

The effect of the T6 heat treatment on the surface structure and oxide layer of an Al-Si coat

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The paper presents investigation results for an Al-Si protective coat deposited from a liquid phase on the ferritic steel surface. A coat of chemical composition of Al-6.5 wt.% Si was subjected to a T6 heat treatment at temperatures of 420 °C (solutionizing), and 80 °C and 120 °C (ageing). The effect of soaking on the structure of the Al-Si coat was determined by microscopic examination. By XRD examination, the effect of soaking on the phase composition of the coat, while by GXRD examination, the oxide layer composition were determined. It was found that relaxation of the coat surface layer (a decay of the technological cold work effects) occurred, and a highly dispersed oxide layer Al_2SiO_5 formed as a result of the heat treatment.

Keywords: Al-Si coatings, T6 treatment, oxides $\text{Al}_2\text{O}_3/\text{SiO}_2$, XRD/GXRD measurements.

1. Introduction

Protective coatings provide effective and long-lasting protection for steel constructional elements operating in an industrial atmosphere. An example of the widespread application of coatings on steels are exhaust system elements, whose operation environment is highly aggressive. In the course of operation of a car, its exhaust system is exposed to a wide variety of agents, *e.g.*, condensate forming from water vapour, harmful chemical substances originating in the combustion process, and mechanical impacts.

The most widely used protective coatings include aluminium and Al-Si coatings. These coatings are characterized by good anticorrosion properties owing to the aluminium oxide film forming on their surface, which effectively protects an item against harmful action of exhaust gas, and resistance to high temperatures. The addition of silicon enables the item operation temperature to be increased and prevents the growth of the intermetallic compound layer at the steel substrate. The film of Fe-Al-Si phases that is being formed provides good adhesion of the coat to

the substrate, which facilitates deep drawing of exhaust system elements in subsequent technological processes.

Many methods of aluminium protective coating application are used at present, including: electroplating, dip coating, spraying, or cladding. In addition to the classical methods, as mentioned above, also modern methods are used, which include ion implantation and laser techniques, among others [1]. Due to their high costs, however, they are rarely used in industry yet. The most common and straightforward method of aluminium-silicon coating application is the hot-dip coating method. Flux-coated steel parts are introduced to a molten Al-Si alloy bath at a temperature of 670–800 °C for the duration ranging from a dozen or so to several seconds, depending on the coat thickness required. The thickness of aluminium coats normally does not exceed 0.05–0.5 mm. The coats are subjected to finishing treatment, consisting in surface smoothing, thickness equalization, improving the properties and aesthetics. The properties of coats can be enhanced, *e.g.*, by heat treatment [2].

The aim of the investigation described in the paper was to determine the effect of heat treatment by solutionizing and artificial ageing (T6) on the condition of the Al-6.5wt.%Si coat structure and the surface oxide layer [4–6].

2. Material and methodology of research

2.1. Material

An Al-Si coat applied on high-chromium steel X2CrTi12 (1.4512) on both sides under industrial conditions was tested. Chemical composition of the coat is given in Tab. 1.

2.2. Methodology

The coats were subjected to a two-stage heat treatment. In the first stage, the coats were held at a temperature of 420 °C in a laboratory furnace in the air atmosphere for 2 hrs, and then quenched in water at room temperature. Rapid, non-equilibrium cooling of the AlSi alloys causes its supersaturation (solutionizing). Supersaturation means an enrichment of the solid solution Al(Si) in silicon and reduction of the share of large Si crystals in the bulk of the coat, being the result of a shift in the solubility limit line in the Al-Si phase equilibrium system (Fig. 1).

In the second stage of heat treatment, the coats were aged at temperatures of 80 and 120 °C for the duration of 0.5 and 2 hrs, respectively. During ageing, the excess silicon precipitates from the supersaturated solid solution Al(Si) in the form of highly refined secondary crystals.

T a b l e 1. Chemical composition of coat.

