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IMPACT OF THE PLASTIC DEFORMATION MICROSTRUCTURE ON THE CORROSIVE RESISTANCE OF METALLIC MATERIALS – THE STATE OF THE ART AND THE EFFECT OF MICROSTRUCTURE REFINEMENT ON THE EXAMPLE OF THE 2000 SERIES ALUMINUM ALLOY

The article discusses the role of the microstructure formed through plastic deformation in the corrosion resistance of metallic materials. Additionally, a review of the existing knowledge in this area is conducted. In particular, the role of the refinement of intermetallic phases is emphasized. For that purpose, investigations of as-cast aluminum alloy, as well as after plastic deformation, from the 2000 series have been performed. Metallographic tests of the examined materials have been carried out, and electrochemical tests as well as SEM examinations of the surface after the corrosion tests have been conducted. It has been documented that the presence of large precipitates existing at distances typical of as-cast alloys favours intensive corrosion. In turn, a significant amount of fine-dispersive precipitates at the initial stage of corrosion can work as a barrier counteracting the corrosion processes.

Keywords: Microstructure; corrosion resistance; aluminum alloys; refinement; plastic deformation

1. Introduction

The characteristics of the microstructure are strictly connected with its mechanical properties as well as corrosion resistance. For this reason, issues related to corrosion resistance are concentrated on its microstructural aspects. The corrosion resistance of materials is affected by the phase composition but also by the fraction of the particular phase components and the degree of their refinement. Not without significance is also the dislocation density caused by plastic deformation as well as the grain size of the material exposed to a corrosive environment. All the mentioned microstructure characteristics are very strongly dependent on the manufacturing technology. And so, in order to fully describe the corrosive behaviour of metallic materials, it is necessary to consider the role of the microstructure formed in technological processes. This makes it possible to ensure an in-depth understanding of the synergy existing between the material's microstructure, the technological process and the material's response to the corrosive environment.

Considerations referring to the microstructure evolution during metal forming include e.g. phase transformations caused by thermo-mechanical operation, dynamic recrystalization, the occurrence of a crystallographic texture, changes in the grain size and morphology, obtaining refinement and a uniform distribution of the secondary phases, as well as increasing the dislocation density. In some cases, however, as a result of phase transformations caused by plastic deformation, we can also observe undesirable structure components, such as martensite induced by plastic deformation in austenitic steels [1,2].

The article sums up the current knowledge on the role of metal forming in the corrosion resistance of metallic materials, taking into account the features of the material's microstructure. To that end, an analysis was performed of the existing state-of-the-art in this scope. The authors' own research to the effect of microstructure refinement on the corrosion resistance of aluminium alloys, based on the example the 2000 series, was an extension of the existing state-of-the-art.

2. Analysis of the state-of-the-art

The effect of plastic deformation on the corrosion resistance of alloys has been discussed in [3,4]. Together with the cold working degree, a shift of the potential value to more negative values was recorded, and an increase of the corrosion current density value was observed, which was directly proportional to the corrosion rate [3]. The cold working also favoured an easier initiation of corrosion pits [3]. The results referring to the relation of the

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corrosion resistance to plastic deformation realized by different methods have also been presented in other studies. A worse corrosion resistance of austenitic steel after cold working have also been recorded by other authors [1,2]. According to Abreu et al. [1] and Barbucii et al. [2], a lower resistance to the formation of pits in the deformed material is connected with a strongly defected microstructure, metastablity of austenite and the occurrence of a martensitic phase induced by plastic deformation, which becomes the area of pit initiation. The susceptibility to the formation of martensite in austenitic steels increases under the effect of deformation, which results in the possibility of its formation at ambient temperature. This tendency depends on the chemical composition and, for example, for steel AISI 304, it is higher than for AISI 316 [1]. A different opinion on the matter is expressed by Phadnis et al. [5], who established an improvement of corrosion resistance after cold working. They attributed the better corrosive properties of a rolled material to a higher chromium content in the surface passive layer after rolling, leading to its better protective characteristics. At the same time, they point out that the increased diffusion of chromium into the passive layer is connected with the deformation texture obtained after rolling. Meanwhile, Hamdy et al. [6] observed a clear dependence of the corrosion resistance of austenitic steel with niobium on the deformation degree. A smaller degree of plastic deformation improved the corrosion resistance but a higher one decreased it. Similar observations have been recorded by Mudali et al. [7] for steel AISI 316L alloyed with nitrogen. These results are in agreement with the numerous data pointing to the possibility of forming the corrosion resistance through a proper use of the deformation texture in the surface area [8-11]. The crystallographic texture is formed in metallic materials during their metal forming, such as rolling, drawing, severe plastic deformation techniques (SPD), as well as, in consequence, phase transformations and recrystallization. The preferred crystallographic orientations which then occur can significantly affect their corrosion resistance. The effect of the texture on the development of passive layers has been extensively discussed by Gerashi et al. [9] on the example of magnesium alloys. They point out that a crystallographic texture affects the thickness and type of oxides forming the passive layer. The effect of cold working on the density of the passive layers which are formed according to a specific crystallographic dependence has been pointed out by Tomaszow [12], who emphasized that cold working can lead to the formation of passive layers with different protective properties.

Metal forming is usually connected with a clear refinement of the existing microstructure. Despite the fact that, commonly, high angle grain boundaries are prone to corrosion, the literature includes also opinions that technologies enabling grain refinement to nanometric sizes through severe plastic deformation (SPD) favour an improvement of corrosion resistance of metallic materials. Depending on the type of material, this can be connected with refinement of the grain boundaries and, in multi-phase alloys, also of the intermetallic phases to nanometric sizes. Jiang et al. [13] stated that the application of multipass equal-channel angular pressing (ECAP) for a hyper-eutectic alloy

from the Al-Si system improved its corrosion resistance through refinement of primary silicon crystals. Brunnera et al. [14] attributed the increase of resistance to intergranular corrosion (IGC) of a 2000 alloy after the same process of its homogenization and a decrease of copper segregation, which reduced the sensitization of the grain boundaries. The grain refinement in the surface area through surface mechanical attrition treatment (SMAT) improved the corrosion resistance of ferritic chromium stainless steel AISI409 [15]. The authors relate this effect to the properties of the formed passive layers, including their higher ability for secondary passivation and a higher chemical stability [15-17]. In the case of iron alloys with chromium, another considered reason is also the increased diffusion of chromium reinforced through the high grain boundary density [18]. This remains in agreement with the discussion undertaken by Ralston et al. [19], who suggest that the observed increase of corrosion resistance together with the grain refinement refers exclusively to materials which are prone to passivation. In the case of lack of passive layer, they expect it to lead to a lower corrosion resistance. This theory is in agreement with the one referring to a lowered corrosion resistance of materials in the case of increasing the total surface area of the grain boundaries through grain refinement as an effect of increased reactivity of the grain boundaries. At the same time, Balusamy et al. [15] and Hamu et al. [20] emphasize the role of dislocation density, which can negatively affect the corrosion rate. In some examples, grain boundaries may be important for the development of stress corrosion cracking (SCC) as there have been cases when cracks were stopped at high angle grain boundaries [21], despite the fact that, at the same time, low angle boundaries are indicated as those more resistance to intercrystaline cracking.

