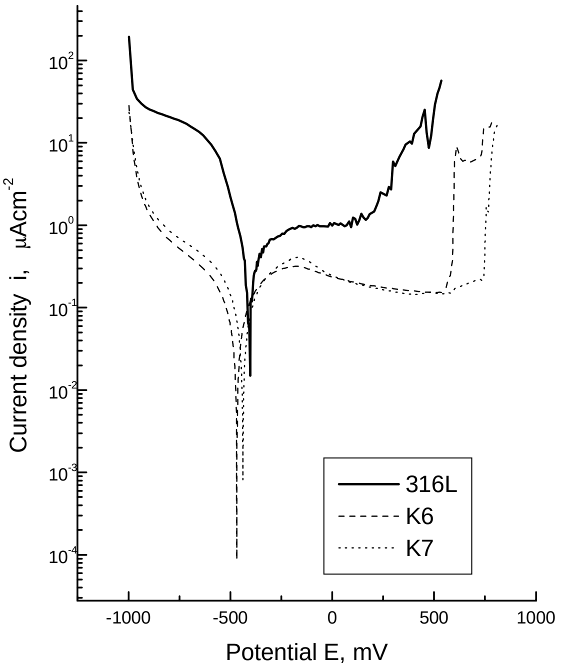

Fig. 4. Polarization curves for sol-gel coated stainless steel 316L

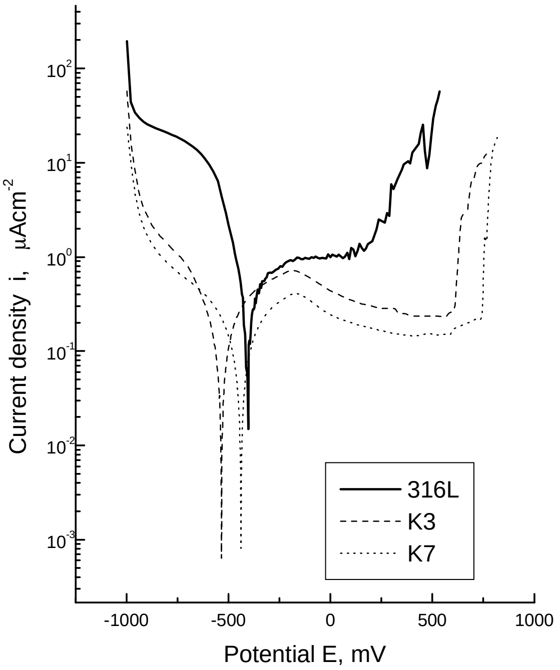

Fig. 5. Polarization curves for sol-gel coated stainless steel 316L

The fourth layer of the coating, which is not the external one and has no direct contact with the solution, exerts an influence on the cathodic-to-anodic transition potential ($E_{\mathrm{C-A}}$). There is also a distinct change in the values of the anode currents and corrosion pit nucleation potentials (Fig. 5). A similar pattern can be observed for the coated samples K2 and K3 where the sequence of the layers deposition from the sol A and the sol B has been changed. Figure 2 reveals a distinct change in the values of the $E_{\mathrm{C-A}}$ transition and the anode currents.

To assess the behaviour of the coatings, two quantities have been chosen from the polarization curves, i.e. the current density obtained from the cathodic curves recorded at – 750 mV (the porosity measure) and the potential obtained from the anodic region corresponding to the current density of 2 $\mu\mathrm{A/cm}^2$. The explanation supporting this choice of parameters can be found in our previous paper [18]. The potential chosen can be considered as the pitting potential. Figure 6 presents (in the current-potential co-ordinates) the parameters $i_{-750\mathrm{mV}}$ and $E_{2\mu\mathrm{A/cm}^2}$ which correspond to each of the polarization curves. Thus, the best and the worst protective properties are supposed to be those of the coating in the top left-hand corner and bottom right-hand corner of the figure, respectively. Figure 6 introduces the electrochemical parameters which are needed for assessment of the anticorrosive properties of the coatings. Analysis of these data demonstrated that, although each of the samples displays protective properties, those of K5 are the most advantageous.

