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COMPOSITES THEORY AND PRACTICE

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TRIBOLOGICAL PROPERTIES OF NANOCOMPOSITE Ni/GRAPHENE COATINGS PRODUCED BY ELECTROCHEMICAL REDUCTION METHOD

The paper presents the results of tribological studies of nanocomposite nickel/graphene (Ni/G) coatings and, for comparative purposes, of nanocrystalline nickel coatings produced by the electrochemical method on a carbon steel S235JR substrate. To prepare the composite coatings, graphene in the form of flakes was used. The characteristics of the graphene flakes were determined by means of Raman spectroscopy and scanning as well as transmission electron microscopes. The results of studies on the structure and morphology of nickel and Ni/G coatings produced in a bath containing different amounts of graphene are presented. The microhardness of the produced coatings was examined by Vickers measurements. The tribological testing was carried out using Amsler type machines. The wear depth of the coatings as a function of time for the tested Ni and Ni/G coatings were determined. Nanocrystalline Ni/G coatings produced by the electrochemical method exhibit a greater degree of surface development, increased hardness and better wear resistance when compared with nickel nanocrystalline coatings.

Keywords: **graphene, nanocomposite coatings, electrocrystallization, tribology, wear**

WŁAŚCIWOŚCI TRIBOLOGICZNE POWŁOK NANOKOMPOZYTOWYCH Ni/GRAFEN WYTWARZANYCH METODĄ REDUKCJI ELEKTROCHEMICZNEJ

W pracy przedstawiono wyniki badań tribologicznych wytwarzanych metodą elektrochemiczną na podłożu ze stali węglowej S235JR powłok nanokompozytowych nikiel/grafen (Ni/G) oraz w celach porównawczych nanokrystalicznej powłoki niklowej. Do wytworzenia powłok kompozytowych stosowano grafen w postaci płatków. Charakterystykę płatków grafenu określano za pomocą spektroskopii Ramana oraz skaningowej i transmisyjnej mikroskopii elektronowej. Przedstawiono wyniki badań struktury, morfologii powłok niklowej oraz kompozytowych Ni/G wytworzonych w kąpieli o różnej zawartości grafenu. Mikrotwardość badanych powłok określono metodą Vickersa. Badania tribologiczne realizowano za pomocą maszyny typu Amsler. Wyznaczano głębokość zużycia powłok w funkcji czasu oraz współczynnik tarcia dla badanych powłok Ni oraz Ni/G. Wytworzone elektrochemicznie nanokrystaliczne powłoki Ni/G odznaczają się większym stopniem rozwinięcia powierzchni, większą twardością oraz lepszą odpornością na zużycie ścierne w porównaniu z nanokrystalicznymi powłokami niklowymi.

Słowa kluczowe: **grafen, powłoki nanokompozytowe, elektrokrystalizacja, tribologia, zużycie ścierne**

INTRODUCTION

Over the last two decades, quite a lot of studies have been devoted to research on new materials with increasingly better functional properties. As is well known, the characteristic feature of most materials is that after long-term usage under unfavorable conditions, one or more of their functional properties can deteriorate. In areas such as computing, sensors, biomedical and many other applications in different industrial sectors, especially, for the automotive, aerospace and aeronautic as well as defense industries, it is necessary to continuously strive to assure the high quality and safety of products. In order to meet such needs, the field of nanoscience has blossomed recently and the importance of nanotechnology has proved to be irreplaceable.

It has been established so far that metallic nanocomposites possess a higher wear resistance compared to that of a pure matrix material. The damage of metal nanocomposites characterized as a depth scar is lower. The roughness of the nanocomposites has found to be the essential factor affecting their wear resistance.

