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Metallic and other inorganic coatings — Simultaneous thickness and electrode potential determination of individual layers in multilayer nickel deposits (STEP test)

Revêtements métalliques et autres revêtements inorganiques — Détermination simultanée de l'épaisseur et du potentiel d'électrode de couches individuelles dans des dépôts de nickel multicouches (essai STEP)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by the European Committee for Standardization (CEN) (as EN 16866:2017) and was adopted, without modification, by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The abbreviated term “STEP” represents “Simultaneous Thickness and Electrode Potential determination”.

The STEP test can be used to measure, in one single operating step, the parameters (thickness of the individual nickel layers and the potential differences among them) relevant for the course of corrosion in a multilayer nickel system. Provided suitable instruments are applied, it can also be used to document them.

The test is a modification of the well-known coulometric method for the measurement of the coating thickness. This method takes advantage of the fact that, following the anodic dissolution of a nickel coating, a potential jump takes place of which the magnitude can be measured against a reference electrode.

Although, nowadays, the STEP test has been incorporated into a number of company standards, particularly in the automobile industry, there are currently no uniform and generally acknowledged potential difference values available. At present, values between 80 mV and 150 mV are assumed for double nickel layers, with the semi-bright nickel layer always being nobler than the bright one.

Likewise, no obligatory numerical values are available, currently, regarding the potential difference between bright nickel layers and existing special nickel layers (e.g. in the case of micro-porous chromium plating). According to the current practical experience, the potential difference is larger than approximately 20 mV, with the bright nickel layer always having to be less noble than the special nickel layer.

Metallic and other inorganic coatings — Simultaneous thickness and electrode potential determination of individual layers in multilayer nickel deposits (STEP test)

1 Scope

This document specifies a method for measuring the thickness of the individual nickel layers in electroplated multilayer nickel coatings and measuring the potential differences between the individual nickel layers in electroplated multilayer nickel coatings.

The measurement of coatings or layer systems other than electroplated multilayer nickel coatings is outside the scope of this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2177, *Metallic coatings — Measurement of coating thickness — Coulometric method by anodic dissolution*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

