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The interface between metallic substrates and layers of electrodeposited Co–W amorphous alloys

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Abstract

The process of formation of deposits of Co–W amorphous alloys on copper and mild steel substrates has been studied. For the alloy layers plated on copper, the content of Co and W in the amorphous coverage has been examined and found to be a function of the distance from the substrate surface. The examination was based on the quantitative EDS and WDS analysis of the cross-sections of the alloy layers. It has been found that an intermediate inner layer is formed on the copper substrate, and the adhesion of the alloy to this substrate is very good. The adhesion of the alloy layers to steel was much weaker compared to copper. We relate this difference to the absence of the interface layer between the alloy and steel. The difference found for the two substrates correlates well with the differences in the crystal structures of the substrates and the deposited metals.

Keywords: Amorphous alloy; Cobalt–tungsten; Substrate influence

1. Introduction

Tungsten and tungsten alloys are technologically and economically important in a variety of applications, ranging from ultra-large scale integration to fuel elements for nuclear reactors. The high-temperature and premium mechanical properties of tungsten alloys are most attractive in engineering applications. However, the high melting temperature of tungsten makes the preparation and processing of tungsten alloys very difficult. Because of this the common processing methods used for other metals and its alloys are useless in tungsten metallurgy. To prepare tungsten alloys, other advanced processing methods such as powder metallurgy, chemical vapor deposition, and electrodeposition are used [1].

Electrochemical plating is a good method for the deposition of tungsten alloys [1–5]. The advantages of this method include the ability to form tailored microstructures, epitaxial layers, and compositional graded microstructures. The deposits obtained by this way can be used for various purposes. One of the applications of the tungsten alloys is the formation of protective layers on the elements and parts of machines that work under extremal conditions. A combination of the premium properties of the tungsten based alloys with the amorphous structure [1,6] may results in very special material properties. Layers of the amorphous tungsten alloys are deposited on pistons of combustion engines [7], printer heads [8], parts of battle arms [9] and other systems exposed to high temperature and wear.

The quality of the protective coatings depends on several parameters. The most important ones are the structure the surface properties and the adhesion to the substrate. The relationship between the interactions in the system deposit-substrate and the adhesion of the layer to the substrate was reported for numerous cases, among others for Au–GaAs [10], Au–Cu [11], and Au–Ni (crystalline and amorphous) [11]. If there are specific interactions between the electrodeposited layer and the substrate, a modification of the layer structure and its composition is also expected. The changes in the structure and the composition of the amorphous Co–W alloy layers grown on two different substrates have been investigated in the frame of this work.

2. Experimental

Depositions were done with an EG&G PARC potentiostat/galvanostat model 173, which was controlled by a National Instruments Lab PC 12-bit 48-channel ADDA card. The software, which allowed e.g. to program a

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current waveform of arbitrary shape was developed in our laboratory. Co–W alloy layers were deposited on copper and steel foils. Before the experiments the foil was polished, washed with a detergent, and rinsed with water and acetone. This was followed by immersing the foil into a 5% H_2SO_4 solution for 20 s to activate the foil surface. The copper and steel cathodes (4 cm^2) were placed between two platinum anodes (8 cm^2 each). The anode compartments were separated from the cathode compartment by glass frits. 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 [3] (sodium tungstate 81.5 $g\,l^{-1}$; ammonia citrate 59 $g\,l^{-1}$; conc. phosphoric acid 7.69 $ml\,l^{-1}$; boric acid 10.25 $g\,l^{-1}$; $Co(NO_3)_2\times 6H_2O$ 3.89 $g\,l^{-1}$; 1,4-butyndiol 0.05 $g\,l^{-1}$, and ammonia water to keep pH at 8.5). BPO_4, according to the patent procedure, should be present at the concentration of 17.5 $g\,l^{-1}$. Instead, phosphoric and boric acids at concentration 7.69 and 10.25 $g\,l^{-1}$, respectively, were used [4]. Such a substitution improves considerably the stability of the bath.

