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## Influence of corrosion on mechanical properties and microstructure of 3xxx, 5xxx, and 6xxx series aluminum alloys

### Wpływ korozji na charakterystykę własności i struktury stopów aluminium serii 3xxx, 5xxx i 6xxx

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#### **Abstract**

Growing demands imposed on passenger car producers concerning the reduction of exhaust emission to the environment are forcing a search for new materials and design solutions. One of the most-important factors that can reduce this emission is the low mass of a vehicle, leading to a decrease in its average fuel consumption. A reduction in weight can be obtained by the use of aluminum elements instead of steel; e.g., in air conditioning pipes, decreasing the specific weight of the construction by nearly three times. In the present study, the influence of the SWAAT corrosion test on A/C piping made from 3xxx, 5xxx, and 6xxx series aluminum alloys was investigated. The study focused on changes in the mechanical properties of samples before and after a SWAAT test determined by a tensile test and Vickers hardness measurements. Additionally, microstructure examinations were performed with the use of optical and scanning microscopy. Corrosion products on the surface of pipes were identified by Energy Dispersive X-ray Spectroscopy. Pipes made from the EN AW 6063 alloy revealed an almost 50% decrease in its strength properties after the tests. The largest decline in plastic properties was observed in pipes made from the EN AW 6060 alloy.

**Keywords:** corrosion resistance, aluminum alloys, pitting corrosion, intergranular corrosion

#### **Streszczenie**

Wobec rosnących wymagań stawianych producentom samochodów osobowych, dotyczących ograniczania emisji spalin do środowiska, poszukiwane są nowe rozwiązania materiałowo-konstrukcyjne. Jednym z czynników ograniczających emisję jest obniżenie masy pojazdów, które prowadzi do obniżenia średniego spalania. Efekt ten uzyskuje się między innymi przez stosowanie elementów z aluminium, którego ciężar właściwy jest prawie trzy razy mniejszy od stali. Aluminium jest stosowane w produkcji przewodów klimatyzatorów samochodowych. Ważną cechą przewodów ze stopu aluminium jest wysoka odporność korozyjna, umożliwiająca jego pracę przez kilkanaście lat. W prezentowanym opracowaniu przedstawiono wpływ testu korozyjnego

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SWAAT na właściwości przewodów układu klimatyzacyjnego wykonanych ze stopu aluminium serii 3xxx, 5xxx oraz 6xxx. Określono zmianę własności mechanicznych przed testem korozyjnym i po nim w próbie jednoosiowego rozciągania oraz przeprowadzono pomiary twardości metodą Vickersa. Dodatkowo prowadzono obserwacje mikrostruktury za pomocą mikroskopii optycznej oraz skaningowej. Za pomocą detektora EDS (Energy Dispersive X-ray Spectroscopy) zidentyfikowano produkty korozji na powierzchni rur po teście korozyjnym.

Badane rury ze stopu EN AW 6063 po teście korozyjnym charakteryzowały się prawie 50-procentowym spadkiem własności wytrzymałościowych w porównaniu do materiału przed testem. Największe zmiany własności plastycznych po teście zgodnym z procedurą SWAAT zaobserwowano w przypadku rur ze stopu aluminium EN AW 6060.

**Słowa kluczowe:** odporność korozyjna, stopy aluminium, korozja wżerowa, korozja międzykrystaliczna

## 1. Introduction

Weight reduction is the driving force of progress in the design and application of innovative materials for various car components. The pursuit of ever-lighter materials in the automotive industry is due to the expectations of car users to reduce their consumption of fuel, which has risen significantly in price due to the rise in oil prices imposed by Middle East countries starting in 1970 [1]. This is one of the elements of the competitiveness of individual automotive companies and the innovation index.

Another factor that inspires innovation is the introduction of restrictions on car exhaust emissions by the EU. It is estimated that reducing a vehicle's weight by 10% reduces its combustion by ~6% and allows a significant reduction of CO<sub>2</sub> emissions into the atmosphere [1]. The use of aluminum alloys in the automotive industry can reduce vehicle weight by about 40–50% [2].

Wrought alloys from the 3xxx, 5xxx, and 6xxx series were the first materials used in the production of car body parts. Due to the high plastic workability and corrosion resistance of these alloys, they have also been used for automotive heat exchangers and air conditioning ducts. This applies in particular to alloys 3003, 3103, 5049, 5052, 6061, and 6063 [3]. The corrosion resistance of aluminum and its alloys is due to the rapid formation of an Al<sub>2</sub>O<sub>3</sub> oxide film, stable at pH 4–9 [4, 5] and protecting the alloy surface against further oxidation. However, atmospheric chemicals such as SO<sub>2</sub> and SO<sub>3</sub> cause degradation and corrosion in aluminum and its alloys. Oesch and Fallner showed the significant effect of atmospheric SO<sub>2</sub> on the appearance of local corrosion cells in these alloys. It has been found, however, that at a relative humidity of 66%, the progress of corrosion is negligible. In environments with a relative humidity of 98%, the corrosion rate was observed to increase to 1.8 mg/cm<sup>2</sup> [6]. The presence of SO<sub>3</sub> compounds, the formation of sulfuric acid with water and the occurrence of Cl<sup>-</sup> ions that destroy the resulting protective film are also dangerous for both aluminum and its alloys [4, 6, 7].

