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Influence of Retrogression and Re-Aging Heat Treatment to Stress Corrosion Cracking Resistance on Al-Zn-Mg-Cu Alloy

Deraman R.[1], Aziz M. R. and Y. Yaakob

Faculty of Mechanical Engineering
Universiti Teknologi MARA (UiTM), Malaysia
[1]Email: rasdi925@ppinang.uitm.edu.my

ABSTRACT

The Al-Zn-Mg-Cu alloy is classified as a high strength to weight ratio material and is widely used in the aerospace structures. This alloy is susceptible to severe localized corrosion induced by heat treatment. The objective of this study is to elucidate alternative heat treatment techniques, which reduce the alloys susceptibility to Stress Corrosion Cracking (SCC). A series of different heat treatments have been performed in the Al-Zn-Mg-Cu alloy using cube shaped and C-ring specimens that had been T6- and T7-tempered and undergone Retrogression and Re-aging (RRA) heat treatments. The specimens were exposed to hardness testing, optical testing and immersion testing in a corrosive environment. The effectiveness of the heat treatments was evaluated with respect to improvements in corrosion resistance and the longevity of the Al-Zn-Mg-Cu alloy. The susceptibility of the Al-Zn-Mg-Cu alloy to SCC has been directly related to the precipitation of $MgZn_2$ particles at the grain boundaries. Precipitation hardening of Al-Zn-Mg-Cu alloy increases the hardness of the material, but increases susceptibility to SCC failure. RRA treatment greatly improved the corrosion resistance and longevity of the alloy combined with minimal strength reduction.

Keywords*: Al-Zn-Mg-Cu Alloy, Stress Corrosion Cracking, Precipitation, Retrogression, Re-aging*

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Introduction

Aluminium and its alloys are categorized as low density materials, with respect to steel, possessing high electrical and thermal conductivities, and resistant to corrosion in atmospheric environments. The strength and hardness of some metal alloys may be enhanced by the formation of extremely small uniformly dispersed particles of a second phase within the original phase matrix, which interfere with the motion of dislocations; such phase transformations may be induced by appropriate treatments [1]. The formation of these particles occurs slowly at room temperature (natural aging), but can be promoted through heating in a temperature range of 100-200 °C (artificial aging).

Heat-treated Al-Zn-Mg-Cu alloy is widely used in many aircraft structure industries, but it is susceptible to Stress Corrosion Cracking (SCC). The susceptibility of this alloy is inherently linked to heat treatments, which change the microstructure of the alloy to yield more optimum mechanical properties. The low resistance to localized corrosion of particular microstructures represents a problem in the application of the Al-Zn-Mg-Cu alloy in the aerospace industry [2]. For the purpose of use in aircraft, the Al-Zn-Mg-Cu alloy is normally aged up to the T6 temper condition in order to increase the strength. However the T6 temper conditioned alloy is highly susceptible to SCC due to the exposure to continually applied stress. In order to produce an alloy with a more acceptable SCC resistance, the alloy has to be over-aged, which equates to the T7 tempered condition.

An investigation by Andrzej *et al*. [3] proposed exposing the Al-Zn-Mg-Cu alloy to Retrogression and Re-aging (RRA) treatment after achieving the T6 tempered condition to improve both the strength and SCC resistance. Viana *et al*. [4] state that the RRA treatment requires retrogression at higher temperatures than for tempering followed by re-aging. Robinson [5] suggests that retrogression is performed locally on a specimen at temperatures as high as 195 °C for 40 minutes followed by re-aging at 120 °C for 24 hours.

The presented work assesses the effect of the different heat treatments (T6-, T7-tempered and RRA) on the SCC of C-ring Al-Zn-Mg-Cu alloy specimens with a static load in corrosive environment. Microstructural changes, induced by the different heat treatments, are also investigated.

Methodology

The Al-Zn-Mg-Cu alloy chosen for this study was in the form of a recently manufactured thick rolled bar with dimensions approximately 1000 (L-Longitudinal) × 50 (LT-Long Transverse) × 50 mm (ST-Short Transverse). The mechanical properties of the Al-Zn-Mg-Cu alloy are presented in Table 1 [6].

