Protective properties of a multi-layer external coating applied to underground pipes of ductile iron

Właściwości ochronne wielowarstwowej powłoki zewnętrznej nałożonej na podziemne rury z żeliwa sferoidalnego

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In this work the analysis of corrosion for ductile iron pipes with diameters of 350 and 500 mm was performed. Two phenomena regarding the pipes coating deterioration have been recognized: corrosion and abrasion. The corrosion tests performed on different coatings in a neutral salt spray for up to 1000 hours indicate that this method is applicable for a rough external surface of centrifugally casted ductile iron pipes. The abrasion tests have been performed manually, using a grinding paper 1000#, due to an irregular profile of the external pipe surface transferred from the casting mold. It helped to obtain "spotted" sections, which were further microscopically analyzed (layer-by-layer). The last procedure, however not standardized, could be in some regards more convenient comparing to traditional cross-sections.
Keywords: water supply pipes, oxide scale, thermal sprayed coating, sealing paint

W pracy dokonano analizy korozji rur z żeliwa sferoidalnego o średnicach 350 i 500 mm. Wykryto dwa zjawiska związane z pogorszeniem się powłoki rur: korozja i ścieranie. Testy korozyjne przeprowadzone na różnych powłokach w neutralnej mgle solnej przez okres do 1000 godzin wskazują, że metoda ta ma zastosowanie do szorstkiej zewnętrznej powierzchni odlewanych wirowo rur z żeliwa sferoidalnego. Testy na ścieranie przeprowadzono ręcznie przy użyciu papieru ściernego 1000 #, ze względu na nieregularny profil zewnętrznej powierzchni rury przeniesionej z formy odlewniczej. Pomogło to w uzyskaniu „plamkowych" przekrojów, które poddano dalszej analizie mikroskopowej (warstwa po warstwie). Ostatnia procedura, choć nie znormalizowana, może być pod pewnymi względami wygodniejsza w porównaniu do tradycyjnych przekrojów poprzecznych.
Słowa kluczowe: rury wodociągowe, żeliwo sferoidalne, zgorzelina tlenkowa, natryskiwana cieplnie powłoka, farba uszczelniająca

Introduction

Zn and Zn85 Al15 coatings produced by arc spraying technique are one of the methods used to improve an external corrosion resistance of water supply ductile iron pipes in the low to moderate aggressive soil environment [1]. The zinc coating of 99,99 % purity is thermally sprayed in a minimal amount of 200 g/m^2 of the pipe wall, however, for pipe to be installed in a corrosive soil the alloy coating of zinc (85 wt %) and aluminium (15 wt %) has to be applied [2]. This alloy is commercially known as Zinalium. In the case of ductile iron pipes, their external surface is rough after centrifugal casting in rotating forms. Moreover, after annealing the surface is covered by two layers of oxide-skin: an inner one rich in silica and an outer one consisting exclusively of ferric oxides [3]. The recent studies [4] revealed, that the double anticorrosion system zinc-paint was sensitive to external damages, occurring e.g. during pipeline placement. They happen because the zinc anodic layer is usually applied on a brittle oxide-skin (a depth of 30-50 mm) growing during subsequent annealing and cooling of pipes in the metallurgical process [4]. So it is relatively easy to "delaminate" the whole coating during transportation and underground pipeline installation. Silica present in the internal layer of the oxide skin, improves the mechanical strength and attachment of ferric oxides to the pipe matrix surface. It is important to recognize such factors as: stability of the oxide skin, the thickness and mass of zinc, or Zn-Al coating as well as the protective properties of additional protective layers, including paints or PE sleeves. One of the objectives of this study was to assess the applicability of the standard [5] commonly used for testing paints covering steel of smooth surfaces. The other goal was to investigate the abrasive behavior of commercial coatings, using layer-by-layer transversal "grinding spots".