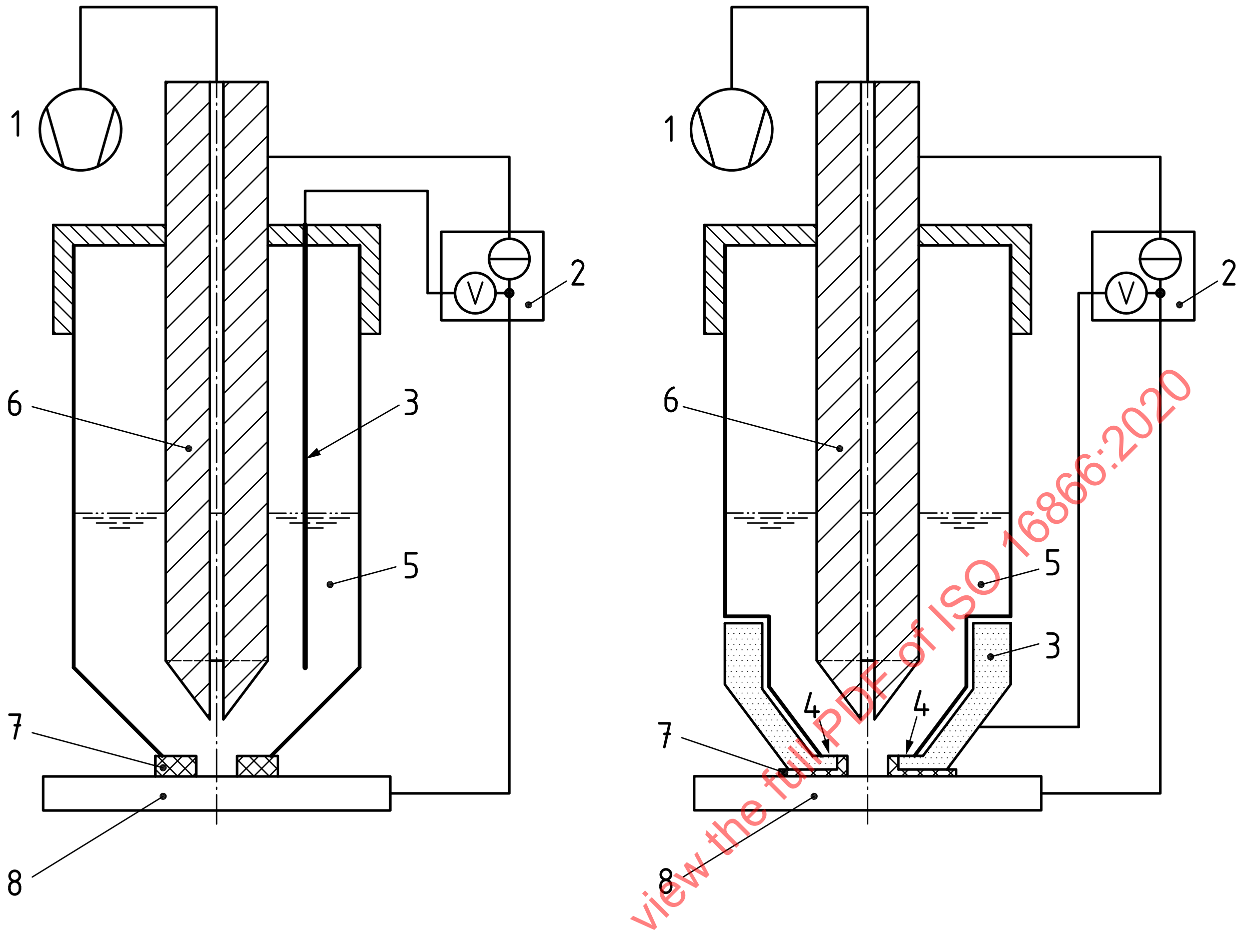
4 Test equipment

4.1 Construction of the measuring cell

Figure 1 shows two examples of the typical schematic construction of a measuring cell used for the simultaneous determination of layer thicknesses and potential differences in multilayer nickel systems. The cells differ with regard to the implementation of the reference electrode. In Figure 1 a), the reference electrode is a silver wire coated with silver chloride and positioned at the edge of the cell; in Figure 1 b), it is a silver ring coated with silver chloride and positioned at the bottom of the cell. With regard to measurement uncertainty, both variants provide the same result for the measurement of the potential difference and (following calibration) the measurement of the layer thickness, independent of the concrete implementation of the reference electrode.

NOTE 1 The silver ring used as the reference electrode in Figure 1 b) is of advantage insofar as the adjustment of the silver wire, which would otherwise be required, becomes unnecessary, leading to results that are more exact and more reproducible.

NOTE 2 The circulated volume of electrolyte solution is typically around 0,1 ml per s.



a) Measuring cell with silver wire, coated with AgCl, used as the reference electrode

b) Measuring cell with silver ring, coated with AgCl in the electrolyte-wetted area, used as the reference electrode

Key

1 pump
2 measuring instrument (with constant-current source and voltmeter)
3 reference electrode
4 electrode surface wetted with electrolyte
5 dissolving electrolyte
6 counter electrode (cathode)
7 gasket
8 working electrode (anode, measurement object with nickel layer system)

Figure 1 — Typical schematic constructions of the measuring cell

4.2 Composition of the test solution

Nickel(II)-chloride hexahydrate ($NiCl_2 \cdot 6\ H_2O$)	300 g/l
Sodium chloride (NaCl)	50 g/l
Boric acid (H_3BO_3)	25 g/l
pH value	3,0

Water of grade 3 in accordance with ISO 3696.

The pH value should be complied with as closely as possible. If required, it is adjusted by means of diluted hydrochloric acid or sodium hydroxide solution.

