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Surface properties of the system: hard metal/Co coating/electrolyte*

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The surface properties of hard metal were studied using *in situ* electrochemical methods (cyclic voltammetry, potentiostatic and galvanostatic methods) in conjunction with *ex situ* techniques (SEM and X-ray diffraction). The samples were prepared by sintering 91% WC and 9% Co binder in vacuum. The present work was inspired by the possibility of eliminating the low wettability of tungsten carbide by means of electrochemical modification of the surface. The hard metal surface was electrocoated with cobalt. In order to improve adhesion of the Co layer an electrolytic method was developed by which the carbide phase was dissolved anodically at 0.2 V with respect to SCE in 4 M NaOH solution. Surface investigations by SEM and X-ray diffraction revealed that electrolytic dissolution of the tungsten carbide leaves the cobalt network (the spongy cobalt layer) with a face-centered cubic lattice (β-cobalt). Considering the substrate's influence on adhesion and the coating quality, particular attention was given to the conditions of electrodeposition of β-cobalt. Low pH values, low temperature, higher current densities strongly promote the deposition of the β-modification of cobalt.

1. Introduction

In the manufacture of hard metal (cemented carbide)-tipped tools the hard metal plates of various shapes and sizes are connected to the base metal materials by brazing. For many years the wetting of cemented carbide parts by molten brazing filler has posed a problem, especially when brazing without a flux. The sintering process influenced the wettability. Carbides packed in alumina and sintered in hydrogen furnaces can present surprisingly great wetting difficulties. Evaporation of Co from the surface in vacuum furnaces or surface contamination with oxides such as Al_2O_3 or ZrO_2, can also cause problems [1–3]. To eliminate the above mentioned difficulties and improve wettability, the cemented carbide surface can be cleaned or modified in one of the following ways: mechanical cleaning with SiC-grit [1], a high temperature salt bath treatment [3–5], coating of the surface with an easily wettable material, such as nickel or cobalt, and thermochemical treatment of the cemented carbide have also been suggested.

To improve the solderability in our investigations, the hard metal surface was electrocoated with a cobalt layer. Electrodeposition of cobalt, i.e. cobalt plating, is much rarer in technical practice than deposition of nickel, which is, in terms of its chemical and electrochemical properties, very similar to cobalt [6, 7]. This is primarily conditioned by the much higher price of cobalt. Electrolytic cobalt and alloy cobalt are applied when some characteristics are needed in which cobalt differs from nickel, e.g. its 'platinum-like' glow, specific magnetic behaviour, higher wear resistance and better solderability.

The aim of the present work was to study the possibility of facilitating, by electrochemical methods, the hard soldering process of hard metal boards to steel tool supports.

2. Experimental procedure

The cathode consisted of plates of hard metal (cemented tungsten carbide, WC = 91% with cobalt binder, Co = 9%) which are applied in the manufacture of tipped tools such as circular saws for cutting wood. The samples were rough ground and polished with diamond paste. On the basis of preliminary investigations, an electrolytic method was suggested and developed to modify the surface of the hard metal so that it consisted solely of the cobalt binder. For this purpose the tungsten carbide phase (WC) was dissolved anodically with a constant current, $i = 0.5$–$1\,A\,dm^{-2}$ or at constant potential, $E = 0.2\,V$ against SCE in 4 M NaOH solution, leaving about a 0.1–5 μm thick spongy cobalt layer. The etching effects were observed by scanning electronic microscope (SEM).

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The cobalt anodes used for electrolysis and the cemented carbide cathodes [8] were sintered in a vacuum furnace ('Sintal', Zagreb). The electrodeposition of cobalt onto hard metal was performed in a rotating electrochemical reactor under the following conditions: basic cobalt sulphate bath: $CoSo_4 \cdot 7H_2O$ . . . 504 g dm^{-3}, NaCl . . . 17 g dm^{-3}, H_3BO_3 . . . 45 g dm^{-3}. Bath temperature, current density and pH were varied from 15 up to 43° C; from 0.5 up to 4.0 A dm^{-2} and from 1.39 up to 5.42 pH.

The structural properties of the surface of the hard metal and of the electrodeposited Co-layer were investigated using a Jeol JXA-50A Scanning Electron Microscope (SEM) and X-ray diffraction patterns were recorded in a Philips PW-1050 diffractometer with CoK_α radiation. Electrochemical investigations were carried out in 1 M and 4 M NaOH solutions with a Wenking Electrochemical System and with a Beckman 'Electroscan 30': galvanostat-potentiostat.

