

Metallurgical aspects of the corrosion resistance of 7000 series aluminum alloys – a review

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This article contains a review of selected studies conducted in the field of corrosion resistance of precipitation-hardenable on the corrosion behavior of these alloys. The article presents the three types of corrosion that occur most commonly in this group of materials in the context of their microstructure. It points to the importance of the chemical composition of a 7000 alloy, including the precipitates present in the microstructure, for the development of corrosion. The aluminum solid solution can act as an anode or cathode in relation to intermetallic particles. Such corrosion features may result in the destruction of the surfaces of elements made of the 7000 series aluminum alloy. It also raises the issue of the mechanism of corrosive destruction of the aluminum solid solution, which is connected with a crystallographic attack. In the case of this process, the nature of the micro-pits formed as a result of their local dissolution is related to the privileged dissolution of specific crystallographic planes de alternations obtained with another popular material for the production of roof tiles \mathcal{L} tiles – Hardox steel, \mathcal{L} t 7000 series aluminum alloys. In particular, it discusses the effect of heat treatment and the role of thus formed microstructure and directions.

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Keywords: *aluminum alloys, 7000 series, microstructure, heat treatment, corrosion*

1. Introduction 1. Introduction

 Γ incredituation of a metallic material $\sum_{i=1}^{n}$ ance $\sum_{i=1}^{n}$ matrix $\sum_{i=1}^{n}$ of $\sum_{i=1$ presence of grain boundaries (GBs) is a factor influencing the corrosion resistance of an annealed μ_{E} is encountered in many branches of μ_{E} in μ_{E} face defect in the structure of polycrystalline materials, in the area of which the rice energy is inglicity. in in the other grain regions. This reads to a higher reactivity of the GBs, because of which a change m the total grain boundary surface area affects the corrosion rate. Dong et al. [\[1\]](#page-16-0), however, in the ϵ example of austenitic steel, point to the fact that example of adstended steel, point to the fact that the activation energy of the oxidation process is not linearly dependent on the increasing surface energy of the GBs. This suggests that it is not the only criterion affecting the progress dia it is not the only criterion affecting the progress of corrosion. omy criterion anceurig are progress or corrosion.
Chen et al. [\[2\]](#page-16-1) demonstrate that the GBs should be $\frac{1}{2}$ considered as areas with a different diffusivity. They propose that the anodic reaction be considered as an effective diffusion process, in which the metal The microstructure of a metallic material significantly affects its final properties. Even the single-phase material, as the GBs constitute a surrials, in the area of which the free energy is higher in the total grain boundary surface area affects the

ions diffuse into the solution and the dissolution stream (equal to the current density) depends on the overpotential. In light of these considerations, the presence, in the surface area, of a metal with fine grains, and thus also with a large grain boundary rea, shound result in an increased corrosion rate compared to a coarse-grained material. This is confirmed by the studies of Niu et al. $[3]$, who observed, in the mixing section of a joint welded using the FSW method, corrosion resistance that worsened with the reduction of the grain size. The polarization resistance determined was lower when
the grain size was smaller. A different view is $\frac{1}{2}$ in Size was smalled. A different view is presented by Ralston, Fabijanic, and Birbilis [\[4\]](#page-16-3), In which corrosion rate was observed to decrease
together with a reduction in grain size. These facts α is an extraction in grain size. These facts are also in agreement with the numerous reports resistance improvement of single-phase metallic materials [\[5–](#page-16-4)[9\]](#page-16-5). In the case of corrosion-resistant $f(x) = f(x)$. In the case of contosion-resistant steels, this is connected with a higher capability for repassivation and a higher chemical stability of the passivation and a light chemical stability of the passive layers formed [\[9\]](#page-16-5). A similar mechanism is p_{d} attributed to an increase in the corrosion resistance area, should result in an increased corrosion rate polarization resistance determined was lower when in which corrosion rate was observed to decrease about a nanometric grain size favoring a corrosion

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of fine-dispersive aluminum [\[8\]](#page-16-6). Ralston et al. [\[10\]](#page-16-7) emphasized that an increase in the corrosion resistance together with a decreasing grain size refers only to materials undergoing passivation. At the same time, they expect a different behavior in the case of materials that do undergo passivation. Yan et al. [\[11\]](#page-16-8) demonstrate that low-angle GBs are more prone to corrosion than high-angle GBs. The authors relate this to the size of the precipitates formed on the GBs. The phenomena described point to a significant complexity of the issues connected with the effect of GBs on the corrosion resistance of metallic materials, which are in the area of interest of grain boundary engineering.

In the case when two connected elements form different phases co-existing in the microstructure, it leads to the formation of corrosion micro-cells. The character of the corrosion processes occurring in the case of such multi-phase systems will be determined by the difference in the standard galvanic potentials as well as the mutual distribution of both phases. Each of the phases formed is characterized in a different electrochemical potential, and the system formed corresponds mostly to a galvanic system with strongly polarized electrodes (shorted by low resistance), as the structural components are characterized in small dimensions [\[12\]](#page-16-9). An important issue in this area is the anodic–cathodic component surface ratio. Another factor affecting the value of the alloy's electrochemical potential is the progressive dissolution of the anodic phase. The relative increase of the amount of the cathodic phase caused by this effect favors an increase of the potential with time [\[12\]](#page-16-9).

Białobrzeski et al. [\[13\]](#page-16-10) propose two schemes for the galvanic micro-cells formed in the case of dual-phase alloys. The first scheme refers to a situation in which one of the phases is distributed inside the grains of the alloy's matrix. An important factor here is also the electrochemical character of the precipitated phase. If the precipitated phase is cathodic, the increase in the dispersion degree of the cathodic inclusion will, in most cases, lead to an increase of the cathode's activity and will favor intensification of corrosion processes [\[12\]](#page-16-9). There is an opinion that a refinement of the cathodic phases to nanometric precipitates causes them to stop playing the role of an active cathode, which in turn favors an improvement of the material's corrosion resistance [\[5,](#page-16-4) [14\]](#page-16-11). If the precipitated phase exhibits an anodic character, its behavior depends on its passivation ability. When it demonstrates such a property, the presence of the cathodic component can facilitate its transition into a passive state, and the corrosion can be hindered (the co-called anodic passivity phenomenon). In such a case, an increase in the dispersion degree of cathodic precipitates favors a deceleration of the corrosion processes [\[12\]](#page-16-9). The other scheme developed by Białobrzeski refers to a situation in which one of the phases is present in the form of precipitates on the GBs. This predisposes the alloy to intergranular corrosion. An analogical scheme can be proposed in the case of a diphase but granular material microstructure. A microstructure of this type usually occurs when one of the phases is formed as a result of a peritectic reaction.

The issue of the microstructure effect on the corrosive behavior of metallic materials includes a range of problems, which still remain valid and in many aspects not completely explained [\[15\]](#page-16-12). This refers especially to alloys whose microstructure consists of many phases synergically interacting. They include aluminum alloys, especially from the precipitation-hardenable 7000 series, which are highly popular owing to the increasing demand for light structural materials with high ultimate and fatigue strength $[16]$, for example, alloy AW 7020 characterized in the R_e/R_m proportions equaling 0.89 [\[17\]](#page-16-14). However, they are prone to localized corrosion forms. Corrosion features can act as initiation sites for corrosion fatigue cracks, which may become an important failure mechanism. The high strength of these alloys is a factor that additionally complicates the situation as the corrosion issues of these materials also refer to the effect of stresses on the corrosion development. The role of the microstructure in the corrosion resistance of 7000 alloys is still a subject of study. Of major importance for the development of these alloys is their application in the aircraft industry owing to their high strength-to-density ratio [\[18\]](#page-16-15).

