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COMPOSITES THEORY AND PRACTICE

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NANOCRYSTALLINE Ni/Cu MULTILAYER COMPOSITE COATINGS

The paper presents the study of multilayer nanocrystalline Ni/Cu coatings produced by the electrocrystallization method on a carbon steel S235JR substrate. Three variants of multilayer nickel/copper coatings of various thicknesses and quantities of the individual layers of nickel and copper were tested. The coating properties were characterized using the following research techniques: X-ray diffraction (XRD), transmission (TEM) and scanning (SEM) electron microscopes, optical microscopy and Vickers microhardness measurements. The paper presents the results of the structure, morphology, surface topography and microhardness measurements of multi-layer nanocrystalline Ni/Cu composite coatings. The produced coatings have a nanocrystalline structure, compact structure, good adhesion to the substrate and a uniform thickness over the entire coated surface. The thickness of the single layers of nickel and copper has an effect on the hardness of the multilayer Ni/Cu composite coatings.

Keywords: Ni/Cu multilayers, nanocomposites, electrocrystallization

WARSTWOWE POWŁOKI KOMPOZYTOWE Ni/Cu O STRUKTURZE NANOKRYSTALICZNEJ

Przedstawiono wyniki badań nanokrystalicznych multiwarstwowych powłok Ni/Cu wytworzonych w procesie elektrokrystalizacji na podłożu ze stali węglowej S235JR. Badano trzy warianty wielowarstwowych powłok nikiel/miedź o różnej grubości oraz ilości pojedynczych warstw niklu i miedzi. Wytworzone powłoki charakteryzowano za pomocą następujących technik badawczych: dyfrakcji promieniowania rentgenowskiego (XRD), transmisyjnej (TEM) i skaningowej (SEM) mikroskopii elektronowej, mikroskopii optycznej oraz pomiarów mikrotwardości metodą Vickersa. Przedstawiono wyniki badań struktury wytworzonych multiwarstwowych kompozytowych Ni/Cu powłok, ich morfologii i topografii powierzchni oraz wyniki pomiarów mikrotwardości. Badane wielowarstwowe powłoki kompozytowe charakteryzują się nanokrystaliczną strukturą, zwartą budową, dobrą adhezją do podłoża oraz równomierną grubością na całej pokrywanej jego powierzchni. Grubość pojedynczych warstw niklu i miedzi ma wpływ na twardość wytworzonego materiału kompozytowego.

Słowa kluczowe: multiwarstwy Ni/Cu, nanokompozyty, elektrokrystalizacja

INTRODUCTION

The electrocrystallization method is one of the main techniques used in surface engineering for the production of metal coatings. The relatively simple technology, low cost and the ability to produce coatings with a different composition and different properties enable this technique to be still used successfully. Surface layers formed by electrocrystallizaton processes are compact, exhibit good adhesion to the substrate, demonstrate uniform thickness over the entire coated surface and provide good protection of the substrate against corrosion [1-7]. Forming a layer composed of alternating layers of nickel and copper may be interesting for the magnetic properties of the obtained structures [8, 9].

The subject of the research carried out within the framework of this study is focused on multilayer composite Ni/Cu coatings of nanocrystalline structures. The aim of this work was to produce multilayer coatings and compare the structure and properties of coatings consisting of different numbers of layers of varying thickness of nickel and copper.

RESEARCH METHODOLOGY

The composite layers of nickel/copper were produced by electrocrystallization processes as a result of electrochemical reduction. The substrate was made of carbon steel S235JR. Before the electrocrystallization process, the substrate was subjected to sanding, degreasing in acetone and activation in a 15% H_2SO_4 solution. These activities were carried out in order to ensure the high quality and good connections of the layers to the substrate. Multilayer nickel-copper coatings were produced in multi-electrolyte solutions containing crystallite growth rate inhibitors. The nickel layers were deposited from a Watts bath consisting of: sulfate(VI) nickel(II), chloride nickel(II), and boric

