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Electrolytic nickel–molybdenum–vanadium alloy coatings as a material with a decreased hydrogen overvoltage

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The process of electrodeposition of Ni–Mo–V alloys from an alkaline tartrate bath was studied. The effect of the cathodic current density on the chemical composition, phase composition and surface morphology of Ni–Mo–V alloy deposits, as well as on the current efficiency of the deposition process, was determined. Codeposition of molybdenum and vanadium with nickel and formation of the Ni–Mo–V alloy is possible due to the effects of depolarization and overpolarization occurring in the process of codischarge of the complex ions of these metals. It was observed that the use of cathodes electrodeposited with Ni–Mo–V alloy containing 9–12% Mo and 0.1–0.2% V for water electrolysis resulted in a decreased overpotential for hydrogen evolution.

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1. Introduction

One of the ways of lowering the electrical energy consumption in water and chlor-alkali electrolysis processes is to reduce the hydrogen evolution overpotential. The deposition of electrocatalytic coatings on the cathode surface has been intensely investigated for many years. Profitable results were obtained with the use of steel, nickel or copper cathodes electrolytically covered by an alloy layer. Most often, the Ni–Mo alloys containing from 5–70% molybdenum were deposited [1–4]. Nickel–molybdenum alloys can be electrodeposited from both acid [5, 6] and alkaline baths [7, 8]. Nickel–zinc alloy coatings have also been used in the water electrolysis processes [9, 10]. Nickel or cobalt with tungsten and phosphorus alloys obtained by chemical reduction have also been used in chlor-alkali cells [11]. Our previous experiments would indicate that the content of vanadium in nickel alloys influences the overpotential for hydrogen evolution [12]. This fact was utilized in the preparation of active coatings for water electrolysis. The ternary Ni–Mo–V alloy coatings were deposited from the Watts' acid bath on a sandblasted steel substrate [13]. On these cathodes the hydrogen evolution overpotential values were of the order of 80 mV.

The above principles were also used by the authors of [14, 15], who deposited the ternary Ni–Mo–V alloys on to a copper substrate. The cathodes prepared in this way gave a hydrogen evolution potential lower by several hundred millivolts than on the nickel or steel cathodes. While the Ni–Mo–V alloys are deposited from an acid bath, some difficulties with the process control and properties of the coatings were noted. Baths containing complex ions of the metals to be deposited allow more control of the chemical composition and properties of the electrodeposited alloys.

The present paper discusses the results of experiments with Ni–Mo–V alloy coatings obtained from an alkaline bath [16]. Some characteristics as H_2 cathodes of these alloy coatings are also presented.

2. Experimental methods

The Ni–Mo–V alloy coatings were deposited on steel plates whose area was 4 x 10^{-3} m^2 and which had been sand-blasted. Prior to deposition, the surfaces were alkaline degreased [17], and afterwards pickled in a 20% sulphuric acid.

The deposition process was carried out under galvanostatic conditions in rectangular electrolytic tanks having a capacity of 1 x 10^{-3} m^3, equipped with a temperature control system. Graphite plates, whose total working area was about 1 x 10^{-2} m^2, were used as anodes. Each alloy coating was deposited using a fresh galvanic bath whose chemical composition was as follows

nickel sulphate $NiSO_4 \cdot 7H_2O$	62.0 kg m^{-3}
disodium molybdate $Na_2MoO_4 \cdot 2H_2O$	15.3 kg m^{-3}
vanadyl sulphate $VOSO_4 \cdot H_2O$	5.0 kg m^{-3}
potassium–sodium tartrate $KNaC_4H_4O_6 \cdot 4H_2O$	76.0 kg m^{-3}
sodium chloride NaCl	18.0 kg m^{-3}
ammonia water $NH_3 \cdot H_2O$	up to pH = 10.0

The correct bath operation depended substantially upon the way it was prepared [16]. The optimum composition of the galvanic bath and deposition parameters were selected on the basis of earlier experiments [18]. The deposition process was carried out at a constant temperature of 30 ± 0.5° C, the bath pH values being 9.9 to 10.2. The cathodic current density ranged from 500 to 1000 Am^{-2}.

The deposition time was chosen so as to obtain a coating about 2 x 10^{-5} m thick. The thickness of the galvanic deposits, as well as the current efficiency of the alloy deposition process were estimated by a gravimetric method. The chemical composition of the alloy was assayed by an atomic absorption method using a Perkin-Elmer M-603 spectrophotometer. The sample was completely dissolved in a mixture of concentrated nitric and hydrochloric acids to be analysed chemically. Alloy steels containing known, similar amounts of iron, nickel, molybdenum and vanadium were used as standards.

The phase composition of the Ni–Mo–V alloys was determined using a Philips X-ray diffractometer with a graphite monochromator and Cu*Kα* radiation.

Surface morphology of the coatings was observed using a Joel scanning microscope with a magnification of 500 x.

