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M. Musztyfaga-Staszuk[1], A. Czupryński[1], M. Kciuk[2]

[1]Silesian University of Technology, Welding Department, Gliwice, Poland
[2]Silesian University of Technology, Institute of Engineering Materials and Biomaterials, Gliwice, Poland
malgorzata.musztyfaga@polsl.plT

INVESTIGATION OF MECHANICAL AND ANTI-CORROSION PROPERTIES OF FLAME SPRAYED COATINGS

ABSTRACT

This article presents the results of an examination of the properties of thermal flame sprayed coatings produced by material in the form of four powders (two polymers: PA11 and PA12 CastoPlast, and two high purity: tin and aluminum) on the substrate of the unalloyed structural steel of S235JR grade. Investigations of coating properties are based on metallography tests (SEM and CLSM), measurement of microhardness (acc. to PN-EN ISO 6507-1:2007), anticorrosive (acc. to PN-EN ISO 9227:2017-06) and bend testing. Results demonstrate properties of flame sprayed coatings that are especially promising in the industrial applications where corrosion-resistant coating properties are required. Consequently, performed experiments show that the highest corrosion resistance is demonstrated by steel samples with a polyamide anti-corrosion system. Accelerated corrosion tests showed the lowest corrosion resistance of the tin coating system, however, they do not fully correspond to the corrosion processes in operating conditions.

Keywords: *Flame spray technology, polymer powder, aluminum powder, tin powder, corrosion-resistant coating*

INTRODUCTION

The constructors struggle every day with the unfavorable phenomenon of metal corrosion [1,2]. Due to its negative impact, efforts are being made to prevent it, because despite many efforts and actions of qualified engineering staff, it cannot be avoided to this day. As a result of many studies and development of engineering materials, only a few ways to prevent it have been created [3]. Corrosion causes many economic losses and negatively affects the properties of metals. In order to prevent this negative phenomenon or for its reduction, materials with special anti-corrosion properties such as stainless steels were developed, unfortunately they are very expensive [4]. Another way to protect the surface from corrosion is to apply coatings [5-7]. There are paint coatings that are characterized by relatively good corrosion resistance, they also fulfill a decorative function, require earlier surface preparation and are exposed to scratches [8] and thermally sprayed ones [9-12], which provide more durable surface protection compared to paint coatings but usually require developing the surface roughness before applying them. They are characterized by porosity and quite good adhesion to the substrate and, in addition to corrosion protection, they provide abrasive, erosive and cavitation resistance. The following thermal spray coatings are distinguished:

- zinc and aluminum coatings (e.g. Zn, Al or alloys of Zn and Al),
- composite coatings (e.g., Al_2O_3-TiO_2 mixture),
- and plastic coatings (thermoplastics, e.g. polyamides, which are obtained as a result of: polymerization and polycondensation).

Spraying regenerative layers from various materials is used to restore the operational properties of the worn out surface (fig. 1).

Fig. 1. Example of regeneration of the element: a) surface of the pump shaft, b) regenerated surface of the pump shaft with the molybdenum layer

Both of these methods are effective and durable, but to increase the surface durability a certain coating system has been developed that consists of a combination of thermally sprayed coatings with paint coatings. This system ensures not only longer durability of the protective layer, but also gives a decorative effect, which is often an important technological aspect required in the performance of the particular surfaces [13].

The use of thin layers, in particular anti-corrosive, heat sprayed, brings many benefits. The use of coatings made of metal materials allows us to cover structures with large dimensions on the spot (working in the open air) and is an ideal substrate for paint coatings. Metal coatings produced as a result of thermal metallization provide much more durable protection against corrosion as compared to paint coatings made of plastic and galvanic [14-16].

Among metallization processes, several coating methods are distinguished due to the material being sprayed, its properties and the functions of the coating produced. Currently, we distinguish three main methods: flame spraying (subsonic and supersonic), arc and plasma spraying. Each of the mentioned methods finds its wide application in various branches of industry and allows to provide the required surface properties of designed structures and machine elements. The following are examples of application areas for each thermal spray method (Table 1) [8].

