

# Ni–Al PROTECTIVE COATING OF STEEL ELECTRODES IN DC ELECTROLYSIS FOR HYDROGEN PRODUCTION

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Hydrogen can be a good alternative to fossil fuels under the conditions of world's crisis as an effective energy carrier derived from renewable resources. Among all the known methods of hydrogen production, water electrolysis gives the ecologically purest hydrogen, so it is of importance to maximize the efficiency of this process. The authors consider the influence of plasma sprayed Ni–Al protective coating of 316L steel anode-cathode electrodes in DC electrolysis. In a long-term (24 h) process the anode corrodes strongly, losing Cr and Ni ions which are transferred to the electrolyte, while only minor corrosion of the cathode occurs. At the same time, the composition of anode and cathode electrodes protected by Ni–Al coating changes only slightly during a prolonged electrolysis. As the voltammetry and Tafel plots evidence, the Ni–Al coating protects both the anode and cathode from the corrosion and reduces the potential of hydrogen evolution. The results obtained show that such a coating works best in the case of steel electrodes.

**Key words:** *DC electrolysis, steel, Ni–Al coating, Tafel plot.*

## 1. INTRODUCTION

Hydrogen is one of the most demanded gases in chemical industry, and nowadays it is used as energy carrier in the hydrogen economy, allowing saving the unused energy from renewable sources (sun, wind, rivers) and as fuel for fuel cells [1]. In the case of sustainable production, hydrogen can be obtained in the water electrolysis using the electricity from renewables. To produce higher amount of hydrogen at a given quantity of electricity the effective electrolyzers are needed. The technology of electrolytic process can be improved by engineering the surfaces of electrodes to reduce the excessive potential of hydrogen evolution. The applied voltage providing a given current and, hence, allowing the desired amount of hydrogen to be produced is [2]:

$$E_{appl} = E_e + |\eta_c| + |\eta_a| + IR, \quad (1)$$

where  $\eta_c$ ,  $\eta_a$  are the cathode and anode potentials, respectively;  
 $E_e = 1.23$  V is the equilibrium cell voltage for decomposition of water;  
 $IR$  are the heat losses in electrolyte.

The nanostructuring and modification of the electrode surfaces are found to reduce the  $\eta_c$  and  $\eta_a$  values thus decreasing the applied voltage and heat loss in an electrolytic cell. In the case of typical electrolysis with steel and nickel electrodes the operating cell voltage is  $\sim 2.0$  V. The effect of electrode surface roughness on the kinetics of hydrogen evolution reaction has been studied for different electrodes [3–6]. For nickel cathodes, the Tafel slope was independent of this parameter, while the exchange current density for a smooth electrode was about twice that for the roughened electrode. For the mild steel cathodes the roughened electrode showed a considerably lower Tafel slope than the smooth one, with the exchange current density being lower for the roughened than for the smooth electrode [3]. In the case of copper electrode, the improvement in hydrogen evolution is due to increase in the surface roughness of copper deposits [4]. It is shown that the nature of hydrogen evolution rate rise on the Ni–P alloys depends on the alloy composition up to the phosphor concentration of 6.5 wt %, while at higher P concentrations significant development of the surface occurs [5].

The electrode coatings for advanced alkaline water electrolysis were produced by applying vacuum plasma spraying (VPS) [6]. To obtain well-bonded and stable layers, careful surface preparation of the substrates is required, especially with Ni–Al precursory alloy, which has to be activated subsequently to the Raney nickel. The nickel-aluminium coatings with a significant porosity of the structure and surface roughness were obtained using thermal flame and plasma spraying technology [7]. The coatings were 400–700  $\mu\text{m}$  thick and had various compositions which determined the corrosion potential. It was found that the greater aluminium content in a coating, the harder the coating is. The flame spray coatings are distinguished by nearly 10-times higher corrosion current density comparing with the plasma spray coatings [7].

In our previous research the electrochemical nickel coatings on steel electrodes were investigated [8]. In the present work the research has been done on steel electrodes coated with a plasma sprayed Ni–Al layer. Prolonged electrolysis was performed to check up the changes of anode and cathode surfaces.

## 2. EXPERIMENTAL

A stainless steel 316L plate (obtained from *VNT System Ltd.*) was used as substrate for plasma spray coating with a 4:1 Ni–Al alloy (produced by the plasma spray method, *Terpa-Service Ltd.* [9]). The thickness of Ni–Al coating in our case was 730  $\mu\text{m}$ . First, fresh coatings were etched in a hot (80 °C) alkali solution, 5 M KOH (*Aldrich*), and only then subjected to electrochemical tests and prolonged electrolysis. The voltammetry and Tafel slope characteristics of electrodes were measured before and after electrolysis in 5 M KOH solution at room temperature (22 °C) by a Voltalab 40 PGZ301 potentiostat using a Calomel electrode as reference (both from *Radiometer-Analytical*). The electrochemical characteristics (exchange current, corrosion stability, hydrogen evolution potential) were compared for both electrodes, fresh and after the 24-h electrolysis at 250 mA/cm<sup>2</sup> current density. The surface of electrode before and after electrolysis was examined using a scanning electron microscope FEI SEM "Quanta 200" (Laboratory of the State Forensic Science Bureau). The elemental composition of electrodes after the 24-h electrolysis was analyzed with X-ray fluorescence micro-analyst system EDAX Eagle III.

