TECHNICAL NOTE

Defect analysis of Ag coatings on aluminum castings

Hagarová M.[1], Baranová G.[1], Mašlejová A.[1], Vorobiov S.[2], Komanický V.[2]

[1] Institute of Materials, Faculty of Materials, Metallurgy and Recycling, Technical University of Košice, Park Komenského 11, 042 00 Košice, Slovakia

[2] Institute of Physics, Faculty of Science, P. J. Šafárik University in Košice, Park Angelinum 9, 041 54 Košice, Slovakia

E-mail: maria.hagarova@tuke.sk

Cast aluminum alloys are one of the most widely used structural materials in electrical engineering due to their good mechanical properties, high thermal and electrical conductivity. Passive Al_2O_3 layer formation on the aluminum surface reduces its electrical conductivity. Thus, the Ag coating electrodeposition on the aluminum substrate material allows increasing the electrical conductivity. The coating quality depends not only on the composition and on the quality of the electrolytic bath and technological parameters of the deposition, but a very important factor is the surface material pre-treatment prior to coating. In this study, the causes of the defect occurrence in the form of blisters on the Ag coating surface were analyzed. Blistering is a characteristic sign of local low adhesion strength of the coating to the substrate. Microscopic analysis showed the presence of AlSi fragments between the coating and the substrate, which were formed during machining of the Al casting surface. The difference in electrical conductivity between the AlSi particles and the aluminum matrix created an inhomogeneous field during electroplating, which led to the formation of defects in the coating. The presence of pores on the Al casting surface, resulting from low-pressure casting conditions, may also have contributed to defects formation in the coating.

INTRODUCTION

Aluminum alloys have high strength, good casting properties, good electrical and thermal conductivity, good corrosion resistance and weldability. They can be used as structural materials in aerospace and construction. Aluminum is an ideal choice for, among other things, components in the electrical and energetic industries, such as semiconductors, transformer tanks, transistors and central processing units (CPUs) [1]. According to the authors [2], cast aluminum alloys are among the most widely used materials for high-voltage connections due to their good mechanical properties, low weight and high thermal and electrical conductivity. However, aluminum forms a continuous passive layer of Al_2O_3 on its surface, which negatively affects the transmission of electrical energy by acting as an insulator. For this reason, silver plating of the aluminum surface can be the solution, as silver has good electrical conductivity and does not easily oxidize when exposed to the atmosphere [3]. Alkaline cyanide baths are used for the deposition of silver coatings, where the main component is potassium dicyanosilver [4]. According to the authors [5], the complex of CN^- and Ag^+ formed in the electrolytic bath during the coating deposition provides higher stability and good dispersion of the plating solution. The bond stability between the silver cyanide layer and the matrix is high and the solution is stable and easy to maintain. However, cyanide is highly toxic and causes great damage to the human body. Therefore, it is necessary to replace the cyanide electroplating process of silver plating. The authors in [6] used thiosulfate baths containing mainly $AgNO_3$ or AgBr salts. In the study [7], the author offered alternatives for silver plating without cyanide, such as electrolytes using silver thiosulfate complexes or silver sulfite complexes, or silver succinimide complexes and last but not least pyrophosphate solutions.

The electrodeposition working conditions depend on the type of bath. The formation of silver-based coating is very challenging and sensitive to the formation of coating defects [8]. It is a common misconception that electroplating deposition conditions are the primary cause of coating defects. In reality, the root of the problem often lies in inadequate surface preparation of the substrate [9]. If the substrate surface is covered with oxides or oils, the plated material adhesion can be greatly reduced. The process of mechanical machining by grinding or polishing is also important.

This study analyses the defects in Ag coating on the surface of cast aluminum alloy using macroscopic and microscopic techniques. It defines the types of defects and possible causes of their formation. It also offers a solution to eliminate the formation of defects in the electrodeposition process.

EXPERIMENTAL

The casting of aluminum alloy AlSi7Mg0.3-T6 (EN AC-42100) with an electrodeposited Ag coating was used to determine the cause of defects. The chemical composition of the AlSi7Mg0.3-T6 alloy is in Table 1.

The surface preparation of Al castings prior to coating, coating parameters and electrolyte composition represents the know-how of the electroplating company that applied the coating. Ni was applied as an interlayer. Nickel coating is used as a barrier layer on the aluminum to prevent adverse effects between the final desired surface finish and the underlying aluminum alloy.

The macroscopic analysis was performed with LEICA WILD M3Z stereomicroscope. The microscopic analysis was performed with OLYMPUS VANOX-T light microscope and Tescan VEGA-3 scanning electron microscope (SEM) using the backscattered electron (BSE) method. Energy dispersive spectroscopic (EDS) SEM analysis was used to determine the chemical composition.