Table 1. *Examples of application areas for thermal spray methods [8]*

Thermal spray method	Area of application of coatings
Flame spraying using wire	Refinery installations, water tanks, aircraft engine cylinders, shafts, bushings, journals
Flame spraying using a rod made of ceramic material	Elements of gas turbines, pump sleeves, pistons, graphite molds, guide rollers
Subsonic flame spraying	Bearings, vanes, bushings, valve seats, crankshafts, pistons
Flame supersonic powder spraying	Aerospace, automotive, energy, chemical, electronics
Plasma spraying	Automotive, aerospace, electronics, production and regeneration of machine parts
Arcing	Elements of friction clutches, gas turbine parts, journals, shafts, bearings

The aim of the investigation is to create anti-corrosive coatings by means of thermal flame spraying technology and to examine their selected properties, which are written in detail below in text (investigation methodology point).

MATERIAL AND SAMPLE PREPARATION

Suitably prepared substrates and powders were used for the experiment. First, the surface of the sheets was subjected to abrasive blasting using a rotary-hook cleaner (type OWH-1.0 x 1.5). Then shot peening was applied using S330 shot to develop the surface of the plates (time: 2 minutes). The following coatings were sprayed onto the prepared surfaces as a result of the thermal flame spray process (Fig. 2): aluminum series 1000 (Al), tin (Sn) and two polymer ones (white polyamide (PA11) and yellow one (PA12)). After the preliminary tests, the coating made of white polymer was abandoned because it fell off during the cutting process. It is believed that this may be due to insufficiently developed surface of the substrate, insufficient for this coating before the coating process. The most beneficial conditions of flame-spraying were selected based on tests (table 2).

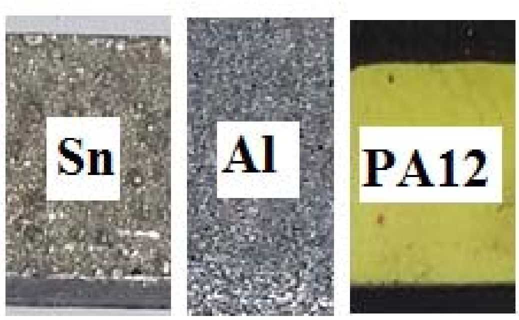

Fig. 2. View of flame coatings prepared in thermal spraying technology

The criterion for the selection of coating material included the creation of a coating characterized by:

- low electrochemical potential Al (-1.33 V) Sn (-0.13 V) polyamide PA 12 (missing),
- good resistance to atmospheric corrosion,

- high plasticity of the coating material,
- low sliding friction coefficient,
- possible application in the automotive and transport industries.

Table 2. *Parameters of flame-sprayed aluminum, tin and polyamide coatings using CastoDyn DS 8000 torch*

Type of powder	Flame setting	Powder Container Mouting (Setting)	Oxygen pressure [bar]	Acetylene pressure [bar]	Air pressure [bar]		Spraying distance [mm]
					Torch	Extention neck	
Al	Neutral	6	4	0.7	4	4	~250
Sn	Neutral	6	4	0.7	4	4	~250
PA12	Neutral	6	4	0.7	4	4	>250
Note: Standard modular nozzles regulating the flame outlet (SSM 40) were used							

The coatings were made under the same technological conditions of the powder flame spray process:

- thermal spray surfaces for each coating material were prepared in the same way, i.e. by abrasive blasting,
- in each case, this spraying system was used (CastoDyn DS. 8000), the same process gases (acetylene, oxygen) and similar parameters of the spraying process.

EXPERIMENTAL

The scope of performed tests included:

- analysis of morphology and multiplicity of powders was made using the Zeiss Supra scanning electron microscopy (using secondary electron detection at accelerating voltage in the range of 5 ÷ 20 kV). The optimal power size was calculated on the basis of six medium measurements from images obtained at this microscope;
- development of coatings using flame thermal spray technology;
- roughness analysis of coatings was carried out using Confocal Laser Scanning Microscope CLSM 5 Exciter from Zeiss, in which the source of light is a 25 mW diode laser emitting radiation with a wavelength of 405 nm;
- bending test with tensile and compression of the coatings. During the test, samples of 20 mm x 150 mm were used, the distance between the supports was 65 mm, while the diameter of the bending mandrel was 10 mm;
- corrosion tests in a salt chamber on 30 x 30 mm samples used for cyclic corrosion tests of CCP 450ip. The device was equipped with appropriate systems to maintain the chamber and its content at the assumed test temperature of 35 ± 2 °C. The exposure of the tested coating systems in the salt chamber took place over a period of 96 hours, the pH of the solution was maintained within 6.5-7.2, with a sodium chloride concentration of 50g / l. The surfaces of the samples without the analyzed coating systems and of the edges were protected against the action of sodium chloride with wax. The test specimens were placed in the salt cell holders at