Material	Chemical composition [wt.%]			
	Al	Si	Fe	Other
Coat	Rest	6.5	0.4	<0.1

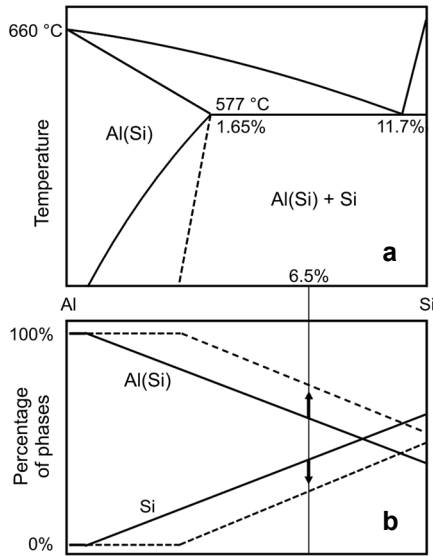


Fig. 1. Changes in Al-Si phase equilibrium system (a) and percentage of phases in coating (b) caused by saturation.

The heat treated coats were subjected to microscopic evaluation and GXRD examination on a Seifert 3003TT apparatus using filtered radiation with $\lambda_{K_{\alpha}Co} = 0.17902$ nm and slits limited the divergence of the diffracted beam to 0.5° . The angle range of $2\theta = 21-49^\circ$ was examined (with a step of 0.05°) with the radiation incidence angle α in the range of $1.5-19^\circ$.

3. Results

The heat treatment used, in agreement with the assumption and conclusions relative to the Al-Si phase equilibrium system, caused a decrease of the share of Si crystals in the bulk of the coat, a reduction in their size, and change of their shape into a new one, more advantageous from the point of view of the plastic properties of the coat. An example of the coat's microstructure is given in Fig. 2.

The SiO_2 oxide was found to be present in the phase composition of both the initial coat and the heat treated coats. In order to find out whether the SiO_2 oxide is distributed within the bulk of the coat (as an impurity of alloys containing Si, and made in typical

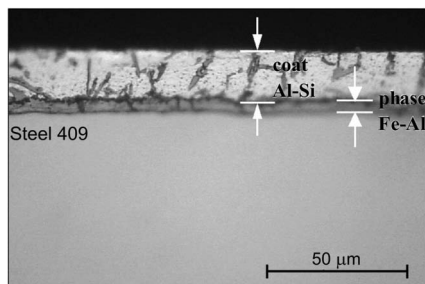


Fig. 2. Structure of the Al-Si coat in the cross section of the coat, etched by 1% HF.

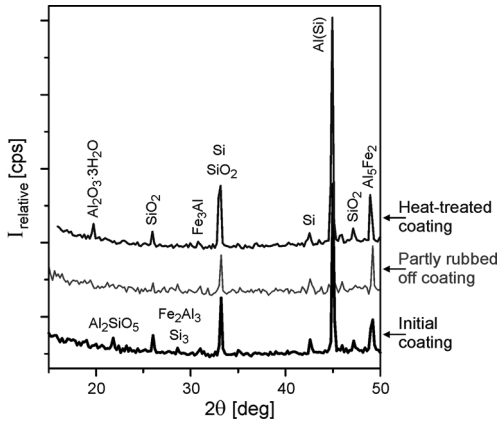


Fig. 3. Sample X-ray patterns obtained in symmetric geometry from coating in different states.

industrial conditions), or is spread on the coat surface, diffraction was performed on the coat with its thickness being partially reduced by mechanical polishing.

The diffraction pattern obtained from the thinned coat showed a weaker reflection originating from SiO_2 , which means that this phase occurs in the entire coat, too (Fig. 3).

In the diffraction patterns obtained from the initial coat the presence of reflection was also found, which comes from the hydrated forms of the aluminium oxide $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and/or $\text{AlO}(\text{OH})$ [3], as well as a reflection originating from the oxide of the Al_2SiO_5 ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) type (Fig. 4). Reflections from the Al_2SiO_5 oxide are best visible in diffraction patterns made at radiation incidence angles α in the range of $9\text{--}13^\circ$.

