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EFFECT OF HEAT TREATMENT ON THE CORROSION RESISTANCE OF ALUMINIZED STEEL STRIPS

WPŁYW OBRÓBKI CIEPLNEJ NA ODPORNOŚĆ KOROZYJNĄ ALUMINIOWANYCH TAŚM STALOWYCH

The paper presents the results of corrosion resistance of heat treated aluminized steel strips. Products coated by Al-10Si alloy are used among others in a manufacturing process of welded pipes as the elements of the car exhaust systems, working in high temperatures and different environments (eg. wet, salty). The strips and tubes high performance requirements are applied to stability, thickness and roughness of Al-Si coating, adhesion and corrosion resistance. Tubes working in elements of exhaust systems in a wide range of temperatures are exposed to the effects of many aggressive factors, such as salty snow mud. It was therefore decided to carry out research on the impact of corrosion on the environmental influence on heat treated aluminized steel strips. The heat treatment was carried out temperatures in the range 250-700°C for 30, 180, 1440 minutes. Then the coatings was subjected to cyclic impact of snow mud. Total duration of treatment was 12 months and it was divided into three stages of four months and at the end of each stage was made the assessment of factor of corrosion. The results are presented in the form of macroscopic, microscopic (using a scanning electron microscope) observations and the degree and type of rusty coating.

W artykule przedstawiono wyniki badań odporności korozyjnej obrobionych cieplnie aluminiowanych taśm stalowych. Taśmy z powłoką Al-10Si stosowane są między innymi do wytwarzania zgrzewanych rur przeznaczonych na elementy układów wydechowych pojazdów samochodowych. Wymagania stawiane taśmom i rurom dotyczą stabilności, grubości i chropowatości powłoki Al-Si, przyczepności oraz odporności korozyjnej. Rury pracujące w elementach układów wydechowych w szerokim zakresie temperatur narażone są na oddziaływanie wielu agresywnych czynników m.in. soli zawartej w błocie pośniegowym. Dlatego zdecydowano się na realizację badań wpływu oddziaływania środowiska korozyjnego na obrobione cieplnie aluminiowane taśmy stalowe. Obróbkę cieplną zrealizowano w zakresie temp 250-700°C w czasie 30, 180, 1440min. Następnie powierzchnie powłoki poddano cyklicznemu oddziaływaniu błota pośniegowego. Całkowity czas badania wynosił 12 miesięcy i został podzielony na trzy, czteromiesięczne etapy po zakończeniu których dokonywano oceny zmian korozyjnych. Wyniki badań przedstawiono w postaci obserwacji makroskopowych, mikroskopowych (z wykorzystaniem skaningowego mikroskopu elektronowego) oraz stopnia i rodzaju skorodowanej powłoki.

1. Introduction

Among many steel products applied in the building industry and automotive sectors is large group of aluminized steel strips produced as galvanized. The process of dip aluminizing was developed after the First World War in Russia, the USA and Japan [1]. There are two types of such tapes. Strips coated with pure aluminum, are referred as Type 2 [1-3]. They are characterized by the presence of diffusion Al-Fe layer between the coating and the substrate, with a thickness approximately 60% of the thickness of the coating (Fig. 1a).

Due to the great fragility of the Al-Fe layer, these tapes have limited formability. The addition to aluminum approximately 8-11% Si affects the creation of a thin diffusion layer Al-Fe-Si, which is about 10-20% of the total thickness of the coating (Fig. 1b) [4-10]. At the same time fine-grained eutectic or hypoeutectic structure is obtained and decreased the temperature of the coating process on strips. Reducing the thickness of the diffusion layer improves the ability of the strips with Al-Si coating to the plastic forming. Strips with Al-Si coating are referred as Type 1 [1, 3, 11].

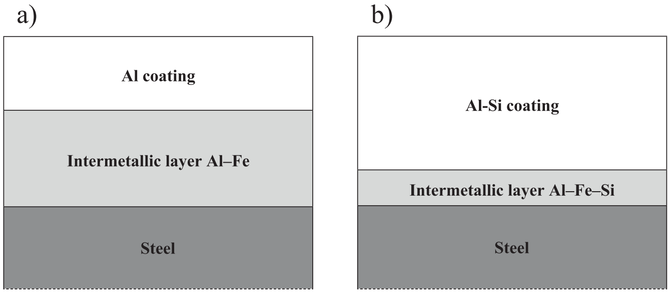

Fig. 1. Schematic cross-section of the steel strip coated with Al (a) and the Al-Si (b)

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The advantages include good dip-coating adhesion, the ability of creation with the steel alloy by diffusion, integrity and uniformity of the coating, wear resistance, corrosion resistance, water resistance, the technical reliability of the method implementation, the ability to automation of the manufacturing process.

