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COMPOSITES THEORY AND PRACTICE

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NICKEL-GRAPHENE COMPOSITE COATINGS

The research on the graphene application for the electrodeposition of nickel composite coatings was conducted. The study assessed the important role of graphene in the increased wear resistance of these coatings. A Watts type nickel plating bath with a low concentration of nickel ions, organic addition agents and graphene as dispersed particles was used for deposition of the composite nickel-graphene coatings. The particle contents in the coatings, surface morphology, roughness and microhardness of the coatings were measured. An Amsler testing machine with a block - ring system was used for tribological tests with Lux oil lubrication. The obtained results suggest that the content of incorporated graphen particles increases with an increasing amount of graphen in the plating bath. The application of organic compounds was advantageous. The nickel-graphene coatings produced during the investigation were distinguished by much better tribological properties than the nickel coating. The tested composite coatings had a relative wear resistance from 3.7 to 6.9 times higher in relation to the relative wear resistance of a nickel coating.

Keywords: nickel, electrodeposition, composite coatings, graphene

POWŁOKI KOMPOZYTOWE NIKIEL-GRAFEN

Prace badawcze nad zastosowaniem grafenu do elektroosadzania niklowych powłok kompozytowych były pierwszą próbą wykorzystania i oceny zalet tego materiału w niklowych powłokach kompozytowych pod kątem wzrostu ich odporności na zużycie przez tarcie. W pracy do osadzania powłok kompozytowych nikiel-grafen użyto kąpieli typu Wattsa z obniżonym stężeniem jonów niklu, dodatków organicznych i grafenu jako cząstki dyspersyjne. Przedstawiono wyniki badań dla powłok nikiel-grafen wytwarzanych z kąpieli o zawartości grafenu 0,33 i 0,5 g/dm^3 oraz w obecności dwóch różnych związków powierzchniowoczynnych. Badano zawartość cząstek w powłokach, morfologię powierzchni, chropowatość i mikrotwardość powłok. Badania tribologiczne wykonano w warunkach tarcia ze smarowaniem na maszynie Amslera. Otrzymane wyniki sugerują, że ilość wbudowanych cząstek grafenu wzrasta ze wzrostem zawartości grafenu w kąpieli. Zastosowanie badanych związków organicznych było korzystne. Kompozytowe powłoki nikiel-grafen wytworzone w tych badaniach odznaczały się znacznie lepszymi właściwościami tribologicznymi od powłoki niklowej. Badane powłoki kompozytowe miały względną odporność na zużycie od 3,7 do 6,9 razy większą od względnej odporności na zużycie powłoki niklowej.

Słowa kluczowe: nikiel, elektroosadzanie, powłoki kompozytowe, grafen

INTRODUCTION

Graphene is an sp^2-hybridized unsaturated compound (alkene). It forms a single flat layer of carbon atoms packed in a two-dimensional (2D) honeycomb structure.

Since the discovery of graphene in 2004 [1, 2] numerous publications on its properties and possible applications have been published [3-5].

There are many different types of graphene, each offering a different set of properties. The differing parameters include: number of layers, purity, oxygen content, crystallinity and form (powder or sheet). Depending on the specifics of these parameters, the quality of the so-called graphene may differ from an ideal graphene material to graphite oxide. Each type of graphene is manufactured using a different technique, and all of the techniques differ in terms of cost structure, production capacity and ultimately, potential target markets.

Among the methods for the preparation of graphene the following can be mentioned: mechanical graphite exfoliation [1], thermal decomposition of SiC [6], epitaxy on metals [7], reduction of graphite oxide [8, 9], from nanotubes [10], thermal CVD [11, 12] and plasma enhanced chemical vapor deposition (PECVD) [13]. Graphene oxide derived from graphite using exfoliation is also being increasingly widely used [14, 15]. The extraordinary chemical and physical properties of graphene, such as: it is an excellent heat conductor, it has a low current resistance, absorbs approximately 2.3% light and is almost completely transparent, it is 100 times harder than steel, but it is also incredibly flexible at the same time, it is characterized by high mobility of electrons at normal temperature, it does not allow large amounts of elementary substances to pass through, a current flows very fast through it, meaning that there are more and more potential applications in different areas, such as: solar energy processing [16], superconductors [17], lithium batteries [18] or fuel cells [19].