The structure of the alloys deposited was determined by X-ray diffraction using a DRON-1 instrument with a cobalt X-ray tube equipped with a CoKL filter. The mean concentrations of Co and W were determined by EDS electron micro-probe spectroscopy using either an JEOL JXA 50A or a CAMECA SX-50 instrument. Optical inspection of the alloy surface was done with a metallurgical microscope, Olympus, type PM3. Cobalt concentrations in the solutions were determined by atomic absorption spectroscopy. The microhardness of the material was tested by measuring the diagonal length of the indentations obtained with a Vickers diamond pyramid. The pressure used in the measurements was 5 g. Micrographs of the indentations were taken with a JEOL JSM-5400 electron scanning microscope.

The plating temperature was maintained at 65°C. Special attention has been paid to protect the substrates against dissolution (Cu) and passivation (Fe). Firstly, the substrates were connected to the galvanostat before entering the bath solution and secondly, the current density was fixed at such a level that hydrogen evolution took place parallel to the plating process. Since the cathode potential under such conditions was −1.3 V versus SCE, and the initial efficiency of the plating process was very low. There was a good chance that the iron surface was not passivated prior to deposition of the amorphous alloy. Volume and pH of the bath were corrected by adding water and ammonia, respectively.

All solutions were made of analytical grade chemicals and distilled water. The samples for the cross-section analysis were prepared from thick (40–50 μm) layers of the alloy by immersing the layers together with the substrate in melted Wood alloy. The samples deposited on copper and iron substrates were placed into melted Wood alloy. After solidification, the samples were cut appropriately and polished: first with sand papers of increasing grade, and finally with diamond paste.

3. Results

A test of the exfoliation of the deposits plated on copper and steel substrates was done first. An analysis of the coverage exfoliation indicated that there was a difference in adhesion of the alloy to copper and steel. It is possible that the different adhesion of the alloy is a result of either the differences in the structure of the substrates or the interactions between the alloy components and the substrate material. The interaction between the substrate material and the alloy component may modify the structure and the composition of the alloy.

Another result of the influence of the substrate properties on the deposition process is the change in the deposition efficiency with time. The increase in weight of the coverage plotted versus deposition time is shown in Fig. 1. A significant difference in efficiency of the deposition (growth rate) of the alloy layers plated on iron and copper during the first hour of the electrolysis is illustrated in Fig. 1. For copper, the efficiency of the electrodeposition of the alloy decreases during the first hour; such a trend is not observed when the iron substrate is plated. A large difference in the shapes of the efficiency plots obtained for copper and iron may be related to a strong interaction between copper and the Co–W alloy. The linear time-dependent increase in weight of the deposit which was reduced on iron. This suggests that there are no strong interactions between iron and the Co–W alloy.

Further analysis of the alloy layers deposited on copper has shown that the irregularities in the deposition efficiency are accompanied by variations in the layer struc-

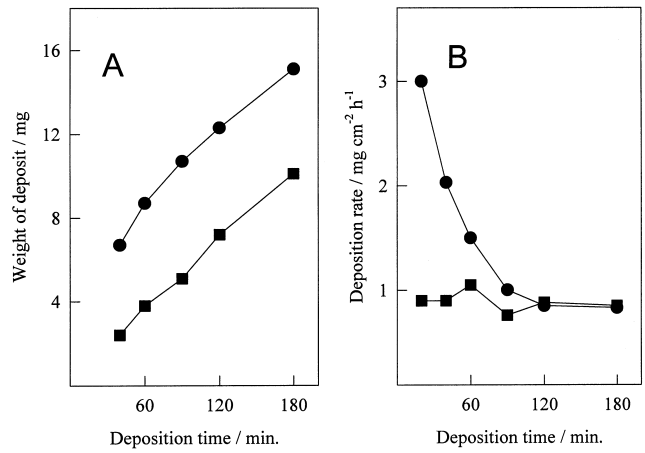

Fig. 1. Electrodeposition of Co–W amorphous alloy on copper and iron substrates. (A) Weight of the alloy deposited on copper substrate (solid line) and iron substrate (dashed line) plotted versus deposition time. (B) Changes in deposition efficiency observed during a three hour period of deposition of Co–W amorphous alloy on copper (solid line) and iron (dashed line).