This article aims to present a complex review of the recent progress in the description and

characterization of different basic processes connected with the corrosion of 7000 aluminum alloys as well as their existing interrelations. The purpose of the review is to shed light on the key challenges and also fill in the gaps of the existing knowledge in this area. Despite the many positive properties of aluminum alloys, there are limits in their corrosion resistance, which makes it justifiable to continuously expand the knowledge of the effect of microstructure on corrosion resistance. In order to determine the resources in the literature, the following phrases were entered into the WOS indexing database: "7xxx alloys" and "corrosion," which allowed us to find 22 works in this field for 2023. Adding the additional word "microstructure" to the search showed that as many as 17 of them concerned these issues. It should be emphasized, that such a search certainly does not fully reflect all the possible results, because entering the specific alloy grade "AW 7075" and "corrosion" locates 48 works in 2023 created in this field. A large number of works clearly indicate that further research in this area is still relevant and necessary.

2. Microstructure of 7000 aluminum alloys

The basic alloying element in this series is zinc in the amount of 9wt%. As can be inferred from the diagram presented by Hosford [\[19\]](#page-16-16), this element can significantly reduce the value of electrochemical potential of the solid solution α (Fig. [1\)](#page-2-0). Besides zinc, almost all the alloys from this series contain magnesium in the amount of up to 4wt%, and some of them also contain copper up to 3wt%. The role of copper as an alloying addition is to reduce the tendency of 7000 alloys for intergranular corrosion and stress corrosion cracking [\[20,](#page-16-17) [21\]](#page-16-18). The presence of copper in the 7000 series aluminum alloys has a beneficial effect on strength, because the addition of copper reinforces the aluminum solid solution. However, it reduces the hardenability, the weldability, and the toughness of alloy. The presence of copper in the chemical composition of the solid solution can also have a significant influence on the corrosion behavior of

Fig. 1. Effect of selected alloying elements on the standard potential of a solid aluminum solution [\[19\]](#page-16-16). The effect of zinc is marked in red

the aluminum alloy. For this reason, it is assumed that these alloys are divided into copper-free and copper-containing alloys.

These alloys belong to the precipitationhardened group, which leads to the formation of precipitates of phase η (Zn₂Mg) crystallizing in a hexagonal system. An exemplary microstructure of alloy AW 7075 after precipitation hardening has been shown in Figure [2.](#page-3-0) We can see finedispersive precipitates of phase η forming bands oriented along the direction of metal working. Besides the precipitation hardening phases, we can also observe precipitates of other intermetallic phases, which do not dissolve at the supersaturation stage. In consequence, they constitute precipitates of quite large sizes. They are mostly precipitates of phase α -AlFeSiMn [\[15\]](#page-16-12).

The sequence of the formation of precipitates in 7000 alloys is subject to constant discussion [\[22,](#page-16-19) [23\]](#page-17-0). The commonly assumed order is the one in which the decomposition of the solid solution during the aging of 7000 alloys runs analogically to those from the 2000 series $[20-26]$ $[20-26]$ and $[27]$:

Solid solution
$$
(\alpha) \rightarrow \text{zone GP} \rightarrow \eta'(Zn_2Mg)
$$

\n $\rightarrow \eta(Zn_2Mg)$

\n(1)

The early stages of aging preceding the precipitation of the GP zones have also been identified; however, they refer mainly to the course of natural aging [\[27\]](#page-17-2). Depending on the aging temperature, we observe two types of GP zones [\[23,](#page-17-0) [28,](#page-17-3) [29\]](#page-17-4). The

Fig. 2. (a) Microstructure of alloy AW 7075-T6. Visible bands of fine-dispersive precipitates of precipitation hardening phases and grey precipitates of phase α -AlFeSiMn; (b) a magnified fragment of the area from (a). Light microscopy, etched state

Fig. 3. A diagram presenting the effect of the phases in the strengthening of 7000 alloys [\[61\]](#page-18-0)

semi-coherent metastable transient phase η' characterizes in a hexagonal cell with the parameters: $a = 0.496$ nm and $c = 0.868$ nm. It is formed in the temperature of 120° C to 250° C [\[23,](#page-17-0) [30\]](#page-17-5). The incoherent equilibrium phase η (Zn₂Mg) (84.32%) Zn) belongs to the Laves phases and also has a hexagonal cell, yet with the following lattice parameters: $a = 0.521$ nm and $c = 0.860$ nm [\[23,](#page-17-0) [28\]](#page-17-3). This phase is formed in the temperature range of 150 \degree C to 300 \degree C [\[30,](#page-17-5) [31\]](#page-17-6). The number of formed particles η increases together with the proceeding aging time [\[28,](#page-17-3) [32\]](#page-17-7). Some authors point to the fact that, at high temperatures, the formation of phase η precedes the precipitation of intermediate phase η_P , which is morphologically similar to η' ; however, it characterizes in lattice parameters

close to those of phase η [\[22\]](#page-16-19) and [\[23\]](#page-17-0). The strengthening mechanism has been well described for alloys from the Al-Cu system. Based on the diagram presented by Ashby and Jones [\[33\]](#page-17-8), the effect of the hardening phases on the strengthening can be presented according to the scheme shown in Figure [3.](#page-3-1) Metastable η' phase is believed to be the main hardening phase and responsible for the peak hardness of these alloys.

3. Recent progress and key challenges

3.1. Effect of phase η on the corrosion mechanism

Phase η characterizes in a strongly anodic character in reference to the aluminum solid solution, which is reported by many authors [\[20,](#page-16-17) [27,](#page-17-2) [35,](#page-17-9) [36\]](#page-17-10). Andreatta et al. [\[37\]](#page-17-11) state that this phase demonstrates a fundamentally anodic character in Al-Zn alloys, however, the supersaturation of the aluminum solid solution can cause this phase to become cathodic with respect to it. The corrosive potential of this phase is estimated at the level of about −1 V (with respect to Saturated Calomel Electrode) [\[20,](#page-16-17) [38,](#page-17-12) [39\]](#page-17-13). At the same time, Birbilis [\[40,](#page-17-14) [41\]](#page-17-15) points out that the corrosive potential value only slightly changes in a wide pH scope of the corrosive solution, and the change of its value caused

Fig. 4. A scheme of the consecutive stages of corrosion in the case of the occurrence in the microstructure of isolated precipitates of phase $Zn₂Mg$, anodic with respect to the aluminum solid solution [\[15\]](#page-16-12)

by this is within the scope of -999 to -1012 mV (with respect to SCE). The anodic character of phase Zn_2Mg causes the mechanisms connected with corrosion of 7000 aluminum alloys to be more complex than in the case of the 2000 series, in which the formed precipitates are cathodic. For this reason, the investigations referring to the corrosion of these alloys mainly concentrate on the role of the precipitates occurring on the GBs and within the grains, as well as the precipitate free zone (PFZ).

Microscopic observations of the samples' surfaces after the realized electrochemical tests confirm an anodic nature of phase η (Zn₂Mg) with respect to the aluminum solid solution. The strongly negative potential value compared to the aluminum solid solution leads to a significant difference between it and the aluminum solid solution and generates the formation of galvanic microcells. In consequence, in the case of the operation of a corrosive environment, selective dissolution of these anodic precipitates takes place as well as the formation of corrosive micro-pits (Fig. [4\)](#page-4-0). And so, the presence of small amounts of precipitates uniformly distributed in the microstructure leads to a quasi-single-phase microstructure in the surface area, which can limit further development of corrosion.

