COMPARATIVE STUDY OF ZINC COATINGS TRIBOLOGICAL PROPERTIES IN A DRY FRICTION CONDITIONS

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Abstract

The paper presents a comparative study of zinc coatings tribological properties in dry friction conditions in the context of assessing coating wear intensity. For this purpose, three zinc coatings were analyzed: hot-dip, galvanic and lamellar, put to steel bolts made of 23MnB4 steel normally applied in the automotive industry. The tests were conducted using a T-11 tester. As a result of tribological tests the friction coefficient of investigated coatings were determined. The investigations were supplemented by nano-hardness measurements using the Anton Paar NHT2 device. In addition, the microscopic analysis of the surface changes supplemented by surface texture measurements was conducted in order to clarify the destruction mechanisms. Based on the studies, the diversity of the tribological properties of the tested coatings was evaluated. Results achieved for steel samples were compared to the results that were determined in earlier studies for samples made of EN-GJL-250 grey cast iron. It has been shown that the tested coatings on both the steel and the cast iron have similar tribological properties, and the most wear resistant zinc coating is a lamella.

Keywords: Tribological wear, friction coefficient, zinc, nano-hardness

1. INTRODUCTION

New construction materials before putting into industrial production are subjected to extensive laboratory tests and next additional trials with prototypes applications are conducted. It regards also zinc coatings which in addition to the high resistance to corrosion should also demonstrate good resistance to mechanical damage [1]. To determine the resistance to mechanical damage also tribological tests are used, which have essential meaning during reasons analysis of the variable durability of zinc coatings exposed to external loads.

In practice, as the fasteners corrosion protection three methods of Zn galvanizing are used: hot-dip galvanizing, electroplating and lamella. Hot-dip galvanizing is the immersion method, widely used to protect steel parts against corrosion. The process consist in immersing the element prepared in advance in the liquid zinc, which gives the opportunity to thoroughly cover elements even with complex shape [2]. The final product after hot-dip galvanizing is resistant to corrosion, abrasion and mechanical damage. Depending on the coating thickness, the aggressiveness of the environment and mechanical erosion the coating lifetime can be prolonged from 10 to 100 years [2]. Hot-dip galvanizing utilizes the phenomenon of diffusion. Iron atoms penetrate the inner layer of the zinc coating. Dipping is carried out at high temperature (approx. 450º C), that results in iron-zinc alloyed layer creation on the surface of galvanized element [3]. The coating consists of several layers: pure zinc and iron-zinc phases (Γ - Fe_3Zn_{10}, δ- $FeZn_7$, ζ - $FeZn_{13}$ and iron solid solution in zinc - η). An important advantage of electroplated zinc coatings is their good adhesion to the substrate and at the same time greater plasticity than achieved by other methods [4]. Zinc as a metal more electronegative than iron, creates on iron alloys anodic coatings. In humid air the corrosion products formed on the surface create a relatively dense layer insulating substrate from the environment. Very good corrosion resistance of the electroplated zinc coatings can be achieved by introducing into an electroplating bath for example: chromium and cobalt salts that build in metallic cobalt and chromium oxide in the coating during its deposition [4].

Particularly large amounts of zinc are used in the engineering and automotive industry. Galvanized elements are also bicycles, household appliances, electrical equipment.

Lamella zinc technology is gaining more and more market share especially in the area of fasteners, i.e. bolts, screws, nuts, springs, etc. This method combines suitable properties of base and sealing coats. Base coat technology lamella is a kind of paint containing "flakes" of zinc and aluminum. The whole reacts with the steel surface and forms after heating a good adhering, conductive and non-toxic zinc-aluminum coating. The applied layer does not contain lead, mercury, cadmium or chromium. Base coat may have different color: silver, black or dark gray. Base coats can be finished by the application of a suitable inorganic or organic seal. Proper selection of coatings provides to achieve very high corrosion resistance, it is also possible to obtain coatings with a specific friction coefficient - by introduction of special additive - which is also important during screws tightening using the assumed moment [5]. An important advantage of lamella coatings is absence of hydriding risk of galvanized machine parts. [5]. The purpose of this study was to compare the tribological properties of zinc coatings applied both to steel and cast iron surfaces.