Additionally, in materials that are characterized by the presence of intermetallic phases or individual particles of Cu and Si, local electrochemical cells are formed

between the matrix and the precipitated phases, significantly reducing the corrosion resistance [7, 8].

Numerous applications have been found for 5xxx series alloys, which belong to hardly deformable and non-heat-treatable alloys. The mechanical properties achievable in these alloys are certainly superior to the 3xxx or 6xxx series [1]. The 5xxx series alloys are also characterized by better corrosion resistance in alkaline environments [9].

This article presents the results of research on the effect of corrosion on the mechanical properties, surface conditions, and structures of pipes made from EN AW 3103, 5049, 6060, and 6063 aluminum alloys used for automotive air conditioning ducts.

## 2. Research methodology

Tests were carried out on pipes made from EN AW 3103, 5049, 6060, and 6063 alloys used for automotive air conditioning ducts. The pipes were delivered as semi-finished products in the H12 condition (strain hardening by rolling). The chemical composition of the tested materials according to EN 573-3: 2014 is given in Table 1.

Table 1. Chemical composition of EN AW 3103, 5049, 6060, and 6063 alloys

3103									
Element	Mg	Mn	Fe	Si	Cr	Zn	Cu	Ti	Al
weight %	0.3	0.9–1.5	0.7	0.5	–	0.2	0.1	–	remainder
5049									
Element	Mg	Mn	Fe	Si	Cr	Zn	Cu	Ti	Al
weight %	1.6–2.5	0.5–1.1	0.5	0.4	0.3	0.2	0.1	0.10	remainder
6060									
Element	Mg	Mn	Fe	Si	Cr	Zn	Cu	Ti	Al
weight %	0.35–0.6	0.1	0.1–0.3	0.3–0.6	0.05	0.15	0.1	0.1	remainder
6063									
Element	Mg	Mn	Fe	Si	Cr	Zn	Cu	Ti	Al
weight %	0.45–0.9	0.1	0.35	0.2–0.6	0.1	0.1	0.1	0.1	remainder

The corrosion test was performed in a CTS CA 3.1.1 salt chamber according to DIN SPEC 74106: 2015-08, applying the ASTM G85: A3 SWAAT Test (Sea Water Acetic Acid Test). The main component of the corrosive environment was a sea salt solution with the addition of acetic acid and distilled water to obtain a solution pH ranging from 2.8 to 3. The test time was 20 days.

From each test alloy, 5 pipes with an outer diameter of 18 mm and a wall thickness of 1.5 mm were made and tested for tensile strength at room temperature. Studies were made on the materials before and after the corrosion test. To avoid material deformation, steel mandrels were used in the jaws. The tensile test was carried out at room temperature on a Zwick/Rockwell Z050 machine. The strain rate on the length of the parallel part was  $8 \cdot 10^{-3}$  1/s. The length of the measuring base and of the mandrel was calculated according to the guidelines comprised in PN-EN ISO 6892-1: 2016.

A surface analysis was performed using an SEM Hitachi SU-70 scanning electron microscope. The corrosion products on the surface of aluminum pipes used for automotive air conditioning ducts (among others) were identified with an EDS (Energy Dispersive X-ray Spectroscopy) detector.

### 3. Evaluation of corrosion effect on surface condition of pipes after corrosion test (SEM)

Surface examinations of pipes made from the EN AW 3103, 5049, 6060, and 6063 alloys were done by the technique of scanning electron microscopy (SEM). Figure 1 shows the results obtained before and after the SWAAT corrosion test. Surface defects such as micro scratches, micro cracks, and material discontinuities (Figs. 2, 3a, and 3c) are visible on the surface of the examined pipes. All of these defects favor the further spreading of corrosion into the material. Additionally, the pH of the solution in a range of 2.8–3 enhances the pitting and intergranular corrosion in aluminum alloys [4]. Figures 2 and 3b, 3d show the morphology of corrosion products found on the surface of the tested pipes after a corrosion test lasting 20 days.