Table 1: Mechanical Properties for as Received Sample of Al-Zn-Mg-Cu Alloy

Designation	Al-Zn-Mg-Cu
Young's Modulus (GPa)	70.33
Yield Strength (MPa)	515
Ultimate Strength (MPa)	557
Elongation (%)	14.7

In this investigation, two types of specimen were produced: the C-ring for stress corrosion cracking testing and cubes for hardness and microstructure testing. The cube shape was machined to 15 mm × 15 mm × 10 mm with a tolerance of ±0.05 mm. The Vickers hardness was measured using a load of 20 kg and a loading time of 20 seconds at various locations on the cube shaped specimens. Six C-ring specimens were produced using a CNC turning machine according to the ASTM standard G 38, Figure 1.

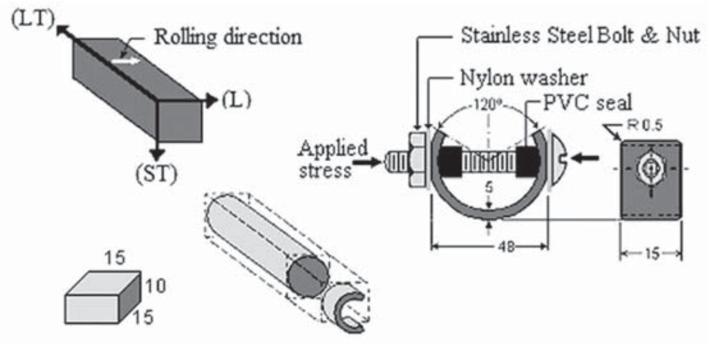


Figure 1: Sketches of the Orientation of Cube Shape and C-ring Specimens Employed
(All dimensions are in millimeters)

Two heat treatment methods were applied to the Al-Zn-Mg-Cu alloy; namely a conventional method (Table 2) and an RRA heat technique (Table 3). The RRA heat treatment required Retrogression (R) of T6 tempered specimens in a heated stirred oil bath. Upon completion of the retrogression the specimens were immediately cooled under a stream of flowing water. Finally the specimens were re-aged (RA) at 120 ± 5°C for 24 hours in an air-circulating electric oven. The final RRA specimens were stored in a refrigerator to avoid any adverse effects from exposure to ambient conditions.

Table 2: Conventional Heat Treatment Method Parameters

Test		1st stage		2nd stage		3rd stage	
Code	Condition	Temp. (°C)	Time (min)	Temp. (°C)	Time (hr)	Temp. (°C)	Time (hr)
CR1	As machined	-	-	-	-	-	-
CR3	T6 temper	490	30	120	24	-	-
CR7	T7 temper	490	30	120	24	175	5

Table 3: RRA Heat Treatment Method Parameters

Test		3rd stage (Retrogression)		4th stage (Re-aging)	
Code	Condition	Temp. (°C)	Time (min)	Temp. (°C)	Time (hr)
CR4	T6 + RRA	160	29	120	24
CR5	T6 + RRA	180	9	120	24
CR6	T6 + RRA	200	2	120	24

SCC tests were performed using C-ring specimens immersed in an aerated 3.56 wt % NaCl solution at a pH of 3 with a 2.75 mm deflection stress level. The failure time of the heat treated specimens is used to evaluate the SCC susceptibility. Jones [7] recommended that any two dissimilar metals or alloys are coupled in the presence of a corrosive electrolyte; one is preferentially corroded while the other is protected from corrosion. Thus, to avoid the bolt and nut holding the specimen in place from coming in electrical contact with C-ring specimen during the SCC test, a nylon washer and PVC seal were used, Figure 1. The C-ring specimen was stressed by tightening the bolt and the nut until the desired final outer diameter was attained. The stress applied to the C-ring specimens has been calculated according to Equation (1), Lesmana [8].

$$\sigma_{app} = \frac{4.\Delta E.t.Z}{\pi\left(\varphi_0 - t\right)^2} \qquad (1)$$

where

σ_{app} is applied stress (MPa),
E is the modulus of elasticity (MPa),
Δ is the change of out side diameter of C-ring due to stress applied (mm),
Z is the correction factor for curved beams,
t is the wall thickness (mm),
φ_0 is the outside diameter of C-ring before stressing (mm).