Basic corrosion protection of steel substrate is carried out by forming an impermeable barrier in the form of a passive oxide layer which forms on the surface of Al-Si coating. The barrier is formed due to the ability of aluminum to a rapid preparation of a very thin (typically with a thickness of 5-25nm) and durable oxide layer which is practically impermeable and insoluble in most common oxidizing agents. Thus aluminum, although it is more anodic than iron or zinc, has a very limited ability to cathodic protection of steel [2].

On the basis of test results [12], it can be concluded that the galvanized aluminized steel products are characterized by high resistance to oxidation and corrosion, both at room temperature and elevated temperatures. Resistance depends on the physical and mechanical properties of the alloy and the chemical bond between the aluminum and steel. In other studies [13-14] follows that in both the industrial and without significant air pollution, aluminized steel is much more resistant to corrosion than galvanized or zinc-aluminum coated. Nevertheless, a number of researchers indicate that, unlike zinc coatings, uncoated points, pores or fine cracks are a possible source of damaging the aluminum coatings on steel [15-16]. It is believed that the cause is the lack of cathodic protection of aluminum, which is manifested by spots red rust on the uncoated edges. However, the author of [17] shows that such spots it's basically just a cosmetic issue and the results of his research in an urban environment, carried out by more than 40 years show no damage to the coating in the stained areas or delamination of the coating at the edges.

During the heat treatment of aluminized steel at a certain point is reached the temperature at which begins interdiffusion coating and a substrate with high speed. Diffusion reactions cause the primary coating is slowly turning into, and becomes dull gray layer of intermetallic compounds. There is a substantial mismatch between researchers, on the temperature at which the alloy formation is initiated between the coating and the substrate. In the case of low carbon steel of Al-Si coating temperature range is 360-580°C [18, 22]. The initial deformation and deformation of the substrate during the production of aluminized products significantly lower the temperature at which occurs violent reaction in the solid state diffusion [17, 18, 23]. A number of studies on the influence of heat treatment on the structure, physical properties and formability aluminized steel strip is presented in [24-26].

Strip coated Al-10Si are used among other things for the production of welded tubes for the automotive elements of exhaust systems. Requirements for tapes and pipes relate to stability, thickness and roughness of Al-Si coating, adhesion and corrosion resistance. Pipes operating in components of the exhaust systems in a wide range of temperatures are exposed to the effects of many aggressive factors include salty snow mud. It was therefore decided to carry out effect of environment impact study on corrosion on heat treated aluminized steel strips. The heat treatment was carried out in the temperature range of 250-700°C for 30, 180, 1440 min. Then the surfaces of coating were subjected to cycle impact by snow mud. The total duration of treatment was 12 months, and was divided into three, four-month stages, after which the assessment made of corrosion were obtained. The results are presented in the form of macroscopic and microscopic observations (using a scanning electron microscope), and the degree and type of rust coating.

2. Experimental technique

Steel strips of DX52D+AS120 grade, of a thickness app. 1.5 mm, with the Al–10%Si coating of a thickness app. 20 mm were chosen for testing. The chemical composition of the aluminized steel strip base is shown in Table 1. Determinations of the chemical composition was performed by the optical emission spectrometry method by means of SPECTROLAB M7.

Samples of dimensions 250x250 mm were cut from steel strips. Then samples were heated in a chamber furnace in the air atmosphere at temperatures from 250 to 700^{o}C, every 50^{o}C, for 30, 180 and 1440 minutes After heating, the samples were air cooled outside the furnace until a temperature of 23±2^{o}C was achieved.

The next step was testing the corrosion resistance of the coating. The study was based on a cyclic spraying surface one side of the samples, equal portion of snow mud in the amount 5ml/sample. The ionic composition of snow mud, made in the Department of Hydrogeology and Water Protection, University of Science and Technology, presented in Table 2.

The spraying was carried out in a constant temperature of 20°C once a day, about the same time. Materials containers and tools with which the samples have been in contact, were resistant to the corrosive environment and do not affect the reaction between the sample and the solution. The total duration of treatment was 12 months, and was divided into three, four-months stages, after which the assessment of corrosion were made. After each step, prior to the evaluation, samples were purified from loose deposits and corrosion products from the salts with distilled water and dried.