Although twin boundaries, as a special case of wide angle coherent boundaries, have a lower interfacial energy compared to high angle grain boundaries, it is expected that the existence of twins on the external surfaces will have a negative effect on the corrosive behaviour of metallic materials [9]. This is the responsibility of the atoms located in the twin area, which are more active (with higher energy) than atoms located in the normal lattice positions. There are, however, contradictory results referring to the effect of twins on the corrosive behaviour. Aung et al. [22] and Sabbaghian et al. [11] demonstrated that the presence of twin boundaries clearly accelerated corrosion. This is also in agreement with the studies of Hamu et al. [23], who recorded a stronger corrosion in the case of samples with a microstructure containing numerous twins as well as samples which contained hardly any twins. There are, however, reports that the presence of twin boundaries can, in some cases, positively affect the corrosive behaviour [24]. Still, such an effect is attributed to a change in the orientation of the crystallographic plane for one which is more resistant to dissolution. Liu et al. [25] point to a potential role of twins in the corrosion resistance of magnesium alloys. On the one hand, their presence worsens the corrosion resistance as a result of the creation of a galvanic cell between the particular grain areas. On the other hand, it favours the formation of a passive layer, which translates to an improvement of this

resistance. These results seem to be in agreement with those obtained by Xiong et al. [26], who proved also on the example of a magnesium alloy that a small number of twin boundaries decreased its corrosion resistance whereas their high density favoured an improvement of the material's corrosion resistance. At the same time, Wanga et al. [27] ascribe such an effect to the decrease of the diversity of crystallographic orientation between the particular areas as a result of the appearance of twins.

The role of crystallographic orientation in the development of corrosion comes down to anisotropy of corrosion between differently oriented surfaces [10]. The crystallographic orientation is becoming the subject of studies also in the context of mechanical properties [28]. The activation energy needed for the dissolution of a densely packed surface is higher than in the case of a loosely packed surface [10]. Thus, we observe that, in the case of densely packed planes, corrosion proceeds slower compared to planes with a lower degree of packing [29]. And so, the crystals oriented to low surface energy (i.e. close-packed planes) can cause an increase of the corrosion resistance [30]. In order to limit the effect of other factors, the studies in this area are conducted mainly for pure metals [29]. Shkatulyak et al. [31] pointed to the importance of carbon and a crystallographic texture for the anisotropy of corrosion on the example of non-alloy steel. The literature contains observations also of the effect of the type of rolling on the formed texture, which further translates to the corrosion resistance [10]. This is also confirmed by the studies conducted by Kumar et al. [32]. It was established that the presence of densely packed crystallographic planes parallel to the sample surface improves the resistance to corrosive proprieties. In a measurable way, this non-uniform progress of corrosion in the case of aluminium alloys is manifested through the formation, in the solid solution, of corrosive changes with a step-like character, which consist of many forms with jagged edges [8]. Corrosion of this type is usually described as a "crystallographic attack" [33,34]. The forming morphology is connected with the different rates of dissolution of the grain surfaces caused by their increased reactivity along certain crystallographic planes and

directions. Planes belonging to those densely packed with atoms demonstrate the lowest value of potential of pitting corrosion initiation, and so they are the most prone to pitting corrosion initiation [35,36]. An exemplary view of a crystallographic attack observed after corrosion tests in alloy AW7075 has been presented in Fig. 1. The literature shows that reaching the plane wall (100) stops the corrosion process due to the fact that it is the plane with the highest thermodynamic stability and the most resistant to dissolution in reference to planes (011) and (111) [34]. Treacy et al. [35] point out that the propagation of pits on the surface of (100) requires dissolution of the most tightly bound (111) subsurface atoms, which cause the crystallographic plane (100) to be more resistant to a pitting attack. In the aspect of the issue discussed above, we should expect that the texture present in the material caused by metal forming will significantly affect the general corrosion of metallic materials.
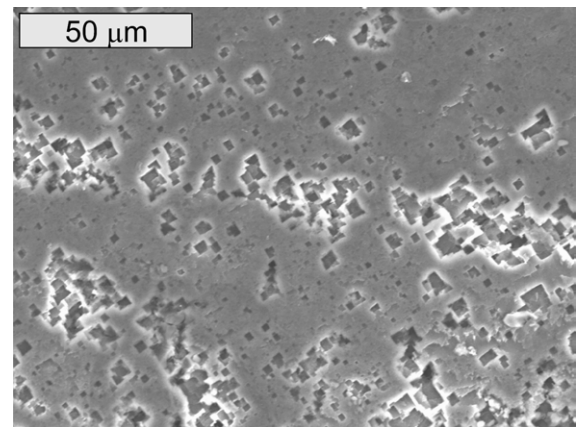

Fig. 1. A general view of a "crystallographic attack" observed in the solid solution of aluminium alloy AW7075 [unpublished own materials]

