Available online at www.sciencedirect.com
ScienceDirect
J. Mater. Sci. Technol., 2010, **26**(12), 1083-1088.
JMST
www.JMST.org

Hardness-Lattice Parameter Correlation for Aged Al-Zn-Mg Alloys

P. Fernandez, G. Gonzalez†, I. Alfonso and I.A. Figueroa
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Cd. Universitaria, Del. Coyoacán, México, DF. 04510, Mexico

[Manuscript received August 31, 2009, in revised form May 18, 2010]

Two ternary Al-2.2Zn-0.95Mg and Al-5.5Zn-2.1Mg (in wt pct) alloys, with Zn:Mg ratios close to 2.5 were produced by conventional ingot casting metallurgy. The ingots were solution heat treated at 500°C for 0.5 h and aged at 180°C for times between 0.5 and 80 h. The structural characterization was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and Vickers microhardness measurements (HV). The study was focused on the investigation of the precipitates formation and the relationship between hardness and lattice parameter for α-Al. The results showed that there was an inverse correlation for all the experimental conditions, and the aged peaks coincided with lattice parameter minima. Significant precipitates formation only occurred for the alloy containing 5.5 wt pct Zn and 2.1 wt pct Mg, provoking an important strengthening and variations in the lattice parameter, however, this was not observed for the alloy containing 2.2 wt pct Zn and 0.95 wt pct Mg. A plausible explanation of the increment of hardness values could be the presence of a well distributed η phase ($MgZn_2$). At initial stages of the precipitation process, η' was the most abundant precipitate while the phase τ was observed at overaged conditions. These results showed that the aging response of the conventionally cast Al-Zn-Mg alloys could be obtained using the lattice parameter of the α-Al matrix, even for alloy systems with low precipitates formation.

KEY WORDS: Aluminum alloy; X-ray diffraction; Precipitation; Lattice parameter; Hardness

1. Introduction

Precipitation hardening in aluminum was discovered at about 100 years ago. Since then, different hardenable aluminum alloys have been developed and commercialized[1]. The 7XXX series is one of the most widely used aluminum alloys being employed in diverse fields such as aerospace, space exploration, extreme sports, automotive, military and nuclear industries[2]. The advantages of these alloys are high strength, wide solution range for solution treatment, age hardenability and readily weldable[2]. Chemical composition and heat treatment exert an important influence on the mechanical properties for these alloys. The most widely employed heat treatment is the T6, which consists of a solution treatment followed by an aging required for the precipitation of hardening constituents. The relatively high solubility of Zn and Mg in aluminum makes it possible to produce a high density of precipitates, which results in a strength enhancement. The usual precipitation sequence of 7XXX series can be summarized as follows[3,4]:

Solid solution→Guinier preston zones (GPZ)→Metastable η'→Stable η ($MgZn_2$)

However, there are still considerable controversies in the literature regarding the nature of the strengthening precipitates (*i.e.* GP zone, η' or η) formed in the heat treated commercial 7XXX series[5–8]. The chemical composition of η phase is close to $MgZn_2$, and precipitates as nanosized particles after the T6 treatment. The precipitation of τ phase ($Al_2Mg_3Zn_3$) has also been reported[9–11]. T6 treatment seems to

† Corresponding author. Ph.D.; Tel.: +52 55 56224647; E-mail address: joseggr@unam.mx (G. Gonzalez).