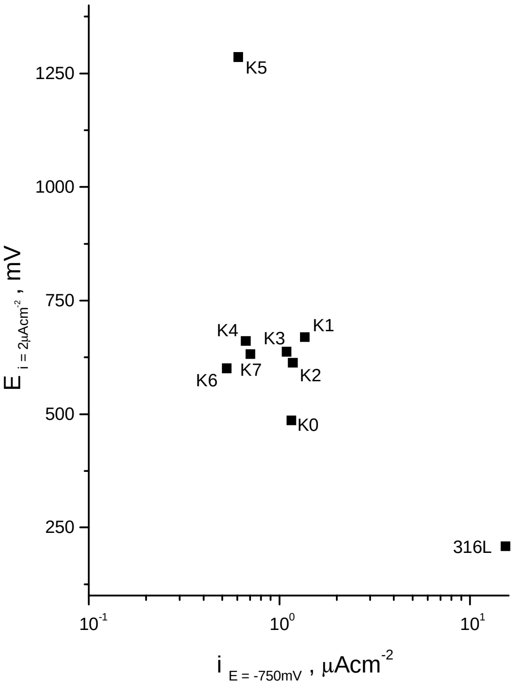

Fig. 6. Electrochemical parameters used for estimation of the protective properties of the coatings

Another parameter useful for the quality assessment of coatings is the polarization resistance $R_p$. To determine its value, we have used the data chosen from the proximity of the cathodic-to-anodic transition potential. In the linear system (*E–i*) one obtains a straight line with a slope yielding directly the polarization resistance. The $R_p$ values were determined using the linear regression method and are plotted in Fig. 7.

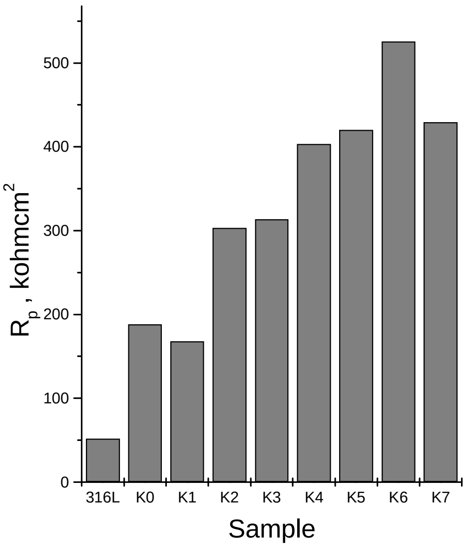

Fig. 7. Comparison of polarization resistances $R_p$ for coated and uncoated stainless steel 316L

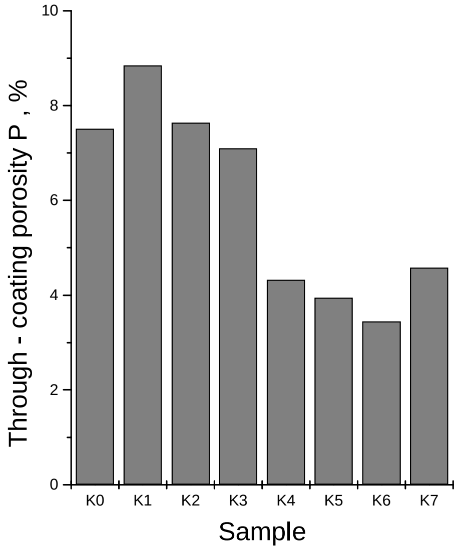

Fig. 8. Comparison of the through-coating porosity for coated stainless steel 316L

From these plots it can be seen that a change in the method of deposition is connected with a change in the values of polarization resistance of the samples of coated stainless steel 316L. This is particularly evident when comparing K2 with K3, K2 with K4, K3 with K7 and K6 with K7. It can be concluded that each sample of stainless steel 316L with the coating displays protective properties. However, the best ones are those of the K6 sample.