an angle of 20 °, in such a way that they did not touch each other and the chamber and so that the surfaces of the material were exposed to the free circulation of the sprayed liquid;

- the microhardness tests of the tested samples were made using a Vickers hardness tester with an automatic measurement path using Future-Tech FM-ARS 9000 image analysis. Eight measurements were taken on each sample. An indenter was used in the form of a diamond pyramid with a square base and an angle between opposite walls of 136 ° and a load of 50g. The measurements were made on metallographic microsections;
- tests of thickness, surface topography and cross-section of the prepared coating with the substrate were made using scanning electron microscopy, mentioned earlier.

RESULTS AND DISCUSSION

Observations of powder morphology in the scanning electron microscope show that Al powder particles and polyamides have an irregular shape, while Sn particles are globular. In order to select the optimal granulation powder, the following granulations were used for the tests: Al=132 µm, Sn=17 µm, PA12=167 µm and PA11=166 µm (Fig. 3).

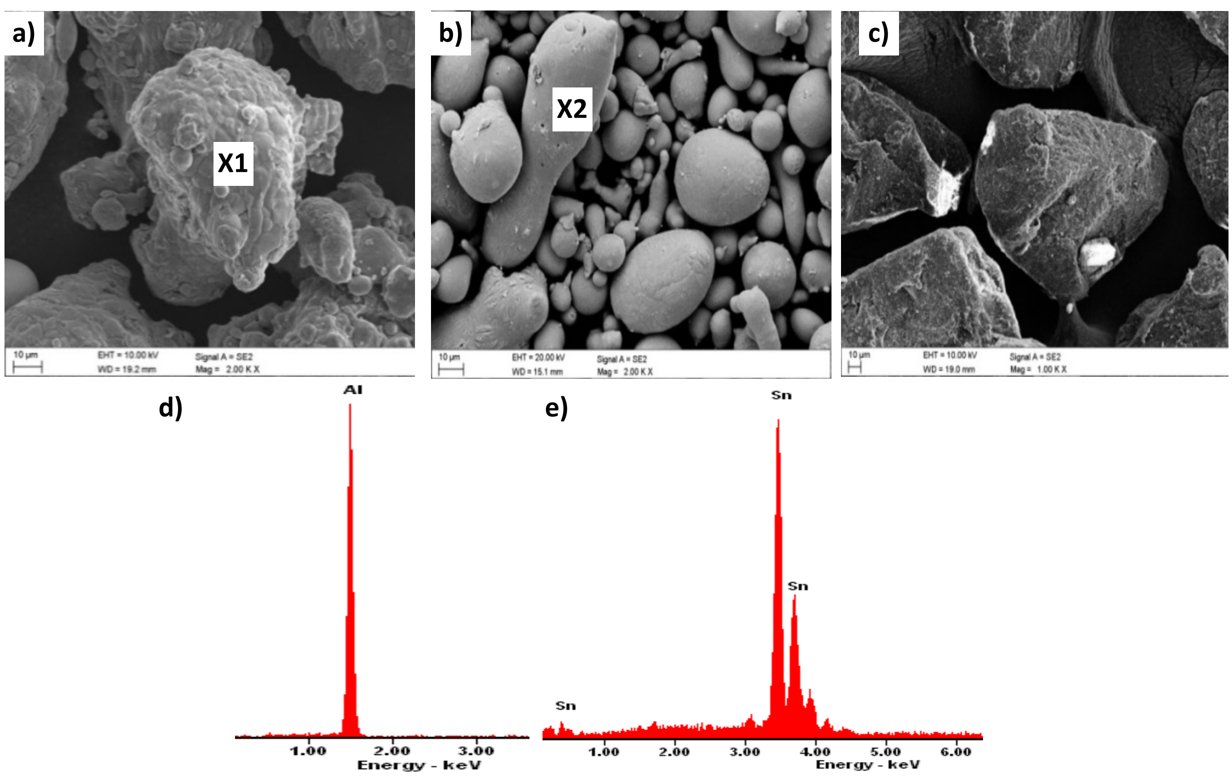

Fig. 3. Powder with granulation: a) 140 µm - aluminum, b) 25 µm - tin, c) 150 µm - polymer yellow (SEM), energy scattered X-ray chart from the micro-area d) X1 and e) X2

The roughness of the coatings with the substrate was determined on the basis of the surface topography measurements performed in a confocal laser scanning microscope (Fig. 4). On the basis of the obtained test results, it was found that the smallest surface roughness was obtained for the PA12 coating (1.55 μm), intermediate for the Sn coating (11.28 μm), and the largest for the Al coating (29.05 μm). The high roughness of the coating contributes to the accumulation of impurities and formation of corrosive cells, which promotes the emergence of new corrosion centers.