RESULTS AND DISCUSSION

In Figs. 1a-c, the defects on the Ag coating surface are visible. The stereomicroscope images confirmed the occurrence of defects with different sizes, Figs. 1d-e. Figs. 1a and 1d represent sample 1, Figs. 1b and 1e represent sample 3, Figs. 1c and 1f represent sample 5. According to [10], the lack of coating adhesion can be manifested by blisters formation. Coating adhesion problems are almost always caused by deficiencies in pre-treatment operations, such as incomplete removal of grease, oils, impurities or oxides.

As can be seen mainly in the stereomicroscope images, Figs. 1d-f, the Ag coating surface roughness is high and follows the surface roughness and texture of the AlSi7Mg0.3-T6 alloy aluminum casting surface after its machining (turning and milling). The average roughness value determined from five measurements, expressed by the mean arithmetic profile deviation, was at Ra ~ 6.3 µm. The surface micro geometry contributes significantly to ensuring a quality coating after deposition in terms of its uniform thickness and sufficient

Tab. 1 Chemical composition of the AlSi7Mg0.3-T6 alloy

Element	Al	Si	Mn	Mg	Fe	Cu	Zn	Ti	Sr
(%)	91.89	7.35	0.02	0.35	0.16	0.007	0.015	0.172	0.028

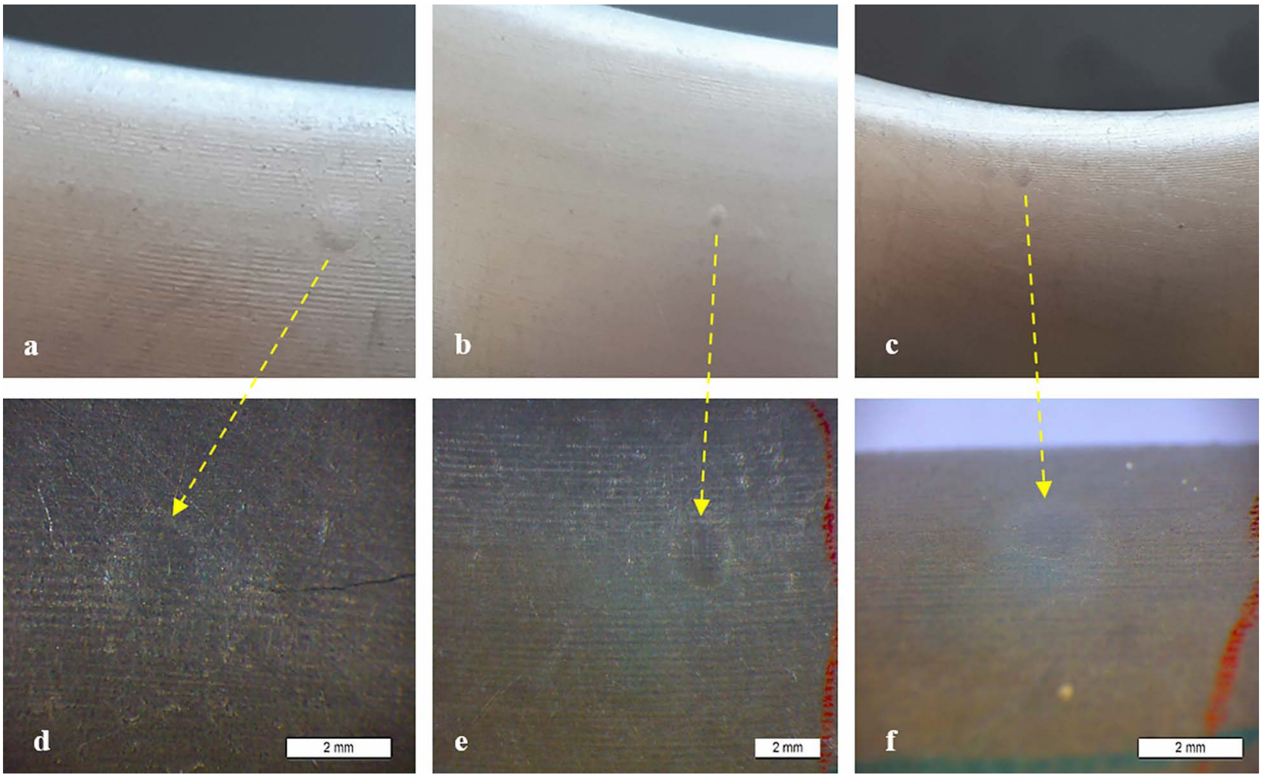


Fig. 1. Defects on aluminum casting surface (indicated by arrows): a) and d) represent sample 1, b) and e) represent sample 3, c) and f) represent sample 5, d)-f) were documented on the stereomicroscope

adhesion to the substrate material. The silicon present in the aluminum casting remains on the surface of the casting as a component that cannot be chemically removed in the casting pre-treatment, thus leaving the surface rougher [10]. Silicon that is part of the microstructure cannot be chemically removed, but silicon that is on the surface can be removed. Si which is part of the surface increases its roughness.