Nickel matrix composite coatings are applicable especially in the automotive and aerospace industries due to their very good mechanical properties and corrosion resistance. The preparation of composite coatings with super hard particles and enhanced mechanical properties compared to nickel coatings have been described by several authors [20-23]. Other authors deposited Ni-nanotube composite coatings [24, 25] which were characterized by increased microhardness, as compared to nickel. Nanotubes are not resistant to crushing. Owing to their flexibility and empty structure, they can be easily bent and deformed under the influence of bending or compressive forces, as presented in the findings by Jeon et al. [25].

The tensile strength of multilayer nanotubes reaches 63 GPa and in the case of graphene it is 130 GPa. It can be assumed that graphene composite coatings are characterized by superior mechanical properties to nanotube coatings.

The advatageous properties of graphene as a lubricant in rolling friction were shown by Berman et al. [26]. When a graphene film was deposited on steel surfaces with a 1 g/dm^3 solution of ethanol and tested on a Kulotester apparatus at a humidity of 30%, it caused a six-time lower consumption of steel and six-time reduction in the friction coefficient in test conditions.

Kuang et al. [27] deposited nickel-graphene composite coatings of sulfamate electrolyte using graphene oxide (GO) for this purpose, which reduced to graphene under electrodeposition conditions. The content of graphene in the nickel coating was 0.12 wt.%. These particles forced a change in the crystallographic orientation of the nickel matrix from (200) to (111). The deposited composite coating was characterized by an improved microhardness and thermal conductivity, in relation to the nickel coating.

Another approach was used by Kumar et al. [28]. They reduced graphene oxide obtained by exfoliation with hydrazine and deposited the composite coating with a diluted electrolyte containing nickel sulfate and sodium, and boric acid. This layer was characterized by increased hardness and corrosion resistance as compared to the nickel coating. The graphene particles changed the nickel matrix orientation from (220) to (200) and caused a grain-size reduction of the matrix from 30 to 20 nm. The grain-size reduction of the matrix and incorporating graphene particles resulted in increased microhardness of the layer by 100 HV. The corrosion rate of the composite coating was two and a half times less than the corrosion rate of the nickel coating. Wang et al. [29] also deposited a nickel-graphene coating producing graphene oxide from graphite using the modified Hummers method [30, 31] and reducing the graphene oxide during nickel electrodeposition. The deposited composite coating was characterized by good catalytic properties for urea oxidation in a 1M KOH solution. Such a catalyst has a potential application in hydrogen production and in fuel cells.

The range of potential applications of graphene includes materials engineering (durable composite materials). It is also possible to use graphene in the form of composites in the aerospace and automotive industries, and because of its high strength, ductility and tightness of covering as a layer - in the form of laminated composites, modifying the substrate by improving its resistance to an aggressive environment of exploitation and oxygen corrosion.

Leading industries in Europe have shown serious interest in graphene, including the fields of mobile telecommunications and automobile production. The present work on the use of graphene for the electrodeposition of nickel composite coatings is an attempt to assess the use and advantages of this material in nickel composite coatings in terms of increasing their resistance to abrasive wear.

EXPERIMENTAL SECTION

Characteristics of graphene

Graphene iGP2 by Graphene Chemical Industries Co. (G) was used as the dispersion particles, with a diameter of 5 μm, thickness 5÷8 nm and surface area 120÷150 m^2/g in the amounts of 0.33 and 0.5 g/dm^3 of bath.

The SEM image of iGP2 graphene particles is shown in Figure 1.

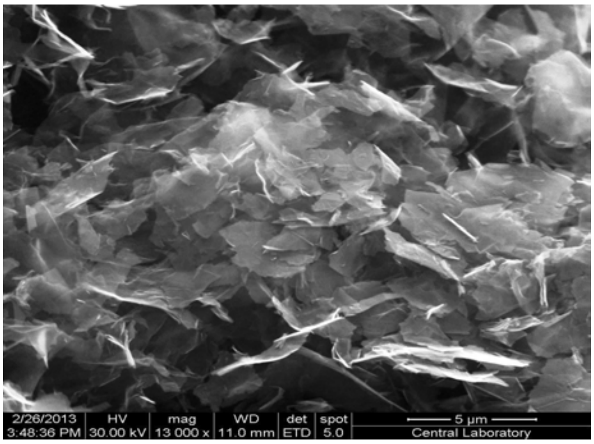

Fig. 1. SEM image of graphene iPG2. 13 000x magnification. From www.grafen.com.tr

Rys. 1. Obraz SEM grafenu iPG2. Powiększenie 13 000x. Reprodukcja z www.grafen.com.tr

