

Pulse electroplating of rich-in-tungsten thin layers of amorphous Co–W alloys

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Received 29 May 1995; revised 1 December 1995

A combination of an improved plating bath and pulsed current was shown to lead to a substantial increase in tungsten content in amorphous Co–W alloys. This increase was associated with selective oxidation of cobalt during the rest times of the deposition process. The tungsten content reached 41.4 at % under the following conditions: current density 35 mA cm^{-2} , ratio of pulse time to rest time 1/1, and pulse frequency 10 Hz. The alloy layers were of similar hardness and of much better smoothness, ductility, adhesion to the substrate, and resistance to corrosion compared to those plated according to the US 4 529 668 patent.

1. Introduction

An increased interest in amorphous alloys has been triggered by their attractive properties and potential applications [1, 2]. Some of these alloys are known to be resistive to corrosion, others have unusually soft magnetic characteristics, which makes them an interesting material for production of storage devices. Amorphous alloys are usually prepared by very rapid cooling of liquids, but for thin coatings electrolysis is often used. A thin layer of alloy plated on a conducting substrate can considerably improve the properties of the substrate.

We have focused our attention on amorphous Co–W alloys; boron and phosphorous are present in these alloys as minor components. It is worth noting that tungsten alone cannot be reduced to metallic form from aqueous solutions. Co–W alloys are hard and very inert in both acidic and alkaline solutions [3–6]. An application of the original patent procedure [7] leads to an alloy composition of 75 and 25 at % of Co and W, respectively. The patent bath was recently improved by us [8]. BPO_4 , the use of which was recommended in the patent, dissolves very slowly in water, decomposes, is relatively expensive, and causes precipitation of $\text{Co}(\text{NH}_4)\text{PO}_4$. We have found that boron phosphate can be replaced in the plating bath by a mixture of phosphoric and boric acids (or their salts), and, in addition, the amount of phosphate can be decreased by 25% compared to that introduced as BPO_4 . Such a change eliminates precipitation of $\text{Co}(\text{NH}_4)\text{PO}_4$, increases the content of tungsten from 25 to 30%, increases the life time of the bath, preserves the efficiency of the alloy deposition in consecutive runs and improves the smoothness of the alloy surface. All this was achieved without affecting the amorphousness and hardness of the deposited layers.

One aim of the work described in this paper is to further improve the quality of the alloy layers by

applying pulse-plating. This approach led to better results for other crystalline alloys [9–12]. Another aim was to increase considerably the tungsten contents.

2. Experimental details

Depositions were carried out using an EG&G Parc potentiostat/galvanostat model 173, which was controlled by a Lab PC 12-bit 48-channel adda card. The software, which produced a current waveform of arbitrary shape was developed in house. Co–W alloy layers were deposited on copper and platinum foils. Before experiments the foil was polished, washed with a detergent, and rinsed with water and acetone. This was followed by immersing the foil in a 5% H_2SO_4 solution for 20 s to activate the foil surface. The copper cathode (4 cm^2) was placed between two platinum anodes (8 cm^2 each). Mass and thickness of the layers were determined by weighing. The concentrations of the plating bath components, except for BPO_4 , were as given in the patent [7] (sodium tungstate 81.5 g dm^{-3} ; ammonium citrate 59 g dm^{-3} ; conc. phosphoric acid 7.69 ml dm^{-3} ; boric acid 10.25 g dm^{-3} ; $\text{Co}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ 3.89 g dm^{-3} ; 1,4-butyndiol 0.05 g dm^{-3} , and ammonia water to maintain the pH at 8.5). BPO_4 , according to the patent procedure, should be present at a concentration of 17.5 g dm^{-3} . Instead, phosphoric and boric acids at concentration 7.69 and 10.25 g dm^{-3} , respectively, were used [8].

The structure of the deposited alloys was determined by X-ray diffraction using a DRON-1 instrument with a cobaltous X-ray lamp equipped with a CoKL filter. The mean concentrations of Co and W were found by electron microprobe spectroscopy using either a Jeol JXA 50A or a Cameca SX-50 instrument. Optical inspection of the alloy surface was done with an inverted metallurgical microscope, Olympus, type PM3. Cobalt concentration in the

