



## EFFECT OF HEAT TREATMENTS ON THE CORROSION BEHAVIOR OF HIGH STRENGTH ALUMINUM ALLOY

Azarias Mavropoulos<sup>1\*</sup>, Stefanos Skolianos<sup>2</sup>

<sup>1,2</sup>Department of Mechanical Engineering, Faculty of Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece.

### Abstract

7xxx series aluminum alloys (Al-Zn-Mg-Cu) have been widely used in recent decades in aerospace applications because of their high strength and low density. However, these alloys are susceptible to various forms of localized corrosion such as exfoliation corrosion (EC), intergranular corrosion (IC) and stress corrosion cracking (SCC). In order to evaluate the corrosion behavior of the alloys various laboratory accelerated corrosion tests have been developed, which, useful though they may be, are nonetheless unable to simulate the actual corrosive environment and reveal the actual mechanism of corrosion. In this work the progress of corrosion of solution heat treated, aged and overaged AA7075 aluminum alloy specimens was studied systematically by using a controlled humidity chamber that is a milder environment than that of laboratory tests and thus closer to operating conditions. The systematic study of the specimens indicated that the corrosion behavior improved with heat treatment of aging and overaging, while the mechanism of corrosion starts as pitting and progresses as intergranular corrosion.

**Key Words:** AA7075, corrosion, humidity controlled chamber, aging, overaging.

### 1. INTRODUCTION

Aluminum alloys of series 7xxx (Al-Zn-Mg-Cu) are widely used in the production of aircraft components and structures that generally require a combination of high mechanical strength and corrosion resistance [1, 2]. However, these alloys are susceptible to various forms of localized corrosion such as exfoliation corrosion (EC), intergranular corrosion (IC) and stress corrosion cracking (SCC). Exfoliation corrosion is a form of intergranular corrosion, which occurs at the boundaries of grains, elongated in the rolling direction. Since the volume of the corrosion products is greater than that of the original metal the surface layers of the metal are lifted giving rise to its exfoliation [3, 4].

To evaluate the strength of the alloys in the various forms of localized corrosion various tests have been developed. In particular, the corrosion tests of aluminum alloys are divided into two

categories, namely long-term tests and laboratory tests. In long-term tests specimens of material are exposed to certain natural environments such as a marine, rural, urban or industrial environment [5-7]. A major drawback of these tests is the long time needed for evaluating the corrosion resistance, because of the relatively mild corrosive environment. This time can vary from a few years to decades depending on the material and the corrosive environment. On the other hand, due to the actual operating conditions, contrary to the laboratory tests, these tests provide a reliable assessment of the corrosion resistance of materials.

The laboratory tests were developed to provide a quick corrosion resistance assessment of materials since often the rapid development of new alloys and procedures allows no time for their evaluation through extensive testing. The accelerated laboratory tests have come to address this gap. However, simulating real environment and deriving reliable comparable results with the long duration tests constitute major challenges for laboratory testing [8-9].

It is noteworthy that the majority of the works on the corrosion behavior of aluminum alloys rely on accelerated laboratory tests in an effort to draw fast results. Few studies on the corrosion of alloys exposed to the atmosphere are available [5-7] as they require several years to extract reliable results, while a very small amount of studies are related with humidity controlled chambers.

The corrosion resistance of 7xxx series aluminum alloys and their mechanical properties are in general directly affected by specific heat treatments. Specifically, alloys having undergone hardening heat treatment by precipitation - aging (T6) show little resistance to localized corrosion. To increase their resistance, they are subjected to various overaging heat treatments such as T73, which nevertheless reduce their mechanical strength by 5% -10% [10]. In order to address the above problem the heat treatment of retrogression and re-aging (RRA) has been introduced. According to this, the alloy is initially subjected to T6 heat treatment, and then retrogresses to an intermediate temperature below the solvus for a short period of time to partially or fully dissolve precipitates such as GP zones and MgZn<sub>2</sub>. Finally, the alloy undergoes reaging similar to T6, where  $\eta'$  precipitates within the grains of the material as in T6, and  $\eta$  at the grain boundaries as in T7. This characteristic microstructure greatly improves resistance to stress corrosion cracking without concomitant reduction in the mechanical strength [10]-11].