Table 1 Average chemical composition for the alloys produced (wt pct)

	Zn	Mg	Cu	Fe	Mn	Si	V	Al
C1	2.27	0.95	<0.01	0.04	<0.01	0.03	<0.01	Bal.
C2	5.53	2.14	<0.01	0.04	<0.01	0.03	<0.01	Bal.

be particularly suitable for alloys with high content of alloying elements and Zn:Mg ratios above 2.0[12,13]. The response of a heat treatment for Al alloys can be measured using different characterization methods such as hardness, microscopy and X-ray diffraction (XRD), which compile the resulting effect of contributing factors for the strengthening of Al alloys: solid solution, Hall-Petch hardening from the α-Al cell size and precipitation hardening. Changes in lattice parameters during aging have shown to yield useful information about composition changes and precipitated phases[14]. Lattice parameter can be changed after quenching depending on the size of alloying elements in solid solution, while the presence of precipitates provokes lattice parameter to decrease due to compressive stresses. At overaging conditions, the coalescence and growth of the precipitates cause their incoherence and the stresses tend to disappear. Some works reported lattice parameter determinations using XRD and its relationship with the precipitation process for Al alloys, *e.g.* Al-Si-Mg[15], Al-Zn[16] and Al-Si-Cu-Mg[17] alloys and, in general, a good correlations between hardness and lattice parameter were obtained under certain conditions. Lattice parameter-hardness relationship resulting from precipitation has not been reported in the literature for Al-Zn-Mg alloys. In the present work, we intend to gain further insight by providing information about the relationship between precipitation process and lattice parameter for alloys with low and high Zn+Mg contents. Our objective is to investigate the precipitates formation during aging and their influence on the hardening response, relating them with the matrix lattice parameter behavior. If a defined correlation between them is found, the lattice parameter could be employed to obtain aging response behavior under conditions where hardness measurement is impossible, *e.g.* thin ribbons.

2. Experimental

Two Al-Zn-Mg alloys were conventionally cast using aluminum shots (>99.9% purity), zinc pellets (>99.9% purity) and magnesium bars (>99.9% purity). The alloys were produced in a Leybold-Heraeus induction furnace with controlled argon atmosphere with graphite crucibles. The molten alloys were poured into a conventional mould (10.0 cm×2.0 cm×4.0 cm) without preheating, to avoid pore formation and metal oxidation inside the furnace chamber. Chemical composition for the experimental alloys is shown in Table 1. As can be observed, Zn:Mg ratios are similar, *i.e.* 2.4 for the alloy C1 and 2.6 for the alloy C2. The ingots were homogenized at 500°C for 24 h and laminated to obtain homogeneous grains and minimize micro porosity and segregation. The samples obtained after this process were solution heat treated at 500°C for 0.5 h in a molten salt bath. It is worth mentioning that the selected solution temperature is lower than the critical dissolution temperature to avoid localized melting[1].

After the solution treatment, the samples were quenched in water at room temperature (20°C), in order to freeze the microstructure, aged at 180°C for times ranging from 0.5 to 80 h and then cooled in air. Assuming that the precipitation process should change the microhardness even in the early stages of the process, time *vs* microhardness was plotted. XRD analysis was used to study the lattice parameter behavior. Fine details of microstructure were revealed by transmission electron microscopy (TEM) and related to microhardness and lattice parameter plots. XRD measurements were carried out in a Bruker AXS D8 Advance diffractometer Cu$K\alpha$ (λ=0.15418 nm), operated at 35 kV and 30 mA. Silicon was used as internal standard to determine lattice parameter for α-Al matrix. TEM investigations were carried out in a 120 kV JEOL 1200EX and in a 200 kV field emission JEOL 2010 transmission electron microscope, respectively. Specimens for TEM were prepared by dimpling in a Gatan 656 Dimple Grinder followed by argon ion milling using a Gatan 691 precision ion polishing system. Microhardness measurements were made with a Vickers diamond indenter in a Matsuzawa MXT30-UL microhardness tester employing a load of 50 g for 30 s. Statistical procedures were carried out to ensure repetitive and accurate results.

