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CORROSION BEHAVIOR OF THE Al-Zn-Mg-Cu ALLOYS WITH NICKEL ADDITIONS

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In this research, comparative study of corrosion resistance of aluminum based alloys and Al-alloys with nickel have been investigated. Several processes are conducted for the Al-Zn-Mg-Cu alloys and Al-Zn-Mg-Cu-0.5%Ni alloys were homogenized, aged then retrogressed and reaged; also, alloys were homogenized then the extruded thereafter heat treated. Al-Zn-Mg-Cu alloy and AlZn-Mg-Cu-Ni alloy samples after different treatments were subjected to corrosive media (acidic: 1.0M HCl) using weight loss method to evaluate their corrosion resistance. The consequences present that the precipitation for the base alloy samples treated led to enhance their resistance of corrosion. Furthermore, the gain of corrosion resistance for the Al-Zn-Mg-Cu-Ni alloy samples after the RRA treatment and thermomechanical with the RRA about of 52 and 75 %, respectively, more than what the Al-Zn-Mg-Cu alloy samples under same conditions. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to show the corroded surfaces.

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1. Introduction

In aeronautical industries due to their attractive comprehensive properties, such as low density, high strength, ductility, toughness and resistance to fatigue, Al–Zn–Mg–Cu alloys have been widely used as structural materials [1, 2]. However, Al–Zn–Mg–Cu alloys are susceptible to local corrosion, like pitting, inter-granular corrosion (IGC), exfoliation corrosion (EXCO) and stress corrosion cracking (SCC). [3-5]. A major corrosion issue with Al is the localized breakdown of the passive film, which lead to the induction and growing of corrosion cavities in chloride containing environments. New heat treatments of the Al–Zn–Mg–Cu alloys can be improved the corrosion resistance, optimum mechanical properties which changes the microstructure of the alloy in order to obtain [6, 7]. The specific microstructure of corrosion limits the application of the Al-alloys (7xxx) in the aerospace industry. Recently, investigators interested about reducing the corrosion susceptibility by controlled grain sizes, manufactured by means of severe plastic deformation, such as surface mechanical attrition and equal channel angular processing [8, 9] or adding rare earth elements as grain refiner, Bobby Kannan and Raja [10] and Fang and Chen [11] found that the resistance to SCC or EXCO of the Al-Zn-Mg-Cu alloy can be substantially improved by conquering recrystallization through Sc or Cr, Yb and Zr additions, respectively. Have been developed for the Al–Zn–Mg–Cu alloys several catalogs of ageing processes, among these processes in our previously studied, the retrogression and reageing has greatly promoted the application of Al-Zn-Mg-Cu alloys [12, 13]. In our research have achieved [14, 15], indicated that addition of nickel into the Al-Zn-Mg-Cu alloys, the greatest potential for developing new lightweight structural materials with excellent mechanical properties due to the formation of extremely fine which is offer, dispersed of the Al-Ni intermetallic compounds, that can effectively fine tune grains and stamp down recrystallization. However, to data, reports have not found about investigation the consequence of Ni additions and the retrogression and reaging on the corrosion behavior of the Al-Zn-Mg-Cu alloys. Therefore, the aim of this work is to study the synergistic

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effects of Ni micro alloying additions and the retrogression and reaging on the corrosion behavior of the Al-Zn-Mg-Cu alloys.

2. Experimental procedures

The materials used in this study were the Al-Zn-Mg-Cu alloys with and without Ni additions which produced with the chilling cast process cited in our previous studies [12-15]. The nominal compositions of the studied alloys are listed in Table 1. The terms “Base alloy”, “Alloy A” and “Alloy B” refer to as produced alloy, alloy with 0.1 and 0.5 wt. % Ni respectively. The chemical composition analysis was carried out using the arc-spark spectrometer.