The distribution of these micro-pits observed in the SEM image after the electrochemical tests confirms the influence of PFZ on the development of corrosion (Fig. [5\)](#page-5-0). The formation of this zone is connected with the presence of phase Zn_2Mg or its intermediate phase on the GBs [\[24,](#page-17-16) [42,](#page-17-17) [43\]](#page-17-18). The presence of the PFZ zone is the cause of the formation of another galvanic cell between the narrow-depleted area near the GBs and the grains rich in zinc and magnesium, and in alloys containing copper—also in this element. It is agreed that the presence of complex precipitates on the GBs, as well as the presence of PFZ, favor the dissolution of the GBs [\[44,](#page-17-19) [45\]](#page-17-20). For this reason, alloys in aged states or after slow cooling are more prone to intergranular corrosion (IGC) [\[46\]](#page-17-21). In turn, there is no agreement about the effect of a wide *PFZ* zone on the tendency for stress corrosion cracking (SCC). Some authors state that it favors SCC [\[44\]](#page-17-19), others claim that it increases the resistance to this type of corrosion [\[43\]](#page-17-18).

Most alloys from the 7000 series demonstrate a medium resistance to different types of electrochemical corrosion. It is assumed that, in the case of this series, an important role is played by three mechanisms related to localized corrosion, that is, IGC, SCC, and exfoliation [\[3,](#page-16-2) [20,](#page-16-17) [27,](#page-17-2) [36,](#page-17-10) [38,](#page-17-12) [47](#page-17-22)[–52\]](#page-18-1). A literature analysis makes it possible to state that the type of the dominating mechanism depends on the alloy's chemical composition, the size and geometry of the grains, as well as the conditions of heat treatment and the resulting microstructure of their boundaries. The selection of the conditions of artificial aging can contribute to an improvement of the alloy's resistance to one type of corrosion and at the same time increase its tendency for another.

3.2. Role of heat treatment

The presence of intermetallic phases in the microstructure of aluminum alloys creates a wide spectrum of possibilities for forming their properties aluminum. In the case of the alloys from the 7000 series, both the conventional methods of precipitation hardening and the RRA technology (retrogression and re-aging) are applied [\[25,](#page-17-23) [34,](#page-17-24) [51–](#page-18-2)[58\]](#page-18-3). Figure [1](#page-2-0) presents a scheme of the course of aging in reference to the hardness of an aluminum alloy subjected to conventional aging. The highest hardening effect is achieved at the stage of the formation of intermediate phases, which is connected with the change of the mechanism of interaction between the precipitates and the

Fig. 5. (a) Microscopic image (SEM) of the surface of an AW 7020 alloy sample after electrochemical tests ended at the potential of +250 mV with respect to *Ecorr*. Visible lower intensity of corrosion processes in PFZ [\[15\]](#page-16-12); (b) a magnified fragment of the area from (a) in the PFZ zone [author's own unpublished research]

dislocations. State T6 leads to the formation of a continuous distribution of the grain boundary precipitates (GBPs) [\[51,](#page-18-2) [59\]](#page-18-4). In the case of matrix precipitates (MPs), a properly conducted heat treatment should end when the intermediate phase is still coherent with the matrix. This state ensures high strength and hardness; however, it increases the tendency for SCC.

The multi-stage process of RRA includes aging of the alloy at the temperature of that of state T6, and next another aging to temperatures below 200◦C, followed by another cooling and another aging. This is accompanied, depending on the size of precipitates, by dissolution of metastable phases η' or their transformation into precipitates of equilibrium phase η . Ultimately, RRA leads to a microstructure characterization in the presence of fine-dispersive MPs, which are characteristic of state T6. In the scope of GBPs, this makes it possible to obtain a microstructure closer to that of states T7X [\[57\]](#page-18-5). The data in the literature demonstrate that delivery states T7X clearly decrease the susceptibility to SCC and exfoliation [\[18\]](#page-16-15). As a result, the grain boundary blocked in state T6 by the linearly continuous particles of GBPs transits after RRA into a state in which the GBPs of phase $η$ become coarse-grained and discontinuous [\[47,](#page-17-22) [51,](#page-18-2) [56,](#page-18-6) [59,](#page-18-4) [60\]](#page-18-7). This ensures an increased resistance to SCC. The presence of discontinuous precipitates GBPs also favors a high resistance to the initiation of fatigue cracks and a high impact strength [\[6,](#page-16-20) [14,](#page-16-11) [15\]](#page-16-12). At the same time, we observe resistance to general corrosion to state T6 as well as hardness close to that state, which ensures good tribological properties [\[34,](#page-17-24) [61\]](#page-18-0).

With the aim of increasing the resistance to SCC, double aging (DA) is applied. The first stage of DA characterizes in a lower temperature compared to conventional aging. This enables diffusion and a uniform distribution of the GP zones. More coarse-grained precipitates are formed during the second aging and contribute to the achievement of top hardness. MPs are thicker and partially incoherent with phase η compared to single-stage aging [\[62,](#page-18-8) [63\]](#page-18-9). The interfacial energy of the GP zone in the Al–Zn–Mg system is low enough for small sized precipitates (∼3 nm) to already be formed in the scope of ambient temperature up to 120◦C [\[27,](#page-17-2) [32\]](#page-17-7). For this reason, these alloys can also be delivered in the naturally aged state T4. There are also other types of treatments, including multistage aging, which affects the corrosion resistance of alloys from this series. In every case, the role of the heat treatment comes down to ensuring a proper microstructure, which translates, in turn, to the possibility of obtaining the assumed properties. For this reason, heat treatment should be considered in reference to the microstructure formed.

A literature review suggests a large influence for heat treatment on corrosion as it affects not

only the morphology but also the chemical composition of the precipitates formed. For example, a heat treatment leading to the obtaining of a lower copper content in the GBPs favors the alloy's susceptibility to SCC. This is connected with a big difference in the electrochemical potential between phase $\text{Zn}_2\text{Mg}(\eta)$ and the aluminum solid solution, in the case when it is depleted of copper. This intensifies the emission of hydrogen as a result of the occurring electrochemical reactions [\[44,](#page-17-19) [49\]](#page-18-10). Kumar et al. [\[53\]](#page-18-11) state that enriching copper with GBPs improves the kinetics of oxygen reduction.