TABLE 1

Chemical composition of strip (wt.%)

C	Mn	Si	P	S	Cr	Ni	Nb	Cu	Al	Fe
0,017	0,16	0,007	0,008	0,011	0,025	0,021	0,015	0,019	0,03	Bal.

TABLE 2

The ionic composition of snow mud

Cations	Content [mg/dm^3]	Anions	Content [mg/dm^3]
Na^+	276,60	Cl^-	439,0
K^+	2,06	SO_4^{2-}	55,54
Mg^{2+}	7,69	HCO_3^-	268,0
Ca^{2+}	89,52	CO_3^{2-}	<0,5
Fe^{+2}	2,186	NO_3^-	4,7$^-$
Σ K	37,056	Σ A	762,54

Results of corrosion tests are shown in a photograph of coating surface, on which, using CorelDRAW Graphics Suite 12, was imposed grid consisting of 266 squares, facilitating calculation of the degree of surface coating corrosion. The degree of corrosion (S) was calculated according to equation (1):

$$S = \frac{n_Q}{N_Q} \times 100\%, \tag{1}$$

where:

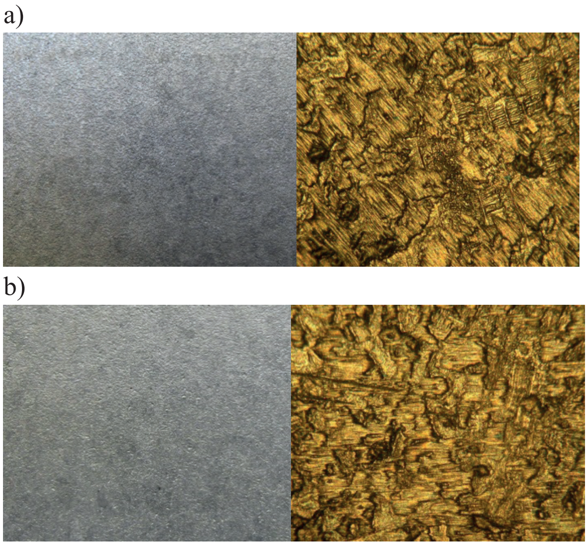
- n_Q - the number of squares covered with corrosion products on the surface of at least 50% of the square
- N_Q - the total number of squares

The results are also shown in the graphs on which are marked numerical values of the corrosion of the surface S, the number of dark D and red R areas on the surface of the coating before and after heat treatment and impact of snow mud for 4, 8 and 12 months.

3. Results and discussion

3.1 Results of the coating surface observations before and after heat treatment

Macroscopic observations of the surface of Al-Si film before and after heat treatment at 250-700ºC for 30, 180, 1440 min. on selected samples are shown in Fig. 2.