Table 1. The nominal compositions of the studied alloys

No.	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Al
Base alloy	0.078	0.234	1.774	0.044	2.886	0.187	-	6.676	0.027	balance
Alloy A	0.114	0.265	1.543	0.043	2.665	0.188	0.557	7.076	0.053	balance

Alloys were casted. After the casting; two kinds of Al-Zn-Mg-Cu and Al-Zn-Mg-Cu-Ni alloys are homogenizing treated which followed by quenching in cold water immediately after each step. Thereafter the ageing at T6 temper then the retrogression and re-aging (RRA) process were conducted alloys according to [12, 16]. The second type of the process is after the homogenizing treatment an extrusion process was performed on the cast bars as in detail [13, 17] then also the ageing and the retrogression and reaging were conducted. To preparation of specimens for the corrosion tests, the specimen surfaces were ground with 1200 grit silicon carbide paper and then polished using 3µm diamond paste to obtain a good surface finish. The coupons were then washed in distilled water, followed by acetone, and then allowed to dry thoroughly. The corrosion tests were static immersion tests conducted at room temperature using the conventional weight loss method to an accuracy of 0.1 mg. Each specimen was first weighed before being immersed in 250 ml open beakers containing 200 ml of 1 M HCl solution and later taken out after 24, 48 and 72 h respectively. HCl acid solution was chosen as the corrodent for accelerated consequences. After each corrosion test, the specimen was immersed in Nitric acid for 1 min and gently cleaned with a soft brush to remove adhered scales. After drying thoroughly, the specimens were weighed again. The weight loss was measured and converted into corrosion rate expressed in millimeters per year (mm/y) as according to Eq. 1.

$$Corrosion\ rate\ (C.R) = \frac{K\ x\ W}{A\ x\ T\ x\ D} \tag{1}$$

Where,

$W = weight\ loss\ in\ mg = W_0\ - W_f$

$W_0 = original\ weight\ of\ the\ sample,\ W_f = final\ weight\ of\ the\ sample\ after\ immersion$

$D = Density\ of\ the\ sample\ in \frac{g}{cm3}$ $A = Total\ surface\ area\ of sample\ in\ cm^2$ $T = exposure\ time\ in\ hours$

The corroded surfaces were analyzed using scanning electron microscopy (SEM) coupled with the energy dispersive X-ray spectroscopy (EDS) was used.

3. Results and discussions

Generally it is assumed that aluminum reacted with oxygen to signifier the protective layer as follows:

$$2Al_{(metal)} + 3/2O_{2(gas)} \leftrightarrow Al_2O_{3(solid)} \quad (2)$$

From the solution, the oxide formed acted as a static barrier that isolated the metal. However, acid solutions may bear upon its properties. On the characteristics of the medium, disintegration of the protective layer or repassivation of the metal may come about depending [18].

$$\frac{1}{2}\, Al_2O_3 + 3H^+ \leftrightarrow Al^{+3} + \frac{3}{2}H_2O \quad (3)$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + e^- \quad (4)$$

The reformation of oxide layer under the conditions used in this study appears not to come about since an increased dissolution of Al was observed in all cases. Al dissolution in chloride solutions was largely investigated and its chemical mechanism almost clearly understood. It is agreed that several staircase are involved in the chemical mechanism of Al dissolution including the adsorption of chloride ions at the oxide surface, penetration of the oxide film by chloride ions, dissolution which come about beneath the oxide film at the metallic element oxide at the metal/oxide interface and Cl^-aided. This can be represented as follows [19]:

$$Cl^-(bulk\ solution) \rightarrow Cl^-(adsorbed\ on\ Al_2O_3.nH_2O) \quad (5)$$

$$Al^{3+}(in\ Al_2O_3.nH_2O) + 4Cl^- \rightarrow AlCl_4^- \quad (6)$$

Leads to oxide film thinning this process [20] and commencing the corrosion of the metal. Table 2 shows the result s of all the corrosion tests conducted on the base matrix alloy and the alloy A in as quenched, kinds of heat treatments and extruded then heat treated conditions in 1 M HCl solution for interval time included 24 h, 48 h and 72 h. These results are represented graphically in Figs. 1 and 3. Each tabulated is an average obtained from three identical tests.