2. OWN RESEARCH

The research were conducted on samples made of 23MnB4 steel with typical chemical composition according to the standard EN 10263-4-2001 (**Table 1**). Samples were taken from the hexagonal screws used frequently e.g. in the automotive industry. The galvanizing process as the next stage of the experiment was made by three different methods: hot-dip, galvanic and lamellar. Galvanizing process parameters and the method of surface preparation are shown in **Table 2**. The research of zinc coatings included coating thickness measurement where the method using the phenomenon of magnetic induction and microscopic structure observations were applied (**Figure 1**). The achieved results were compared to data determined for the EN-GJL-250 cast iron samples.

Table 1 Chemical composition of investigated bolts

Chemical composition [%] 23MnB4 (1.5535): EN 10263-4-2001							
C	**Si**	**Mn**	**P**	**S**	**Cr**	**Cu**	**Ni**
0.2 - 0.25	max 0.3	0.9 - 1.2	max 0.025	max 0.025	max 0.3	max 0.25	Max 0.005
Chemical composition [%] EN-GJL-250: PN-EN 1560: 2001							
C	**Si**	**Mn**	**P**	**S**	**Ni**	**Cu**	**Cr**
3.25	2.00	0.55	0.065	0.035	0	0	0

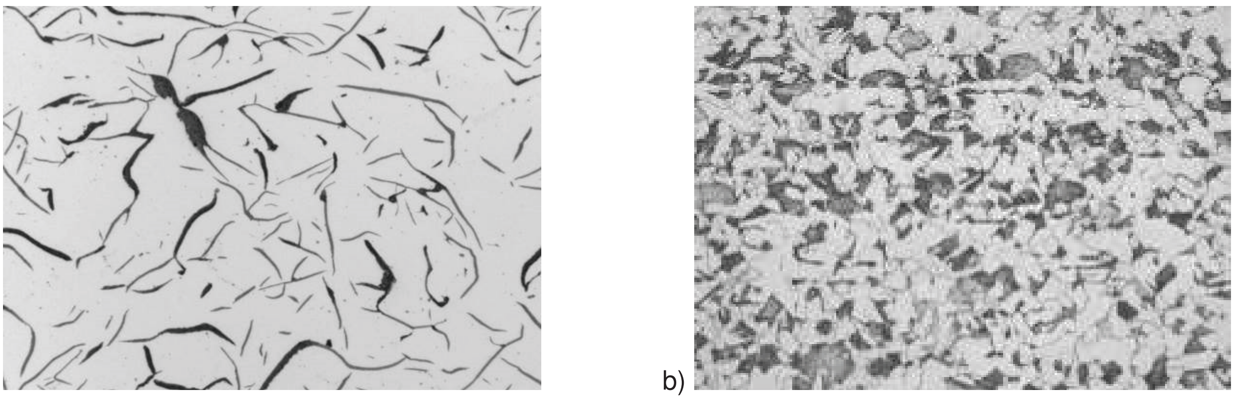
a) b)

Figure 1 Typical microstructure of the tested materials: a) cast iron GJL-250, b) steel Mn23B4

Table 2 Parameters of Zn coating process

No	Kind of process	Surface preparation
1	Electro-galvanizing acc. PN-EN ISO 4042 [6]	• chemical degreasing, temp. 60 ºC • etching in 18% HCl and 10% H_2SO_4 with inhibitors • degreasing and electro-polishing, temp. 60 ºC, 1000 A • galvanization in the weak acid chlorine Zn bath, temp. 35 ºC, • passivation - ions Cr^{3+}, Co^{2+}, NO_3^- temp. 45 ºC, pH 1.9
2	Hot-dip acc. PN-EN ISO 10684 [7]	• etching in 12% HCl • fluxing • galvanizing in the bath: Zn with additions Al, Bi, Ni; temp. 460 ºC • cooling in water
3	Lamellar acc. PN-EN ISO 10683 [8]	• shotblasting 0.4 mm • triple painting (95% Zn, 5% Al) • holding in temperature 120 ºC, cooling to temp. 25 ºC - air jet

The determination of friction characteristics were performed on a T11 stand according to a fixed testing program. During test the following parameters were recorded continuously: friction force, temperature and time. Additionally, the study was supplemented by roughness measurements of the test surface defining the maximum pit depth of roughness profile - Rv. Examples of test results are shown in **Figure 2** and **Table 3**.

