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COMPOSITES THEORY AND PRACTICE

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PREPARATION AND PROPERTIES OF Ni-P/CNT COMPOSITE SURFACE LAYERS PRODUCED BY CHEMICAL REDUCTION METHOD

The chemical reduction method, as one of the processes very often applied in surface engineering, allows one to obtain materials with good performance properties. Electroless Ni-P layers have been extensively applied in industry, microelectronics and materials engineering due to their unique and exceptional properties. Thanks to the addition of carbon nanotubes as a dispersion phase, it is possible to obtain layers with improved properties. Solid particles in a nickel matrix have been developed to achieve better wear resistance, corrosion resistance, microhardness and tribological properties. The study is concerned with composite layers consisting of a nickel-phosphorus (Ni-P) matrix and a dispersed carbon nanotube (CNTs) phase. The Ni-P layers and composite layers were deposited on a S235JR carbon steel substrate by the chemical reduction method. The process of manufacturing both layers was carried out by means of sediment electroless depositions in a nickel sulfate bath. The paper describes the technique of manufacturing Ni-P/CNT layers, the methods of CNT identification in the Ni-P layer, and presents the results of examinations of the mechanical properties (micro-hardness examinations) of the layers of the final products. The CNTs introduced into the Ni-P matrix improve the properties of the Ni-P layers and thereby the useful properties of the products covered by Ni-P/CNT coatings.

Keywords: carbon nanotubes, Ni-P layers, chemical reduction method, Ni-P/CNT composite layers

OTRZYMYWANIE I WŁAŚCIWOŚCI WARSTW KOMPOZYTOWYCH Ni-P/CNTS WYTWORZONYCH METODĄ REDUKCJI CHEMICZNEJ

Metoda chemiczna osadzania, jako jedna z metod inżynierii powierzchni, pozwala otrzymywać materiały o dobrych właściwościach użytkowych. Warstwy Ni-P wytworzone tą metodą, dzięki swym unikalnym i wyjątkowym właściwościom, są obecnie intensywnie badane z punktu widzenia możliwości ich wykorzystania w przemyśle, mikroelektronice i inżynierii materiałowej. Dzięki wprowadzeniu cząstek innej fazy do niklowej osnowy możliwa jest modyfikacja właściwości warstw kompozytowych. Stałe cząstki wprowadzane są do osnowy w celu polepszenia odporności na zużycie, odporności korozyjnej, twardości i właściwości tribologicznych gotowych wyrobów. W niniejszej pracy węglowe nanorurki (CNTs) wprowadzane zostały do osnowy niklowej w celu polepszenia właściwości mechanicznych wytworzonych warstw kompozytowych. Badane warstwy Ni-P/CNTs wytwarzane były w kąpieli z dodatkiem dyspersyjnej fazy CNTs w procesie bezprądowego osadzania (chemicznego osadzania). Skład stosowanej kąpieli był następujący: 28 g/l $NiSO_4$, 30 g/l NaH_2PO_2, 35 g/l CH_3COONa, 20 cm^3 kwas mlekowy. Wartość pH kąpieli utrzymywana była na poziomie 4,5. Morfologia i topografia warstw Ni-P oraz Ni-P/CNTs obserwowana była za pomocą skaningowego mikroskopu elektronowego S-3500 N. CNTs i wytworzone warstwy kompozytowe Ni-P/CNTs charakteryzowane były obrazami uzyskanymi z transmisyjnej mikroskopii elektronowej JEOL-1200. Zbadano mikrotwardość wytworzonych warstw Ni-P i Ni-P/CNTs metodą Vickersa przy obciążeniu 20 G. Przedstawione w niniejszej pracy wyniki badań wskazują, że wprowadzenie CNTs do kąpieli implikuje znaczne polepszenie właściwości mechanicznych warstw kompozytowych Ni-P/CNTs.

