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# MODIFICATION OF SILICON CRYSTALS IN THE Al-Si COATING BY MEANS OF HEAT TREATMENT

# MODYFIKACJA KRYSZTAŁÓW KRZEMU W POWŁOCE Al-Si NA DRODZE OBRÓBKI CIEPLNEJ

The paper presents the results of investigation into the improvement of the quality of protective coatings applied in the automotive industry. Coating was dip applied on steel. The main application of the coatings are the exhaust system parts, which must be characterized by adequate anticorrosive properties, while maintaining high plasticity (during the final forming of the part). The addition of silicon increases the service temperature of coatings, but, at the same time, lowers the plastic properties of the alloy. Large sharp-edged Si crystals in a dip coating are preferential locations of coating decohesion during the plastic forming of parts. The large difference in hardness between aluminium and silicon may cause numerous Si crystals chipping out from the matrix during plastic forming, causing a discontinuity in the protective coating, and hence an impairment in its anticorrosive properties.

By means of heat treatment, a modification to the morphology of silicon crystals was made with the aim of improving the plasticity of the coating. An industrial Al-Si coating was subjected to the two-stage heat treatment process. An Al-Si coating (containing approx. 7 wt Si) was investigated for the possibility of optimizing the structure with the aim of improving the deformability under the conditions of press forming of products. Two-stage heat treatment was applied, as a result of which some reduction of the volumetric fraction of silicon crystals was obtained, along with the change of their morphology to a new one, more advantageous from the point of view of plastic forming. The change of the coating microstructure did not result in any increment in intermetallic phases responsible for coating adhesion.

In the investigation, microscopic techniques and computer image analysis (Image ProPlus for Windows) were used. In addition, the scratch test (Scratch Tester) was performed.

The investigation carried out has shown that, as a result of heat treatment, part of Si from crystals have passed to the solution, while the remaining crystals have undergone a slight size reduction and rounding, which has a favourable effect on the plastic properties of the alloy.

W pracy przedstawiono wyniki badań dotyczących poprawy jakości stosowanych w przemyśle motoryzacyjnym powłok ochronnych Al-Si. Powłoki nakładane są na stal metodą zanurzeniową. Głównym przeznaczeniem powłok są elementy układów wydechowych, które muszą charakteryzować się dobrymi własnościami antykorozyjnym przy jednoczesnym zachowaniu wysokiej plastyczności (podczas formowania finalnego elementu). Dodatek krzemu podwyższa maksymalną temperaturę eksploatacji powłok, ale jednocześnie obniża własności plastyczne stopu. Duże, ostrokrawędziowe kryształy Si w powłoce zanurzeniowej są preferencyjnymi miejscami dekohezji powłoki podczas formowania plastycznego detali. Duża różnica w twardości, między aluminium a krzemem, podczas formowania plastycznego może powodować również wykruszanie twardych kryształów Si z osnowy powodując nieciągłość warstwy ochronnej, a co za tym idzie, obniżenie własności antykorozyjnych powłoki. Na drodze obróbki cieplnej dokonano zmiany morfologii kryształów krzemu w celu poprawy plastyczności powłoki. W pracy badano technologiczną powłokę Al-Si (zawierającą 7% wag. Si) pod kątem możliwości optymalizacji struktury na potrzeby poprawy odkształcalności w warunkach tłoczenia wyrobów. Zastosowano dwuetapową obróbkę cieplną, w wyniku której uzyskano pewne zmniejszenie udziału objętościowego kryształów krzemu oraz zmianę ich morfologii na bardziej korzystną, z punktu widzenia formowania plastycznego. Zmiana mikrostruktury powłoki nie spowodowała przyrostu warstwy faz międzymetalicznych odpowiedzialnych za adhezję powłoki.

W badaniach wykorzystano techniki mikroskopowe (mikroskop optyczny i scanningowy) oraz komputerową analizę obrazu (Image ProPlus for Windows). Dodatkowo przeprowadzono test rysy (Scratch Tester).