Metallographic cut sections from the defect region were prepared for microscopic analysis, according to Fig. 1. Metallographic cut sections were prepared from marked analyzed and cut sections, Figs. 2a-c, labelled: sample 1, 3 and 5. Figs. 2d-f represent prepared samples for metallographic analysis.

In the regions where no defects in the coating were detected, the average nickel layer thickness was measured using a light microscope, which had a value of 29.64 μm for sample 1; 30.44 μm for sample 3; respectively 28.07 μm for sample 5, Fig. 3. The nickel layer uniformly covered the Al alloy surface. Fig. 3 also shows the casting surface with the Ag layer of coating. The average Ag coating thickness showed a value of 21.66 μm for sample 1; 22.17 μm for sample 3 and 21.67 μm for sample 5.

Table 2 shows the measured values of all samples, supplemented by the number of measurements and standard deviation.

Tab. 2 Thickness (μm) of internal Ni layer and external Ag layer of coating on AlSi7Mg0.3-T6 cast

Sample	Layer	Number of measurements	Average thickness	Standard deviation
1	internal Ni	12	29.64	1.87
	external Ag	10	21.66	1.99
3	internal Ni	10	30.44	2.09
	external Ag	9	22.17	1.79
5	internal Ni	12	28.07	1.83
	external Ag	10	21.67	1.11

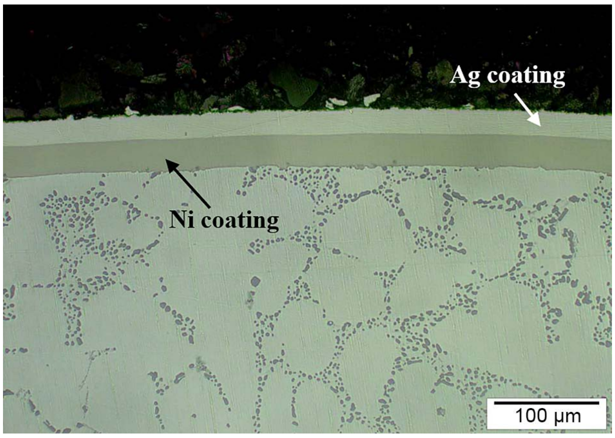


Fig. 3. Coating composed of Ni interlayer with an average thickness of 29.64 μm and Ag coating with an average thickness of 21.66 μm (sample 1), non-etched state

