SUMMARY

A kinetic study of the dehydration of propan-2-ol on kyanite suggests that catalysis is effected by the free $3d_{yz}$, $3d_{xz}$, and $3d_{xy}$ orbitals of aluminium.

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REFLECTANCE AND STRUCTURE OF THIN LAYERS OF ELECTRODEPOSITED NICKEL

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Study of the physicochemical properties of thin layers of an electrodeposit on different substrates has become very important for several new fields of technology. The present paper reports an investigation on the effect of the nature of the metal substrate and the chemical condition and relief of the surface on the reflecting power of nickel deposited in thin layers.

EXPERIMENTAL

The reflectance of the electrodeposit was determined during electrolysis in an apparatus developed in the Institute of Physical Chemistry of the USSR Academy of Sciences[1]. The instrument enables simultaneous recordings to be made of the variation in reflectance from the magnitude of the photocurrent and in the electrode potential. The electrolyte used contained per litre 300 g $NiSO_4.7H_2O$ + 60 g $NiCl_2.6H_2O$ + 38 g H_3BO_3, and had pH 4; the cathodic current density D_c was 40 mA cm^{-2} and the temperature 40°. The effect of the nature of the metal substrate on the reflectance of the deposits was studied on polished copper, nickel, and steel specimens.

The experimental results are plotted in Fig. 1 as the photocurrent (in μA) against the thickness of the deposit (μm). The initial horizontal plateaux correspond to the reflectance of the initial surface of the specimens, before the current has been switched on. It is seen from Fig. 1 that, when this occurs, there is a brief and slight drop in reflectance, which then rises again, this change occupying about 3 s. This is followed with further deposition of nickel by a smooth fall in reflecting power. It is seen that, with the same mechanical treatment of the electrode surface, the nature of the metal (nickel, iron, or copper) has no significant effect on the reflectance of the electrodeposit. The slight differences observed at the instant the current is switched on may, perhaps, be associated with the chemical state of the electrode surface.

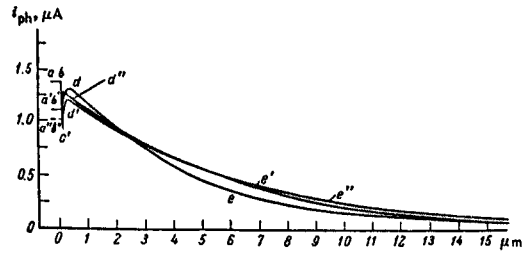


Fig.1. Effect of nature of metal substrate on reflectance of nickel deposit during electrolysis: *abcde*) on polished copper; *a'b'c'd'e'*) on nickel; *a"b"c"d"e"*) on steel; *ab*) reflectance of specimen before current switched on; *bcde*) during electrolysis.

Fig. 2 illustrates the effect of the surface state of the electrode on the reflectance of the nickel deposit during electrolysis. Nickel deposition was carried out both on the active surface of a nickel specimen (curve *abcde*) and on the surface of a nickel electrode of different degrees of passivation (curves *a'b'c'd'e'*–*a'''b'''c'''d'''e'''*). It is seen from the curves that the reflecting power of the deposits deteriorates sharply with increasing degree of passivation of the nickel electrode surface. When nickel is deposited on passive specimens, the deposit cracks and partial exfoliation from the substrate is observed. At the instant of exfoliation the reflectance changes sharply, as can be seen from the curves. Similar results are obtained for the deposition of nickel on passivated iron and copper specimens. Comparison of the curves in Figs. 1 and 2 shows that with these metals the chemical state of the metal surface has a greater influence than has the nature of the metal substrate on the change in reflectance of the deposit. The deterioration in the reflecting power of

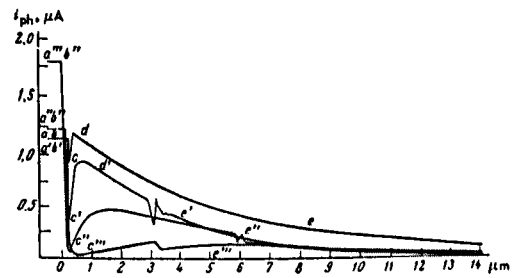


Fig.2. Effect of state of electrode surface on reflectance of nickel deposit during electrolysis: *abcde*) on active electrode surface; and on surface passivated in CrO_3 solution (250 g $litre^{-1}$) for (min): *a'b'c'd'e'*) 20; *a"b"c"d"e"*) 50; *a'''b'''c'''d'''e'''*) 60; *ab*) reflectance of specimen before current switched on; *bcde*) during electrolysis.