In the diffraction patterns obtained from the heat treated coats, a very broad reflection, being typical of highly dispersed phases, was additionally recorded in

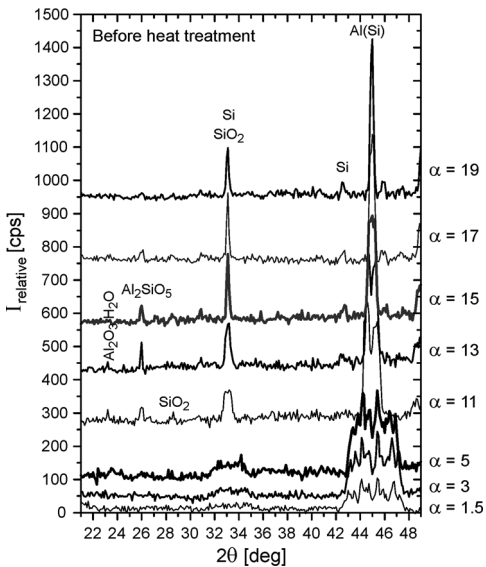


Fig. 4. GXR diffraction patterns obtained from the Al-Si coat before heat treatment (the technological state).

the angle range of Al_2SiO_5 oxide occurrence (Fig. 5). The broad reflection, similarly to the SiO_2 -originating reflections, is best represented in diffraction patterns made at X-ray radiation incidence angles of $\alpha \geq 5^\circ$. At angles α smaller than 5° no reflection from oxide was recorded, despite that the reflections from the solid solution $\text{Al}(\text{Si})$ were clearly seen. This means that there is a relatively small amount of oxide in superficial volume of the coat, and the protective layer is very thin. Therefore, it can