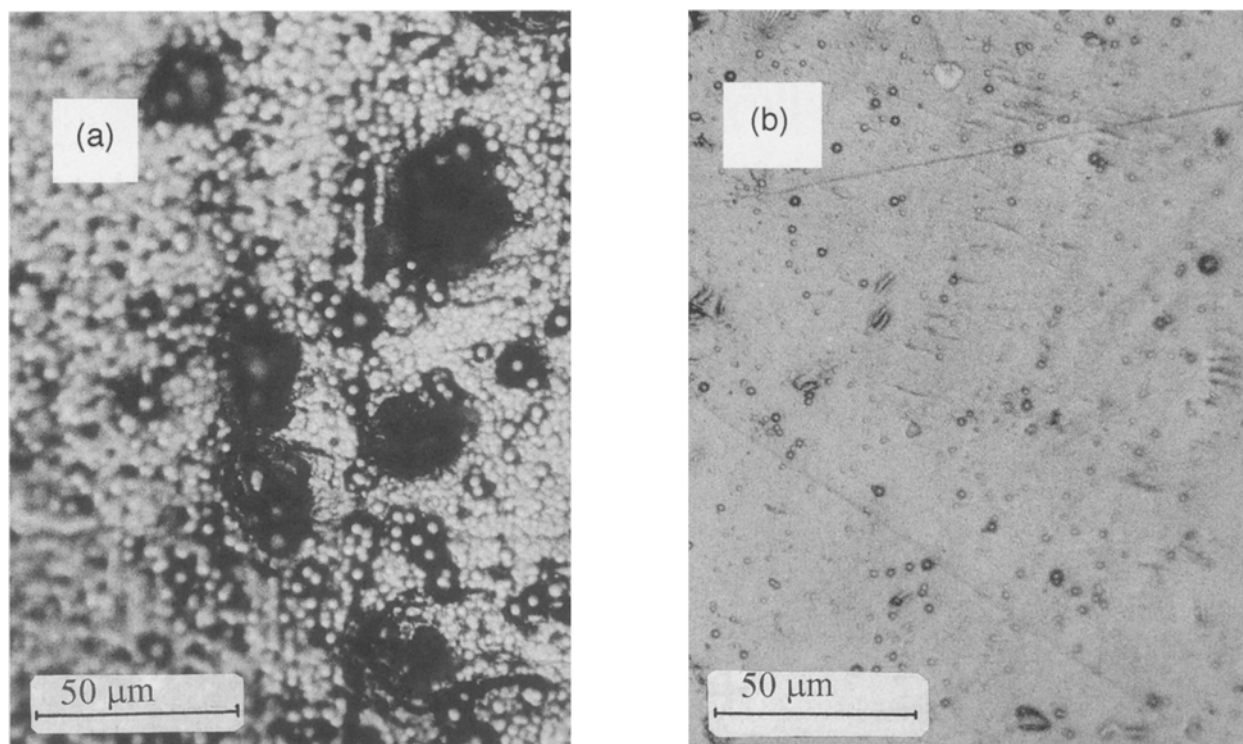


Fig. 1. Micrographs of alloy layers. Thickness $8\ \mu\text{m}$. Current density: $35\ \text{mA cm}^{-2}$. (a) constant current, (b) pulsating current, $t_d/t_r = 1/1$, frequency: 25 Hz.

solutions was determined by atomic absorption spectroscopy. Microhardness of the material was tested by measuring the diagonal length of the indentations obtained with a Vickers diamond pyramid. The load used in the measurements was 5 g. Micrographs of the indentations were taken with a Joel JSM-5400 electron scanning microscope.

Plating temperature was maintained at $65\ ^\circ\text{C}$. The volume and pH of the bath were corrected by adding water and ammonia, respectively.

3. Results and discussion

3.1. Influence of pulsed deposition on physical properties of alloy layers

For all examined samples, pulsed deposition distinctly improved the quality of the coatings. For all pulse plating current parameters, improved deposit smoothness was obtained compared to constant current deposition which always led to the formation of an irregular,