ture and composition. Fig. 2 presents a micrograph of a scanning electron microscope image of a cross-section of an alloy layer exfoliated from the copper substrate. As it can be seen in the micrograph, the coverage consists of two layers. The inner layer, originally stacked to the copper substrate, consists of smaller ''grains'' and is 2–3 μm thick. The structure of the external layer is more grainy. No similar split in the alloy layer was found for the coverages obtained on the iron substrate.

An EDS examination of the alloy layers exfoliated from both types of the substrates demonstrated that the compositions at the inner and the external surfaces of the layers of the alloy deposited on copper are significantly different. On the other hand, these compositions are very similar for the alloys deposited on iron. The EDS spectra of both sides of the alloy layers plated on Cu are shown in Fig. 3. For the layers deposited on the copper substrate the difference in the tungsten content is significant. The content of tungsten on the external side of the coverage is close to the mean composition of the Co–W alloys (approximately 28 at.%) obtained by electroplating under constant-current conditions. Taking into account that the EDS method collects and processes the data from roughly 1 μm thick layers, the differences in the compositions measured exactly on the surfaces could be larger.

The determination of Co and W contents in cross-sections of the electrodeposited layers of Co–W alloy have been done using the WDS method. A micrograph of a typical cross-section of the alloy prepared for the WDS analysis is shown in Fig. 4. For performing this type of analysis, 30–50 μm thick layers were deposited on both (copper and iron) types of substrates. The results of the WDS cross-section scanning are shown in Fig. 5. It is clear that composition of the layer electrodeposited on iron is constant in function of distance from the substrate surface. Contrary, the composition of the alloy plated on copper differs significantly in the region next to the substrate, compared to the mean values obtained for the external part of the layers. Taking into account the determination uncertainty related to the WDS method and the limitations such as electron beam diameter and volume of the material from which the signals are collected, the agreement between the thickness of the inner layer of lowered tungsten concentration (WDS analysis) and the layer of finer grain shown at the micrograph of Fig. 2 is very good.

The WDS examination, which under applied experimental conditions gave only qualitative results, was followed by the EDS microprobe quantitative analysis. The results of the measurements are given in Table 1. The results of the EDS analysis confirmed that the decrease in the