acid, while the copper layers were manufactured in a solution having the composition of: sulfate(VI) copper(II), sulfuric acid(VI), and hydrochloric acid. The process of depositing the copper and nickel layers was performed at a constant current density of 3 A/dm^2 in electrolyte solutions with temperatures of 45°C for nickel and of 25°C for copper. The deposition time was chosen in accordance to the *a priori* estimated thickness of the individual layers of Ni and Cu. Analysis of the surface topography of the produced coatings was performed using a scanning electron microscope, SU-70 HITACHI. Examination of the produced coating structures was performed using a transmission electron microscope, JEOL JEM 1200 EX, and an X-ray diffractometer, Philips PW 1830. The thickness of the layers and the structure were assessed by analyzing metallographic specimens in sections perpendicular to the surface using an optical microscope, Nikon ECLIPSE 150 LV. The microhardness of the layers was examined on cross-sections by the Vickers method at a load of 25 g (HV 0.025) by an INNOVATEST hardness tester.

RESULTS OF STUDIES

The multilayer nickel/copper composite coatings were prepared by the electrocrystallization process with alternating immersion of the samples in electrolyte solutions of copper and nickel. This process was carried out at a constant current density equal to 3 A/dm^2. The duration of the process was controlled according to the planned thickness of the individual nickel and copper layers. It is possible by using this method to prepare multilayer composite materials of any thickness of individual layers. In the present work, multilayer coatings with the following amounts and thicknesses of individual layers of nickel and copper were prepared and tested:

1. 30 layers of Ni and Cu, single layer thickness equal to 1 μm
2. 60 layers of Ni and Cu, single layer thickness equal to 0.5 μm
3. 120 layers of Ni and Cu, single layer thickness equal to 0.25 μm.

Due to the different efficiency of copper and nickel electrocrystallization processes, to obtain a uniform thickness of the nickel and copper layers in the coating, the depositions of these metals were performed for different durations.

For all the variants of the manufacturing process of multilayer coatings, the first layer was made of nickel on the steel substrate, because the aim was to ensure good connection of the produced coating to the substrate material - S235JR carbon steel. The last layer was also made of nickel. For comparative purposes, copper and nickel layers produced in the same electrolyte solutions and at the same process parameters as the Ni/Cu multilayers were also prepared and tested. Images of the surface topography of the copper and nickel layers are shown in Figure 1.

The surface of the copper layer is smooth and glossy while the nickel layer is also glossy but has a higher degree of distribution. The results of the microstructure of the copper and nickel layer using a transmission electron microscope are shown in Figure 2.

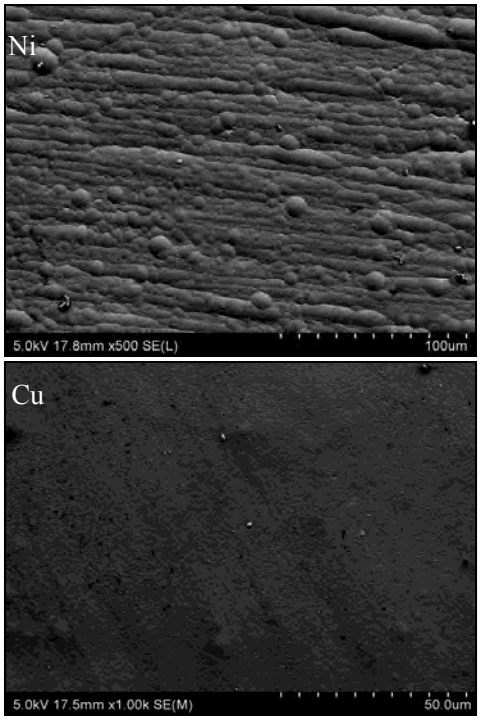

Fig. 1. Surface topography of of nickel and copper layers

Rys. 1. Topografia powierzchni warstw niklowej i miedzianej

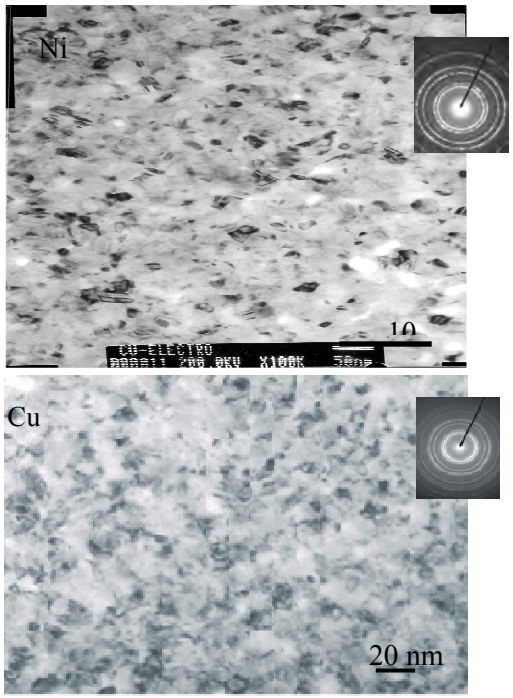

Fig. 2. TEM images of structure and diffraction of copper and nickel layers in plane parallel to surface