3.3. Stress corrosion cracking

An important problem connected with high strength aluminum alloys from the 7000 series is their susceptibility to SCC. States T7X significantly reduce the susceptibility to SCC of 7000 alloys, which limits the problem of SCC on thick cross-sections [\[18\]](#page-16-15). According to the literature, the main mechanisms leading to SCC are: slip dissolution, film-induced cleavage, hydride formation, hydrogen-enhanced localized plasticity, adsorption-induced dislocation emission, hydrogen-enhanced decohesion, and corrosionenhanced localized plasticity [\[47,](#page-17-22) [64\]](#page-18-12). Burleigh [\[65\]](#page-18-13) states that alloys from the 7xxx series are mostly susceptible to hydrogen-induced cracking. The literature data show that the critical value of tensile stresses needed for the initiation of this type of corrosion depends on the alloy's chemical composition, the features of its microstructure, the environmental parameters, the state of the surface, and the internal stresses occurring in the element. The highest susceptibility to this type of corrosion is exhibited by alloys in which the direction of principal stresses is perpendicular to the direction of grain elongation [\[66\]](#page-18-14). The presence of compressive stresses formed at the stage of technological processes in the surface area leads to an increase of the element's resistance to SCC [\[66\]](#page-18-14). The cracks formed are usually initiated on the surface discontinuities, and corrosive pits present on the surface [\[47\]](#page-17-22). The corrosion products formed demonstrate a larger specific volume and thus cause a wedge effect, generating high tensile stresses, which contribute to the continuation of the initial crack $[36, 48]$ $[36, 48]$ $[36, 48]$. The dominant mechanisms considered in the scope of SCC of aluminum alloys are hydrogen brittleness and anodic dissolution [\[47\]](#page-17-22). SCC is promoted by the recrystallization of the α solid solution [\[66\]](#page-18-14). There is an opinion that the presence of precipitate-free zones increases the susceptibility of 7000 aluminum alloys to SCC [\[44\]](#page-17-19) and $[66]$. Data in the literature point to a significant role in this aspect of the character of the precipitates present on the GBs, especially their sizes, manner of distribution, and volume fraction. It is also possible that the presence of isolated precipitates increases the SCC resistance of these alloys. We can see that, at the initial stage of aging, the further apart the precipitates obtained through heat treatment, the higher the SCC resistance [\[44,](#page-17-19) [49,](#page-18-10) [50\]](#page-18-16). This can be affected by two factors. On the one hand, the force accompanying the formation of corrosion products is lower for overaged alloys than for alloys aged under optimal conditions [\[48,](#page-18-15) [57\]](#page-18-5). Reducing the volume of corrosion products favoring the formation of lower tensile stresses causes, in consequence, a more hindered propagation of the initiated microcracks. On the other hand, obtaining significant distances between the precipitates results in a lowered rate of their anodic dissolution and thus also a reduced hydrogen concentration at the end of the crack [\[44\]](#page-17-19). As a result, a higher SCC resistance is exhibited by alloys in an insufficiently aged or overaged state [\[48\]](#page-18-15). These views are in agreement with the scheme presented in Figure 6×67 6×67 . It is also partially in agreement with the opinion that the SCC resistance increases when the alloy's strength decreases [\[66\]](#page-18-14). We should, however, point out that the authors of $[44, 50, 51]$ $[44, 50, 51]$ $[44, 50, 51]$ $[44, 50, 51]$ $[44, 50, 51]$ observed that the technological processes leading to an excessive growth of precipitates can cause a drop in SCC resistance of alloys from the 7000 series. In particular, this refers to a case when there is a growth of precipitates inside the aluminum solid solution, which is accompanied by a drop in hardness and a reduction of their sizes on the GBs, with a tendency to form more continuous precipitates. The heat treatment leading to the formation of continuous GBPs will favor SCC as their presence constitutes a "trap"

Fig. 6. Effect of the aging time on the strength and SCC resistance of 7000 alloys [\[64\]](#page-18-12)

for the atomic hydrogen, leading to nucleation of molecular hydrogen [\[44\]](#page-17-19). At the same time, the presence of continuous precipitates also favors the propagation of cracks on the GBs. In the scope of mechanical properties, this also translates to a low impact strength of the alloy [\[56\]](#page-18-6). For example, the presence of fine-dispersive (∼20 nm) but continuous precipitates and a narrow precipitate-free zone (PFZ) was obtained by Chen et al. [\[44\]](#page-17-19) as a result of supersaturation of alloy AW 7085, followed by cooling in water (150 $°C/s$), which resulted in a high susceptibility to SCC.

Studies show that the SCC resistance is connected not only with the morphology of the precipitates present on the GBs but also with the chemical composition of the alloy, especially the presence of copper [\[44,](#page-17-19) [49,](#page-18-10) [51\]](#page-18-2). Lowering the copper and chromium content with an increased Zn/Mg ratio made it possible to improve the SCC resistance of alloy AW 7049 with respect to AW 7001 [\[18\]](#page-16-15). In the case of alloy AW 7075, better SCC resistance was also obtained when its purity was improved, which led to the formation of alloy AW 7475 [\[18\]](#page-16-15). In this way, this alloy is considered to be the most resistant to SCC of all the copper-containing alloys. Also, replacing chromium with zirconium enables an increase in the SCC resistance [\[18\]](#page-16-15). A big role in the corrosion resistance of coppercontaining alloys is played by the segregation of the chemical composition and the formation of precipitates enriched with copper. A literature analysis suggests, however, that views referring to the effect of the chemical composition of precipitates on the occurring corrosion processes are not unequivocal. Kairy et al. [\[20\]](#page-16-17) point out that the role of precipitates enriched with copper present on the GBs in the microstructure of aluminum alloys is similar in the case of intergranular corrosion (IGC) and SCC. At the same time, they claim that the formation of copper-rich phases favors a susceptibility to both types of corrosion of the 7000 series alloys, as a result of a tendency for localized corrosion on the GBs. In turn, Umamaheshwer Rao et al. [\[47\]](#page-17-22) state that the presence of precipitates rich in copper in these alloys favors a puncture of the passive layer in its vicinity and initiation of corrosion cracking.

3.4. Exfoliation and intergranular corrosion

Studies have also been conducted of the susceptibility of aluminum alloys from the 7000 series to exfoliation [\[36,](#page-17-10) [46,](#page-17-21) [48\]](#page-18-15). This corrosion type is characteristic of alloys in which anisotropy of the grains elongated through cold working takes place [\[36,](#page-17-10) [46\]](#page-17-21). Figure [7](#page-8-0) illustrates the differences in the development of exfoliation along the GBs obtained in the longitudinal section and cross-section with respect to the direction of metal working of the same element.

Exfoliation is stimulated by the formation of tensile stresses on the GBs, caused by the formation of corrosion products as a result of a galvanic effect of the GBs [\[36\]](#page-17-10). As long as the wedging forces are too low to cause mechanical deformations, the only path for the development of corrosion are the tunnels formed on the GBs. This enables distribution of a fresh electrolyte onto the alloy as well as a further dissolution of the GBs. A successive increase of the corrosion product volume leads to an increase in the stresses present on the GBs. The mechanism is controlled by the hydrogen absorbed into the grain boundary areas, which are formed as a result of the occurring corrosion reactions, which leads to their cracking and ultimately lifting the entire surface layers off the alloy [\[46\]](#page-17-21). The issues

Fig. 7. (a) Advanced intergranular corrosion of grains deformed in the metal working direction on a longitudinal section with respect to the metal working direction; (b) surface corrosion observed on a cross section with respect to the metal working direction. Light microscopy, etched state [author's own unpublished research]

related to a microstructure favoring the tendency of 7000 alloys for exfoliation are not completely clear. Wloka et al. [\[36\]](#page-17-10) point out that the alloys' susceptibility to this type of corrosion decreases for overaged alloys, which is connected with thickening of the precipitates present on the GBs and a loss of their continuity. They obtained, as a result of overaging of the alloy, a microstructure with separated precipitates and a wide precipitate free zone. An overaged alloy characterized in a precipitate size of the order of 50 nm and a very narrow precipitate free-zone, not exceeding 20 nm. At the same time, they point out that the susceptibility to exfoliation is related, similarly to SCC, to the presence of continuous precipitates on the GBs. Their views are shared by the authors of [\[46\]](#page-17-21), who also demonstrated that an increase of the cooling rate lowers the exfoliation susceptibility. A slower cooling favors a microstructure in which the degree of coverage of the GBs with intermetallic phase precipitates will be higher, which will stimulate the corrosion mechanism connected with the effect of dissolution of anodic precipitates on the GBs. The Wloka et al. [\[36\]](#page-17-10) point out that an increase in the zinc content of the alloy's chemical composition favors the occurrence of exfoliation. In turn, the studies of McNaughtan et al. [\[48\]](#page-18-15) demonstrate an opposite tendency. Lowering the content of impurities is a factor that increases the resistance to exfoliation [\[18\]](#page-16-15).