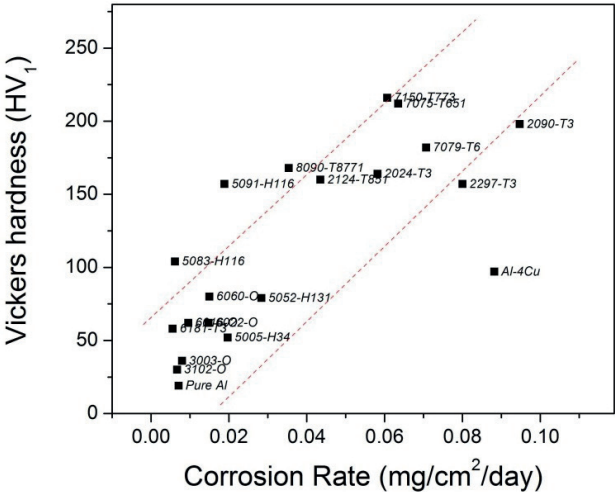


Fig. 1. Corrosion rate versus hardness of aluminum alloys [10]

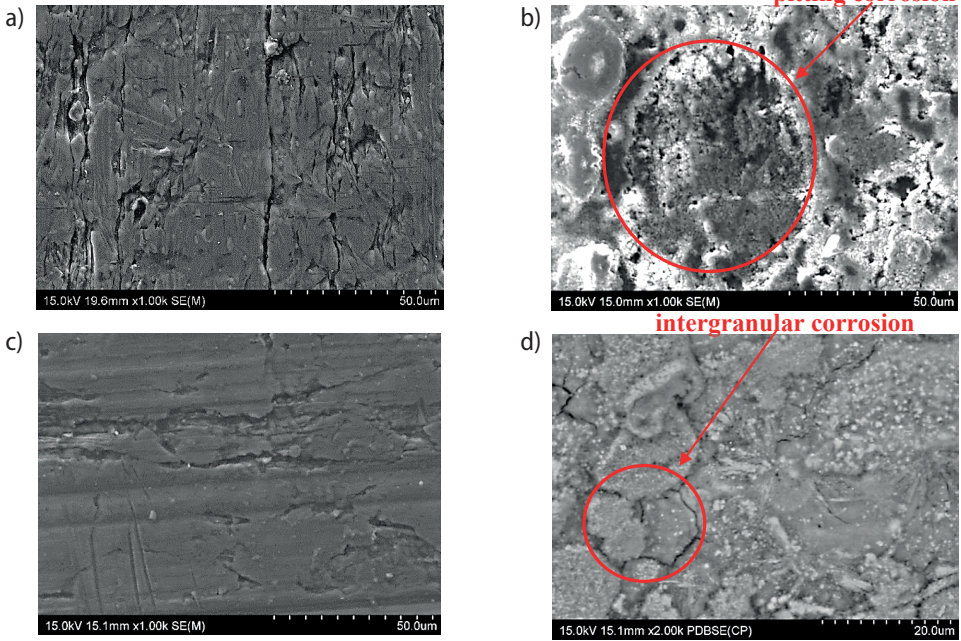


Fig. 2. Surface of EN AW 3103 and 5049 alloy pipes: (a, c) before SWAAT corrosion test; (b, d) after SWAAT corrosion test

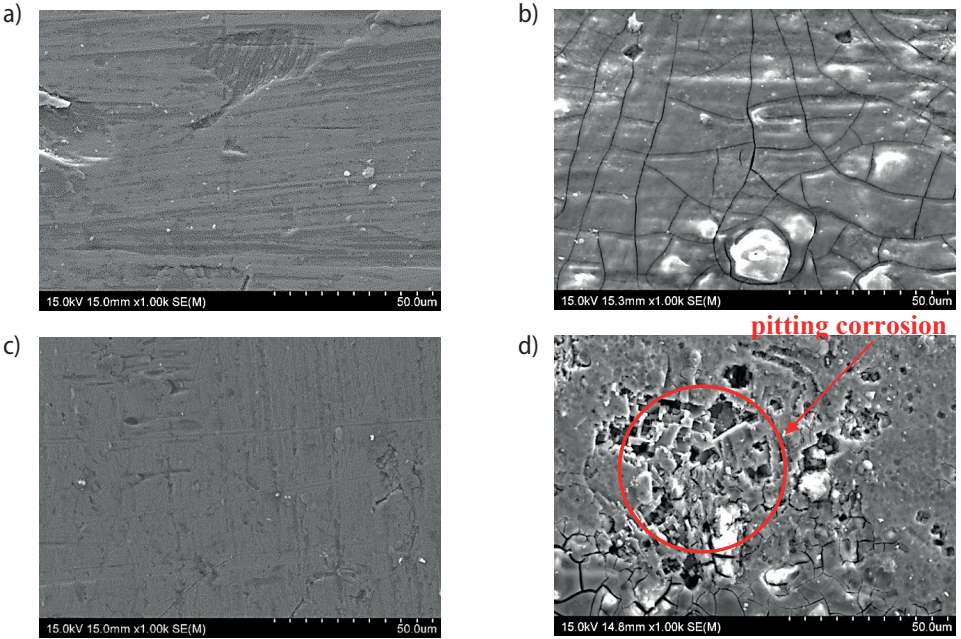


Fig. 3. Surface of EN AW 6060 and 6063 alloy pipes: (a, c) before SWAAT corrosion test; (b, d) after SWAAT corrosion test

In the case of pipes made from EN AW 3103, 5049, and 6063 alloys, a non-homogeneous aluminum oxide ( $\text{Al}_2\text{O}_3$ ) protective film was developed on the surface; its chemical composition was identified by EDX. Locally, in the  $\text{Al}_2\text{O}_3$  layer, the effects of pitting corrosion in the form of numerous pores were observed (Figs. 2b and 3d). Additionally, traces of linear corrosion running along and across the surface tested and often forming lines surrounding fragments of the surface were noticed (Fig. 2d) [4, 11–14].