At the microscopic level, the heterogeneous microstructure with bands can affect the differentiation of the corrosion mechanism in individual areas of the material. This effect can be observed, for example, in Fig. 2, which shows the course
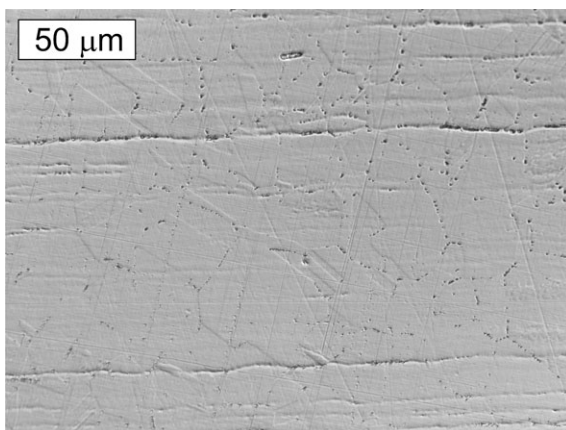
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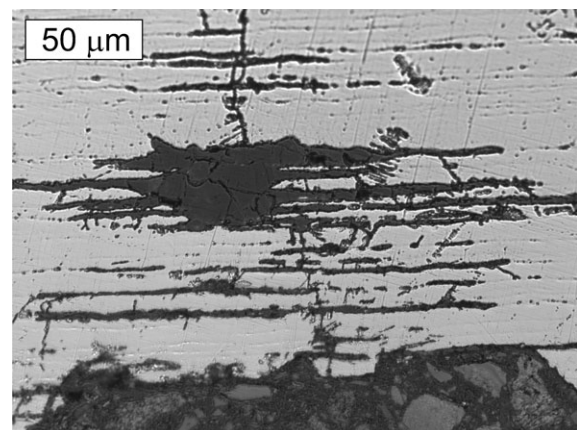
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Fig. 2. Stress corrosion cracking (SCC) of austenitic stainless steel X5CrNi18-10: a) the microstructure with carbide precipitates arranged along the plastic deformation direction and present on the grain boundaries; b) an advanced stage of SCC. Visible locally selective character of corrosion conditioned by the presence of carbide bands. Light microscopy, etched state with a 10% aqueous solution of oxalic acid [unpublished own materials]

of stress corrosion cracking (SCC) in austenitic stainless steel X5CrNi18-10 grade. A characteristic property of the formed cracks is their strong branching (resembling a tree root) as well as orientation perpendicular to the maximal tensile stresses. The formed crack becomes an active anode, which catalyzes a further development of corrosion. In the presented case, the number of branches connected with SCC is small, due to the presence of band-oriented precipitates of carbides as well as ferrite δ in the structure of the examined metal sheet. This contributed to a local occurrence of selective corrosion. The forming crack created a path for the corrosive solution, which released other corrosion mechanisms, at the same time limiting the number of cracks caused by SCC.

A similar effect has been observed in the case of austenitic stainless steel X5CrNiMo17-12-2, shown in Fig. 3. Also in this case, selective corrosion was observed, caused by the presence of ferrite δ. However, here, the degree of selective corrosion

advancement was clearly lower. The cracks caused by SCC obtained a more branched form.

At the macroscopic level, such banded microstructure may manifest itself in anisotropy in the development of corrosion, influencing the nature of the features in the exploative surface layer. This effect can be observed, for example, in banded ferritic-pearlitic steel (Fig. 4).

Another measurable effect of corrosion is the mechanism of exfoliation, which is characteristic for alloys with anisotropy of grains elongated by cold working [37-39]. Exfoliation is stimulated by the formation of tensile stresses on the grain boundary caused by the creation of corrosion products as a result of the galvanic effect of the grain boundaries [38]. The tunnels formed on the grain boundaries elongated according to the grains' plastic deformation direction enable distribution of the fresh electrolyte and their further dissolution. The successive increase of the corrosion products' volume leads to an increase of the stresses
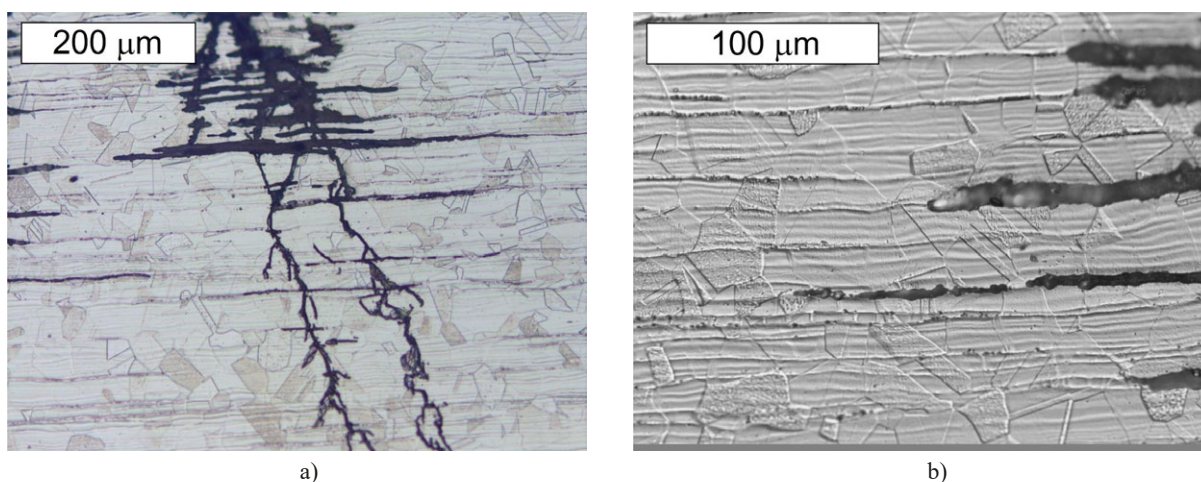

a)   b)

Fig. 3. a) SCC of austenitic stainless steel X5CrNiMo17-12-2; b) a magnified fragment of the area with ferrite δ showing the development of selective corrosion. Light microscopy, etched state with a 10% aqueous solution of oxalic acid [unpublished own materials]

a)   b)
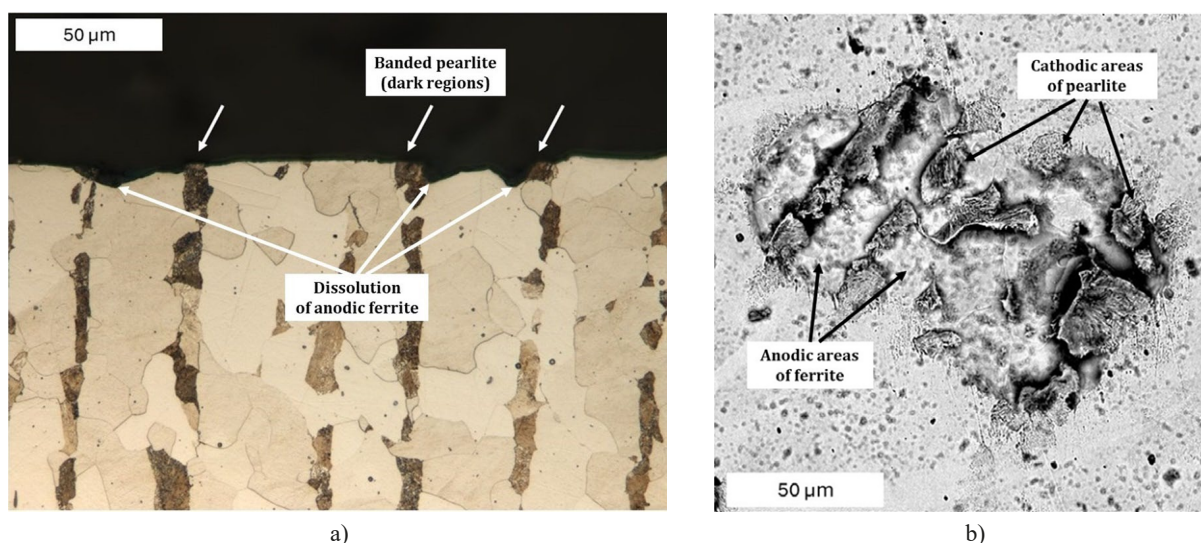
Fig. 4. a) Banded ferritic-pearlitic steel. A cross-section made of a sample after electrochemical tests. Visible dissolution of the anodic ferrite areas while maintaining the cathodic pearlite unchanged. The arrows mark the places where perlite occurs. Light microscopy, etched state with 3% Nital; b) The surface of the same steel after electrochemical tests. Bands of pearlite as a result of ferrite dissolution are visible. SEM [unpublished own materials]