3.5. Synergic interactions between different corrosion types

The concepts presented in the literature on the scope of the corrosion of aluminum alloys make it possible to state that there is a range of interactions among the corrosion mechanisms of alloys from the 7000 series. For example, there are studies pointing to the role of IGC in exfoliation [\[36,](#page-17-10) [68\]](#page-18-18). On the basis of our literature analysis, we can state that both mechanisms (IGC and exfoliation) have similar etymologies, whereas their courses depend on the geometry of the GBs. Exfoliation takes place along the paths of IGC and next develops along the elongated grains at a higher rate under specific conditions [\[68\]](#page-18-18). In the case of exfoliation, no corrosion is observed on individual grains, as can be the case with IGC [\[36\]](#page-17-10). Such tendencies within the microstructure scope favoring the development of both corrosion types are similar. An important role in exfoliation is played by the stress, which causes corrosion products formed as a result of the galvanic effect of the GBs [\[36\]](#page-17-10). Stresses are also the key factor in the course of SCC. There is also a lot of evidence for SCC being related to IGC [\[36,](#page-17-10) [46](#page-17-21)[–48\]](#page-18-15). Most of all, both mechanisms are strongly dependent on the structure of the GBs as well as the heat treatment conditions. Umamaheshwer Rao et al. [\[47\]](#page-17-22) state that SCC is often initiated on the already existing surface discontinuities, for example, corrosion pits and areas initiated by the mechanism of IGC. The wedging force accompanying the formation of corrosion products is strongly related to the susceptibility of an aluminum alloy to SCC, and, at the same time, it is dependent on the susceptibility of the GBs to IGC [\[48\]](#page-18-15). On the other hand, however, the presence of stresses connected with the corrosion products formed is insufficient for SCC [\[36\]](#page-17-10). Umamaheshwer Rao et al. [\[39\]](#page-17-13) and Chen et al. [\[47\]](#page-17-22) observe an important effect of hydrogen in the aspect of SCC susceptibility. Marlaund et al. [\[46\]](#page-17-21) point to hydrogen's role, also at the initial stage of exfoliation, and its control by way of an intergranular mechanism at a later stage.

3.6. Effect of crystallographic orientation

The literature emphasizes the role of crystallographic orientation in the development of corrosion. Mai et al. [\[69\]](#page-18-19) point out that areas with a higher atom density corrode more slowly, which translates also to the corrosion rate, dependent on the crystallographic orientation of the grains and resulting from a nonuniform distribution of the planes with the densest arrangement of atoms. The effect of the crystallographic orientation of the grains on the corrosion rate is also mentioned by other authors [\[1,](#page-16-0) [70](#page-18-20)[–72\]](#page-18-21).

The microscopic observations on samples after performing the electrochemical tests presented earlier show that the morphology of the corrosion changes formed in the aluminum solid solution area had a step-like character, consisting of many forms with a cubic shape and rugged edges (Fig. [5\)](#page-5-0). The initiation of a corrosive micro-pit takes place as a result of a puncture of the oxide layer on the alloy's surface at its weakest point, whereas the propagation of corrosion proceeds along certain privileged areas. Corrosion of this type is described in the literature as a crystallographic attack [\[73,](#page-18-22) [74\]](#page-19-0). In the case of a solid solution formed on an aluminum base, the privileged paths along which corrosion propagates are crystallographic planes ${100}$ as well as directions ${100}$. The morphology formed is connected with a different rate of dissolution of the grains' surface caused by their increased reactivity along certain crystallographic planes and directions. Such an interpretation is confirmed by the results obtained by Treacy et al. [\[75\]](#page-19-1), who considered different susceptibilities of the particular crystallographic planes in the category of differences in the free surface energy of the planes. In the case of a face-centered cubic cell (FCC), in which aluminum crystallizes, the number of atoms per surface unit increases in the order: (100) < (110) < (111) , whereas the value of surface energy of the crystallographic planes decreases in the opposite order, that is, $(100) > (110) > (111)$ [\[75–](#page-19-1)[77\]](#page-19-2). In consequence, the family of planes {100} characterizes in a higher rate of the cathodic reactions occurring as well as a higher value of critical potential of pitting corrosion. This translates to the following susceptibility to the initiation of pitting corrosion in chloride solutions: ${111} > {110} > {100}$ [\[75,](#page-19-1) [76,](#page-19-3) [78,](#page-19-4) [79\]](#page-19-5). The highest value of local dissolution occurs in planes {111}. Planes {111}, which, in the case of aluminum crystallizing in lattice A1, belong to those densely packed with atoms and exhibiting the lowest potential value of pitting corrosion initiation. Thus, they are the most susceptible to the initiation of pitting corrosion [\[75,](#page-19-1) [76\]](#page-19-3). At the same time, in the case of planes {100}, less densely packed with atoms, the required value of this potential should be higher in order to reach a specific current density and maintain the conditions necessary for an active dissolution $[80]$. In consequence, the pits nucleating on the surfaces of planes {110} and {111} develop faster than on {100}. The morphology of the pit formed in the case of planes {100} favors local tunneling and a reduction of the adsorbed oxygen compared to the ordered planes {111} [\[76\]](#page-19-3). The facilitation of the reduction reaction in areas less density packed with atoms of planes {100} is connected with a more effective course of $O₂$ and H^+ adsorption [\[75\]](#page-19-1). Other authors relate the limited corrosion in planes {100} to a lower energy of elastic deformation, which favors the formation of a more stable aluminum oxide during the repassivation [\[76\]](#page-19-3). Regardless of these considerations, however, all authors agree that reaching the wall of one of planes {100} stops the corrosion process, owing to the fact that it is more resistant to

dissolution. In consequence, it leads to the creation of forms visible in a microscopic image. It can also be related to a different rate of diffusion taking place with respect to the direction of movement of the diffusing oxygen atoms, which determines the rate of the occurring electrochemical reactions [\[15\]](#page-16-12). The facilitated diffusion of oxygen can favor the development of corrosion in areas of energetically favored planes, that is those with a lower surface energy, i.e. {111}. In such a case, the better oxygenated areas will exhibit a cathodic character in reference to the worse oxygenated zones, as a result of the formation of a local microcell of a dissimilar aeriation. The ultimate effect on the formation of privileged paths of corrosion propagation along planes {100} can be related to both mechanisms simultaneously. It should be noted that the theory presented is in agreement with the theory included in an article by Treacy and Breslin [\[75\]](#page-19-1), which points out that, in areas of planes {100}, which is less densely packed with atoms, a more effective O_2 and H⁺ adsorption takes place, which facilitates the reduction reaction. It has been established that the presence of alloying elements such as: Li, Mg, Zn, Ag, and Cd in the aluminum solid solution can lower the density of corrosion current and decelerate the rate of anodic dissolution [\[77\]](#page-19-2).

Several authors have observed a relation between the slip bands and the corrosion initiation through a crystallographic attack [\[72,](#page-18-21) [81](#page-19-7)[–83\]](#page-19-8). This observation provides an energetic explanation in that the free energy supply of plastically deformed materials is higher than in other materials and therefore the diffusion along the slip bands will occur more slowly. This is the result of the fact that they characterize in a higher value of free energy due to a more defected structure, and thus the energetic state of these areas reduces the value of the activation energy needed for the diffusion. Huang et al. [\[82\]](#page-19-9) also established an existing dependence between the GP zones and the crystallographic attack. Donatus et al. [\[83\]](#page-19-8) point to a mechanism of corrosion propagation along the slip bands. Zhang et al. relate the bands formed in lithium-containing alloys with phase T1 (Al_2CuLi), whose nucleation takes place preferentially on the slip bands [\[84\]](#page-19-10).