Przeprowadzone badania wykazały, że w wyniku obróbki cieplnej część krzemu z kryształów przeszła do roztworu, natomiast pozostałe kryształy uległy niewielkiemu zmniejszeniu i wyobleniu, co korzystnie wpływa na własności plastyczne stopu.

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## 1. Introduction

The exhaust system of the motor car undoubtedly continues making new demands from the designers. The increasing parameters of exhaust system operation – the increasingly high temperature (reaching 900°C), the aggressive environment containing a very harmful condensate (chemical substances originated from the combustion process), and the high probability of mechanical damage during driving are all the cause of constant searching for new technological ideas to improve the durability of its parts.

The solution of recent years have been widely used protective coatings applied on steel, most often, in the dip coating process. Considering the economical aspect, aluminium-based coatings are most frequently used. Due to the addition of silicon (lowering the alloy melting point), these coatings show too low plasticity during plastic forming. The large difference in hardness between aluminium and silicon may cause numerous Si crystals chipping out from the matrix during plastic forming, causing a discontinuity in the protective coating, and hence an impairment in its anticorrosive properties [1,2].

The complete elimination of the adverse effect of silicon crystals on the plasticity and corrosion properties of the coating is not possible, though it can be minimized through the modification of its structure by applying appropriate heat treatment.

An aluminium-based coating used for exhaust system elements was put to the toughening test within the present work. Two-stage heat treatment was proposed, which was intended to change the morphology of silicon crystals (with water cooling) and the relaxation of possible stresses (with air cooling) [3,4].

## 2. Material and methodology of researches

### 2.1. Material

An Al-Si coating, as applied on both sides on the X2CrTi12 high-chromium steel (1.4512) in the dip coating process, was subjected to examination. The structure of the coating is made up of the Al(Si)+Si eutectic mixture. In the plane parallel to the sheet (substrate) surface, the eutectic mixture has a lamellar form [5] (Fig.1a). The observations of the structure in the plane parallel to the sheet surface have revealed that the lamellas are preferentially perpendicular to the substrate. In extreme cases, the silicon lamellas reach the size equal to the entire coating thickness (Fig. 1b). Chemical composition of the coating examined is given in Table 1.

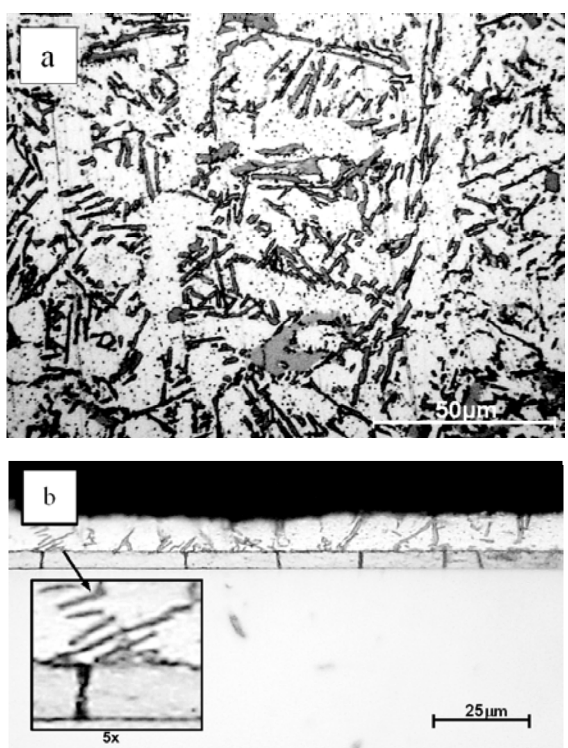


Fig. 1. Microstructures of the initial coating, a) in parallel plane to the substrate of the metal sheet, b) on the cross section of the coat, etched by 1%HF

TABLE 1
Chemical composition of the coating (EDX)

| Material | Chemical composition, weight % | | | |
|---|---|---|---|---|
| | Al | Si | Fe | other |
| Coating | balance | 6.5 | 0.4 | <0.1 |