specimens at the start of electrolysis is most probably due to the non-uniform distribution of current over the electrode surface and the deposition of metal predominantly on active portions of the electrode [2]. These experiments show that the high reflectance of thin layers of the deposits is maintained only with a thoroughly cleaned active electrode surface.

The reflectance of thin layers of deposit is substantially dependent on the relief of the substrate surface. The curves in Fig. 3 show the variation in reflectance and polarisation during electrolysis for initial electrode surfaces differing in relief. Curve *I* relates to the deposition of nickel from an electrolyte containing no additives on a well polished electrode surface, and curve *II* to its deposition from a solution containing thiourea (0.3 g litre^{-1}) on a rough electrode surface. The rough substrate was a nickel deposit obtained from an electrolyte containing no surface-active addition, its structure being shown in Fig. 4*a*1. It is seen from curve *I* in Fig. 3 that the deposition of nickel is accompanied by a gradual increase in roughness of the electrode surface, as a result of which the reflectance falls. This decrease ceases when the deposit is 7–8 μm thick, owing to the formation of crystals of definite size corresponding to the conditions of electrolysis.

When nickel is deposited on a rough electrode surface in the presence of levelling additives (curve *II*), the reflecting power practically reaches its maximum value at a deposit thickness of 1.5 μm, and does not change further during electrolysis.

It is seen from the accompanying curves that the levelling of a rough surface requires the deposition of a far smaller quantity of metal than is needed for the formation of a rough deposit of the same structure on a smooth surface. The reason for this difference is that, in order to obtain a bright surface in the presence of levelling additives in the former case, it is mainly sufficient to fill with metal only the deep portions of the electrode, whereas in the latter case several layers of crystals must be obtained, combining to a deposit thickness of around 7–8 μm.

The variation with thickness in the structure of nickel electrodeposits obtained from an electrolyte in the absence and in the presence of added thiourea (0.3 g litre^{-1}) is illustrated in Figs. 4*a* and 4*b* respectively. Comparison of

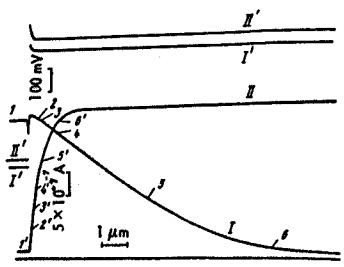
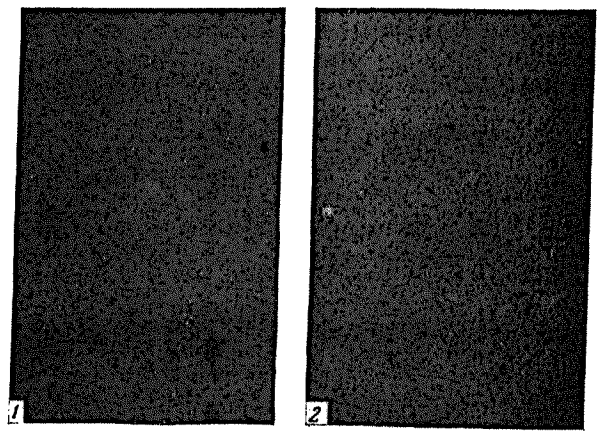
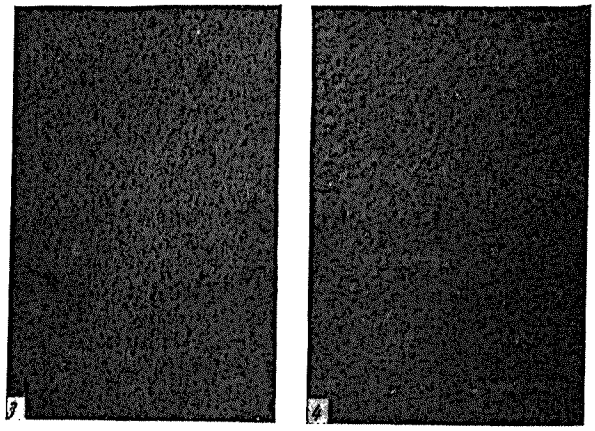


Fig. 3. Variation in reflectance (I, II) and in polarisation (I′, II′) of electrode during electrolysis for two surfaces differing in relief, nickel being deposited from: I) electrolyte containing no additive, on a polished surface; II) from a solution containing thiourea (0.3 g litre^{-1}), on a rough surface.