Material and experimental methods

The material investigated was cut from two standard water pipes (Fig. 1 and Fig. 2). The pipes nominal diameter (DN) was 350 mm and 500 mm. The surface of each sample was approximately 400 cm^2. Both samples were made of a ductile iron matrix covered with oxides of approximately the same thickness from 35 to 55 micrometers [4], and then covered by a Zinalium coating exceeding slightly the mass of 400 g/m^2. Concluding, the undercoat could be recognized to present identical properties in both samples. The tested surface was degreased with ethanol. The

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Fig. 1.
Standard water pipe before using in a municipal pipeline. View from the socket
Ryc. 1. Standardowa rura wodociągowa przed montażem do rurociągu miejskiego. Widok od strony kielicha

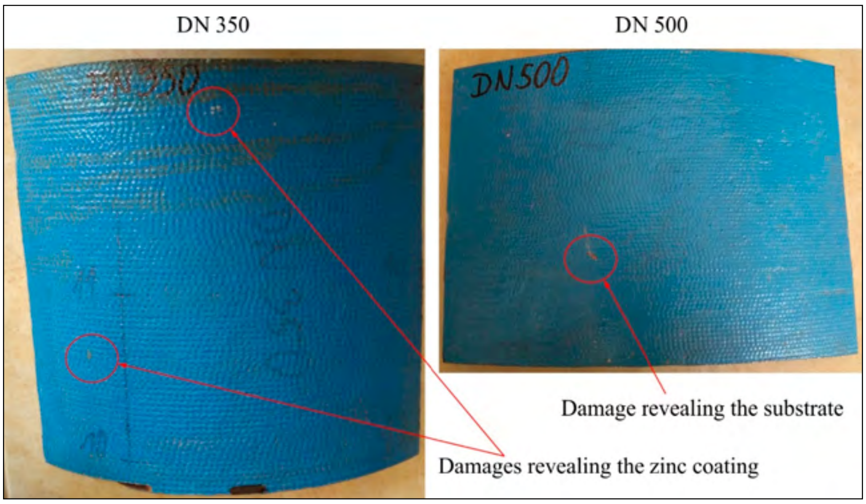

Fig. 2.
Images of the material cut from the pipes with diameter of 350 mm and 500 mm
Ryc. 2. Zdjęcia materiału wyciętego z rur o średnicy 350 mm i 500 mm

samples were visually examined for potential damages in the coating (Fig. 2).

Natural salt spray test (NSS)

A salt spray test was performed according to the European standard [6] using the chamber type SC/KWT 450 from Weiss Umwelttechnik GmbH. A neutral salt spray (NSS) test took place at temperature of 35°C, at a pH range of 6.5-7.1 and with a NaCl concentration of about 50-55 g/l. After the test, the samples removed from the chamber were washed and dried. The edges of the NSS samples have not been protected and thus not evaluated. The inspection photos were taken after every 100 hours. The assessment of the rusting degree (Ri) of samples during the tests was carried out after 1000 h [5]. A protection rating (Rp) and an appearance rating (Ra) for an anodic zinc coating have been specified [7]. The protection rating Rp is a number assigned to the ability of the coating to protect the base material from corrosion and the rating Ra is a number of symbols assigned to describe the overall appearance of the specimen, including all defects caused by exposure.

Abrasion test

Abrasion test was performed manually using a grinding paper of gradation 1000# (grain size 4.5+1mm) in a plane tangential to the pipe external surface. The pipe outer surface showed a regular wave pattern associated with the casting process (Fig. 3 and Fig. 4). Thus the abrasion might lead to many regular "spots", each containing images of layer-by-layer external coating components: sealing paint, thermally sprayed Zn-Al, ferric oxides covering the surface of the ductile iron pipe and finally the iron pipe itself. Visual inspection of the grinding paper reveals different colored residues coming from the scraped outer coating: a blue color for the pipe DN 350 (Fig 3 left) and a gray one for the pipe DN 500 (Fig. 3 right). The morphology and chemical composition of that spots were studied using scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS).

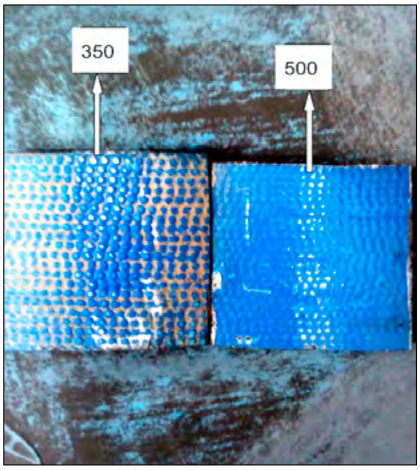

Fig. 3.
Images of samples abrasion using paper of 1000#. Blue sediment for the pipe DN 350 and gray sediment for DN 500, respectively.
Ryc. 3. Widok próbek ścieranych na papierze o gradacji 1000 #. Niebieski osad dla rury DN 350 i szary osad odpowiednio dla rury DN 500.