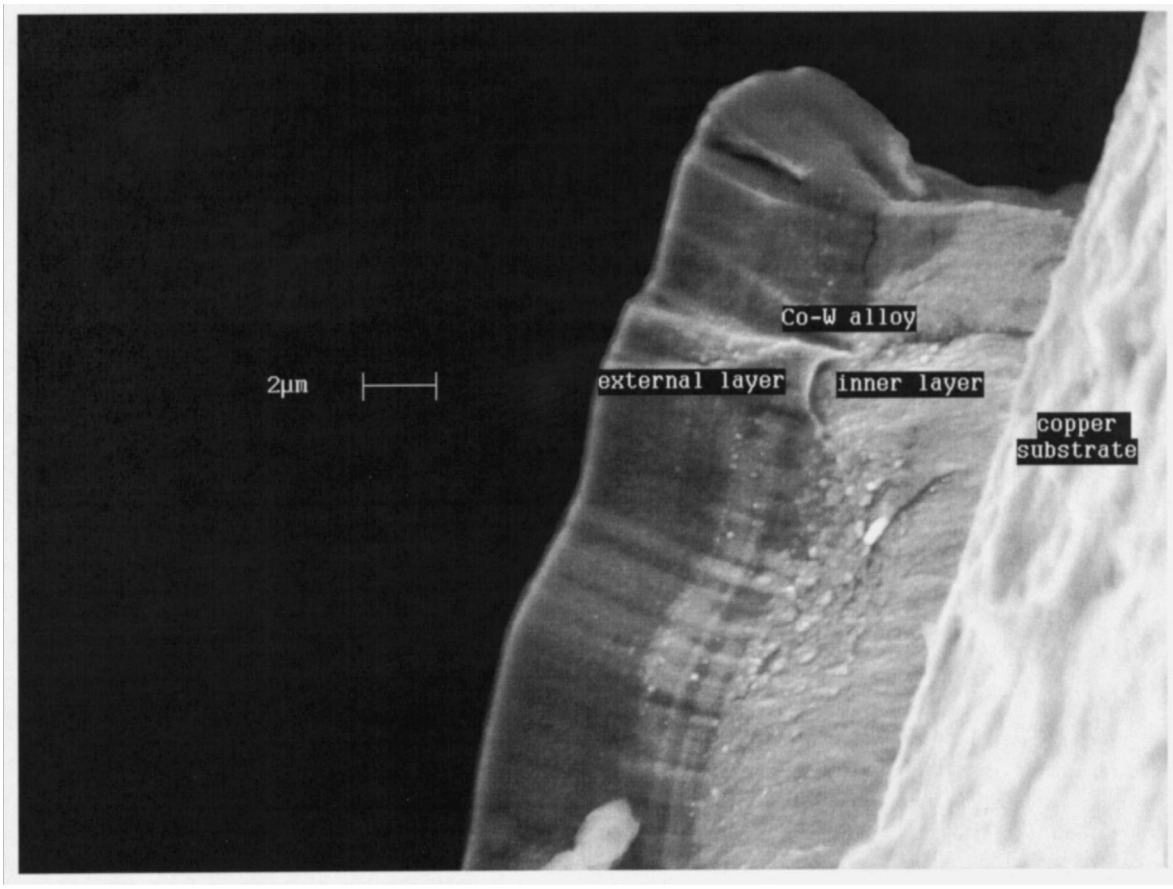

Fig. 2. SEM micrograph of a broken, 8 μm thick Co–W amorphous alloy layer.