Table 2 Corrosion rate of alloys samples for different procedures in HCL solution

Alloys	**Types of procedures**	**Corrosion rate (mm/y)**		
		After 24h exposure	**After 48h exposure**	**After 72h exposure**
Base Alloy	As quenched	30.414	21.735	17.942
	T6-H.T= (heat treated)	20.659	17.146	15.862
	RRA-H.T= (heat treated)	19.794	13.854	12.732
	T6-E.=(extruded then heat treated)	13.384	10.189	9.628
	RRA-E.(extruded then heat treated)	10.294	9.394	8.541
Alloy **A**	As quenched # 0.5%Ni	26.183	16.051	13.421
	T6-H.T # 0.5%Ni	15.571	13.289	12.634
	RRA-H.T # 0.5%Ni	14.491	11.465	10.531
	T6-E # 0.5%Ni	8.523	7.671	6.632
	RRA-E. # 0.5%Ni	7.471	6.331	5.439

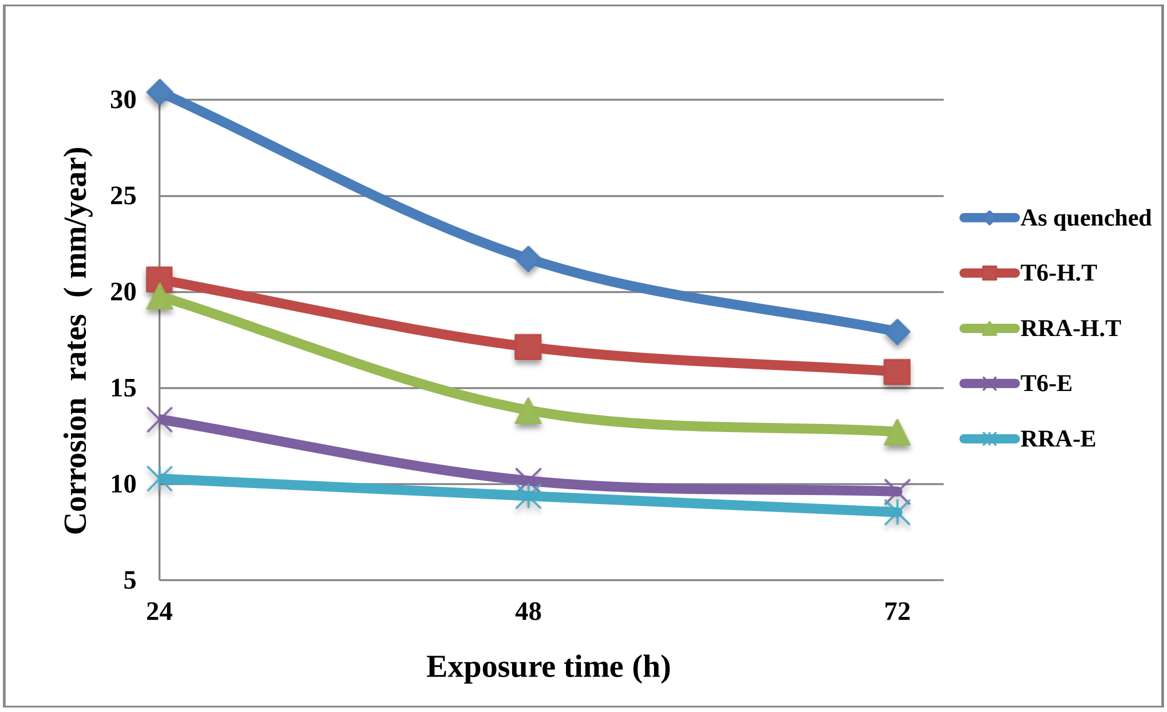

Fig. 1. Graphs of corrosion rates of an Al-Zn-Mg-Cu alloy for several of heat treatments and extrusion process vs. exposure time in 1 M HCl solution