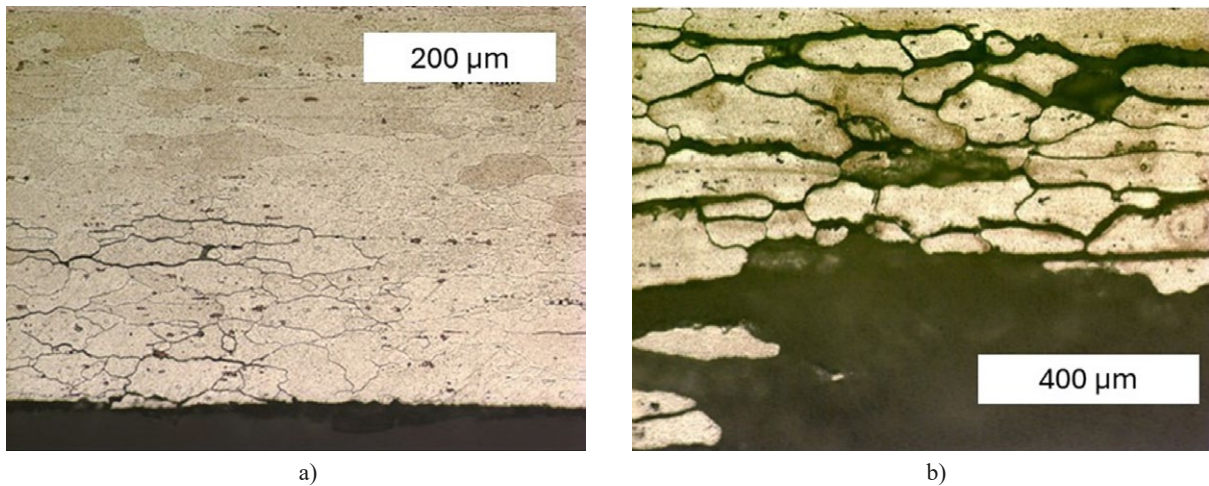a)   b)

Fig. 5. a) Advanced exfoliation of AW2017A aluminium alloy on the longitudinal-section in respect of the plastic deformation. b) An enlarged fragment of the microstructure in the near-surface area Light microscopy, etched state with a 2% HF aqueous solution [unpublished own materials]

present on the grain boundaries, which, in turn, leads to their cracking and, ultimately, to lifting of the alloy's whole surface layers. This effect can be observed, for example, in Fig. 5. The grain boundaries formed longitudinally to the plastic deformation direction become active zones responsible for the penetration and transport of the corrosive solution into deeper areas of the aluminium components. The alloy's pulverization occurring in grains arranged according to the plastic deformation direction favours surface exfoliation in products made of alloys from the 2000 series [8,37,39].

It is symptomatic of exfoliation that the progress of corrosion and the depth of penetration in the grain boundary area are strictly related to the way of grain boundary arrangement in respect of the plastic deformation direction. On the cross-section, we observe a different character of corrosive changes [8]. The corrosive damage related to the grain boundaries characterized in a wider scope in the longitudinal direction in respect of the plastic deformation. In the transverse direction, the electrochemical processes refer mostly to the aluminium solid solution, whereas the grain boundaries arranged transversely remain free of corrosion (Fig. 6). This means that the corrosion initiated on the grain boundary is not limited only to its areas but, in certain situations, it propagates and develops into its inside. This can be considered in the context of the level of internal energy of the grain boundaries [8]. For this reason, it is necessary to perform studies in the scope of the relation between IGC and the grain boundary orientation. Conducting further studies in this area can make it possible to select the technological processes which will enable optimization of the corrosive properties at the microscopic level. It is purposeful to obtain the preferred grain boundary arrangement, which will reduce the sensitivity to IGC. This, in turn, will translate to the properties of elements made from aluminium alloys at the macroscopic level. It can be prospective in this scope to apply thermomechanical treatment as well as incremental techniques.

The presented examples document the important role of plastic deformation and the formed microstructure on the devel-
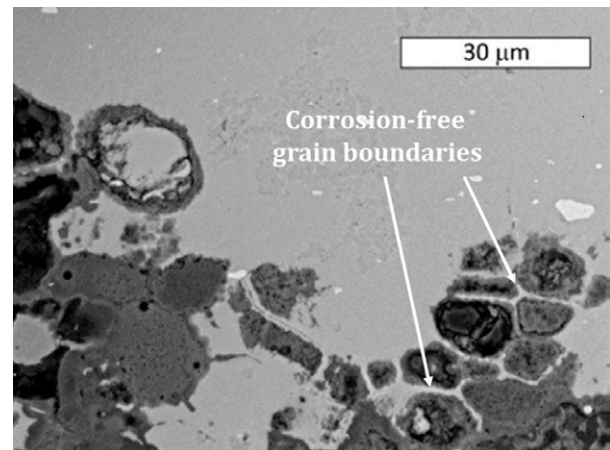

Fig. 6. Exfoliation features in the AW2017A aluminium alloy on the cross-section in respect of the plastic deformation, non-etched state. SEM [8]

opment of corrosion. At the same time, the performed analysis shows that this effect is very complicated, which is connected with the number of factors and their mutual synergy, which translate to the final effect on the corrosion mechanism. At the same time, it clearly emphasizes the need for further studies in this area.