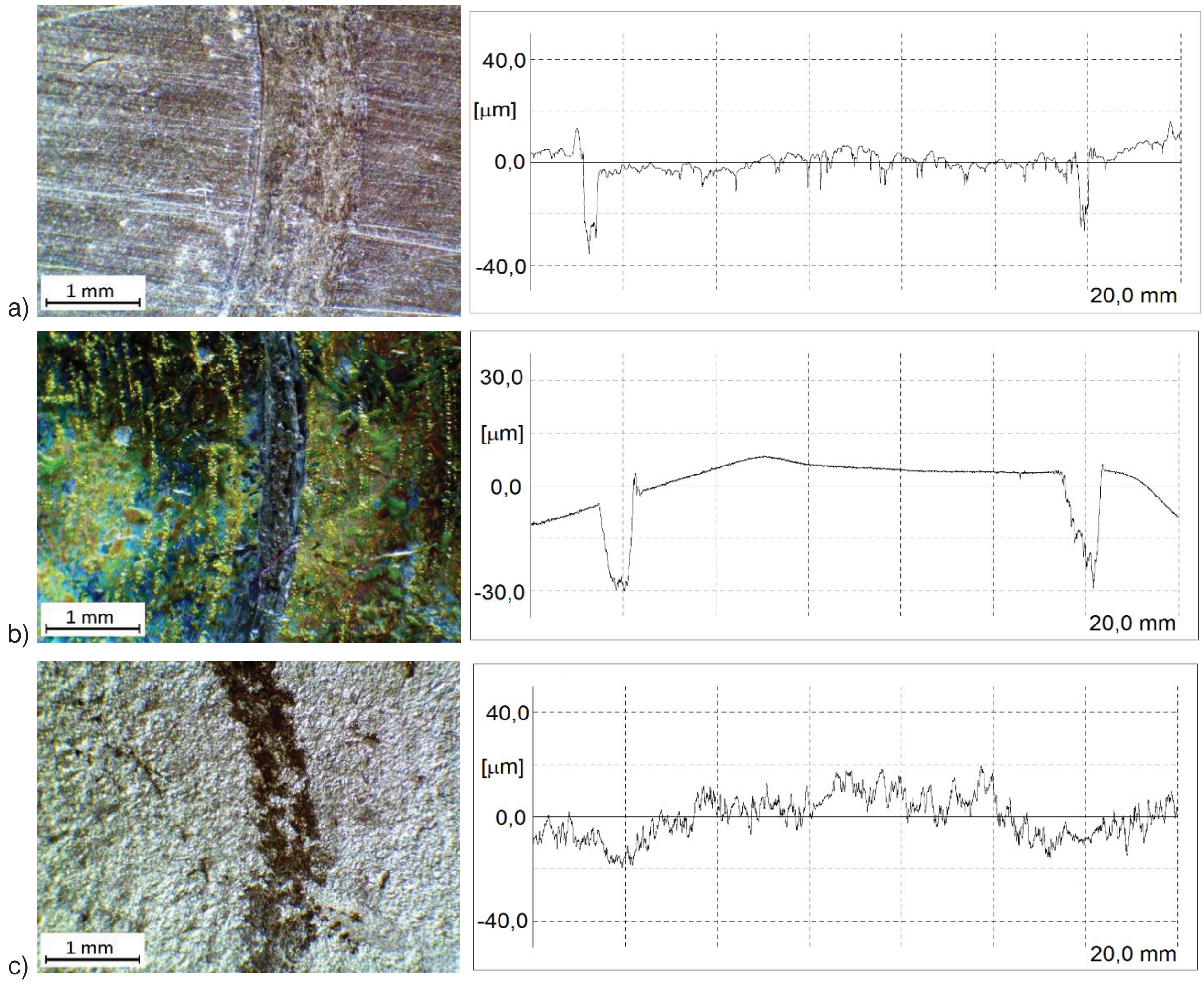

Figure 2 The surface profile and the view of the outside surface of coating: a) galvanic, b) hot-dip, c) lamellar