3. Results and discussion

3.1. *Electrochemical, X-ray and SEM investigations of hard metal substrates*

Having in mind the influence of the preliminary treatment of the hard metal surface on the quality and adhesion of the electrolytic cobalt coating, electrochemical investigations of its behaviour were performed using cyclic voltammetry. The results are shown in Fig. 1. From the thermodynamic data it follows that tungsten is a base metal, as its domain of stability lies completely below that of water [9]. Tungsten does not dissolve, if it is anodically polarized, in the presence of solutions of HCl, H_2SO_4 and HNO_3. Voltammetric results, see Fig. 1, clearly show that the electrodissolution process of hard metal in 4 M NaOH becomes most remarkable in the potential range $E \geqslant 0.2$ V. The abrupt current increases corresponds to tungsten dissolution in the hexavalent state (in the form of tungstic ions WO_4^{2-}) according to the following mechanism [10]

$$WC \longrightarrow W + C \tag{1}$$

$$2OH^- - 2e^- \longrightarrow O + H_2O \tag{2}$$

$$W + 3O \longrightarrow WO_3 \tag{3}$$

$$WO_3 + 2OH^- \longrightarrow WO_4^{2-} + H_2O \tag{4}$$

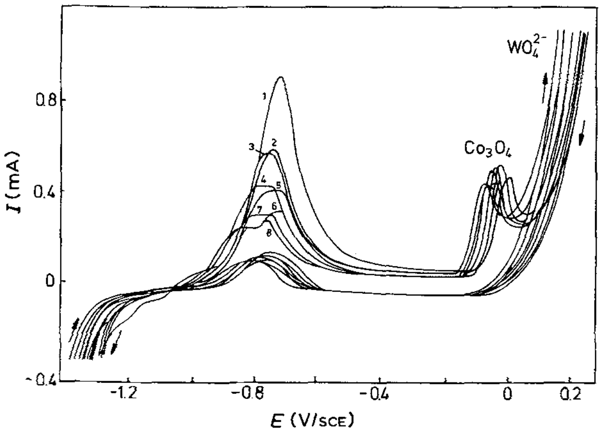

Fig. 1. Cyclic voltammograms of hard metal (91% WC, 9% Co) in 4 M NaOH solution. The numerals indicate changes in the profile during successive potential cycles at a sweep rate dE/dt = 10 mV s^{-1}.

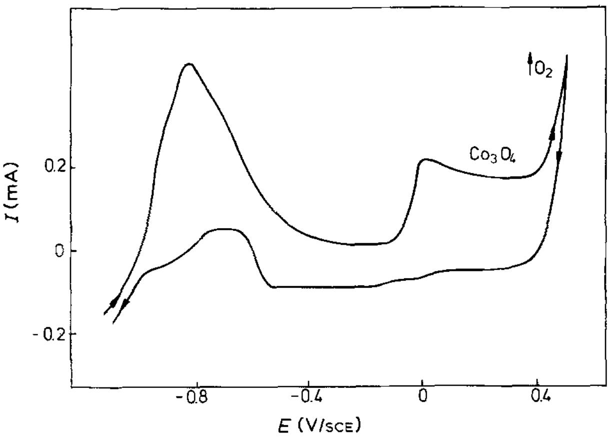

Fig. 2. Cyclic voltammograms of sintered cobalt 'Sintal' in 4 M NaOH. Sweep rate = 10 mV s^{-1}. The stabilized E/I profiles are attained after a few potential cycles.

By contrast, the polarization of cobalt in this potential range causes a net decrease of the amount of soluble species (compare Figs 1 and 2).

A comparison of micrographic pictures from the emission of secondary electrons shows a considerable difference in the surface structure of anodically treated and non-treated hard metal samples. Transmission electron micrographs are shown in Fig. 3. Electrolytic dissolution of tungsten carbide creates a surface consisting solely of very fine-grained cobalt. At $E \geqslant 0.2$ V the cobalt binder surface is coated with a thin passive film of Co_3O_4-oxide which prevents the dissolution of the cobalt into solution (compare Figs 2 and 3).