Corrosion rates of the base alloy under different treatments for various durations in HCl solution as shown in Fig.1. It can be observed that the rates of corrosion for T6-H.T, RRA-H.T, T6.E and RRA.E are decreased than as quenched about of 32, 35, 56 and 66%, respectively. These enhancements of corrosion resistance of samples of the base alloy attributed to the distribution precipitations particles under impacts of the aging at T6 and RRA as reported [7, 21]. On the other hand, The data points indicate that the corrosion resistance significant improved for the samples conducted the extrusion process subsequently heat treatments, so due to the role of extrusion process to cut down the grains size with dispersion of precipitations [22]. Fig.2 displays corrosion rates of an alloy A after carried series of the homogenizing and heat treatments as well as thermo-mechanical process and subsequently the aging and retrogression and reaging. Corrosion resistance of as quenched of alloy A (after nickel added) about 14 % more than as quenched of base alloy in same conditions work. Besides, Maximum corrosion rate decrease is obtained for samples of alloy A included T6-H.T# 0.5%Ni, RRA-H.T# 0.5%Ni, T6.E# 0.5%Ni and RRA.E# 0.5%Ni about 32, 26, 36 and 27 % what the corresponding than the base alloy samples. Increasing in corrosion resistance of alloy A owing distribution of the Al-Ni intermetallic compounds created during Aluminum matrix. Aburada et al [23] reported that the beneficial of addition of nickel alloying in pitting resistance wherein alteration in repassivation potential. Moreover, it can be seen that in every case as in Figs. 1 and 2, there is a decrease in corrosion rate with increase in duration of exposure to the corrodent, implying that the corrosion resistance of the materials tested increases as the exposure time is increased. Visible inspection showed that there were no hydrogen bubbles clinging onto the surface of the test specimens. The phenomenon of monotonically decreasing corrosion rate with respect to time indicates some passivation of the matrix alloy. Garcia et al [24] observed in the suit of localized corrosion in HCl solution, the surfaces of aluminum alloys are passive and back up a relatively thick alumina film that does not allow hydrogen to evolve. Ma et al [25] believe that the black film formed on the surface consists of an Al hydrated oxide compound which protects the bulk stuff from further corrosion in the acid medium. However, it can be seeing in each graphical record that as duration of exposure is increased, the beneficial consequence on corrosion resistance degrees off, probably due to the protective layer reaching a steady state with time.

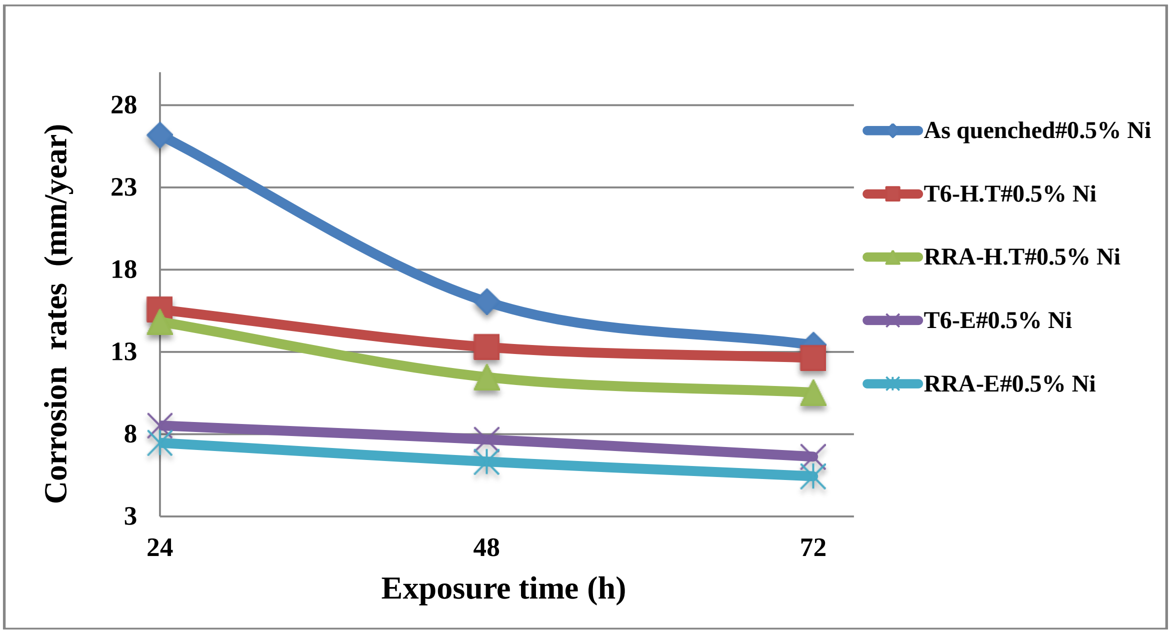

Fig. 2. Graphs of corrosion rates of an alloy A for different of thermo-mechanical treatments vs. exposure time in 1 M HCl solution.

