

## NATURAL AGING INFLUENCE ON THE ACTIVATION ENERGY OF THE PRECIPITATION SEQUENCE OF Al-Mg-Si ALLOY

Ines Hamdi<sup>1</sup>, Zakaria Boumerzoug<sup>2</sup>

<sup>1</sup>Industrial Chemistry Department  
University of Biskra, Biskra, Algeria

<sup>2</sup>Department of Mechanical Engineering  
University of Biskra, Biskra, Algeria  
E-mail: ines.hamdi@univ-biskra.dz

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### ABSTRACT

*The effect of long natural aging on the kinetics of precipitation sequence of Al-Mg-Si alloy has been investigated by differential scanning calorimetry (DSC) and Vickers microhardness measurements. To understand the mechanism of the precipitation sequence in this kind of alloys, we calculated the activation energy using the Kissenger model. The results showed that the long natural aging speeds up the formation of the strength phase  $\beta''$ . Furthermore, the measured activation energy for precipitate formation in the case of the naturally aging samples for 8 and 24 months was compared. The results show that the long natural aging makes precipitation more difficulty by increasing the activation energy.*

*Keywords:* Al-Mg-Si, activation energy, DSC, natural aging, precipitation.

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### INTRODUCTION

Aluminum alloys are increasingly used in industry due to their valuable properties: weightlessness, resistance to corrosion, thermal and electrical conductivity, medium strength and high extrudability [1 - 3]. They are structural hardening alloys with mechanical properties related to their constituents, particularly more or less hardening phases that precipitate during appropriate heat treatments. These alloys gain most of their strength through an adequate distribution of strengthening particles, which can be precipitated with a dedicated heat treatment or integrated into the manufacturing process [4]. Natural aging refers to the long-term storage of Al-Mg-Si alloys at room temperature (NA). Natural aging (NA) can significantly reduce the maximum strengthening potential during artificial aging (AA); it has a negative effect on the Al-Mg-Si properties, which is attributed to the formation of Mg and Si clusters [5 - 7] and a variety of suggested influences on the AA

precipitation process [8 - 14].

There is considerable interest in this natural aging (NA) since it influences the subsequent artificial aging (AA) step. In the Al-Mg-Si alloys, this response is negative; i.e., AA is much slower and leads to lower peak strengths after NA, [15] expressed by the decrease in number density and an increase in the length of the strengthening phase  $\beta''$  in the peak-aged condition [16, 17].

The general sequence precipitation phase in the 6000 series alloys is: [18, 20].

(SSS)  $\rightarrow$  GP zones  $\rightarrow \beta' \rightarrow \beta \rightarrow \beta' \rightarrow \beta$  ( $Mg_2Si$ ).

However, the precipitation sequence of the Al-Mg-Si alloys stored at room temperature determined by DSC is:  $\beta'' \rightarrow \beta' \rightarrow \beta$  ( $Mg_2Si$ ) [21, 22].

Because a high density of fine, coherent or semi-coherent precipitates nucleates and grows, the strength is increased. Controlling precipitation during artificial and natural aging is essential for achieving optimal mechanical properties of the Al-Mg-Si alloy [23]. To understand the mechanism of precipitation sequence in

the Al-Mg-Si alloy during long natural aging, the kinetic parameters must be evaluated.

One of the most important kinetic parameters is the activation energy. There are numerous methods for calculating activation energy from experiments with non-isothermal conditions and a linear heating rate. The most commonly used methods are isoconversional methods, which allow activation energy to be determined as a function of the transformed fraction.

This work aims to investigate the effect of long natural aging on the precipitation kinetics, and on the alloy hardening using differential scanning calorimetry (DSC) and hardness test. In order to clarify the precipitation kinetics of the Al-Mg-Si alloy, the activation energy of each phase formed in this alloy is calculated using Kissinger method [24].

## EXPERIMENTAL

The chemical composition of the investigated Al-Mg-Si alloy was in at. %; 98.45 Al, 0.653 Mg, 0.595 Si, 0.014 Cu and 0.215 Fe. The calorimetric measurements were carried out on a DSC Q 20 TA analyzer. The samples were cut from rods with 3 mm diameter and 2 - 2.5 mm height. They were aging at room temperature for 8 and 24 months before DSC testing. The DSC tests were conducted in an Argon atmosphere, from 20°C to 550°C, with three different heating rates of 10, 20 and 30°C/min.

The specimens for the Vickers hardness measurements were aging at 150°C for different times (5 min to 120 h) previously stored at room temperature for 8 and 24 months. Micro-Vickers hardness measurements were conducted with a 200 g load. Each hardness value is the average value from five individual tests.

## RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the DSC thermo-grams at different heating rates of 10, 20, and 30°C/min of the Al-Mg-Si alloy stored at room temperature for 8 and 24 months. The DSC scans were carried out from room temperature to 550°C, and three exothermic reactions could be identified from DSC thermo-grams indicated by 1, 2, and 3. These reactions are shifted towards higher temperature as the heating rates increases. This information indicates that these reactions are thermally

activated. The exothermic reaction 1, 2, and 3 are attributed to the formation of the  $\beta''$ ,  $\beta'$ , and  $\beta$  stable successively [21, 22]. The maximum peak temperatures of the exothermic peaks are shown in Tables 1 and 2 for the samples stored at room temperature for 8 and 24 months, respectively.