Słowa kluczowe: nanorurki węglowe, warstwy Ni-P, metoda redukcji chemicznej, warstwy kompozytowe Ni-P/CNTs

INTRODUCTION

Since Iijima [1] discovered carbon nanotubes (CNTs) in 1991, they have been intensively studied. This has been so because of their unique properties and specific atomic structures. CNTs possess unique topological hollow tube structures, strong C-C bonds and they are the most typical one-dimensional nanomaterial (length of the order of micrometers and a nanometric diameter). Thanks to these features, CNTs have attractive mechanical (high tensile strength, high elastic modulus), optical, chemical, magnetic, and tribological properties as well as high thermal and electrical conductivities. These properties make them useful in many industrial branches, materials engineering, nanoscience and nanotechnology [1-10].

Recently, great interest has aroused in composites modified with carbon nanotubes whose mechanical, electrical, and tribological properties, as well as corrosion resistance, thermal and electrical conductivities are better than those of the host materials.

The chemical reduction method is an effective approach to the preparation of Ni-P surface layers and composite surface layers that contain a dispersed CNT phase. This technique has been widely used for producing composite coatings and is also effective in the manufacture of surface-coated products with various shapes. Layers produced by the chemical reduction method are characterized by good adhesion and high hardness. Traditional materials which were added to composite materials in the form of a dispersed phase were: SiC, Si_3N_4, PTFE, Al_2O_3 and carbon allotropes such as graphite. CNTs with their unique topological hollow-tube structure and advantageous properties open new applicative perspectives for composite materials with a disperse phase [11, 12].

The paper describes how the dispersed CNT phase introduced into Ni-P layers affects their morphology, structure and properties. Composites containing CNTs appear to have much better properties than traditional Ni-P coatings.

EXPERIMENTAL PROCEDURE

The Ni-P layers and Ni-P/CNT composite layers were produced by the chemical reduction method. The layers were deposited on S235JR carbon steel. The plating bath contained $NiSO_4$, NaH_2PO_2, CH_3COONa, and $C_3H_6O_3$. The pH value of the bath was maintained at 4.5. During the deposition process, the bath temperature was held at about 90°C. 0.2 g/l of CNTs was added to the bath.

Prior to the process, the bath was intensively stirred ultrasonically in order to obtain a homogenous CNT suspension. During the entire deposition process, the bath was stirred mechanically at a speed of 300 rev/min.

The structure of the CNTs was analyzed with a high-resolution scanning electron microscope - SU-70 (SEM), JEOL-1200, JEM-3010 transmission electron microscopes (TEM) and by Raman spectroscopy. The morphology and topography of the Ni-P layers and of the Ni-P/CNTs composite layers were examined with S-3500N and SU-70 scanning electron microscopes. For the sake of comparison, the structure of the Ni-P layers and the Ni-P/CNTs composite layers was also analyzed by Raman spectroscopy. The microhardness of the layers was determined with a Vickers hardness indenter, under a load of 20 G.

RESULTS AND DISCUSSION

The CNTs which were used as the disperse phase in the Ni-P/CNTs composite layers had various shapes and sizes. They showed the tendency to form agglomerates irrespective of whether in dry or hydrous environments.

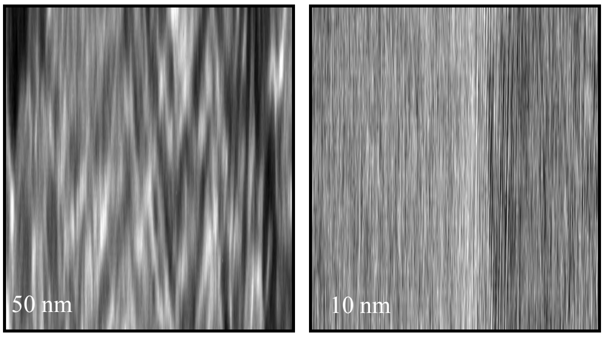

Fig. 1. TEM images of CNTs

Rys. 1. Obrazy TEM nanorurek węglowych

The diameters of the CNTs were varied and ranged from 20 to 30 nm whereas their lengths even amounted to a few micrometers. The images of the multiwalled carbon nanotubes used as the dispersed phase are shown in Figure 1.

