ARCHIVES OF METALLURGY AND MATERIALS
Volume 59 2014 Issue 4
DOI: 10.2478/amm-2014-0257

N. GIDIKOVA*, A. CIAŚ**, V. PETKOV*, M. MADEJ**, M. SUŁOWSKI**, R. VALOV*

WEAR RESISTANT CHROMIUM COATINGS MODIFIED WITH DIAMOND NANOPARTICLES

ODPORNOŚĆ NA ZUŻYCIE ŚCIERNE POWŁOK CHROMOWYCH MODYFIKOWANYCH NANOCZĄSTKAMI DIAMENTU

Electrochemical chromium coatings on steel, modified with diamond nanoparticles (NDDS), were produced by detonation synthesis. Their particle size was from 10 to 50 nm. Galvanization conditions, current density, etc., concentration of NDDS, were studied in relation to the characteristics of the chromium coatings. The optimal conditions were determined to attain the maximal values of the physical and mechanical properties of the coating. Surface topography after wear testing was examined. Compared to unmodified chromium coating, microhardness of the surface increased to 1100 kg/mm^2, wear resistance, expressed as % of mass loss, increased from 3 to 10 times.

Keywords: diamond nanoparticles, chrome galvanization, microhardness, wear resistance

Powłoki chromowe, wytworzone elektrochemicznie na stali, modyfikowane nanocząstkami diamentu, zostały wyprodukowane w procesie syntezy detonacyjnej. Ich wielkość cząstek mieściła się w zakresie od 10 do 50 nm. W artykule przedstawiono wpływ warunków galwanizacji, gęstości katodowej prądu, koncentracji nanocząstek diamentu na grubość powłoki chromowej. Podczas badań wytypowano optymalne warunki wytwarzania, pozwalające na uzyskanie warstwy chromowej o najlepszych własnościach fizycznych oraz mechanicznych. Przeprowadzono również badania odporności na ścieranie uzyskanych warstw. Na podstawie badań stwierdzono, że w porównaniu do powłok chromowych nie modyfikowanych nanocząstkami diamentu, mikrotwardość na powierzchni wzrosła do 1100 kg/mm^2, a odporność na zużycie ścierne, wyrażona jako % ubytek masy, wzrosła od 3 do 10 razy.

1. Introduction

Electrochemical chromium coatings on steels have a wide practical application. They increase the hardness and the wear resistance of the base material and possess increased corrosion resistance. The modification of the chromium galvanic coatings with diamond nanoparticles additionally increases these chemical and mechanical properties [1-3]. Therefore such investigations are widely performed in recent years. The aim of the present study was to investigate the influence of diamond nanoparticles and their concentration in the electrolyte on the performance and properties of the chromium layer, and especially on the hardness of the surface and its wear resistance.

2. Experimental procedures

The electrochemical chrome plating was carried out with acid solution of CrO_3 on samples of carbon steel C45. The current density was varied from 35 to 80 A/dm^2 and the duration of the process was 45 min. The diamond nanoparticles (NDDS) were obtained by detonation synthesis. They were added to the electrolyte as a water suspension in concentration from 0.6 to 42 g/l after an activation process was performed. The temperature of the electrolytic bath was 50°C. The anode was lead. The chromium yield, the thickness of the layer, its microstructure and microhardness were determined by weight and metallographic analysis methods. Their changes with the change of the current density and the concentration of the diamond nanoparticles in the electrolyte was studied. Dry friction wear resistance was investigated by the block on ring test.

3. Results and discussion

As was shown in Figure 1, the chromium yield (the accumulated quantity of Cr) on the cathode increased with the increase of the current density and the concentration of the diamond nanoparticles in the chrome plating electrolyte (Fig. 1).

The microstructure and the respective thickness of the chromium coating at different concentrations of the diamond nanoparticles in the electrolyte was presented in Figure 2. The coating is soundly joined to the basic material and visually it is homogenous. The thickness of the layer is increased with increasing diamond nanoparticles concentration at constant current density and duration of the galvanization.