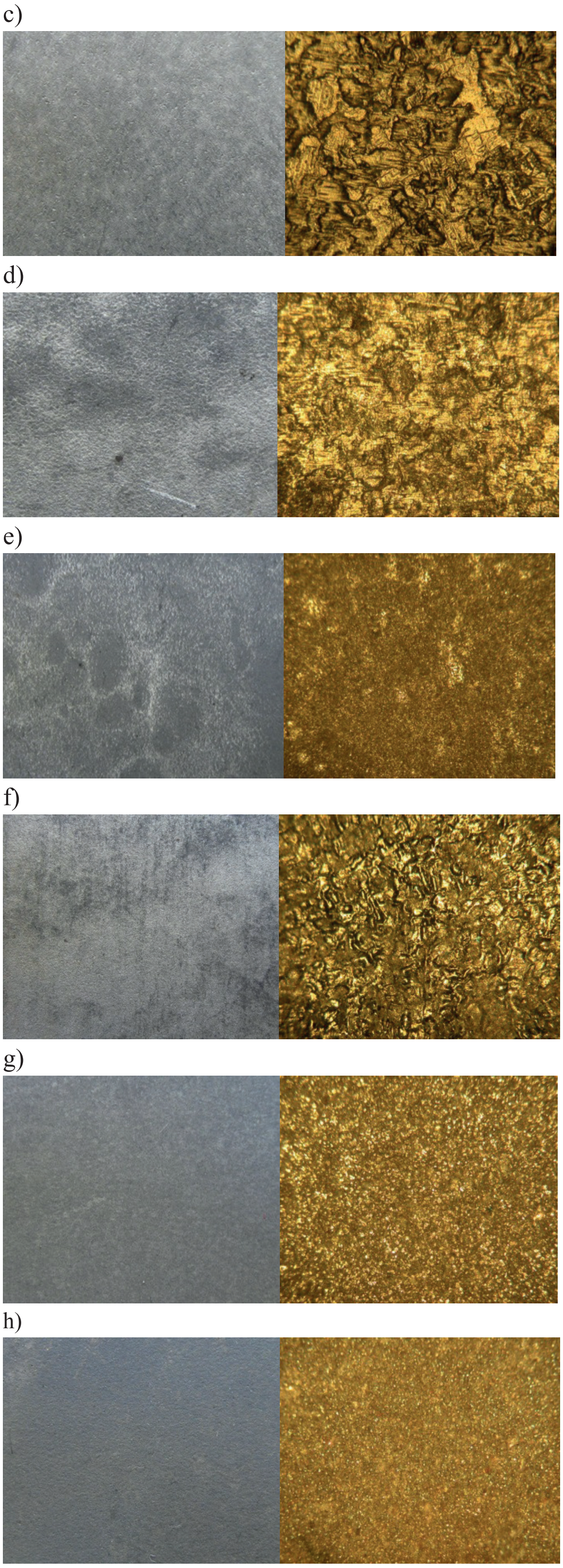


Fig. 2. Macro- and microscopic observation of the surface of the Al-Si coating without and after heat treatment
a) Initial state, b) 250ºC – 1440min, c) 450ºC – 1440min, d) 500ºC – 1440min, e) 550ºC – 180min, f) 600ºC – 30min, g) 650ºC – 30min h) 700ºC – 180min

The surface appearance of the coating depends on the temperature and time of heating. To a temperature of 450°C heat treatment time has no effect on the appearance of the surface. Surface coating after heat treatment in this area is not different from the coating in the original state (Fig. 2a), that is bright, silvery with a clear luster (Figure 2b-c). Partial changes appear on the surface of the coating in the range of 500-600°C. Coating in many irregular areas changes in the darker and matte (Fig. 2d-f). This diversity, according to the research, due to uneven thickness of the coating. The smaller thickness of the coating causing the darker and matt areas, thicker maintains the brighter appearance of the coating. At a temperature of 650-700°C in a time interval implemented the entire surface of the coating is a dark, matt and porous (Fig. 2g-h), regardless of the thickness of the coating.

3.2 Results of the corrosion coating surface observation without heat treatment

Observations of the surface layers without the influence of heat treatment and snow mud for 4, 8 and 12 months are shown in Fig. 3

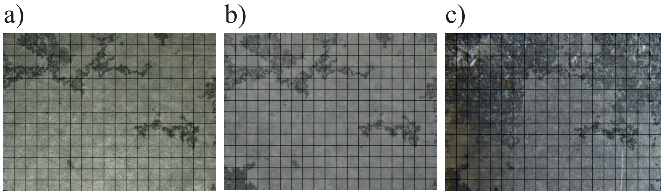


Fig. 3. Surface of Al-Si coating without heat treatment, and after the influence of snow mud for a) 4 months, b) 8 months, c) 12 months

In each case, the coating surface was covered with a dark gray coating corrosion (Fig. 3a-b), whereas after 12 months there were also slight changes in the form of red corrosion products - small pits (Fig. 3c).

3.3 Results of the corrosion coating surface observation after heat treatment

Influence of heat treatment on the corrosion resistance of the coating is visible in the observations of the coating surface after testing in the environment of snow mud. The results of macroscopic observations of the coating after heat treatment and corrosion study after, 4, 8 and 12 months are shown in Fig. 4-24.