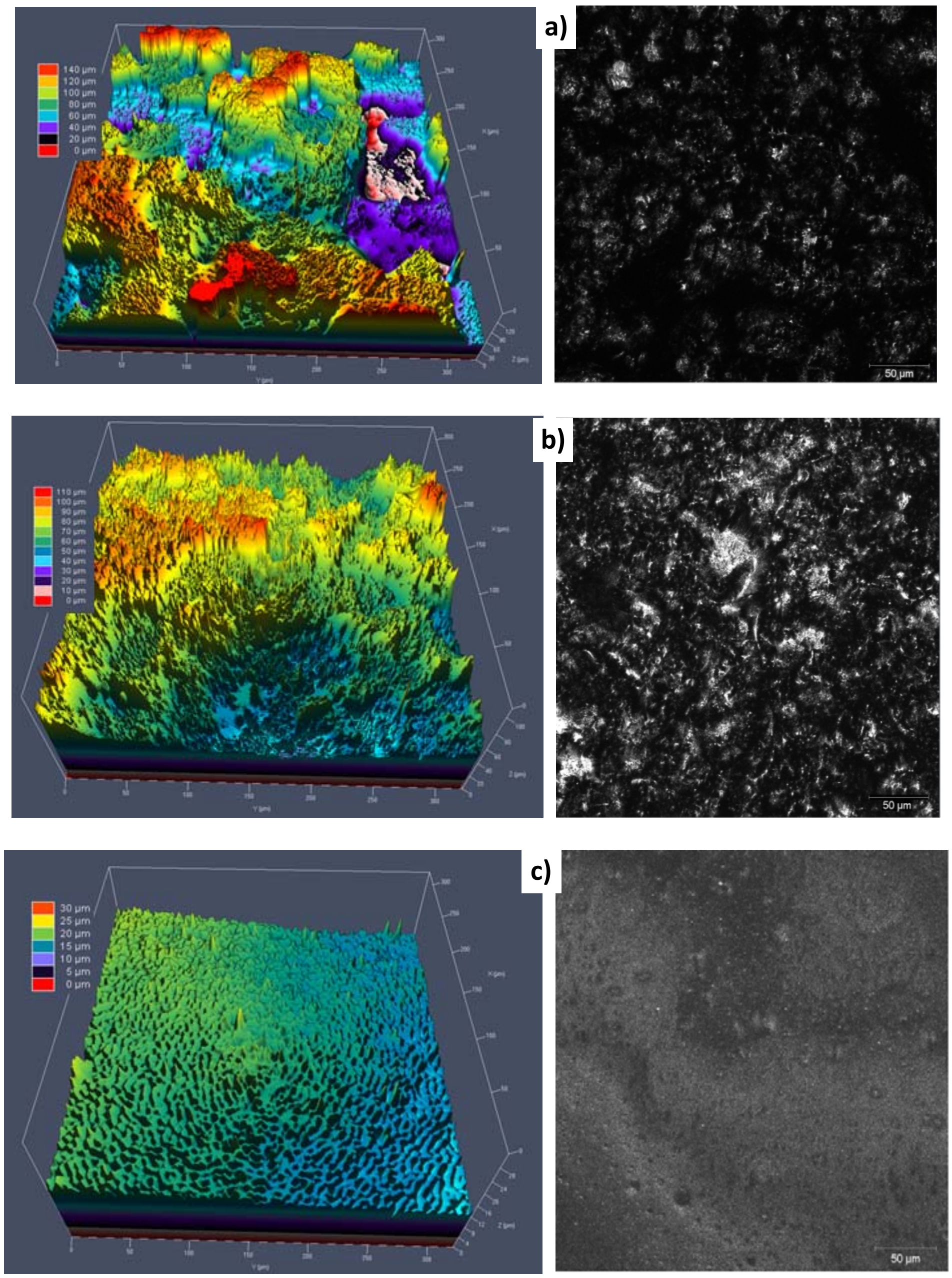

Fig. 4. Three- and two-dimensional surface topography of the coating made of a) Al, b) Sn, c) PA12

On the basis of the test results obtained in the case of tensile tests (Fig. 5) it was found that the coating made of Al did not break, while the coatings made of Sn and PA broke. In the compression tests (Fig. 6), it was found that none of the coatings were damaged.

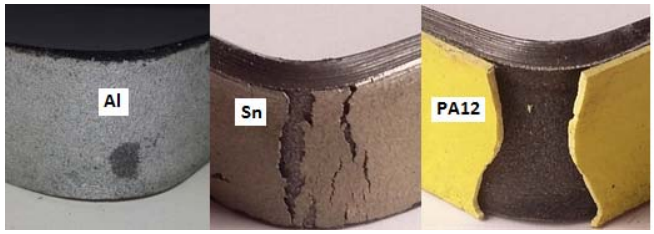

Fig. 5. View of samples after bending test with tensile of the coatings

Fig. 6. View of samples after bending test with compression of the coatings

The description of the corrosion resistance test against neutral salt spray (NSS) was performed based on the PN-EN ISO 9227 standard, which makes it possible to estimate the corrosion resistance of metal materials with permanent or temporary corrosion protection.

For this purpose, a salt cell Ascott CCP450ip for cyclic corrosion tests was used, all of whose elements were made of corrosion-resistant materials. The evaluation of the surface appearance of the samples during the tests was carried out after 24, 48 and 96 h (Figs. 7 to 9). Exposure of the tested coating systems to the aggressive agent in the form of chlorides (5% NaCl solution) had the greatest impact on the system obtained by thermal spraying of flame tin. As a result of the insufficient protective properties of this metal coating, numerous corrosion centers are visible on the steel substrate and the so-called red corrosion products appear, which shows that the barrier coating has been perforated and the protection of this coating has been exhausted in samples already after 24 hours (Fig. 8b). Therefore, the tin spray coating system should not be used on steel machine components used in the natural environment, in particular marine one.