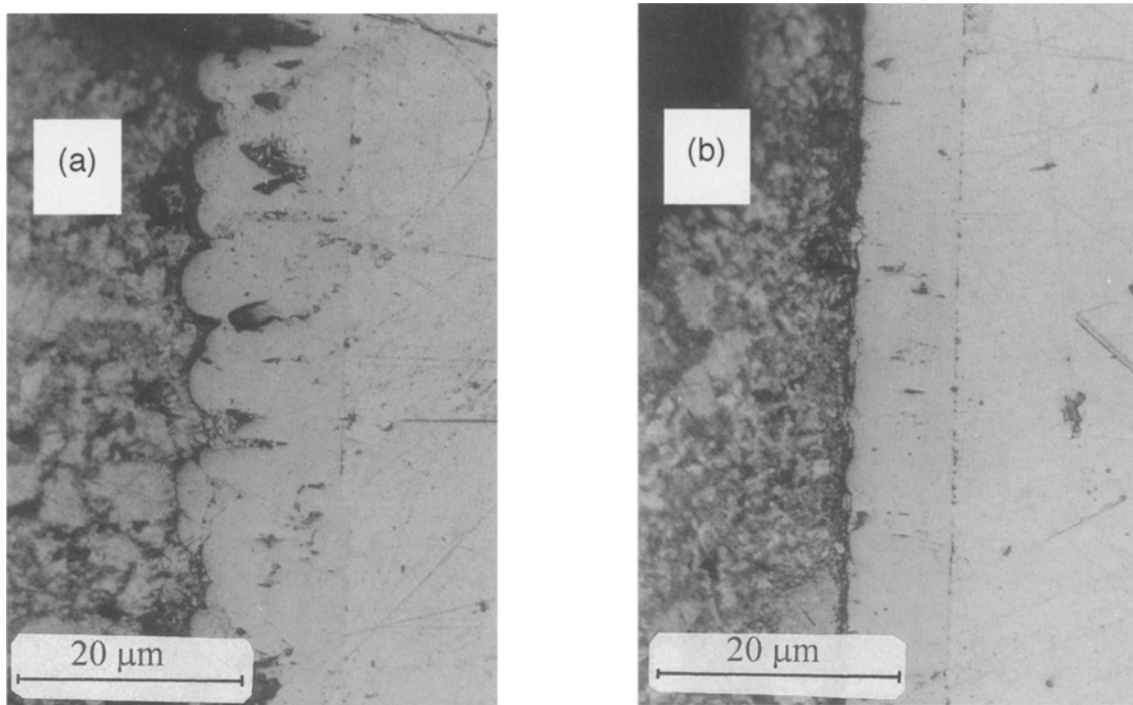


Fig. 2. Cross sections of the alloy layers from Fig. 1. (a) Constant current, (b) pulsating current, $t_d/t_r = 1/1$, frequency: 25 Hz. The layers from right to left are: Cu, Co-W, filler.

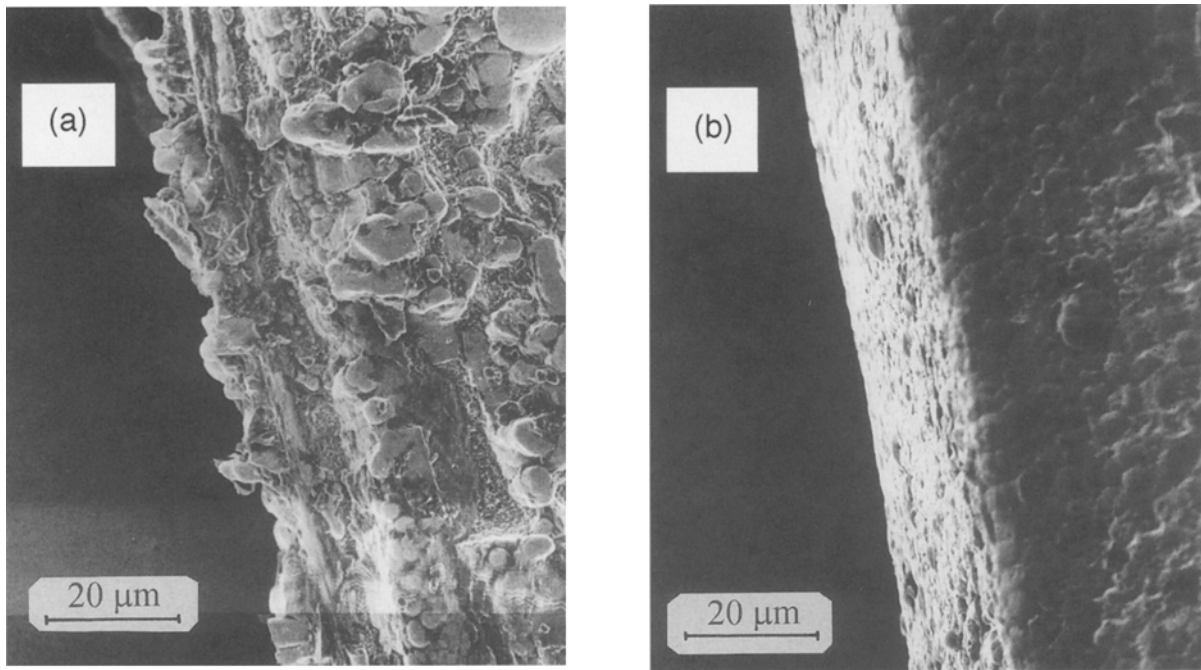


Fig. 3. Micrographs of the edge of a Cu foil covered with a $5\ \mu\text{m}$ layer of Co–W alloy. (a) Constant current, (b) pulse current, $t_d/t_r = 1/5$, frequency: 25 Hz.

nonflat surface, sometimes cauliflower like. A typical difference between the smoothness of the deposits obtained by constant and pulsed electroplating is illustrated in Fig. 1.

A detailed examination of the deposition process revealed that both the shape of the current waveform and its frequency affected the smoothness/roughness of the alloy surface. The smoothest layers were obtained for symmetrical (both current and rest components of the same duration) current waveforms of 10 and 25 Hz. The smoothness was evaluated by inspecting cross sections of the layers using a microscope. Typical micrographs of the layer cross sections are presented in Fig. 2. A layer obtained using a symmetrical current waveform of frequency 25 Hz (b) is compared in the figure with a typical layer obtained by constant current deposition (a). The difference is striking. The irregular surface structure produced by the constant current deposition is replaced by a very uniform and smooth layer when the reduction current is separated by rest periods.