---

* INSTITUTE OF METAL SCIENCE, SOFIA, BG
** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

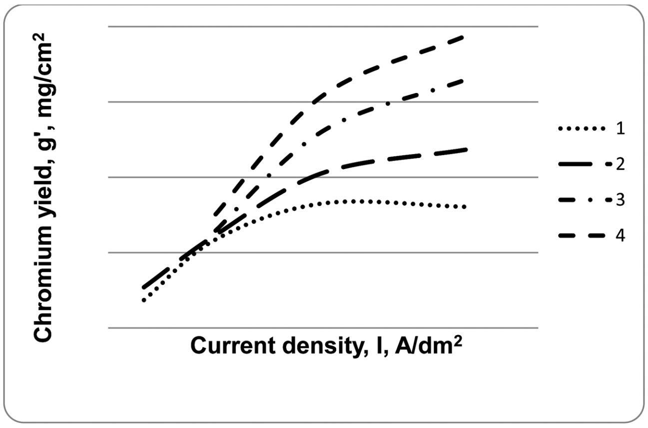
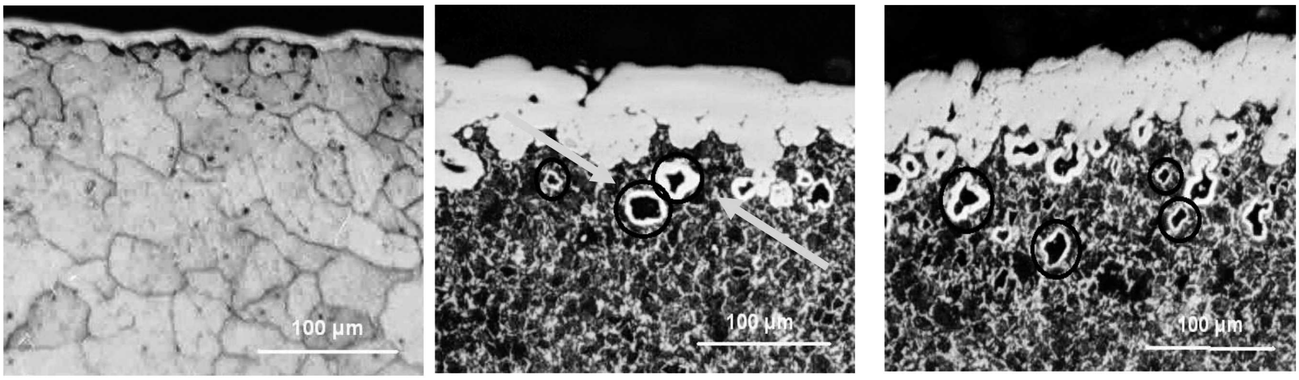


Fig. 1. The change of the chromium yield (g') with the change of the current density (I) and the nanodiamond particles concentration (C_{NDDS}): 1) C_{NDDS} = 0; 2) C_{NDDS} = 0.6 g/l; 3) C_{NDDS} = 10 g/l; 4) C_{NDDS} = 25 g/l



a) b) c)

Fig. 2. Microstructures of chromium galvanic coatings on steel, produced with different concentrations of diamond nanoparticles C_{NDDS} in the electrolyte (I = 45 A/dm^2, t = 45 min): a) C_{NDDS} = 0; b) C_{NDDS} = 25 g/l; c) C_{NDDS} = 42 g/l

Mini-sections, examples of which are marked as circles in Figure 2b, 2c, were formed in the zone adjacent to the chromium coating when the concentration of diamond nanoparticles is equal to or more than 25 g/l. This phenomenon occurs no matter what the current density and other galvanic conditions are. The formation of the mini-sections depends only on the presence of diamond nanoparticles and their concentration. The mini-sections contain pure chromium shell covering steel grains. The chromium layer gradually gets thicker, overlaps totally the section and "sticks" to the inner surface of the base coating. This type of mechanism of building the electrochemically deposited layer is not described in the literature. These processes can be explained only by the active participation of the diamond nanoparticles. The chromium containing ions are absorbed on the surface of the diamond nanoparticles, which turn into "donors" of chromium while moving to the cathode, and in this way accelerate the electrochemical process. Chromium deposition and layer thickness are increased. On the other hand with increasing concentration of the diamond nanoparticles in the electrolyte, an electron exchange of the ions absorbed on the surface of the nanoparticles intensifies. Chromium ions are reduced and neutral chromium is deposited on the steel grains situated under the layer.

The microhardness was determined at points of the surface zone with a load of 50 g, duration 10 s and loading speed 10 g/s. The value of the microhardness is the average of 30 measurements. Samples were made with different concentration of the diamond nanoparticles in the electrolyte and at different galvanizing conditions. The results are presented in Figure 3. Current density does not influence considerably the microhardness of the coating. The rise in the concentration of the NDDS increases the microhardness of the coatings, and at C_{NDDS} = 42 g/l it is 1100 kg/mm^2. This microhardness is 2 times greater than that of the pure chromium coating obtained at the same galvanizing conditions and 8 times greater than that of the substrate material. The microhardness of the Fe matrix in the zone adjacent to the chromium coating is also increased. The results of microhardness tests are presented in Figure 3.