3. Results and Discussion

Figure 1(a) and (b) show the microhardness (continuous lines) and lattice parameter (discontinuous lines) behaviors for the aged experimental alloys as a function of aging time. For both alloys, the microhardness and lattice parameters follow inverse behaviors. For C1 alloy, the microhardness increases until 4 h, reaching a maximum (close to 686 MPa) remaining without noticeable changes for further time (Fig. 1(a)), while lattice parameter decreases down to a value close to the lattice parameter of pure aluminum, which could be mainly attributed to the loss of alloying elements in solid solution, leading to lattice relaxation. The insufficient precipitation response does not provoke lattice compression or significant microhardness improvement. This fact is related to a low driving force originated for the insufficient Zn+Mg

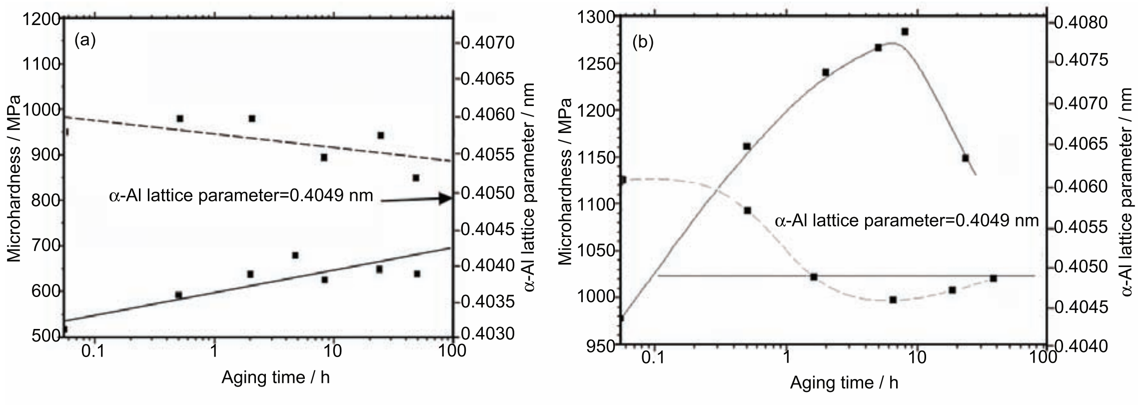

Fig. 1 Microhardness (continuous lines) and matrix lattice parameter (discontinuous lines) behaviors as a function of aging time for the alloys C1 (a) and C2 (b), aged at 180°C. Inverse correlations can be observed

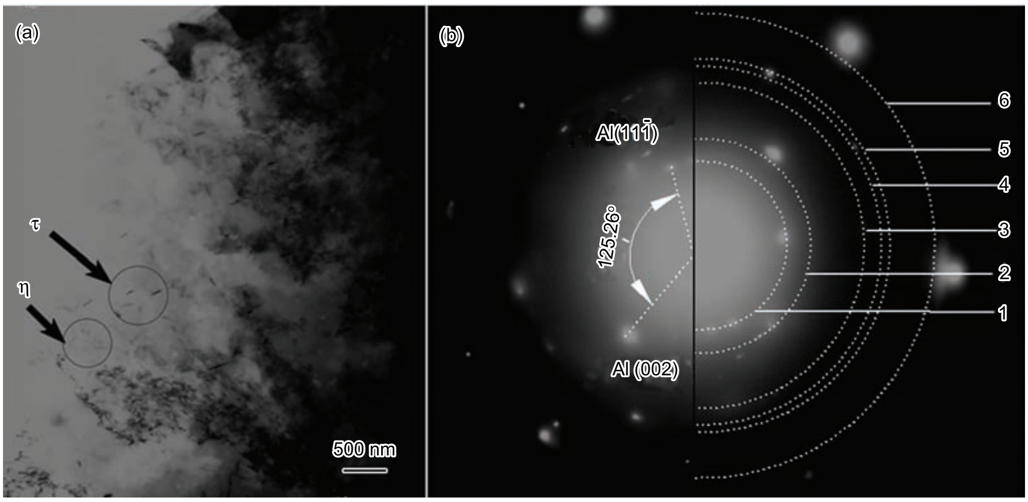

Fig. 2 (a) Bright field TEM image for the C1 alloy (2.2 wt pct Zn and 0.95 wt pct Mg) aged at 180°C for 4 h, (b) the corresponding SAED pattern