Rys. 2. Obrazy TEM struktury i dyfrakcji warstw niklowej i miedzianej w płaszczyźnie równoległej do powierzchni

Studies using a transmission electron microscope showed that the nickel and copper layers have a polycrystalline structure with nanometric grain sizes. Polycrystalline materials with nano-sized grains are characteristic on the diffraction images of the produced layers. The rings are arranged symmetrically relative to the central reflex.

The XRD analysis of the Ni/Cu multilayers is shown in Figure 3.

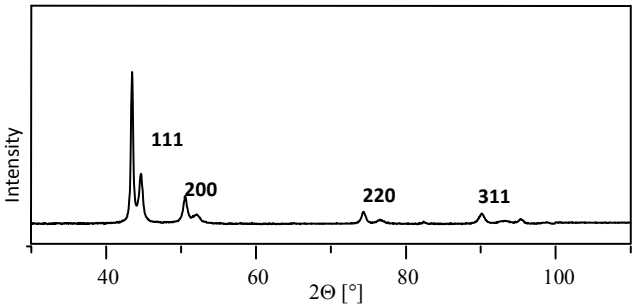

Fig. 3. Difractogram of multilayer Ni/Cu composite coating

Rys. 3. Dyfraktogram wielowarstwowej powłoki kompozytowej Ni/Cu

The X-ray analysis showed that the resulting multilayer Ni/Cu composite coating exhibits crystalline structures. Broadening of the individual peaks on the diffraction pattern indicates the nanocrystalline structure of the multilayer Ni/Cu coatings. Cross-section images of the Ni, Cu and Cu/Ni coatings are shown in Figures 4 and 5, respectively.