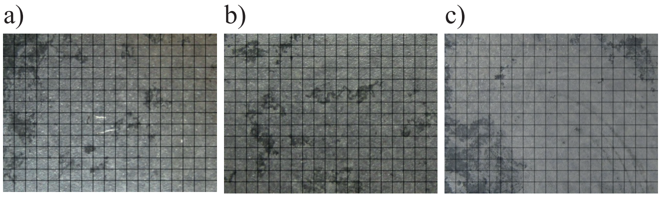


Fig. 4. Surface of Al-Si coating after the heat treatment at 250°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

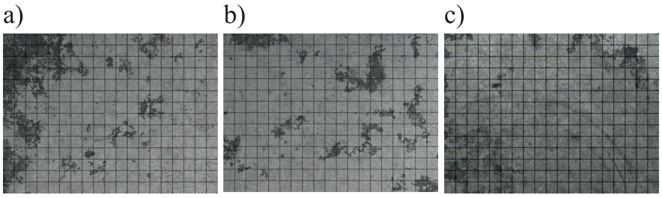


Fig. 5. Surface of Al-Si coating after the heat treatment at 250°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

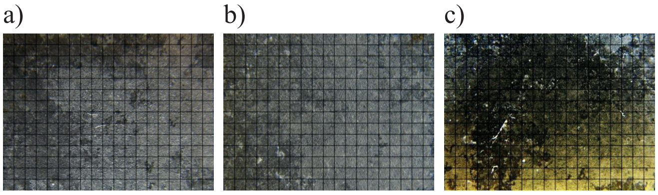


Fig. 6. Surface of Al-Si coating after the heat treatment at 250°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

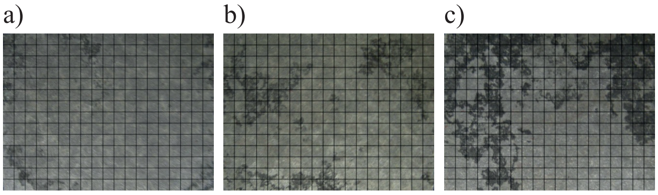


Fig. 7. Surface of Al-Si coating after the heat treatment at 450°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

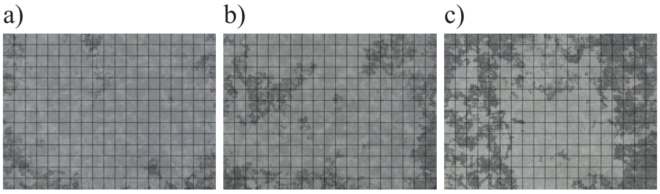


Fig. 8. Surface of Al-Si coating after the heat treatment at 450°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

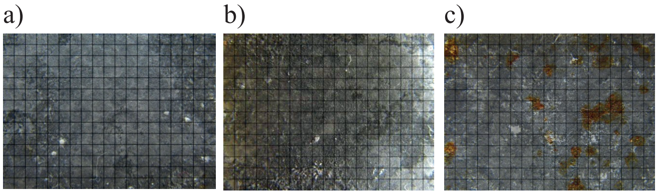


Fig. 9. Surface of Al-Si coating after the heat treatment at 450°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

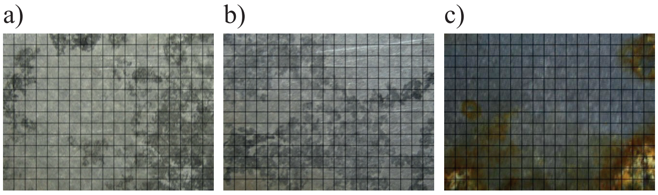


Fig. 10. Surface of Al-Si coating after the heat treatment at 500°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

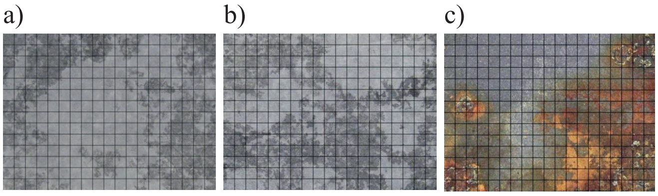


Fig. 11. Surface of Al-Si coating after the heat treatment at 500°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

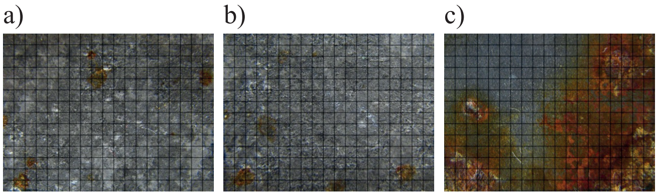


Fig. 12. Surface of Al-Si coating after the heat treatment at 500°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

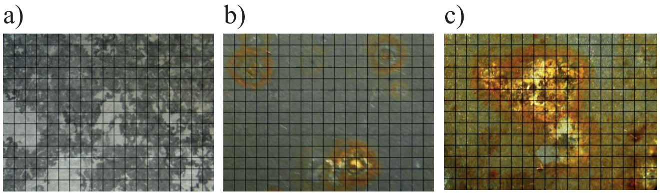


Fig. 13. Surface of Al-Si coating after the heat treatment at 550°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