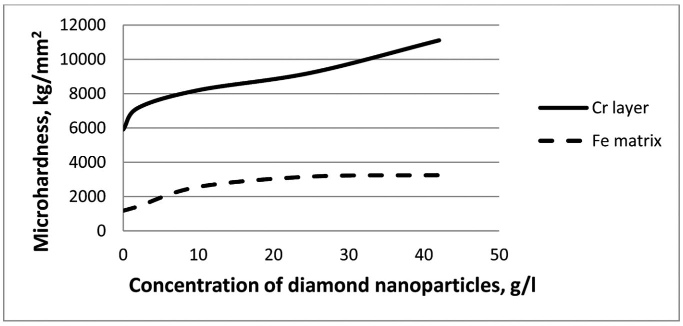


Fig. 3. Relation of microhardness to diamond nanoparticles concentration

4. Tribological testing

The wear tests were carried out using the block-on-ring tester (Figure 4). During the test a rectangular 15×5×10 mm wear sample (1) was mounted in a sample holder (4) equipped with a hemispherical insert (3) ensuring proper contact between the test sample and a steel ring (2), heat treated to 55 HRC, which was rotated at a constant speed of 136 rpm. The wear surface of the sample was perpendicular to the loading direction. Double lever system was used to force the sample towards the ring at 156±1% N. The loss of sample mass was measured after a sliding distance of 500m (Figs. 5 and 6).

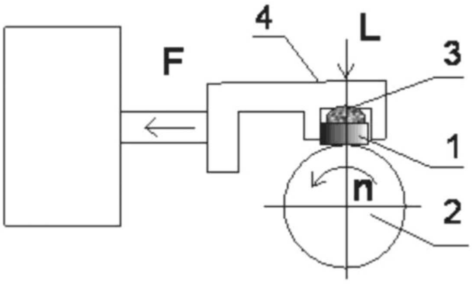


Fig. 4. Schematic view of the block-on-ring tester

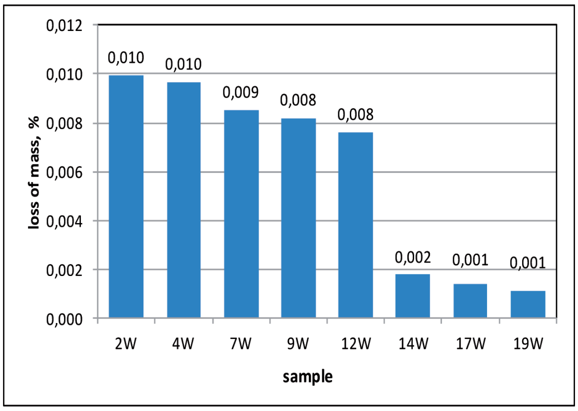


Fig. 5. Loss of mass of the samples after sliding distance of 500 m

Characteristic surface topographies after wear testing are presented in Figs 7-10. The friction coefficient was calculated as mean force F [N] during the whole wear test divided by load (in Newtons). The galvanic parameters for the preparation of the samples are shown on Table 1.

TABLE 1

The electroplating conditions for samples preparation

Sample No	C_{NDDS}, g/l	Current density, A/dm^2
2W	0	45
4W	0	60
7W	1	45
9W	1	60
12W	5	45
14W	5	60
17W	10	45
19W	10	60

