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COMPOSITES THEORY AND PRACTICE

Maria Trzaska*, Grzegorz Cieślak

Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warsaw, Poland
**Corresponding author: E-mail: maria.trzaska@imp.edu.pl*

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Ni-P/GRAPHENE COMPOSITE LAYERS PRODUCED BY CHEMICAL REDUCTION METHOD

The paper presents the results of studies of nickel-phosphorus/graphene (Ni-P/G) composite layers and, for comparative purposes, Ni-P layers produced by the electroless deposition method. The layers were prepared in multi-component solutions. The used graphene was in the form of flakes of different sizes. The characteristics of the grapheme were determined by means of Raman spectroscopy and scanning electron microscopy. The diffraction analysis of the material, morphology and surface topography of the Ni-P and Ni-P/G layers are presented. The micro-hardness of the material of the produced layers was examined by Vickers measurements. The conducted studies have shown that the Ni-P/G layers prepared by the chemical reduction process are characterized by a higher degree of surface roughness and three times higher hardness in comparison with the Ni-P composite layers.

Keywords: graphene, composites layers, electroless deposition, Ni-P and Ni-P/G coatings

WARSTWY KOMPOZYTOWE Ni-P/GRAFEN WYTWARZANE METODĄ REDUKCJI CHEMICZNEJ

Przedstawione w niniejszej pracy wyniki zrealizowanych badań odniesione są do powierzchniowych warstw kompozytowych nikiel-fosfor/grafen (Ni-P/G) oraz, w celach porównawczych, do warstw Ni-P, wytworzonych metodą redukcji chemicznej. Warstwy wytwarzano w wieloskładnikowej kąpieli, a w przypadku warstw kompozytowych jako fazę dyspersyjną stosowano grafen w postaci płatków o zróżnicowanych wymiarach. Charakterystykę grafenu wyznaczano za pomocą spektroskopii Ramana oraz skaningowej mikroskopii elektronowej. Przedstawiono wyniki analizy dyfrakcyjnej materiału warstw Ni-P, Ni-P/G oraz morfologię i topografię ich powierzchni. Mikrotwardość materiału wytworzonych warstw określono metodą Vickersa. Zrealizowane badania wykazały, że warstwy kompozytowe Ni-P/G wytworzone metodą redukcji chemicznej charakteryzują się znacznie większym stopniem rozwinięcia powierzchni oraz trzykrotnie większą twardością w porównaniu z warstwami Ni-P.

Słowa kluczowe: grafen, warstwy kompozytowe, metoda elektrochemiczna, warstwy Ni-P oraz Ni-P/G

INTRODUCTION

Currently, there is a great deal of interest in new materials with favorable functional properties. Among such kinds of materials, the attention of researchers is focused on graphene which is formed of a single layer of carbon atoms and exhibits unique physical and chemical properties. The use of graphene as a disperse phase in the production of composite materials offers a favorable potential for shaping their properties. One of the basic methods used in surface engineering to modify the properties of products consists in introducing to the surface layer another material having advantageous functional properties. Important in the production of such surface layers are chemical and electrochemical reduction methods, which allow the production of layers composed of different materials and different structures [1-3]. The incorporation of graphene particles in the metal matrix by these methods makes it possible to form a new composite surface layer formed by different materials [4-6].

The research presented in this paper concerns nickel-phosphorus/graphene (Ni-P/G) surface layers produced by the electroless method. For comparative purposes, studies were also performed on Ni-P layers. The completed studies included the forming of Ni-P/G layers by the chemical reduction method as well as studies of their structures and selected properties.