Hardness measurements were made in accordance with PN-EN ISO 14577-1: 2015-09 standard using a NHT2 Anton Paar device. The research carried out for the maximum load of 20 mN using a diamond indenter type Berkovitch. The arithmetic average of measured hardness is shown in **Table 2.**

Additionally, a microscopic observation within the hardness measurement area was conducted (**Figure 3**). The coating thickness was determined by using the phenomenon of magnetic induction (**Table 2**) and as the result of microscopic observation.

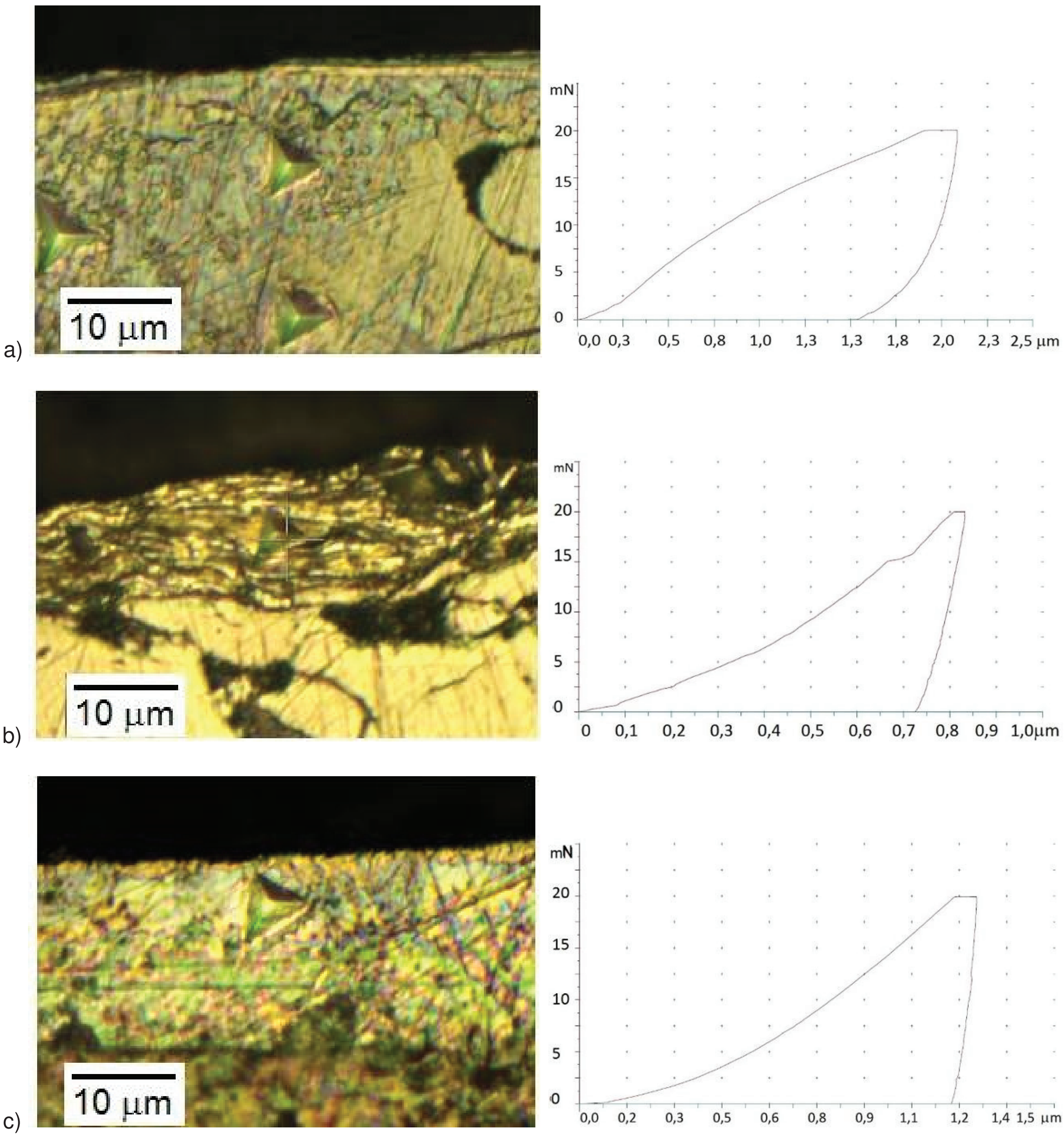

Figure 3 The microstructure of the tested coatings cross-section and example of graphs recorded during the coatings hardness measurement: a) hot-dip, b) lamella, c) galvanic