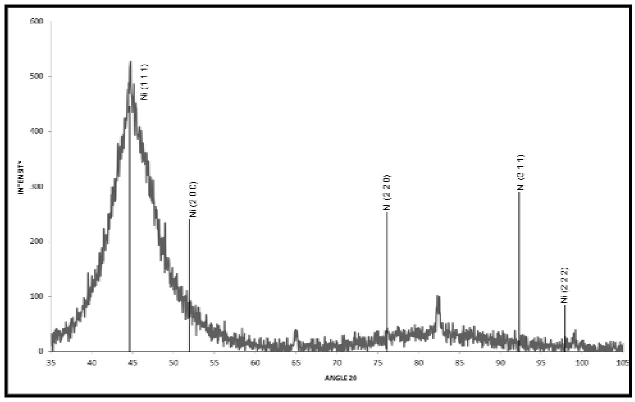

Fig. 2. Diffraction patterns of Ni-P layers

Rys. 2. Dyfraktogram rentgenowski warstwy Ni-P

The results of the XRD analyses (Fig. 2) indicate that the phase structure of the deposited Ni-P layers is an amorphous state.

Figure 3 shows the structure of the Ni-P and Ni-P/CNTs composite layers. The CNTs built into the Ni-P layers affected their morphology and structures. The surfaces of the composite layers were rougher than those of the Ni-P layers, and CNTs, covered with nickel (to various degrees), could be seen on them.

It can be observed from Figure 4 that uniform and continuous surface layers with a thickness of about 20 μm were formed and the surface of the sample was uniformly covered with the electroless deposition.

The CNTs incorporated in the composite layers occur either as single nano-tubes or in agglomerates (Fig. 5).

The presence of CNTs in the Ni-P layers was confirmed by Raman spectroscopy. Figure 6 shows the Raman plots obtained for (a) CNTs, (b) Ni-P layer and (c) Ni-P/CNT composite layer. The two well-marked peaks, the D-band around 1330 cm^{-1} and the G-band at 1580 cm^{-1}, occurring in the Raman spectrum obtained for the composite Ni-P/CNT layer, are characteristic of CNTs.

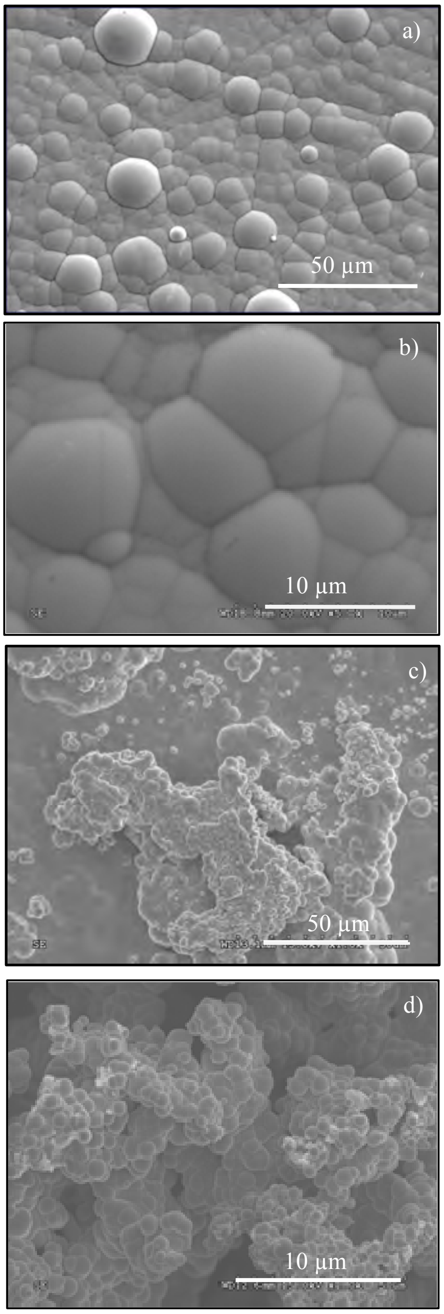

Fig. 3. Morphology of: a) and b) Ni-P layers, c) and d) Ni-P/CNTs composite layers

