

MODIFICATION OF THE Cu-ETP COPPER SURFACE LAYER WITH CHROMIUM BY PHYSICAL VAPOR DEPOSITION (PVD) AND DIFFUSION ANNEALING

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In the study, an attempt was made to increase durability of copper by creating a surface layer saturated or supersaturated with chromium only in the area of the highest thermo-mechanical loads during the welding process. There was developed a two-stage technological process, consisting of: application of chrome coating of the thickness approx. 1 μm on the Cu-ETP copper surface using the PVD method, and then performing the process of its diffusion by annealing at a temperature of 950 $^{\circ}\text{C}$ in the vacuum. As a result, a diffusion CuCr layer with a thickness of approx. 20 μm was obtained, with hardness of approx. 120 HV0,01.

Keywords: Cu-ETP and Cu-OF copper, surface, CuCr layer, PVD, annealing, x-ray analysis, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS)

INTRODUCTION

Chromium copper contains no more than 0,5-1 wt.% of Cr. Small amounts of chromium added to copper significantly boost its strength and technological properties. One of the most important features of chromium copper is its ability to maintain strength properties obtained by dispersion, hardening up to a temperature of approx. 400 $^{\circ}\text{C}$. High hardness and slightly lower electrical conductivity make chromium copper suitable for point electrodes used in spot welding or shielding electrodes used in welding, thus replacing pure copper. This has resulted in an increase in durability of spot welding electrodes, which is one of most important technological issues, especially in relation to welding galvanized sheets, mainly in the automotive industry [1-3].

Currently sought after are the possibilities of increasing the functional properties of copper and copper alloys through the use of intensive plastic working methods or introduction of alloying additives which refine the microstructure [4-7].

In the study, an attempt was made to increase durability of copper by creating a layer saturated or supersaturated with chromium (chromium bronze) only on its surface in the area of the highest thermo-mechanical loads during the welding process. It was assumed that the diffusively produced chromium-rich coating would increase the surface hardness whilst maintaining good adhesion to the substrate. There was developed a two-stage technological process, consisting of: application of chrome coating on the Cu-ETP copper surface using

the PVD method, followed by performing the process of its diffusion annealing at a temperature of 950 $^{\circ}\text{C}$.

The homogenization annealing process of CuCr alloy copper (most often produced by casting and cold or hot plastic working) is usually carried out in the temperature range from approx. 950 to 1 000 $^{\circ}\text{C}$. It was assumed that carrying out the heat treatment process in this temperature range would enable dissolution of chromium in the copper solid solution and would also cause its partial supersaturation. The annealing process was carried out in air and in a protective atmosphere.

EXPERIMENTAL PROCEDURE

Chromium coatings on Cu-ETP and Cu-OF copper substrate were deposited in the process of physical vapour deposition in a vacuum chamber, under pressure of 1 Pa, using nano PVD apparatus from Moorfield Nanotechnology. There were produced pure chromium coatings with a thickness of approx. 0,5, 1,0, and 2,0 μm (Figure 1). Prior to the process, the surface of the samples was polished using MD-Mol polishing cloths and 9,6, and 3 μm polycrystalline DP-type diamond suspen-

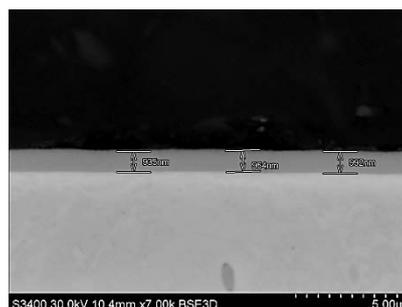


Figure 1 Cross-section of the chromium coating applied on Cu-ETP by the PVD method

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sions from Struers. The polished samples were washed in ultrasonic cleaner in isopropyl alcohol for 5 minutes and then placed in the working chamber of the PVD device. A target containing 99,95 wt. % of chromium was used as the source of chromium in the process.