## 2.2. Methodology

The influence of heat treatment on the morphology of silicon crystals in the coating was determined. The starting material for the production of exhaust silencers (10 x 10 mm test pieces made from commercial sheet of a thickness of approx. 1 mm with an Al-Si coating of an average thickness of approx. 15 m applied on both sides) was subjected to the heat treatment process. The heat treatment consisted of two stages: Stage I (420°C /2h / water cooling) and Stage II (120°C / 2h / air cooling). The heat treatment parameters were determined experimentally. It was ascertained that the solutioning temperature of 420°C is the maximum temperature, at which the undesirable increase in the thickness of the intermediate phases layer does not occur. Heat treatment by solutioning and ageing in an alloy, where there are no precipitates of Mg, Cu, Mn in the structure, is not effective because of the inability of the hardening dispersion phases to precipitate [5]. Therefore, the heat treatment applied in the experiment was not intended to cause the dispersion hardening of aluminium, but only to improve the silicon crystal morphology in respect of plastic forming [6, 7]. The second stage of heat treatment, herein referred to as ageing, was carried out with the aim of elimination possible stresses formed in the coating as a result of rapid cooling.

The examination carried out included observations of the coating structure (on an Axiovert 25 microscope by ZEISS and a JSM 5400 Jeol scanning microscope). Successively, the average crystal size was determined (on an NEOPHOT 21 microscope) and, using the computer program Image ProPlus for Windows, the volumetric fraction of silicon crystals in the heat treated coating was established. Additionally, the comparison of both coating, i.e. before and after the heat treatment coating by use the Scratch Test was done.

## 3. Result of researches and discussion

Observations of the structure on the cross-section of the coating in its initial state (Fig. 1b) found that Si crystals take preferentially the position parallel to the substrate. The largest Si crystals attain the length equal to the coating thickness and have strongly elongated shapes (the cross-section of lamellar precipitates). Between the Al-Si and the steel substrate is a layer of intermetallic phases (mainly Fe-Al) resulted from the mutual diffusion of Al and Fe in the aluminizing process. Microscopic observations indicated that the applied heat treatment had decreased the number and sizes of Si crystals and that the silicon crystals had been rounded. In addition, macroscopic observations from different locations on the initial sheet showed a very uneven arrangement of silicon crystals and a variation in the coating thickness reaching 30%. As a consequence, after heat treatment, differential heat treatment effects were observed in different locations of the coating.

Examples of coating microstructure within the same heat treated specimen are shown in Figure 2.

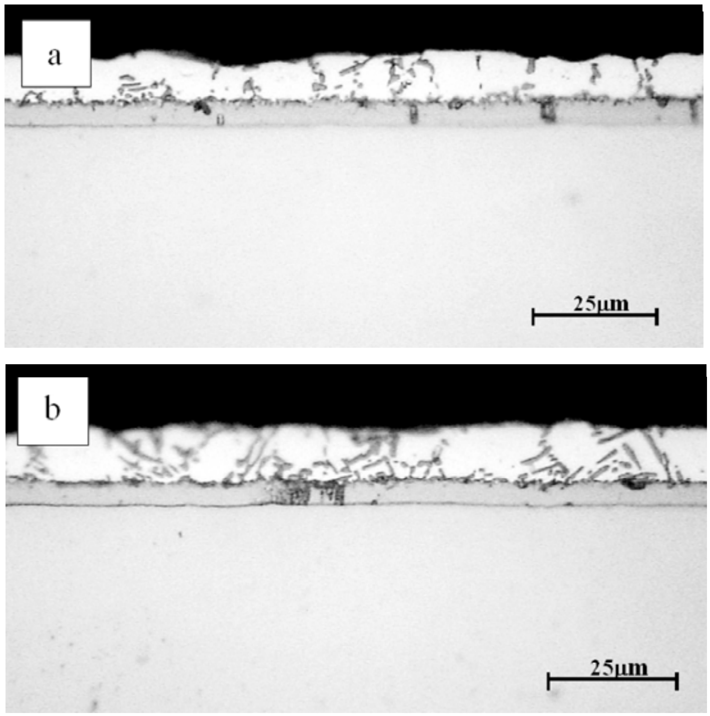


Fig. 2. a, b) Microstructures of coating after heat treatment, etched by 1 % HF

In Figure 2a, distinct effects of decreasing silicon crystal size (defragmentation and spheroidizing) are found. In Figure 2b, on the other hand, the effect of heat treatment is less visible (successful), but also in this microphotograph can an edge rounding, as against the initial structure, be noticed.