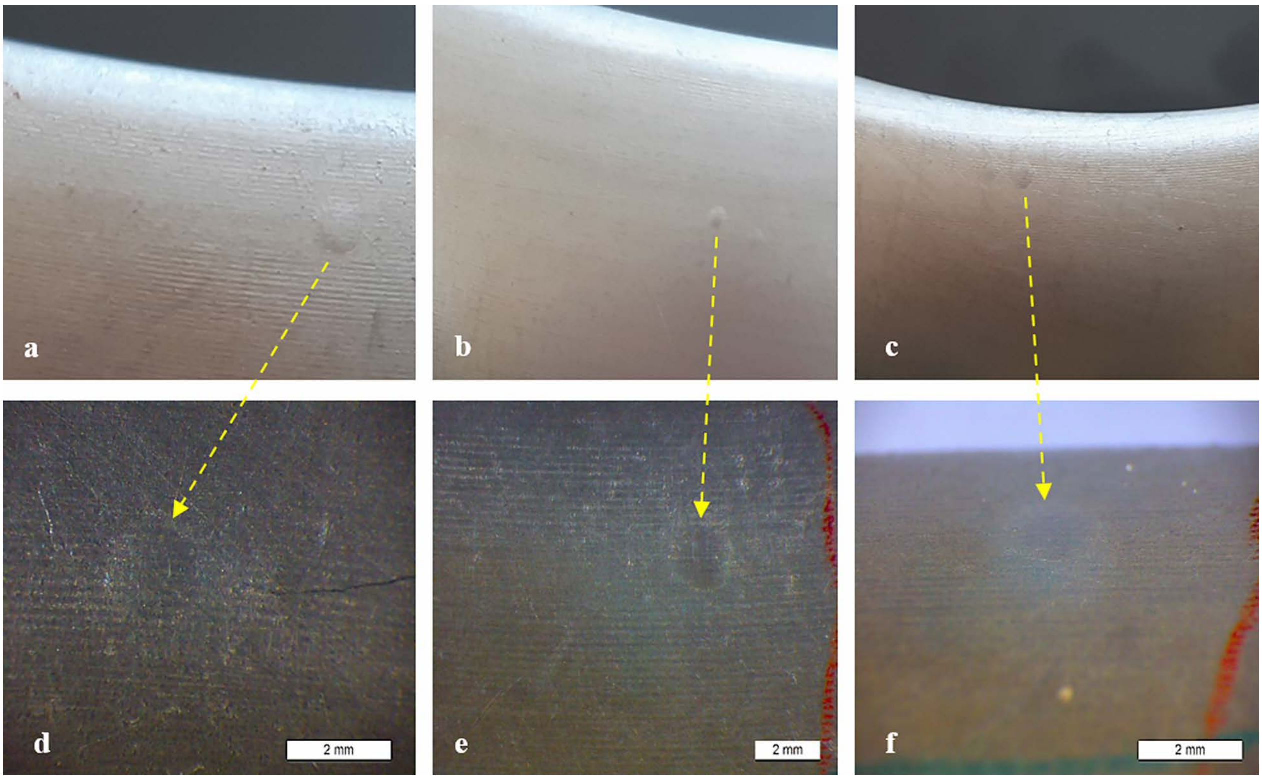


Fig. 2. Cuttings and metallographic cut sections of samples with analysed regions marked with the arrow

In Figs. 4 to 8, sample 1 (according to Fig. 2) is shown after cross-sectioning. Fig. 4 shows a cross-section of sample 1 with Ag coating and Ni coating missing at the observed defect location (according to Figs. 1a, d). The Ni coating adhesion to the aluminum substrate material was very weak, therefore the coating detached from the surface.

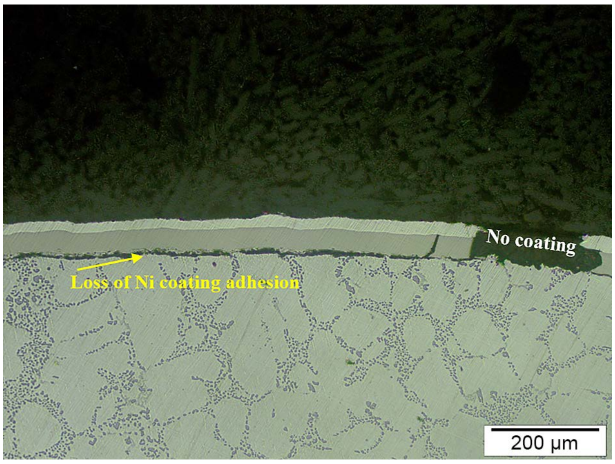


Fig. 4. Coating defects on sample 1: missing coating and loss of Ni coating adhesion, non-etched state

On closer observation, in Figs. 5 and 6, it could be seen that the region between the separated coating and the casting surface is formed by fragments (in Fig. 5, some fragments are indicated by arrows). As mentioned before, the lack of adhesion strength of the electroplated metallic coating to the substrate material is most often due to the pre-treatment quality of the substrate surface, but as the authors in [11,12] state, with nickel deposition being a process highly sensitive to impurities in the electrolyte as well.

Fig. 7 shows a cross-section of sample 3 (according to Figs. 2b,e showing the presence of pores in the AlSi7Mg0.3-T6 aluminum alloy, which were partially covered by Ni coating. Pores in aluminum alloys are the result of the production process; they are related to higher gas content during refining, insufficient or high-

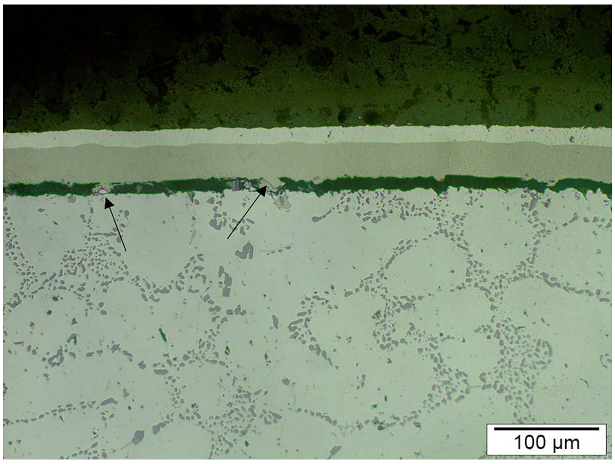


Fig. 5. Closer look at the Ni coating separation from Al material, non-etched state