Pulse plating also leads to a smooth coverage of the edges. This is illustrated in Fig. 3, where two photos of copper-plate edges are shown. Due to the very uniform deposition with pulsed current the copper-plate shape is very well preserved compared to the situation for regular deposition.

The first chemical consequence of pulse plating is improved resistance to corrosion. This is, among others, a result of elimination of irregular objects on the surface. Such objects, most often the shape similar to a sphere segment, are especially easy targets for corrosion, probably because of their varying composition. Tungsten content at these points drops to 20% while the average level in the layer is 30% (see Fig. 4(a)). These changes in the composition lead to

internal stress and, further, to the formation of cracks during anodic polarization. The history of a prolonged anodization of a selected spherical object is shown in Fig. 4b.

Pulse electroplating has also led to reduced brittleness and improved adhesion to the substrate of the Co–W layers. Figure 5 presents a result of a test of bending copper plates covered with $6\ \mu\text{m}$ alloy layers. The plates were bent through 180° and straightened again. This test clearly showed that the pulse deposited layers were superior in terms of adhesion and ductility against the layers plated by constant current.

Since the present alloys are thin and plated on an electrochemically active material, regular potentiostatic examination of passivation/corrosion, which require sufficiently long polarization time, were not appropriate; copper would interfere. It was decided to shorten the time scale of polarization and, therefore, the following experiment was done. Two samples: one obtained by constant, and the other one by pulsed, current deposition were exposed to anodization at a gradually increasing current density at a rate of $0.2\ \text{mA cm}^{-2}\ \text{s}^{-1}$. It was assumed that the surface was fully passivated when the potential of oxygen evolution (app. +1.8 V) was reached. The dependencies of the anode (alloy) potential against anodic current density are presented in Fig. 6. For the pulse-deposited $6\ \mu\text{m}$ layer the current density causing complete passivation was four times lower compared to that for the layer obtained by constant current plating. This ratio of passivation times in terms of the ratio of the charges required to passivate the layers was 10.

A similar comparison, under currentless conditions, was made by immersing alloy samples into solutions containing ions and molecules that promote corrosion: Cl^- , NH_3 , and citrate anion. The alloy