3.7. Influence of copper in the chemical composition of alloy on corrosion resistance

As was pointed out earlier, an important role in the development and course of corrosion is played by the chemical composition of the precipitates formed. Also, the tendency of these alloys towards localized forms of corrosion depends on the content of this alloying element. However, the influence of copper on the corrosion resistance is not clear and sometimes appears contradictory. There are reports stating that a copper addition to the chemical composition of alloys from the 7000 series favors their corrosion [\[68\]](#page-18-18). On the other hand, a more common view states that enriching precipitates of phase η present on the GBs with copper reduces the difference of potentials between the aluminum solid solution and this phase, making the precipitate nobler $[20, 45]$ $[20, 45]$ $[20, 45]$. This is due to the fact that copper atoms substitute zinc atoms in the crystallographic lattice of hardening precipitates. Even with a high copper content, however, as is possible in the case of phase $Mg_2(Zn, Al, Cu)$, it still maintains its anodic character [\[20\]](#page-16-17). Yang et al. [\[45\]](#page-17-20) proposed the following scheme of corrosion development in the case of an aluminum solid solution rich with copper and precipitates occurring on the GBs:

- 1. At the initial stage of aging, the forming precipitates are copperless and in consequence the corrosion develops on the GBs;
- 2. At the following stage of aging, the number of particles present inside the grains increases, which reduces the difference in the copper content between the grain center and its boundaries. For this reason, the corrosion refers to both the grain and its boundaries;
- 3. A wide PFZ and large precipitates rich in copper are present on the GBs formed as a result of long-term aging, favor corrosion proceeding along the PFZ areas.

The presence of copper in the chemical composition of 7000 alloys, especially in the precipitates formed on the GBs, affects the course of SCC [\[44,](#page-17-19) [49,](#page-18-10) [51,](#page-18-2) [53\]](#page-18-11). The presence of copper in the

composition of the precipitate increases the value of the electrochemical potential of phase η , which reduces the difference in potential between it and the aluminum solid solution. The increase in the copper content in the precipitates is stimulated by a higher temperature of artificial aging, which is connected with a slower diffusion of copper into alu-minum than that of zinc and magnesium [\[27,](#page-17-2) [45\]](#page-17-20). Besides the temperature, the presence of copper in the precipitates formed is also affected by the aging time [\[46\]](#page-17-21) as well as the cooling rate [\[44\]](#page-17-19). For example, Chen et al. [\[44\]](#page-17-19) observed an increased copper content on the GBs in alloys rapidly cooled after supersaturation. Owing to cooling after supersaturation in oil, they obtained a high SCC resistance as a result of the presence of isolated precipitates of intermetallic phases on the GBs and a simultaneous preservation of copper in them. It can be expected that, in the case of the presence of copper-rich precipitates on the GBs, a dominating mechanism will be IGC. This is confirmed by, for example, the studies of Yang et al. [\[45\]](#page-17-20), who demonstrated that it runs along the precipitates' free zone which is rich in copper. The precipitation of copper-rich phases during aging favors depletion of the PFZ of this element and in consequence also of the corrosion proceeding along the GBs. Copper is also present in micrometer-sized intermetallic particles, which include Al₂CuMg (S phase), Al₂Cu (θ phase), and Al7CuFe. The presence of these copper-rich particles is important for the corrosion of 7000 series aluminum alloys. Wang et al. [\[85\]](#page-19-11) showed that the presence of copper in some precipitates of intermetallic phases (especially $Al₇Cu₂Fe$) other than the η phase may contribute to much more serious corrosion damage in copper-containing than copperless alloys. He attributed this to strong galvanic coupling between intermetallic phase and aluminum solid solution.

The copper content in the solid solution plays a key role in the localized corrosion of 7000 series alloys [\[85\]](#page-19-11) and [\[86\]](#page-19-12). Figure [8](#page-11-0) shows exemplary polarization curves obtained for alloys AW7020 and AW7075 presented in a study by Lachowicz [\[15\]](#page-16-12). Comparing the copperless alloy AW 7020- T4 with an alloy containing copper AW 7075, the former characterized in a lower value (by

Fig. 8. Exemplary potentiodynamic polarization curves obtained for copperless alloy AW7020 and copper containing alloy AW7075 [\[15\]](#page-16-12)

about 100 mV) of corrosion potential. This should be related to the operation of copper on alloy AW 7075-T4, which causes a change of the electrochemical potential value of a solid solution α to a more positive one. The value obtained for alloy AW 7020-T4 is close to that obtained for the overaged alloy AW 7075. In all the materials examined, the course of the anodic reaction exhibits an intensive growth, which points to a significant rate of general corrosion. In the case of alloy AW 7075, we observe a difference at the level of 100 mV in the values of corrosion potentials for the alloy as delivered and after overaging. The anodic nature of $Zn₂Mg$ phase compared to the aluminum solid solution causes changes in E_{corr} potential of overaged alloy towards more negative values (caused by its precipitation during heat treatment) when its amount in the microstructure is increased. The effect of reducing the copper content in the aluminum solid solution was also enhanced during over-aging [\[85,](#page-19-11) [86\]](#page-19-12). Sha et al. [\[87\]](#page-19-13) also showed that Zn and Mg concentrations in the aluminum solid solution tend to decrease with aging time.

3.8. Presence of iron-rich phases

Phases rich in iron are present in practically all aluminum alloys as a consequence of contamination by this metal, whose removal is too expensive, as well as low solubility of iron in aluminum. There are generally two types of iron rich-phase particles found in aluminum alloys. The first is the large particles, several micrometers in size and often also rich in silicon, which precipitate

during solidification. These particles do not dissolve during the solution treatment. The second type is the submicrometer-sized dispersoid particles, also often rich in iron and silicon, formed during heat treatment. This type of particle is mainly used to control grain growth. Due to the low solubility of iron in aluminum in a solid state, it demonstrates a high tendency to form diversified and complex intermetallic phases [\[88–](#page-19-14)[90\]](#page-19-15). Most of their grains also contain manganese and silicon in their chemical composition. In the case of a series of alloys containing alloying elements such as copper and magnesium, in aluminum alloys, we observe the formation of phase rich in iron, additionally enriched with their atoms. The parameter that determines the tendency for the precipitation of iron-rich phases in aluminum alloys is the iron equivalent value (IEV), described by a formula in which iron, manganese, and chromium are consid-ered in [wt%] [\[91\]](#page-19-16): IEV = 1Fe + 2Mn + 3Cr.