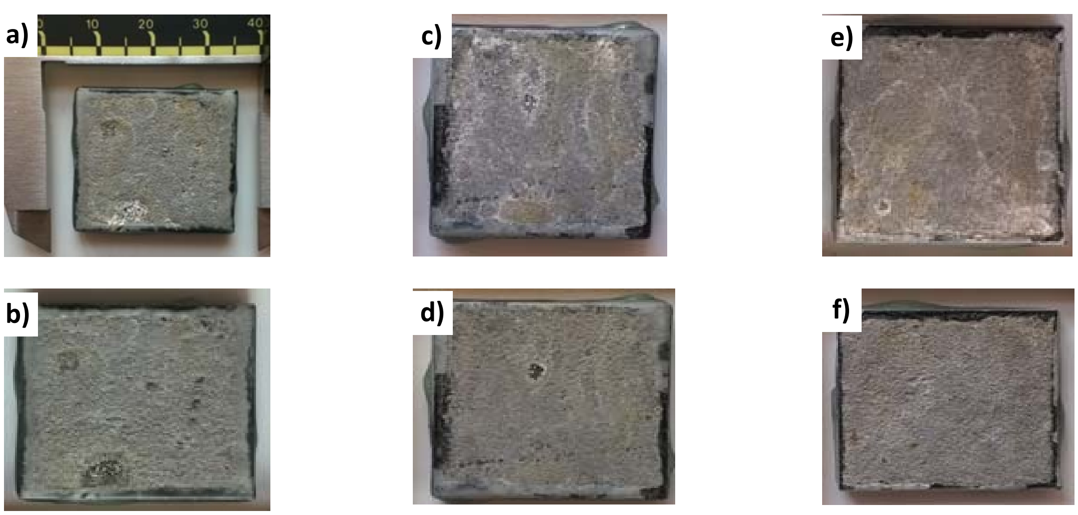

Fig. 7. Sample with the Al coating in the salt chamber: after day 1 of the test a) before cleaning, b) after cleaning,

after day 2 of the test c) before cleaning, d) after cleaning, after day 3 of the test e) before cleaning, f) after cleaning

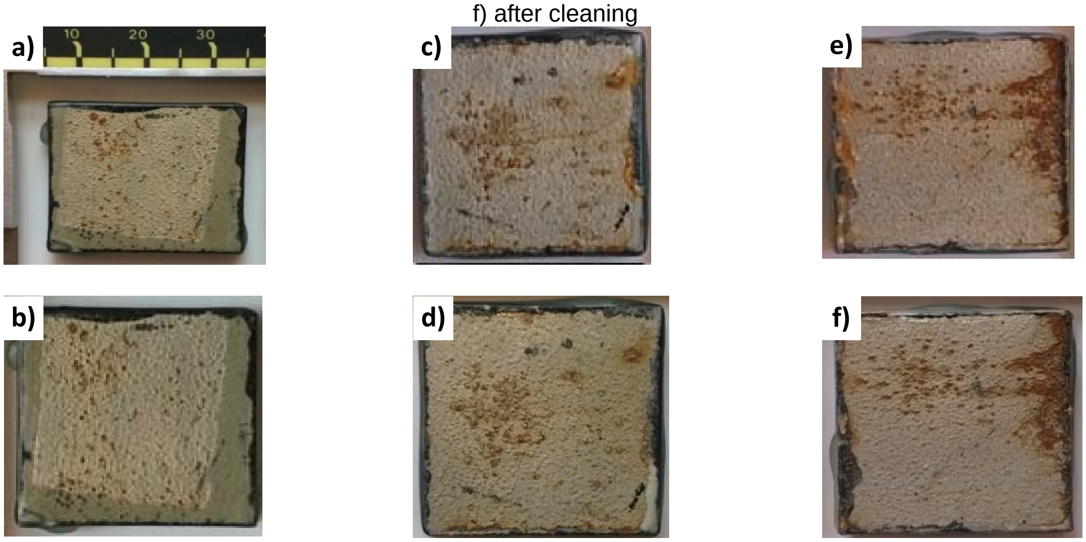

Fig. 8. Sample with the Sn coating in the salt chamber: after day 1 of the test a) before cleaning, b) after cleaning, after day 2 of the test c) before cleaning, d) after cleaning, after day 3 of the test e) before cleaning, f) after cleaning