Potentiodynamic polarization curves were estimated for four electrolytes with different chemical composition (Table 1), in a three-electrode electrochemical vessel with a silver electrode area 5 x 10^{-4} m^2. The electrode potential was measured in relation to a saturated calomel electrode (SCE). A platinum gauze served as an auxiliary electrode. Measurements were conducted at a temperature of 25 ± 0.5° C. The silver electrode was polarized from a generator via a potentiostat with a linear potential sweep rate of 2 x 10^{-3} V s^{-1}. The dependence of the current upon the potential was monitored with a *x–y* recorder.

Samples coated with the Ni–Mo–V alloy were then used as cathodes in a test H_2O electrolysis cell (Fig. 1). This process was carried out in an electrolyser whose volume was 3 x 10^{-3} m^3. In the central part of the electrolyser, a segment was placed in which the following were fixed: a steel plate coated with a layer of Ni–Mo–V alloy, 2 x 10^{-5} m thick, serving as the cathode; a nickel-plated steel plate, with a coating 5 x 10^{-5} m thick, serving as the anode, and an asbestos diaphragm made of an AT-7 fabric. A 20% aqueous solution of potassium

Table 1. Chemical composition of electrolytes for which the potentiodynamic polarization curves were estimated

Compound	*Concentration* [kg m^{-3}]			
	1	*2*	*3*	*4*
$NiSO_4 \cdot 7H_2O$	62.0	62.0	–	–
$Na_2MoO_4 \cdot 2H_2O$	–	15.3	15.3	–
$VOSO_4 \cdot H_2O$	–	5.0	5.0	–
$KNaC_4H_4O_6 \cdot 4H_2O$	76.0	76.0	76.0	76.0
NaCl	18.0	18.0	18.0	18.0
$NH_3 \cdot H_2O$	pH = 10	pH = 10	pH = 10	pH = 10

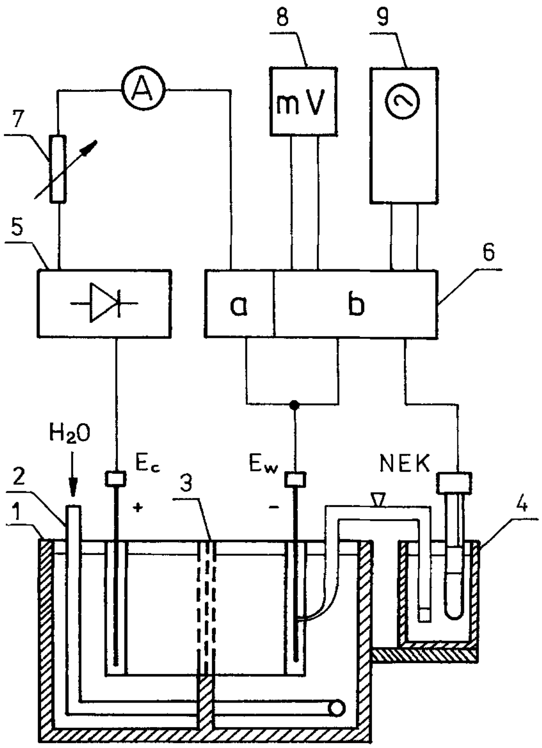

Fig. 1. A scheme of the measurement system used to test cathodes for the electrolysis of water: 1 – electrolyzer; 2 – glass coil; 3 – asbestos diaphragm; 4 – salt-bridge with a Ługgin capillary; 5 – stabilized current source; 6 – automatic control system; 7 – regulated resistor, 8 – photoelectric millivoltmeter; 9 – oscilloscope with a photographic camera.

hydroxide was used as electrolyte; its temperature was kept at 80 ± 1° C using glass coils connected with an ultrathermostat. The electrolyser was fed from a stabilized current source through a specially constructed automatic control system consisting of time relays, a potentiometric potential compensator, and an electronic analog switch. Part (a) of the system controlled the switching on and -off of the water electrolysis process. Part (b) controlled the measuring of changes in time of the hydrogen evolution polarization in the water electrolysis process. The cathode potential was measured (with a photoelectric millivoltmeter with an input resistance of 10^{12} Ω) versus the saturated calomel electrode (SCE) connected with the electrode-edging area through a Ługgin capillary and a salt-bridge. The end of the capillary which was filled with a 20% solution of KOH was placed in a specially moulded cathode aperture. The salt-bridge was filled with a saturated solution of potassium chloride. The hydrogen evolution polarization ΔE was assessed as the difference between the cathode potential value under conditions of the current flow in the electrolysis circuit $E_w(i)$ and the cathode potential after disconnection of the water electrolysis circuit $E_w(0)$:

$$\Delta E = E_w(i) - E_w(0). \qquad (1)$$

The potential value $E_w(i)$ was measured 600 s after switching on the electrolysis process at a current density ranging from 1000 to 5000 $\mathrm{Am^{-2}}$, calculated per geometric area of the cathode. The $E_w(0)$ value was measured 120 s after disconnecting the water electrolysis circuit. At 600 s after switching on the water electrolysis system with an analog switch the estimated cathode potential value $E_w(i)$ was measured with a photoelectric millivoltmeter and potentiometrically compensated to 0. Afterwards the control system released the spot course on the oscilloscope screen and opened the diaphragm of the photographic camera. After 5 s the water electrolysis circuit was disconnected and the oscilloscopic recording of changes in time of the cathode potential $E_w(0)$ started; the latter changes were equivalent to those in the hydrogen evolution polarization ΔE.

3. Results

3.1. *The deposition and characteristics of the Ni–Mo–V alloy coatings*

The chemical composition of the Ni–Mo–V alloy coatings obtained from the tartrate bath altered with the cathodic current density (Fig. 2). The percentage content of molybdenum in the alloy decreased from about 12% to about 5%, whereas the content of vanadium increased from about 0.05% to about 0.3%; at the same time the cathodic current density increased from 500 to 1000 $\mathrm{Am^{-2}}$. The current efficiency for the alloy deposition process also varied with the applied current density (Fig. 2). A distinct maximum of the current efficiency, estimated at ca. 60%, at a current density of 700 $\mathrm{Am^{-2}}$, could be observed. In the case of higher and lower values of the cathodic current density the current efficiency of the process fell to about 15–20%.

Over the whole current density range the deposition of Ni–Mo–V alloy took place under