The SEM micrograph of the base alloy sample after RRA-H.T as shown in Fig. 3a reveals corroded surface of aluminum matrix. The α-Al with existent major alloying elements of Zn, Mg and Cu which are evident as presented in Fig. 3b. Further, the presence high percentage of chloride ions due to reactions taken place in the base alloy during the immersed in acidic medium as mentioned former (Eq. 5 and 6). The SEM image of an alloy A after RRA-H.T in Fig. 4a shows dark area as α-Al matrix as well as dispersion particles as light which consist of the intercompounds and precipitations. Fig. 4b reveals the EDS spectrum the having of nickel element as a evidence about create compounds.

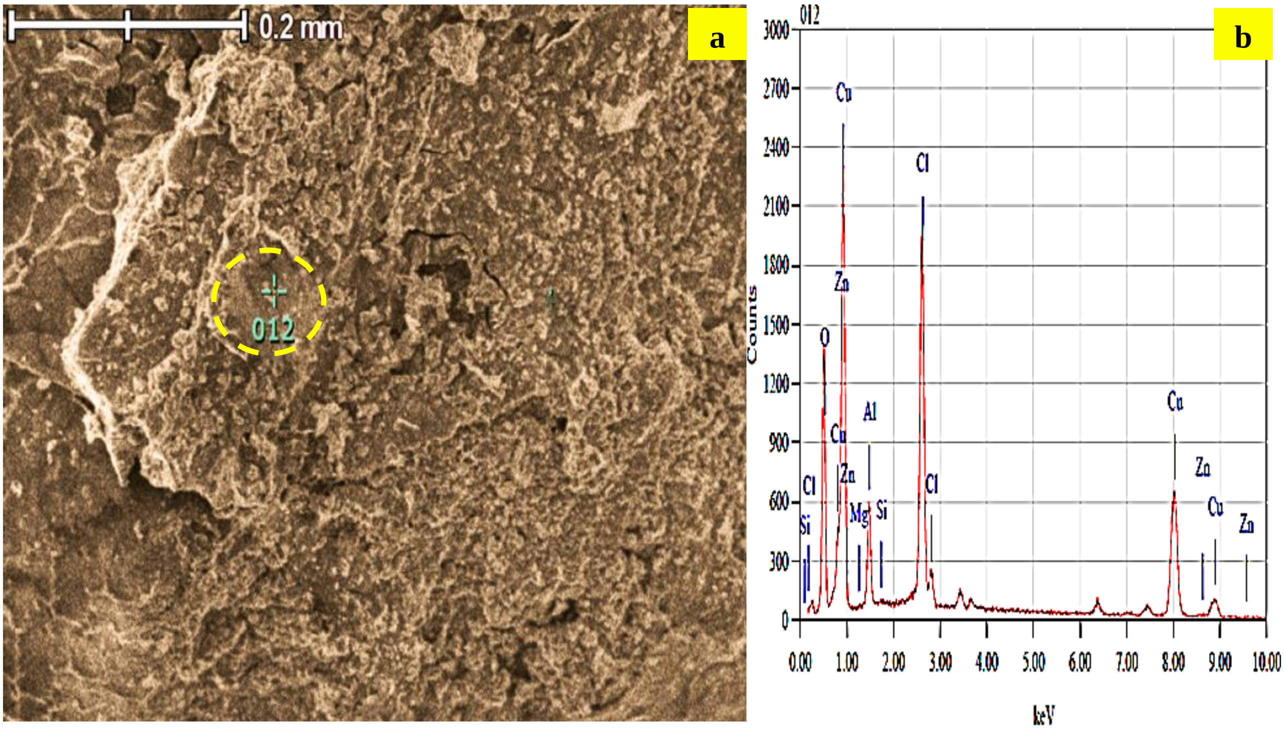

Fig. 3. a) SEM micrograph of corroded surface of base alloy in 1 M HCl solution after 72 hours, and b) Corresponding EDS analysis showing the attacked surface and chemical composition of corroded surface.