In the present investigation, the development of corrosion of AA7075 in solutionized, aged and overaged conditions, was systematically studied in an environment milder than the one of the laboratory tests and closer to operating conditions by using a controlled humidity chamber.

## 2. Materials and Methods

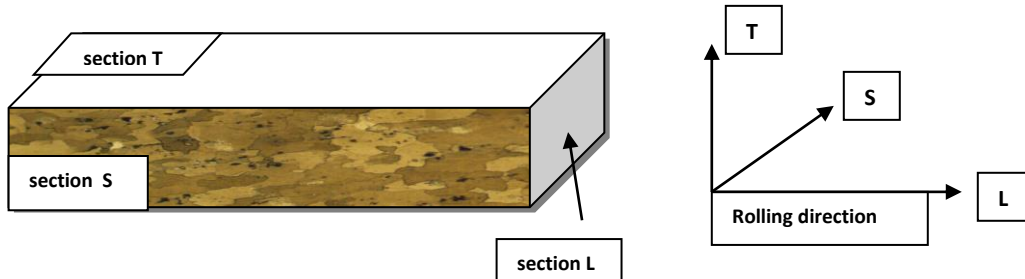
Aluminum alloy AA7075 -T651 was supplied as a plate, 1020x2020x10mm. The chemical composition of the material is shown in Table 1:

**Table 1:** Chemical composition of the original alloy AA 7075 T651

Element	Zn	Mg	Cu	Fe	Si	Cr	Mn	Ti	Ni	Al
w.t %	5.8	2.5	1.5	0,15	0.06	0.2	0.06	0.03	0.06	bal.

### 2.1 Specimen preparation

Specimens for the heat treatments were properly prepared from the above material. More specifically, samples 50x10x3mm were removed from the plate so that the large dimension would be in the direction of rolling. This orientation of the test specimens was selected because the T surface has elongated grains due to rolling, thus being more sensitive to various forms of localized corrosion. The T surface of specimens was polished with an 800-grit polishing paper. The metallographic sections of the original alloy plate are shown in Figure 1.



**Figure 1.** Metallographic sections of the initial AA 7075 aluminum alloy

## 2.2 Heat treatment

The following heat treatments were performed [12]:

- a) solution heat treatment (SW): the specimens were solutionized at 480°C for 1h and then water quenched.
- b) precipitation aging treatment (T6): solutionized specimens (SW) were aged at 120°C for 24h and then air-cooled.
- c) overaging treatment (T73): solutionized specimens (SW) were kept at room temperature for 24 hours then heated at 107°C for 7 hours to start the formation of GP zones and then at 163°C for 24 hours to form mainly  $\eta$  but also  $\eta'$  phase.
- d) retrogression and re-aging (RRA): aged specimens (T6) were heated at 200°C for 1 hour and then re-aged at 160°C for 16 hours [15]. In this way the microstructure of the T6 heat-treatment within the grains ( $\eta'$  phase) is maintained while at the same time the development of precipitates in the grain boundaries as in T7 heat-treatment is enhanced.

Following heat treatments, the T surface of the specimens was polished to 1 $\mu$ m and etched with Keller's reagent (190ml H<sub>2</sub>O, 5ml HNO<sub>3</sub>, 3ml HCl, 2ml HF) for 25 sec. The microstructures were studied by optical and scanning electron microscope (SEM) while the intermetallic compounds were characterized by EDS.

## 2.3 Transmission Electron Microscopy (TEM)

Also the specimens studied in transmission electron microscopy (TEM), JEOL 100 CX (100KV), to investigate the precipitates having a size of a few nanometers and can not be detected by other methods. More specifically, in order to observe in TEM specimens were ground mechanically to a thickness of about 100 microns. Then cut into 3mm diameter disk form, followed by electrochemical polishing on Struers device (Tenupol-3) with a solution of 20% HNO<sub>3</sub> and 80% CH<sub>3</sub>OH.