RESEARCH METHODOLOGY

The nickel-phosphorus/graphene (Ni-P/G) composite surface layers were produced on a carbon steel

S235JR substrate by the electroless chemical reduction process. The deposition process was carried out in a bath containing: $NiSO_4$, NaH_2PO_2, CH_3COONa, $C_2H_4OHCOOH$. As the disperse phase, graphene in the form of flakes with the dimensions: thickness 5÷8 nm, diameter 5 μm and specific area 120÷150 m^2/g, made by Graphene Chemical Industries Co. was used. The composite layers were produced in a bath with a content of 0.5 g/dm^3 graphene flakes. The characteristics of the graphene flakes were examined by using a scanning electron microscope (SEM) and Raman spectroscopy. Before the electroless deposition 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 adhesion of the layers to the substrate. The process of electroless deposition was carried out in a bath pH of 4.5 and temperature of 90°C and the process took up 6 hours. During the process, the bath was stirred by a mechanical stirrer at the speed of 50 rpm. The topography and morphology of the nickel-phosphorus layers, and the nickel-phosphorus /graphene composite were tested by using a scanning electron microscope (SEM) manufactured by ZEISS. The chemical composition of the produced composite layers was tested by using an EDS analyzer. The thickness of the Ni-P and Ni-P/G layers and their structures were assessed by analyzing metallographic specimens in sections perpendicular to the layer surface using an optical microscope - Nikon ECLIPSE 150 LV. The microhardness of the layers was examined on cross-sections by the Vickers method at an indenter load of 10 g (HV 0.01) by an INNOVATEST hardness tester.

The phase structures of the Ni-P layers were examined by X-ray diffraction using a Rigaku Ultima IV diffractometer.

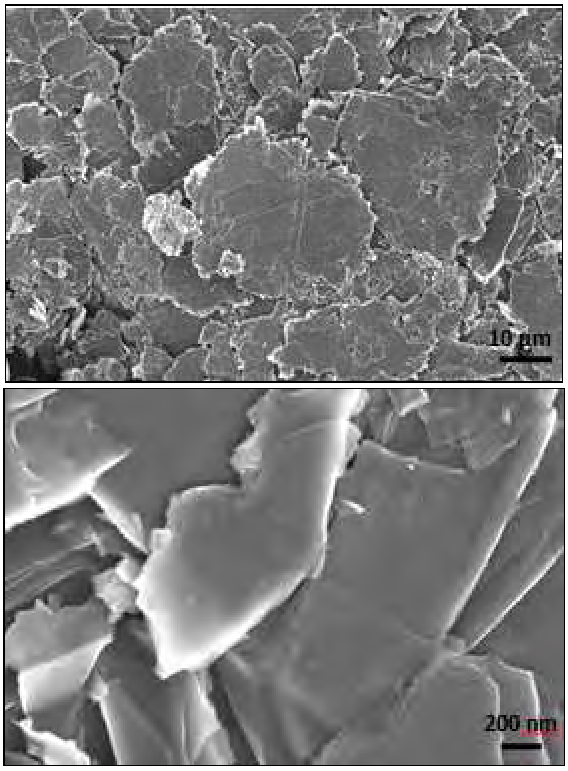

Fig. 1. Images (SEM) of graphene flakes

Rys. 1. Obrazy (SEM) płatków grafenu

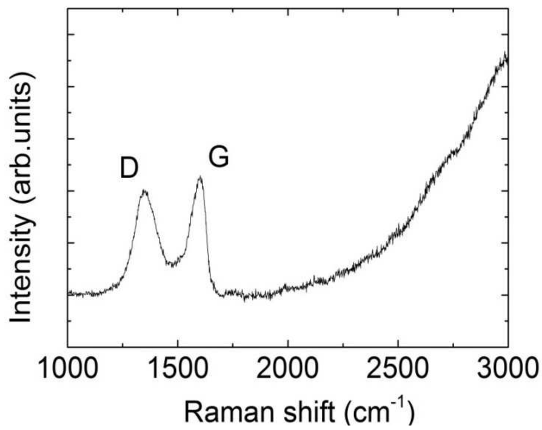

Fig. 2. Raman spectrum of graphene flakes

Rys. 2. Widmo Ramana płatków grafenu

RESULTS OF STUDIES

Graphene in the form of polydisperse flakes was used for preparations of the studied surface layers. The images of the graphene flakes are shown in Figure 1.

The graphene flakes used in the production of the composite layers are characterized by a great diversity in their dimensions. The Raman spectrum of the used graphene is shown in Figure 2.