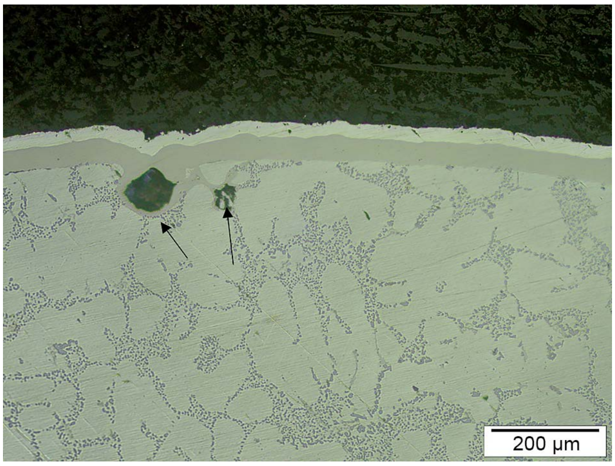


Fig. 7. Pores in the microstructure of Ni-coated aluminium alloy casting, non-etched state

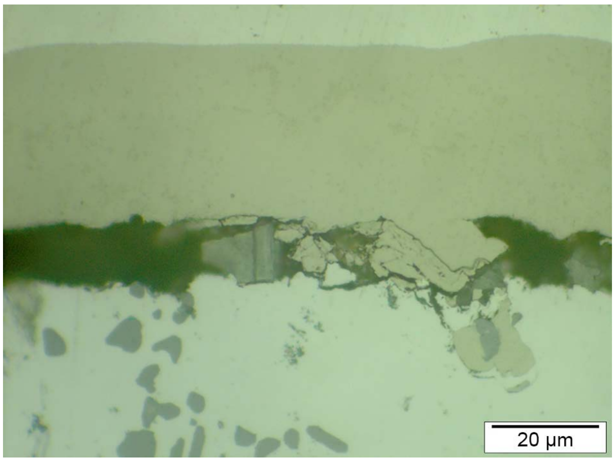


Fig. 6. Close-up view at 1000 x magnification of the location of Ni coating separation from Al alloy with the presence of fragments, non-etched state

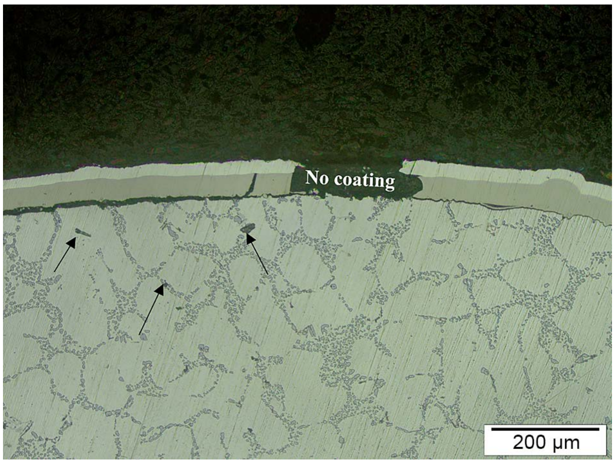


Fig. 8. Pores in the microstructure of the aluminium alloy after etching (some are marked with arrows) on sample 3, etch. 0.5% HF

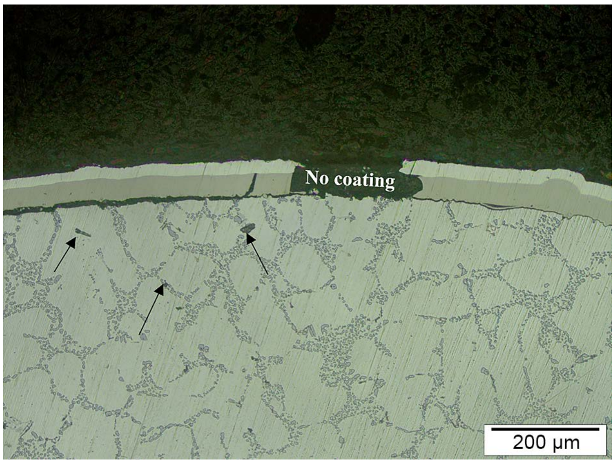


Fig. 9. Sample 5 with a layer of Ni and Ag on the surface. The arrow indicates the region of pores at the aluminium alloy/Ni coating interface, etch. 0.5% HF