In a corrosive atmosphere, the active particles were  $\text{Cl}^-$  ions contained in the sodium chloride solution used in the corrosion experiment to simulate the operating conditions of air conditioning components. As a result of the surface condition assessment and based on an analysis of the reference literature, it has been concluded that, due to the reaction of the  $\text{Cl}^-$  ions, the  $\text{Al}_2\text{O}_3$  film was most likely damaged and its consistency broken with the resulting penetration of corrosion into the material.

On the other hand, in the case of the EN AW 6060 alloy, a uniform aluminum oxide film with characteristic cracks was formed on the entire surface; this was probably due to changes in the stress level resulting from the conditions of the corrosion process (Fig. 3b). Surface observations of this alloy did not reveal the presence of typical corrosion centers, such as the pitting found in the 3xxx and 5xxx series alloys and in 6063.

It should be emphasized that brine is one of the most-corrosive agents that cause damage to aluminum alloys. It is particularly well-known for its ability to enhance the susceptibility to electrochemical corrosion, activated by both the environment and the non-homogeneous phase structure of the alloy. The high solubility of the passive  $\text{Al}_2\text{O}_3$  film is associated with a solution pH reduced to a level below 4 [10]. Under these conditions, the reaction of the decomposition of  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$  takes place. The corrosion resistance is stable within a pH range of 4–9, while in the basic range (above  $\text{pH} = 9$ ), the  $\text{AlO}_2^-$  compound is formed.

A graph based on the data given in the literature [10] interrelating the hardness of aluminum alloys with their corrosion resistance shows that the higher the hardness of the alloy, the higher the corrosion rate in the presence of NaCl (Fig. 1) [10].

Magnesium added to aluminum alloys improves the corrosion resistance, but a lot depends on the form in which this element occurs in the alloy. If the precipitation of  $\text{Al}_3\text{Mg}_2$  or  $\text{Al}_3\text{Mg}_2$  phases takes place, and these are the phases that tend to place themselves along the grain boundaries and act as an anode relative to the matrix (which becomes a cathode), then the result is the progression of corrosion.

The presence of manganese is beneficial and reduces corrosion. Manganese forms the precipitates of  $\text{Al}_6\text{MnFe}$  characterized by a potential similar to Al matrix, thus counteracting the corrosion.

The alloy structure strongly influences the corrosion resistance. Phase-homogeneous alloys and pure aluminum are the materials most-resistant to corrosion. An increase in the content of intermetallic phases in alloys containing different elements makes them heterogeneous (especially alloys from the 2xxx, 6xxx, and 7xxx series) and leads to a corrosive attack in the environment conducive to electrochemical corrosion.

The investigations of intermetallic compounds present in aluminum alloys showed significant variations in their corrosion potential [15]. Phases such as  $\text{Al}_{32}\text{Zn}_{49}$ ,  $\text{MgZn}_2$ , and  $\text{Mg}_2\text{Si}$  are commonly included in the group of corrosion-promoting compounds. On the other hand, phases such as  $\text{Al}_3\text{Fe}$ ,  $\text{Al}_7\text{Cu}_2\text{Fe}$ ,  $\text{Al}_2\text{Cu}$ , and  $\text{Al}_3\text{Ti}$  support the formation of a passive film.

#### 4. Chemical analysis of corrosion products (EDS)

Maps of the distribution of elements on the surface areas of pipes subjected to corrosion testing are illustrated in Figure 4. The examinations were made with an EDS detector. It has been found that corrosion products include elements such as Al, O, Na, and Cl (among others). Studies have shown the presence of an  $\text{Al}_2\text{O}_3$  oxide film on the surface of alloys as well as an area containing sodium and chlorine originating from the corrosive solutions used in the corrosion test.