Electrodeposition parameters

The electrodeposition experiments of composite nickel-graphene coatings were carried-out using a low-concentration Watts nickel plating electrolyte of the following composition: 0.45 M $NiSO_4$. 7H_2O, 0.3 M $NiCl_2 \cdot$ 6H2O, 0.85 M H_3BO_3. The bath was prepared in the usual manner, oxidized and preelectrolyzed to remove organic and metallic impurities and then refilled with a dispersion of particles and addition agents. The GRN addition agent was used as an antipitting and leveller addition. For the production of graphene dispersion, two surface-active substances were used: Z1 - [3-(heptadekafluorineoctyl)-sulphonyl]-amino-propyl-trimethylammonium jodide and Z2 - N-ethyl-N(heptadekafluorineoctyl) sulphonylglicyn potasium salt purchased from Aldrich. The electroplating process was realized at a current density of 4 A/dm^2, temperature of 318 K and pH = 4 during 30 min. Composite nickel coatings were deposited on a copper metal substrate by stirring with a magnetic stirrer at a speed of 100 rev/min. The substrate was prepared as follows:

- degreasing with calcium carbonate and pickling with hydrochloric acid 1:1 (to test surface roughness and microhardness),
- passivating in 10% sodium dichromate to make it possible to remove the deposited coating layer (for testing of particle contents).

Measurement methodology

The content of the dispersion particles in the composite coating was determined by titration. The roughness of the nickel layers was measured using a TR 100 profilograph by Elcometr Instruments Ltd. The microhardness of the deposited coatings was measured on the cross section by a Vickers microhardness tester under the load of 0.05 kg.

To study the tribological properties of the produced composite layers, the method according to IMP procedure LB-4 No. PB/2-19/LB-4 for sliding friction processes (rotation) on an Amsler friction machine at a constant unit pressure was employed. The methodology of work at this station is standardized (PN-82/H-04332). The conditions in the Amsler A-135 machine were: block-ring friction system, sample composite coating-counter sample 41Cr4 steel heat treated (ca. 70 HRC) friction pairs, counter sample rotational speed n = = 200 rpm, friction speed v = 0.35 m/s, load: P = 25 daN, test duration t = 3 h, conditions of surface mating: lubricated with Lux oil by immersion; diameter of ringcounter sample ca. 35 mm. Wear was measured every 30 minutes by weighing with a precision of 0.5 mg. Measurements of the transient friction coefficient were taken every 30 minutes by measuring the moment of friction.

Observations of the Ni-graphene composite coating surface were performed using a scanning item for the JEM 100C transmission electron microscope. Chemical composition analyses were performed on sample surfaces using an ISIS 300 energy dispersive X-ray spectrometer at an accelerating voltage of 40 kV.

RESULTS AND DISCUSSION

Table 1 summarizes the numbers of samples, bath compositions with the addition of GRN, graphene particle content in the composite coating, roughness parameter R$_a$ and microhardness. The microhardness of the nickel coating was 4.8 HV 0.05.

TABLE 1. **Results of measurements of graphene particles in composite coating C_p, roughness parameter R_a and microhardness HV 0.05**

TABELA 1. **Wyniki pomiarów zawartości cząstek grafenu w powłoce kompozytowej C_p, parametru chropowatości R_a i mikrotwardości HV 0,05**

No	Bath composition	C_p [%]	R_a [µm]	*HV* 0.05 [GPa]
1	G(0.33g/l)+Z1	0.82	0.49	3.4
2	G(0.5g/l)+Z1	1.3	0.45	3.5
3	G(0.33g/l)+Z2	0.5	0.37	4.7
4	G(0.5g/l)+Z2	1.9	0.23	5.0

Figures 2 to 5 show the results of the tribological tests.

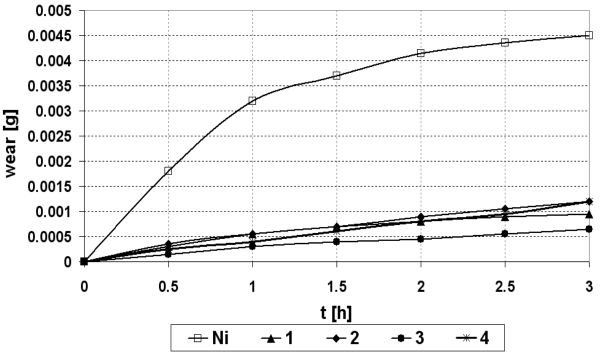

Fig. 2. Dependence of weight wear of Ni-graphene composite and Ni coatings on friction time. Amsler machine, lubrication with Lux oil. Sample number as in Table 1