5 Requirements

The geometry of the parts to be tested shall be such that the measuring cell can be attached to the surface in a liquid-tight way, at the respective points to be measured.

Prior to this, the surface to be measured shall be appropriately de-chromed and activated (e.g. in a 1:1 dilution of chemically pure, concentrated hydrochloric acid). When selecting the de-chroming and activating procedures, it shall be ensured that the nickel coating is not visibly damaged by these procedures.

6 Sampling

Sampling from the ongoing production of parts should be performed in accordance with ISO 2859-1 and ISO 2859-2. The tolerable margin of error is specified by the client.

7 Factors influencing measurement accuracy

7.1 Electrolyte

Each measurement shall be carried out using a fresh electrolyte. Used electrolytes can result in falsified measurement results.

7.2 Conditioning

New reference electrodes or ones which have not been in use for an extended period of time shall be conditioned (creation of a silver chloride layer at the electrode surface) prior to use. The lack of or inadequate conditioning results in falsified or atypical courses of measurement that cannot be correctly interpreted. Any conditioning and potentially required cleaning are carried out in accordance with the instrument manufacturer's information.

NOTE The conditioning quality is checked on the basis of comparative measurements using reference standards of known potential differences and layer thicknesses.

7.3 Ni deposits

As a result of repeated measurements, Ni is gradually deposited on the surface of the cathode. From a certain thickness onwards, these Ni deposits can become dissolved from the cathode and move around in the electrolyte in the form of “flocs”, leading to very noisy measurement curves and a faulty evaluation. It is, therefore, necessary to remove any Ni deposits early enough from the surface of the cathode (this is done mechanically or, in the case of persistent deposits, chemically).

7.4 Surface cleanliness

In order to achieve a uniform dissolution process across the whole measurement area, the surface of the test specimen shall be free from contaminations and oxide layers (see also Clause 5).

7.5 Measurement area and contact pressure

Depending on the size and shape of the test specimen, different gaskets defining the measurement area can be selected. The measurement area influences the measurement uncertainty. Usually larger measurement areas result in smaller uncertainties.

The contact pressure exerted on the test specimen by the measuring cell shall be sufficiently high to enable a leakage-free sealing between the cell and the sample surface. Too high a pressure, on the other hand, can lead to a reduction of the active dissolution surface (increase of the sealing surface with regard to a calibration carried out beforehand), thereby causing measurement errors. When placing the measuring cell, the relevant manufacturer's provisions shall be met.

7.6 Electrical contact

Good contacts shall be ensured at the electrical connections of the installation. It is particularly a lack of cleanliness or the occurrence of corrosion at the contact surfaces that leads to increased contact resistances, which, in turn, can result in very noisy courses of measurement.

7.7 Complete dissolution

For a correct thickness measurement, the last Ni layer shall have been completely dissolved from the basis material once the measurement is complete. This shall be checked visually following the removal of the measuring cell (with optical means, if appropriate). If there are still any Ni residues detectable, meaning that the dissolution process is incomplete, the measurement shall be rejected.

8 Procedure

8.1 General

Nickel can be deposited from both plain baths (in the form of dull or semi-bright layers) and from additive-containing baths with different properties regarding brightness, levelling, ductility, hardness, internal stress, porosity, abrasion resistance, etc. The additives change the structure of the precipitation; they are partly incorporated as such and partly in the form of their decomposition products.

Structure and composition manifest themselves by a certain activity of the nickel precipitation that can be determined on the basis of stationary electrochemical measurements.

In the STEP test, the layer thicknesses are determined by measuring the dissolution time. The layer thicknesses shall be calculated in accordance with ISO 2177. The dissolution potentials of the different types of nickel coating are obtained by measuring the voltage between the reference electrode and the anode (test specimen).

NOTE 1 In both measurements, a uniform dissolution rate is achieved by a pre-defined constant dissolution current.

NOTE 2 With most commercially available instruments, the thickness of the dissolved layer is automatically calculated from the dissolution time, and the measured potential curves are represented as a function of the layer thickness (µm) in order to facilitate the evaluation.