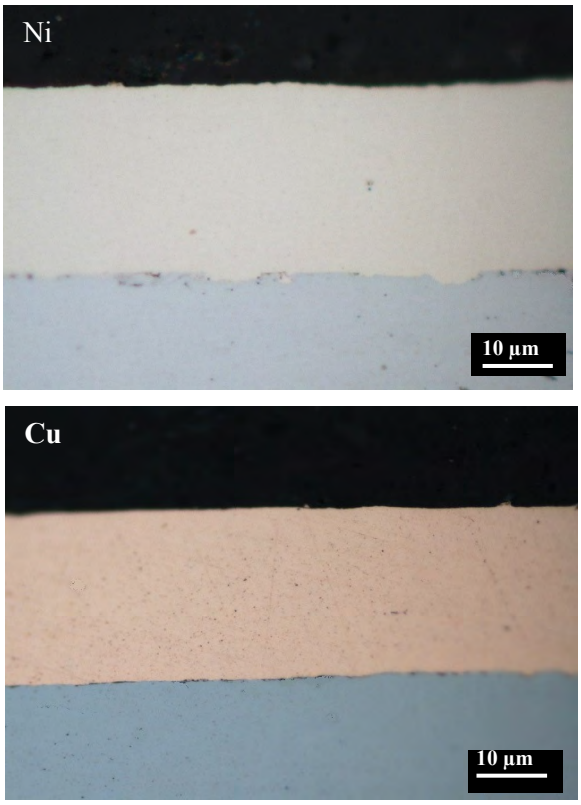

Fig. 4. Structure of nanocrystalline Ni and Cu coating in cross section

Rys. 4. Budowa nanokrystalicznych powłok Ni i Cu w przekroju poprzecznym

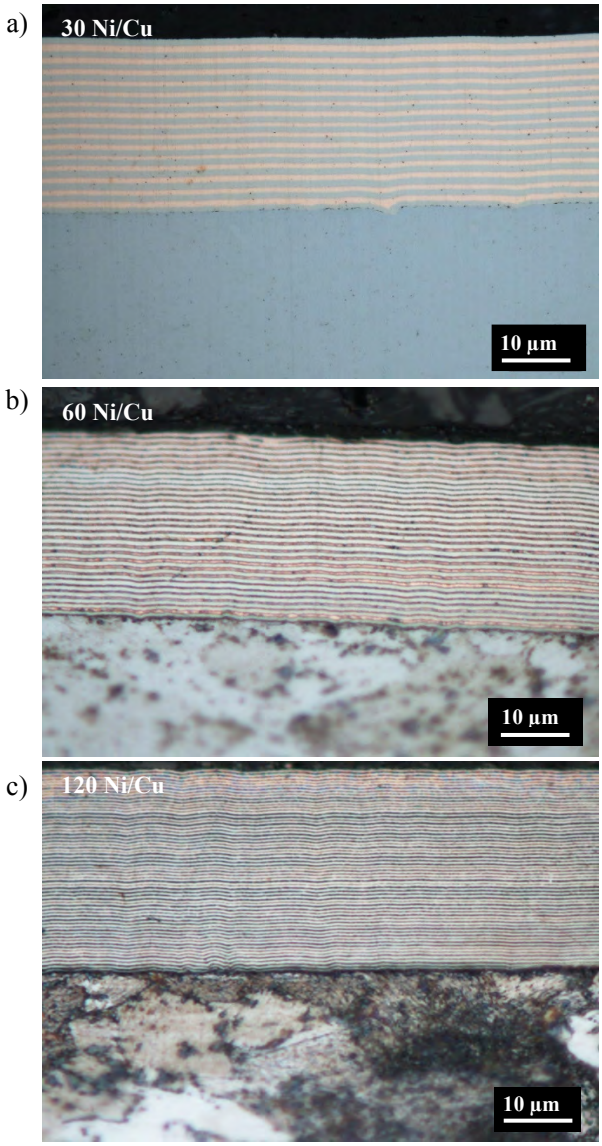

Fig. 5. Structures of nanocrystalline Ni/Cu coatings in cross sections of different thicknesses of individual layers: a) 1 µm, b) 0.5 µm, c) 0.25 µm

Rys. 5. Budowa nanokrystalicznych powłok Ni/Cu w przekroju poprzecznym o różnej grubości pojedynczych warstw: a) 1 µm, b) 0,5 µm, c) 0,25 µm

All the produced multilayer composite coatings are compact, with uniform thickness throughout the coating and the individual layers coat the entire surface area and demonstrate good adhesion between the layers of nickel and copper materials as well as between the coating and the steel substrate.

The material properties are the result of the properties of the composite materials from which the composite is built and the interaction between the materials.

Microhardness measurements were conducted on metallographic cross sections of the coatings. The microhardness measurement results of the substrate material and the nanocrystalline Ni, Cu, and Ni/Cu layers are presented in Table 1. The greatest hardness of the coatings is demonstrated by a nanocrystalline nickel; it has a five times greater hardness than the nanocrystalline copper coating and the steel substrate,

and is two times harder than the multilayer coatings. Among the produced multilayer composite coatings, the highest hardness belongs to the coating consisting of 60 alternating layers of Ni and Cu with a thickness of 0.5 microns.

TABLE 1. **Microhardness HV 0.025 layers and substrate materials**
TABELA 1. **Mikrotwardość HV 0,025 materiałów warstw i podłoża**

Material	HV 0.025
Steel S235JR	106
Ni	537
Cu	95
Ni/Cu (1 μm layer)	237
Ni/Cu (0,5 μm layer)	280
Ni/Cu (0,25 μm layer)	256

CONCLUSIONS

Nanocrystalline coatings of nickel, copper, and multilayer Ni/Cu made by the electrocrystallization process are characterized by a compact structure, uniform thickness over the entire coated surface and good adhesion to the steel substrate. In the case of the multilayer coatings of nickel and copper, all the individual layers also demonstrate uniform thickness and good adhesion between both the layers of nickel and copper as well as between the coating and the steel substrate. Moreover, the thickness of the individual layers of nickel and copper determine the thickness of the produced composite coating as well as influence the hardness of the coating material.

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