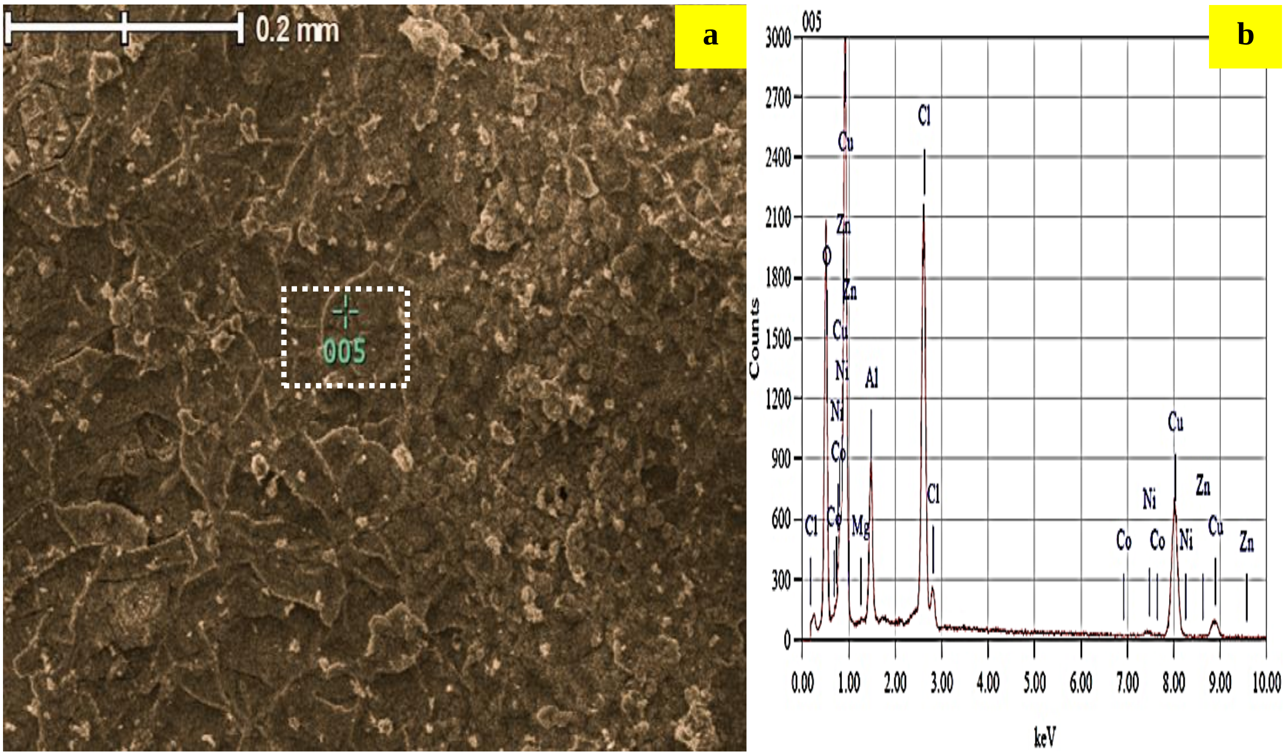

Fig. 4. a) SEM micrograph of corroded surface of Al-Zn-Mg-Cu-0.5% Ni alloy, in 1 M HCl solution after 72 hours, and b) Corresponding EDS analysis showing the attacked surface and chemical composition of corroded surface.

4. Conclusions

The results for this study reveals that corrosion rate is decreased of the base alloy samples after applying the aging; retrogression and reaging, additional thermo-mechanical process with heat treatments. On the other hand, regard to the corrosion resistance of the RRA, T6-H.T and RRA, T6-E samples of the base alloy possess higher than as quenched sample, because of the precipitations partials are occurred. Furthermore, Corrosion resistance of an alloy A is enhanced more than the base alloy due to the additions of nickel led to create dispersion intermetallics as well the precipitations particles.

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