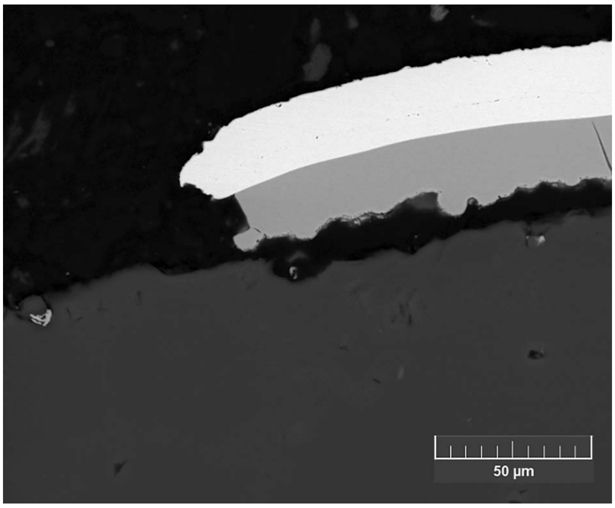
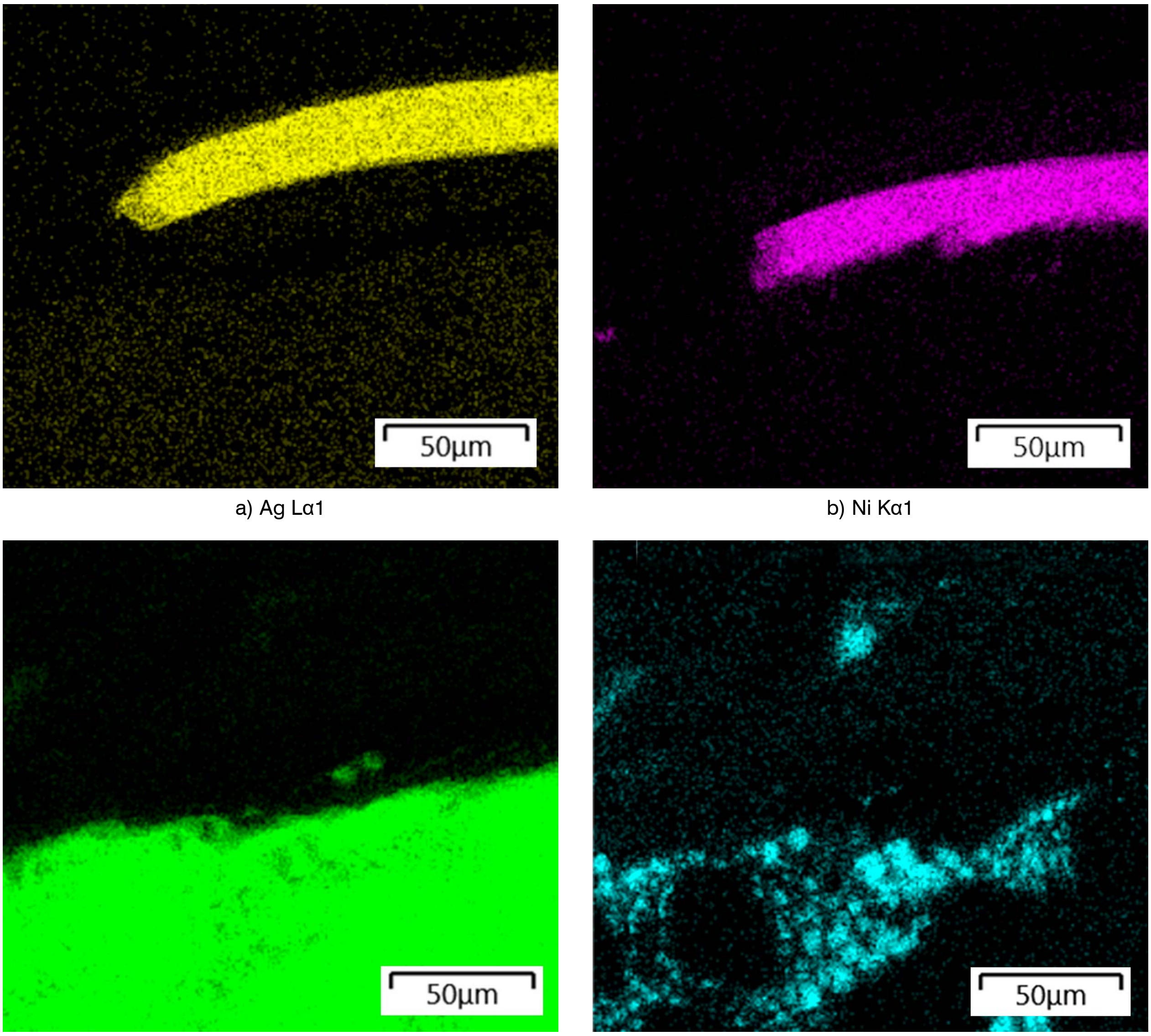


Fig. 10. Location of Ni coating adhesion loss to aluminium substrate material (SEM)



a) Ag Lα1

b) Ni Kα1

c) Al Kα1

d) Si Kα1

Fig. 11. Map of the analysed coating elements distribution and Al alloy (from Fig. 10)

speed during casting, or improper setup. Casting shape with uneven wall thickness may also be the cause. Product shape with excessive wall thickness difference is also a common problem [13]. Pores in Al castings are also formed e.g. due to inappropriate low-pressure casting parameters [14].