Observations of coating cross-sections using the scanning microscope confirmed the influence of heat treatment on the morphology of silicon crystals. The scanning images (Figs. 3a and 3b) clearly show rounding of silicon crystal edges and their tendency to taking on regular forms.

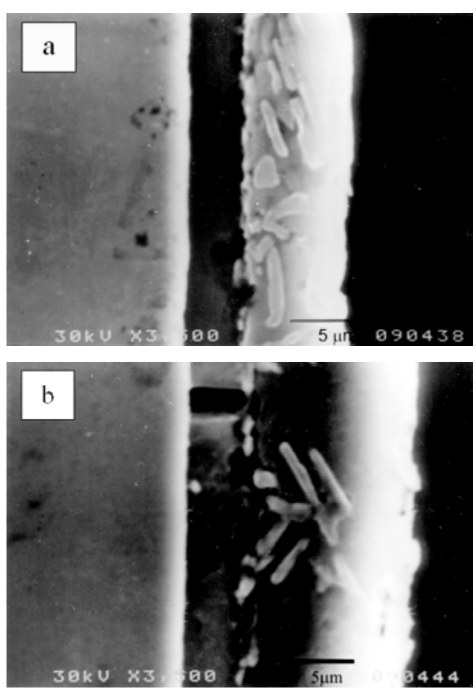


Fig. 3. a, b) Microstructures of coating after heat treatment taken from two different areas

Similarly as in Figure 2, different heat treatment effects, depending on the location of taking the test coating section from the initial sheet, and thus on the coating thickness, are revealed here.

The silicon crystals were also characterized by measuring their dimensions in the direction parallel to the substrate, as per the diagram in Figure 4.
Due to the uneven distribution of Si crystals in the structure, the measurements of the crystal sizes by the microscopic method with the graduation might be burdened with a large error.

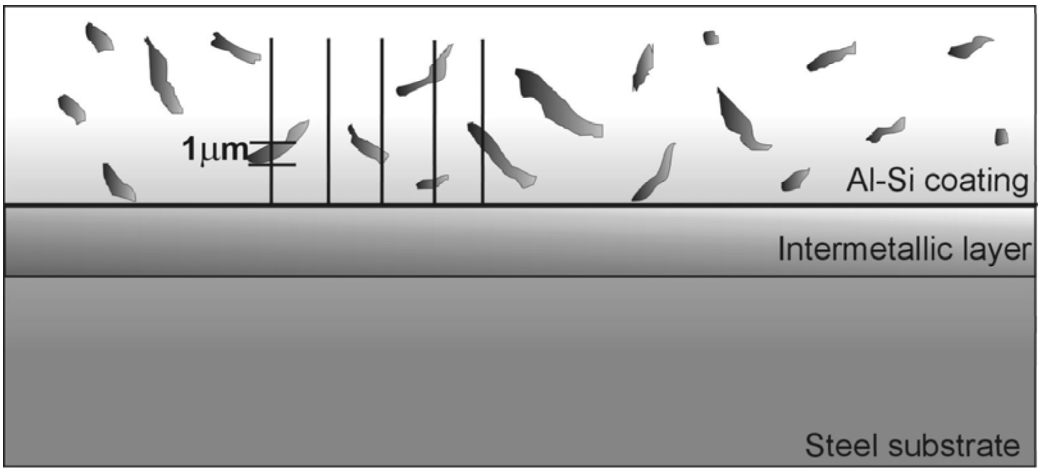


Fig. 4. Diagram of the measurement of the Si crystal size using the microscope graduation

Therefore, the volumetric fraction of Si crystals of the matrix was additionally estimated using the Image ProPlus 30 for Windows software. By offering the capability to analyze a larger area, this method yields, as a result, a more accurate estimation compared to the previous microscopic method. A sample area of analysis is shown in Figure 5. The results of the measurements of the average size of silicon crystals and their volumetric fraction of the coating are given in Table 2.