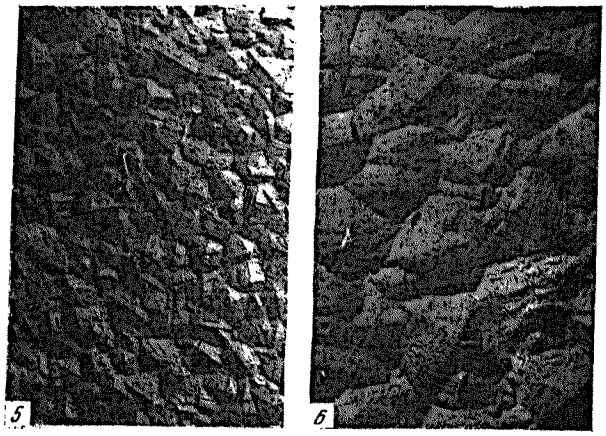


Fig. 4*a*. Variation in structure (magnification 11 200 ×), of nickel electrodeposited from electrolyte containing no additive, with thickness (μm) of deposit: 1) initial specimen; 2) 0.2; 3) 0.3; 4) 1; 5) 5; 6) 10.

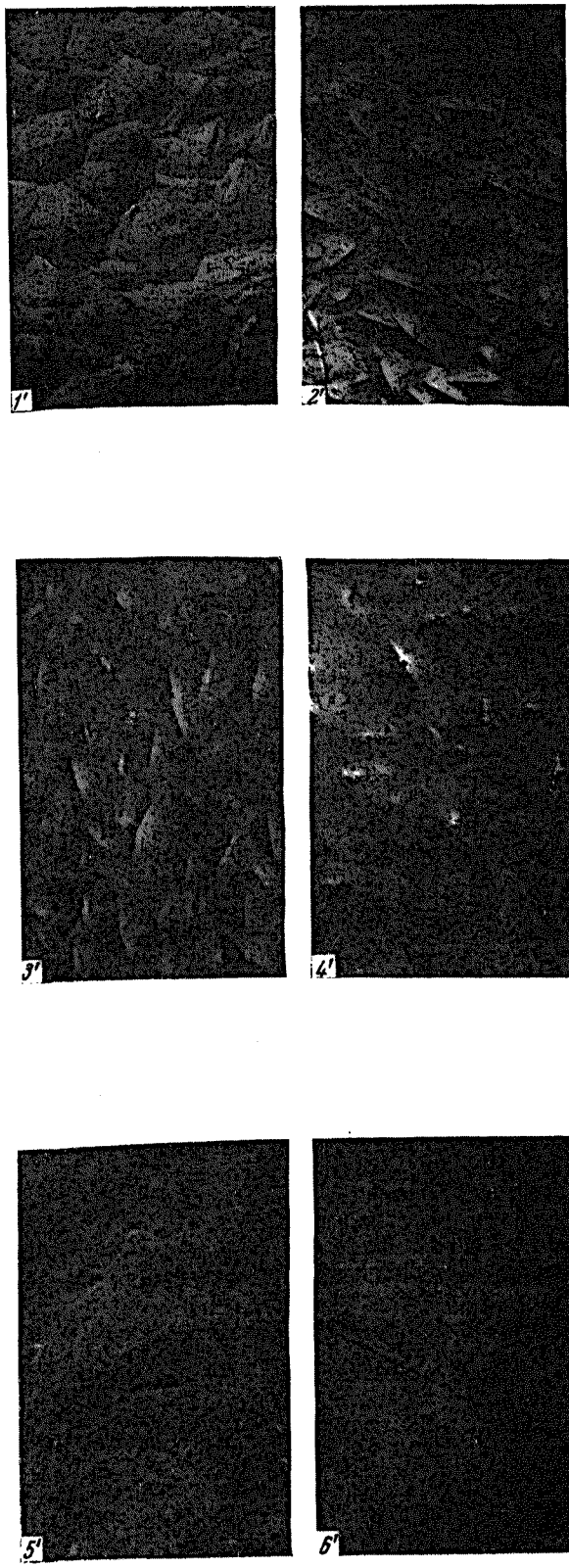


Fig. 4*b*. Variation in structure (magnification 5600 ×), of nickel electrodeposited from electrolyte containing thiourea (0.3 g litre^{-1}), with thickness (μm) of deposit: 1') initial specimen; 2') 0.06; 3') 0.13; 4') 0.2; 5') 0.3; 6') 1.

the reflectance (Fig. 3, curve *I*) with the structure of an electrodeposit (Fig. 4*a*) shows that the decrease in photocurrent is associated with a coarsening of the nickel crystals during electrolysis and an increase in roughness of the electrode surface. When the reflectance increases (Fig. 3, curve *II*), the electrode surface is levelled out as the nickel is deposited, as a result of the deposition of metal predominantly in the depressed portions of the electrode (Fig. 4*b*). Peaks — projecting faces of the original surface — remain only to thicknesses of around 0.30 μm, and these faces become unnoticeable at deposit thicknesses exceeding 1 μm, after which no further change in the structure of the deposit takes place.

The degree of roughness and the true surface of the electrode can be roughly estimated from the data given here. For this purpose a curve is recorded rapidly, and with different sensitivities to the photocurrent, for the variation with thickness in the reflectance of a nickel deposit obtained from an electrolyte containing thiourea (0.3 g litre^{-1}) (Fig. 5).

The curve in Fig. 5 is seen to comprise two sections differing in slope. Comparison of the photocurrent–time curve with the structure of the electrodeposit shows that the first section corresponds to deposition of metal mainly at depressed sites, and the second section to completion of smoothing and the deposition of metal on the whole electrode surface. The end of the first section