Figure 8 depicts the through-coating porosity $P$, defined as the ratio of the cathode current density of the coated samples $i$ to the current density of the uncoated substrate $i'$ at the potential of –750 mV.

$$P = \frac{i}{i'} \cdot 100\%$$

There is a correlation between the polarization resistance $R_p$ and the through-coating porosity $P$. Thus, the sample K6 (which has the highest $R_p$ value), shows the lowest $P$ value, while the sample K2 exhibits the highest $P$ value at the lowest polarization resistance. The complex nature of the system causes, however, that no general criteria seem to apply to the assessment of the protective properties when the coatings are prepared by the sol-gel method. It should be also stressed that the corrosion resistance is strongly influenced not only by through-coating porosity but also by the character of the coating–substrate interface [19].

## 4. Conclusions

Addition of nanosilica and the cation surfactant DoDAB has a favourable effect on the protective properties of the sol-gel coatings on stainless steel substrates of the type 316L. It is also the sequence of deposition at the layers that contributes to the protective properties of the coatings obtained.

## References

[1] BRINKER C.J., SCHERER G.W., *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990.

[2] GŁUSZEK J., *Tlenkowe powłoki ochronne otrzymywane metodą sol-gel* (*The protective oxide coatings prepared by the sol-gel metod*, in Polish), Ofic. Wyd. Politechniki Wrocławskiej, 1998.

[3] GŁUSZEK J., ZABRZESKI J., Inżynieria Powierzchni, 3 (1996), 16.

[4] GUGLIELMI M., J. Sol–Gel Sci. Techn., 8 (1997), 443.

[5] ATIK M., DE LIMA P., AVACA L.A., AEGERTER M.A., ZARZYCKI J., J. Mater. Sci. Letters, 13 (1994), 1081.

[6] ULRICH D.R., J. Non-Cryst. Solids, 100 (1988), 174.

[7] HENCH L.L., ULRICH D.R., *Ultrastructure Processing of Ceramics, Glasses and Composites*, Wiley, New York, 1984.

[8] STRAWBRIDGE I., JAMES P.F., J. Non-Cryst. Solids, 82 (1986), 366.

[9] ZARZYCKI J., [in:] L.L. Hench and D.R. Urlich (Eds.), *Ultrastructure Processing of Ceramics, Glasses and Composites*, Wiley, New York, 1987, p. 27.
[10] GARINO T.J., Mater. Res. Soc. Symp. Proc., 180 (1990), 497.
[11] GALLARDO J., GALLIANO P., DURAN A., J. Sol-Gel Sci. Techn., 19 (2000), 393.
[12] JURCZYK M., *Nanomatriały* (*Nanomaterials*, in Polish), Wyd. Politechniki Poznańskiej, 2001.
[13] CHĘCMANOWSKI J.G., GŁUSZEK J., MASALSKI J., KRYSZTAFKIEWICZ A., Inż. Mat., 5 (2002), 359.
[14] CHĘCMANOWSKI J.G., GŁUSZEK J., MASALSKI J., JESIONOWSKI T., Ochrona przed Korozją, 11A (2002), 214.
[15] WEST J.M., *Basic Corrosion and Oxidation*, Wiley, New York, 1986.
[16] MASALSKI J., CHĘCMANOWSKI J.G., SOBAŃSKA D., Raport SPR 13/2001 ITNiNM Politech. Wrocł. 2001.
[17] CHĘCMANOWSKI J.G., GŁUSZEK J., MASALSKI J., Proc. 7th Polish Symp. Sci.-Tech. 83, Poraj 2001.
[18] GŁUSZEK J., MASALSKI J., KUCHARCZYK B., GOLUBSKI Z., Inż. Mat., 5 (2002), 355.
[19] PENTTINEN I.M., KORHONEN A.S., HARJU E., TURKIA M.A., FORSEN O., RISTOLAINEN E.O., Surf. Coat. Tech., 2 (1992), 161.

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