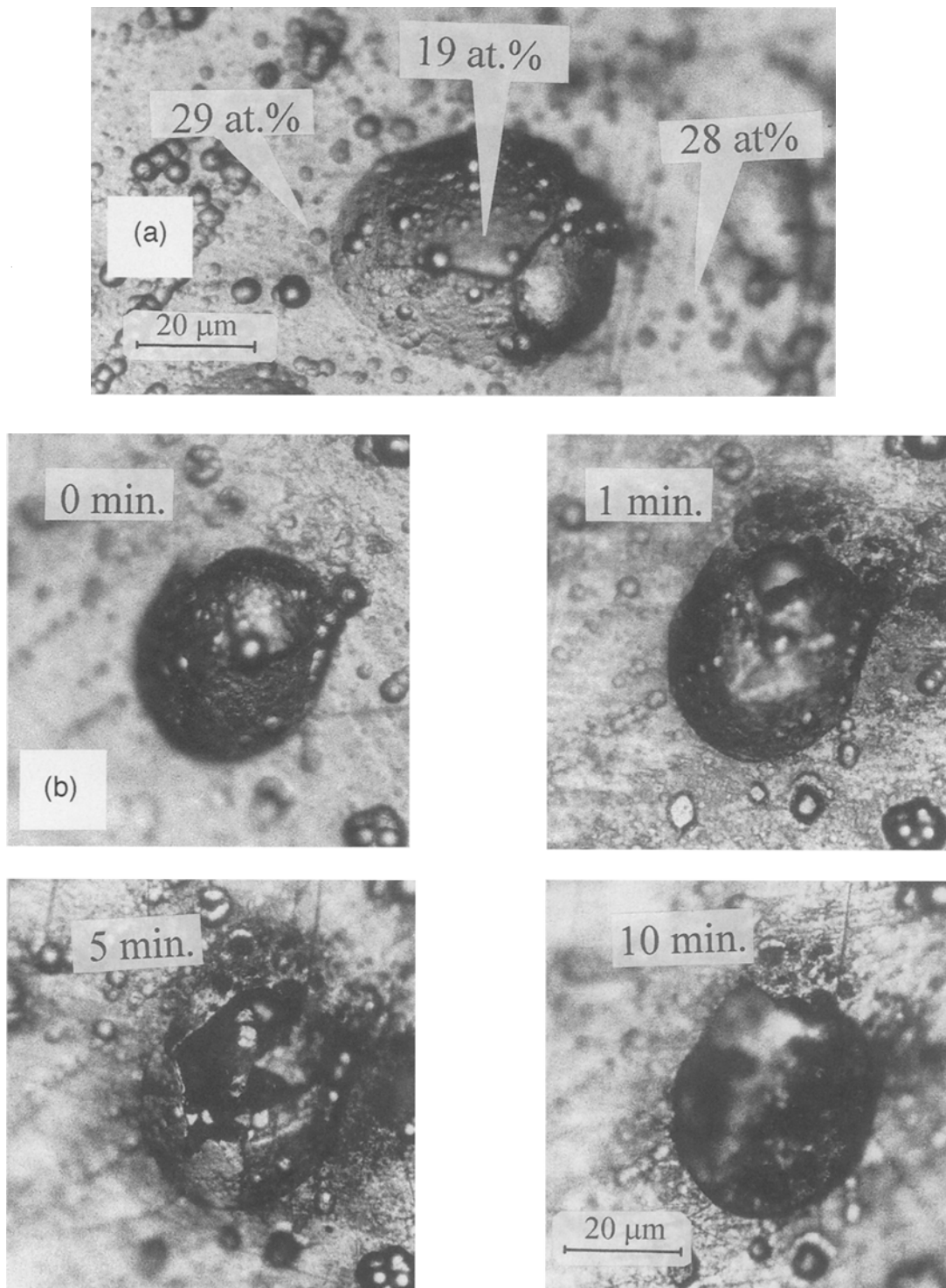


Fig. 4. Irregularities at the alloy surface. Constant current deposition (35 mA cm^{-2}). (a) Content of W at selected places, (b) formation of a pit during anodic polarization in $0.1 \text{ M K}_2\text{SO}_4$ of pH 2.

layers obtained by constant current electrolysis were attacked faster. Pits appeared at the irregularities on the surface. A prolonged exposition of the layers to these solutions finally led to the appearance of cracks moving radially from the pits. The situation is depicted in Fig. 7 by a photograph of a pit formed in a $1 \text{ M NH}_3/\text{NH}_4\text{Cl}$ solution (pH = 9.2). Cracks are usually interpreted as evidence for the existence of internal stress in alloys. The layers obtained by pulse deposition remained shiny, unpitted and uncracked for a several times longer time.

3.2. Influence of pulsed deposition on alloy composition and deposition efficiency

The ratio of the deposition time to the rest time, t_d/t_r , was found to be a key factor in alloy composition. Three values of this ratio were chosen for electroplating: 1/5, 1/1 and 5/1. The frequency of the current waveform was 5, 10, 25, 50 and 100 Hz. In the first series of platings, done for $t_d/t_r = 5/1$, no distinct differences in the alloy amorphousness and composition were found between the samples obtained by constant