corresponds to a mean thickness of the deposit of 0.275 μm (Fig. 4*b*, *3* and *4*). During this time the volume of nickel deposited to level off unit surface of the electrode is 2.75×10^{-5} cm^3. This value has been obtained from the formula $V_1 = itk$, where $k = M/2dE$, in which M is the molecular mass, d the density of the metal, and F Faraday's constant.

If the crystals are assumed to be in the form of regular pyramids, the depth h can be approximately estimated as

$$h = \frac{3V_1}{2S_g} = \frac{3}{2}\,\frac{2.75 \times 10^{-5}\ \text{cm}^3}{1\ \text{cm}^2} = 4 \times 10^{-5}\ \text{cm} = 0.4\ \mu\text{m},$$

where V_1 is the volume of metal required to fill only the depressed portions, and S_g = 1 cm^2 is the geometrical surface of the electrode. In the present case the roughness is 0.4 μm, which is the height of a pyramid the side of whose base is l = 0.8 μm, the value of l being determined statistically from electronmicrograms on the hypothesis that the bases of the pyramids are of constant area.

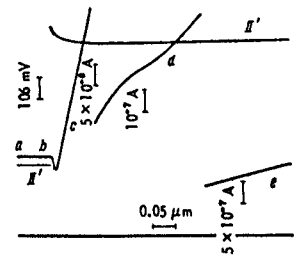


Fig. 5. Variation in reflectance and polarisation of nickel deposit obtained from electrolyte containing thiourea (0.3 g litre^{-1}): *ab*) before current switched on; *bcde*) during electrolysis.

These results make it possible to assess how many times the true surface of the original specimen exceeds the geometrical surface. The ratio of true to geometrical surfaces will be numerically equal to the ratio of the apothems of the pyramid A and of the base a, where $A = (a^2 + h^2)^{\frac{1}{2}}$, h being the height of the pyramid. In the case of a four-sided pyramid with $l = 0.8\ \mu m$ and $h = 0.4\ \mu m$, we have

$$\frac{S_{tr}}{S_g} = \frac{\sqrt{a^2+h^2}}{a} = \frac{\sqrt{\left(\frac{l}{2}\right)^2+h^2}}{\frac{l}{2}} = \frac{\sqrt{0.4^2+0.4^2}}{0.4} = 1.41.$$

The calculations show that the true surface of a nickel deposit obtained from the standard electrolyte with $D_c = 40$ mA cm^{-2} at 40° exceeds the geometrical surface by a factor of 1.41†.