Rys. 3. Morfologia warstw: a) i b) Ni-P, c) i d) kompozytowych Ni-P/CNTs

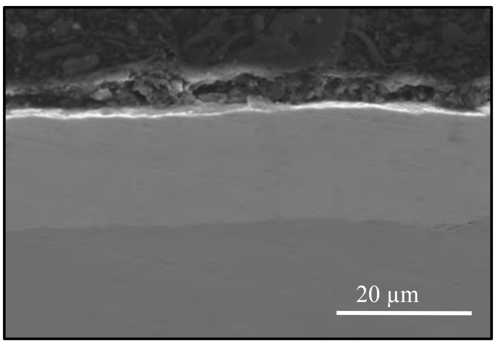

Fig. 4. Cross-section morphology of Ni-P/CNTs composite layers

Rys. 4. Przekrój poprzeczny warstwy kompozytowej Ni-P/CNTs

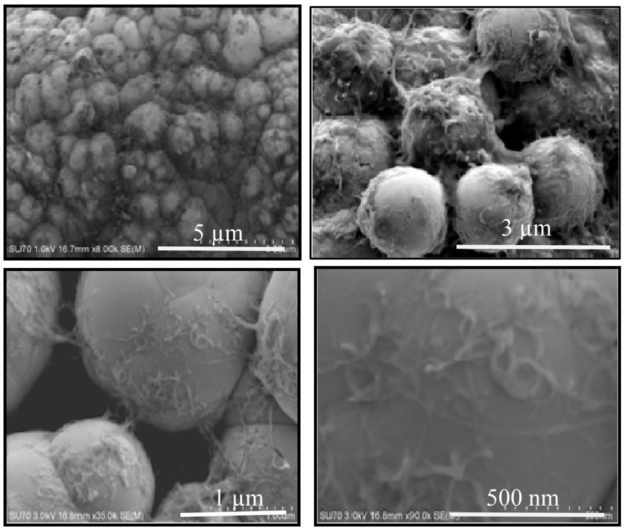

Fig. 5. CNTs in Ni-P/CNT composite layer not fully coated by nickel

Rys. 5. Obrazy nanorurek węglowych w warstwach kompozytowych Ni-P/CNTs niecałkowicie pokryte niklem

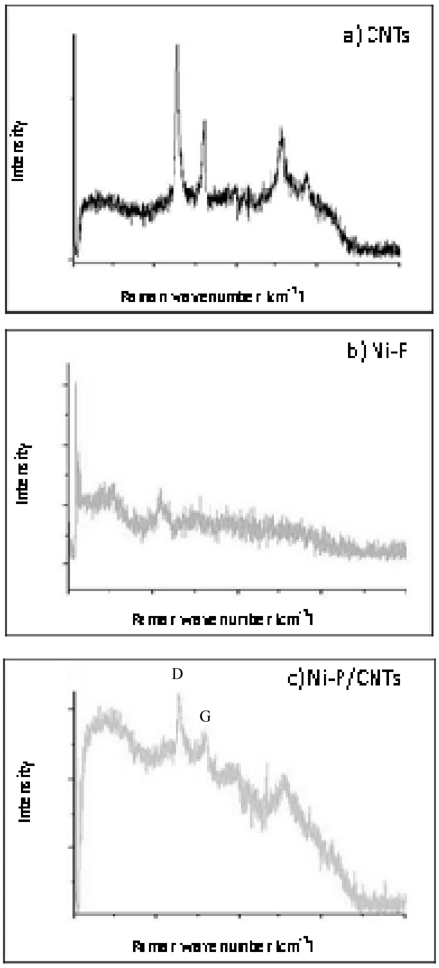

Fig. 6. Raman plots of: a) CNTs, b) Ni-P layer, c) Ni-P/CNT composite layer

Rys. 6. Widma Ramana: a) nanorurek węglowych: b) warstwy Ni-P, c) warstwy kompozytowej Ni-P/CNTs

The modification of the layer structure by introducing CNTs in the form of a dispersed phase was aimed at improving the mechanical properties of the Ni-P layers.