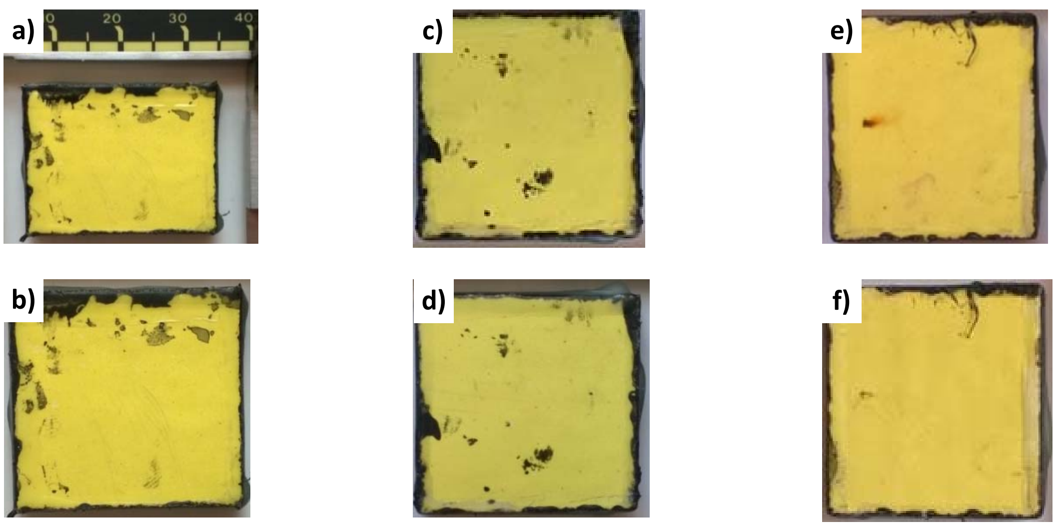

Fig. 9. Sample with the PA12 coating in the salt chamber: after day 1 of the test a) before cleaning, b) after cleaning, after day 2 of the test c) before cleaning, d) after cleaning, after day 3 of the test e) before cleaning, f) after cleaning

Steel sheets protected with aluminum coating in the first hours of the test show no signs of corrosion (Fig. 7b), only as a result of prolongation of the corrosion process up to 48h the first penetrations to the sheet substrate are observed, which manifests as a change in the color of corrosion products (Fig. 7d). Further exposure of the coating system under investigation to neutral salt mist caused only a slight intensification of corrosion processes (Fig. 7f).

The highest corrosion resistance in the analyzed conditions was demonstrated by samples with a polymer system. The surface appearance of steel specimens with polyamide PA12 coating is shown in Fig. 9. In this case, there are only a few single corrosion centers Fig. 9e after 96 hours of the process, which is probably caused by the uneven coating application. The coating itself shows no anti-corrosion properties, no cracks, blisters or signs of point corrosion.

On the basis of the obtained microhardness results, the highest hardness was characterized by the Al coating, which was 32 HV, the average Sn 12 HV, and the lowest PA12 9 HV. In each case, a narrow heat affected zone was observed in the parent material, corresponding to Al 255 HV, Sn 138 HV and PA12 168 HV, respectively.