In technical aluminum alloys, very often, we observe the presence of phase α -AlFeSiMn with a regular lattice. The following formula is attributed to this phase: $Al_{15}(Fe, Mn)_{3}Si_{2}$ [\[88,](#page-19-14) [91](#page-19-16)[–95\]](#page-19-17). Its light grey precipitates in the microscopic image demonstrate a characteristic branched shape [\[96,](#page-19-18) [97\]](#page-19-19). This phase exhibits a high affinity to phase β -AlFeSi, which is considered to be especially harmful from the point of view of the mechanical properties because, during crystallization, it forms acicular precipitates, which at the same time make it easy to differentiate in a microscopic image from phase α-AlFeMnSi [\[89,](#page-19-20) [96,](#page-19-18) [98\]](#page-19-21). Homogenization of aluminum alloys allows the use of the transformation of the β -AlFeSi phase into α -AlFeMnSi and removes the negative effects of the presence of the β-AlFeSi phase in the microstructure. The literature describes this transformation, which occurs at temperatures between 530 and 600 $°C$, as the "β to α transformation" [\[90,](#page-19-15) [99,](#page-19-22) [100\]](#page-20-0). In aluminum alloys, phase α -Al₈Fe₂Si (or α -Al₁₂Fe₃Si₂) can also be formed, which crystallizes in a hexagonal lattice. It is described in the literature as α -AlFeSi, and in the presence of manganese, as α -AlFe (Mn)Si [\[88,](#page-19-14) [91,](#page-19-16) [94\]](#page-19-23). The literature also contains a description of phase β -Al₆Mn(Fe), which is isomorphic also to phase $Al₆Fe$ [\[92,](#page-19-24) [101,](#page-20-1) [102\]](#page-20-2). Precipitates of the β -Al₆(MnFe) phase can be transformed directly into the α -AlFeMnSi phase as a result of the absorption of silicon atoms from the solid solution, which is called in the literature "6 to α transformation" [\[103\]](#page-20-3). A negative impact of this cathodic phase in relation to the solid solution on the corrosion resistance of aluminum alloys was noted [\[104\]](#page-20-4). Several authors [\[88,](#page-19-14) [89,](#page-19-20) [96,](#page-19-18) [105\]](#page-20-5) have pointed out that the predisposition for the formation of the above-mentioned phases is determined by the chemical composition of the alloy. Manganese is mostly used up during the formation of most intermetallic phases rich in iron, as the iron and manganese atoms can replace each other in the crystalline lattice [\[88\]](#page-19-14). Wang et al. [\[85\]](#page-19-11) pointed out that Al3Fe particles serve as local cathode and provide sites for the oxygen-reduction reaction, and thus result in the development of pitting at the particle–solid solution interface.

Authors are in agreement in pointing to a cathodic character of the phase most commonly present in aluminum alloys: α -AlFeSiMn [\[40,](#page-17-14) [73,](#page-18-22) [106](#page-20-6)[–108\]](#page-20-7). This does not mean, however, that the effect of phases rich in iron should be completely omitted from consideration. We should also point out that the diversity of the phases present in aluminum alloys make it impossible to formulate such a thesis in reference to all iron-rich phases. The variability of the chemical composition of the phases formed rich in iron can, in some cases, favor corrosion. For example, there are reports about a strong corrosion of iron-rich phases in alloys from the 2000 series containing lithium, which is connected with depletion of the aluminum solid solution with copper and lithium around the forming precipitates [\[81,](#page-19-7) [108\]](#page-20-7). Andreatta et al. [\[37\]](#page-17-11) observed that supersaturation of alloy AW 7075 leads to a stronger galvanic corrosion between the cathodic phase Al_7Cu_2Fe and the aluminum solid solution. This suggests that the enrichment of the aluminum solid solution with zinc and magnesium, connected with the dissolution of the phase that precipitate/hardens the alloy, reduces the value of its electrochemical potential. On this basis, we can conclude that areas with a lower content of these elements will be cathodic in reference to the other zones.

3.9. Corrosion in welded joints

Alloys from the 7000 series are popular in their application owing to their high mechanical strength, but they characterize in a difficult weldability [\[109\]](#page-20-8). The data in the literature point to such problems with weldability as, for example, susceptibility to hot cracking and a drop in strength in the weld area in the case of the application of traditional welding methods [\[31,](#page-17-6) [66,](#page-18-14) [110](#page-20-9)[–113\]](#page-20-10). A big technological challenge is ensuring a high corrosion resistance for the whole welded joint produced [\[114,](#page-20-11) [115\]](#page-20-12).

In practice, we can encounter attempts at connecting alloy AW 7020 by means of traditional electrodes, included in the norm PN-EN ISO 18273:2007. A lower melting point of the weld should limit the tendency for cracking in the heataffected zone (HAZ) because of the lower stresses formed during the weld's crystallization. For this reason, the electrode materials are often alloys from the 4000 series 4000 [\[15,](#page-16-12) [66,](#page-18-14) [109\]](#page-20-8). In the literature, in the case of the 7000 series, alloys with magnesium are usually used for this purpose [\[15,](#page-16-12) [30,](#page-17-5) [39,](#page-17-13) [66,](#page-18-14) [116\]](#page-20-13). Both cases, however, cause the chemical composition of the weld to deviate significantly from the native material, which is not without an effect on the issues of the welded joints' corrosion.

In the case of these alloys, there is considerable interest in the friction stir-welding method (FSW) [\[3,](#page-16-2) [29,](#page-17-4) [54,](#page-18-23) [66,](#page-18-14) [109,](#page-20-8) [117](#page-20-14)[–119\]](#page-20-15). This method is also not devoid of flaws connected with microstructural changes. In particular, flaws can arise when FSW is applied to connect 7000 aluminum alloys with some other series. Bocchi et al. [\[117\]](#page-20-14) examined the effect of friction welding on the corrosive behavior of joints of alloy AW 7075-T6 with a 2000 series alloy. They observed precipitation of phases on the GBs as well as an anodic character of the formed weld. A reduction of the corrosion resistance in the weld's nucleus during the connecting of a 2000 aluminum alloy with alloy AW 7075 was also observed in [\[3\]](#page-16-2). An anodic character of a singlesign joint weld made on alloy AW 7020 was also recorded by Dudzik and Charchalis [\[118\]](#page-20-16). Shah and Badheka [\[119\]](#page-20-15) demonstrated that the corrosion resistance is directly proportional to the heat inflow

during friction stir welding. Boards connected at a lower rotational speed of the tool, a higher welding speed, and with a lower shoulder diameter exhibited a higher corrosion resistance.

The authors' own studies [\[15\]](#page-16-12) of the heataffected zone (HAZ) of the welded joints examined made on alloys from the 7000 series showed that we can distinguish between its two characteristic areas. The first one is a relatively narrow zone directly adhering to the weld and depleted of precipitates present inside the grains. In the HAZ zone, directly adhering to the weld, the temperature during welding can exceed 400◦C [\[30,](#page-17-5) [120\]](#page-20-17). Rapid heating initiates, in the solid solution zone, dissolution of hardening precipitates after the temperature reaches a value over their maximal solubility. The temperature of the fading of phases characteristic for 7000 alloys equals: 50◦C–150◦C for GP zones, 200 $^{\circ}$ C–250 $^{\circ}$ C for phase η' , and 300 $^{\circ}$ C–350 $^{\circ}$ C for phase η [\[30\]](#page-17-5). The dissolution of intermetallic phase $Zn₂Mg$ and the intermediate phases enriches the solid solution with alloying elements. The second observed HAZ area is characterized by the presence of grains deformed according to the metal working direction and clearly intensified aging processes. The presence of a solid solution zone and a super-aging zone located slightly away from it is also confirmed by the studies of other authors [\[30,](#page-17-5) [112\]](#page-20-18). The data in the literature point out that, in the superaging area, we observe mainly precipitates of semi-coherent phase η' and equilibrium phase η (with a clearly lower degree of dispersion than in the native material) [\[30\]](#page-17-5). The temperature increase in this area reaches the stability scope of equilibrium phase η , which leads to an increase of the precipitates' size, with a simultaneous decrease of the density of their occurrence. The authors' own observations [\[15\]](#page-16-12) have demonstrated, however, that both in the solid solution area and the superaged zone, we can encounter phase precipitates on the GBs. In the microstructure of the welds, we observe, as a result of the thermal cycles, equilibrium partial melting as well as the presence of the so-called "ghost GB" network in the microstructure [\[15,](#page-16-12) [121\]](#page-20-19). In this case, the partial melting is connected with the initiation of dissolution of intermetallic phases present on the GBs [\[121,](#page-20-19) [122\]](#page-20-20).