The stressed specimens were immersed into a test solution in a transparent corrosion cell using a glass holder. The immersion C-rings were observed periodically until specimen failure occurred.

Results and Discussion

The standard composition of the Al-Zn-Mg-Cu alloy is presented in Table 4 together with the specimen chemical compositions determined from XRF analysis. The results indicate that the chemical compositions of the machined alloy specimens are very similar to those of the standard Al-Zn-Mg-Cu alloy, where Zn and Mg are the major elements. The addition of Zn and Mg to the aluminium wrought alloys improves the strength of the alloy, especially in the range of 3-7.5 % Zn. Magnesium and zinc form $MgZn_2$, which results in a far greater response to heat treatment than that for the binary aluminium-zinc system. Smith [9] stated that the intermetallic compound, $MgZn_2$, is the main strengthening precipitate for this alloy and may be attributed to the high solubility of zinc and magnesium, which enables the formation of high density precipitates with intrinsic high strength. The improved stress corrosion cracking resistance may be attributed to the presence of chromium.

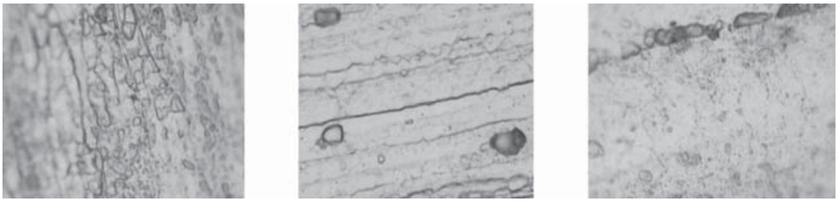
Although alloys tend to be relatively more isotropic, they can exhibit significant anisotropic behaviour. Bayoumi [10] reported that the failures do not usually occur as result of engineering applied stresses, but rather that residual stresses may be compounded and result in failure. Residual stresses may be inherent aspects of the fabrication process. To evaluate such residual stresses cube shaped specimens were viewed using an optical microscope in three different directions to elucidate the alloy

Table 4: Standard and Sspecimen Al-Zn-Mg-Cu alloy Chemical Composition

Elements	Weight Percent (wt %)	
	Standard Composition of Al-Zn-Mg-Cu alloy	As-machined sample Composition
Aluminum (Al)	90.07	89.971
Zinc (Zn)	5.6	5.200
Magnesium (Mg)	2.5	2.800
Copper (Cu)	1.6	1.500
Chromium (Cr)	0.23	0.160
Others	…	0.369

structure on a microscopic level and ascertain the existence of residual stress points.

The orthographic micrographs of an Al-Zn-Mg-Cu alloy specimen, Figure 2, shows the grain structures of the specimen after RRA heat treatment. The figure clearly illustrates that these alloys have a highly directional grain structure. The directional effects relate to the rolling direction and based on the fragment grain flow it is evident that the Al-Zn-Mg-Cu alloy specimen derives from a flat rolled product. RRA treatment produces microstructures that closely match those found in the SCC resistant T7 specimens. Furthermore, dislocations which invariably develop during quenching from solution are annealed during the retrogression treatment, which contributes to better SCC performance [11]. The specimen was etched in order to enable distinction between the recrystallized grains (clear) and the unrecrystallized grain fragments, which appear dark due to the precipitation of fine subgrains at the boundaries.



(a) L–LT plane (b) L–ST plane (c) ST–LT plane

Figure 2: Optical Microscope Pictures (magnification 500×) of Cube Shaped Specimen C4 Grains in Different Planes Retrogressed at 200 ºC for 2 minutes followed by Re-aging at 120 ºC for 24 hours

The average hardness values for the differently treated Al-Zn-Mg-Cu alloy are presented in Figure 3. The conventional treatment, which constitutes solution heat treatment followed by quenching (CS2), results in a significant drop in hardness compared to the untreated received specimen (CS1). The decrease in hardness is caused by the dissolution of $MgZn_2$ particles (η phase), which provide greater strength to the Al-Zn-Mg-Cu alloy, and the formation of a single solid phase, which is relatively soft and weak.