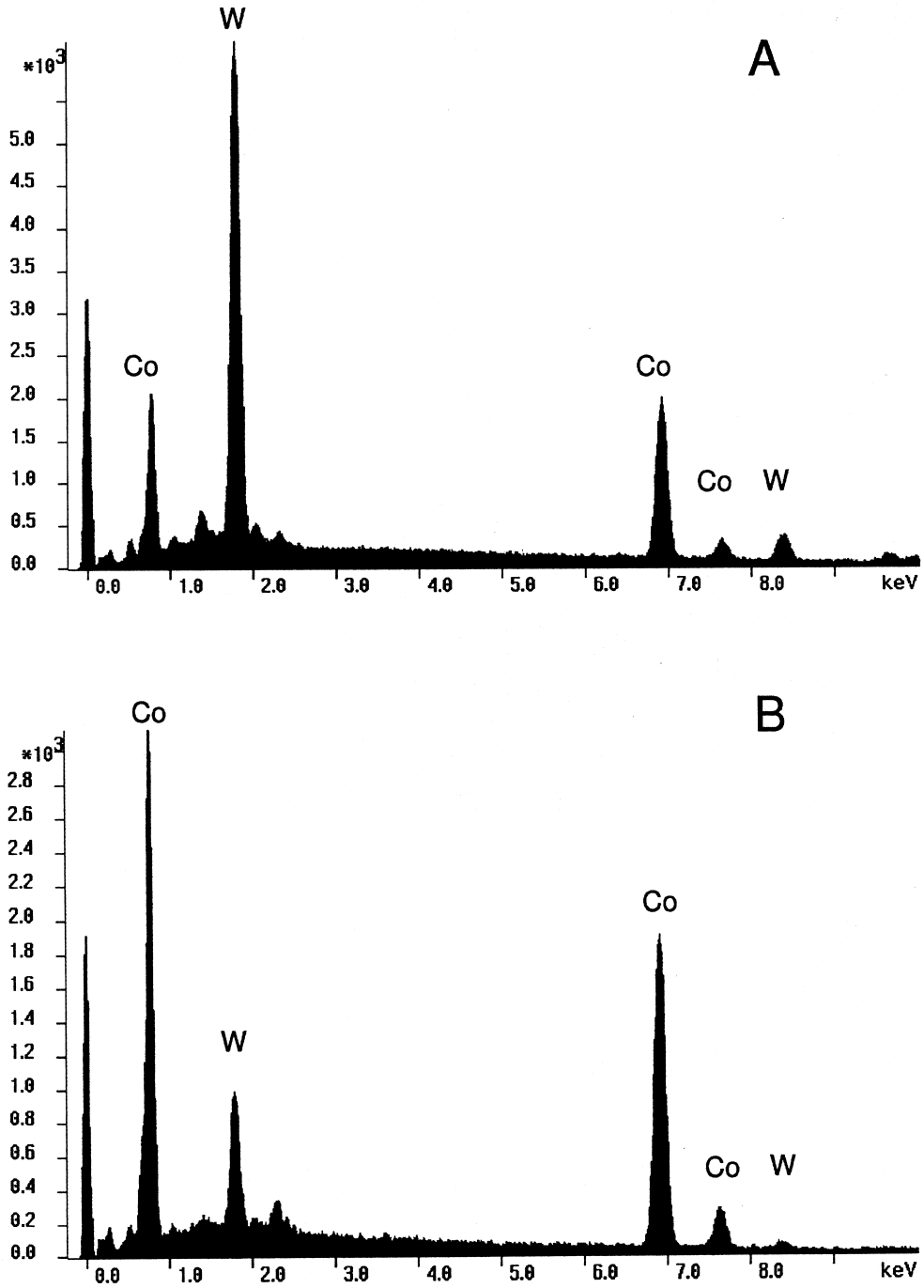

Fig. 3. EDS spectra of solution side (A; W:Co=5.8: 94.2) and substrate side (B; W:Co=27.5:72.5) of Co–W amorphous layer deposited on copper substrate.

tungsten concentration in the region next to the copper substrate is significant. It can not be excluded, that the first monolayers of the deposit plated on the copper substrate consist of almost pure cobalt.

The structure of the alloy layers was examined by the X-ray diffraction spectroscopy using alloy samples of different thickness. This type of analysis also revealed some differences between the deposits obtained on the copper and iron substrates. The X-ray diffractograms obtained for the Co–W alloy layers of various thickness are identical for the alloys deposited on iron. The diffractograms of the Co–W deposits on copper were obtained under the same conditions but their shape changed with a change in alloy layer thickness. For layers thicker than 10 μm, all X-ray diffractograms obtained are identical. The diffraction peak is located at 50.6 degrees (2Θ angle), and the half width equals 5.65 degrees. This broad diffraction peak, typical for an amorphous-substance, changes with