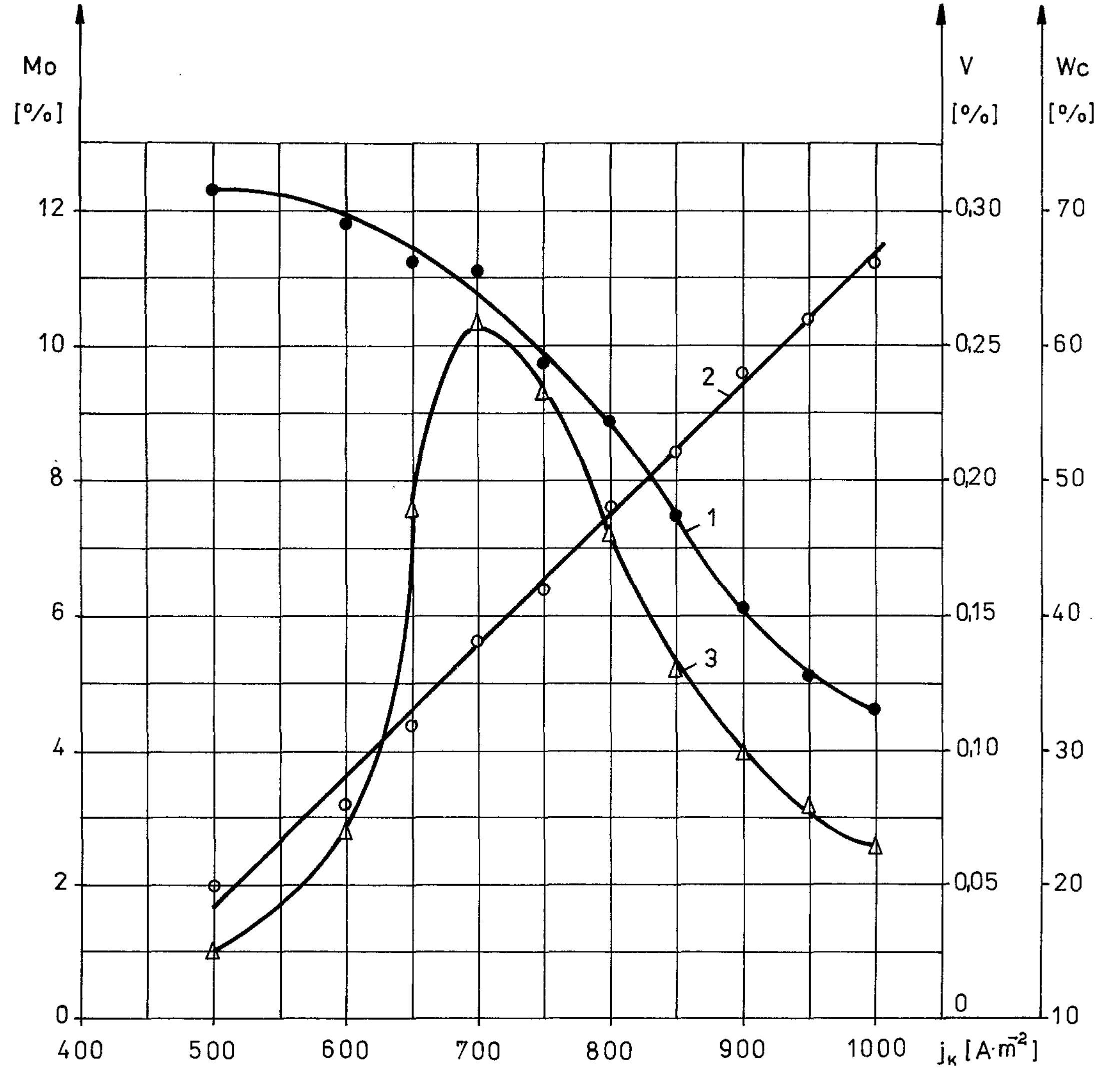

Fig. 2. Dependence of the percentage content of molybdenum and vanadium in the Ni–Mo–V alloy coatings and the current efficiency of the process (W_c) upon the current density.

conditions of hydrogen co-evolution. A great number of gas bubbles were observed on the cathode; they effectively mixed the electrolyte at the electrode-surface. The intensive hydrogen evolution, accompanying an increase in the cathodic current density, may account for the fall in the current efficiency of the process. However, hydrogen co-evolution is probably not the only cause of the low efficiency of the cathodic alloy deposition process.

Deposition of Ni–Mo–V alloys from the complex electrolyte is a very complicated process. In the electrolyte, there coexists various complex ions because both tartrate and ammonia may play the role of ligand [7]. Formation of polyligand complexes cannot be excluded, either. Four depolarizers participate in the cathodic process leading to co-deposition of nickel, molybdenum, vanadium and hydrogen. It is well known that in such circumstances there are changes in the discharge rate of the ions in comparison with their rate of discharge when alone [19].

Potentiodynamic polarization curves throw some light on the course of this complex cathodic process (Fig. 3). Deposition of the Ni–Mo–V alloy starts at quite a negative potential, about – 1.1 V, whereas nickel deposition from a tartrate electrolyte begins at a less negative potential, by about

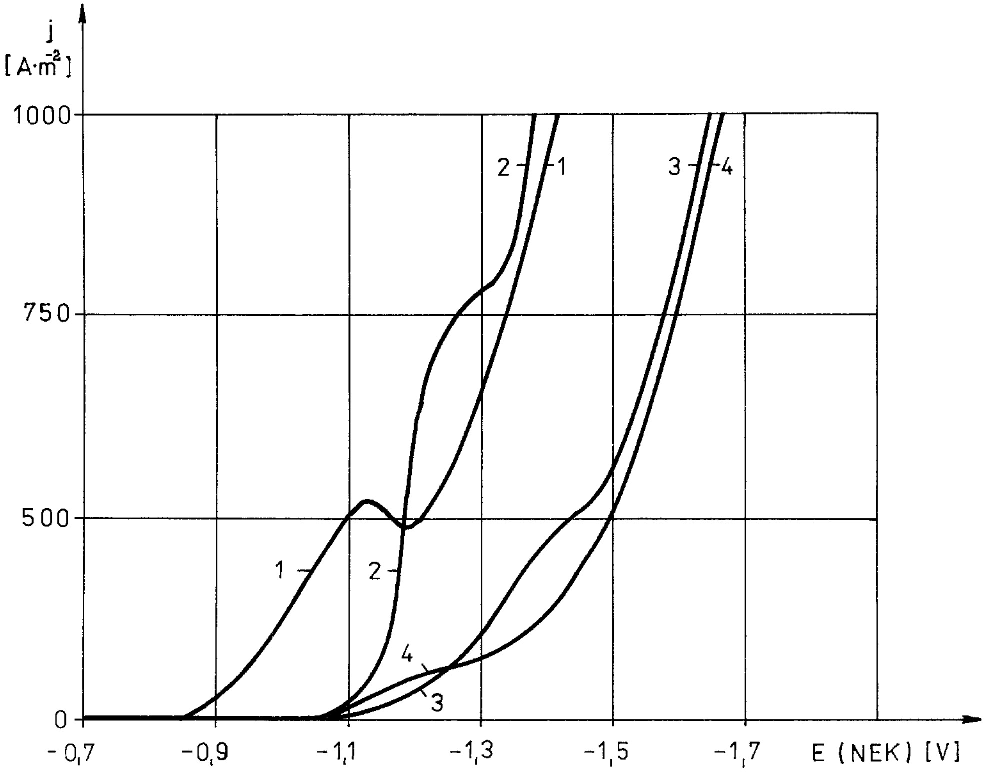

Fig. 3. Potentiodynamic polarization curves obtained for the electrolytes with their compositions presented in Table 1. $v = 0.002\ \mathrm{V\,s^{-1}}$.