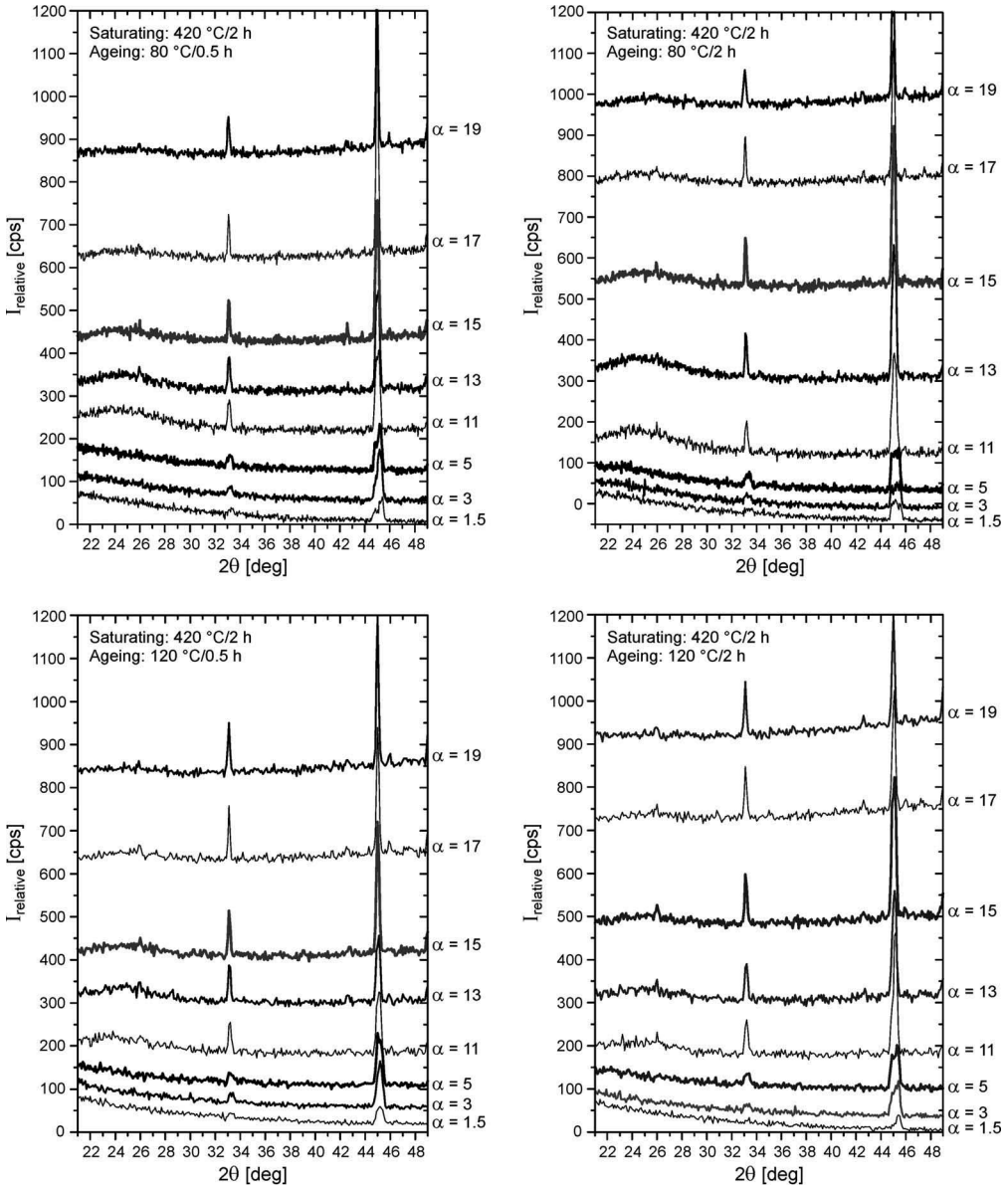


Fig. 5. GXR D diffraction patterns obtained from the Al-Si coat after heat treatments.

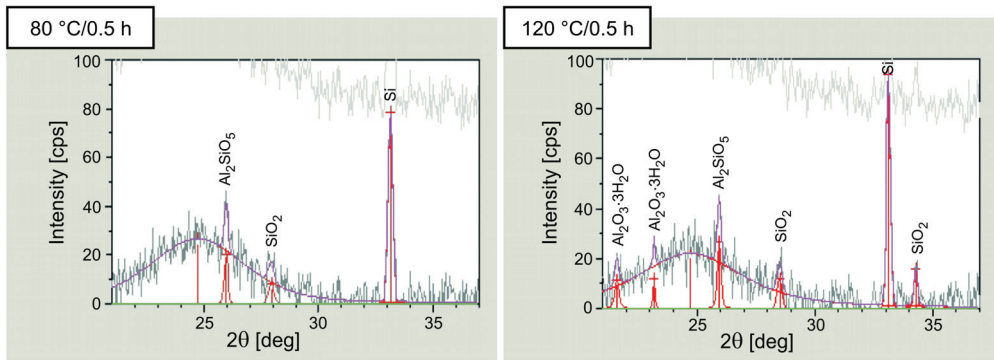


Fig. 6. Sample pseudo-Voigt fit in the diffraction angle range of fine crystalline oxides.

be assumed that the radiation incidence angle of $\alpha \geq 5^\circ$ is the minimum angle needed for the phase analysis of the AlSi coat under the apparatus conditions applied. In the diffraction patterns obtained from the Al-Si coat after heat treatment no reflection from $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was recorded. One should suppose that because of the soaking it became decomposed to Al_2O_3 which was incorporated in the SiO_2 spinel structure. The integral (total) intensities of the broad reflection obtained from the coat aged at 80°C are greater than those of the reflections from the coat aged at 120°C , as well as the intensities of the coats aged for 2 hrs are greater than those of the coats aged for 0.5 hrs.

Using the Scherrer equation, the average size of oxide crystallites was estimated as follows:

$$D_{hkl} = \frac{K \lambda}{\text{FWHM} \cos(\theta_{hkl})}$$

where: FWHM – half-reflection width, K – Scherrer constant (~ 1), λ – X-ray radiation wavelength, θ_{hkl} – Bragg angle.

The calculation was performed for the measurement at a radiation incidence angle $\alpha = 13^\circ$. The half-reflection widths were determined after they had been previously described with the pseudo-Voigt curve (Fig. 6). The results of calculation of oxide crystallite sizes are given in Table 2.

The GXRd diffraction patterns obtained from the initial coat indicate a strong plastic deformation of the coat surface. The reflection (111) from the Al(Si) solid solution is strongly widened and has several maxima (Fig. 4). This form of reflections

Table 2. The average size of oxide crystallites formed at surface of the Al-Si coat in the heat treatment process.

Heat treatment	420°/2 h/water	420°/2 h/water	420°/2 h/water	420°/2 h/water
	80°/0.5 h/air	80°/2 h/air	120°/0.5 h/air	120°/2 h/air
Average size of crystallites	1.5 nm	1.7 nm	2.6 nm	2.5 nm

is the result of the final plastic deformation in the last technological stage of coating application designed to smooth the coat surface. In Figure 7, a comparison is made of the shape of the reflection (111) from the Al(Si) solid solution in the initial coat and in the heat treated coats for three X-ray radiation incidence angles, namely 1.5° , 5° and 9° .

The comparison shows that the soaking has caused a considerable mitigation of the effect of surface plastic deformation (relaxation) – the reflection has narrowed, and the number of local maxima has decreased from 4–5 to 1–2. Figure 6 indicates that the most effective relaxation has occurred within the surface layer of coats aged at 120°C .