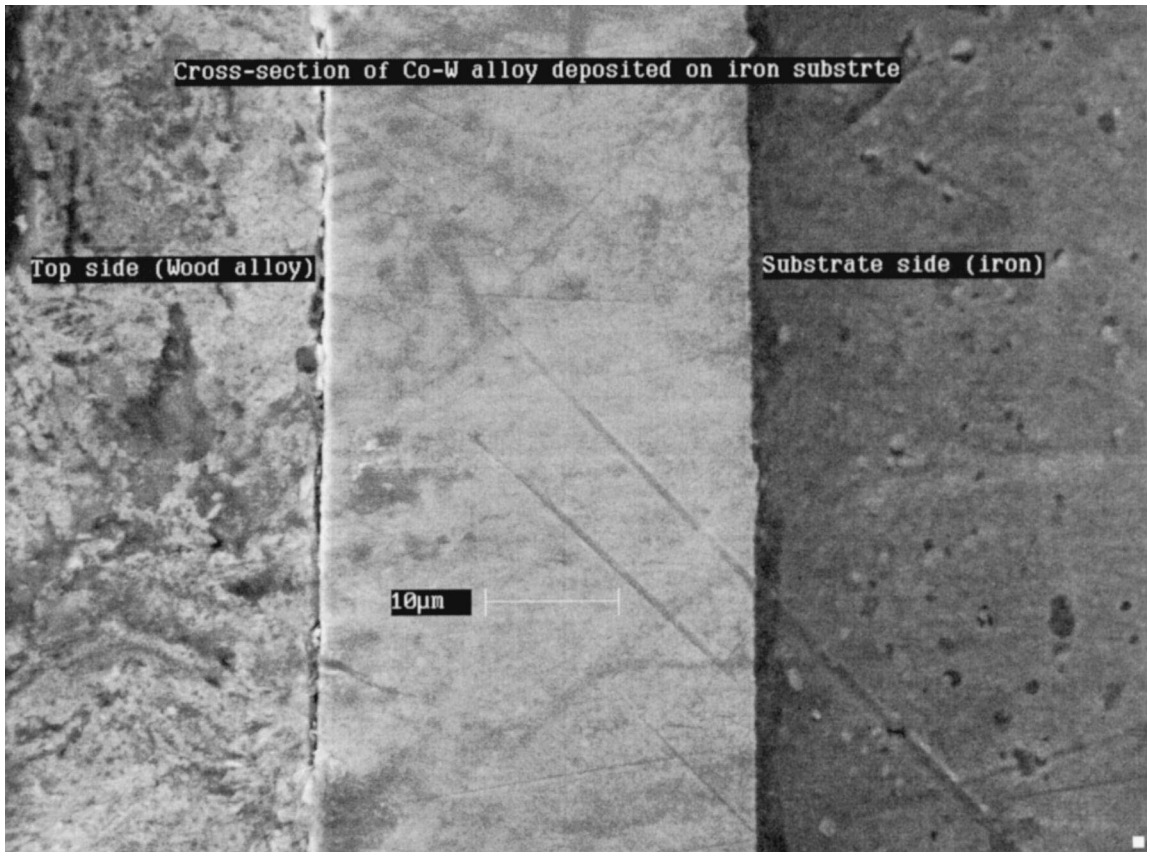

Fig. 4. SEM image of a Co–W amorphous-alloy cross section prepared for EDS/WDS analysis.

decreaseing in layer thickness. Both peak position and peak half width change. Fig. 6 illustrates the regularity of these changes. The half width of the peak increases and the peak position shifts to larger 2Θ values. The appearance of these changes suggests that the distance between metal atoms in the layer next to the copper substrate decreases. The range of the changes of the diffraction peak parameters is in agreement with the electron microscopy observations regarding the structure of the inner layer of the alloy plated on the copper substrate. An increase in half width of the diffraction peak means the the structure of the inner layer is less ordered. A shift of the peak position to larger 2Θ angle observed for the thinner layers can be explained as a decrease of tungsten contents in the part of the layer close to the Cu substrate.

Finally, it is clear that the results obtained by electron microscopy, the WDS/EDS techniques, and the X-ray structure analyses are in good agreement.

4. Discussion

The process of transferring the substrate structure into the materials deposited on that substrate was observed frequently [12,13]. This phenomenon was noticed for vacuum deposition [12,13] as well as for electrodeposition [14] of various materials on many substrates. For a crystalline material the transfer of the substrate structure into the deposit is called epitaxy. Epitaxial layers can be formed when the structure of the substrate is the same as the deposit structure, and the parameters of the lattices are similar [12]. When an amorphous layer is formed on a crystalline substrate, the phenomenon of the influence of the substrate structure on the deposit cannot be exactly the same as for the crystalline deposit, however the existence of some similarities is possible.