8.2 Measurement

The work piece, which has previously been de-chromed and activated by the appropriate means (see Clause 5, 7.2 and 7.4), is positioned in accordance with Figure 1 a) or Figure 1 b) below the measuring cell and pressed against the gasket from below, in a liquid-tight manner (consider 7.5). Following the filling of the measuring cell with the test solution (see 4.2) and, if required, the adjustment of the conditioned reference electrode, the measurement is performed in accordance with the instrument manufacturer's provisions.

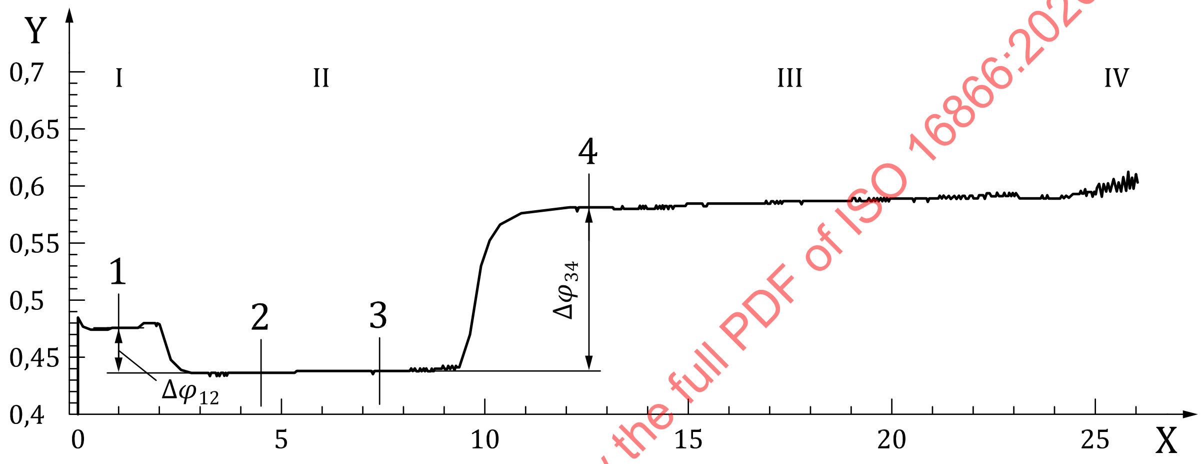
The number and position of the measurements should be chosen as agreed between the supplier and the customer.

The instrument's measurement accuracy shall be checked in regular intervals by means of a calibration sample. The manufacturer's instruction should be considered.

The calibration sample provides both the calibration values for the individual layer thicknesses of a multilayer nickel system and the potential difference between the individual nickel layers. For control purposes, the total thickness of all nickel layers is stated (measured, e.g. by applying the X-ray spectrometric method in accordance with ISO 3497).

8.3 Evaluation

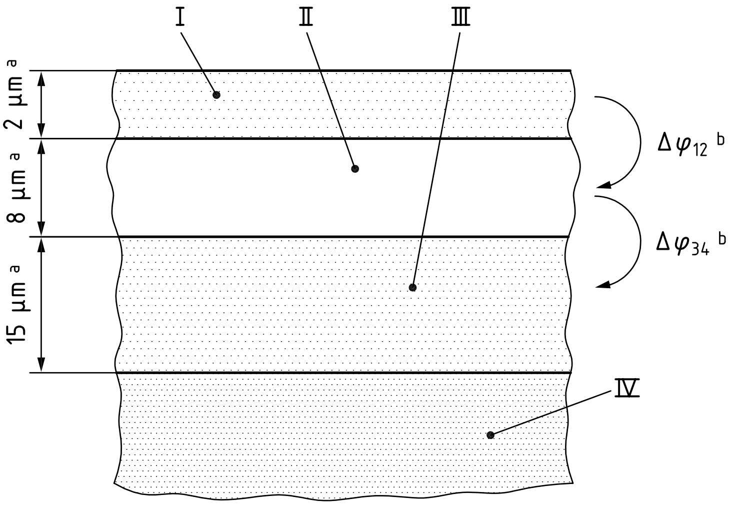
Figures 2 and 4 show typical developments of layer thickness/potential curves of multilayer nickel systems. In Figure 3, the coating structure corresponding to the course of measurement given in Figure 2 is represented schematically.