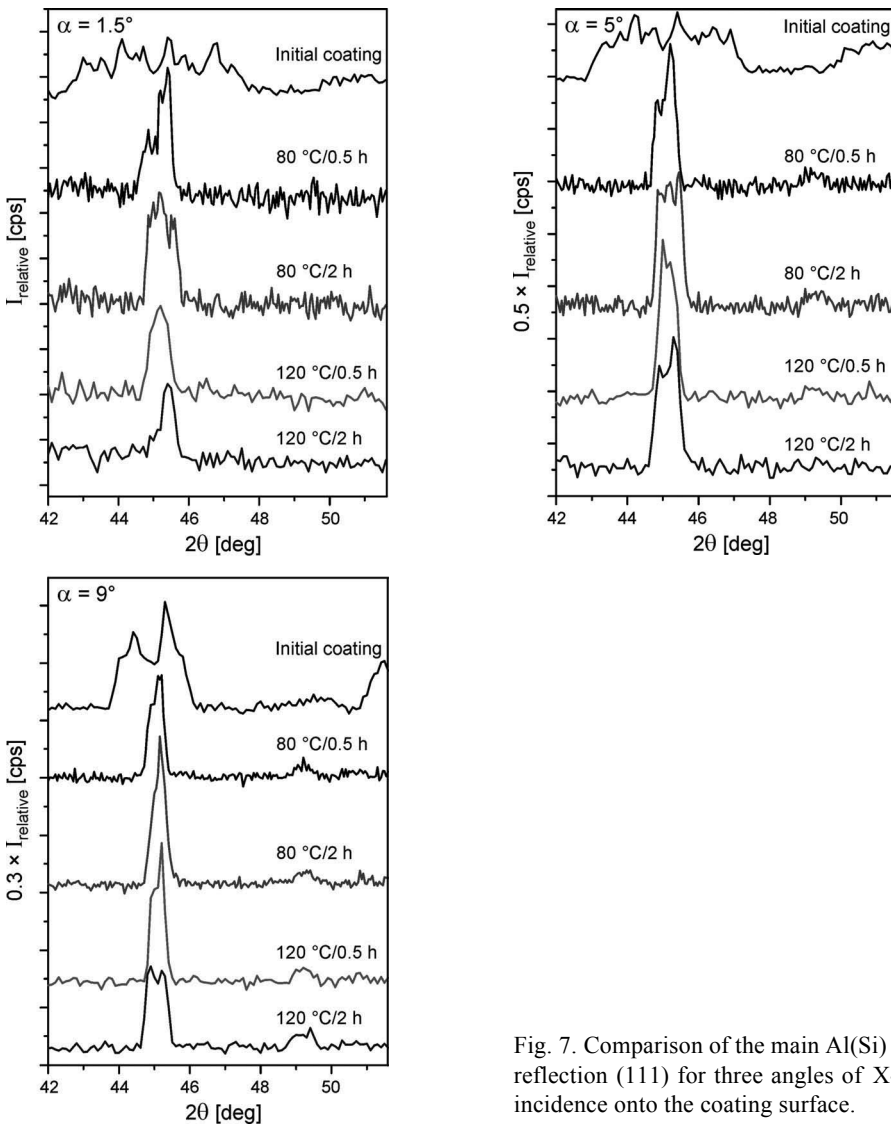


Fig. 7. Comparison of the main Al(Si) solid solution reflection (111) for three angles of X-ray radiation incidence onto the coating surface.

4. Conclusions

The T6 heat treatment (solutionizing at 420 °C/2 hrs/water + ageing at 80–120 °C/0.5–2 hrs/air) of the AlSi coat favourably influences the morphology of Si crystals in the coat. The heat treatment causes also the effects of plastic deformation of the surface coat layer to have vanished, this being more effective in coats aged at 120 °C.

In the course of heat treatment, a film of dispersed $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ oxide spinel forms on the coat surface, which had on average a crystallite size as determined by the X-ray method 1.5–1.7 nm (after ageing at 80 °C) and 2.5–2.6 nm (after ageing at 120 °C). This means that a lower oxidation temperature favours the fine crystallinity of the oxide layer, while the oxide crystallites grow with oxidation time.

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