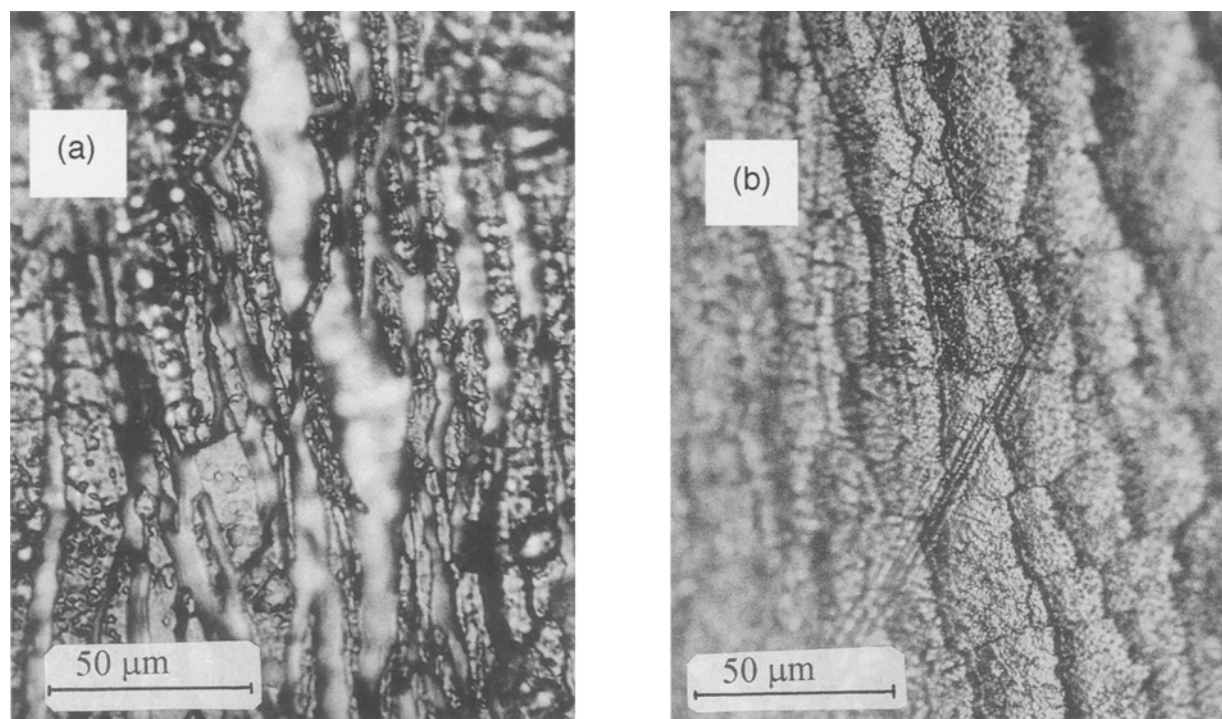


Fig. 5. Micrographs of copper foils covered with 6 μm layers of Co-W alloy and then bent (through 180°) and straightened up again. (a) Constant current, (b) pulse current, $t_d/t_r = 1/1$, frequency: 25 Hz.

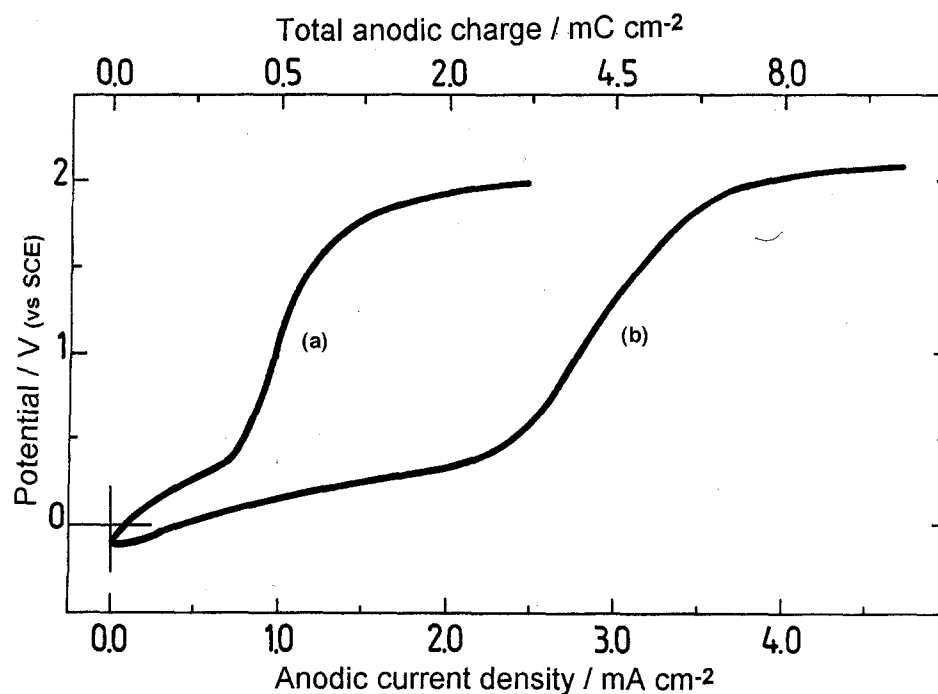


Fig. 6. Polarization curves. E measured against linearly increased anodic current density. Alloy deposited by (a) pulsating current, (b) constant current.

and pulse electroreduction. The alloy contained approximately 28–29, and 71–72 at % of W and Co, respectively. Hardness and deposition efficiency were also similar for all samples, and equalled 780–940 Hv and 9%, respectively. However, as stated in the previous section, smoothness and homogeneity of the samples obtained by the pulse method were improved.

Noticeable changes in the alloy composition were found for $t_d/t_r = 1$. Although the alloys remained amorphous, the tungsten content increased by several

percent, and reached 41.4 at % for a frequency of 10 Hz. Data characterizing the layers are given in Table 1. Taking into account all parameters, it may be concluded that the optimal conditions for electrodeposition of Co-W alloys are $t_d/t_r = 1$ and frequency 25 Hz. To our best knowledge, these are the richest W alloys obtained from aqueous solutions.

A similar dependence of the alloy parameters on current waveform frequency was obtained for the ratio $t_d/t_r = 1/5$. Generally, the W content was

