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Indentation hardness and modulus of electrochemically deposited triple protective-decorative Cu-Ni-Cr system

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Abstract. With respect to the corrosion-protective and decorative characteristics of the Cu-Ni-Cr systems the advance of the technology resulted in products covering the required technical and economic norms and indicators. However, the knowledge about the mechanical characteristics such as elastic and plastic properties of the individual layers and the whole multilayered system is still sparse. The objective of this study is to obtain by means of nanoindentation experiments the mechanical characteristics of standard triple Cu-Ni-Cr coating system whose morphology, structure, texture, composition, and the copper-, nickel- and chrome-layer thickness are predefined. A series of nanoindentation tests in vertical direction to the layered coating and in the lateral direction (along a vertical cut) is analyzed to assess the changes of the mechanical properties of the investigated system in depth and along the layer as well as at layer-to-layer and layer-to-substrate interfaces.

1 Introduction

Multi-layered protective-decorative Cu-Ni-Cr systems became well accepted after an operating period of over 90 years [1-3]. Nowadays this type of systems is widely recommended by national and international standards being an inherent component in the automated production lines for plating with application to the motor-car construction and other branches of the modern engineering industry.

With respect to the corrosion-protective and decorative characteristics of the Cu-Ni-Cr systems the advance of the technology resulted in products covering the required technical and economic norms and indicators. However, the knowledge about the mechanical characteristics such as elastic and plastic properties of the individual layers and the whole multi-layered system is still sparse.

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The plating process involves specific organic and non-organic agents to the electrolytes resulting in co-deposition of these additives (S, C, N, P, H, etc.) into the metallic layers and their embedding in the metal lattice. This leads to lattice deformation and severe deviation of the mechanical and physical properties of the metal layers as compared to their metallurgically obtained counterparts. This may lead to high internal stresses in and between the layers, degradation of the adhesion of the coating to the substrate as well as between the coating layers themselves, unexpected and unwanted changes in the hardness and the wear resistance. In this context, the objective of this study is to obtain by means of nanoindentation experiments the mechanical characteristics of standard triple Cu-Ni-Cr coating system whose morphology, structure, texture, composition, and the copper-, nickel- and chrome-layer thickness are predefined. A series of nanoindentation tests in vertical direction to the layered coating and in the lateral direction (along a vertical cut) is analysed to assess the changes of the mechanical properties of the investigated system in depth and along the layer and layer-to-substrate interfaces.

2 Experimental

2.1 Materials and coating process

The multilayer Cu-Ni-Cr system was obtained by consecutive electrodeposition on a steel substrate of each of the individual copper, nickel and chromium layers. The working specimens were of rectangular form with sizes 3 x 6 cm, and the substrate samples were cut from 08KP steel sheet with a thickness of 1 mm. All samples were subject of standard chemical degreasing in organic solvent and inorganic solution followed by etching and surface activation in aqueous solution of HCl [1-3].

These pre-treatment operations of the steel substrate were completed with a deposition of a very thin copper layer from cyanide electrolyte in order to ensure the necessary adhesion for the multilayer system to the steel substrate.

The ultrafine crystalline copper layer was deposited in an electrolyte whose composition was: $CuSO_4.5H_2O$ − 220 g/l; H_2SO_4 − 50g/l; NaCl – 0.090g/l; Brightening additive THB-6-II [4] – 5 ml/l. Elliptic phosphorus-containing (0.07 wt.%) copper anodes were used. The electrolyte temperature was 25°C. The standard two-electrode electrochemical working cell in which the electrolysis was carried out was equipped with an air-agitating device for the electrolyte. The air-agitating was performed with specially purified compressed air, supplied at a rate of 13 $m^3/m^2/h$. The cathode current density was 4.5 A/dm^2 and the thickness of the obtained bright copper layer was ~8.92 μm. The electrochemically obtained ultrafine crystalline copper layer is characterized by a mirror reflective surface (96% vs. Silver mirror).

The deposition of the bright nickel layer was performed electrochemically by cathodic deposition using working electrolyte with the following composition: $NiSO_4.7H_2O$−270 g/l; $NiCl_2.6H_2O$−70 g/l; H_3BO_3 – 40 g/l; saccharin - 1.1 g/l; butanediol - 0.3 g/l, at a pH ~ 4.5. The working temperature was 55°C. Rolled de-passivated sheet nickel with a purity of 99.7% was used for the soluble anodes. The electrochemical deposition was performed in an analogous standard two-electrode electrochemical cell at cathode current density of 5 A/dm^2 and air agitation of the electrolyte. The thickness of the obtained bright nickel layer was ~19.6 μm.