Table 3 Results of measurements of the thickness, hardness and the coefficient of friction for the coatings tested

Group No. Kind of process		Layer thickness [μm]		Rv [μm]		Friction coefficient, μ		Hardness Penetration depth [μm]
		steel	cast iron	steel	cast iron	Steel	cast iron	steel
1	Galvanic	18.9	20.2	19.1	20.2	0.201	0.212	1.3
2	Hot-dip	87.8	82.1	17.3	16.2	0.223	0.285	1.2
3	Lamellar	10.5	9.8	5.2	4.5	0.122	0.131	0.8

3. RESULTS ANALYSIS

The presented results of the research determine the mechanical properties, and in this way allow to predict performance of the three most popular protective coatings used in the automotive industry.

Because of the laminar structure and the presence of a pure zinc in outer layer, the lowest resistance to dry friction conditions showed zinc coatings deposited by the hot-dip galvanizing. The friction coefficient for this coating was equal to 0.223. A similar friction coefficient value was measured for galvanic coating. Additional observations of the surface condition of the analyzed sample showed that there was completely no zinc coating in the place being in contact with the counter-specimen. The highest resistance to frictional wear was measured for lamellar coating. Arithmetic average of friction coefficient was here equal to 0.122. As a investigation - tribological tests complement coatings hardness measurements with application of Anton Paar NHT2 device were conducted. Hardness tests were performed on the surface of each sample taking the 15 measurements in accordance with the standard. In the case of hot-dip zinc coating additional measurements on cross-section were made. The highest hardness and in consequence the highest resistance to mechanical damage was measured for the sample with lamellar coating. The average depth of penetration of the indenter was equal to 0.8 microns. For the hot-dip and galvanic zinc coating depth of the indenter penetration was at a similar level and amounted to 1.2 microns.

On the basis of microscope observations it can be unambiguously stated that the tested zinc coatings demonstrate conventional, compatible with standard structure and thickness. Additionally in order to determine the zinc coatings thickness samples were measured using magnetic induction method. On this basis it was confirmed that the greatest thickness of the coating was achieved in the case of hot-dip galvanizing. The arithmetic mean coating thickness was equal to 87.8 microns. For galvanic coating the average value of the thickness was 18.9 microns. The smallest thickness of the coating was measured in the lamellar case which amounted to 10.5 microns.

The results determined for steel coatings were compared with data achieved for the coatings deposited on cast iron surface. In both cases, the coating thickness reach similar values, in accordance with the standards. Particular importance attaches the higher coefficient of friction measured for the coatings deposited on cast iron surface. Microscopic observation have shown that the graphite from the surface layer of cast iron can penetrate into the zinc coating and forms a discontinuities. In the process corrosion resistance and resistance to mechanical damage are reduced.

4. CONCLUSIONS

On the basis of the presented tests the following conclusions can be formulated:

- The thickness of the zinc coating is not a decisive parameter influencing their resistance to mechanical damage

- Tribological tests and hardness measurements have shown that both in the case of cast iron and steel the highest resistance to mechanical damage was determined for lamellar coating
- The achieved results indicate that the galvanic and hot-dip coatings reveal similar parameters of friction wear
- As a result of tribological tests the whole galvanic coating was removed from the steel and cast iron surface in the place of contact with counter-specimen
- In the case of cast iron and steel a similar character of tribological wear of every tested coating is observed
- The penetration of graphite into the hot-dip zinc coating may be the reason of increasing the value of the friction coefficient measured for the coatings deposited on cast iron in relation to the steel samples.

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