Generally, the substrate can be homogeneous or heterogeneous, identical with or different from the coating [1]. It can greatly influence the quality of the deposited metal coating [11]. Therefore, the activity of the substrate at small distances of the order of several atomic radii is dominant until the surface is covered with the first layer of deposited metal [12, 13]. The next layer then grows on a homogeneous substrate and the activity of the original substrate diminishes, while the influence of the deposition parameters such as current density, bath concentration and content, electrolyte stirring, pH and temperature, prevails.

According to the X-ray diffraction patterns, in hard metal, cobalt is present primarily in the form of a high temperature allotropic modification (β-cobalt) with a face centered cubic lattice, (see Fig. 4), which, under 420° C, is metastable and slowly turns to the low temperature modification (α-cobalt) with a hexagonal close packed lattice [14]. Taking into consideration these facts, it was supposed that, under certain electrolysis conditions, if a compact cobalt coating with as

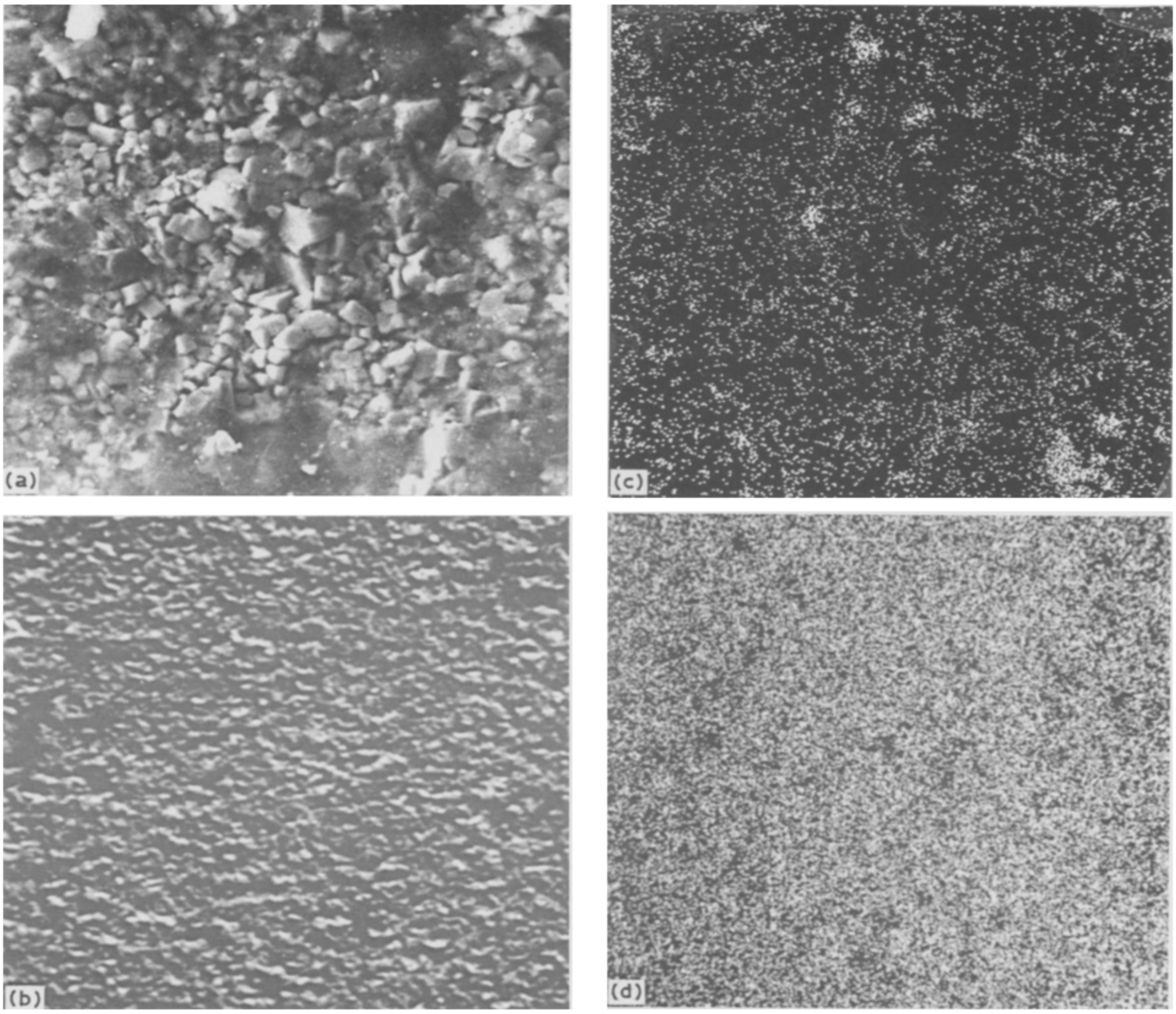

Fig. 3. X-ray image of CoK_α (Co distribution) and SEM micrographs for hard metal specimens: (a) and (b) untreated surface and (c) and (d) after 1 h etching in 4 M NaOH at 0.2 V against SCE. Magnification 1000 ×.