The lack of a peak at 2700 cm^{-1} (2D) on the registered spectroscopic spectrum, characteristic for graphene monolayers, indicates that the used powder contains multilayer graphene flakes. As the material of the nickel-phosphorus layers produced by chemical reduction and of the matrix layers was a composite amorphous solid solution of phosphorus in nickel Ni-P containing 9% P by weight. The SEM images of the surface and the result of X-ray diffraction analysis for nickel-phosphorus layers formed by the chemical reduction process are shown in Figures 3 and 4.

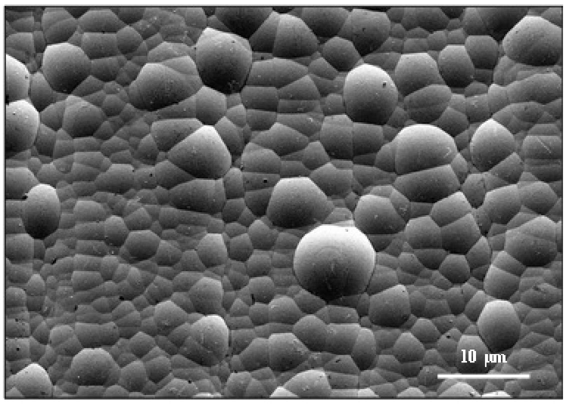

Fig. 3. Image (SEM) of morphology and topography of Ni-P layer

Rys. 3. Obraz (SEM) morfologii i topografii powierzchni warstwy Ni-P

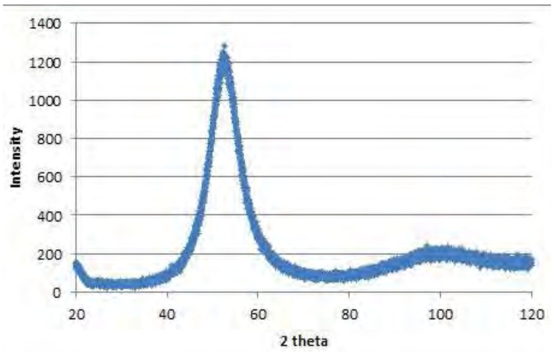

Fig. 4. Diffraction pattern of Ni-P layer

Rys. 4. Dyfraktogram warstwy Ni-P

The diffraction spectrum of the Ni-P layers indicates the amorphous structure of the material deposited in the used bath. The topography and morphology of the Ni-P/G composite layers are shown in Figure 5.

The graphene flakes of relatively large sizes that were incorporated into the nickel-phosphorus matrix contribute to the large surface development of the layers. The images have also shown that the graphene flakes are incompletely incorporated into nickel-phosphorus matrix.

The results of EDS analysis of the chemical composition of the produced composite layers are shown in Figure 6 and Table 1, respectively.

