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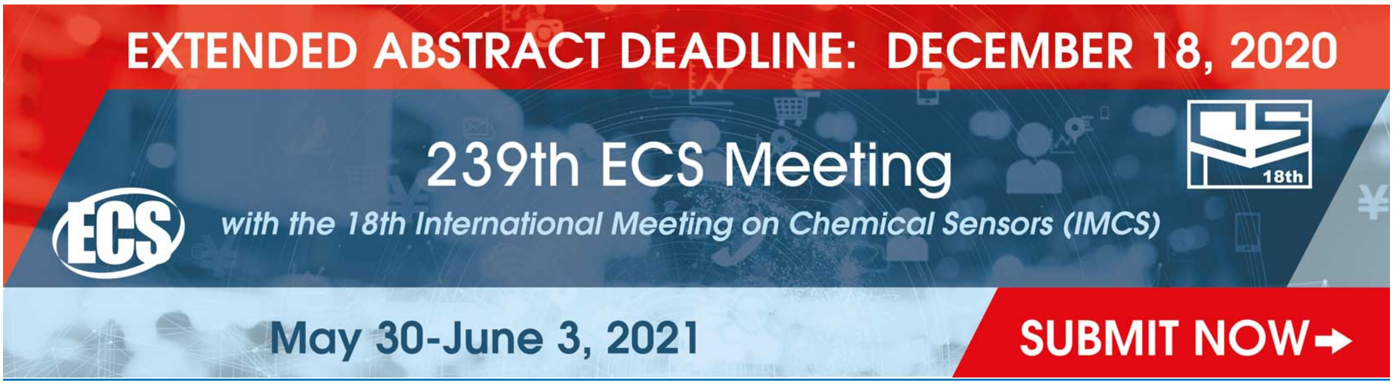

Wear resistance of WC/Co HVOF-coatings and galvanic Cr coatings modified by diamond nanoparticles

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Abstract. The efforts in the recent 20 years are related to search of ecological solutions in the tribotechnologies for the replacement of galvanic Cr coatings in the contact systems operating under extreme conditions: abrasion, erosion, cavitation, corrosion, shock and vibration loads. One of the solutions is in the composite coatings deposited by high velocity gas-flame process (HVOF). The present paper presents comparative study results for mechanical and tribological characteristics of galvanic Cr coatings without nanoparticles, galvanic Cr coatings modified by diamond nanoparticles NDDS of various concentration 0.6; 10; 15 и 20% obtained under three technological regimes, and composite WC-12Co coating. Comparative results about hardness, wear, wear resistance and friction coefficient are obtained for galvanic Cr-NDDS and WC-12Co coatings operating at equal friction conditions of dry friction on abrasive surface. The WC-12Co coating shows 5.4 to 7 times higher wear resistance compared to the galvanic Cr-NDDS coatings.

1. Introduction

For more than 70 years galvanic Cr coatings played the role of „gold standard" for high wear resistance of details operating under extreme conditions: abrasion, erosion, cavitation, corrosion, shock and vibration loads.

Modifying galvanic Cr coatings by nanosize particles improves their mechanical and tribological characteristics. This is the reason for their multiple studies in the field of nanotechnologies and nanotribology [1,2,3,4].

The specific production conditions of galvanic Cr coatings containing hexavalent chromium require higher measures of labor safety and environment protection from the toxic wastes of Cr electrolyte [5,6].

Basic disadvantages of galvanic Cr coatings are:

- Irregular distribution of coating thickness on the coated surface;
- High porosity and internal stress, which worsen the resistance against fatigue wear and corrosion;
- High sensitivity of structure, mechanical and tribological characteristics to electrolyte composition, parameters and the kinetics of the electrolysis;
- Impossibility to regenerate highly worn details because of the brittleness of thicker Cr coatings;

- Impossibility for deposition of galvanic Cr coatings on special steels with higher W and Co content, as well as on cast irons with higher hardness.