## 2.4 Corrosion tests in a controlled humidity chamber

Using a controlled humidity chamber the corrosion behavior of three sets of samples subjected to the heat treatments described above (SW, T6, T73 and RRA) was investigated. The conditions inside the chamber were: relative humidity 90 % Rh and temperature 35°C. These conditions were selected in such a way to accelerate corrosion in a relatively mild corrosive environment. Prior to corrosion in the humidity chamber the specimens were pre-corroded in a salt spray chamber for 72 hours to activate corrosion. The three sets remained in the chamber for 30, 90 and 120 days respectively in order to monitor the progress of corrosion.

The specimens were also weighed before and after the exposure in order to quantify the corrosion resistance. More specifically, there were three weighings, one before the exposure, one immediately after the exposure without cleaning the samples from the corrosion products and one after the removal of the corrosion products. The cleaning of corrosion products was performed with HNO<sub>3</sub>, sp gr 1,42, according to the ASTM G1-03 standard [13].

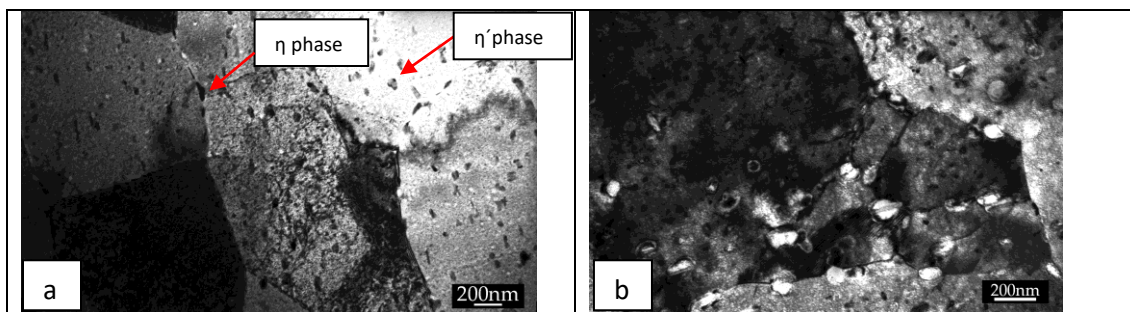
Stereomicroscope and SEM were used to study the morphology of the corroded specimens before and after chemical cleaning and to identify the corrosion products. was studied by a stereo microscope to evaluate the corrosion behavior.

Finally, metallographic sections were made in order to measure the depth of corrosion and quantify the progress of the phenomenon.

## 3. Results – discussion

As already noted the changes that occur in the microstructure of the material when submitting to various heat treatments involving the precipitation and maturing of  $\eta$  phase precipitates, having a size of several nanometers. Therefore was considered appropriate to study the material in the transmission electron microscope (TEM).

In the following Figure 29 are shown microphotographs of the specimen AA7075 T651 AR and over-aging T73 by transmission electron microscopy.



**Figure 2:** Microstructure of aluminum alloy AA7075 by heat treatment, a) aging precipitation T651 (AR), b) over-aging T73. Transmission electron microscope (TEM).

In the above figure 2 presents comparative microphotographs TEM of the specimens AA7075 T651 (AR) and AA7075 T73

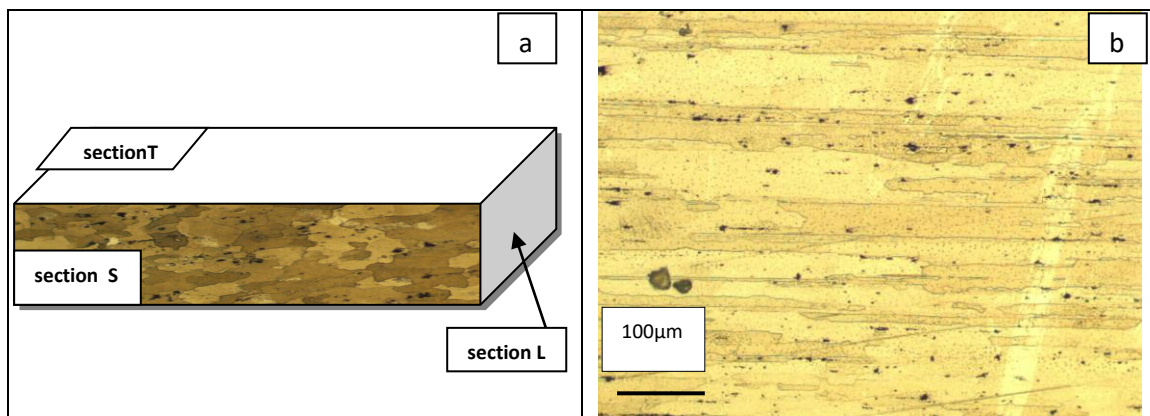
Figure 2a shows the precipitates of the  $\eta'$  phase into the matrix and precipitates of the  $\eta$  phase at the grain boundaries [14]-[16].