### 3. RESULTS AND DISCUSSION

The surface morphology of steel electrodes is seen in the SEM pictures of Figs. 1–3. The starting material and substrate for coatings (a stainless-steel 316L plate with typical industrially-rolled raw steel surface) is shown in Fig. 1a.

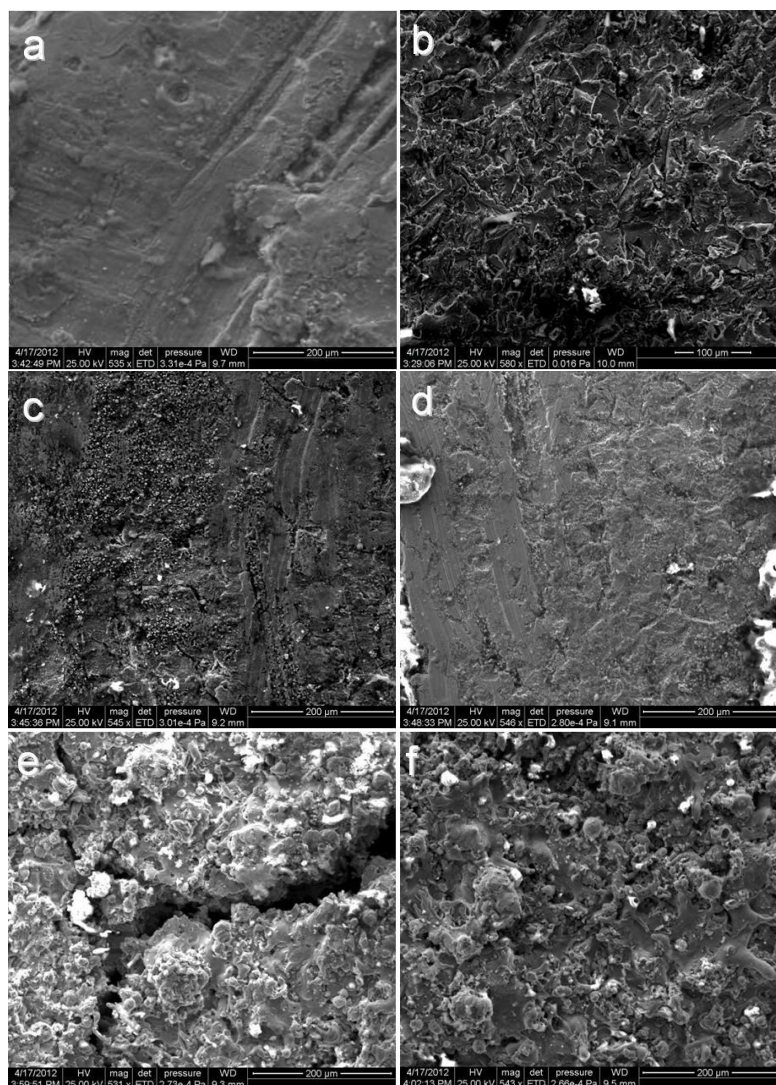


Fig. 1. Surfaces of as-obtained steel plate (a), steel coated with Ni–Al layer (b), steel plate cathode (c) and anode (d) after 24 h electrolysis; steel coated with Ni–Al layer: cathode (e) and anode (f) after 24 h electrolysis. White crystals might be from alkali residuals not removed after electrolysis.

During the plasma spraying process a micro-structured coating is formed (Fig. 1b). Prolonged electrolysis with high current density changes the morphology and elemental composition of both steel electrodes – anode and cathode (Figs. 1c,d Table 1). The surface of steel cathode after electrolysis is coated with 3–4  $\mu\text{m}$  spherical grains (Fig. 1c) originating in the corrosion process during electrolysis (as was also noticed by Nikiforov *et al* [10]), while the surface of anode (Fig. 1d) is smooth and looks etched. Prolonged electrolysis changes the morphology and

elemental composition of Ni–Al coated steel electrodes, both anode and cathode (Table 1, Figs. 1e,f). Smoothing of surface and formation of large cracks in coating is observed on the cathode (Fig. 1e), while coating on the anode looks less smooth and is free from cracks (Fig. 1f). The formation of cracks can be explained with reactive nature of the hydrogen evolved on the cathode – it may diffuse through the coating, accumulate and then destroy the coated layer.