Recently, graphene has attracted both academic and industrial interest because it can produce a dramatic improvement in properties at a low filler content. Graphene has been considered by many material specialists as a revolutionary material with electronic and structural properties that surpass those of conventional metals and semiconductors. Furthermore, graphene is also quite unusual electronically since its electric carriers behave as if they were massless and relativistic, so-called Dirac particles [1]. The utilization of graphene-based materials in the fabrication of nanocomposites with different metallic or polymer matrices has been intensively explored [2-7]. This is due to the fact that graphene-based nanocomposites show superior mechanical, thermal, gas barrier and electrical properties, compared to a neat matrix material. Therefore, thanks to its properties, including high mechanical resistance, graphene can be used to increase the mechanical resistance of machine parts. One of the main methods of surface layer deposition is electrocrystallization. By controlling the parameters of the deposition process, it is possible to produce coatings which improve the mechanical properties of work pieces. In papers [8-13] are examples of composite surface coatings with a metal matrix and graphene as the disperse phase.

The present article mainly concerns the study of the tribological properties of nanocomposite Ni/graphene coatings produced in a bath containing different amounts of graphene, namely, 0.1 g/dm^3 - Ni/G (1), 0.2 g/dm^3 - Ni/G (2). Moreover, for comparison purposes nanocrystalline nickel coatings are also investigated.

RESEARCH METHODOLOGY

The nickel (Ni) and nickel/graphene (Ni/G) composite coatings were deposited on a carbon steel S235JR substrate by the electrochemical reduction process. To produce the composite coatings, we used graphene manufactured by the Graphene Chemical Industries Co (Turkey) in the form of flakes with the following dimensions: thickness 5÷8 nm, diameter 5 μm and specific area 120÷150 m^2/g. Before the electrodeposition process, the substrate was subjected to sanding, degreasing in $CaCo_3$ and activation in a 15% H_2SO_4 solution. The deposition process was carried out in a containing $NiSO_4$, $NiCl_2$, H_3BO_3 and additions of organic matters. The composite coatings were produced in a bath with a content of 0.1 g/dm^3 Ni/G (1) and 0.2 g/dm^3 Ni/G (2). The electrodeposition process was carried out in a bath of pH 4.0÷4.5, at the temperature of 45÷47^{o}C, for 45 minutes. During the process, the bath was stirred mechanically at the speed of 100 rpm. The characteristics of the used graphene flakes were obtained by using Raman spectroscopy and transmission as well as scanning electron microscopes. The topography and morphology of the produced Ni and Ni/G coatings were tested by means of a scanning electron microscope (SEM) made by ZEISS. The microhardness of the Ni and Ni/G coatings were examined on cross sections perpendicular to the surface by the Vickers method at an indenter load of 10 G (HV 0.01) by a T1202 WILSON-HARDNESS (BUEHLER) hardness tester. Tests of resistance to abrasion were implemented in sliding friction appliances of an Amsler A135 type machine. The abrasion wear tests were carried out according to procedure PN-82/H-04332. The tribological system in the friction pair was a sample of the tested coating and a counter specimen in the form of a ring of chrome steel 41Cr4. The study was conducted in LUX-10 oil using a constant force of 10 N and constant speed of 200 rpm. The friction test was performed for 30 minutes. Evaluation of the wear resistance of the tested layers was made by analyzing the wear depth as a function of the test time. The wear resistances of the coatings were analyzed by an optical microscope, Nikon Eclipse 150 LV.

RESEARCH RESULTS

To produce the composite coatings, graphene in the form of flakes (Fig. 1) was used.