Figure 29b clearly shows that the microstructure of the alloy AA7075 by over-aging heat treatment T73, exhibits larger in size,  $\eta$  phase particles at grain boundaries and within them, in relation to the aging precipitation treatment T651. This is due to the largest aging time during overaging the alloy leading to the maturation of the  $\eta$  phase particles. The largest size of the  $\eta$  phase particles in the over-aging treatment explains the higher resistance to localized corrosion because reduced preferential anodic paths at grain boundaries which promote intergranular corrosion.

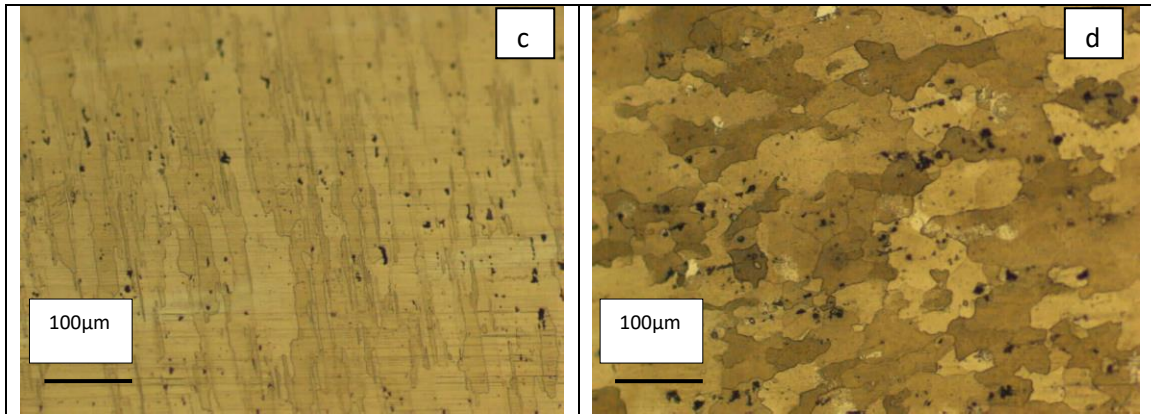
Laboratory exfoliation corrosion tests (exco tests) presented in a previous work were not able to distinguish the effect of heat treatment on corrosion resistance, as they provided only qualitative results about the localized corrosion of 7xxx series aluminum alloys. Tests carried out in a salt spray chamber provide a better simulation of the natural environment, as the corrosive medium is milder than that of the exco test [17]. However, in order to better simulate the natural environment and to study the corrosion behavior of 7xxx series aluminum alloys in conditions close to the operating, corrosion tests were performed in a controlled humidity chamber. The main advantage of these tests was a better simulation of the atmospheric conditions. On the other hand longer time is required for the development of the phenomenon.

To clarify the mechanism of corrosion of 7xxx series aluminum alloys, morphological characteristics of corroded surfaces of alloys were combined with their microstructure characteristics.

The microstructure of the initial AA7075-AR on sections L, T and S is shown in Figure 3. On section T, strongly elongated grains, due to successive rolling, are evident, Fig. 3b, while on section L the grains are less elongated, Fig.3c. Finally, on the rolling surface, Fig. 3d, the grains appear more equiaxial. The difference of grain elongation that observed in the three sections of the material affects the corrosive behavior of the alloy.