The elemental compositions of as-obtained steel and of plasma coating given in Table 1 are Ti:Cr:Fe:Ni (2:18:70:10) and Al:Si:Cr:Fe:Ni:Mo:Cd (39:20:8:7:2:17), respectively. As seen in the table, during prolonged electrolysis of non-coated steel most of Cr and Ni ions are dissolved from the surface of anode, while only minor amount of Cr and Ni ions are dissolved from cathode. In turn, for plasma coating the composition drastically changes after etching in hot alkali: the Al, Si, Cd, Cr contents almost disappear, whereas after prolonged electrolysis the composition of the cathode and anode changes but slightly. Potassium in all electrodes after prolonged electrolysis arrives from the electrolyte (KOH).

Table 1

**Elemental composition of steel 316L electrode and steel coated with Ni–Al layer as-obtained and of the cathodes and anodes after 24-h electrolysis**

Element	Steel as-obtained	Steel after prolonged electrolysis		Ni–Al layer as coated	Ni–Al layer after etching	After prolonged electrolysis	
		cathode	anode			cathode	anode
Al	<0.5	<0.5	<0.5	39	5	5	4
Si				20	<0.5	<0.5	<0.5
K	<0.5	<0.5	1	<0.5	1	3	5
Ti	2	<0.5	<0.5				
Cr	18	16	2	8	3	2	1
Fe	70	76	97	7	6	6	0
Ni	10	8	<0.5	7	82	84	90
Mo				2	1	<0.5	<0.5
Cd				17	2	<0.5	<0.5

Assessment of the materials for their hydrogen evolution behaviour and corrosion stability can be done based on electrochemical measurements, using classic voltammetry and Tafel slope analysis [11]. From the voltammetry curves it follows that the steel electrode with Ni–Al plasma coating is characterized by higher currents at potentials < 0.4 V (Calomel electrode). Larger hysteresis of the electrode with coating points to the oxidation-reduction and hydrogen adsorption-desorption processes on the coating at cathodic potentials <0.4 V comparing with a smooth steel electrode. The Tafel slope analysis tool built up in VoltaMaster software of Voltalab 40 PGZ301 potentiostat provides a quick estimation of the corrosion rate and polarization resistance  $R_p$  (Fig. 2). The corrosion rate is calculated from the estimated corrosion current,  $i_{corr}$ , obtained from the intercept of two linear segments of the Tafel slope, whereas corrosion potential  $E_c$  (in our case also the potential characterizing the start-up of hydrogen evolution) is read from the position of the peak heights in log (current) plot (see Table 2).

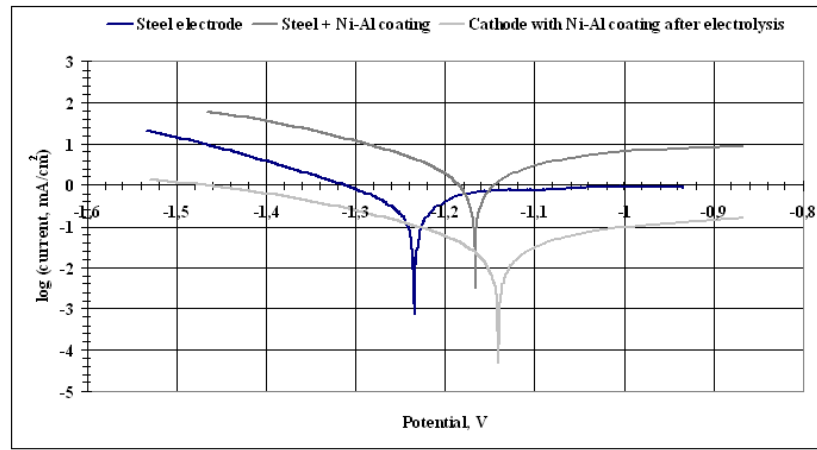


Fig. 2. Tafel plot of steel electrode (dark), steel electrode with Ni–Al plasma coating before etching (gray) and after prolonged electrolysis (light gray).