Key

X	dissolved layer/µm	1,2,3,4	position for evaluation
Y	potential/V	$\Delta\varphi_{12}$	potential difference between the layers I and II
I	micro-porous nickel	$\Delta\varphi_{34}$	potential difference between the layers II and III
II	bright nickel		
III	semi-bright nickel		
IV	basis material (e.g. brass, Cu, steel)		

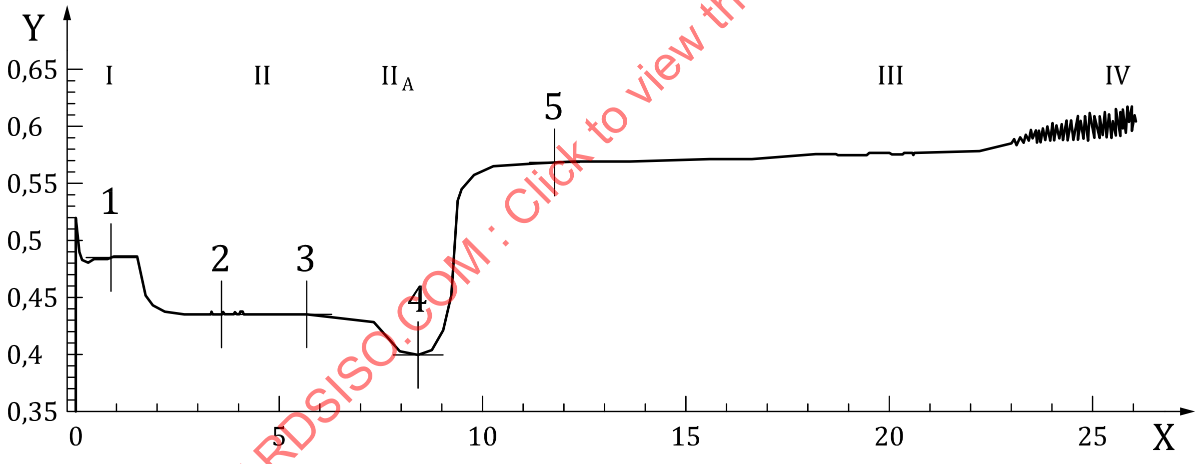
Figure 2 — Measured potential/layer thickness curve of the Ni layer system in accordance with Figure 3 — Evaluation for the purposes of determining the potential differences



Key

I	micro-porous nickel
II	bright nickel
III	semi-bright nickel
IV	basis material (e.g. brass, Cu, steel)
a	Layer thickness.
b	Potential difference.

Figure 3 — Schematic representation of the coating structure of the Ni layer system of Figure 2