3. Research methodology

Microscopic tests aiming at an evaluation of the microstructure of the examined alloys were performed on microsections with the use of a Leica DM6000 microscope. The tests were conducted in a non-etched state as well as in an etched state by means of a 10% water solution HF. The microscopic tests, whose purpose was to evaluate the microstructure of the investigated alloys as well as the changes made after the corrosion tests, were realized by means of scanning electron microscopy methods (SEM) with the use of a Phenom ProX microscope by Thermo

Fisher Scientific integrated with an EDS analyser (accelerating voltage 15 kV). The chemical composition tests of the examined materials were performed with the use of the glow discharge optical emission spectroscopy method (GD OES) on a GDS 500A device by Leco.

The corrosion wear resistance of the examined materials was evaluated based on electrochemical measurements, which were conducted by methods including a measurement of the open circuit potential (stationary) E_0 and the recorded relations $i = f(E)$ during the polarization tests in a three-electrode measurement system. The measurement system, fully automatized, consisted of a measuring vessel, a potentiometer ATLAS 0531 ELEKTROCHEMICAL UNIT&IMPEDANCE ANALYSER and a computer controller, equipped with the processing program AltasCorr05. The auxiliary electrode (counter-electrode) made of austenitic steel was placed directly inside the measuring vessel. A saturated chlorosilver electrode (Ag/AgCl) was used as the reference electrode. The value of the electrode potential in respect of a standard hydrogen electrode equals +0,196 V. The time between the test sample preparation and the tests equalled a minimum of 24 h. The surface of the examined electrode (sample) was 0,785 cm^2. Before the beginning of the measurement, each sample was held for 30 min in a 5% NaCl solution with pH = 7,5±0,2 and at the temperature of 20°C in order to stabilize the stationary potential, after which it was subjected to polarization in the anodic direction in the same solution at the rate of $dE/dt = 1$ mV/s. The initial potential value was determined based on the stationary potential values, assuming a value lower by about 200 mV. The tests were realized on three samples. The results were presented in the form of an exemplary polarization curve and compiled in the form of electrochemical parameters: stationary potential E_0, corrosion potential E_{corr} and corrosion current density i_{corr}. The parameters were marked as the average from the three measurements. The surfaces of the samples before the test underwent a treatment consisting in grinding with abrasive papers, with gradation from 220 to 1200, on rotational grinders. The samples were subjected to cleaning in an ultra-sonic washer in acetone followed by drying with compressed air. The corrosion tests were supplemented with microscopic observations SEM of the surface, performed after the conducted electrochemical tests in order to describe their state after the operation of the corrosive factor.

4. Test material

The first of the examined materials was a sheet made of aluminium alloy AW2017A in the T451 state. The second tested material was as-cast aluminium alloy AlCu4MgSi (AC 2017A). The casting nature of the alloy should be connected with an increase of not only the sizes of the intermetallic phases but also the distance between them. The chemical compositions of the examined alloys obtained by the glow discharge optical emission spectroscopy method have been compiled in TABLE 1. They are similar to the wrought AW2017A, which makes it possible to formulate a dependence on its effect during the inference.

TABLE 1

Chemical composition of the examined aluminium alloys from the 2000 series, in % wt.

GRADE	Mg	Cu	Mn	Zn	Si	Fe	Cr	Ti+Zr	Al
AW 2017A	0,98	4,00	0,48	—	0,42	0,50	0,09	0,15	rest
AC 2017A	0,75	4,06	0,68	0,22	0,46	0,66	0,04	—	rest

The performed metallographic tests of alloy AW2017A demonstrated that its microstructure was characteristic of wrought aluminium alloys. It consisted of aluminium solid solution grains with precipitates of intermetallic phases (Fig. 7). The irregular precipitates observed in a light microscopic image constitute phase α-AlFeMnSi (grey, in the light microscopy image). Also observed were single globular primary precipitates of phase Al$_2$Cu (light colour, in the microscopic image). Detailed metallographic tests have been presented in [8]. The hardness
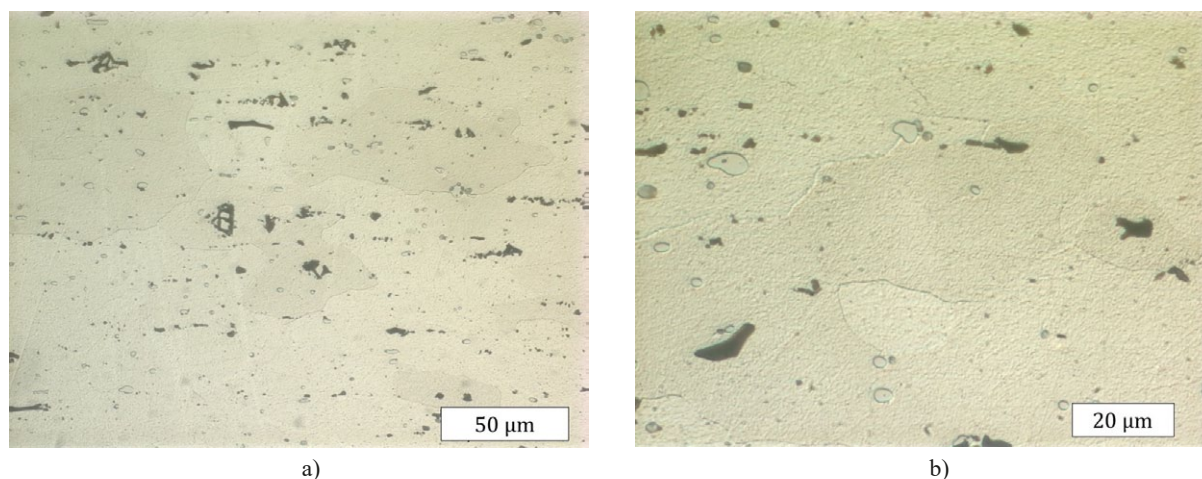

a)

b)

Fig. 7. a) Microstructure of the examined aluminium alloy AW 2017A - T451. Visible precipitates of phase α-AlFeMnSi (dark colour, in the microscopic image) and single primary precipitates of phase Al$_2$Cu (θ) in the aluminium solid solution. b) A magnified fragment of the area from Fig. a, Light microscopy, etched state

of the material as-delivered equalled 115±7 HV3, which is confirmed by the state of delivery.