The occurring local changes in the microstructure and the properties of the welded joints are not without an effect on their corrosion behavior [\[117,](#page-20-14) [118\]](#page-20-16).

Studies show that the differences in the corrosion potential values between the particular welded joint areas are important enough to lead to the formation of corrosion macro-pits [\[15\]](#page-16-12). We should, however, point out that the cathodic polarization is mainly controlled by the diffusion and galvanic corrosion between different regions and is also connected with the distances between them [\[30\]](#page-17-5). When the areas are located far from each other, the effect of galvanic corrosion will be weaker.

The process of welding modifies the alloy's microstructure and, in consequence, also the mechanisms of corrosion development in the macroareas of the welded joint [\[15\]](#page-16-12). In the case of a welded joint obtained with the use of an additional material, for example, an alloy from the Al-Mg system, strong and localized corrosion occurring on the GBs was observed in areas with the intermetallic phase precipitates localized on the GBs. The formation of anodic precipitates with a discontinuous character does not favor extensive corrosion, and it mainly leads to dissolution of the aluminum solid solution around these precipitates [\[15\]](#page-16-12). The corrosion of the aluminum solid solution present in the weld exhibits clear traits of a crystallographic attack. The effect of strong corrosion in the superaged area of HAZ is attributed to the formation of a complex galvanic system, in which it constitutes an intermediate electrode. The diversification in the corrosion development between the particular welded joint zones is illustrated in Figure [9.](#page-14-0)

An especially disadvantageous corrosive behavior was observed in the case of a welded joint made with a binder constituted using an aluminum alloy with silicon, as we observed a strong corrosion of the weld area [\[15\]](#page-16-12). It was stated that the initiation of corrosion occurred on the rain boundaries. The continuous eutectic precipitates present there led to the formation of a preferential corrosion path. Oya et al. [\[116\]](#page-20-13) demonstrated that the presence of a Si-depleted layer along the GBs favors intermetallic corrosion.

Jha et al. [\[124,](#page-20-21) [125\]](#page-20-22) reported a case of SCC damage in welded elements made by means of the

Fig. 9. SEM image illustrating the different degrees of corrosion advancement in different areas of a welded joint made on alloy AW 7020 [author's own unpublished research]

GTA method from alloy Al-Zn-Mg. They established that the anodic dissolution of phase η is a factor that ensures a privileged path of SCC propagation [\[125\]](#page-20-22).

3.10. Recent advances and future perspectives for corrosion protection of 7000 series aluminum alloys

As the analyses conducted show, aluminum alloys are susceptible to various types of localized forms of corrosion. Corrosion is a permanent process that cannot be entirely prevented in any corrosive environment. For this reason, an important aspect that should be considered in further research on aluminum alloys is, in addition to the role of microstructure, also any potential method of protecting them against corrosion.

Corrosion protection strategies for 7000 series aluminum alloys may include surface engineering methods. Applying protective coatings seems to be one of the best approaches to prevent corrosion of the metallic surfaces. This is typically achieved by applying chromate conversion coatings or chromic acid anodized coatings with chromate-pigmented primers [\[126,](#page-21-0) [127\]](#page-21-1). Chromate-based inhibitors are known to be the best inorganic corrosion inhibitors [\[128\]](#page-21-2). Unfortunately, hexavalent chromate ions cause many environmental problems, and their toxic and carcinogenic properties are well

documented. For this reason, extensive research has been carried out to find environmentally friendly alternative protection systems. In particular, various cerium compounds have been widely considered [\[126\]](#page-21-0). The formation of a cerium oxide/hydroxide film on the cathode particles was considered to be the reason for the cathodic inhibition of the AW7075 alloy. Organic inhibitors have also been used successfully [\[129\]](#page-21-3). Protection of the metallic surfaces against corrosive media using organic coatings is considered to be the most conventional and cost-effective method [\[130\]](#page-21-4). Research has also been undertaken to use organic coatings to protect aluminum alloys [\[131\]](#page-21-5). Corrosion protection of metallic substrates by solgel coatings is an intensely debated issue in the scientific community. For this reason, coatings of this type may be of great practical importance for protecting aluminum alloys against corrosion [\[132,](#page-21-6) [133\]](#page-21-7). Attempts to use the cold-spray method have also been made [\[123,](#page-20-23) [127,](#page-21-1) [134,](#page-21-8) [135\]](#page-21-9). In the field of surface engineering technology, the anodizing method is also widely used [\[136\]](#page-21-10).

The development of surface strengthening technologies also creates an opportunity to increase the corrosion resistance of 7000 series alloys. The formation of a passive film on aluminum alloy surfaces is significantly related to the residual stress field. For this reason, the shot-peening method is also promising [\[137\]](#page-21-11). Numerous opinions being advanced in the literature indicate that technologies enabling grain refinement to nanometric sizes through strong plastic deformation can improve the corrosion resistance of aluminum alloys [\[138,](#page-21-12) [139\]](#page-21-13). Prospective research on additive technologies is also being done [\[140\]](#page-21-14).

The examples above do not exhaust all possibilities for improving the corrosion resistance of 7000 series aluminum alloys. It only shows how wide the spectrum of possibilities is in this respect, especially since it is also possible to combine various corrosion protection strategies.

4. Summary

This article presents a review of selected research studies conducted in the field of corrosion resistance of alloys from the 7000 series. The data in the literature unequivocally demonstrate that, in the case of this series, an important role is played by three mechanisms related to localized corrosion, i.e., IGC, SCC, and exfoliation, about which we have paid special attention was paid here. The authors also discuss the effect of heat treatment on the corrosive behavior of these alloys in reference to the forming of microstructure, especially the precipitates of anodic phase $\text{Zn}_2\text{Mg}(\eta)$ as well as the intermediate phases formed during the heat treatment. A particular focus was put on the role of the RRA treatment among the possibilities for forming the corrosion resistance of 7000 alloys. It was demonstrated that an important role in corrosion resistance is also played by the chemical composition of an Al-Zn alloy. The changeability of the chemical composition of precipitates is also an important factor, which can be reflected in the character of the developing corrosion. It was also shown that, in the case of aluminum solid solution corrosion, the destructive mechanism is connected with a crystallographic attack, which is related to the privileged dissolution of specific crystallographic planes and directions.

On the basis of this review, we can unequivocally state that a scientific approach that takes into consideration the role of the microstructure in the corrosion of alloys from the 7000 series is deeply important in drawing conclusions about corrosion resistance. Experimental studies are of particular importance, because they enable an evaluation of the surface morphology after the operation of corrosive factors.

Although previous studies have made great progress, further research on the role of heat treatment in influencing the corrosion resistance of 7000 series aluminum alloys is still greatly needed. The key to this, however, requires a deep understanding of the role of the microstructure in this process. Similar problems can be seen in the case of forming the properties of welded joints made with the use of 7000 alloys. The operation of the welding heat leads to changes in the microstructure of the alloys, which clearly translates to their corrosive behavior. This emphasizes the role of the selection of additional materials and the choice of the welding technology. And so, the job of the technologist is not only to ensure a cathodic character of the weld but also to maximize the optimal microstructure of this area. Meanwhile, the use of additive manufacturing is associated with high cooling rates, which translates into clear differences in microstructure compared to materials produced using traditional techniques.

Another prospective issue regarding 7000 series aluminum alloys is the search for surface engineering methods aimed at improving the corrosion resistance of these alloys. The search for corrosion inhibitors is also not over. All the issues raised in this article allow us to conclude that extensive research on the corrosion resistance of 7000 series aluminum alloys is still required.

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