Results and discussion

The photographs of the samples after the salt spray test are presented in Fig. 5. After 100 hours of the test three areas with red corrosion (corrosion products of cast iron substrate) were noticed on the pipe sample DN 350. Two of these spots matched the damages observed before the test. The areas with red corrosion spots did not increase throughout the test. The first symptom of white corrosion (the corrosion product of the metallic coating) was spotted only at one point (at the upper edge) after 200 hours of the test. Except this single point, no other changes related to the corrosion of the zinc coating were noticed for next 700 hours of the test. After 1000 hours in the salt chamber, the sample DN 350 looked much better than the sample from the pipe DN500.

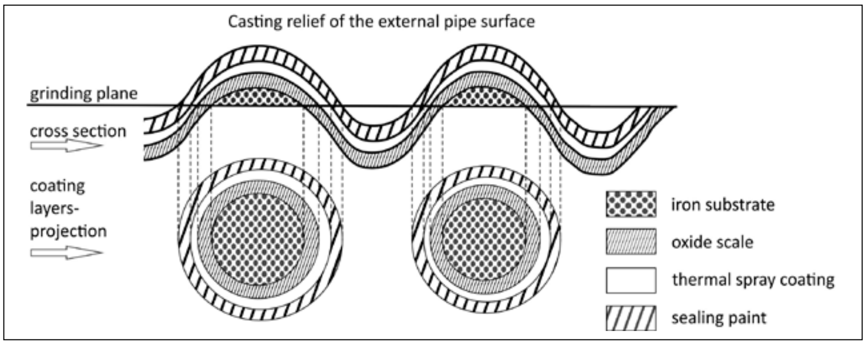

Fig. 4.
Diagram of the grinding plane tangential to the external pipe surface - theoretical appearance of flat "spots" for a further metallographic study has been shown.
Ryc. 4. Schemat płaszczyzny szlifowania stycznej do powierzchni zewnętrznej rury - pokazano teoretyczny wygląd płaskich „plam" do dalszych badań metalograficznych.

In case of the sample DN 500, the first symptoms of white corrosion were observed after 100 hours of the test. After this time, two areas with red corrosion were found; one of them matched the dam-

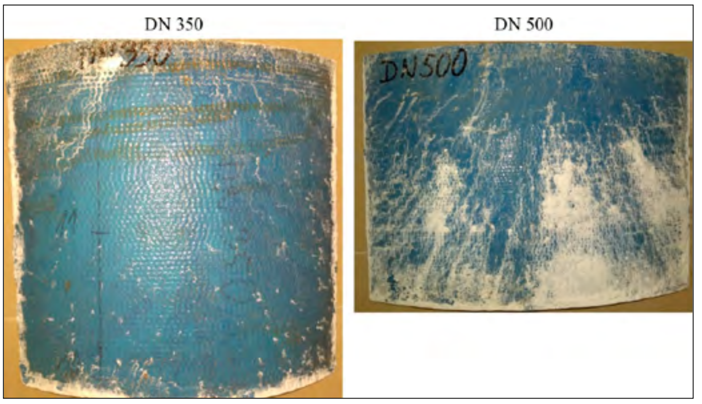

Fig. 5.
The samples after 1000 hours of the salt spray test.
Ryc. 5. Próbki po 1000 godzinach testu w mgle solnej.

age of the coating observed before the test. After each subsequent stage of the test, the other areas with corrosion products of the metallic coating (white corrosion) were observed. It proves a low quality of the paint coating.

The coated surface, except for the edges, was evaluated according to the Standard [5] for the paint coating evaluation. Assessment of the degree of rusting was presented in Table 1. The degree of rusting shown in this table refers to both white corrosion (corrosion products of the zinc coating) and red corrosion (corrosion products of the cast iron substrate). The analysis of the zinc coating performance during NNS shows significant differences between the quality of the samples' surfaces (Tab. 2).

Tab. 1. Assessment of degree of rusting according to [5]
Tab. 1. Ocena stopnia rdzewienia zgodnie z [5]

Sample	Degree of rusting	Minimum (the best)	Maximum (the worst)
DN350	Ri1	Ri0	Ri5
DN500	Ri4	Ri0	Ri5

Tab. 2. Protection rating and appearance rating according to [7] °C – corrosion products from anodic coatings; vs – very slight amount; m – moderate amount.
Tab. 2. Stopień ochrony i wygląd zgodnie z [7] °C - produkty korozji z powłok anodowych; vs - bardzo niewielka ilość; m - umiarkowana ilość.