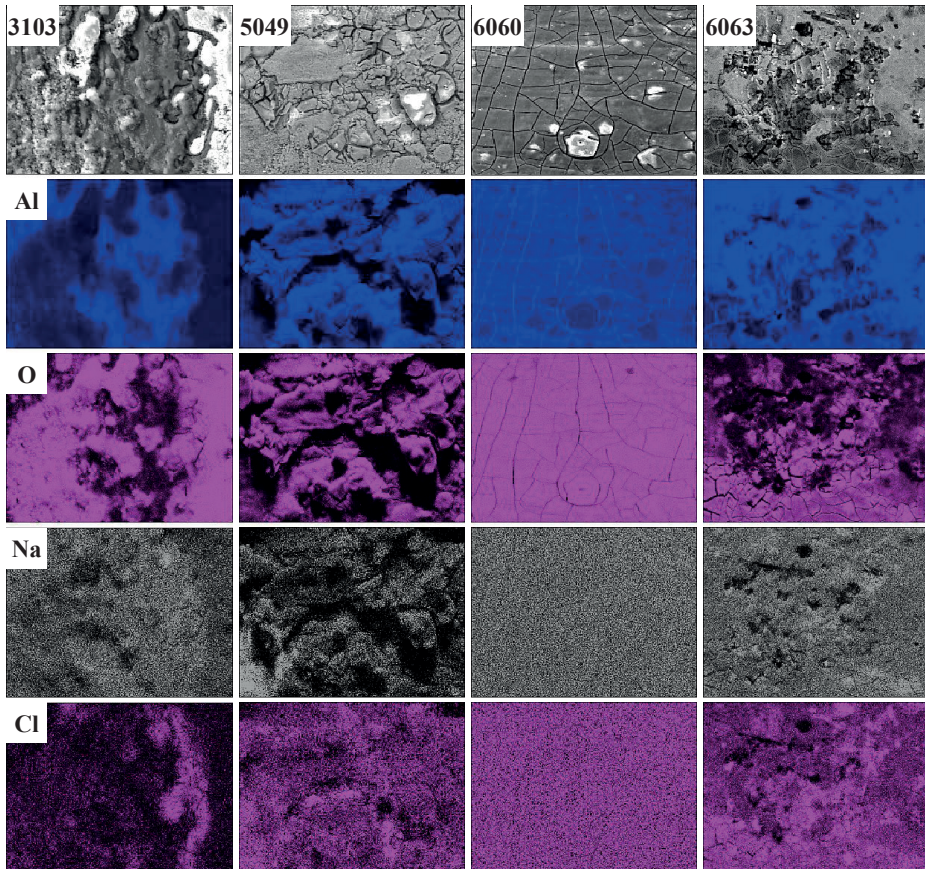


Fig. 4. Maps of distribution of Al, O, Na, and Cl on surface of pipes made from EN AW 3103, 5049, 6060, and 6063 alloys after SWAAT corrosion test

According to the point defect model [16], Cl<sup>-</sup> ions displace the oxygen present in the oxide layer on the alloy surface and form AlCl aluminum chloride. As a result of this effect, a degradation of the Al<sub>2</sub>O<sub>3</sub> protective layer takes place, and pitting corrosion occurs in the places of Cl absorption [14]. The role of Cl<sup>-</sup> ions has been described in more detail by Wang *et al.* in [14], by Lucent and Scully in [17], and by Lunt's team. The results of these studies prove that this is the most-common mechanism of corrosive attack taking place in chloride atmospheres [18].

## 5. Identification of corrosion effects

Figures 5–7 show the microstructure on a cross-section of the tested materials after the corrosion test. The pitting corrosion is visible in each case.