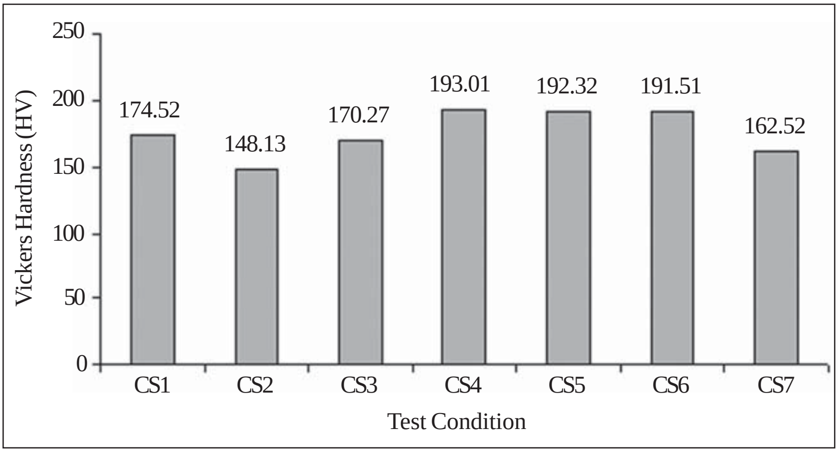


Figure 3: Average Hardness of Different Heat Treated Al-Zn-Mg-Cu Alloys

After solution heat treatment the hardness of the T6 tempered specimen (CS3) has increased due to the effect of aging, whereby the solute particles diffuse into clusters that distort and strengthen the material. The formation of finely dispersed second phase particles in the alloy induce lattice strain in the aluminium matrix that restricts dislocation flow and is the same phenomenon which occurs during the RRA heat treatment (CS4, CS5 and CS6). It is of note that the hardness for the over-aging specimen (CS7) decreases, because the precipitates begin to coarsen and the average particle spacing gradually increases due to heating at a high temperature (175 ^{o}C) for about 5 hours. The conclusion is that the RRA heat treatment is the best hardening technique, because both the RRA specimens exhibit improved hardness compared to the specimens acquired using the conventional treatment method.

The SCC investigation evaluated 6 C-ring units, which had undergone different heat treatments and been immersed in an aerated 3.56 wt%

NaCl solution at pH 3 held at room temperature under a stress level of 2.75 mm. The applied stress for each specimen was obtained using Equation (1), Table 5. The CR1 specimen is subjected to the lowest applied stress (274.35 MPa), all the other specimens are exposed to an applied stress in the range 282.37-309.83 MPa.

Table 5: Stress Level and Applied Stress for Each Specimen

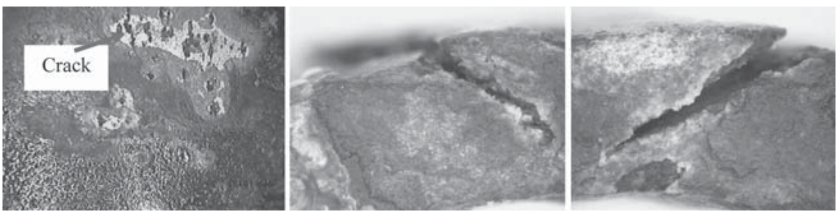
Code	t (mm)	$Ø_o$ (mm)	$Ø_f$ (mm)	Δ (mm)	$Ø_f/t$	Z	E (GPa)	σ_{app} (MPa)
CR1	4.96	47.91	45.52	2.75	9.66	0.934	31.20	274.35
CR3	4.97	47.85	45.46	2.75	9.63	0.931	33.39	294.21
CR4	4.99	48.05	45.64	2.75	9.63	0.931	34.76	304.95
CR5	4.98	47.94	45.54	2.75	9.63	0.931	34.82	306.28
CR6	4.99	48.04	45.64	2.75	9.63	0.931	35.30	309.83
CR7	5.00	48.03	45.63	2.75	9.61	0.930	32.11	282.37