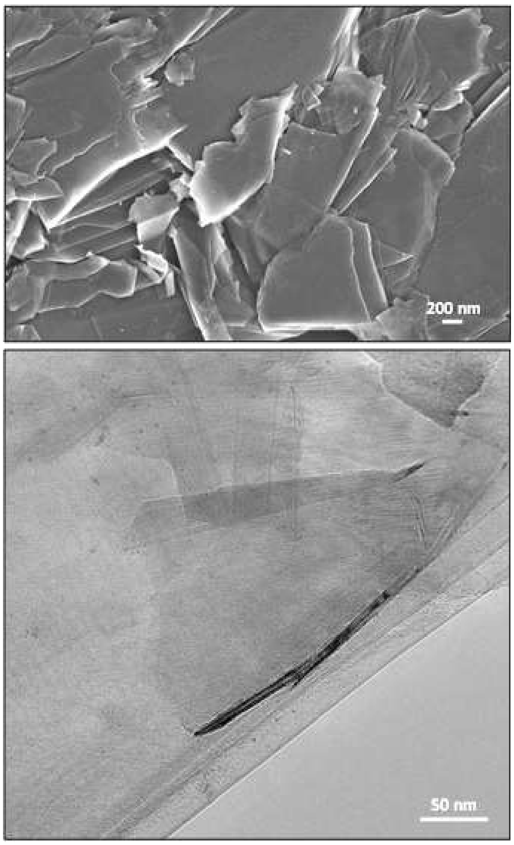

Fig. 1. SEM and TEM images of graphene flakes

Rys. 1. Obrazy SEM oraz TEM stosowanych płatków grafenu

The graphene flakes used to prepare the composite Ni/G coatings are characterized by a great diversity in their dimensions, as indicated by the images of the transmission and scanning electron microscope images The Raman spectrum of the graphene flakes is shown in Figure 2.

The results demonstrate that the Raman spectrum has characteristic D (1350 cm^{-1}), G (1,580 cm^{-1}) peaks for graphene and identifies the individual layers of the graphene 2D peak (2700 cm^{-1}). It should be noted that the graphene flakes when added to the bath have had a tendency to agglomerate. The images of the nickel Ni and Ni/G (1) and Ni/G (2) surface coatings produced in baths containing different amounts of graphene flakes are shown in Figures 3-5.

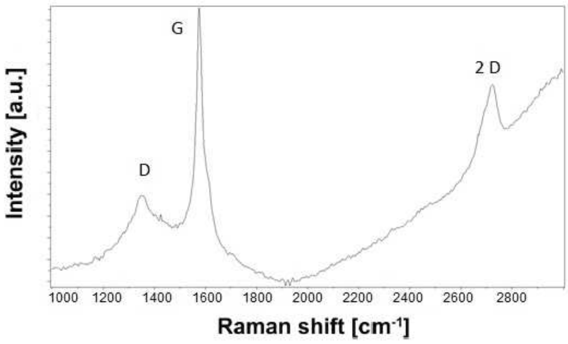

Fig. 2. Raman spectrum of graphene flakes

Rys. 2. Widmo Ramana płatków grafenu

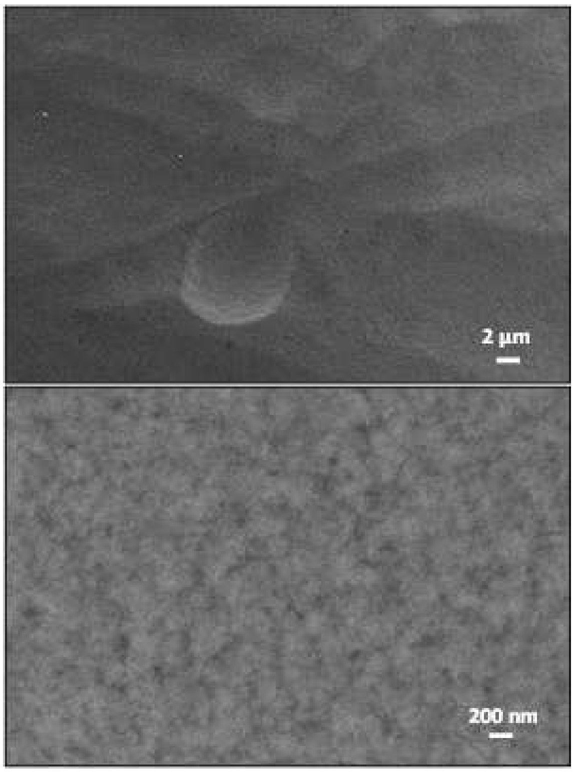

Fig. 3. Images of nickel layer of nanocrystalline structure

Rys. 3. Obrazy powierzchni powłoki niklowej o nanokrystalicznej strukturze

The results of the X-ray diffraction of the nickel coating are shown in Figure 6.