We used the Kissinger method [24] to calculate the activation energy  $E$  for precipitation of the exothermic peaks shown in Fig. 1 and Fig. 2. This method was created primarily to investigate the variation of the maximum peak temperature with heating rates using the following expression:

$$\ln \frac{\alpha}{T_P^2} = \frac{E}{RT_P^2} \quad (1)$$

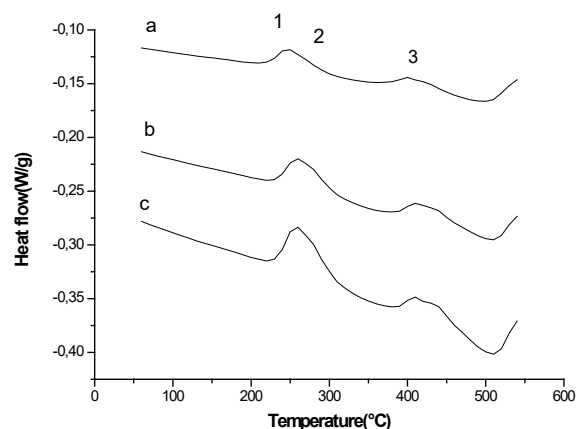


Fig. 1. DSC curves of the Al-Mg-Si alloy aged at room temperature (RT) for 8 months at different heating rates: (a) 10° C min<sup>-1</sup>, (b) 20° C min<sup>-1</sup> and (c) 30° C min<sup>-1</sup>.

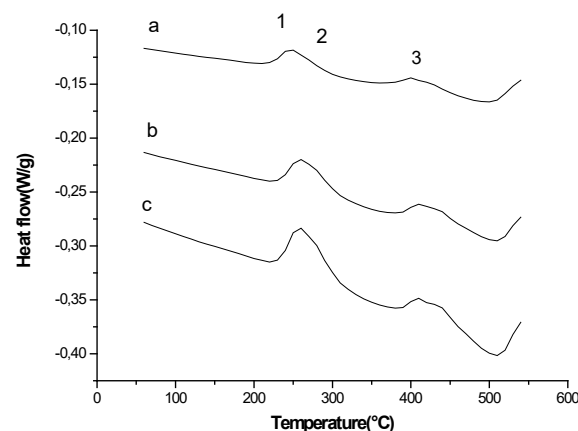


Fig. 2. DSC curves of the Al-Mg-Si alloy aged at room temperature (RT) for 24 months at different heating rates: (a) 10°C min<sup>-1</sup>, (b) 20°C min<sup>-1</sup> and (c) 30°C min<sup>-1</sup>.

Table 1. Variation of DSC peak temperature with heating rate  $\alpha$  (natural aging alloy for 8 months)

phase \ $\alpha$	$\beta''$	$\beta'$	$\beta$
10°C/min	240.82	265.42	414.42
20°C/min	250.22	277.24	419.84
30°C/min	256.49	280.63	425.43

Table 2. Variation of DSC peak temperature with heating rate  $\alpha$  (natural aging alloy for 24 months).

Phase \ $\alpha$	$\beta''$	$\beta'$	$\beta$
10°C/min	250.96	277.13	428.83
20°C/min	252.22	284.94	432.87
30°C/min	260.49	290.07	438.14

where:  $\alpha$  is the heating rate;  $T_p$  is the temperature of the peak maximum;  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

Fig. 3 and Fig.4 show the linear relationships between  $\ln(1/T_p)$  and  $1000/T_p$  for quenched and natural aging Al-Mg-Si alloys. Each slope determines the activation energy  $E$  (Table 3).

In the comparison, the activation energies obtained from the  $\beta''$ ,  $\beta'$ , and  $\beta$  formation in the naturally aged specimen for 24 months are higher than the naturally aged specimen for 8 months. This result shows different features compared to the quenched alloy obtained in our previous work [22]. The activation energy value of samples stored at room temperature for 8 and 24 months was not constant but increased with increasing of storage time. It reveals that the formation of the  $\beta''$ ,  $\beta'$ , and  $\beta$  is very difficult during natural aging, and the increase in the natural aging time makes the formation of these phases more challenging. The increase in the activation energy for longer natural aging times and the decrease in formation time of  $\beta''$  can be attributed to the reducing in the solute super-saturation and vacancy concentration for subsequent artificial aging, which also causes an increase in the critical nucleation size for the most important strengthening phase  $\beta''$  [25].