After visualizing the AlSi7Mg0.3-T6 alloy microstructure after etching, pores at several locations in the microstructure became apparent (some are indicated by arrows in Fig. 8).

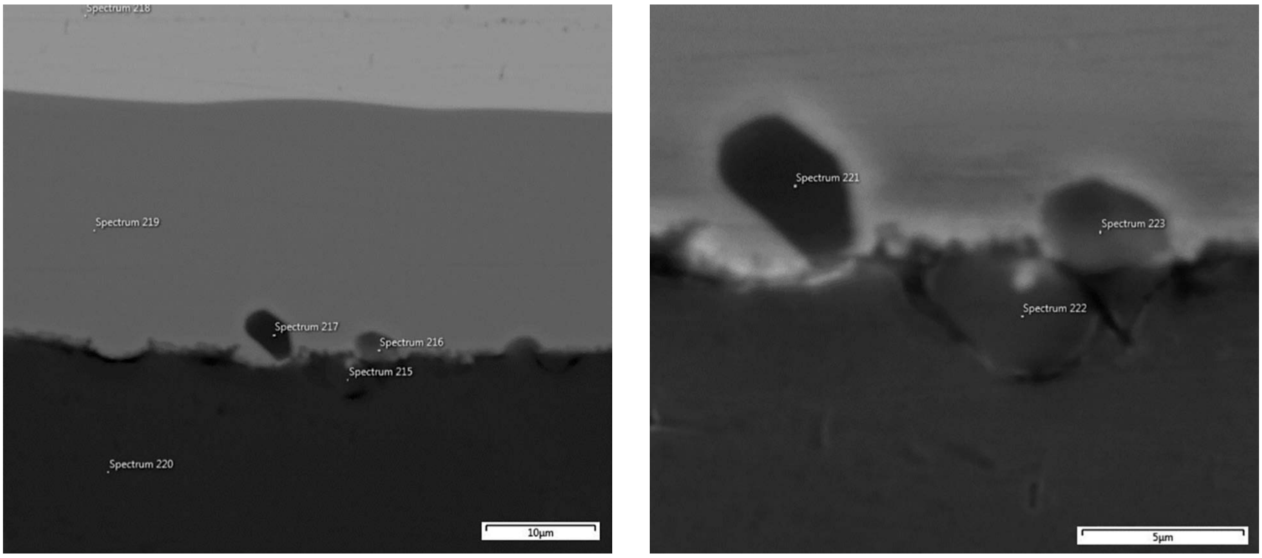
In Fig. 9, sample 5 (according to Figs. 2c,f is documented after cross-sectioning. Pores were observed on the aluminum casting surface (under Ni coating). There were also residues of Ni coating in the pores.

Scanning electron microscope (SEM) analysis of defects was performed using the backscattered electron method (BSE analysis). Observation results with the determination of the coating and the aluminium casting chemical composition by EDS analysis are shown in Figs. 10 to 12 and Tabs. 1 and 2. Fig. 10 shows a detail of the separation location of Ni coating from the aluminum substrate material, which was observed on sample 1 (Fig. 4).

A map of the distribution of the analyzed elements from the SEM observations is shown in Fig. 11. While Ag coating is well adherent and uniformly covers Ni coating, Ni coating itself is non-uniform and without adhesion to the Al alloy substrate material.

Documentation in Fig. 5 and the close-up in Fig. 6 showed the presence of debris at the location of Ni coating separation from the Al alloy. That location was analyzed by SEM and is shown in Fig. 12. EDS SEM analysis showed the presence of AlSi-based particles and Tabs. 3 and 4, which were part of the structure of the Al alloy. These particles are brittle and already during the surface mechanical pre-treatment they crumble into smaller fragments and separate from the surface. If they remain attached to the surface after electro-nickel-plating, they contribute to the loss of the adhesive strength of the deposited coating to the substrate material.

As reported by the authors [15], particles in Al alloys adversely affect the adhesion of electroplating coatings. The difference in electrical conductivity between the particles (in our case AlSi) and the aluminum matrix of the alloy creates an inhomogeneous field during electroplating, which leads to defects formation in Ni layer [16].



a) b)

Fig. 12. Particles at the Ni coating and Al alloy interface: a) Spectrum 215-220 with EDS SEM analysis, b) detail on particles present, Spectrum 221-223 (SEM)

Tab. 3 EDS SEM analysis of monitored elements from regions in Fig. 12a

Element	Spectrum 215	Spectrum 216	Spectrum 217	Spectrum 218	Spectrum 219	Spectrum 220
Al	34.99	17.06	1.12	–	0.37	78.30
Si	42.21	24.49	12.62	–	0.09	0.73
Mg	0.29	–	-	–	–	–
Ni	21.88	58.45	67.11	0.69	99.46	0.32
Ag	–	–	–	99.31	–	2.19