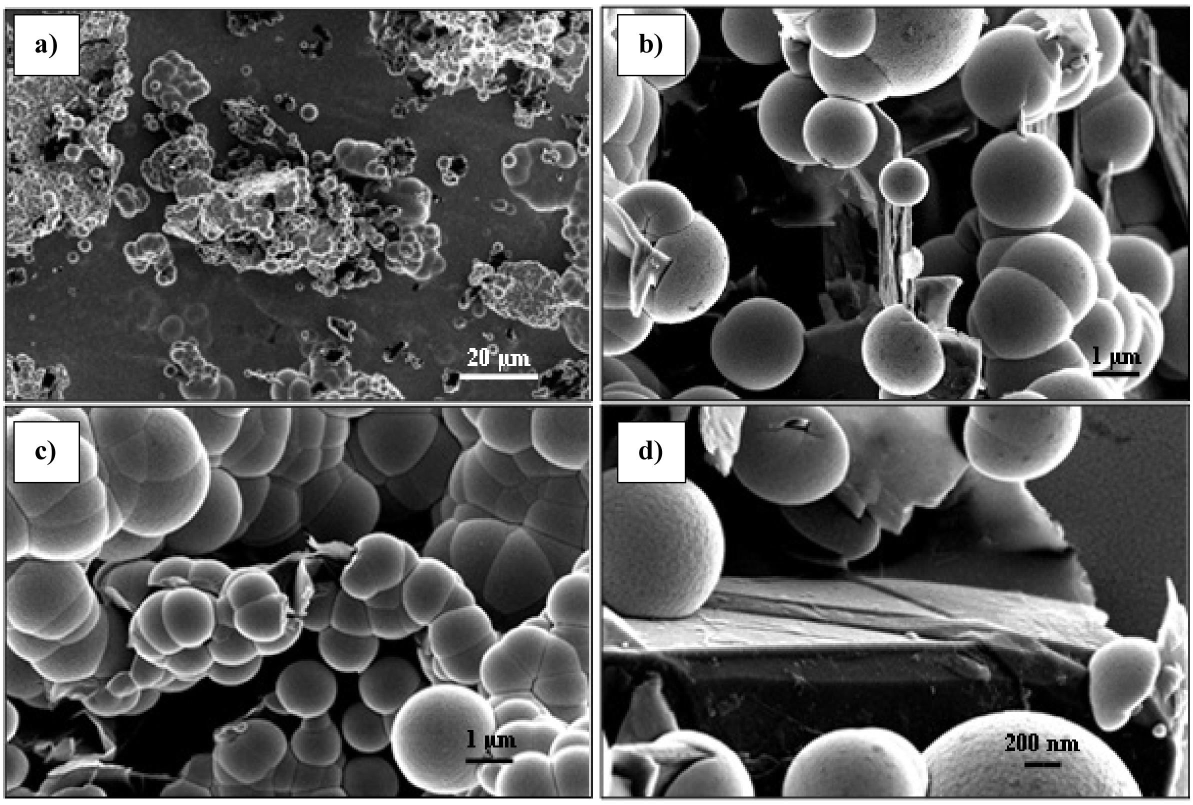

Fig. 5. Images (SEM) of Ni-P/G layer surfaces: a) surface topography, b-d) graphene flakes incorporated into Ni-P matrix

Rys. 5. Obrazy (SEM) powierzchni warstwy Ni-P/G: a) topografia powierzchni, b-d) płatki grafenu wbudowane w osnowę Ni-P

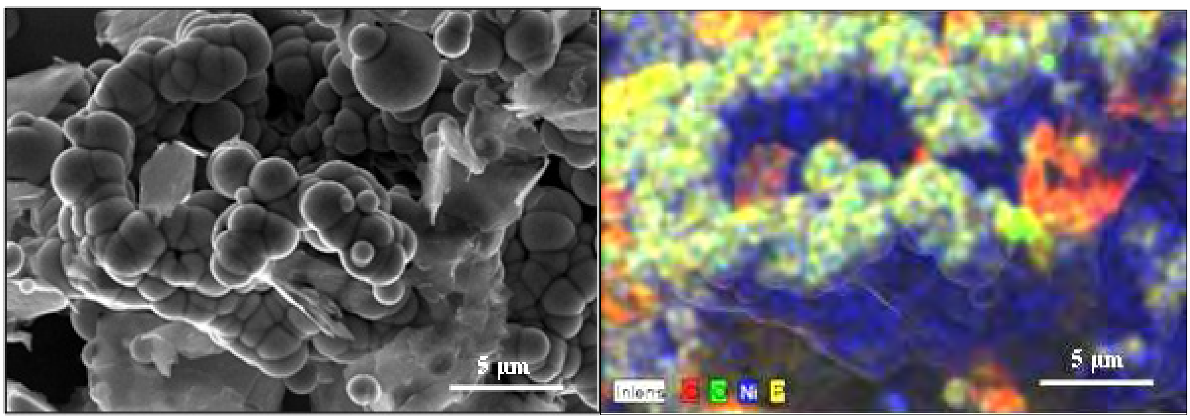

Fig. 6. Map of element distribution in studied area of Ni-P/G layer

Rys. 6. Mapa rozkładu pierwiastków w badanym obszarze warstwy Ni-P/G

TABLE 1. **Chemical composition of Ni-P /G layers**
TABELA 1. **Skład chemiczny warstwy Ni-P/G**

Element	[wt. %]	[at. %]
Ni	79.2	54.38
C	8.9	29.87
P	9.36	12.17
O	0.76	1.93

The EDS analysis of the chemical composition on the surface of the Ni-P/G composite layer indicates a carbon content of approx. 30% at. The cross sections perpendicular to the surface of the Ni-P and Ni-P/G layers are shown in Figure 7.