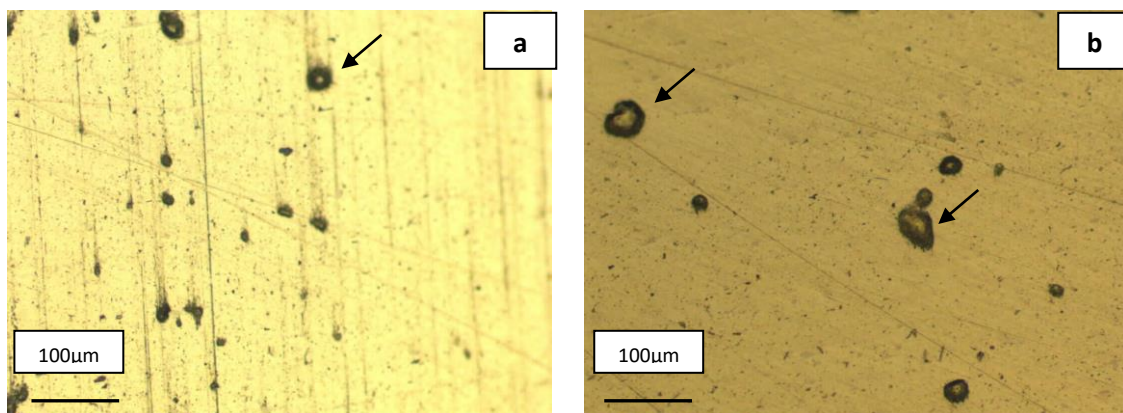


**Figure 3:** Microstructure of AA 7075-AR, a) surface encoding, b) cross section T, c) cross section L, d) cross section S (optical microscopy).

The microstructure of the initial alloy consists of Al, Zn and Mg solid solution and of intermetallic compounds at the grain boundaries and within them. The intermetallic compounds were formed during casting by the interaction of alloying elements with insoluble impurities such as Fe and Si [18-19]. They are easily detected by optical and scanning electron microscopy because their size ranges from few microns to 20 microns. Their shape is irregular and aligned in the direction of rolling. The intermetallic compounds identified by EDX were  $Al_7Cu_2Fe$ , and  $Al_4Si$ .

In 7xxx series aluminum alloys  $MgZn_2$  precipitations are more anodic compared to the matrix [20-21]. Therefore, precipitation of these particles at the grain boundaries during aging makes the grain boundaries more anodic in relation to the matrix. This provides an anodic path for localized corrosion along the grain boundaries, and is responsible for the susceptibility of the alloys to intergranular corrosion.

In order to verify that the intermetallic compounds serve as nucleation points for pitting corrosion, the T surface of AA7075 alloy specimens with T651 (AR), SW, T73 and RRA heat treatments was studied with optical microscopy, after 90 days exposure to controlled humidity chamber without etching (Figure 4).

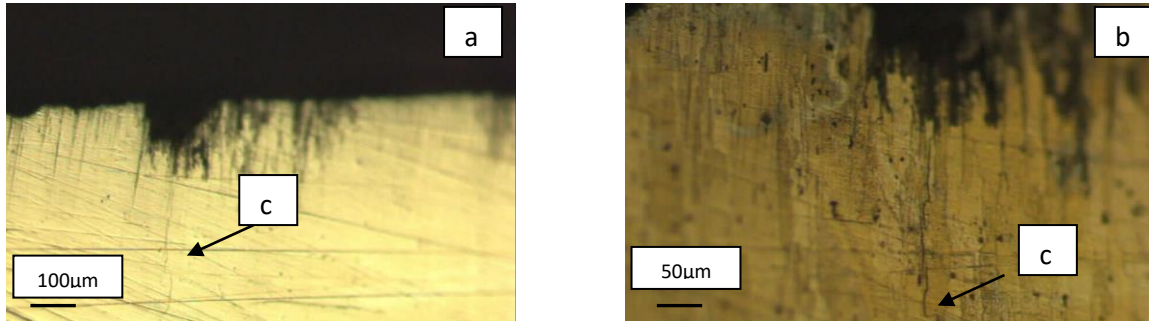


**Figure 4:** T section of AA7075 with a) T73 and b) RR heat treatments after pre-corrosion and 90 days exposure to controlled humidity chamber. No etching. (optical microscope)

It is evident from figure 3 that intermetallic compounds cause dissolution of the adjacent region of the matrix (arrows).