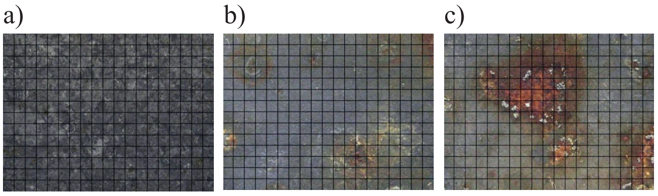


Fig. 14. Surface of Al-Si coating after the heat treatment at 550°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

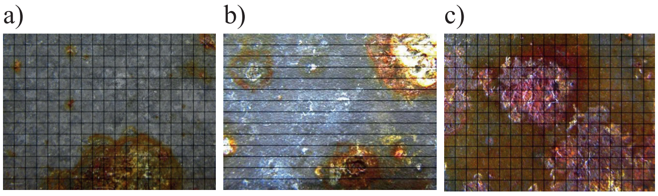


Fig. 15. Surface of Al-Si coating after the heat treatment at 550°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

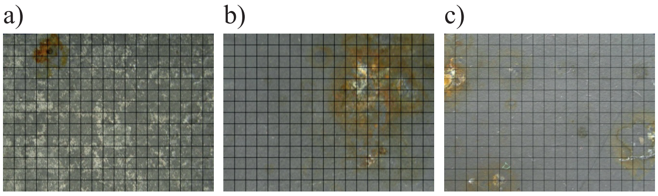


Fig. 16. Surface of Al-Si coating after the heat treatment at 600°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

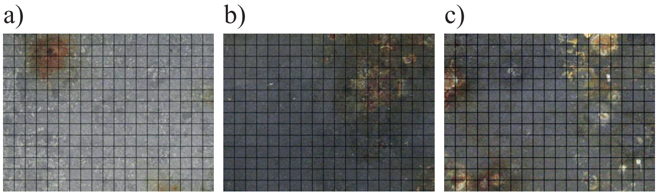


Fig. 17. Surface of Al-Si coating after the heat treatment at 600°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

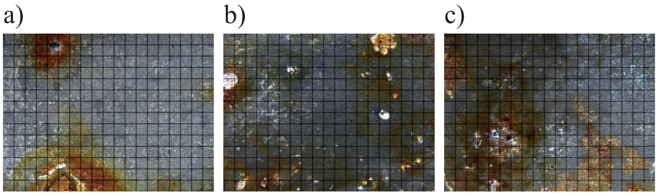


Fig. 18. Surface of Al-Si coating after the heat treatment at 600°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

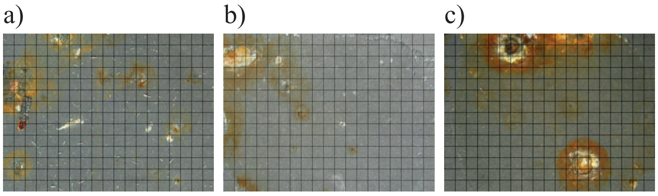


Fig. 19. Surface of Al-Si coating after the heat treatment at 650°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

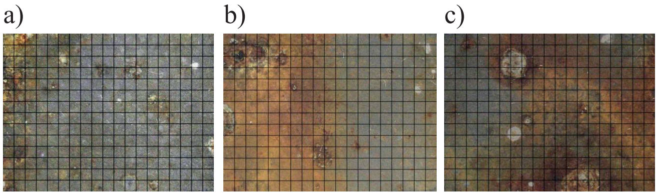


Fig. 20. Surface of Al-Si coating after the heat treatment at 650°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

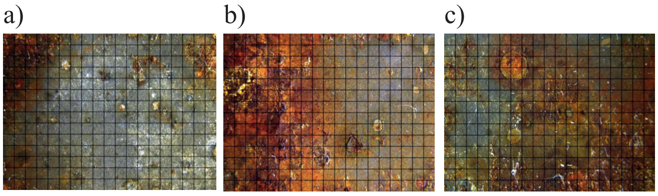


Fig. 21. Surface of Al-Si coating after the heat treatment at 650°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