Key

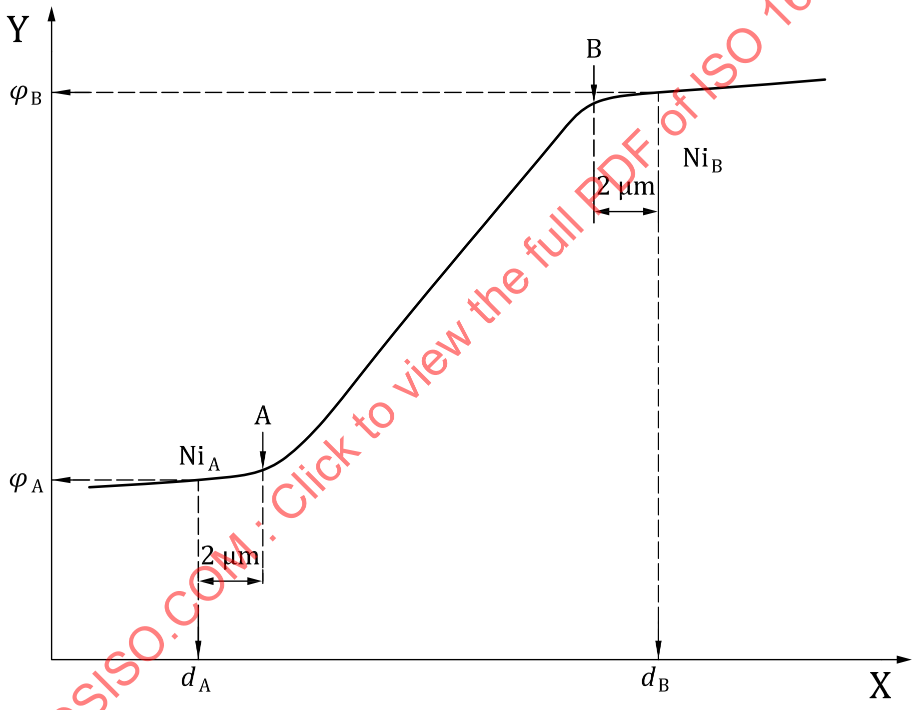
X	dissolved layer/µm
Y	potential/V
I	2 µm of micro-porous Ni
II	6 µm of bright nickel
II_A	2 µm of high-sulfur Ni
III	14 µm of semi-bright nickel
IV	on brass basis material (In the case of a different basis material, e.g. steel, the curve can be different.)

Figure 4 — Measured potential/layer thickness curve of the Ni layer system — Evaluation for the purposes of determining the potential differences

In the ideal case, the dissolution process of each individual nickel layer results in a constant potential curve (no rise). In the case of the curve shown in Figure 2 or Figure 4, as applicable, this situation is approximately implemented. Here, the potential difference to be determined is the direct difference between the respective potential heights; the selection of the dissolution depth for the purposes of determining the potential height is almost irrelevant.

In the practical case, additional minor drifts can complicate a comparable evaluation, i.e. the potential height varies with the dissolution depth. In order to obtain an unambiguous result regarding the potential difference, the following evaluation method shall be applied (see Figure 5):

- the point of transition between the rising (or falling) potential curve of nickel layer Ni_A and the subsequent slope of the transition area is determined (arrow A);
- starting from this point, the associated value φ_A is read off at a distance of 2 µm in the direction of the lower layer depth, at point d_A; φ_A represents the potential of nickel layer Ni_A;
- starting from the following point of transition between the slope and the subsequent rising (or falling) potential curve of nickel layer Ni_B (arrow B), the potential height φ_B is read off at a distance of 2 µm in the direction of the higher dissolution depth, at point d_B; φ_B represents the potential of nickel layer Ni_B;
- the absolute value of the potential difference to be determined, $\varphi_\mathrm{AB} = |\varphi_\mathrm{A} - \varphi_\mathrm{B}|$, results from the difference between the two potentials.