Sample	Protection rating, R_p	Appearance rating, R_a	Area of defect, A
DN350	7	6 vs C*	0.25 < A £ 1.0
DN500	2	2 m C	10 < A £ 25

The composition of paint coatings of the samples DN 350 and DN 500 was analyzed to determine which paint ingredients provide better protective properties. A method of paint collection was developed, as described in the paragraph 2 (Material and Experimental – Abrasion test).

Figures 6, 7 and 8 show results of examination of the as-prepared tangential abrasive spots; the images made at the same magnifications were compared. The representative flat section image of a Zn-Al coating was strongly diffused and did not comply with the theoretical considerations undertaken in Fig. 4; it means an irregular thickness of the protective coating, as described by [8]. A thickness of a thermal diffusion zinc coating is not homogeneous, which can be seen in Fig. 7, presenting a photograph of a pipe wall cross-section. In spite of this, it can be seen that ferric

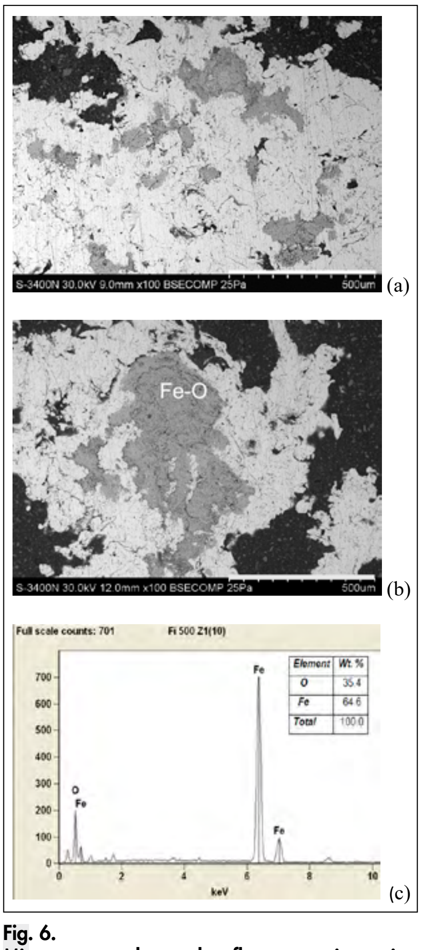

Fig. 6.
Microstructure observed on flat spot-sections using the SEM microscope: a, b) two different "spots" of the sample DN500; c) EDS analysis of the ferric oxide area (magnification bar of 0.5 mm)
Ryc. 6. Mikrostruktura zaobserwowana na płaskich przekrojach plamkowych za pomocą mikroskopu SEM: a, b) dwa różne „punkty" próbki DN500; c) Analiza EDS obszaru tlenku żelaza (pasek powiększenia 0,5 mm)

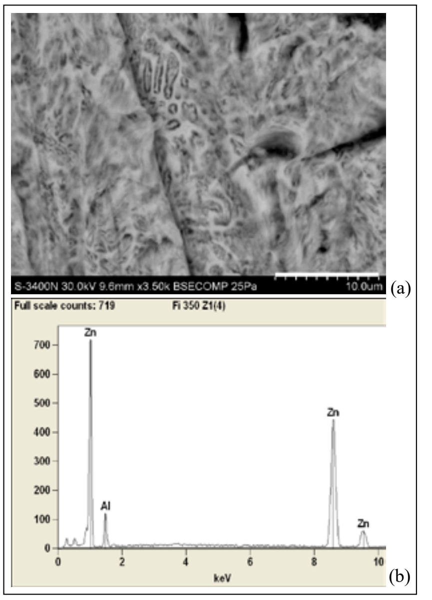

Fig. 7.
Microstructure of the Zn-Al coating: a) flat section of the sample DN500 (magnification scale of 10 mm), b) EDS analysis of the coating
Ryc. 7. Mikrostruktura powłoki Zn-Al: a) płaski przekrój próbki DN500 (skala powiększenia 10 mm), b) Analiza powłoki EDS

oxides are continuously surrounded by the Zinalium protective layer (Fig. 6 a,b). The EDS analyze indicates that the visible oxide spot contains exclusively iron and oxygen. This means that the uncovered layer of ferric oxides is external, as the lower layer always contains silica in the concentration between 3-7 wt. % [4].