TABLE 2
The average size of Si crystals and their volumetric fraction of the coating, respectively, before and after the heat treatment

| Coating | The average size of Si crystals, µm | The volumetric fraction of Si crystals, % |
|---|---|---|
| Initial | 0.70 ± 0.27 | 9.00 |
| After heat treatment | 1.16 ± 0.78 | 8.50 |

Fig. 5. The structure analysis area for the computation of the volumetric Si fraction of the Al-Si coating the Image ProPlus 30 for Windows software

The effect of heat treatment on the mechanical properties was illustrated by the scratch test. Figure 6 shows comparison of the depth of scratching along its length for both coatings. It was demonstrated that the penetrator sunk into the heat treated coating faster, which was resulted from a reduced share and size of Si crystals caused by the heat treatment.

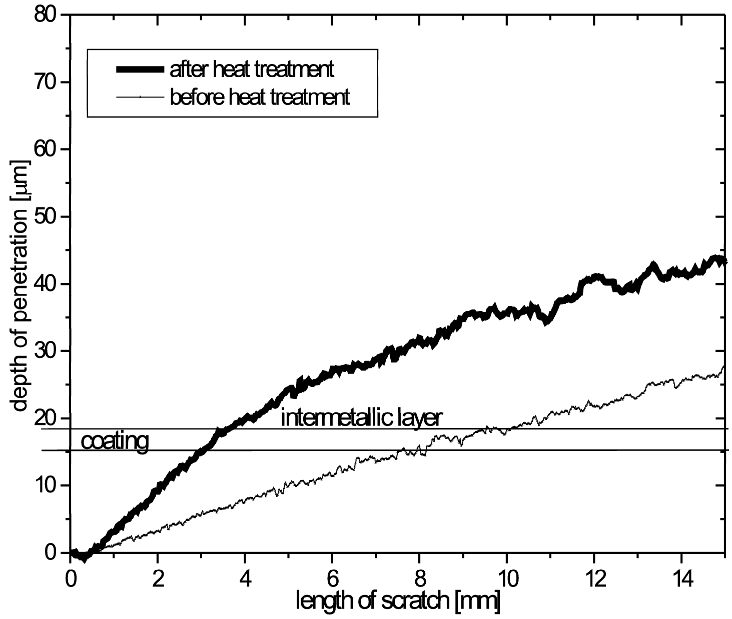


Fig. 6. Depth of penetration (ScratchTest) into coating before and after the heat treatment

## 4. Conclusions

It was found from the analysis of the volumetric silicon crystal fraction of the Al-Si that the heat treatment consisting in soaking at a temperature of 420°C for 2 hrs followed by water cooling, and then soaking at a temperature of 120°C for 2 hrs followed by air cooling reduced the volumetric Si crystal fraction of the matrix only to a small extent. It was found that approx. 5% of the Si crystal volume had passed to the solution. It was determined, however, that the applied heat treatment effectively changed the morphology of silicon crystals from the sharp-edged form to forms with rounded edges and more regular shapes.

In summary it can be stated that the obtained investigation results have demonstrated possibilities for modifying the Si crystal morphology to become more advantageous in terms of the suitability for plastic deformation (press forming processes), while not causing the increment in the thickness of the intermediate phase.

The optimization of the coating structure with the aim of improving plastic deformability by means of the size reduction of Si crystals is associated with a reduction in scratch resistance. The explanation of how the impairment in this property along with the simultaneous improvement of plastic deformability affect the technological process of exhaust silencer press forming will be the subject of further investigation.

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