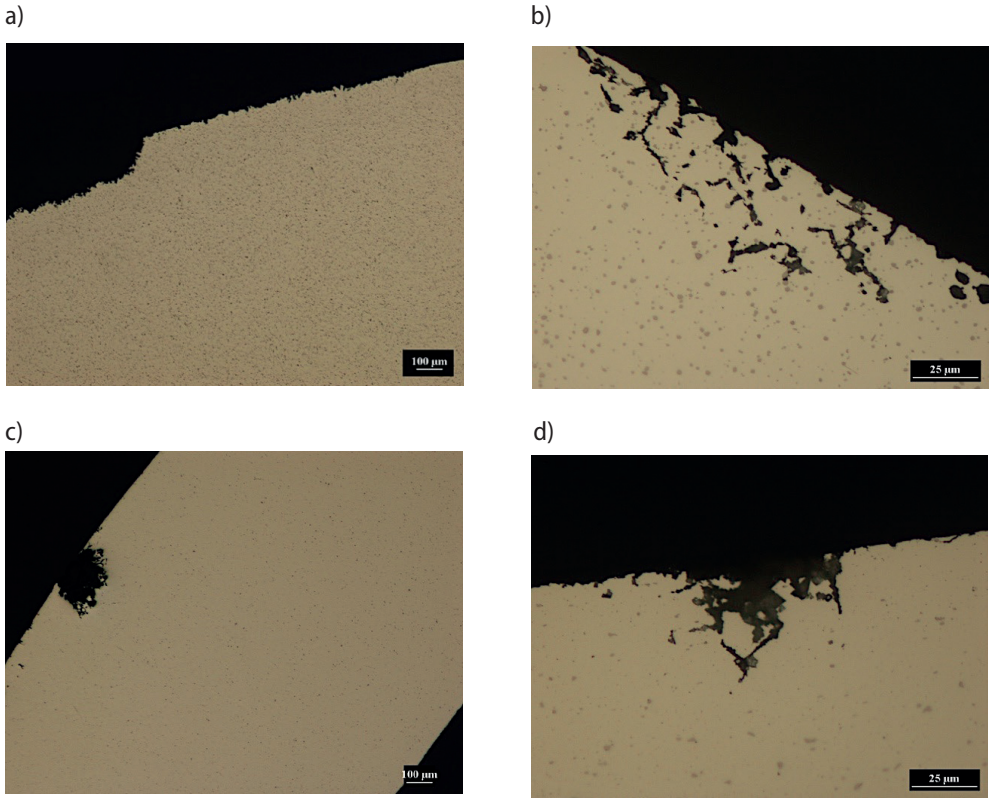


Fig. 5. Cross-section of pipes after corrosion test showing visible pitting and intergranular corrosion in alloys: (a, b) EN AW 3103; (c, d) EN AW 5049 – optical microscopy

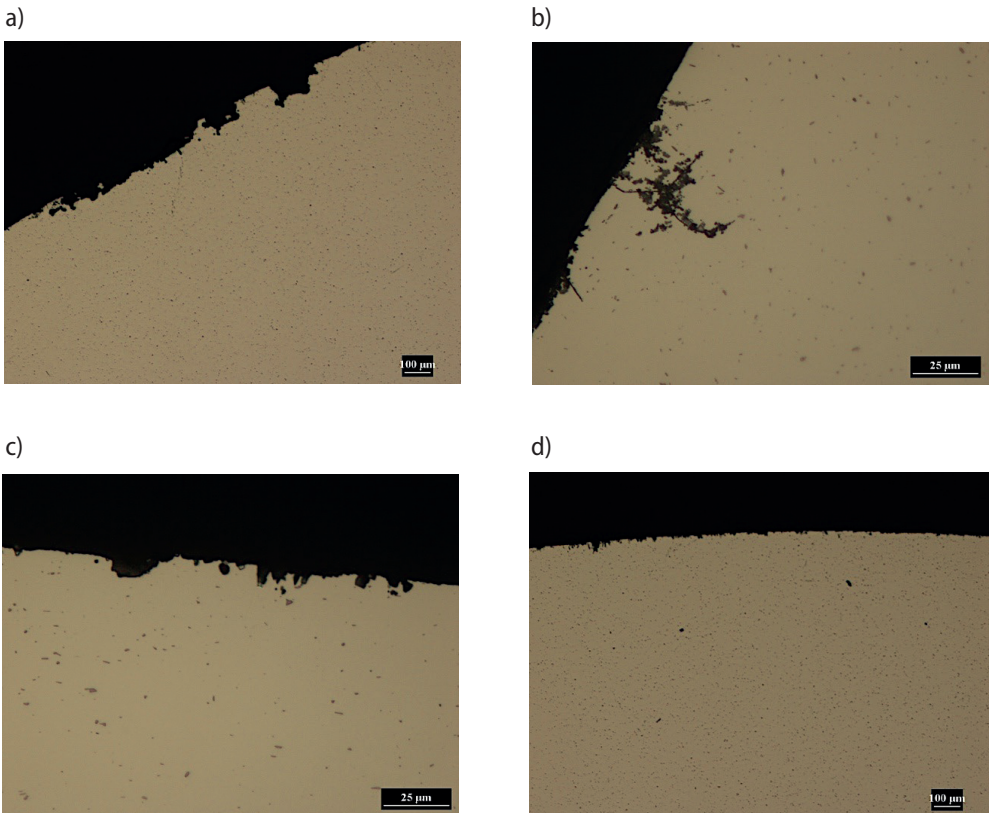
Figures 5a, 5c and 6a, 6c reveal details of the surface corrosion found in the EN AW 3103, 5049, 6060, and 6063 alloys. In the case of alloy 3103, all-grain pitting corrosion