The deposition of the chromium layer was performed electrochemically by cathodic deposition using a working electrolyte with the following composition: CrO_3−250 g/l; H_2SO_4 – 2.5 g/l. The working temperature was 55°C. In this case unsoluble Pb anodes were employed. The electrochemical deposition was performed in an analogous standard two-electrode electrochemical cell at cathode current density of 12 A/dm^2. The thickness of the obtained chromium layer was ~0.234 µm.

2.2 Characterization

The surface morphology and the structure of the obtained coatings were investigated by JEM 200-CX scanning electron microscopy in secondary electron imaging regime (SEI). The texture of the coating system was studied by Philips X-ray diffractometer. The micro profile of the samples was analysed with Perthen profilometer. The interpretation of the nanoindentation data rely on the information about the thickness of the layers obtained using X-ray fluorescence analysis (FISHERSCOPE X-RAY XDVM).

2.3 Sample IPC-3-6

Figure 1 depicts the sample IPC-3-6 and the area where the indentations were done can be seen there marked with black dots.

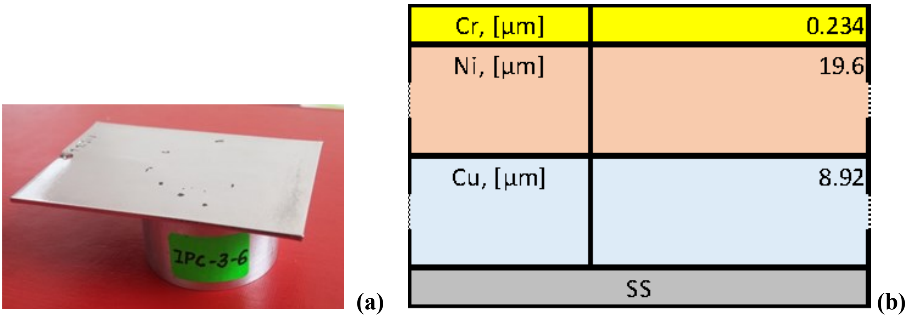

Fig. 1. (a) Sample IPC-3-6 mounted on the punch; (b) sketch of the cross section.

2.4 Sample IPC-4-4 (cross section of IPC-3-6)

Figure 2a presents schematically the way the sample IPC-3-6 had been cut in order to prepare probes for depth-sensing indentation tests along the sample cross section. The red cut side in Fig. 2a indicates the cut used to prepare sample IPC-4-4, while the solid black line shows the side used to prepare sample IPC-1-1. The mechanical properties of the Cu layer, the interface between the Ni and Cu layers and the steel substrate were investigate using this sample IPC-4-4 and IPC-1-1. Here we will discuss only the tests and the results obtained using sample IPC-4-4.

3 Nanoindentation

The mechanical properties of the obtained triple-layer protective-decorative coating and of the 08KP steel substrate were investigated by depth-sensing nanoindentation at room temperature, using Nano Indenter G200 (Keysight Technologies, USA) with a sharp diamond Berkovich tip. The geometrical characteristics of the tip are: centerline-to-face angle 65.3°◦ and a rounding radius of 20 nm. The maximum load that can be applied is 500 mN. The recording resolution for displacement is 0.01 nm and for the load is 50 nN.

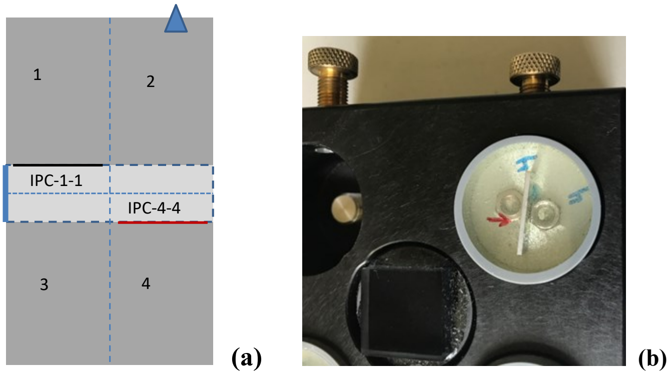

Fig. 2. Cutting scheme for obtaining the cross section samples;(b) sample IPC-4-4 in the tray.