It is worth mentioning that the nickel coating has a smooth and shiny surface. Widening diffraction peaks indicate a nanocrystalline structure. In the case of the Ni/G composite coatings, the large size of the used graphene flakes incorporated into the nickel matrix and the tendency to agglomerate contribute to increasing the level of development of surface coatings being formed. In Figures 4 and 5 incompletely built-up flakes of graphene can be seen. The microhardness measurements using an indenter of 10 G (HV 0.01) were performed on cross sections perpendicular to the layer surface. The results of the Vickers microhardness measurements and thickness of the Ni and composite Ni/G coatings are presented in Table 1.

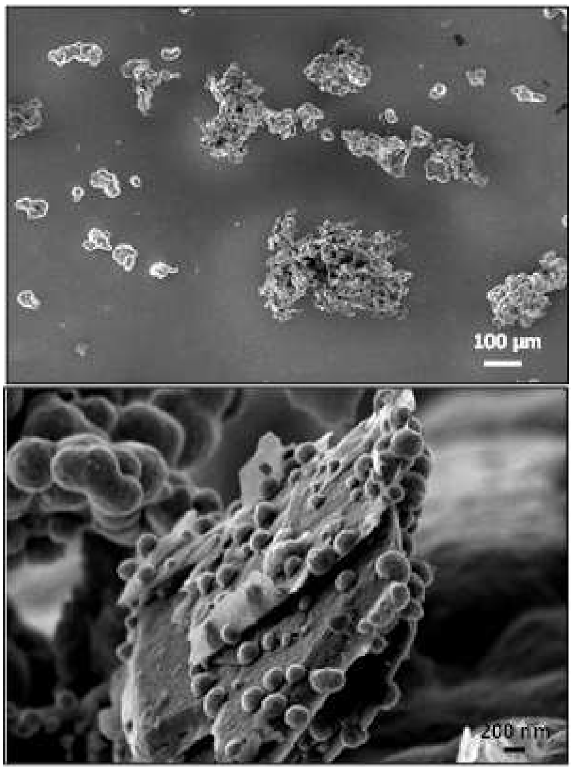

Fig. 4. Images of Ni/G (1) coating surface

Rys. 4. Obrazy powierzchni powłoki Ni/G (1)

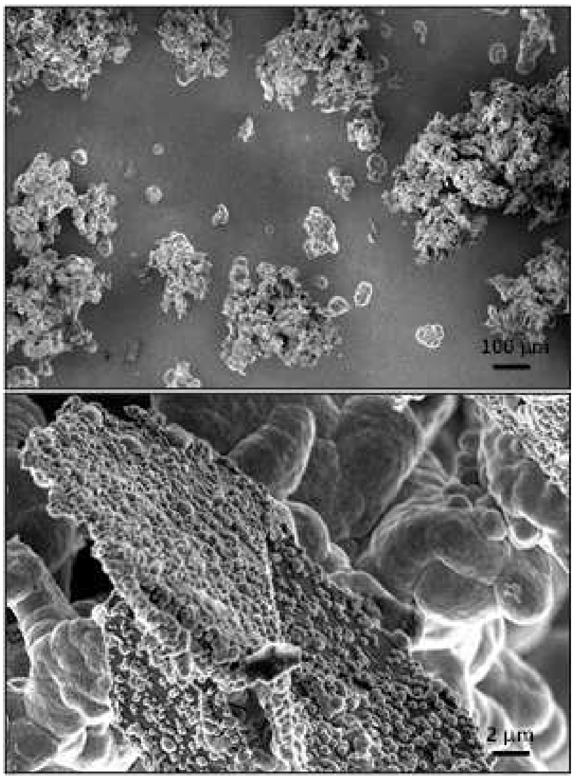

Fig. 5. Images of Ni/G (2) coating surface

Rys. 5. Obrazy powierzchni powłoki Ni/G (2)