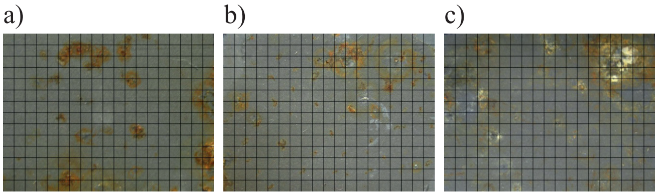


Fig. 22. Surface of Al-Si coating after the heat treatment at 700°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 4 months

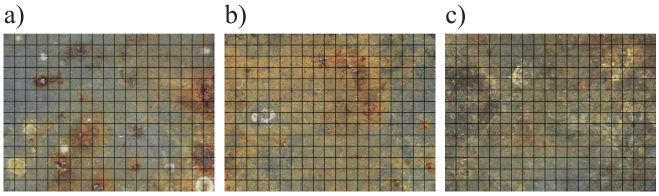


Fig. 23. Surface of Al-Si coating after the heat treatment at 700°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 8 months

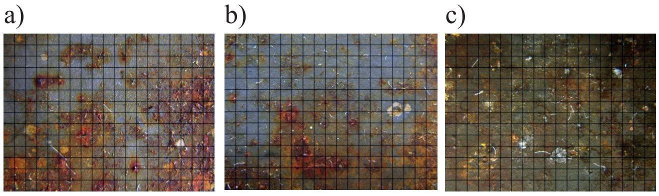


Fig. 24. Surface of Al-Si coating after the heat treatment at 700°C during a) 30 min, b) 180 min, c) 1440 min and influence of snow mud during 12 months

The percentage of the degree of corrosion, the surface in the form of gray areas and redheads are shown in the graphs (Fig. 25-27).

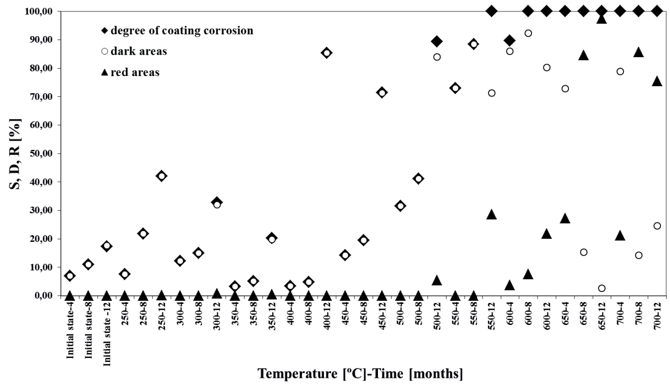


Fig. 25. Results of degree of surface corrosion Al-Si coating before and after heat treatment at 250-700°C at the time 30 min

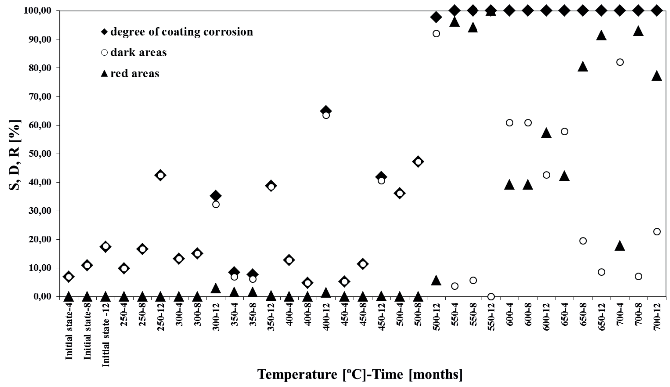


Fig. 26. Results of degree of surface corrosion Al-Si coating before and after heat treatment at 250-700°C at the time 180 min

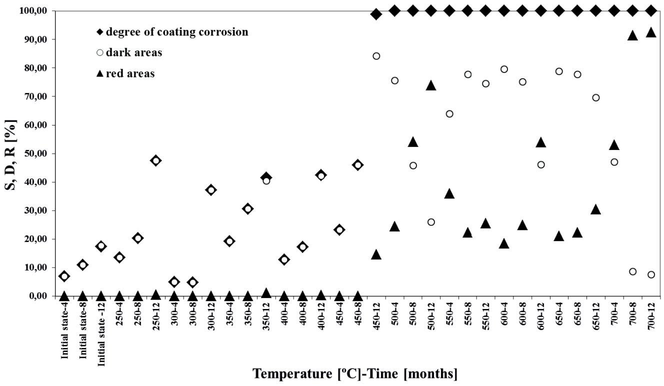


Fig. 27. Results of degree of surface corrosion Al-Si coating before and after heat treatment at 250-700°C at the time 1440 min

The results indicate a very strong influence of heat and corrosive environment applied (snow mud) for corrosion resistance.