much β-modification as possible could be achieved, the adhesion of the coating to the substrate would be improved. In this paper, therefore, particular attention is given to the conditions under which β-cobalt is deposited, taking into consideration the coating quality.

3.2. *Electrochemical, X-ray and SEM investigations of the electrodeposited Co-layer on hard metal substrate*

The influence of pH, bath temperature and current density on the appearance, structure and texture of the deposited cobalt layer was followed using the technique of X-ray diffraction, see Fig. 5. The results showed that electrolytic conditions having a favourable effect on the codeposition of hydrogen at the cathode – low pH values, low temperature, higher current densities – strongly promote the deposition of the β-modification of cobalt. This is in conformity with the theory of hydrogen occlusion into the cobalt coating and a larger number of defects in the electrocrystallization process [6, 15–17]. Table 1 gives the results of the influence of varied electrolysis parameters on the crystallographic characteristics of the cobalt deposited on a hard metal surface. The degree of orientation changes in the directions [0 0 2] and [1 1 1] at lower current densities and lower temperatures, or in the directions [1 0 0] and [0 0 2] at higher current densities and higher temperatures. Tests of the adhesion of the cobalt coating to the hard metal substrate in Fig. 6 showed that satisfactory adhesion – as one of the preconditions for a good brazed joint – can be achieved with electrochemical modification of the sur-

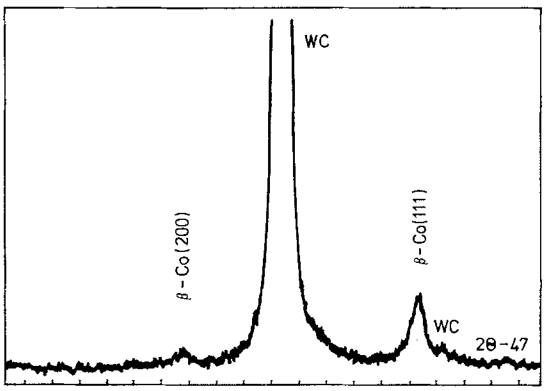

Fig. 4. X-ray diffraction patterns of hard metal specimen (91% WC, 9% Co) sintered in a vacuum furnace.

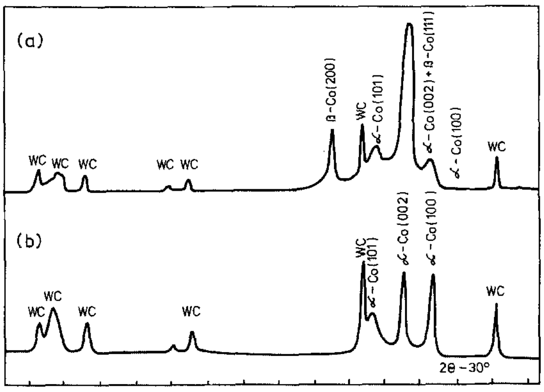

Fig. 5. X-ray diffraction patterns of Co-coatings deposited in a cobalt sulphate bath on the anodically etched hard metal substrate under the following conditions: (a) pH = 1.91, j = 1.0 A dm^{-2}, t = 293 K; (b) pH = 5.00, j = 4.0 A dm^{-2}, t = 316 K. Time of etching in 4 M NaOH at 0.2 V against SCE was 1 h.