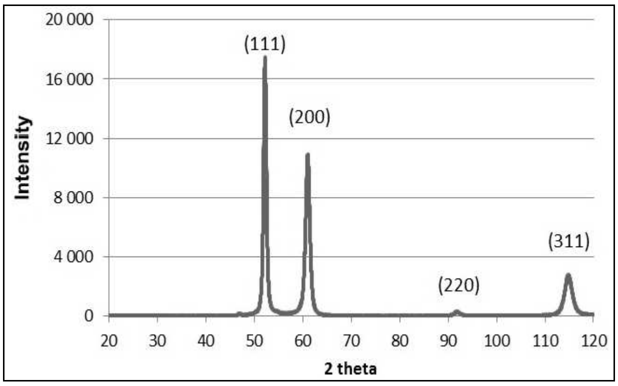

Fig. 6. Diffraction pattern of Ni coating

Rys. 6. Dyfraktogram powłoki Ni

TABLE 1. **Microhardness HV0.01 of Ni, Ni/G coatings**
TABELA 1. **Mikrotwardość HV0,01 powłok Ni, Ni/G**

Material	HV0.01	Thickness [µm]
steel	134	-
Ni	315	22
Ni/G (1)	393	19
Ni/G (2)	452	17

The graphene flakes embedded in the nickel matrix substantially affected increasing the hardness of the material coatings. The Ni, Ni/G (1) and Ni/G (2) coatings were subjected to wear tests. In the conducted studies, the wear depth, which was adopted as a measure of abrasive wear and related to a loss in mass of the test coatings, was expressed as a function of time of the friction pair action. The results of the tribological tests are shown in Figure 8.

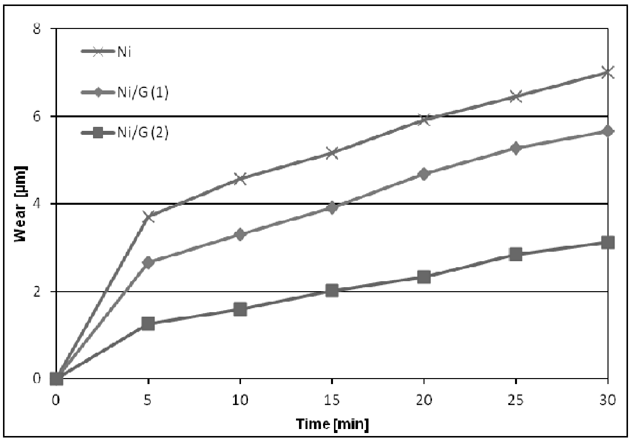

Fig. 8. Intensity of tribiological wear of Ni and Ni/G coatings as function of friction pair collaboration time

Rys. 8. Intensywność zużycia tribologicznego powłok Ni oraz Ni/G w funkcji czasu współpracy pary trącej

The images of the Ni and Ni/G (1) and N/G (2) surface coatings after the tribological tests are shown in Figure 9.

The wear studies show that the nickel coating exhibited the lowest wear resistance under the given conditions. The composite coatings containing graphene as the disperse phase are characterized by a greater resistance to wear. The Ni/G (2) coating has twice less wear than the coating without the addition of graphene. The amount of graphene in the coating has an essential influence on the resulting wear. On the surfaces of deposited coatings after tribological tests are visible characteristic signs of wear due to the work of the tested sample-ring friction pair.