— 0.2 V. The polarization curve for alloy deposition is steeper than the polarization curve for nickel deposition; moreover, it is shifted towards more negative potential values. It may be assumed, therefore, that in the alloy deposition process the discharge of complex nickelous ions is connected with overpolarization. The maximum current density for pure nickel deposition occurs in the potential range — 1.10 to — 1.15 V; it corresponds to the limiting current value. A plateau is also visible on the polarization curve for the Ni–Mo–V alloy deposition at potentials of from —1.25 to —1.35 V but only as a point of inflection. It is interesting that this point is found at a current density of 700 to 800 $\mathrm{Am^{-2}}$; therefore, it occurs within the range where the Ni–Mo–V alloy deposition process proceeds at the maximum current efficiency.

Molybdenum and vanadium belong to the group of metals which cannot be deposited electrolytically from aqueous solutions [20]. The polarization curve obtained for the tartrate electrolyte devoid of nickelous salts resembles the polarization curve obtained from an electrolyte without metal salts (Fig. 3). In both cases only hydrogen evolution takes place on the cathode. Thus molybdenum and vanadium are not deposited individually from the tartrate electrolyte. The possibility of co-deposition of these metals with nickel is connected with the occurrence of a considerable depolarization accompanying the process of co-discharge of complex molybdenum and vanadium ions and the formation of Ni–Mo–V alloy on the cathode.

Using the X-ray method, the phase composition was determined. The electrodeposited Ni–Mo–V alloys constitute solid solutions of molybdenum and vanadium in nickel (γ-Ni phase). The interplanar distances, *d*, of this phase increase as the content of molybdenum and vanadium in the alloy rises (Table 2). The electrolytic Ni–Mo–V alloys have a fine-crystalline structure, which is shown by broad peaks on X-ray diffractograms.

The surface morphology of the Ni–Mo–V alloy deposits changes according to the alloy chemical composition and deposition conditions (Fig. 4). Alloy coatings containing more than 9% Mo are

Table 2. Phase composition of Ni–Mo–V

Content of molybdenum and vanadium in alloy (%)		*Measured value* d (nm)	*Value* d (nm) *from ASTM sheets*	I/I_0	*Phase*
Mo	V				
4.64	0.28	0.204	0.203	100	γ-Ni
		0.180	0.176	50	
		0.125	0.124	32	
		0.107	0.106	32	
		0.090	0.0881	8	
6.10	0.24	0.205	0.203	100	γ-Ni
		0.182	0.176	50	
		0.126	0.124	32	
		0.107	0.106	32	
		0.091	0.0881		
8.90	0.19	0.206	0.203	100	γ-Ni
		0.185	0.176	50	
		0.126	0.124	32	
		0.108	0.106	32	
11.16	0.14	0.208	0.203	100	γ-Ni
		0.187	0.176	50	
		0.128	0.124	32	
		0.109	0.106	32	
12.30	0.05	0.209	0.203	100	γ-Ni
		0.188	0.176	50	
		0.129	0.124	32	
		0.110	0.106	32	

light, silver-grey, and are characterized by considerable internal stresses which cause their cracking. Coatings containing 11.16% Mo and 0.14% V, obtained at the cathodic current density of 700 $\mathrm{Am^{-2}}$, have the best developed surface, covered with a network of deep microcracks and domed irregularities. Coatings obtained at higher current densities, containing 4 to 5% Mo and 0.26 to 0.28% V, are darker, powdery in places, with a more uniform surface displaying no cracks.

3.2. *The Ni–Mo–V alloy coatings as the cathode material in the water electrolysis process*

The use of steel cathodes with the Ni–Mo–V alloy coating, 2×10^{-5} m thick, for the water electrolysis results in a decreased hydrogen overvoltage compared with overvoltage values observed on nickel cathodes. The values measured for the hydrogen evolution polarization, ΔE, on the cathodes with Ni–Mo–V coatings ranged from 63 to 82 mV, whereas on the cathodes with nickel coatings the ΔE value amounts to about 300 mV, when the cathodic current density was 2000 $\mathrm{Am^{-2}}$. The ΔE values depend on the chemical composition of the Ni–Mo–V alloy (Fig. 5). The lowest ΔE values, about 64 mV, are found for the deposits obtained within the current density interval of 650 to 800 $\mathrm{Am^{-2}}$; they contain 9 to 11% Mo and 0.1 to 0.2% V. On the basis of data showing the dependence of ΔE upon the composition of molybdenum and vanadium in the alloy it might be assumed that there exists an optimum value range for this ratio. However, having considered the phase composition of the Ni–Mo–V alloys and the morphology of deposit surfaces, it can be concluded that the degree of cathode surface development has a considerable effect on the hydrogen evolution polarization value.

The crystal lattice of nickel, molybdenum and vanadium are changed causing an increase in the number of crystal defects and altering the electronic structure of the metallic matrix, especially the number of electrons in the d-band. In this connection the Ni–Mo–V alloy may also have a catalytic effect on the hydrogen evolution process.