Promising replacements of galvanic Cr coatings are WC/Co composite coatings deposited by high velocity oxy-flame process (HVOF). HVOF-technology is a modern high technology with higher productivity and better ecological and economic characteristics compared to galvanic chrome plating.

WC/Co coatings deposited by HVOF-technology are new generation powder composite coatings with essential application in aircraft, space and power industry, petrol and chemical industry, etc. Table 1 shows characteristics of WC/Co composite coating and galvanic Cr coating from literature [5].

Table 1. Comparative values of some of the parameters of galvanic Cr coating and HVOF WC/Co coating.

Parameter	Galvanic Cr coating	HVOF WC/Co coating
Hardness, HRc	60-70	>70
Microhardness, DPH 300	750-850	>1050
Adhesion strength, MPa(psi)	41 (60 00)	> 80 (10 000)
Porosity, %	Sub-microcracks	< 1
Thickness, mm	< 0.13	> 1
Oxides, %	> 1	<1

The present paper aims a comparative study of abrasive wear and friction coefficient of galvanic Cr coatings without nanoparticles, galvanic Cr coatings modified by diamond nanoparticles of different concentration and WC/Co (88/12) coating operating at equal friction conditions [6].

2. Experimental procedures

Galvanic Cr-diamond nanoparticles composite coatings are deposited on cylindrical steel specimens of 30 mm diameter and 10 mm height. Table 2 shows the steel composition.

Table 2. Composition (wt. %) of the steel specimens, basis for the galvanic Cr-diamond nanoparticles composite coatings.

Element	C	S	Mn	P	Si	Cr	Ni	Fe
%	0.4	0.045	0.55	0.45	0.20	0.30	0.30	Balance

Cr electrolyte is composed by: CrO_3 – 220 g/l, H_2SO_4 – 2.2 g/l. Cr-diamond nanoparticles coatings are obtained under three technological regimes by variation of current density: 45 and 60 A/dm^2 and deposition duration: 35 and 45 minutes (table 3).

Table 3. Technological regimes of deposition of galvanic Cr coatings with different diamond nanoparticles concentration.

Regimes	R1	R2	R3
Current density, A/dm^2	45	45	60
Duration, min	35	45	35

Diamond nanoparticles of equal size 25 nm with variation of nanoparticles concentration: 0.6 g/l, 10 g/l, 15 g/l and 20 g/l are used for the three regimes R1, R2 and R3. The nanoparticles are added to the electrolyte in the form of water suspension. The process of coatings deposition runs along with intensive electrolyte stirring. The temperature in the electrolyte tray is kept stable in the interval 52-55^{o}C.

Table 4. Technological regime parameters for HVOF coating deposition.

№	Parameter	Technological regime
1.	Propylene/oxygen ratio, %	55/100
2.	Jet velocity, m/s	1000
3.	Distance „nozzle-coating" L, mm	120
4.	Angle between orifice axis and surface, α °	90
5.	Air pressure from compressor, bar	5
6.	N_2 pressure in the proportioning device, bar	4
7.	Velocity of powder material feeding, tr/min	1.5
8.	Mass flow rate of the powder material, g/min	22

The galvanic chromium-nanodiamond coatings and the WC/Co coating were not subjected to additional heat treating. Coatings thickness is been measured by means of the Pocket LEPTOSKOP 2021Fe device using eight point of the contact surface, and the coatings hardness – by Equotip Bambino 2 measuring device. Abrasive wear of galvanic chromium coating, chromium-nanodiamond coating and WC/Co (88/12) HVOF-coating are studied under conditions of dry friction on the surface with fixed abrasive particles using the „pin-on-disk" tribotester shown schematically in figure 1.