Rys. 2. Zależność zużycia wagowego próbki od czasu tarcia. Maszyna Amslera. Powłoki: niklowa i kompozytowe Ni-G, smarowanie olej Lux. Numery próbek jak w tabeli 1

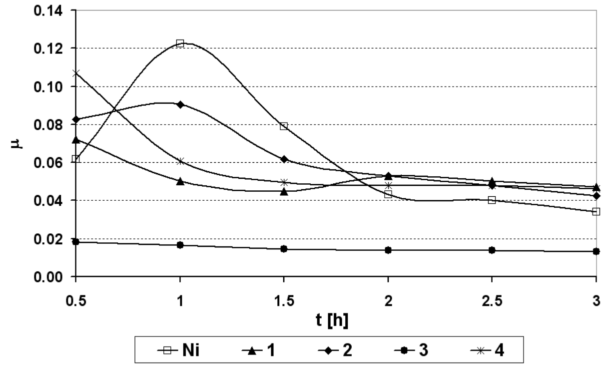

Fig. 3. Dependence of instantaneous coefficient of friction on test duration. Amsler machine. Ni and Ni-graphene composite coatings, lubrication with Lux oil. Sample number as in Table 1

Rys. 3. Zależność chwilowego współczynnika tarcia od czasu trwania próby. Maszyna Amslera. Powłoki: niklowa i kompozytowe Ni-G, smarowanie olej Lux. Numery próbek jak w tabeli 1

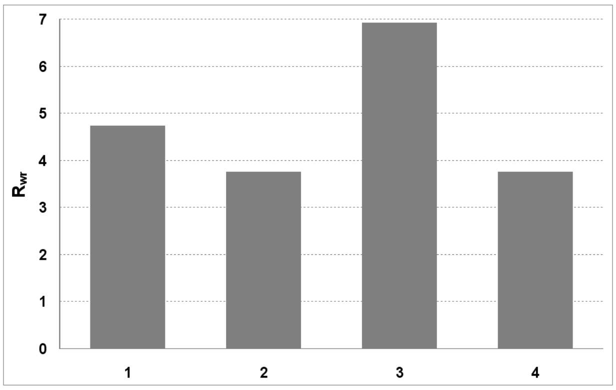

Fig. 4. Relative wear resistance of Ni-graphene composite coatings relative to nickel matrix without graphene. Amsler machine, 3 h friction, lubrication with Lux oil. Sample number as in Table 1

Rys. 4. Względna odporność na zużycie powłok kompozytowych Ni-G w stosunku do osnowy niklowej bez wbudowanego grafenu. Maszyna Amslera, 3 h tarcia, smarowanie olej Lux. Numery próbek jak w tabeli 1

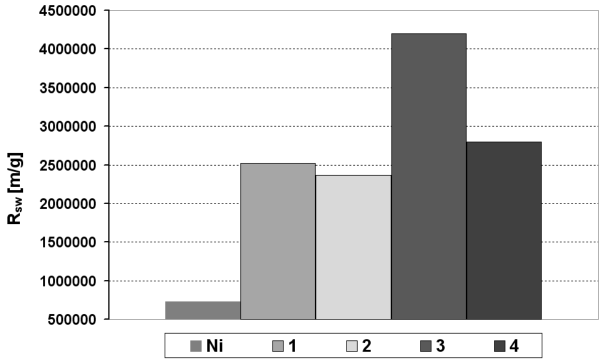

Fig. 5. Wear resistance of Ni and Ni-graphene composite coatings after 3 h of friction. Amsler machine, lubrication with Lux oil. Sample number as in Table 1

Rys. 5. Odporność na zużycie powłok: niklowej i kompozytowych Ni-G po 3 h tarcia. Maszyna Amslera, smarowanie olej Lux. Numery próbek jak w tabeli 1

Figure 6 presents the SEM image of the Ni-graphene coating and Figures 7 and 8 show the EDS spectra of the selected area in Figure 6.