The microstructure of the as-cast alloy Al4CuMgSi (AC2017A) was constituted by irregular precipitates of a phase rich in iron α-AlFeMnSi and globular precipitates of phase θ-Al$_2$Cu in the aluminium solid solution (Fig. 8). Precipitates of phase Al$_2$Cu in casting alloys have also been observed by other authors [40,41]. They occurred both in the form of large block-like precipitates and fine dispersive ones, whose formation is favoured by a high cooling rate or heterogeneous nucleation [41]. According to the expectations, the density of their presence was clearly lower than in the case of an alloy after plasticdeformation.
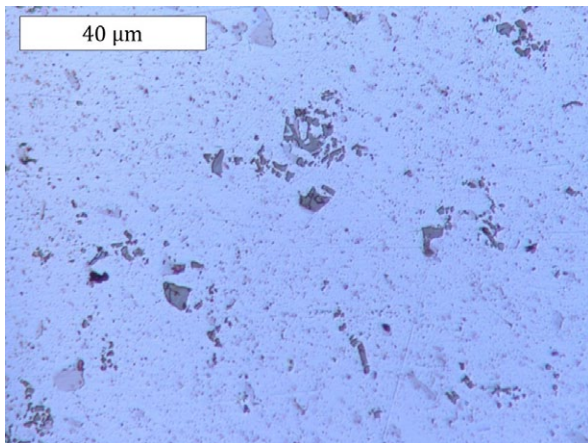

Fig. 8. Microstructure of the examined as-cast alloy from the Al-Cu system. Visible irregular precipitates of phase α-AlFeMnSi(Cu) and single primary precipitates of phase Al$_2$Cu. Light microscopy, Nomarski contrast, etched state

5. Results

5.1. Electrochemical tests

Alloys AW2017A and AC2017A were used for the evaluation of the microstructure effect on the corrosion resistance of the examined aluminium alloys with copper. As shown by the conducted literature studies, the refinement of the phases may play an important role in the occurring corrosion processes.

The aim of the realized investigations was to determine the way in which an increased distance typical of casting alloys, as well as its reduced dispersion degree occurring between the intermetallic phase precipitates typical of alloys formed through plastic deformation, affect the corrosive behaviour of aluminium alloys from the 2000 series. For that purpose, the potentiodynamic curves were determined for both tested alloys. The rate of corrosion development should be related to the number and size of the cathodic-anodic centres. Exemplary polarization curves obtained for both alloys have been shown in Fig. 9, whereas the average values of electrochemical parameters obtained from the three curves have been compiled in TABLE 2.

TABLE 2

Electrochemical parameters obtained in polarization tests conducted in a 5% NaCl solution for wrought alloy AW 2017A and as-cast alloy AC 2017A

Parameter	$E_0 (I = 0)$ [mV]	E_{corr} vs Ag/AgCl [mV]	i_{corr} [µA/cm^2]
AW 2017A	−589±7	−569±6	0,83±0,31
AC 2017A	−690±15	−650±8	3,66±0,60

In the case of both alloys, the course of the anodic reaction exhibited an intensive increase, which points to a significant rate of their general corrosion. However, significant differences in the obtained polarization curves were observed. The alloy as-cast demonstrated a lower value of corrosion potential E_{corr}, as well as higher values of anodic currents compared to alloy AW2017A in state T451. This proves a more intensive oxidation reaction taking place on the surface of the as-cast alloy. A higher value of corrosion current i_{corr} translates to a higher corrosion rate of alloy AC2017A. Both alloys corroded under cathodic control, that is, the oxidation reaction took place "more easily" than the reduction reaction.

5.2. State of the surface after electrochemical tests

Macroscopic and microscopic observations of the sample surfaces were performed after the electrochemical tests. Their purpose was to compare the morphological characteristics
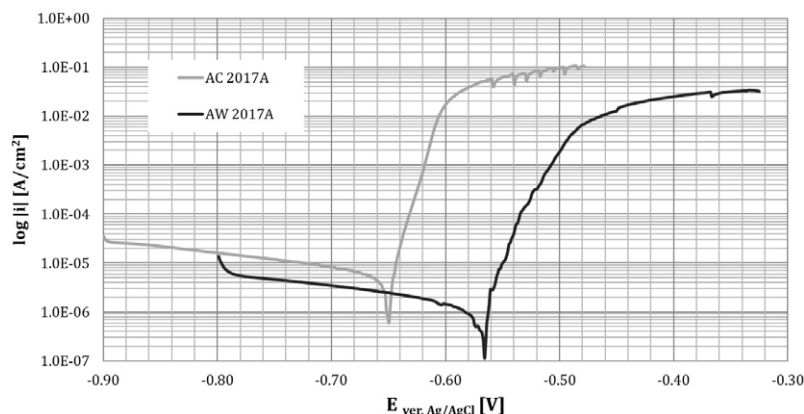

Fig. 9. Exemplary potentiodynamic polarization curves obtained for wrought alloy AW 2017A and as-cast alloy AC 2017A

of the sample surfaces of the alloy in both states after they underwent local corrosion. In the case of alloy AW2017A, the presence of dispersive cathodic precipitates of phase Al_2Cu in the grains surrounded by a zone depleted of copper leads to selective dissolution of the aluminium solid solution, which predisposes the alloy for changes in the form of general pitting corrosion (Fig. 10). The initiation of corrosion at a macroscopic level is connected with the formation of corrosion micro-pits in the areas of the presence of large intermetallic precipitates (Fig. 11). Also observed was a corrosive attack of the grain boundaries (marked with arrows), which points to sensitization of the grain boundaries. The microscopic observations SEM showed that the corrosion of the solid solution has the character of a crystallographic attack (Fig. 10). While growing, these changes occupy an increasing area of the substrate surface. This will be favoured by the presence of a big amount of fine-dispersive precipitates of the precipitate-hardening phase, which, though invisible in a microscopic image, will be present in state T451. Observations performed with higher magnifications show that precipitates of phase Al_2Cu were cathodically

protected, owing to which no dissolution of particles of this phase was observed in the microscopic image. In the case of the examined alloy, no significant effect of the iron-rich phase AlFeMnSi on the intensity of the corrosion processes occurring on the alloy surface was established either. The surface of phase α-AlFeMnSi remained unchanged (Fig. 12). This is connected with its cathodic character, which has been confirmed by many other authors [8,33].