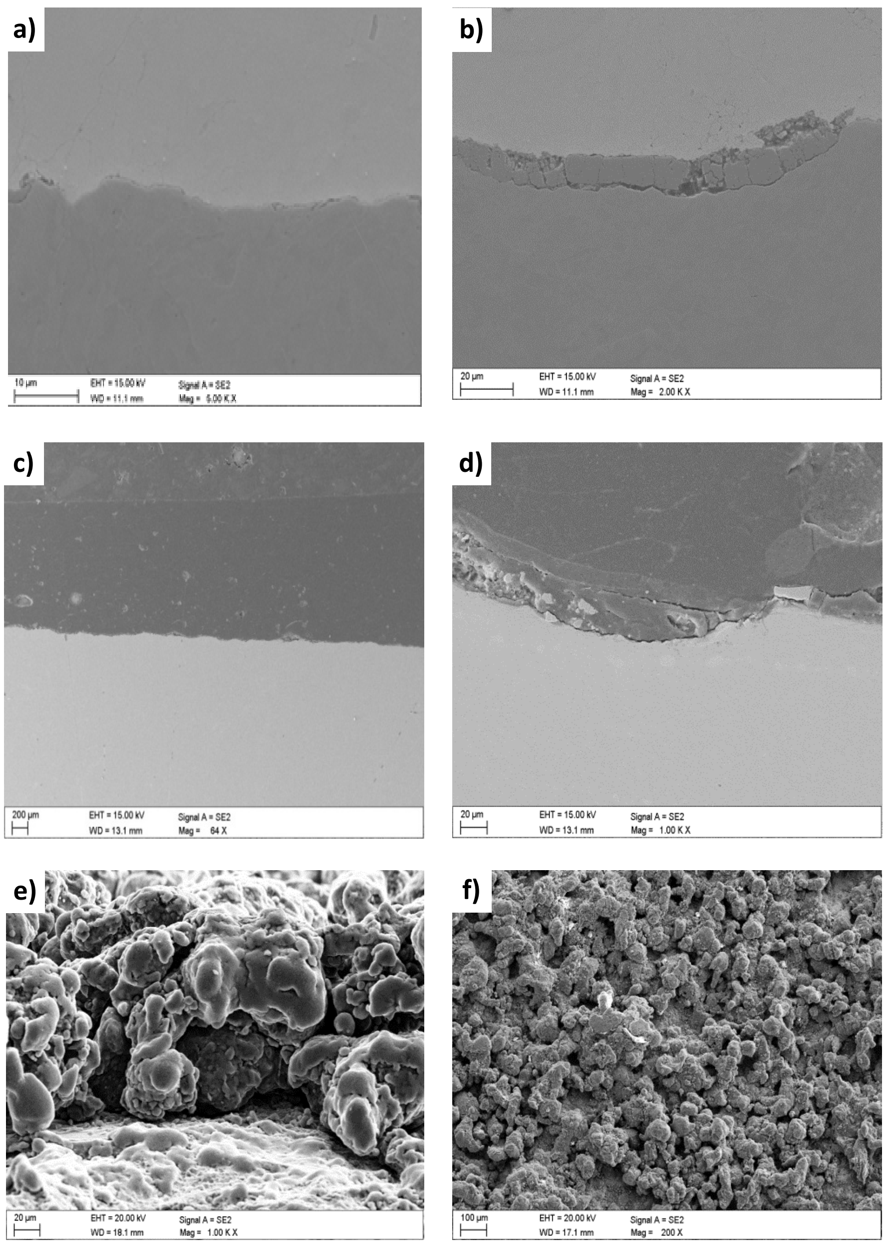

Fig. 10. Cross-sectional area of the coating made of a, b) Sn; c, d) polyamide-PA12, e) Al; f) topography of the coating layer from Al

Observation of the thickness of the tested coatings in the scanning electron microscope allowed to state that the thickest coating was obtained with Sn = 292 μm, intermediate with Al = 125 μm, and the thinnest with PA12 = 1.43 μm. On the basis of fractal analysis, it was found that all applied coatings show a connection with a steel substrate with defects (showing a microcracks network) and delamination (Fig. 10 a-e). In addition, combinations of these coatings with a steel substrate, only in places are close to continuous, in most cases they are only point connections (eg Fig. 10e). However, the coating made of PA12 is the least defective. Metallographic observations in the scanning electron microscope allow to state that the morphology of the obtained structures of all coatings shows a porous structure containing a dense network of connections between grain agglomerates of variable size. Figure 10f shows an example of surface topography made of Al.

SUMMARY

Based on the investigations and the results discussed, it was found that:

- Applied powders with Al particle sizes: 131.64 μm, Sn: 16.79 μm, PA: 166.14 μm, despite their irregular shape, allowed for their stable feeding to the device during the manufacture of coatings in a thermal flame spray process.
- The coating's roughness is influenced by the properties of the materials used. The lowest roughness was characterized by a PA coating of 1, 90 μm, and the highest Al coating of 27.3 μm. Differences in roughness are probably caused by different melting points and different thermal conductivity coefficients.
- Among the coatings subjected to mechanical tensile investigations the best strength was obtained by the aluminum coating, and the worst coating from PA12, which most probably results from its low plasticity.
- The thickness of the tested coatings did not affect their corrosion resistance. It depends on the electrochemical potential, which polyamides do not have, thanks to which they do not undergo electrochemical corrosion.

Moreover, conducted corrosion tests in neutral salt spray (NSS) were of comparative nature and made it possible to determine the corrosion resistance of the tested materials in the conditions of their application.

The conducted experiments show that the highest corrosion resistance is demonstrated by steel samples with a polyamide anti-corrosion system. The inert sodium chloride solution is also characterized by low aggressiveness towards the protective aluminum coating [17].

Accelerated corrosion tests showed the lowest corrosion resistance of the tin coating system. Flame sprayed coatings are characterized by high porosity and strong oxidation, which reduces their corrosion protection capacities [18,19].

The laboratory tests carried out do not fully correspond to the corrosion processes in work conditions. In particular, it is not possible to translate the exact number of hours of the protective coating's resistance to the corrosive agent in the salt chamber to a specific number of years of durable protection against corrosion in real conditions. These tests can be used to confirm and compare the effectiveness of individual corrosion protection.

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