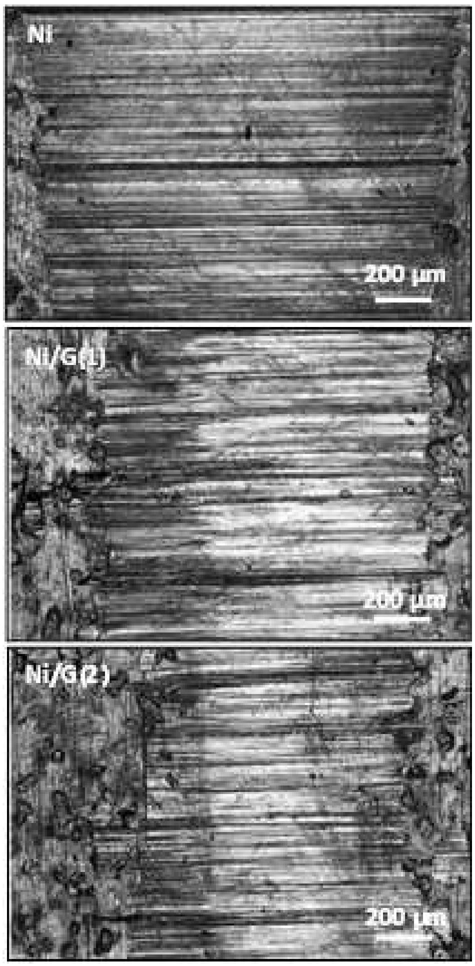

Fig. 9. Surface of Ni, Ni/G (1) and Ni/G (2) coating after tribological tests

Rys. 9. Powierzchnia powłok Ni, Ni/G (1) oraz Ni/G (2) po badaniach tribologicznych

CONCLUSIONS

The conducted studies have shown that in the case of nickel coatings, the incorporation of graphene flakes into the nanocrystalline structure has a significant influence on the mechanical and tribological properties of the produced material. The graphene flakes embedded in the nanocrystalline nickel matrix increase the hardness and the wear resistance of the coating material. The properties of such coatings are also affected by the amount of built-in dispersed phase in the form of flakes of graphene. Nanostructured nickel-graphene coatings can be widely used in industry to increase the wear resistance of elements working in friction.

REFERENCES

[1] Medelienė V., Stankevič V., Grigucevičienė A., Selskienė A., Bikulčius G., The study of corrosion and wear resistance of copper composite coatings with inclusions of carbon nanomaterials in the copper metal matrix, Materials Science (Medžiagotyra) 2011, 17, 132-139.

[2] Huang G. et al., Preparation and characterization of the graphene-Cu composite film by electrodeposition process, Microelectronic Engineering 2016, 157, 7-12.

[3] Saleem H., Habib A., Study of band gap reduction of TiO_2 thin films with variation in GO contents and use of TiO2/Graphene composite in hybrid solar cell, Journal of Alloys and Compounds 2016, 679, 177-183.

[4] Cygan T. et al., Influence of graphene addition and sintering temperature on physical properties of Si_3N_4 matrix composites, Int. Journal of Refractory Metals and Hard Materials 2016, 57, 19-23.

[5] Sun X. et al., Graphene foam/carbon nanotube/poly(dimethyl siloxane) composites for exceptional microwave shielding, Composites: Part A 2016, 85, 199-206.

[6] Ma Z. et al., Graphene oxide/chitin nanofibril composite foams as column adsorbents for aqueous pollutants, Carbohydrate Polymers 2016, 144, 230-237.

[7] Woźniak J. et al., Preparation and mechanical properties of alumina composites reinforced with nickel-coated graphene, Ceramics International 2016, 42, 8597-8603.

[8] Trzaska M., Cieślak G., Composites layers of Ni-P/graphene produced by chemical reduction method, Composites: Theory and Practice 2015, 3, 137-140.

[9] Cieślak G., Mazurek A., Trzaska M., Warstwy kompozytowe Ni/grafen wytwarzane metodą redukcji elektrochemicznej, Inżynieria Powierzchni 2015, 3, 44-47.

[10] Szeptycka B., Gajewska-Midziałek A., Powłoki nanokompozytowe nikiel-grafen wytwarzane metodą redukcji elektrochemicznej, Inżynieria Materiałowa 2015, 3, 112-115.

[11] Liu X. et al., One-step electrochemical deposition of nickel sulfide/graphene and its use for supercapacitors, Ceramics International 2014, 40, 8189-8193.

[12] Kuang D., Xu L., Liu L., Hu W., Wu Y., Graphene-nickel composites, Applied Surface Science 2013, 273, 484-490.

[13] Chen J. et al., Preparation and tribological behavior of Ni-graphene composite coating under room temperature, Applied Surface Science 2016, 361, 49-56.