The method of measuring the time variation of the reflectance of the deposit makes it possible also to estimate the smoothing power (S.P.) of surface-active additions. Quantitative assessment of the percentage levelling power is usefully based on the relationship S.P. = $100V_1/V_2$, where V_1 is the volume of metal necessary to fill only the depressed portions (in the present case $V_1 = 2.75 \times 10^{-5} \times$ $\times$ cm^3) and V_2 is the quantity of metal actually electrodeposited before maximum reflectance, defined on the basis of photocurrent–time curves (Fig. 3, curve *II*), is reached. It is seen from the curve that maximum reflectance of the specimen is achieved at a thickness of 1.5 μm, so that the volume of metal deposited is $V_2 = 1.50 \times 10^{-4} \times$ $\times$ cm^3. From the above relationship we obtain S.P. = 18%. The use of photocurrent–time curves to estimate the levelling power of an electrolyte has the advantage that separate experiments are not required, measurements being made at the same time as metal is deposited under the actual conditions of electrolysis.

A conclusion of practical value can be drawn from the above results: bright nickel deposits having good mechanical properties are obtained by depositing on ordinary electrodeposited nickel, which is quite elastic, a thin layer (1.5–2 μm) of bright nickel. The first layer ensures good mechanical and corrosion properties, and the second makes the coating bright without further mechanical treatment.

The electronmicrographs were obtained in the laboratory of V. M. Luk'yanovich by Z. E. Shishenina, for which the authors are grateful.

SUMMARY

1. The nature of the metal forming the substrate (copper, iron, or nickel) has less influence on the reflectance of a nickel electrodeposit then has the chemical condition of the surface.
2. The reflectance of nickel deposits is determined mainly by the relief of the electrode surface.
3. Curves of reflectance plotted against thickness of coating can be used to estimate the levelling power of additives and the roughness and true surface of the electrode.

† If the calculation is made for the two extreme cases — a cone and a three-sided pyramid — the difference in the ratio of the areas will be 10%; in the case of a hemisphere the discrepancy is 40% ($S_{tr}/S_g = 2$).

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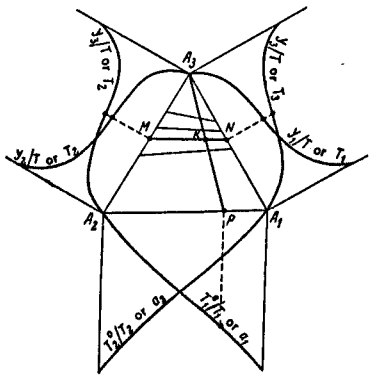
CALCULATION OF CONSTANT-PRESSURE LIQUID–VAPOUR EQUILIBRIUM IN A TERNARY SYSTEM HAVING TWO COMPONENTS WHICH FORM NEARLY IDEAL BINARY SOLUTIONS

M. P. Susarev and A. N. Gorbunov

A method has been proposed previously[1] for calculating the isothermal equilibrium in a ternary system from data for binary systems one of which comprises components of similar chemical character[1]. For practical distillation and fractionation processes, however, constant-pressure and rather than constant-temperature data are of greater importance. The present paper attempts to extend the principles of the proposed method to constant-pressure conditions. It also suggests a modified calculation of isothermal equilibrium, based on the use as initial data of the excess chemical potentials or activity coefficients of the components of binary solutions.



The assumptions underlying the proposed method for calculating constant-pressure equilibrium and the method which has been used to calculate constant-temperature equilibrium are analogous: (1) the isolines $T_3 \equiv Ty_3$ (where T is the absolute boiling point of the solution, and y_3 the mole fraction in the vapour of the "aspective" component A_3, which differs in chemical nature from the mutually related components A_1 and A_2) are straight lines