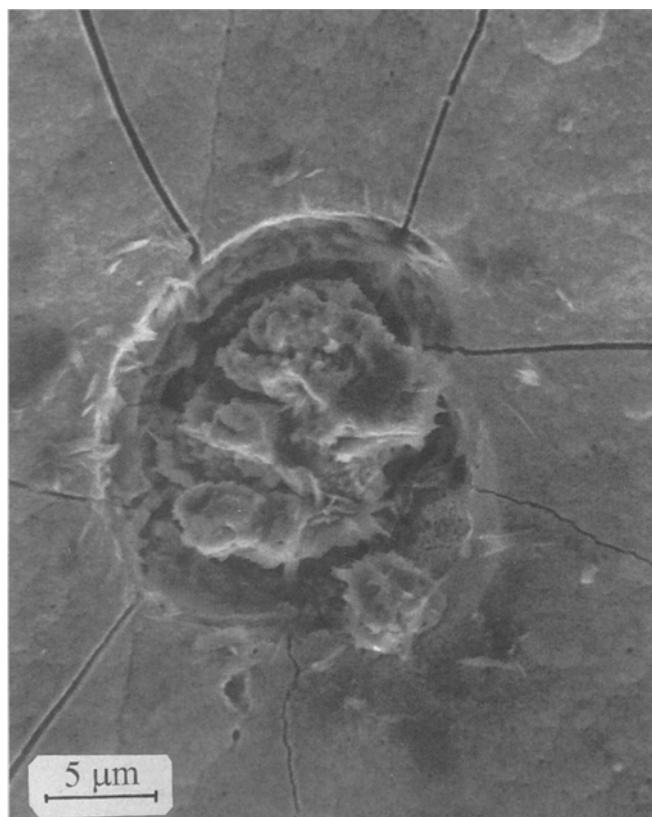


Fig. 7. A result of a 2 h treatment of a bump on the alloy surface with 1 M ammonia buffer at 50 °C.

Table 1. Parameters of deposited amorphous Co–W layers against current-waveform frequency

Current waveform frequency /Hz	Tungsten content /at %	Hardness /Hv	Alloy deposition rate /mg cm ⁻² h ⁻¹	Deposition efficiency /%
5	36.6	880	1.56	8.0
10	41.4	910	1.87	9.6
25	40.1	1035	231	11.8
50	39.3	930	2.80	14.3
100	38.2	1060	3.00	15.3

$$t_d/t_r = 1/1$$

Table 2. Parameters of deposited amorphous Co–W layers against current-waveform frequency

Current waveform frequency /Hz	Tungsten content /at %	Hardness /Hv	Alloy deposition rate /mg cm ⁻² h ⁻¹	Deposition efficiency /%
3	31.2	880	0.93	10.0
5	32.4	835	0.97	10.4
10	33.8	885	1.03	11.1
25	35.3	890	1.07	11.5
50	33.1	935	1.23	13.2
100	32.2	890	1.90	15.0

$$t_d/t_r = 1/5.$$

lower compared to the previous case. The maximum W yield (35.5%) was obtained for 25 Hz. This series of electroplatings is characterized in Table 2.

The increase in W content in the alloy obtained by pulse deposition may be a consequence of selective

oxidation of cobalt from the layers during the rest time. A similar trend observed for crystalline Ni–Mo alloys was explained by an additional reduction of molybdenum by the accumulated hydrogen at the electrode [9]. That explanation cannot be adopted for the Co–W case. The phenomenon of selective oxidation and removal of cobalt from the alloy layers was noted previously during pulsed anodization of Co–W alloys [6]. In this work there was no anodic component in the applied pulse current waveform; however, the plating bath used was sufficiently oxidative for cobalt. An experiment was performed to examine

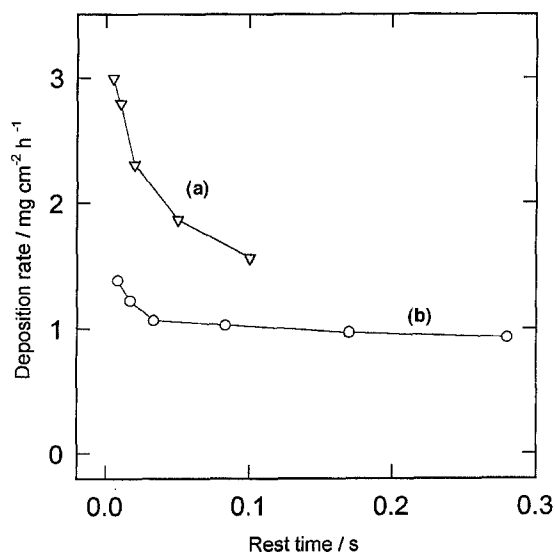


Fig. 8. Dependence of deposition rate on rest time. (a) $t_d/t_r = 1/1$; (b) $t_d/t_r = 1/5$.

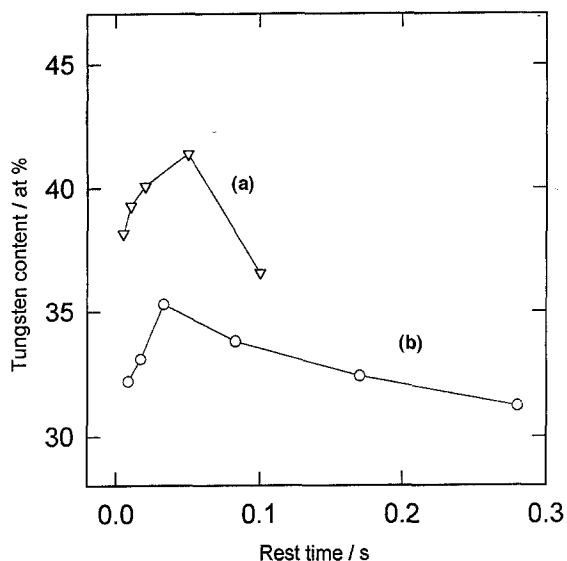


Fig. 9. Dependence of tungsten content on rest time. (a) $t_d/t_r = 1/1$; (b) $t_d/t_r = 1/5$.