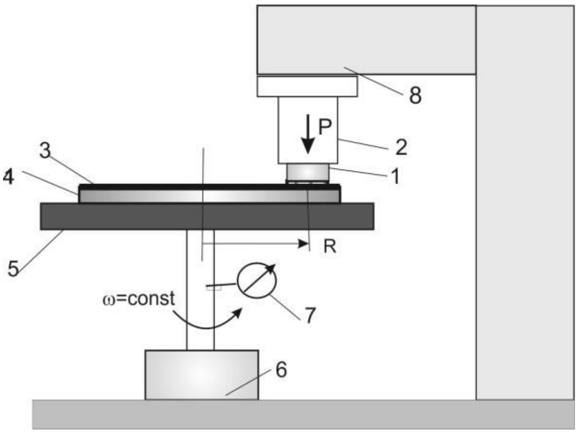

Figure 1. Schematic drawing of the „pin-on-disk" tribotester applied for the study of abrasive wear of coating during friction on the surface with fixed abrasive particles.

The studied cylindrical specimen 1 with the coating is placed in a holder 2 of the loading box 8, so that the coating stays in contact with the abrasive surface 3, fixed on horizontal disk 4 and mounted on the support 5. The disk is driven by the motor 6 and is rotating around its vertical central axis with rotational speed ω = const.

The sliding distance is measured by number of revolutions read on the revolution-counter 7. The device allows sliding speed variation by changing the disk rotational speed through the control unit and/or by changing the distance R between disk axis and specimen axis.

All tests are carried out at equal contact interaction conditions: load, sliding speed, sliding way, type and parameters of the abrasive (see table 5).

The test procedure embraces the measurement of mass wear *m* for each specimen after a given sliding way L followed by wear resistance *I* calculation using the formula:

$$I = \frac{\rho A_a L}{m} \tag{1}$$

where ρ is coating matrix material density, in our case the density of chromium $\rho = 6.92.10^3$ kg/m^3 and tungsten $\rho = 19.25.10^3$ kg/m^3.

Table 5. Abrasive wear test parameters.

Normal load	$P = 10.3$ N
Apparent (nominal) contact area	$A_a = 706.5.10^{-6}$ m^2
Apparent (nominal) contact pressure	$P_a = 1.46$ N/cm^2
Average sliding speed	$V = 0.82$ m/s
Sliding way	$L = 630$ m
Abrasive surface	Corundum P 320

The coefficient of friction is calculated for each test according to Amontons' law:

$$\mu = \frac{T}{P} \tag{2}$$

where T is the friction force, and P the normal load in specimen's center.

The coatings are compared by means of two relative criteria: K_{ND} and K_{WC}. The first one: K_{ND} characterizes the influence of diamond nanoparticles concentration upon the wear resistance of chromium-nanodiamond coatings:

$$K_{ND} = \frac{I(Cr - ND)}{I(Cr)} \tag{3}$$

It is the dimensionless ratio between the wear resistance of Cr coating containing diamond nanoparticles $I(Cr - ND)$ and the wear resistance of Cr coating without diamond nanoparticles $I(Cr)$ under equal friction regimes.

The second criterion $K_{WC/Co}$ indicates how many times the wear resistance of WC/Co (88/12) coating deposited by HVOF-technology is higher than the wear resistance of the chromium-nanodiamond coating. The criterion is given by the ratio of $I(WC / Co)$: the wear resistance WC/Co (88/12) coating and $I(Cr - ND)$: the wear resistance of electrolyte Cr coating with nanodiamond particles, i.e.

$$K_{WC/Co} = \frac{I(WC / Co)}{I(Cr - ND)} \tag{4}$$

3. Experimental results

Figure 2 shows the microstructure of galvanic Cr coating deposited under technological regime R1: without diamond nanoparticles (a) and with diamond nanoparticles with 10 g/l concentration.(b).