The experimental results indicate that the RRA increases the SCC resistance of the alloy. Even though the initial applied stress is higher (for specimens C4, C5 and C6), the time of failure is longer (Table 6) than that for the T6 tempered specimen (CR3). Based on observation, cracking propagation for all specimens did not start at the centre of the C-ring, as shown in Figure 4. Theoretically, if the rectangular bar is bent to form a C-ring shape, the weak point may be located at the centre of the C-ring since it is the point of maximum bending and thus theoretical stress. However, in this investigation the C-ring was machined in the longitudinal and short transverse plane of the rolled bar direction, Figure 4. Thus, the orientation of grain particles will have an inherent effect on the strength of the C-ring, which is in accordance with the work of Bagab [10] who stated that the distribution of particles affects the hardness and yield strength. The short transverse grain orientation is far more susceptible to failure by SCC than the other two orientations, due to the flattening and elongation of the grain structure in the short transverse and longitudinal directions, respectively.

The T6 tempered specimen, which underwent RRA, (CR6) and the over-aged (CR7) specimen (CR7) did not fail for the duration of the test period (30 days). The specimens did however undergo exfoliation corrosion (Figure 5), whereby the surface alloy grains are lifted up by the force of expanding corrosion products occurring at the grain boundaries. Exfoliation

Table 6: Test Results for C-ring Heat Treated Specimens Immersed in an Aerated 3.56 wt% NaCl Solution at pH 3 and Room Temperature Under 2.75mm Stress Deflection

Code	Time of Failure
CR1	Fractured 6 days after immersion.
CR3	Fractured 10 days after immersed.
CR4	Started to crack after 15 days immersed and totally fractured 4 days later.
CR5	Started to crack after 17 days immersed and totally fractured 5 days later.
CR6	Unbroken in 30 days duration testing.
CR7	Unbroken in 30 days duration testing.

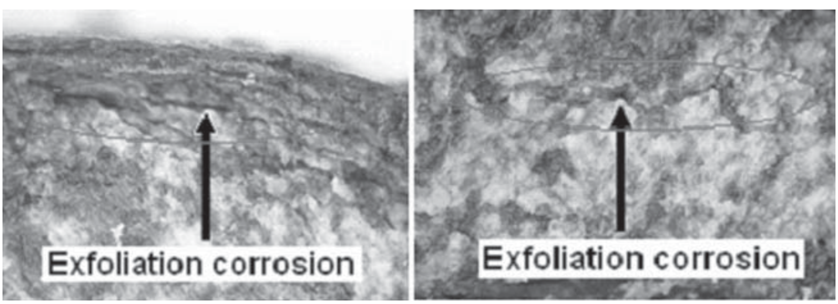


(a) Crack initiation on the topof the C-ring specimen CR1. Magnification 10×.

(b) Side view showed thecrack growth on thespecimen CR3. Magnification 7×

(c) Side view showed thecrack growth on thespecimen CR4. Magnification 7×

Figure 4: The Influence of Orientation and Grain Particles on the Cracking Propagation of the Alloy Specimens



(a) Specimen CR6. Magnification 12×

(b) Specimen CR7. Magnification 12×

Figure 5: Exfoliation Corrosion (a) The T6 tempered/RRA Specimen (CR6) and (b) the Over-aged Specimen (CR7)

[12] is most likely to occur in wrought products such as extrusions, thick sheets and thin plates formed by rolling, because of the resultant highly elongated grain structure. Andreatta *et al.* [2] reported that over-aging distinctly improves resistance to intergranular corrosion, because the size of the $MgZn_2$ particles at the grain boundaries increases their inter particle distance.

Conclusions

In this study, the microstructure and corrosion behaviour of Al-Zn-Mg-Cu alloys exposed to different heat treatments has been investigated and evaluated using a combination of stereo- and optical-microscopy. The following conclusions have been drawn:

1. Generally, Retrogression and Re-aging heat treatment decreases the stress corrosion/cracking susceptibility of the Al-Zn-Mg-Cu alloy in comparison to that for the T6 tempered alloy.
2. Stress-corrosion cracking failure can be minimized through design solutions, which reduce tensile stresses in the short transverse direction of the material.
3. Retrogression and Re-aging is more effective at higher retrogressed temperatures when combined with soaking for a short period of time and results in significant increases in the stress corrosion/cracking resistance of the alloy, but exfoliation corrosion is still evident.

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