The data presented in this paper can not prove that an epitaxial layer is formed. However, the influence of the substrate on the alloy growth is apparent. Structural similarity of the materials, as seen in Table 2, occurs only for cobalt and copper, and this similarity may stand behind the observed changes in the structure and composition within the alloy layers plated on copper. Tungsten and iron have the same crystallographic structure. However, there is a large difference in their lattice constants. This excludes the existence of a serious influence of the iron substrate on the structure and composition of the Co–W alloy.

The almost identical structures of cubic cobalt and copper can explain preferential electrodeposition of cobalt on the copper surface in the early stage of the alloy layer formation. With progress of the process the contribution of the tungsten flux to the total flux increases. Taking into

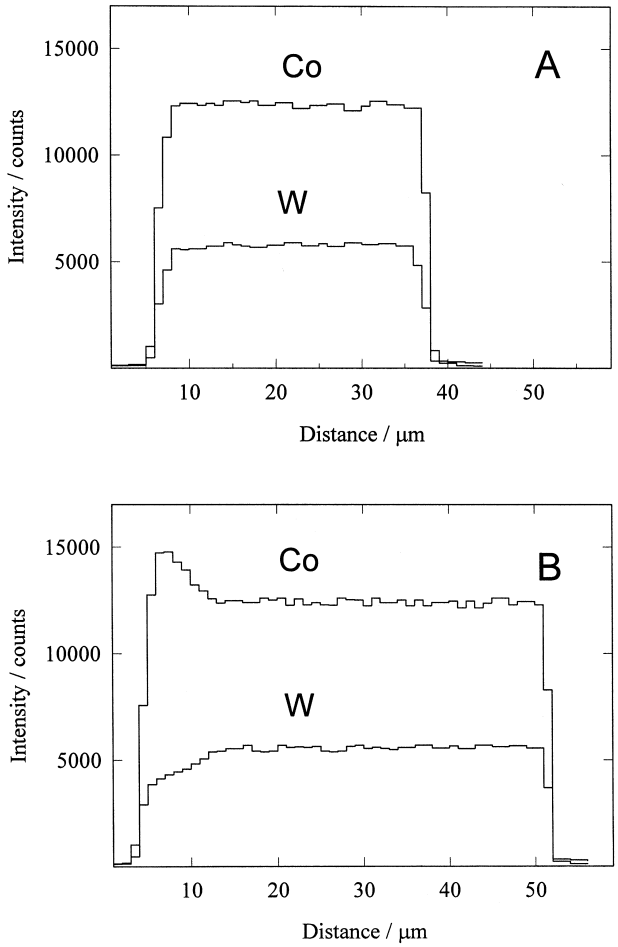

Fig. 5. WDS spectra of cross-sections of Co–W amorphous alloy deposited on iron (A) and copper (B).