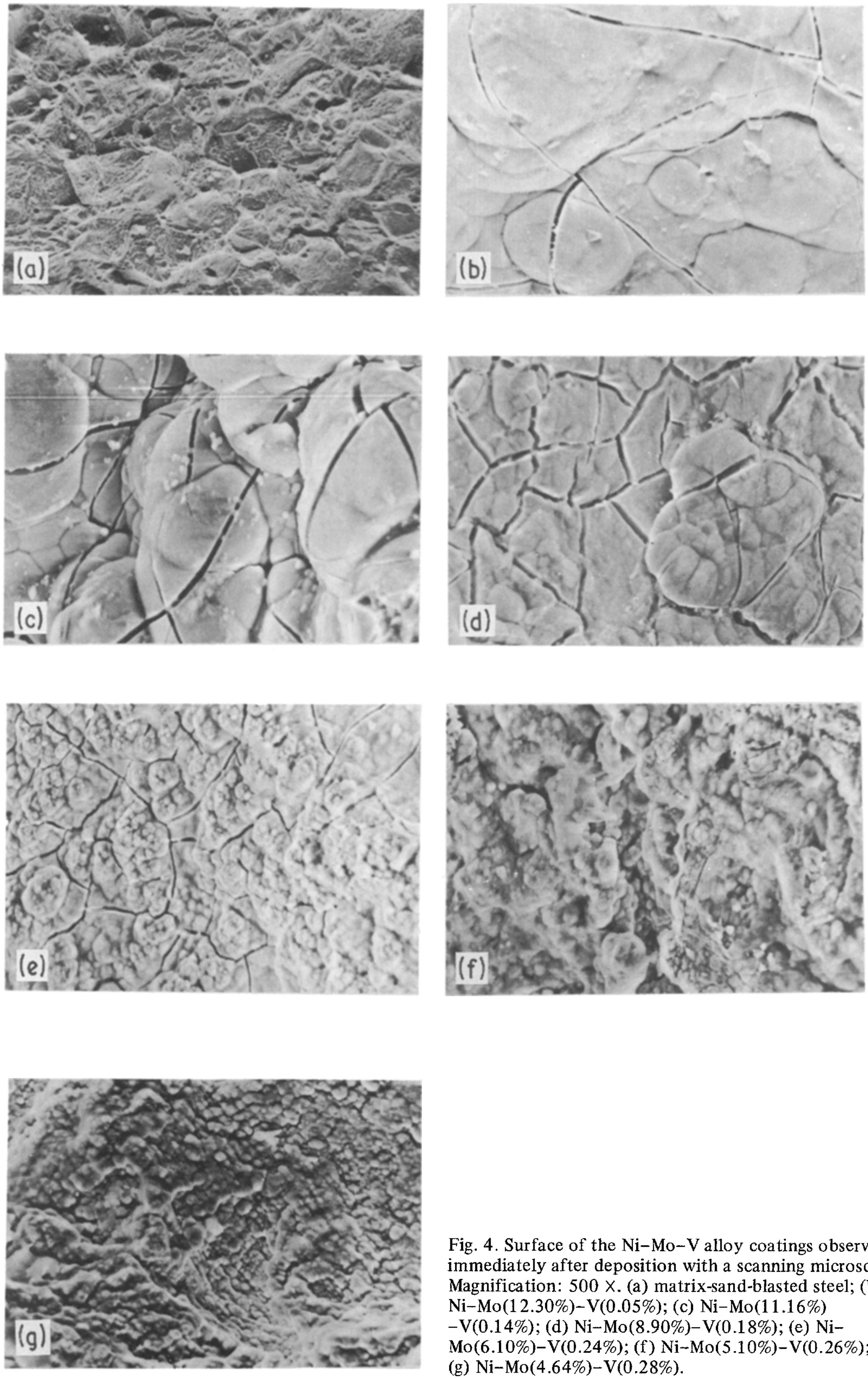

Fig. 4. Surface of the Ni–Mo–V alloy coatings observed immediately after deposition with a scanning microscope. Magnification: 500 ×. (a) matrix-sand-blasted steel; (b) Ni–Mo(12.30%)–V(0.05%); (c) Ni–Mo(11.16%)–V(0.14%); (d) Ni–Mo(8.90%)–V(0.18%); (e) Ni–Mo(6.10%)–V(0.24%); (f) Ni–Mo(5.10%)–V(0.26%); (g) Ni–Mo(4.64%)–V(0.28%).