Key

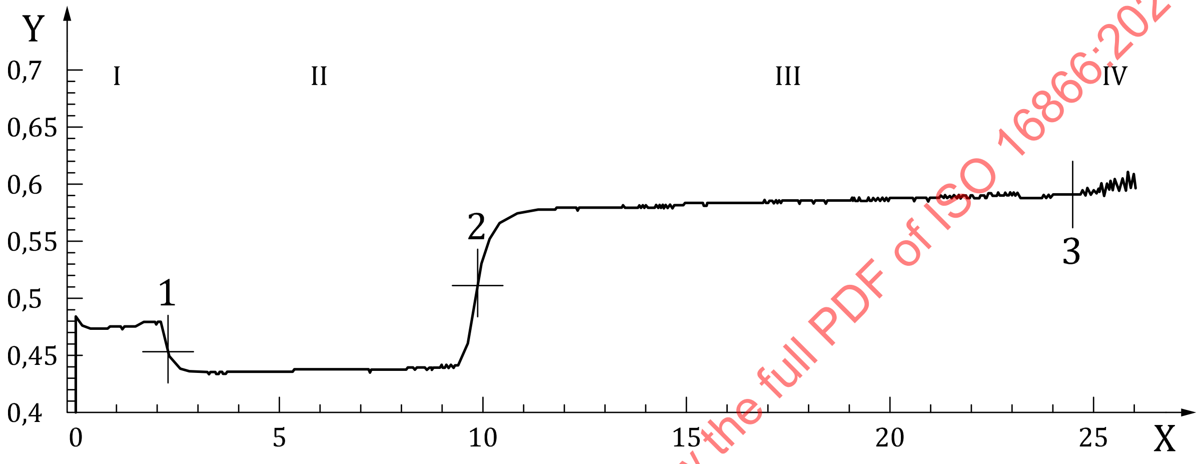
X	dissolved layer/µm
Y	potential/V
A, B	transition points of the curve
d_A	position for the evaluation of nickel layer A
d_B	position for the evaluation of nickel layer B
Ni_A	nickel layer A
Ni_B	nickel layer B

Figure 5 — Schematic representation of the determination of the potential difference between two subsequent nickel layers showing drift behaviour

In Figure 2 or Figure 4, as applicable, the evaluation markers are positioned in accordance with this approach. For example, in Figure 2, the potential difference between the micro-porous nickel (I) and the bright nickel (II) results from the difference between the potentials read off at the points of markers 1 and 2. Accordingly, the potential difference between the bright nickel (II) and the semi-bright nickel (III) results from the difference between the potentials read off at the points of markers 3 and 4.

NOTE 1 If the thickness of the Ni layer in question is too low for the described evaluation (displacement by 2 µm) (d < 2 µm ... 4 µm), the potential is determined in the centre of the potential curve (e.g. Figure 2, marker 1, and Figure 4, markers 1 and 4).

Figure 6 shows the approach taken to determine the layer thicknesses. Here, the evaluation criteria are the slopes between the dissolution ranges of the individual layers. At half height of the slopes, the associated dissolution depth is read off. The difference between the dissolution depths associated with two successive slopes corresponds with the thickness of the enclosed layer. In the example of Figure 6, the dissolution depth of the first slope is the layer thickness of the micro-porous nickel (I), the difference between the dissolution depths of slopes 2 and 1 is the layer thickness of the bright nickel (II), etc. At the point of transition from the lowest nickel layer [here the semi-bright nickel (III)] to the basis material, the difference to the point is determined, at which the measurement curve starts to exhibit a high degree of scatter (marker 3). If the basis material is a copper alloy, the dissolution curve starts to rise slightly. In the case of an iron alloy as the basis material, the dissolution curve starts to fall slightly. If required, this position shall be concretely agreed upon on an individual basis, in order to get unambiguous results.



Key

X	dissolved layer/µm
Y	potential/V
I	micro-porous nickel
II	bright nickel
III	semi-bright nickel
IV	on brass basis material (In the case of a different basis material, e.g. steel, the curve can be different.)

Figure 6 — Measured potential/layer thickness curve for the Ni layer system in accordance with Figure 3 (on brass basis material) — Evaluation for the purposes of determining the layer thickness

NOTE 2 Some manufacturers offer the relevant software that automatically calculates and documents the resulting potential differences or layer thicknesses, as applicable, following the establishment of the evaluation points on the measurement curves.

9 Measurement uncertainty

To a high degree, the measurement uncertainty depends on the way the measuring instrument is handled (see Clause 7) as well as on the uncertainties of the standards used for calibration. With commercially available measuring instruments, uncertainties of about 10 % can be achieved for the measurement of potentials and layer thicknesses (see also Annex A for precision data obtained by a round robin test).

A complete calculation of the measurement uncertainty should be performed in accordance with ISO/IEC Guide 98-3.