Figure 5 shows the microstructure of the L section of a SW sample with no etching, Fig. 5a, and with etching, Fig. 5b. It can be seen from Fig. 5a pitting corrosion on T surface as well as selective dissolution of the grains on the bottom of the pit which proceeds in depth. It is noteworthy that at the point where the dissolution of the grain ends a filament of intergranular corrosion (point c) is developed, which evidently will serve as a starting point for the dissolution of a new grain.

Fig. 5b, shows the same region of the specimen but after etching. The intergranular corrosion at the grain boundaries (point c) is clearly illustrated.

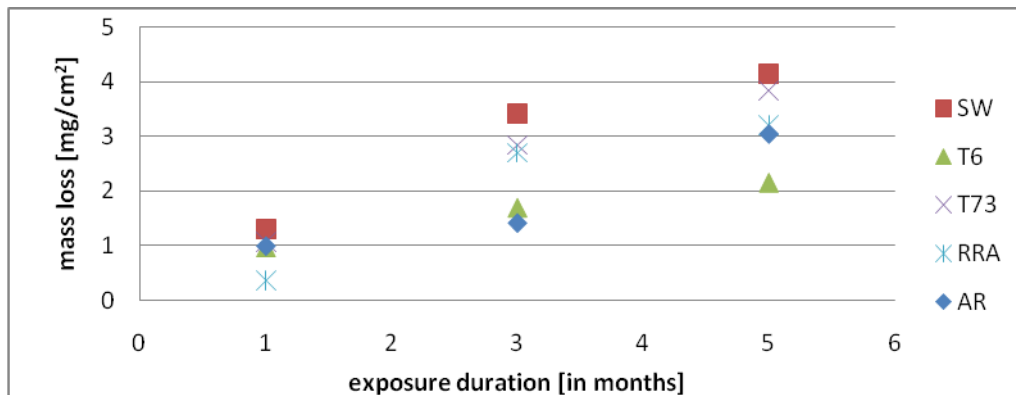


**Figure 5:** Specimen of AA7075-SW after 90 days of exposure in a salt spray chamber a) no etching, b) etching with Keller's reagent (optical microscope).

One of the problems of laboratory corrosion testing, beyond the inaccurate simulation of atmospheric conditions, is the qualitative assessment of the phenomenon and the inability to evaluate it with quantitative data. The experiments in controlled humidity chamber provide the ability to monitor the development of the phenomenon of localized corrosion in conditions similar to the operating conditions of the alloys.

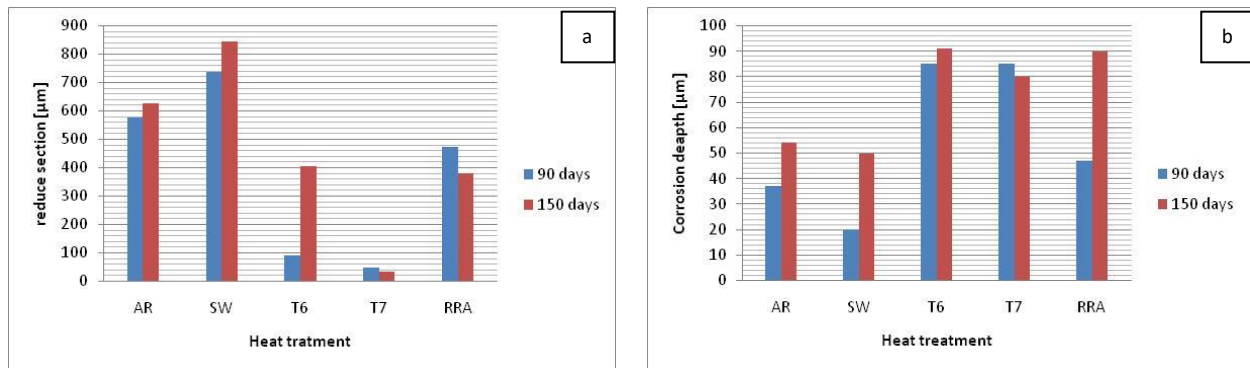
To address this problem, quantitative data on the development and extension of localized corrosion were extracted by measuring the mass loss of the specimens after exposure along with depth measurements of the corrosion that causes a reduction in the cross-section of the specimens.