Table 1. The influence of electrolytic parameters on the structure of the Co-layer deposited on a hard metal substrate

No.	pH	Bath temperature (*K*)	Current density ($A\,dm^{-2}$)	Structure of Co coatings	
				αβ	orientation
1	1.39	293	0.78	+ +	[0 0 2] + [1 1 1]
2	1.61	293	0.91	+ +	[0 0 2] + [1 1 1]
3	1.91	293	1.00	+ +	[0 0 2] + [1 1 1] [2 0 0]
4	3.56	293	0.86	+ +	[0 0 2] + [1 1 1]
5	3.83	293	1.04	+ +	[0 0 2] + [1 1 1]
6	4.30	297	1.00	+ +	[0 0 2] + [1 1 1] [1 0 0]
7	4.95	311	2.70	+ −	[1 0 0], [0 0 2]
8	5.00	316	4.00	+ −	[1 0 0], [0 0 2]
9	5.05	313	2.50	+ −	[0 0 2], [1 0 0]
10	5.41	313	2.08	+ −	[1 0 0], [0 0 2]
11	5.42	289	0.50	+ −	[0 0 2], [1 0 0]
12	5.25	288	1.66	+ −	[0 0 2], [1 0 0]

face by anodically etching in 4 M NaOH at 0.2 V against SCE.

The electrochemical behaviour of Co-coatings electrodeposited on hard metal substrate was compared with the electrochemical properties of 'specpure' cobalt and sintered 'Sintal' cobalt. The potentiodynamic *E*/*I* profiles run with the polycrystalline Co/1 M NaOH interface under repetive triangular potential scans in a potential range exceeding that of the thermodynamic stability of bulk water involve two defined anodic current peaks, one at about −0.8 V (peak I), another at 0.0 V (peak II) and probably a third at about 0.4 V (peak III), see Figs 7, 8 and 2. Beyond peak (III) the contribution of the oxygen evolution current is also depicted. On reversing the direction of polarization at the potential of O_2 evolution, three very small reduction peaks are observed. The reversible characteristics of the electrochemical reactions occurring in the potential range between −1.1 and 0.5 V offer a possibility of a straightforward comparison of the potential corresponding current peak with those predicted by thermodynamics, see Table 2. It is clear that the reactions in the lower potential range should be mainly related to the Co(II)/Co(III) redox systems, while at potentials preceding the discharge of oxygen, the Co(III)/Co(IV) couple should predominate.

Previous results on the behaviour of Co/alkaline solution interfaces have shown the formation of a sandwich-type structure when the electrode was subjected to prolonged potential cycling, namely, a structure such as $Co/CoO/Co(OH)_2$ was proposed, [18–22]. The primary passivity region of the cobalt electrode is regarded as due to the formation of an inner film of CoO next to the metallic surface.

The potentiodynamic response of cobalt in 1 M NaOH (see Table 2; Figs 7 and 8, peak I) in the potential range of the thermodynamic stability of the Co(II) species reveals two limiting electrochemical phenomena. The first potentiodynamic scan involves the large contribution of the metal electro-

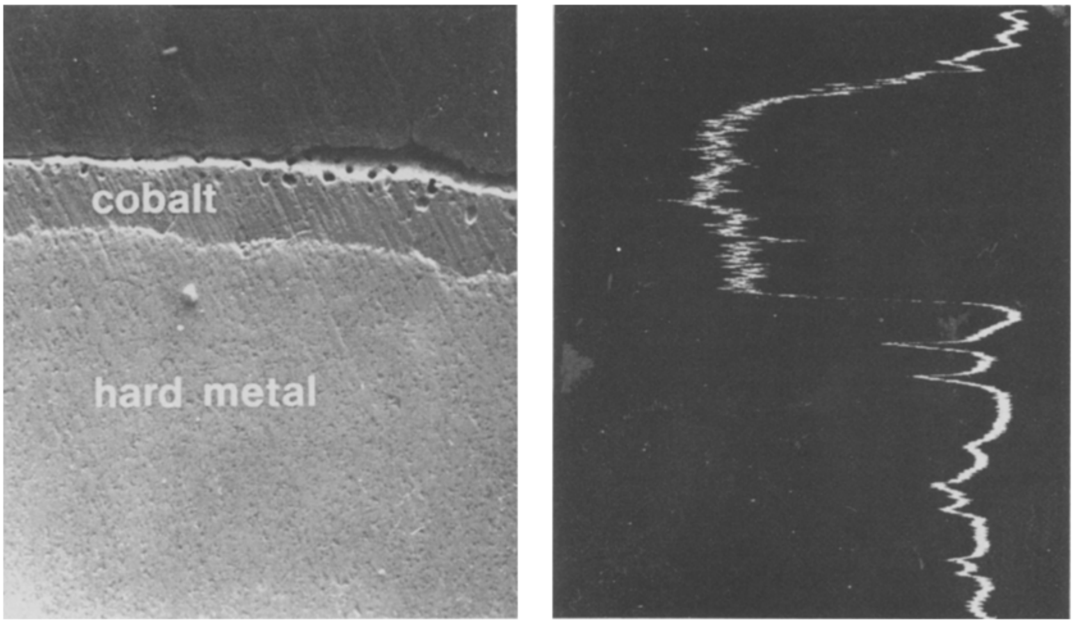

Fig. 6. X-ray image of CoK_α (line analysis), magnification 1000 × and scanning electron microscope (SEM) image of Co-coating deposited on the hard metal under the same conditions as in Fig. 5a. Magnification 300 ×.