3.1 Indentation methods and experimental program

The basic indentation methods employed in this study are Hardness, Modulus via Cyclic Load Control and Basic Hardness, Modulus at a Depth. For all test the unloading was set to be up to 90% of the reached maximum load. The thermal drift effects were corrected for each test using a holding segment before the indentation and after unloading up to 90% of the maximum applied load. The Poisson ratio was predefined to be equal to 0.25. Basic input parameters, used in this indentation method are given in Table 1. The loading programs were selected based on observations and employing the following experimental design strategy. First the loading programs A (load control) and E (displacement control) were applied to the top of the sample (sample IPC-3-4). This way the maximum penetration depth and the force to have maximum displacements not exceeding 25% of the thickness of the upper Cr-layer were determined. It has been taken into account that because of the surface roughness indentation tests below 50 nm penetration depth are not reliable. The average force applied to have a penetration of the indenter ~50 nm (program D) when performing nanoindentations on the top of the examined multi-layer system under the program E was afterwards used to test the response to the indenter penetration of each of the layers. This ensure for having reliable comparison of the mechanical properties. The cyclic loading test programs B and C allow of obtaining the indentation hardness and modulus at various depths from a single indent, from where the variation of these two parameters can be analysed.

Table 1. Input parameters for the experimental programs

Input parameter	unit		Programs			
		A	B	C	D	E
Max Load	mN	500	200	500	1.5	n/a
Number of Times to Load	-	1	10	3	1	n/a
Time to Load	s	10	10	10	10	n/a
Strain Rate Target	1/s	n/a	n/a	n/a	n/a	0.05
Depth Limit	nm	n/a	n/a	n/a	n/a	50

The indentation tests on sample IPC-3-4 consist of 10 indentations under program E, 9 indentations under each of the programs A and B, while the tests performed on sample IPC-4-4 followed the program D (16 indents for the Ni layer and 16 indents for the Cu layer) and the program C (total 17 indents including indents along the Ni and Cu layers, at the interface between them and 9 indents in the steel substrate). The distance between the indents varies but was not less than 20 µm insuring the independent measurements of the deformation at each particular indentation test.

3.2 Nanoindentation results

Figure 3 shows the load-displacement curves (P-h curves) and the imprint images for testing programs A and B (sample IPC-3-6, indentations from the top of the multi-layer system) and C (indentations along the cross section of the multi-layer system - sample IPC-4-4). The indentation data from the tests at the top and in the cross section of the Ni layer show very small scatter indicating the high homogeneity of the Ni layer. The average maximum displacements that can be achieved applying the maximum load of 500 mN to the top of sample IPC-3-6 is 1800 nm. Therefore, considering the thickness of the Ni-layer (~19.6 µm) it is not possible to investigate the properties of the whole multi-layer system using indentation tests from the top of sample IPC-3-6. This is the reason to cut the sample and to prepare samples (Fig. 2b) allowing to perform indentations along the cross section of the triple layer system (IPC-4-4).

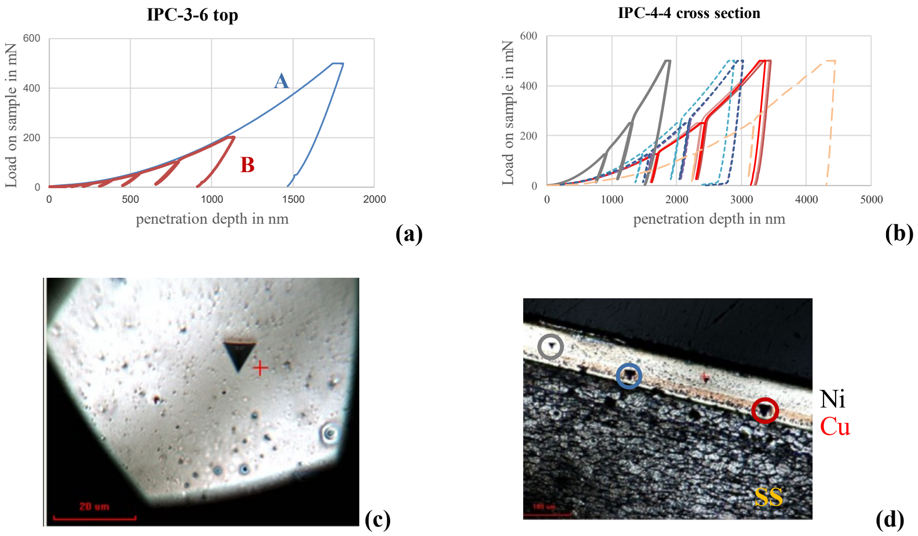

Fig. 3. P-h curves after programs (a) A (sample IPC-3-6) and (b) C (sample IPC-4-4). Imprint images: (c) sample IPC-3-6 (1000x) and (d) sample IPC-4-4 (250x).