Figure 6 illustrates the mass loss measurements for the specimens after heat treatments.



**Figure 6:** Mass loss of AA 7075 alloys with AR, SW, T6, T7 and RRA heat treatments, after exposure for 30, 90 and 150 days to controlled humidity chamber (90% Rh, 35 °C).

The above comparative presentation illustrates an almost linear change in the specimen's weight. However, the results of these measurements should be evaluated and used with particular caution since, as established by the observation on the optical microscope, the damage to these specimens caused by corrosion is extremely localized. The evaluation of corrosion exclusively with mass loss measurements is indicated only in cases that exhibit uniform corrosion. In this particular case this happens only in the case of specimen T73. It was therefore necessary to measure the penetration depth of corrosion in metallographic sections of the test specimens. The penetration of corrosion on the T surface and the S rolling surface was measured on metallographic sections L using optical microscope with the aid of a special software. Figure 7 shows the measurements of the corrosion depth on the S and T surfaces for various treatments. Figure 7a depicts a strong increase in the corrosion depth in T6 heat treatment, while this is not observed in other heat treatments. Figure 6b shows the development of the corrosion depth on the S surface of the specimens after 90 and 150 days of exposure to a controlled humidity chamber. On the S surface, mostly exfoliation corrosion of an approximate depth of 90 microns was observed by a stereomicroscope and an optical microscope. In contrast, at the T surface appears selective dissolution of grains, which grows intensely at a depth of 844 microns in SW treatment. This anisotropic behavior between T and S surfaces, regarding the type and extension of corrosion, is evidently owed to the highly elongated grains on T surface in relation to S surface.



**Figure 7:** Development of cross-section reduction due to corrosion a) on the T surface of the specimens and b) on the S surface of the specimens after 90 and 150 days of exposure in controlled humidity chamber.

#### 4. Conclusions

- Better simulation of the atmospheric conditions and more reliable results are obtained by corrosion testing in controlled humidity chamber than by accelerated laboratory corrosion tests such as salt spray or exco tests. However, more time is needed for the development of the phenomenon.
- The morphological characterization of corroded surfaces in a humidity controlled chamber has shown that corrosion starts in the form of pitting corrosion at the points of intermetallic compounds. The pits then grow in size and develop along the direction of rolling. At the base of



the pits intergranular corrosion is developed, leading to a selective dissolution of the material grains.

- Retrogression and re-aging treatment RRA exhibits improved corrosion resistance compared to the SW and T6 treatments.

In conclusion, we could say that T73 overaging heat treatment could be the answer to problems of localized corrosion in applications that do not require high mechanical strength. However, in applications where a combination of increased mechanical strength and resistance to localized corrosion is required, RRA treatment could be an alternative to T6 maximum strength treatment. In the future, developing aluminum alloys and production processes that reduce the creation of intermetallic compounds should be explored, as the latter are the starting points of pitting corrosion. Equally essential would be to study heat treatments similar to RRA, which will affect the microstructure of the material in such a way as to reduce anodic preferential paths conducive to intergranular corrosion, while maintaining the desired mechanical strength .

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### Author Profile



**Azarias Mavropoulos:** Studied Mechanical Engineering in the Mechanical Engineering Department of the Aristotle University of Thessaloniki in 1998. Received his MSc in "Processing and Technology of Advanced Materials" in the same department in 2000. Also received his Diploma in "Technical Teachers' Training" of the Technical and Vocational Teachers' Training Institute (PATES-SELETE) in Thessaloniki in 2002 and his MEd in "Models of Designing and Planning Educational Units" of the University of the Aegean in 2006. He received PhD from Aristotle University of Thessaloniki in 2011. He has got quite a lot of experience in designing, planning and conducting National and European programs and has also worked for some years as an enterprises consultant. He is a Teaching and research associate in Aristotle University of Thessaloniki.