Table 2. Standard potentials at 25° C

Reaction	*E (V/SCE)*	*Ref.*
$Co(OH)_2 + 2e^- \rightleftharpoons Co + 2OH^-$	(β-) −0.987	[20]
	−0.972	[9]
	−0.959	[19]
	(α-) −0.917	[20]
$CoO + H_2O + 2e^- \rightleftharpoons Co + 2OH^-$	−0.933	[19]
	−0.901	[9]
$Co_3O_4 + 4H_2O + 8e^- \rightleftharpoons 3Co + 8OH^-$	−0.802	[19]
$CoOOH + H_2O + 3e^- \rightleftharpoons 2Co + 3OH^-$	−0.704	[19]
$Co_3O_4 + H_2O + 2e^- \rightleftharpoons 3CoO + 2OH^-$	−0.417	[20]
	−0.290	[9]
$Co_3O_4 + 4H_2O + 2e^- \rightleftharpoons 3Co(OH)_2 + 2OH^-$	−0.333	[19]
	−0.074	[9]
$CoOOH + e^- \rightleftharpoons CoO + OH^-$	−0.313	[19]
$CoOOH + H_2O + e^- \rightleftharpoons Co(OH)_2 + OH^-$	−0.195	[19]
$3Co_2O_3 + H_2O + 2e^- \rightleftharpoons 2Co_3O_4 + 2OH^-$	−0.049	[9]
$3CoOOH + e^- \rightleftharpoons Co_3O_4 + H_2O + OH^-$	+0.081	[19]
	+0.083	[20]
$3CoO_2 + 2H_2O + 4e^- \rightleftharpoons Co_3O_4 + 4OH^-$	+0.335	[20]
$CoO_2 + H_2O + e^- \rightleftharpoons CoOOH + OH^-$	+0.423	[20]

dissolution process. The stabilized E/I profile (Figs 2, 7 and 8) resulting after prolonged potential scanning is explained in terms of the reaction taking place at the sandwich-type structure interface. The current plateau in Figs 7 and 8 may be explained as due to steady growth of soluble cobaltous hydroxide through the underlying film of cobaltous oxide. Anodic peak (II), at about 0 V, indicates the formation of a new oxide layer which blocks the dissolution of cobaltous hydroxide into solution. The observed potential for the beginning of this peak is about −0.3 V as compared to the thermodynamically calculated value of $E_r = -0.333$ V (Table 2) for the reaction

$$3Co(OH)_2 + 2OH^- \longrightarrow Co_3O_4 + 4H_2O + 2e^- \quad (5)$$

According to the X-ray work [23], the trivalent cobalt compound is CoOOH and not $Co(OH)_3$ at higher potentials. Finally, in the region preceding oxygen evolution the electrochemical reaction yielding Co(IV) from Co(III) species should occur at 0.4 V, Table 2.

The passivation of cobalt at more positive potentials, secondary passivity, can be principally assigned to the formation of spinel-type Co_3O_4 oxides in alkaline solutions. Analytical investigations of solutions in the present electrochemical experiments and ring-disc experiments [19] also showed that only Co^{2+} species were produced in NaOH solutions due to the dissolution of $Co(OH)_2$ only. Spinel oxide Co_3O_4 is either insoluble or has negligible solubility so that only Co^{2+} species are predominantly present in NaOH solutions. The electrochemical properties of spinel-type cobalt oxides in alkaline solutions, as well as their chemical and electrochemical stability have been recently analysed [24, 25]. The passive oxide film can be cathodically reduced to obtain an oxide-free cobalt surface. By cathodic reduction, the Co_3O_4 layer is first