The resulting load-displacement curves after indentation tests along the cross section of the layered structure are shown in Fig. 3b, where the black curve represents test data from indentations in the Ni-layer, red curves are from tests in the Cu-layer, blue dashed curves give the response of the interface between the Ni- and Cu- layers and the orange curve depicts the results from the tests in the steel substrate.

The series of nanoindentation tests on the top of the triple protective system (program E) aims to evaluate the mechanical properties of the upper very thin Cr-layer. Figure 4 depicts representative load-displacement curves showing the scatter observed in these test data. The reason for this scatter can be the roughness and the thermal drift correction.

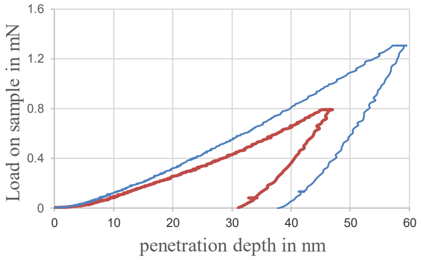

Fig. 4. Load-displacement curves for depths ~25% of the Cr layer's thickness (sample IPC-3-6).

The comparison between the indentation modulus and hardness of the three layers is illustrated in Fig.5. The indentation modulus and hardness are calculated based on Oliver&Pharr approximation method [5] and using for the Ni and Cu layers the data from indentation tests at different locations along the cross section of the layered coating employing the experimental program D, while for the Cr-layer the data from on-top indentions under program E were used. Therefore, the mechanical characteristics of the different layers are determined and compared for an average indentation force of 1.5 mN.

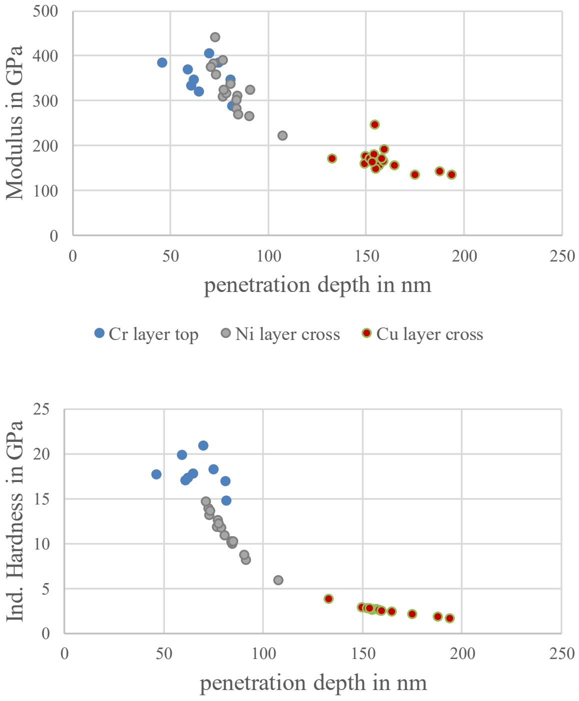

Fig. 5. Indentation modulus and hardness for Cr-, Ni- and Cu-layers at maximum load of 1.5 mN.

Conclusion

In conclusion, nanoindentation measurements were performed on Cr-Ni-Cu triple layered protective coating. In order to assess the mechanical characteristics of all of the layers, the specimen of the coated steel plate was cut and a sample was prepared to allow nanoindentation tests along the cross section of the multi-layered system. A series of nanoindentation tests employing four different experimental programs was performed and the indentation data was used to calculate the indentation modulus and hardness of each of the layers composing the multi-layered coating. The average value of the Cr-layer's nanohardness is superior compared to the corresponding hardness measure for the other two layers. The indentation modules of the Cr- and Ni layers have similar values, while the indentation modulus of the Cu-layer is almost twice lower.

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