If the content of phase Al_2Cu is insignificant in the alloy and it is present in the form of fine-dispersive and isolated precipitates, it plays the role of an active cathode only at the beginning of the dissolution process. The preferential dissolution taking place around the precipitates of this phase will lead in time to its mechanical separation from the aluminium solid solution. This will result in a limitation of the corrosion processes connected with its cathodic operation, as a result of fading of its precipitates in the surface area. This affects the changing content of phase Al_2Cu in the alloy caused by corrosion, which in time causes the material to become quasi-homogeneous on its surface. This will favour a better corrosion resistance of the
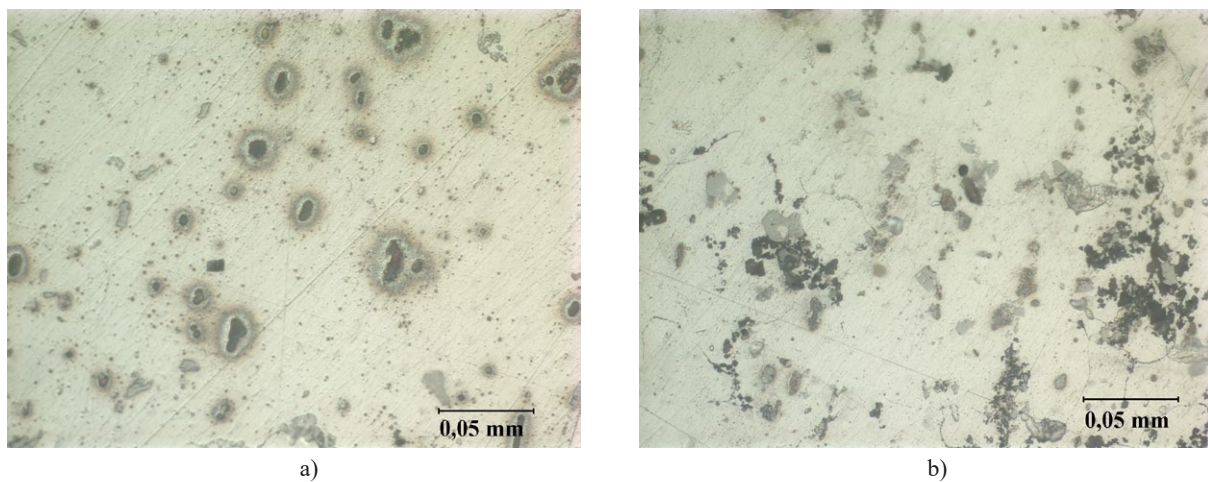

Fig. 10. A macroscopic image of the sample surface of alloy AW2017A as-delivered after electrochemical tests: pitting corrosion, b) an attack on the grain boundaries. Stereoscopic microscopy
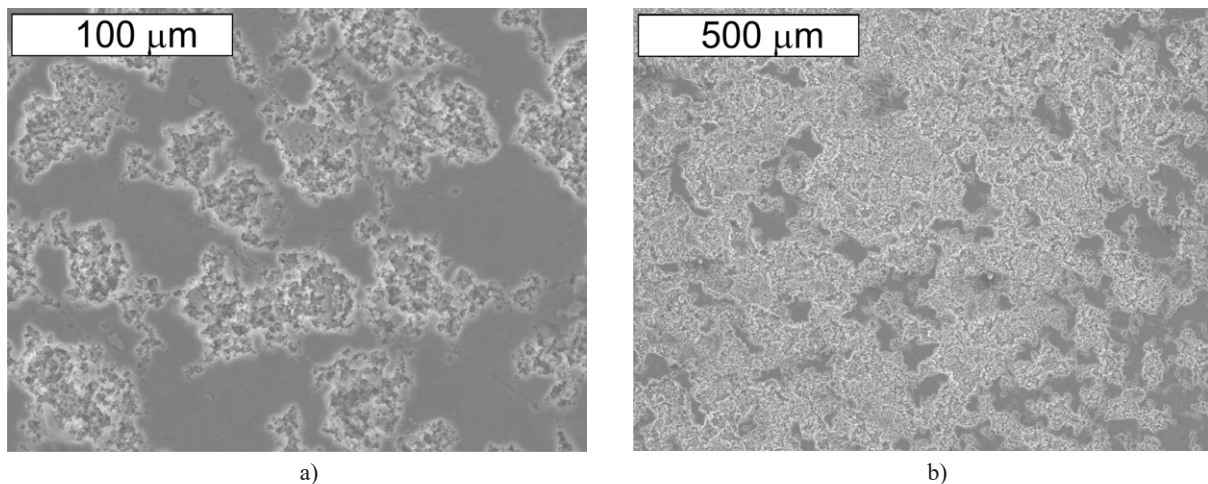

Fig. 11. An image of the sample surface of alloy AW2017A as-delivered after electrochemical tests finished at the potential of: a) +150 mV, b) +250 mV in respect of E_{corr}. SEM
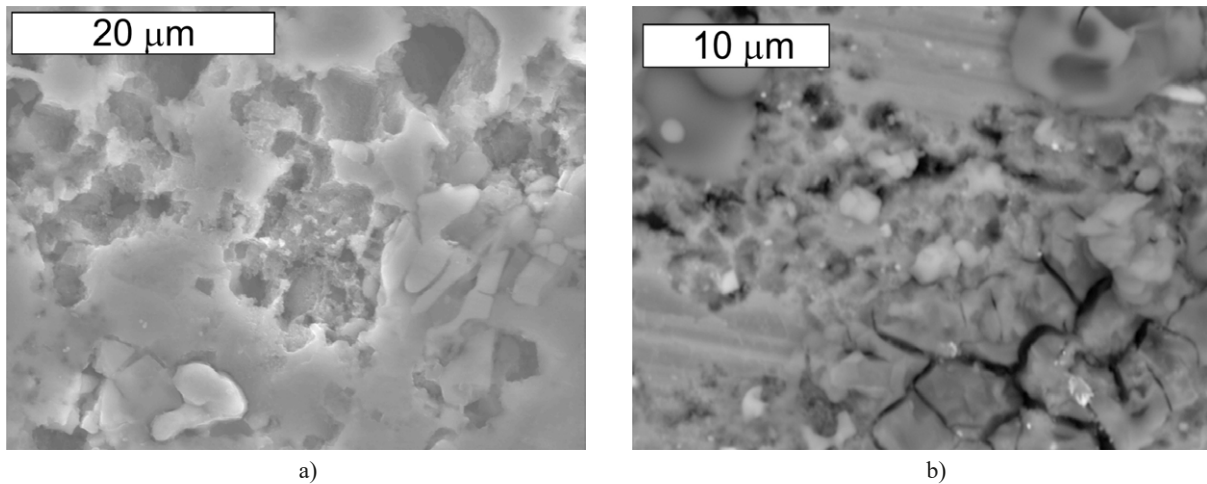
Fig. 12. An image of the sample surface of alloy AW2017A as-delivered after electrochemical tests finished at the potential of: a) +150 mV, b) +250 mV in respect of E_{corr}. SEM

alloy after plastic deformation. At the same time, on the surface, in the areas of its presence, corrosion micro-pits will be formed. On the other hand, we should consider the fact that the precipitates occurring in agglomerations which are not far from the surface can obtain access to the corrosive solution through dissolution of the solid solution around other intermetallic phase precipitates. In such a case, the corrosion will propagate from the surface particles to those located in the deeper areas from the surface, which can result, at a further stage, in the occurrence of intensive local corrosion.