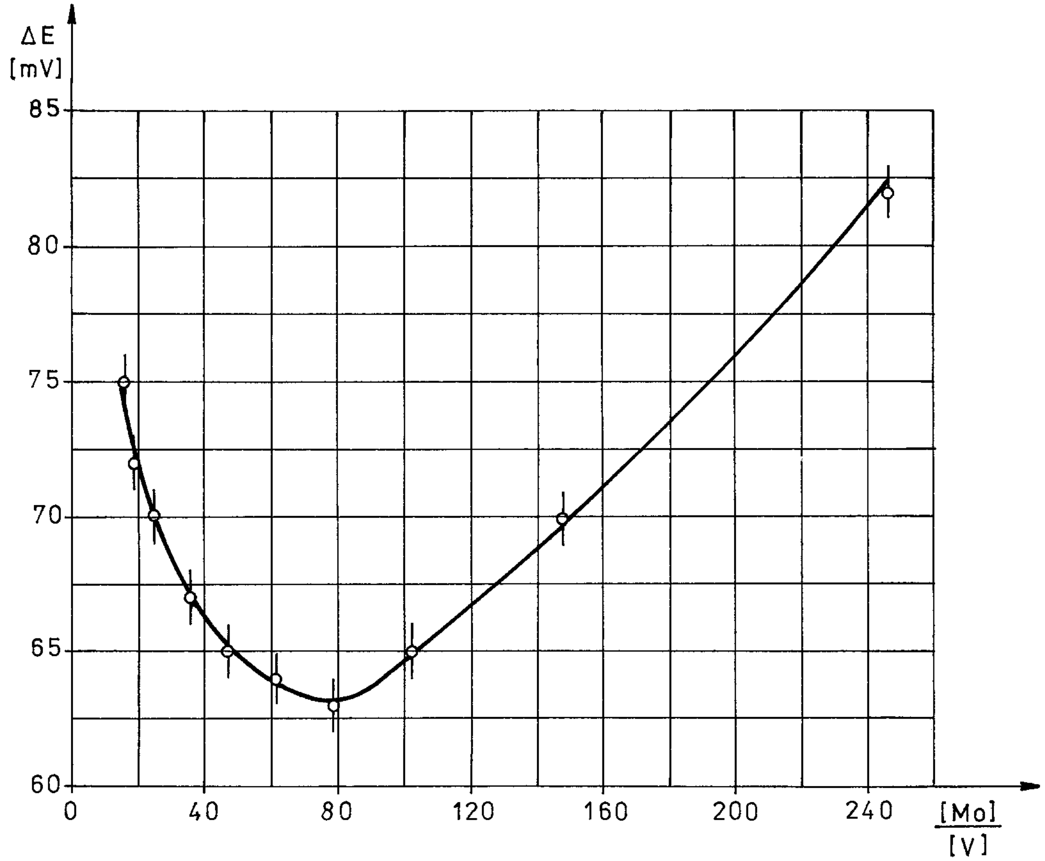

Fig. 5. Dependence of the hydrogen evolution polarization Δ*E* in the water electrolysis process at the cathodic current density, 2000 Am^{-2}, upon the content ratio of molybdenum and vanadium in the Ni–Mo–V alloy deposits.

The changes in the hydrogen evolution polarization, Δ*E*, with time after switching off the electrolysis process (Fig. 6) become flatter and flatter during the time 0 to 60 s, for the electrodes characterized by the lowest polarization of hydrogen evolution. This phenomenon may occur because hydrogen desorption from the surface is impeded; this is evidence for a strong bond between atomic hydrogen and the electrode surface. The percentage content of vanadium in the Ni–Mo–V alloys is low; however, its presence has a considerable effect on the Δ*E* values. On electrodes coated with a Ni–Mo alloy, the values of the hydrogen evolution polarization were about 40 to 60 mV higher than on the electrodes coated with the Ni–Mo–V alloy [5].

The values of the hydrogen evolution polarization also depend upon the current density used in the water electrolysis process (Table 3). A rise in the current density from 1000 to 5000 Am^{-2} causes an increase by about 40 mV in the hydrogen evolution polarization. It is possible, therefore, to intensify the water electrolysis process by using cathodes coated with the Ni–Mo–V alloy deposits.

4. Conclusions

The effects of depolarization and overpolarization observed in the process of codischarge of ions, permit the deposition of ternary nickel–molybdenum–vanadium alloys which constitute a supersaturated solid solution of molybdenum and vanadium in nickel. Conducting the deposition process at a cathodic current density of 700 Am^{-2}, alloy coatings containing 88.70% Ni, 11.16% Mo and 0.14% V may be deposited at a current efficiency of about 60%. These coatings are compact and adhere well to the sandblasted steel substrate. They have a well-developed surface covered with a network of microcracks.