In Figure 7 a fragment of Zn-Al alloy is presented and zinc and aluminium grains can be easily recognized. As it is known, this alloy contains micro-pores created during thermal spraying. According to [9], the pores size is in the range of 2.5 to 10 μm. The zinc coating mass cannot be calculated from the cross section of a pipe wall because of the pores, as presented in Figure 7. Other electrolytical methods can be applied for this purpose. The coating consists of lamellas of the thickness from 10 to 15 micrometers (Fig. 7).

The EDS analysis of two paint coatings applied by two producers to protect the pipes DN 350 and DN 500 are presented in Fig. 8. The paint (A) that gives much better protection to the Zinalium coating contains high concentrations of Ca and Zn, as presented in Table 3 and in the form of X-ray peaks (Fig. 8b).

The EDS analyze does not apply to the five elements of the lowest number of protons and usually overestimates the carbon concentration (Tab. 3). The composition of the less protective paint (B) is significantly different. The paint comprises mostly carbon and traces of other elements: Si, Zn, Ti and Mg.

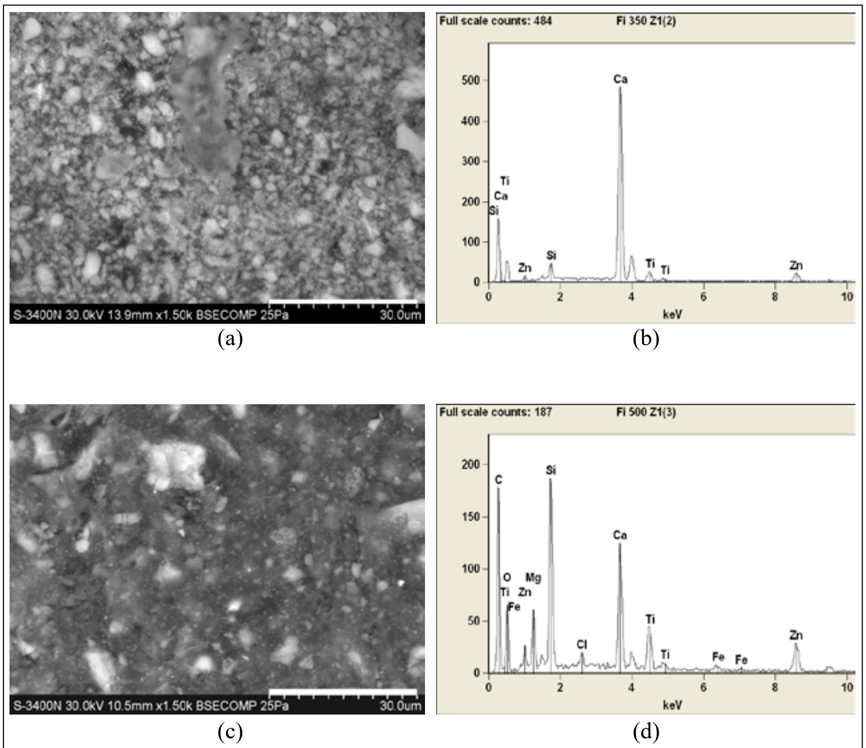

Fig. 8.
Paints morphology and a chemical composition: a) the sample DN 350, b) the respective EDS analysis, c) the sample DN500, d) the respective EDS analysis (magnification scale of 30 mm)
Ryc. 8. Morfologia farb i skład chemiczny: a) próbka DN 350, b) odpowiednia analiza EDS, c) próbka DN500, d) odpowiednia analiza EDS (skala powiększenia 30 mm)

Tab. 3. EDS results from the paint samples investigated
Tab. 3. Wyniki EDS z badanych próbek farb

Paint sample	Chemical composition, wt %.							
	C	O	Si	Ca	Ti	Zn	Mg	Al
A	-	-	6,1	75,0	6,7	12,2	-	-
B	75,8	17,9	1,7	1,3	0,8	1,4	1,0	0,1

Conclusions

The neutral salt spray test of paint coatings, developed mostly for protective layers adhered to a smooth steel surface, is also applicable for testing paints applied on external rough ductile iron pipe walls after casting and annealing processes.

The unconventional method of a paint-zinc abrasion assessment was applied for evaluation of the Zinalium continuity lining around ferric hills covered with ferric oxides. This method was also used for sampling of paints protecting the external zinc coating. The paint with a quite high concentration of calcium and then zinc provided much better anticorrosion protection to the ductile iron pipe. The paint with a high concentration of carbon had worse protective properties.

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