The microscopic observations conducted after the electrochemical tests of alloy AC2017A confirm a similar effect of phase Al_2Cu on the occurring corrosion processes, also in the case of as-cast alloy AC2017A. However, the large precipitates present in the microstructure favour corrosion of the solid solution mainly in their own surrounding (Fig. 13). This

leads to much deeper changes than in the case of the alloy after plastic deformation, and, at the same time, it clears the path for the corrosive solution. This type of circumferential damage present around the cathodic phase is described in the literature as "cathodic corrosion" [42]. Corrosion initiated around the precipitates may lead to a loss of coherence and the formation of micro-pits on the surface of the corroding element. In such a case, the large and hard particles of phase Al_2Cu moving into the working area favour a possible tribological destruction of the details cooperating with it. The surface changes occurring as a result of cathodic precipitates, if they are distributed inside the grains, can be of big importance, not for a material loss caused by corrosion, but rather as potential areas of initiation of corrosive fatigue and formation of fatigue cracks. There are experimental data which confirm that corrosive cracking is often initiated in areas with corrosive pits [43].
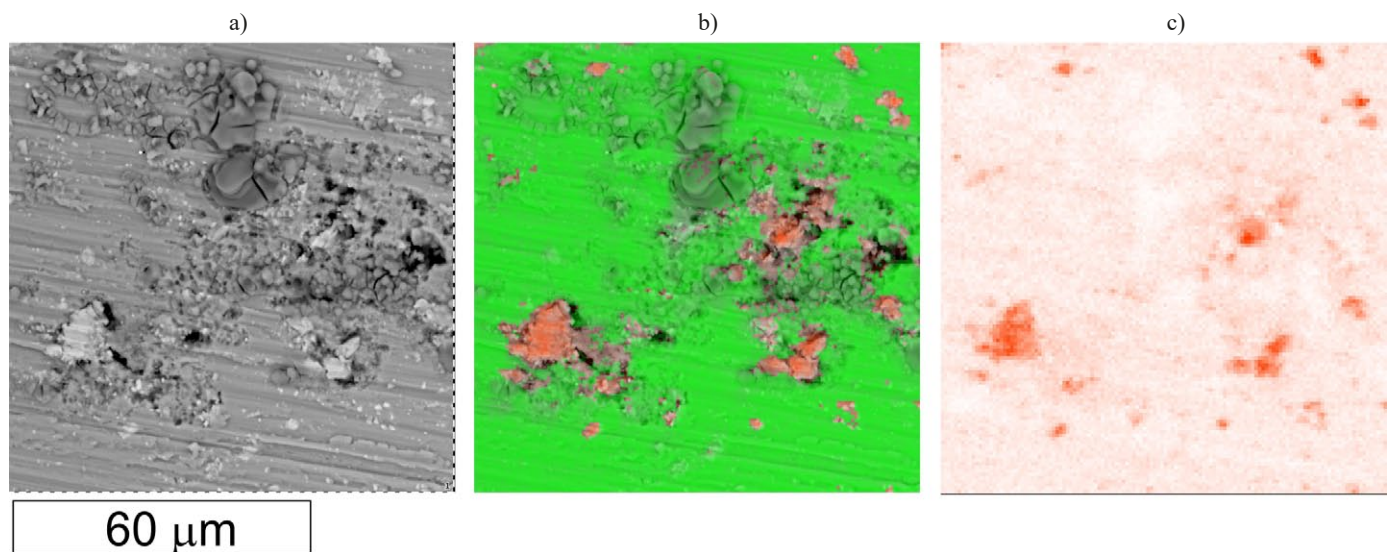

Fig. 13. a) A microscopic image SEM of the sample surface of alloy AC2017A as-cast after electrochemical tests finished at the potential of +150 mV in respect of E_{corr}. Visible aluminium solid solution dissolution around the cathodic precipitates of phase Al_2Cu present in the microstructure of alloy AC2017A, b) a SEM image from Fig. a compiled with the aluminium and copper distribution obtained by the EDS method, c) the copper distribution on the surface of the area shown in Fig. a

Comparing the results obtained in the tests, we can state that the presence of large precipitates located at distances typical of casting alloys favours intensive corrosion. In turn, a significant amount of fine-dispersive precipitates at the initial stage of corrosion can work as a barrier counteracting the corrosion processes. Such an effect can be explained by the ability of anodic phase passivation [12]. In such a situation, the presence of a fine-dispersive cathodic element can facilitate passivation of a more electro-negative phase and initially hinder the corrosion development. This also remains in agreement with the theory that, in the case of a control of the diffusive work of the corrosion micro-cells, the corrosion current intensity is directly proportional to its dimensions [12].

6. Summary

The presented investigation results expand the existing knowledge in the area of the effect of microstructure refinement caused by plastic deformation on the corrosion resistance of metallic materials, especially aluminum alloys. In the summary of the conducted studies, we should conclude that:

1) An increase of the dispersion degree of phase Al_2Cu in a casting alloy causes an intensification of the corrosion processes caused by an increase of their cathodic activity. A significant amount of fine-dispersive precipitates in alloys after plastic deformation at the initial stage of corrosion can work as a barrier limiting the development of corrosion processes as a result of anodic passivation, which limits the corrosion rate. This is manifested by the obtained higher values of anodic currents in the case of as-cast alloy AC2017A compared to wrought alloy AW2017A in state T451. The alloy formed thought plastic deformation demonstrated a more positive value of corrosion potential, which should be connected with the presence of cathodic precipitate-hardening phases in the alloy microstructure.

2) In the case of the presence, in the element's surface layer, of single and isolated precipitates of this phase, they will play the role of an active cathode at the initial stage of corrosion development. The preferential dissolution of the substrate taking place around these precipitates will predispose components made of a material with such properties for pitting corrosion with their simultaneous mechanical separation, especially under the conditions of a coexistence of tribological operation. The reduction of the phase Al_2Cu content occurring in this way will in time limit the corrosion processes as, on its surface, the material becomes quasi-homogeneous.

3) A situation when phase Al_2Cu occurs in agglomerations of precipitates with small distances inbetween will favour a better penetration of the corrosive solution into the material and facilitate the corrosion processes in the aluminium solid solution as the corrosive solution obtains an easier path cleared by the corrosion propagating from the particles on the surface to those located in deeper areas of the material.

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