After 4 months exposure at snow mud, after heat treatment at a temperature of 250-450°C full time range and at a temperature of 500°C for 30 and 180 min for samples whose surface was clear, with no traces of matting, the surface samples cover approximately 2-40% by the dark areas, but the longer heat treatment increases the number of these areas (Fig. 4, 7, 10a-b). After heat treatment at 550°C for 30 min more than 70% of the area is dark areas without red corrosion (Fig. 13a). In these cases, the degree of corrosion, surface coincides with the percentage share of dark areas. In other cases, ie. after heat treatment at 500°C during 1440 min (Fig. 10c), 550°C for 180 and 1440 min (Fig. 13b-c) and at a temperature of 600-700°C full time range the surface samples are both dark and red areas (Fig. 16, 19, 22). In most cases dark areas occupy 10-85%, and red areas occupy about 20-90%. The degree of surface corrosion, which is the sum of the areas of dark and ores, in that the temperature-time exposure in most cases is 100%.

After 8 months, the corrosive effects of the environment (snow mud) for the samples after the heat treatment at a temperature of 250-450°C full time range and at a temperature of 500°C for 30 and 180 min. continue to cover the surface of samples by dark areas, which occupy about 5-50% (Fig. 5, 8, 11a-b). After heat treatment at 550°C for 30 min. about 90% of the area is dark without red corrosion (Fig. 14a). In these cases, the degree of corrosion, surface coincides with the percentage share of dark areas. After heat treatment at 500°C for 1440 min (Fig. 11c), 550°C for 180 and 1440 min (Fig. 14b, c) on the surface of the samples are both dark and red areas, forming, depending on the heat treatment parameters, approximately 10-90%. For the samples heat-treated at 600-700°C full time range, the surface of coating is covered at about 80-90% by the red areas and the rest are the dark areas (Fig. 17b-c, 20b-c, 23). Exceptions are sample after heat treatment at 600°C and 650°C during 30 minutes (Fig. 17a, 20a), with 10-40% red corrosion regions on surface. The degree of surface corrosion, which is the sum of the areas of dark and red, in that the temperature-time exposure of 100%.

After 12 months the corrosive effects of the environment (snow mud), on the samples after heat treatment is greatest. After heat treatment at 250°C at full time range (Fig. 6), and at 450°C for 30 and 180 min (Fig. 9a-b) surface of samples is coated about 40-80% by the dark areas, and at few samples have been noticed red areas. In these cases, the degree of corrosion, surface coincides with the percentage share of dark areas in a number of cases increased by 1-2% due to the residual red areas. After heat treatment at 450°C for 1440 min sample surface is covered with more than 80% by the dark areas, while almost 20% of red areas (Fig. 9c), and the total degree of rust is 100%. In other cases, on all samples appear red areas in an amount of 5-99%, the remainder being of dark areas (Fig. 12, 15, 18, 21, 24). It should be noted that red areas represent greater share than the percentage of dark areas, particularly for samples which were heat-treated surface is completely dark, dull and porous. The total degree of surface corrosion, except the sample after heat treatment at 500°C for 30 min. (90% of the area of rust) is 100%.

4. Conclusions

The paper presents the results of corrosion resistance of heat treated aluminized steel strips. Samples cut out from the DX52D + AS120 grade strips were heat treated at a temperature range 250-700^{o}C for 30, 180 and 1440 minutes. Then the coatings was subjected to cyclic impact of snow mud. Total duration of treatment was 12 months and it was divided into three stages of four months and at the end of each stage was made the assessment of factor of corrosion. The results are presented in the form of macroscopic, microscopic (using a scanning electron microscope) observations and the degree and type of rusty coating. Basing on the analysis of the test results the following conclusions can be drawn:

1. The results indicate a very strong influence of heat treatment and applied corrosive environment (snow mud) for corrosion resistance.
2. Coating without heat treatment has a high resistance to corrosion, regardless of the time the impact of corrosive environment.
3. Coating after heat treatment in the range where there is no change on the surface also has a high resistance to corrosion. However, in some cases, the coating formulation to a greater extent dark areas.
4. In most cases after heat treatment and exposure to conditions of snow mud samples surface is coated by red products of corrosion.

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