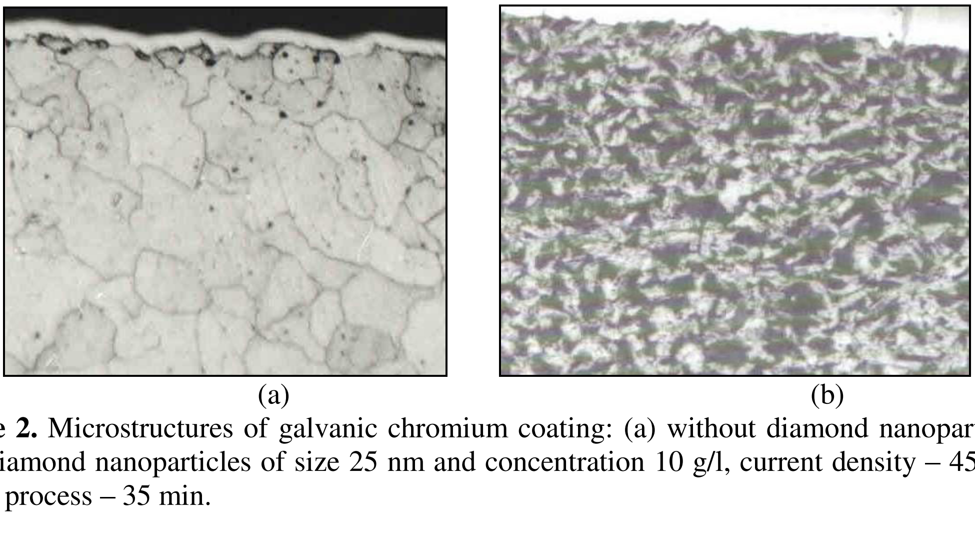
(a) (b)

Figure 2. Microstructures of galvanic chromium coating: (a) without diamond nanoparticles and (b) with diamond nanoparticles of size 25 nm and concentration 10 g/l, current density – 45 A/dm^2, time of the process – 35 min.

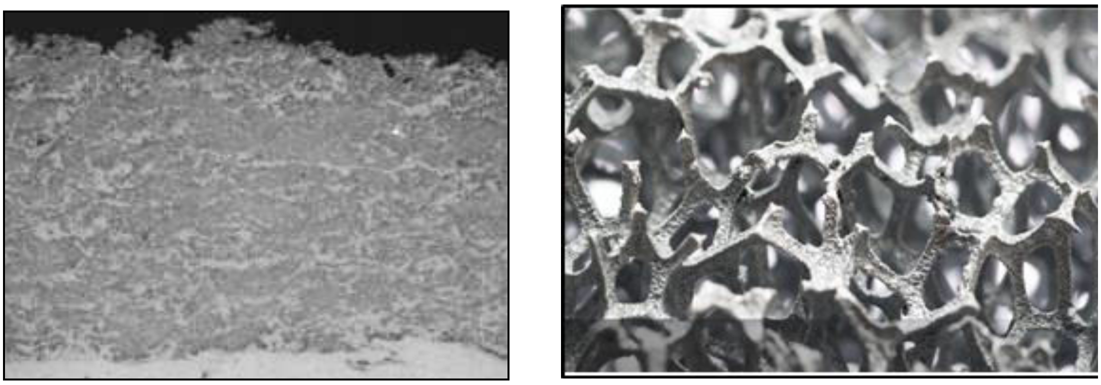
(a) (b)

Figure 3. Morphology (a) and microstructure, x200; (b) of WC/Co (88/12) HVOF coating on steel.

Based on the described procedures and devices, experimental results are obtained for the thickness, hardness, mass wear, wear resistance and friction coefficient of all coatings (see table 6).

Table 6. Experimental results for thickness, hardness, mass wear, wear resistance and friction coefficient of the studied galvanic coatings and WC/Co (88/12) coating.