TABLE 1. **Microhardness of Ni-P and Ni-P/CNT composite layers**
TABELA 1. **Mikrotwardość warstw Ni-P i kompozytowych Ni-P/CNTs**

Layer	HV
Ni-P	410
Ni-P/CNTs	634

The microhardness of the produced layers was determined with a Vickers hardness indenter, under a load of 20 G. The average of three repeated measurements has been reported.

The aim seems to have been achieved since the microhardness of the layers increased from 410 HV in the unmodified Ni-P layers to 634 HV in the Ni-P/CNT composite layers, i.e. it increased by more than 50%.

CONCLUSIONS

Ni-P/CNT composite layers were successfully produced on a carbon steel substrate by the chemical reduction method.

Both the Ni-P and Ni-P/CNT layers had a compact structure. The CNTs incorporated into the Ni-P composite matrix have changed its morphology, topography and structure and also improved the mechanical properties of the composite layers. The Ni-P/CNT composite layers appeared to have a higher microhardness than the Ni-P layers by about 50%. The results of this study have demonstrated that the chemical reduction method can be effectively used for the production of Ni-P/CNT composite layers.

Further stages of the investigations will be a continuation of the structure analysis of the composite layers, and will include optimization of the content of the dispersed CNT phase in the composite layers, and tests of their tribological, electrical and thermal properties.

REFERENCES

[1] Iijima S., Helical microtubules of graphitic carbon, Nature 1991, 354, 56-58.
[2] Trzaska M., Gostomska M., Composite layers Ni/$C_{graphite}$ produced electrochemically, Composites 2009, 1, 84-88.
[3] Trzaska M, Gostomska M., The structure and properties of Ni-P/CNTs composite layers produced by chemical method, The E- MRS Fall Meeting, Warsaw 14-18.09.2009, 217.
[4] Trzaska M., Odporność korozyjna nanokompozytowych warstw nikiel/nanorurki węglowe (Ni/CNTs) wytworzonych metodą elektrochemiczną, Ochrona przed Korozją 2011, 248-51.
[5] Bright I., Koutsos V., Li Q., Cheung R., Carbon nanotubes for integration into nanocomposite materials, Microelectronic Engineering 2006, 83, 1542-1546.
[6] Li Z.H., Wang X.Q., Wang M., Wang F.F., Ge H.L., Preparation and tribological properties of carbon nanotubes-Ni-P composite coating, Tribology International 2006, 39, 953-957.
[7] Popov V.N., Carbon nanotubes: properties and application, Materials Science and Engineering 2004, 43, 61-102.
[8] Chen W.X., Tu J.P., Gan H.Y., Xu Z.D., Tribological application of carbon nanotubes in a metal-based composite coating and composites, Carbon 2003, 41, 215-222.
[9] Chen W.X., Tu J.P., Xu Z.D, Chen W.L., Zhang X.B., Cheng D.H., Tribological properties of N-P-multi walled carbon nanotubes electroless composite coating, Materials Letters 2003, 57, 1256-1260
[10] Chen W.X., Tu J.P, Wang L.Y., Gan H.Y., Xu Z.D., Zhang X.B., Electroless preparation and tribological properties of Ni-P-Carbon nanotube composite coatings under lubricated condition, Surface and Coatings Technology 2002, 160, 68-73.
[11] Yang Z., Xu H., Li M., Shi Y., Huang Y., Li H., Preparation and properties of Ni/P/single-walled carbon nanotubes composite coatings by means of electroless plating, Thin Solid Films 2004, 446, 86-91.
[12] Wang F., Arai S., Endo M., The preparation of multi-walled carbon nanotubes with a Ni-P coating by an electroless deposition process, Carbon 2005, 43, 1716-1721.