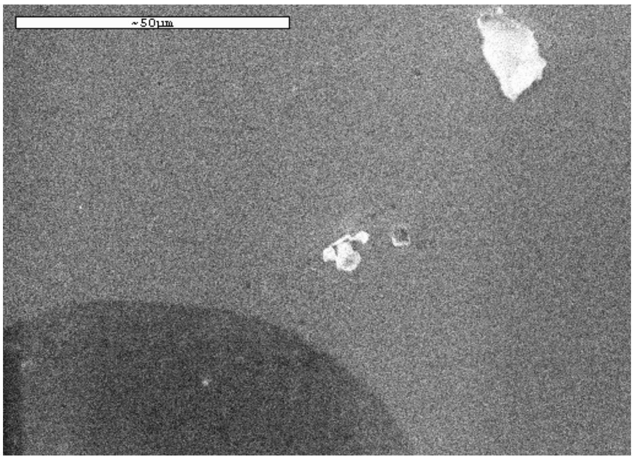

Fig. 6. SEM image of Ni-graphene coating. Sample 4. Graphene particle in nickel coating

Rys. 6. Obraz SEM powłoki Ni-G. Próbka 4. Cząstka grafenu w powłoce niklowej

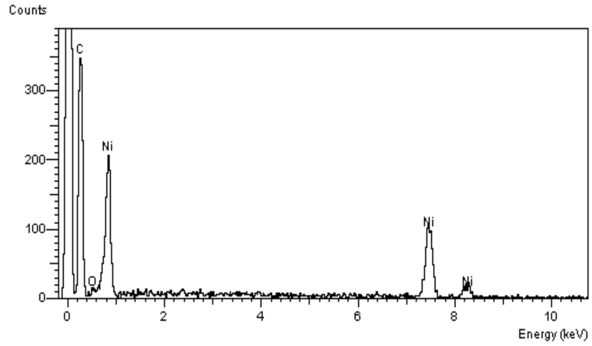

Fig. 7. EDS spectrum of graphene particles shown in Figure 6

Rys. 7. Widmo EDS z cząstki grafenu z rysunku 6

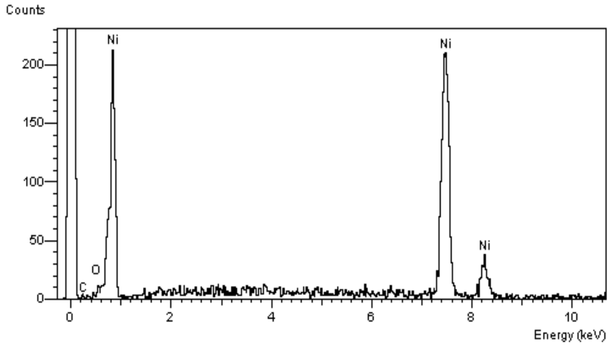

Fig. 8. EDS spectrum from smooth surface of coating in Figure 6

Rys. 8. Widmo EDS z gładkiej powierzchni powłoki z rysunku 6

iGP2 graphene particles in the amounts of 0.33 and 0.5 g/dm^3 were used and the dispersions were prepared with two different surface-active substances. The results of of the graphene particle measurements incorporated in the composite coatings (Table 1) showed that under the selected conditions of deposition, incorporation of these particles is possible in the range from 0.5 to 1.9% by weight. The microhardness of the Ni-graphene coatings was between 3.4 and 5.0 GPa for a load of HV 0.05 (Table 1), and was higher than the microhardness of the Ni-graphene coating obtained by Kumar et al. [28]. Only Sample 4 was characterized by a microhardness greater than that of nickel. Apparently, the incorporated graphene particles in other samples had an insufficient impact on strengthening the nickel matrix.

The coatings deposited in the presence of a cationic wetting agent had a greater roughness than those coatings deposited in the presence of an anionic wetting agent (Table 1).

The thickness of the deposited coatings differed slightly (about 20 ±2 μm) and the cathodic current efficiency was between 90 and 97%.

In the sliding friction conditions used, all of the deposited coatings had less wear (Fig. 2) when compared to the nickel coating. The values of the instantaneous friction coefficient were different (Fig. 3), and it probably depended on the contents of the incorporated graphene particles and roughness parameters. The smallest instantaneous friction coefficient - 0.015 was observed in sample 3 containing 0.5% graphene and an R_a value of 0.37 μm. This sample also had the highest abrasive wear resistance (Fig. 5) and nearly seven times higher relative wear resistance in relation to nickel coatings (Fig. 4). The other tested composite coatings had relative wear resistance from 3.7 to 4.7 times higher in relation to the wear resistance of the nickel coating.

CONCLUSIONS

It has been shown that iGP2 graphene particles can be incorporated into nickel coatings using the electrochemical method. The presence of graphene in composite coatings was confirmed by titration and EDS methods.

Minor roughness of the Ni-graphene composite coatings and greater microhardness were obtained using an anionic wetting agent used to produce graphene dispersion.

All the Ni-graphene composite coatings had better abrasion wear resistance in relation to the nickel coating, but those deposited in the presence of an anionic wetting agent had better resistance than those deposited in the presence of a cationic wetting agent.

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