№	Speci-men	Coating	NDDS g/l	Thickness μm	Micro-hardness MPa	Wear g	Wear-resistance m/kg	COF
1	0-R1	Cr	0	20÷35	5906	$42.2x10^{-3}$	$1.5x10^{7}$	0.35
2	1-R1	Cr-(0.6)ND	0.6	12÷16	8170	$89x10^{-3}$	$0.7x10^{7}$	0.46
3	2-R1	Cr-(10)ND	10	6÷23	7907	$32.4x10^{-3}$	$2x10^{7}$	0.24
4	3-R1	Cr-(15)ND	15	10÷20	8260	$34.3x10^{-3}$	$1.8x10^{7}$	0.26
5	4-R1	Cr-(20)ND	20	13÷17	8401	$40x10^{-3}$	$1.6x10^{7}$	0.32
6	0-R2	Cr	0	7÷11	6010	$40.4x10^{-3}$	$1.6x10^{7}$	0.31
7	1-R2	Cr-(0.6)ND	0.6	33÷40	8172	$72x10^{-3}$	$0.9x10^{7}$	0.42
8	2-R2	Cr-(10)ND	10	23÷38	8196	$68.4x10^{-3}$	$0.9x10^{7}$	0.40
9	3-R2	Cr-(15)ND	15	22÷25	8455	$53.5x10^{-3}$	$1.2x10^{7}$	0.38
10	4-R2	Cr-(20)ND	20	22÷26	8613	$44.4x10^{-3}$	$1.4x10^{7}$	0.36
11	0-R3	Cr	0	18÷32	6890	$80.2x10^{-3}$	$0.8x10^{7}$	0.42
12	1-R3	Cr-(0.6)ND	0.6	29÷34	8075	$49.1x10^{-3}$	$1.3x10^{7}$	0.37
13	2-R3	Cr-(10)ND	10	26÷29	7618	$51.2x10^{-3}$	$1.2x10^{7}$	0.38
14	3-R3	Cr-(15)ND	15	20÷25	8520	$66.4x10^{-3}$	$0.9x10^{7}$	0.40
15	4-R3	Cr-(20)ND	20	18÷24	9820	$96.8x10^{-3}$	$0.6x10^{7}$	0.58
16	WC/Co	WC/Co (88/12)		220	72 HRC	$5.8x10^{-3}$	$10.8x10^{7}$	0.14

Figures 4 and 5 give graphically the variation of thickness and micro hardness of galvanic Cr-nanodiamond coatings with the concentration of the diamond nanoparticles in the electrolyte under the three deposition regimes R1, R2 and R3.

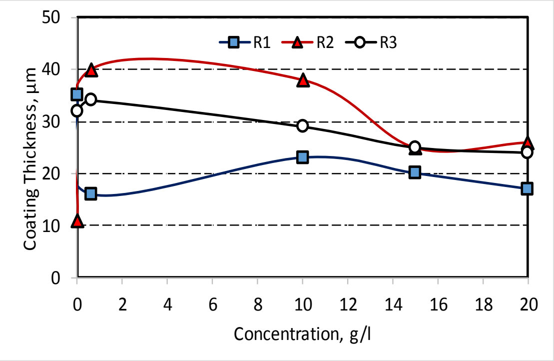

Figure 4. Influence of NDDS concentration on coating thickness.

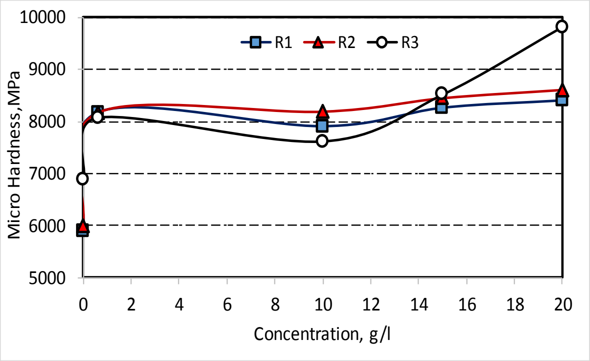

Figure 5. Influence of NDDS concentration on coating microhardness.

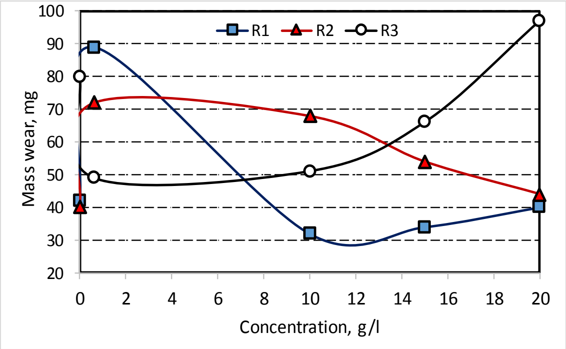

Figure 6. Influence of NDDS concentration on mass wear.