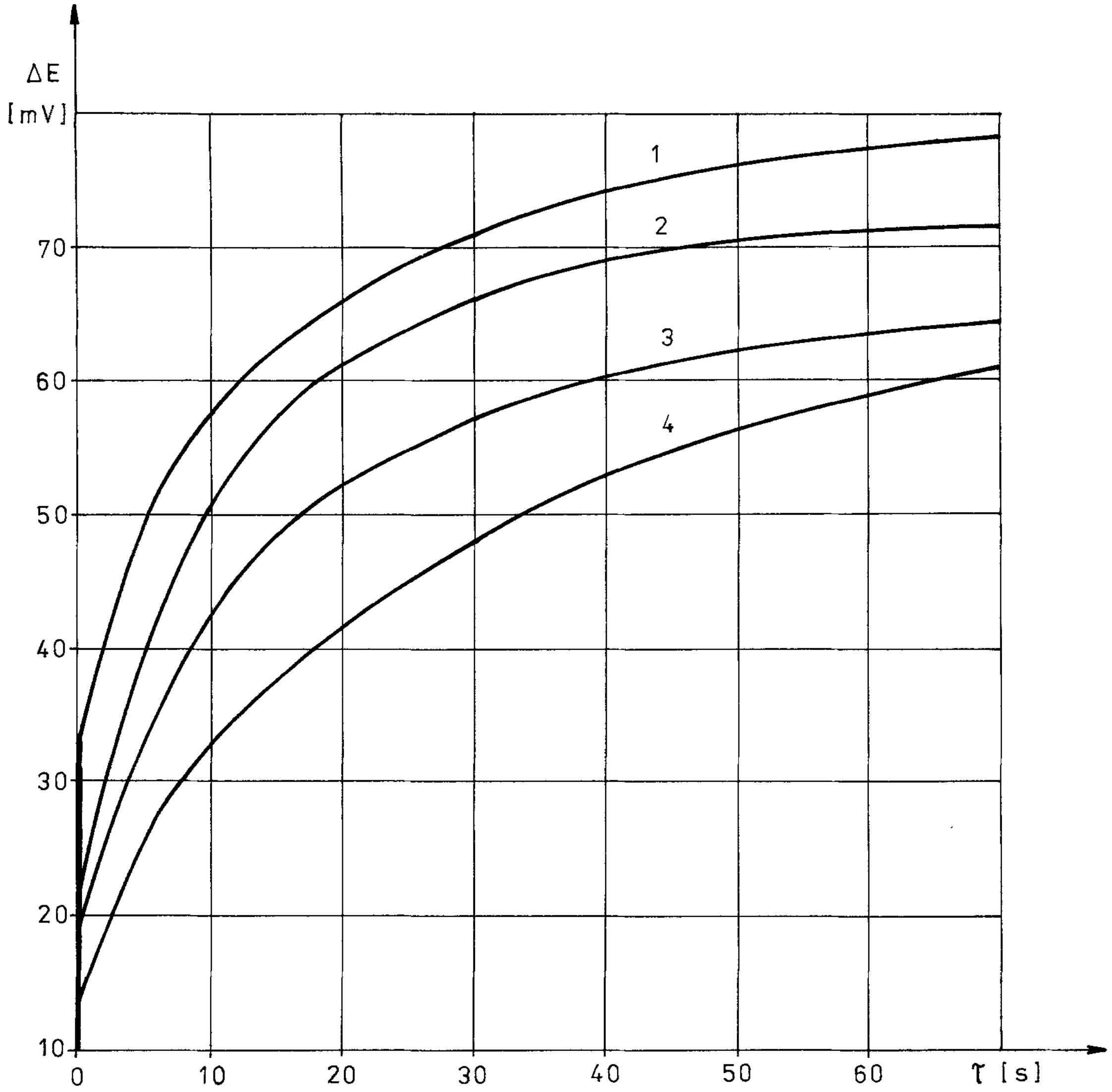

Fig. 6. Dependence of the hydrogen evolution polarization E upon the time after switching off the water electrolysis process (1) Ni–Mo(12.30%)–V(0.05%); (2) Ni–Mo(5.10%)–V(0.26%); (3) Ni–Mo(8.90%)–V(0.19%); (4) Ni–Mo(11.16%)–V(0.14%).

Table 3. Change of the hydrogen evolution polarization ΔE (mV) *with increase in the current density used in the water electrolysis process,* I

Type of the cathodic coating	I (A m^{-2})				
	1000	2000	3000	4000	5000
Ni	262	300	315	330	340
Ni–Mo(12.30)–V(0.05)	59	82	107	112	117
Ni–Mo(11.16)–V(0.14)	50	63	73	83	93
Ni–Mo(8.90)–V(0.19)	53	65	75	87	98
Ni–Mo(5.10)–V(0.26)	57	72	79	90	105

On the cathodes with Ni–Mo–V alloy coatings electroplated from the alkaline tartrate bath, the hydrogen evolution polarization is low and its value amounts to about 70 mV.

The ternary Ni–Mo–V alloy coatings obtained from alkaline tartrate bath have better mechanical properties than those obtained from the Watts' bath.

Sandblasted steel cathodes electroplated with the active Ni–Mo–V alloys can be used for water electrolysis and other processes where reduction of hydrogen overpotential is important.

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