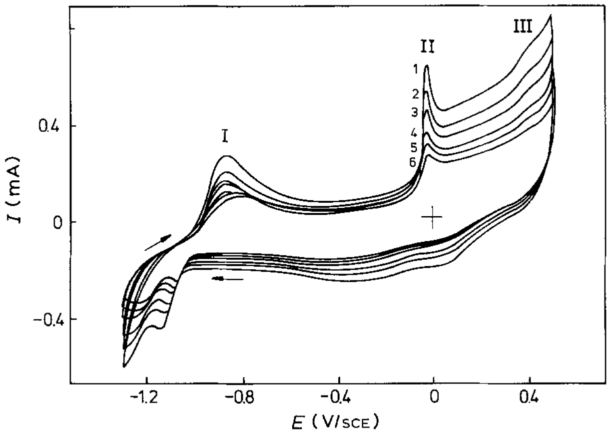

Fig. 7. Cyclic voltammograms of 'Specpure' cobalt (Johnson Matthey) in 1 M NaOH. Influence of the sweeep rate dE/dt = 100, 70, 50, 30, 20 and 10 mV s^{-1}. The stabilized E/I profiles are attained after a few potential cycles.

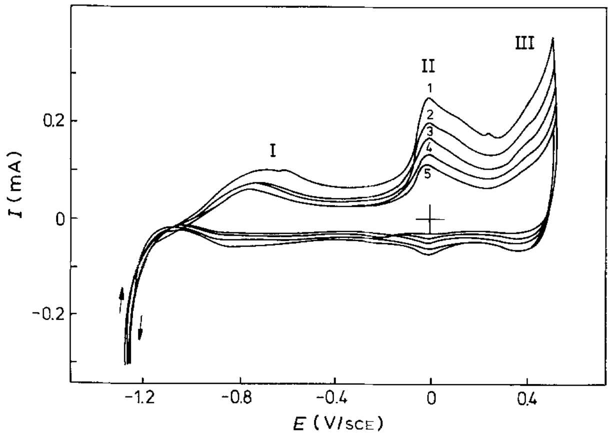

Fig. 8. Cyclic voltammograms of Co-coating on the hard metal substrate in 1 M NaOH. Influence of the sweep rate dE/dt = 150, 100, 70, 50, 30 and 20 mV s^{-1}. The stabilized E/I profiles are attained after a few potential cycles.

reduced to hydrated Co^{2+} ions before the inner Co layer is reduced to metallic cobalt.

4. Conclusions

The low wettability of hard metal is one of the greatest problem in tipped tools manufacture. In order to eliminate this difficulty, the hard metal surface was anodically etched in 4 M NaOH at 0.2 V against SCE and then coated with electrolytic cobalt from cobalt sulphate. Pure cobalt wetted perfectly.

The electrodeposition of cobalt was performed in a rotating electrochemical reactor. Bath temperature, current density and pH were varied from 15–43° C; from 0.5 up to 4.0 A dm^{-2} and from 1.39 up to 5.42 pH. The influence of these electrolytic parameters on the structure and composition of electrodeposited cobalt was followed through X-ray diffraction studies.

Electrochemical investigations of Co-coatings on the hard metal were carried out in 1 M and 4 M NaOH solutions by means of cyclic voltammetry. The results were compared with those obtained on 'specpure' and sintered cobalt under the same conditions. The potential regions of anodic cobalt dissolution, the primary passivity region with a $CoO/Co(OH)_2$ duplex layer and the secondary passivity region with a Co_3O_4 layer were defined. In the potential region of complete cobalt passivity, tungsten carbide dissolves in the form of tungstic ions (WO_4^{2-}).

The X-ray diffraction patterns showed that cobalt is present in the hard metal mostly in the form of a high temperature modification with a face centered cubic lattice (β-cobalt). At temperatures lower than 420° C, this modification is unstable and slowly turns to the low temperature modification (α-cobalt) with a hexagonal closed packed lattice.

Considering the influence of the substrate on adhesion and the coating quality, as well as the above mentioned fact, particular attention was given to the conditions of electrodeposition of β-cobalt and surface pretreatment. Low pH values, low temperature, higher current densities strongly promote the deposition of β-cobalt.

Surface investigations by SEM revealed that electrolytic dissolution of the tungsten carbide leaves the cobalt network with its original structure and chemical composition. In order to improve adhesion of the electroplated Co-layer on the hard metal substrate, on the basis of these results an electrolytic method has been developed by which the carbide phase is dissolved anodically at 0.2 V against SCE in 4 M NaOH solution. The cobalt binding phase oxidizes to Co_3O_4 but remains undissolved.

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