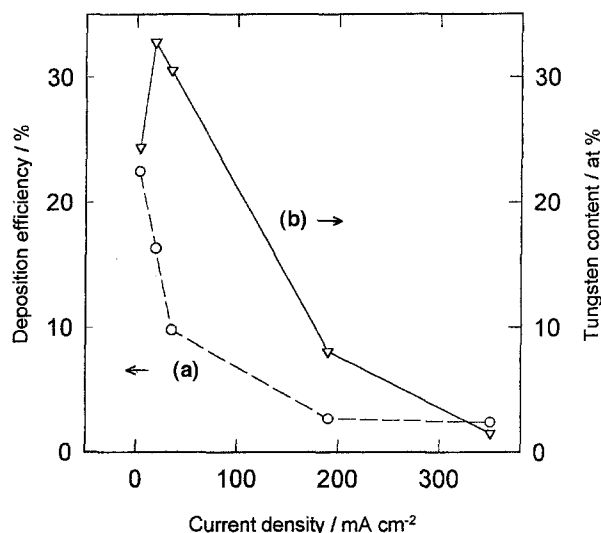


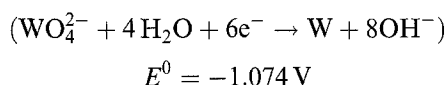
Fig. 10. Plots of (a) deposition efficiency and (b) tungsten content against current density. Constant current deposition.

the corrosive properties of the bath. Samples of the amorphous alloy (plated on Pt) were placed in a bath solution for several hours. Apparently the alloy layers were attacked. The attack was most serious at irregularities such as those shown in Fig. 4(a), and at the sample edges. It was noticed that during a prolonged contact of the alloy samples with the bath solution, tungsten was also dissolved of the alloy. In the most affected places the W content dropped to approximately 20 at %. After several days of contact with the bath the entire layer could be dissolved.

Data presented in our earlier paper on corrosion of the amorphous Co-W alloy [6], supports the view that on the plating time scale the oxidation of cobalt to soluble species which diffuse away is followed by the formation of insoluble cobalt oxides and hydroxides which remain on the alloy surface. The cobalt oxides formed during the rest time of the plating current waveform are immediately reduced

during the plating time. Therefore the cobalt 'loss' cannot be large at longer rest times. Curve (b) in Fig. 8 illustrates the situation for the ratio $t_d/t_r = 1/5$. The efficiency of the deposition process drops with increase in the rest time. The highest drop rate takes place at shorter rest times. In the range of rest time where the drop rate is highest the tungsten content increases and reaches an upper value at the end of this range. For the ratio $t_d/t_r = 1/1$, the deposition efficiency and the W content are represented by curves (a) in Figs 8 and 9. They are similar to those of curves (b); however, for the ratio $t_d/t_r = 1/1$ a very high W content is obtained. It is interesting that, for the 1/1 ratio, the highest W content is observed for the current pulsing at 10 Hz, i.e. for 50 ms rest time. This is close to the rest time of 34 ms needed to obtain the highest W content for the ratio 1/5.

These factors suggest selective removal, by oxidation, of cobalt from the alloy surface during the first tens of milliseconds of the rest time. If the increase in tungsten content is caused by the chemical reduction of tungstate by hydrogen evolved during the rest time, as suggested for molybdenum in pulsed electrodeposition of Ni-Mo alloys [9], the efficiency of the deposition process would increase. Also, the formal potential for the half cell WO_4^{2-}/W in an alkaline media [13]



seems to be too negative to make the direct reduction of WO_4^{2-} to W by elemental hydrogen possible.

An increase in the plating current magnitude did not bring any advantages. The W content and the deposition efficiency dropped. For example: a t_d/t_r ratio of 1/1, and a plating current density of 70 mA cm⁻² led to a 2-3% decrease of the W content and to a 20% drop in the plating efficiency. When the current density was raised to 175 mA cm⁻², the W content and the plating efficiency dropped to 19% and by 50%, respectively. The quality of the deposited layers was also poor (rough surface and increased brittleness). The dependence of W content and deposition efficiency on current density are presented in Fig. 10. The deposition efficiency was calculated as the ratio of the charge equivalent to number of moles deposited and the charge which was passed through the cell. Too low a current density resulted, not only in a decreased W content, but also in the appearance of crystal grains. The plots in Fig. 10 suggest that the optimum current densities in respect of W content, amorphousness, and deposition efficiency are in the region of 30 mA cm⁻².

Acknowledgements

This work was supported in part by the Polish Science and Technology Agency (KBN) under grant number 2.0882.91.01.

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