Adhesion of the chromium coating to the CuETP copper substrate was determined by the “scratch-test” method. Scratching was performed with a load increasing from 0,9 N to 10 N in 30 seconds, over a distance of 5 mm, with simultaneous recording of acoustic emission signal and friction force. The analysis of these values showed that the critical load for the chromium coating was 1,5 N. In the next stage of the research, the samples were subjected to diffusion annealing process at 950 °C for 1 h using the Vacuum Heat Treatment Mono Therm HK.446.N.20.gr furnace in order to introduce chromium atoms into the copper crystal lattice. Two variants of the annealing were applied – first in the air at atmospheric pressure and second in high vacuum (Table 1).

Table 1 **Conditions of the diffusion annealing processes for Cu-OF and Cu-ETP**

Thickness of Cr coating / μm	Substrate	Temperature / $^{\circ}\text{C}$	Time / h	Pressure / Pa	Atmosphere
1	Cu-ETP	950	1	10^5	Air
		950	1	10^{-3}	Vacuum
0,5	Cu-OF	950	2	10^{-3}	Vacuum
2,0				10^{-3}	Vacuum

It was found that the annealing process in the air atmosphere of Cu-ETP copper with chromium coatings with thickness of 1 μm , led to formation of a copper oxide layer Cu_2O with thickness of approx. 20 μm on the copper surface as a result of oxidation processes and in its subsurface zone (as a result of internal oxidation and simultaneous inward oxygen diffusion). Formation of oxygen and chromium enriched crystals in the near-surface zone was also observed, especially at the grain boundaries of copper (Figure 2, Table 2). Their pres-

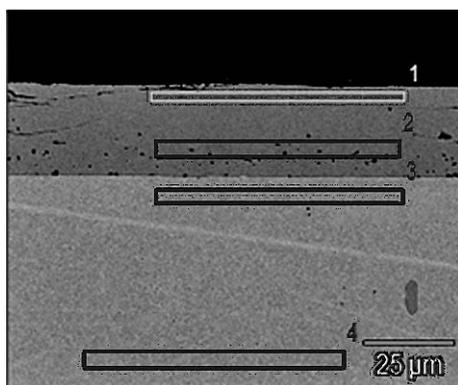


Figure 2 Cross-section of Cu-ETP copper surface layer (SEM) following the high temperature diffusion annealing process at 950 °C/1 h. The microstructure of the oxide layer formed due to the oxidation process is visible.

Table 2 **Chemical composition determined by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) in micro-areas of the surface layer and near-surface zone of Cu-ETP copper after its annealing at 950 °C/ 1 h in air**

Micro-area (Figure 2)	Element content			
	/ wt. %		/ at. %	
	O	Cu	O	Cu
Pt 1	11,20	88,8	33,3	66,7
Pt 2	11,20	88,8	33,3	66,7
Pt 3	-	100,0	-	100,0
Pt 4	-	100,0	-	100,0

ence may result both from oxidation caused by inward diffusion of atmospheric oxygen, and also as a result of the reaction of diffusing chromium atoms with oxygen atoms dissolved in the copper matrix.

As a result of the use of a protective atmosphere during the annealing of Cu-ETP copper at 950 °C/1 h, a diffusion CuCr layer with a thickness of approx. 20 μm was obtained on its surface (Figure 3, Table 3) having hardness of 120 HV0,01 while a substrate hardness was 50 HV1. Chromium diffused into the substrate, dissolved in the copper matrix and formed a saturated copper solid solution. As a result of further saturation of copper with chromium, crystals rich in chromium and oxygen were formed from the super-saturated solid solution.

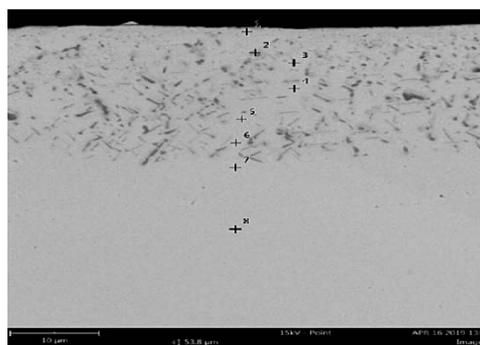


Figure 3 Cross-section of Cu-ETP copper: a) PVD chrome plating; b) diffusion layer formed as a result of chromium diffusion from the coating during annealing at 950 °C/1 h in a protective atmosphere.