Table 2

**Parameters from Tafel plot for the steel electrode, electrode with Ni–Al plasma coating: as-obtained, after etching in hot alkali; as the cathode and anode after 24 h electrolysis.**

Samples	$E_c (i=0)$ , mV	$i_{corr}$ , $\mu\text{A}/\text{cm}^2$	$R_p$ , $\text{k}\Omega/\text{cm}^2$	$B_c$ , mV	Corrosion rate, mm/Y
Steel electrode before electrolysis	–1239	699	0.037	–193	8.18
Steel cathode after electrolysis	–1178	65	0.089	–229	7.6
Steel anode after electrolysis	–1206	440	5.21	–265	22.7
Plasma coating before etching	–1164.6	8878	0.016	–356	103.8
Plasma coating after etching	–1157	276.4	1.194	–546	3.23
Coating cathode after electrolysis	–1140	241.5	1.4	–507	2.82
Coating anode after electrolysis	–1174.6	311.3	0.987	–585	3.64

The hydrogen evolution starts at lower potential  $E_c$  for the electrodes coated with Ni–Al layer (Table 2). The Tafel lines obtained in a polarization curve (Fig. 2) correspond basically to three types of processes, which represent a controlling discharge reaction: barrier-free discharge ( $\alpha = 1$ , the activation energy barrier is high), ordinary discharge ( $\alpha = 0.5$ , the activation energy barrier is modest) and activation-free discharge ( $\alpha = 0$ , the activation energy barrier is negligible) [12]. The  $B_c$  values for our samples in all cases more likely correspond to  $\alpha = 0$ ; however, as seen from Table 2 the activation energy barrier in the discharge reaction is much less expressed for the electrodes coated with Ni–Al. The tabulated data show that the steel electrode sample with plasma coating before etching differs from other samples by very high corrosion current and corrosion rate. This can be explained with high reactivity of aluminium in alkali solution. After etching there

is no more excess of surface aluminium in the sample, and the corrosion rates are much lower. Comparing characteristics from the Tafel plots (Table 2) of non-coated and coated steel electrodes it is seen that lower hydrogen evolution potentials and corrosion rates are for steel electrodes coated with Ni–Al layer and also for a steel cathode after prolonged electrolysis. Explanation for these phenomena can be passivation of the steel cathode surface [10]. As concerns the effect of coating as protection against corrosion of steel electrodes in electrolysis process, it can be said that such a coating protects both the electrodes and reduces the corrosion rates. The disadvantage is that cracks appear in a coating when it is used as cathode during prolonged electrolysis, which can be prevented by choosing a thicker coating.

#### 4. CONCLUSIONS

As can be concluded from the morphology and elemental compositional analysis, a steel 316L anode corrodes more severely during electrolysis in alkali solution than a cathode from the same steel – Ni and Cr ions are dissolved from the anode surface almost completely. The composition of Ni–Al plasma coating drastically changes during etching in hot alkali, whereas during prolonged electrolysis the composition of the cathode and anode varies only slightly.

Assessment of the corrosion stability and the hydrogen evolution potential of non-coated and coated steel electrodes based on the analysis of voltammetry and Tafel plots has shown that the coating protects both electrodes (cathode and anode), reduces the corrosion rates and hydrogen evolution potentials. The disadvantage is that cracks appear in such a coating when it is used as cathode during prolonged electrolysis. Based on the results obtained it is proposed using steel with Ni–Al plasma coating as cathode and anode in electrolysis cell.

#### ACKNOWLEDGEMENT

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## Ni–Al PĀRKLĀJUMA IETEKME UZ TĒRAUDA ELEKTRODIEM LĪDZSTRĀVAS ELEKTROLĪZĒ ŪDEŅRAŽA RAŽOŠANAI

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### Kopsavilkums

Darbā pētīts, kā līdzstrāvas elektrolīzē tērauda 316L elektrodus (anods un katods) ietekmē ar plazmas izputināšanas metodi iegūts Ni–Al pārklājums. Tikko uznestam pārklājumam ir mikrostrukturēta virsma, kas kodināšanas laikā mainās, gan pēc reljefa, gan elementu sastāva. Veicot ilgstošu (24 stundas elektrolīzi), atrasts, ka tikai tērauda elektrods anoda lomā intensīvi korodē un zaudē hroma un niķeļa jonus, kas pāriet elektrolītā, turpretī katods mainās relatīvi maz. Pārklājums Ni–Al pēc uznesšanas tiek kodināts karstā sārmā, kad tiek izšķīdināta daļa sastāvā esošo elementu (Al, Si, Cd), bet ilgstošas elektrolīzes laikā pārklājuma sastāvs mainās maz gan anodam, gan katodam. Elektrodu elektroķīmiskie raksturlielumi noteikti ar voltamperometriju un Tāfeļa līkņu analīzes metodēm. Atrasts, ka Ni–Al pārklājums aizsargā gan anodu, gan katodu no korozijas un samazina ūdeņraža izdalīšanās potenciālu, lai gan ilgstošas elektrolīzes laikā katoda pārklājumā parādās plaisas. No iegūtajiem rezultātiem ieteikts reālai elektrolīzes šūnai par anodu un katodu izmantot tēraudu, kas pārklāts ar plazmas izputināšanas metodē iegūtu Ni–Al aizsargpārklājumu.

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