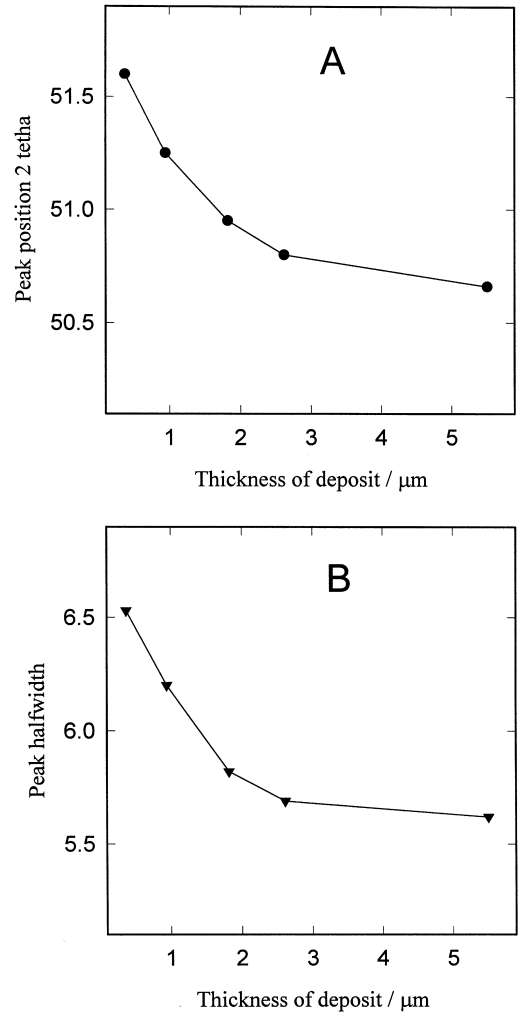

Fig. 6. Dependence of X-ray diffraction peak position (A) and half width (B), for Co–W amorphous alloy, plotted versus layer thickness. The layers were deposited on the copper substrate.

account the fact that the metallic radius of the tungsten atom is significantly larger than that of the cobalt atom, it is apparent that an increase in tungsten content in the deposit leads to an appropriate increase in the mean distance between the atoms in the alloy. This effect is portrayed in the X-ray diffractograms as a decrease in the 2Θ angle. An increase in the amount of tungsten in the growing layer influences the order in the layer. A discussion about the structure of the amorphous alloys seems to be illogical at first. However, these alloys are not ideally amorphous. If they were, the X-ray diffractograms would not be seen at all. We believe that the amorphous Co–W alloys are in fact alloys with a heavily distorted cobalt lattice. At the composition close to 25 and 75 at.% of Co and W, respectively, a kind of seriously deformed Co_3W

Table 2
Crystallographic structures of Cu, Co, Fe and W

Lattice parameters	copper	cobalt	iron	tungsten
Structure	cubic	cubic	cubic	cubic
Space group	*Fm3m*	*Fm3m*	*Im3m*	*Im3m*
Lattice constant	3.615Å	3.545Å	2.866Å	3.165Å

Table 1
Results of EDS microprobe analysis of Co–W amorphous alloy layers deposited on copper and iron

Position	Fe substrate		Cu substrate	
	Co (at.%)	W (at.%)	Co (at.%)	W (at.%)
substrate side	71.7	28.3	94.2	5.8
at substrate edge	70.7	29.3	81.1	18.9
2 μm from substrate edge	69.8	30.2	77.8	22.2
5 μm from substrate edge	70.1	29.9	71.3	28.7
15 μm from substrate edge	69.7	30.3	70.8	29.2

lattice may be formed instead of a solid solution of tungsten in cobalt. The formation of this lattice should lead to an increased atomic order in the layer and to a decrease in half width of the diffraction peak for thicker layers, which is really observed.

All observations made indicate that during the electrodeposition of the Co–W amorphous alloy on copper a transition layer with modified composition and structure is formed on the copper surface. The existence of this transition layer improves the adhesion of the alloy to the substrate. When this type of layer is not formed the deposit can relatively easily be separated from the substrate, as it happens in the case of the alloy deposition on iron. The steps undertaken during the electroplating procedure, and described in the experimental section, rather eliminate the possibility that the differences obtained for the Fe and Cu substrates are due either to passivation of iron or dissolution of Cu in the hot electrolyte. An influence of the hydrogen dissolved in the substrate, as it has been reported for Ni–Mo alloys [15], can also be dismissed in the Cu and Fe cases.

The results of the experiments confirmed the practical observation, that the deposition of crystalline Co–W alloys on steel is easier when it is proceeded by plating a thin copper layer on the steel surface [1].

Acknowledgements

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