Table 3 **Chemical composition (SEM-EDS) in micro-areas of the chromium diffusion layer produced on the Cu-ETP copper substrate in the PVD process and then annealed at 950 °C/1 h (Figure 3)**

Micro-area (Figure 3)	Element content					
	/ at. %			/ wt. %		
	Cu	Cr	O	Cu	Cr	O
1	74,01	4,92	21,06	88,80	4,83	6,36
2	15,85	15,81	68,34	34,46	28,1	37,41
3	99,43	0,57	-	99,53	0,47	-
4	99,54	0,46	-	99,63	0,37	-
5	99,47	0,58	-	99,57	0,43	-
6	99,58	0,47	-	99,62	0,38	-
7	100,0	-	-	100,0	-	-
8	100,0	-	-	100,0	-	-

Table 4 **Vickers hardness of the chromium diffusion layer produced on the Cu-ETP copper substrate in the PVD process and then annealed at 950 °C/1 h**

Vickers scale	Vickers hardness	
	Layer	Substrate
HV0,01	119	-
HV0,02	112	-
HV1	-	50

Then, in accordance with the same methodology as for the PVD chromium coatings produced on the Cu-ETP copper substrate, there were performed annealing processes of Cu-OF copper at the temperature of 950 °C and for 2 hours with the deposited chromium coatings with thickness of 0,5 µm and 2 µm.

As a result of the diffusion annealing process in a high vacuum (0,0133 Pa) at 950 °C/2 h of chromium coatings deposited on the surface of the Cu-OF oxygen-free copper, an outer coating consisting of copper and chromium was obtained. The thickness of the PVD chromium coating did not change during the diffusion annealing, but as a result of outward diffusion of copper from the substrate, a copper-enriched chromium coating was formed (unlike in the case of electrolytic copper containing significantly more oxygen) (Figures 4-7 Tables 5-6).

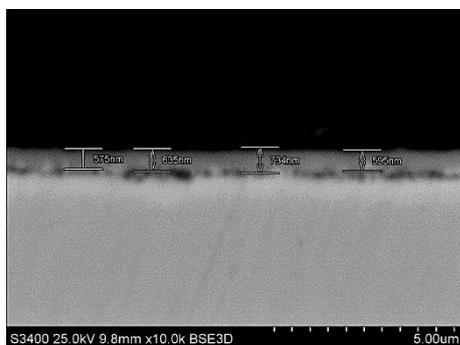


Figure 4 Cross-section (SEM) of Cu-OF copper with a chromium coating with thickness of 0,5 µm – thickness of the coating following the high vacuum annealing process at 950 °C/2 h is marked

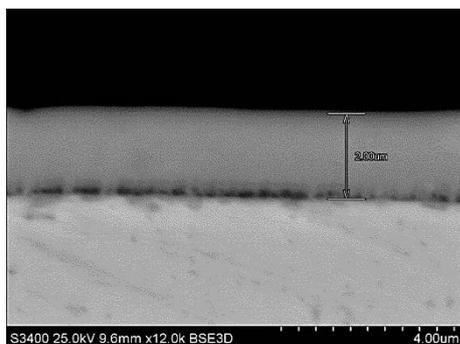


Figure 5 Cross-section (SEM) of Cu-OF copper with a chromium coating with thickness of 2,0 µm – thickness of the coating following high vacuum annealing process at 950 °C/2 h is marked