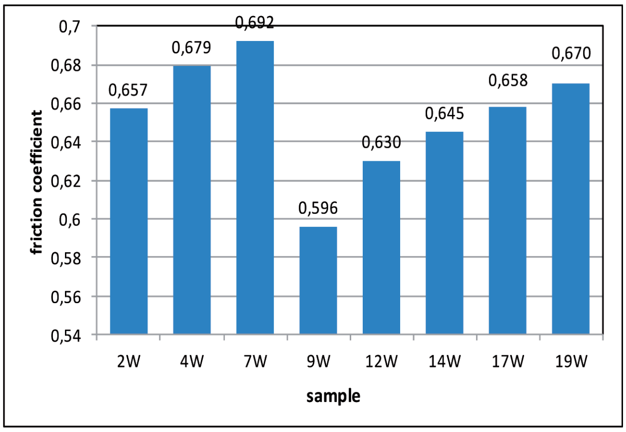


Fig. 6. Friction coefficient of the samples

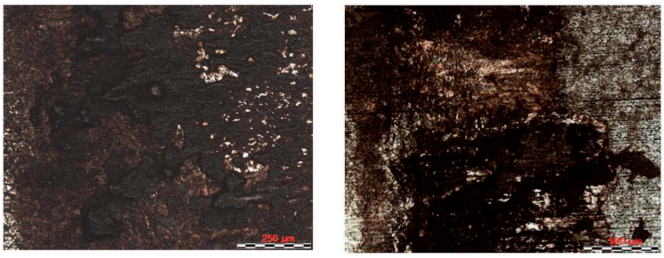


Fig. 7. Surface topographies of 2W (left) and 4W (right) samples after a sliding distance of 500 m

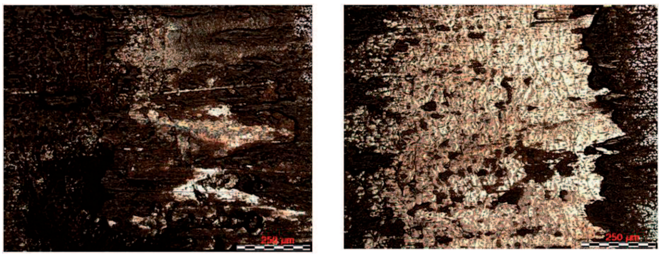


Fig. 8. Surface topographies of 7W (left) and 9W (right) samples after sliding distance of 500 m

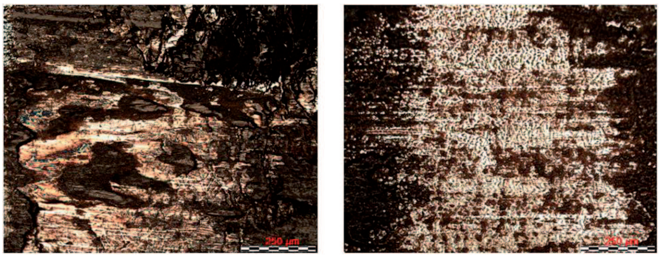


Fig. 9. Surface topographies of 12W (left) and 14W (right) samples after sliding distance of 500 m

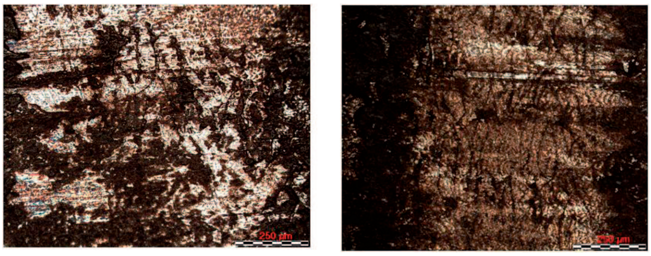


Fig. 10. Surface topographies of 17W (left) and 19W (right) samples after sliding distance of 500 m

The topographies of the friction surface, presented in Figures 7-10, indicate that the dominating mechanism of wear was adhesive wear. There are also some scratches – transverse to the direction of the friction test. The figures show also smearing of material from the steel ring over the surface of the samples, which implies marked contribution of adhesive wear; an extensive formation of iron oxides may occur.

5. Conclusions

The investigations allowed the following conclusions to be drawn:

1. During electrochemical deposition of chromium the modification of the electrolyte with diamond nanoparticles results in increase of the chromium yield and the thickness of the coating.
2. Original data of the behavior and the role of the diamond nanoparticles in the process of electrochemical deposition of chromium are obtained. This data clarifies the mechanism of their action.
3. The wear resistance increases with the increase of the content of the nanodiamond particles in the electrolyte and at concentration 10 g/l it is approximately 10 times greater than the wear resistance of the pure chromium coating.
4. Micrographs of the friction surface indicate that the dominating mechanism of wear is adhesive wear.

Acknowledgements

The financial support of the Ministry of Science and Higher Education under AGH contract No **11.11.110.299** and Bulgarian Academy of Science is gratefully acknowledged.

REFERENCES

[1] V. Dolmatov, T. Fujimura, G. Barkat, E. Orlova, M. Veretennikova, Powder Metallurgy and Metal Ceramics **42**, 11-12 (2003).

[2] N. Mandich, J. Dennis, Metal Finishing, June 2001, 117.

[3] V. Isakov, A. Lyamkin, D. Nikitin, A. Shalimova, A. Solntsev, Protection of Metals and Physical Chemistry of Surfaces **46**, 5, 578-581 (2010).

Received: 20 February 2014.