### Hardness measurements

Fig. 5 presents the hardness variation versus aging time of Al-Mg-Si alloy aging at  $150^\circ\text{C}$  previously stored at room temperature for 8 and 24 months. The hardness

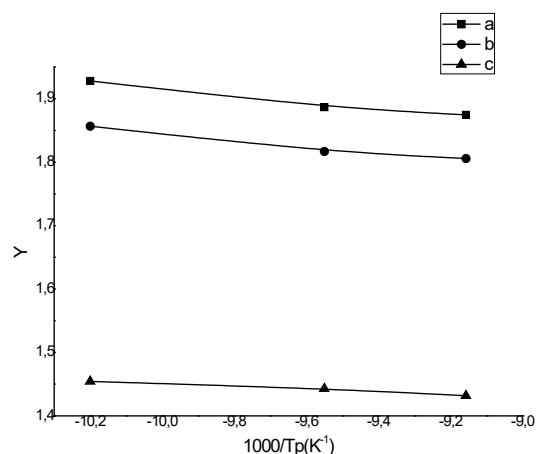
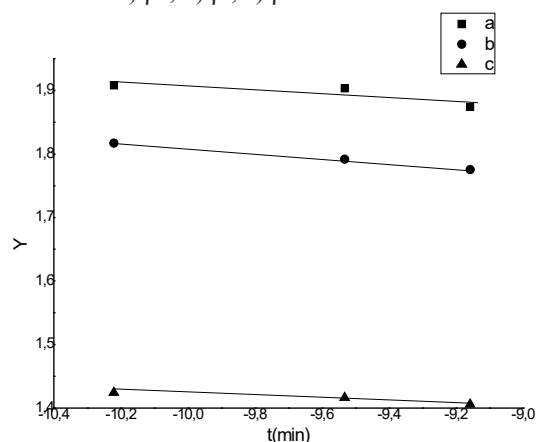
Fig. 3. Y against  $1000/T_p$  of Al-Mg-Si alloy aged at RT for 8 months a)  $\beta''$ , b)  $\beta'$ , c)  $\beta$ .Fig. 4. Y against  $1000/T_p$  of Al-Mg-Si alloy aged at RT for 24 months a)  $\beta''$ , b)  $\beta'$ , c)  $\beta$ .

Table 3. Activation energy of precipitates (KJ/mol) calculated from Kissinger method.

phase \ Sample	$\beta''$	$\beta'$	$\beta$
Natural aging alloy for 8 months	153.975	160.793	394.566
Natural aging alloy for 24 months	201.506	210.195	469.907

curves showed similar profiles. The hardness of the specimen stored for 8 months was much higher than that of the specimen stored for 24 months, although the hardness of the natural aging alloy decreased compared to that of the quenched alloy; the maximum hardening corresponds to the formation of  $\beta''$  phase [22]. The

microhardness value of the quenched specimen aging at 150°C is determined as 88.8 HV [22]. In contrast, it is attributed as 86.4 and 72.1 HV for the specimens aging at 150°C previously stored at room temperature for 8 and 24 months, respectively. It is reported that the long natural aging can significantly influence the age hardening of the 6xxx series alloy [26]. The long natural aging has a negative impact on the microhardness of the Al-Mg-Si alloy.

In comparison to our previous work [22], the formation time of the  $\beta''$  during quenched alloy aging at 150°C (48 h) is longer than that of the specimens aging at 150°C previously stored at room temperature for 8 and 24 months (20 h and 16 h, respectively). The results show that the long natural aging accelerates the formation of the strength phase  $\beta''$ . During natural aging, the formed cluster could not stable at tempering temperature [27]. These clusters are too small to act as nucleation sites for strength phase  $\beta''$  [2]. The latter can explain the decrease of the Al-Mg-Si alloy hardness with the longest NA period.

## CONCLUSIONS

The study of the precipitation kinetics in Al-Mg-Si alloy has been made by DSC technique under non-isothermal conditions and microhardness test. In the present study was used the Kissenger model to calculate the activation energy for all phases of the precipitation sequence during natural aging samples for 8 and 24 months. It has been found that the activation energy value of the natural aging sample increases with the increase of the storage time. The hardness value of the  $\beta''$  phase decrease with the long natural aging and the formation time of the  $\beta''$  phase decrease with the long natural aging.

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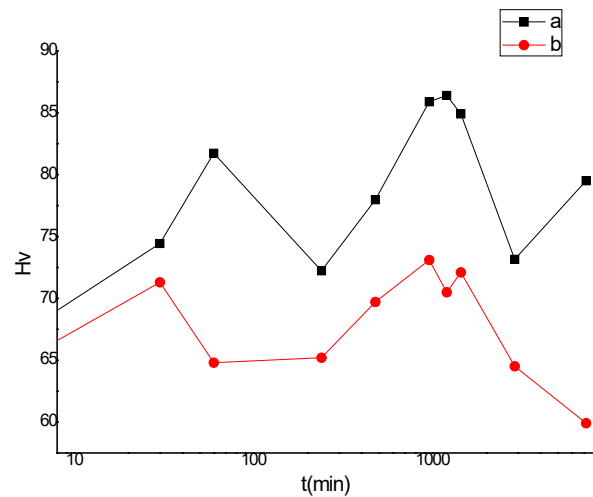


Fig. 5. Vickers hardness of Al-Mg-Si alloy with the time of artificial aging at 150°C after RT storage for a) 8 and c) 24 months.

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