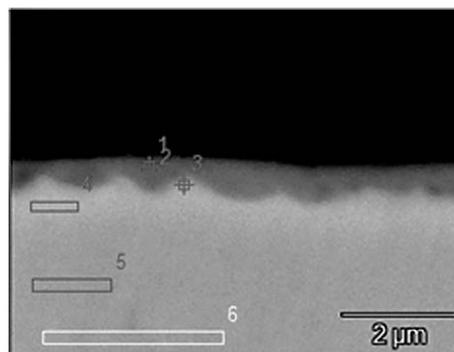


Figure 6 Cross-section (SEM) of Cu-OF copper with a 0,5 µm PVD chromium Cu-enriched coating after high vacuum annealing at 950 °C/2 h, with marked areas of SEM-EDS microanalysis (Table 5)

Table 5 **Chemical composition (SEM-EDS) in micro-areas of the chromium Cu-enriched coating (Figure 6)**

Micro-area no.6	Element content	
	Cr / wt. %	Cu / wt. %
1	76,1	23,9
2	70,2	29,8
3	54,6	45,4
4	23,7	76,3
5	1,1	98,9
6	0,8	99,2

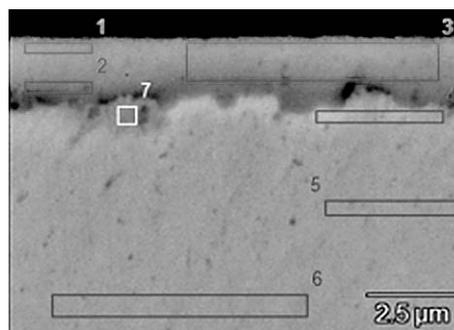


Figure 7 Cross-section (SEM) of Cu-OF copper with a 2.0 µm PVD chromium Cu-enriched coating following high vacuum annealing at 950 °C/2 h, with marked areas of SEM-EDS microanalysis (Table 6).

Table 6 **Chemical composition (SEM-EDS) in micro-areas of the chromium Cu-enriched coating (Figure 7)**

Micro-area no.	Element content	
	Cr / wt.%	Cu / wt.%
1	97,4	2,6
2	83,8	16,2
3	94,4	5,5
4	18,9	81,1
5	1,0	99,0
6	0,7	99,3
7	27,0	73,0

RESULTS AND DISCUSSION

As a result of the research, it was found that the diffusion annealing processes (carried out in the air atmosphere) of PVD chromium coatings produced on the

copper substrate, led to formation of a Cu_2O oxide layer on its surface, as a result of internal oxidation processes. As a result of the simultaneous inward diffusion of oxygen and chromium, there was observed formation of crystals enriched in oxygen and chromium in the near-surface zone, especially at the boundaries of copper grains. It was found that as a result of the diffusion annealing process under high vacuum conditions (at 10^{-3} Pa pressure) of Cu-ETP copper with a chromium coating deposited using the PVD method, a diffusion CuCr layer with thickness of approx. 20 μm and hardness of approx. 120 HV0,01 was obtained, while hardness of the copper substrate was about 50 HV1. During annealing, chromium diffused inward into the substrate, dissolved in the copper matrix and formed a saturated copper based solid solution. As a result of the further diffusion process and saturation of the copper matrix with chromium, crystals rich in chromium and oxygen were formed from the supersaturated solid solution.

CONCLUSIONS

Analysis of the results of the studies indicates that in order to obtain diffusion surface layer enriched with chromium on the copper sample, electrolytic copper should be used as a substrate rather than oxygen free grade – solubility of chromium in copper is a function not only of temperature but also of oxygen content. In the electrolytic copper of the Cu-ETP grade oxygen content can reach 400 ppm, which is even a several hundred higher value than in the oxygen-free Cu-OF grade (usually < 5 ppm). Therefore, because of high chemical affinity of chromium for oxygen inward diffusion of chromium atoms is facilitated and internal oxidation of chromium results in formation of fine dispersed crystals build of oxygen, chromium and copper. They are located both inside copper grains – with a diameter of several dozens of nanometers – and on the grain boundaries – with diameter of several hundreds of nanometers [7,8]. The conclusion was drawn that appropriate oxygen content in the copper facilitates diffusion of chromium atoms into the substrate.

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