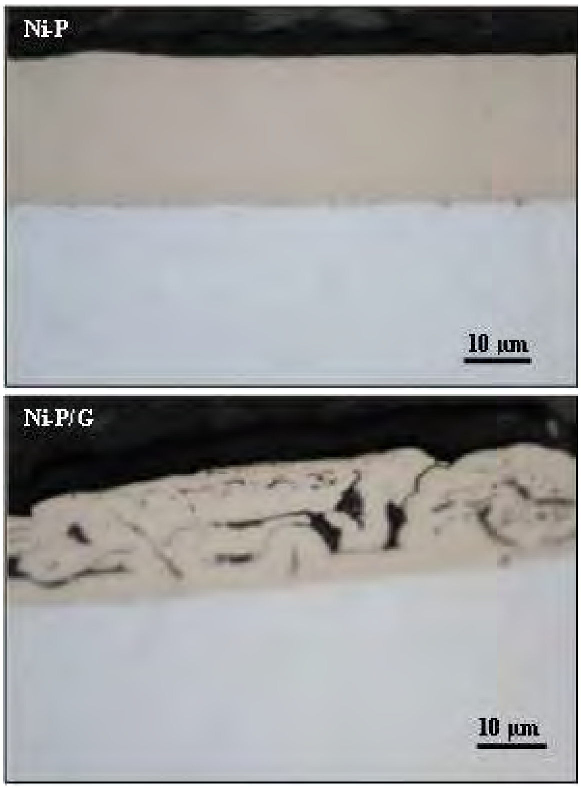

Fig. 7. Cross sections of surface layers of Ni-P and Ni-P/G with graphene aggregates in Ni-P matrix

Rys. 7. Przekroje poprzeczne warstw powierzchniowych Ni-P oraz Ni-P/G z płatkami grafenu w osnowie Ni-P

The Ni-P and Ni-P/G layers produced by chemical reduction method have good adhesion to the steel substrate (Fig. 7). The Ni-P layer exhibits a compact shape and a uniform thickness over the entire coated surface of the substrate. The Ni-P/G composites layers have large multi-layered graphene flakes embedded in the nickel-phosphorus matrix. The large size of the graphene flakes incorporated into the nickel-phosphorus matrix contributes to the large surface development of the layers and forms a non-uniform thickness of the Ni-P/G layer. The microhardness measurements at an indenter load of 10 g (HV 0.01) were performed on cross sections perpendicular to the layer surface. The results of Vickers microhardness measurements of the composite Ni-P/G layers and of Ni-P layers are presented in Table 2.

TABELA 2. **Mikrotwardość HV 0,01 warstw Ni-P oraz Ni-P/G**
TABLE 2. **Microhardness HV 0.01 of Ni-P and Ni-P/G layers**

Layer	HV0.01
Ni-P	130
Ni-P/G	398

The graphene particles embedded in the nickel--phosphorus matrix have an effect on increasing the hardness of the composite layer material. The nickel--phosphorus layers have three times lower hardness in comparison with the composite Ni-P/G layer.

CONCLUSIONS

The conducted studies have shown that by the electroless chemical reduction method, composite surface layers of Ni-P containing graphene flakes can be prepared. The produced composite surface layers have good adhesion to the substrate material. The graphene flakes embedded in the nickel-phosphorus matrix increase the surface area of the produced Ni-P/G layers. The performed studies have also shown that the of Ni-P/G layers deposited by chemical reduction exhibit threetimes higher hardness in comparison with Ni-P layers.

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