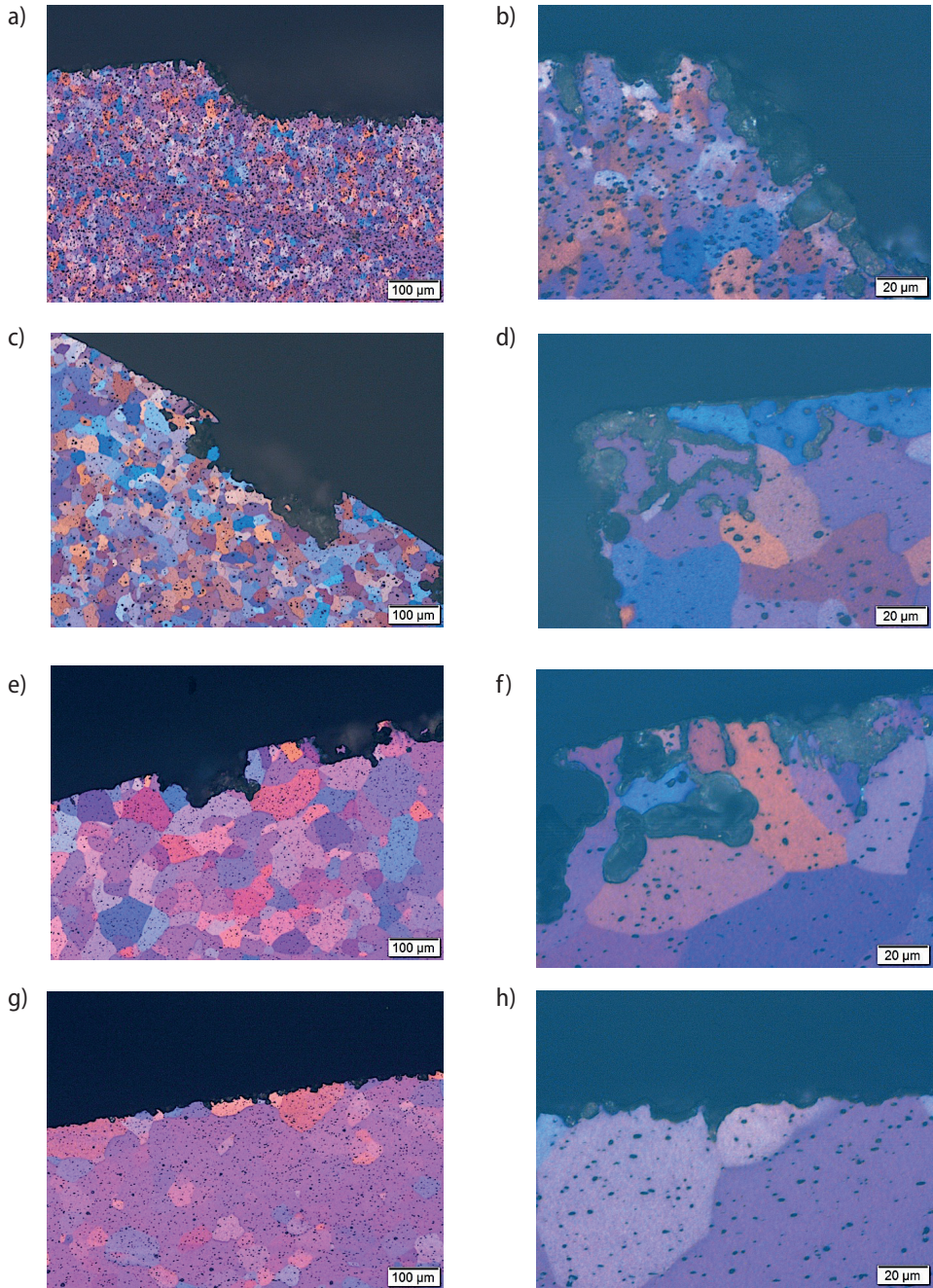
was observed (Fig. 7b). In the case of alloy 5049, a large surface defect is visible that also has the nature of pitting corrosion (Fig. 7c). In contrast, local intergranular corrosion was traced in Figure 7d. Figure 7e, 7f shows the microstructure of the EN AW 6060 alloy after the corrosion test. Visible are the effects of pitting corrosion penetrating to a depth of about 100  $\mu\text{m}$ , accompanied by local intergranular corrosion.

The EN AW 6063 alloy showed the highest resistance to the effect of a brine atmosphere; only some minor pits were found on the surface and at a depth of about 20  $\mu\text{m}$  (Fig. 7g, 7h). Severe pitting corrosion can lead to perforation of the material and loss of its tightness in extreme cases.

In the EN AW 5049 and 6060 alloys, intergranular corrosion has been identified (Fig. 7d, 7f). Corrosion of this type is one of the most dangerous. As a result of intergranular corrosion, the material can suffer failure during operation, even at low loads.



*Fig. 6. Cross-section of pipes after corrosion test showing visible pitting and intergranular corrosion in alloys: (a, b) EN AW 6060; (c, d) EN AW 6063 – optical microscopy*



*Fig. 7. Cross-section of pipes after corrosion test showing visible pitting and intergranular corrosion in alloys: (a, b) EN AW 3103; (c, d) EN AW 5049; (e, f) EN AW 6060; (g, h) EN AW 6063 – optical microscopy and polarized light observations*

## 6. Mechanical properties

The effect of corrosion on the mechanical properties of materials tested at room temperature is shown in Figure 8. The average tensile strength and yield strength obtained in pipes made from the EN AW 3103 alloy assumed similar values before and after the corrosion test (amounting to  $R_m = 134$  MPa and  $R_{p0.2} = 117$  MPa, respectively). After the corrosion test, the deformation decreased by 1% (from  $\varepsilon = 16\%$  to  $\varepsilon = 15\%$ ). In the case of the EN AW 5049 alloy, no significant changes were observed before and after the corrosion test. In both cases, the tensile strength of the starting material was 202 MPa, while the yield strength was 84 MPa and 82 MPa before and after the test, respectively. The unit elongation was 49% before the test, and it decreased to 45% after the test.