Tab. 4 EDS SEM analysis from regions in Fig. 12b

Element	Spectrum 221	Spectrum 222	Spectrum 223
Al	19.43	37.83	12.57
Si	15.00	44.03	20.21
Mg	–	0.17	–
Ni	65.57	17.93	67.22

CONCLUSIONS

Based on the macroscopic and microscopic analysis of the defects present in Ag coating on the aluminum casting surface, the following can be concluded:

- blisters were present on the Ag coating surface, which are a characteristic sign of local coating adhesion loss to the substrate material,
- the Ag coating surface had a relatively high average roughness (at the level of 6.3 µm), while the coating surface followed the surface texture of the Al casting after machining,
- the analyzed AlSi7Mg0.3-T6 alloy included hard and brittle AlSi phases, which increased the casting surface roughness after machining,
- after cross-sectioning the coated samples, insufficient adhesion strength of the Ni coating (this served as a barrier on aluminum to prevent adverse effects between the final desired surface finish and the underlying aluminum alloy) was found with the presence of hard and brittle AlSi particles in the regions between the Al alloy surface and separated coating layer. The difference in electrical conductivity between the particles (AlSi in our case) and the aluminum alloy matrix created an inhomogeneous field during electroplating, leading to defects formation in Ni layer,
- the pores found in the analyzed Al alloy were result of the alloy manufacturing process. Their appearance on the surface could contribute to the weakening of the deposited coating adhesion during electroplating.

Substrate pre-treatment prior to coating is essential to obtaining a high-quality, well adhesive coating. A clean, degreased surface is characterized by high activity for the formation of adhesion forces between the deposited coating and the metallic substrate material. The presence of hard and brittle particles (in our case AlSi phase) impairs the adhesion between the substrate and the coating. In this case, the answer is to use e.g., HF + HNO_3 solution, which removes Si, and the surface will be prepared for plating in this way.

REFERENCES

1. Czerwinski F. Aluminium alloys for electrical engineering: a review, *Journal of Materials Science* **2024**, 59, 14847–14892
2. Luiz, L. A. et al. Failure analysis of corroded 500 kV connectors made of silver plated ASTM 356 aluminum alloy, *Engineering Failure Analysis* **2022**, 136, 106229
3. Chudnovsky B.H. Electrical Equipment in a Corrosive Environment, Transmission, Distribution, and Renewable Energy Generation Power Equipment, 2nd ed. **2017**, CRC Press, 131-193
4. Chovancová M. et al. Základy korózie a povrchovej úpravy materiálov, 1. vyd. **2009**, STU Bratislava
5. Liu C. et al. Preparation of Conductive Polyester Fibers Using Continuous Two-Step Plating Silver, *Materials* **2018**, 11, 2033
6. Ren F. et al. Cyanide-free silver electroplating process in thiosulfate bath and microstructure analysis of Ag coatings, *Transactions of Nonferrous Metals Society of China* **2013**, 23, 3822-3828
7. https://theadvint.com/short_paper/a-sustainable-cyanide-free-silver-plating-development-in-metal-finishing [online, 03.01.2025]
8. Mareška A., Kordová T., Míka M. H. Defects on silver based coatings, *Corrosion and Material Protection Journal* **2022**, 66, 72-80
9. https://www.sharrettsplating.com/blog/electroplating-defects-issues/ [online, 04.01.2025]
10. Mueller G., Žagar G., Mortensen A. In-situ strength of individual silicon particles within an aluminium casting alloy, *Acta Materialia* **2018**, 67-76
11. Gamburg Y.D., Zangari G. Theory and Practice of Metal Electrodeposition, 1st ed. **2011**, Springer New York, ISBN 978-1-4419-9668-8
12. Djokic, S. S. Electrodeposition. Theory and Practice, 1st ed. **2010**, Springer New York, ISBN 978-1-4419-5588-0
13. Michna, Š. et al. Encyklopedie hliníku, 1st ed. **2005**, Adin s.r.o., ISBN 80-89041-88-4
14. Niu Z. et al. Effect of high pressure die casting on the castability, defects and mechanical properties of aluminium alloys in extra-large thin-wall castings, *Journal of Materials Processing Technology* **2022**, 303, 117525
15. Ul-Hamid A. et al. Microstructure and surface mechanical properties of electrodeposited Ni coating on Al 2014 alloy, *Surface and Coatings Technology* **2010**, 205, 2023–2030
16. Molina J. M. et al. Surface modification of 2014 aluminium alloy – Al_2O_3 particles composites by nickel electrochemical deposition, *Materials Science and Engineering: A* **2004**, 383, 299–306