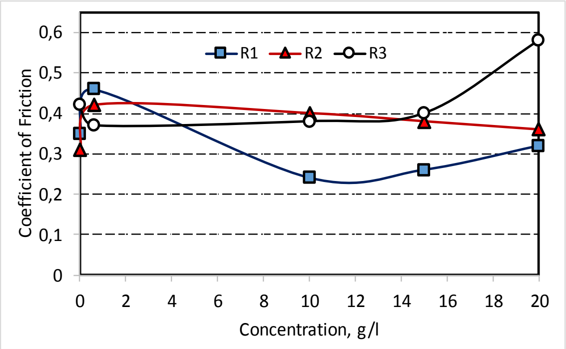

Figure 7. Influence of NDDS concentration on friction coefficient.

Figures 6 and 7 give graphically the variation of mass wear and friction coefficient of galvanic Cr-nanodiamond coatings with the concentration of the diamond nanoparticles in the electrolyte under the three deposition regimes R1, R2 and R3.

Figures 8 and 9 show diagrams of the relative criteria for comparison, K_{ND} and K_{WC}, at different nanodiamond particles concentrations in the Cr coatings for regime R1 and in WC/Co (88/12) coating.

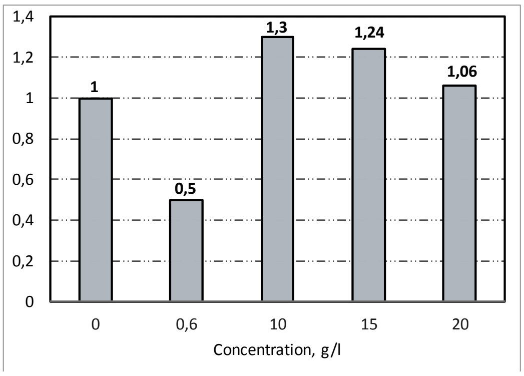

Figure 8. Diagram of criterion K_{ND}.

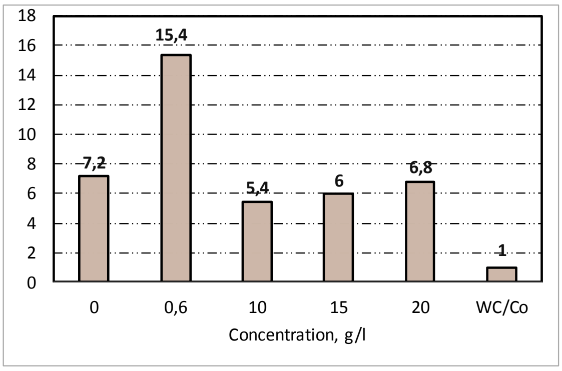

Figure 9. Diagram of criterion $K_{Wc/Co}$.

4. Discussion and conclusions

The comparative study for galvanic Cr and Cr-nanodiamod coatings provides the following interpretations and conclusions:

- Adding nanodiamond particles (NDDS) in electrolytic Cr coating affects the thickness, hardness, wear and friction coefficient. The nature and value of this influence depend on the technological regime of coatings deposition: current density and time of deposition, as well as on nanodiamond particles concentration;
- For small NDDS concentration – 0.6 g/l, wear increases compared to wear of Cr coating without NDDS for the three regimes R1, R2, R3 (figure 6). The wear resistance decreases of 50% compared to wear resistance of Cr coating without NDDS;
- The dependence of mass wear on NDDS concentration is nonlinear, the type of the curve depending on deposition regime – figure 6;
- Lowest wear shows Cr-nanodiamod coating deposited under regime R1 for 10-15 g/l NDDS concentration (figure 6). The wear resistance of these coatings increases by 30% compared to wear resistance of Cr coating without NDDS (figure 8);
- The variation of friction coefficient with NDDS concentration (figure 7) for the same regime R1 has similar character as the variation of wear (figure 6). Increasing NDDS concentration leads to increase of COF from 0.35 to 0.46; then it decreases, passes the minimum value 0.24 at 10 g/l NDDS concentration and increases gradually to 0.32 for concentration 20 g/l (figure 7). By technological regimes R2 and R3 COF keeps its constant value, except for the following: at concentration 20 g/l in regime R3 the COF increases abruptly to maximal value 0.58 for all studied coatings (figure 7). The last corresponds to the maximal wear of the same coating – figure 6, curve R3;
- Electrolyte Cr and Cr-nanodiamond coatings exhibit irregularly distributed thickness. The value depends on the technological regime and NDDS concentration (figure 4). Increasing NDDS concentration leads to thickness increase up to a given value, and then decreases to minimum values for concentration 20 g/l. Minimal thickness show Cr-nanodiamond coatings deposited at technological regime R1, which show the least wear among all studied galvanic coatings (figure 6);
- The presence of NDDS leads to increment in Cr coatings hardness (figure 5). At small concentration 0.6 g/l the hardness of all coatings increases by 42% compared to Cr coatings without NDDS. Further increment of NDDS concentration does not influence the hardness under different regimes. An exception is the coating obtained in regime R3 and concentration 20 g/l, where the hardness increases sharply with 20% compared to the hardness of all other coatings (figure 5). The higher hardness does not however result in increase of the wear resistance of the coating. Its wear resistance $I = 0.6.10^7$ is lower than the wear resistance of coatings obtained at regimes R1 and R2 (table 6). This result confirms again the fact that there is no proportionality between wear resistance and hardness of the surface layers.

Comparing the results for galvanic chromium, Cr-nanodiamond coatings and WC/Co (88/12) composite coating obtained by HVOF-technology points to the following conclusions:

WC/Co (88/12) coating shows the highest wear resistance compared to all electrolyte Cr coatings without and with NDDS, deposited under the three regimes R1, R2 and R3.

WC/Co coating shows 7.2 times higher wear resistance than Cr coating without NDDS in regime R1 and 5.4 to 15.4 times higher wear resistance than Cr coatings with NDDS in the whole interval of variation of their concentration (figure 9).

The higher wear resistance of WC/Co coating is due to its high density and homogeneous small-grain structure made of WC grains linked in an internal contact network of cobalt (Co). The properties and size of this network are of great significance for the contact interaction of the coating during friction: small tangential resistance and corresponding small wear.

The results of the comparative study allow the following basic conclusion to be done: the composite WC/Co (88/12) coating deposited by HVOF-technology can replace the non-ecological chromium and Cr-nanodiamond coatings in tribological systems.

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References

[1] Bhushan B (ed.) 1999 *Handbook of Micro/Nanotribology*, 2nd ed. (CRC Press Series Mechanics and Material Science) (London, New York, Washington D.C.: CRC Press LLC)

[2] Bhushan B 2011 Nanotribology, nanomechanics and materials characterization studies and applications to bio/nanotechnology and biomimetics in *Proc. Int. Conf. on Tribology SERBIATRIB`11* (Kragujevac, Serbia) pp 3-4

[3] Nguen Vict-Hue, Hoang Thi-Nam, Nguyen Ngoe-Thong, Kwon Sik-Choa, Man-Kim and Joo-Yui Lee 2009 Cr/Nanodiamond Composite Plating with Cobalt Cation additive *Trans. Nonferrous Met. Soc. China* **19** 975-978

[4] Kandeva M, Gidikova N, Valov R, Petkov V, Kalchevska K and Torbova M 2011 in *Proc. of 9th International Conference The "A"Coatings* (Tessaloniki, Greece) pp 371-380

[5] Nestler M C, Prenzel G and Seitz T. 1998 in *Proc. of 15th ITSC Vol 2* (Nice, France) pp 1073-1078

[6] Kandeva M, Karastoyanov D and Vencl A 2016 *Advanced Tribological Coatings for Heavy-Duty Applications: Case Studies* (Sofia: Marin Drinov Academic Publishing House)