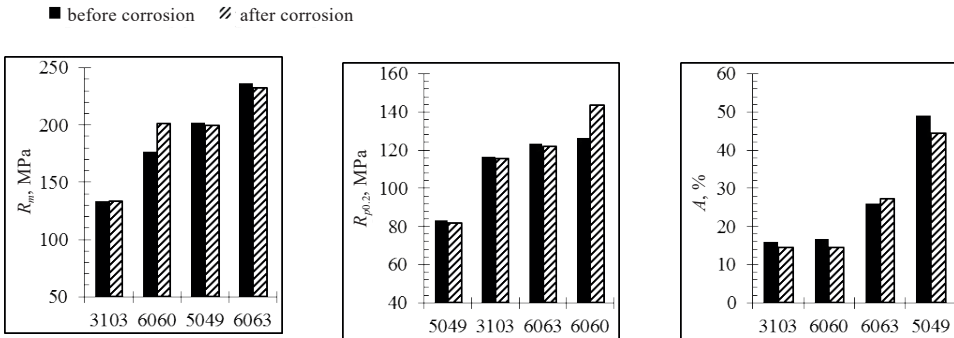


Fig. 8. Effect of corrosion test conditions on changes in tensile strength ( $R_m$ ), yield strength ( $R_{p0.2}$ ), and unit elongation ( $A$ ) obtained in tensile test for EN AW 3103, 5049, 6060, and 6063 alloys before and after SWAAT corrosion test

The EN AW 6060 alloy was characterized by a tensile strength of 177 MPa prior to the corrosion test, reaching 202 MPa after the test. There was also an increase in the yield strength (from 127 MPa to 144 MPa) and a decrease in unit elongation (from 17% to 15%). The tensile strength of the EN AW 6063 alloy pipes was 236 MPa before the test, and it was reduced to 233 MPa as a result of the effect of the corrosive environment. The yield strength decreased from 124 MPa to 122 MPa. After the SWAAT corrosion test, this material was characterized by a 2% increase in unit elongation, ultimately reaching a value of 28%.

A detailed analysis of the obtained results leads to the conclusion that the effect of the performed corrosion test on the properties of each alloy tested is negligible. The observed increase in tensile strength and yield strength after the corrosion test carried out on the EN AW 6060 alloy pipes is probably due to structural and phase transformations resulting from the long-term (20 days) holding of this alloy at a temperature of 50°C. Aluminum alloys from the 6xxx series are included in the group of precipitation-hardened materials. It is possible that, as a result of the impact of increased temperature (50°C for 20 days) during the corrosion test, the precipitation of phases such as  $Mg_2Si$  and  $Mg_5Si_6$  might have occurred [19, 20].

## 7. Summary

Subjected to corrosion test, the properties of aluminum alloys were observed to undergo only a negligible change, which proves their satisfactory behavior. Many authors have confirmed the beneficial properties of aluminum alloys that are widely used in the automotive industry [20–23]. Aluminum alloys EN AW 3103, 5049, 6060, and 6063 are used for ducts and heat exchangers in automotive air conditioners, among other things. The broad application of these alloys in the automotive industry owe mainly to the high stability of their mechanical properties during operation under varying conditions [24].

The 6xxx series alloys are used in automotive applications such as automotive air conditioners, heat exchangers, and car body parts [20, 23]. As a result of the temperature increase due to its chemical composition, alloy 6060 undergoes phase transformations [20, 25]. However, the temperature range that covers the operation of the car air conditioning system does not pose any major risk of significant adverse changes that might take place in this alloy during operation.

As the test results showed, the mechanical properties of the EN AW 6060 alloy (Fig. 8) were improved by a prolonged holding at 50°C. Therefore, it can be concluded that its use will guarantee stable operation and meet the requirements of standards for the use of materials in automotive air conditioning systems.

Based on an analysis of the results, the following conclusions were made:

- after the SWAAT corrosion test at a solution pH equal to 2.8–3.0, numerous pitting and intergranular corrosion centers were observed on the surfaces of the EN AW 3103, 5049, and 6063 alloy pipes;
- on the surface of the EN AW 6060 alloy pipe, an aluminum oxide film with visible cracks was formed, probably due to the effect of tensile stresses activated by temperature changes during the corrosion test;
- despite some corrosion marks visible on the surface of the pipes, the properties of the aluminum alloys after the corrosion test remained at a level comparable to the level obtained before the test.

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