content in solid solution. For C2 alloy, microhardness significantly increases for short aging time (Fig. 1(b)) reaching 1274 MPa at 4 h (aging peak), while lattice parameter decreases until reaching pure aluminum lattice parameter. This could be the result of the loss of alloying elements in solid solution besides precipitates formation. A wide formation of coherent and semi-coherent precipitates at aging peak leads to lattice compression, coinciding with the minimum lattice parameter. When the alloy is overaged, the precipitates coalesce and grow, losing their coherence. This fact causes the matrix relaxation and the lattice parameter to reach the value of Al matrix. The increase in Zn+Mg content from 3.2 to 7.6 (from 2.2 to 5.5 for Zn and from 0.95 to 2.1 for Mg, in wt pct) leads to an increase in the microhardness values of about twice. These relationships show that the lattice parameter measurements for Al-Zn-Mg alloys could be used to analyze the microhardness and precipitation response behaviors during aging.

TEM and selected area electron diffraction (SAED) were used to analyze the presence of the precipitates and its influence on hardness and matrix lattice parameter. At initial stages of the aging process, no precipitates were observed for the C1 alloy (*i.e.* the alloy with lower Zn+Mg content), as shown in Fig. 1(a). It can be seen that neither microhardness nor lattice parameter has a significant variation. Thus, we are speculating that at these stages, the formation of η' phase might have already occurred. Similar results have also been reported in literature [3] and [4]. After an aging time of 4 h (aging peak), a small quantity of τ rods with 150-200 nm in diameter was observed, as shown in the bright field TEM image (Fig. 2(a)). Figure 2(b) shows the SAED analysis of the encircled zone, the presence of η precipitates can also be observed, which are not observable in TEM image mode. The characteristic rings of τ and η are shown in Table 2. The insufficient amount of precipitates explains the low hardness improvement for this

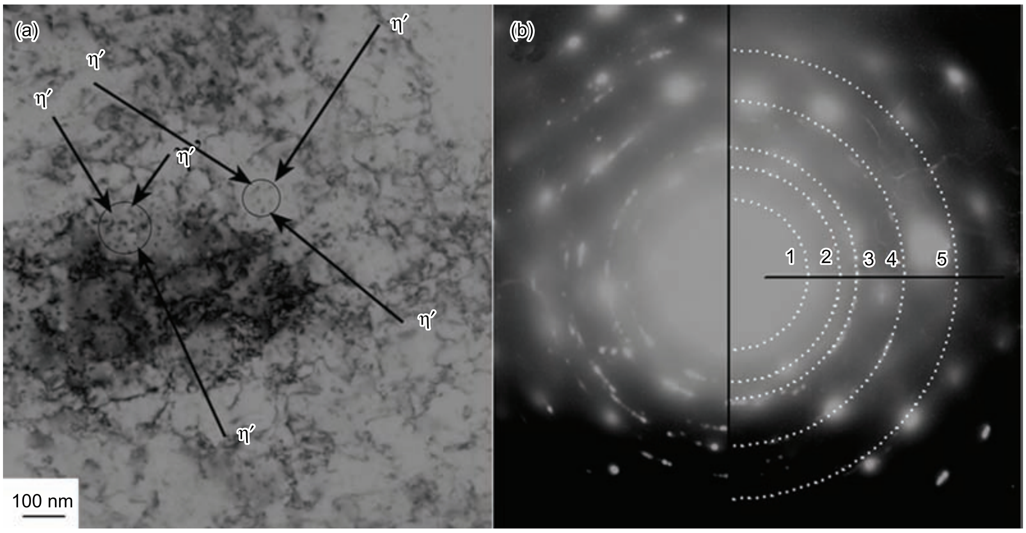

Fig. 3 (a) Bright field TEM image for the C2 alloy (5.5 wt pct Zn and 2.1 wt pct Mg) aged 0.5 h at 180°C, (b) SAED pattern remarking the presence of rings corresponding to η' precipitates

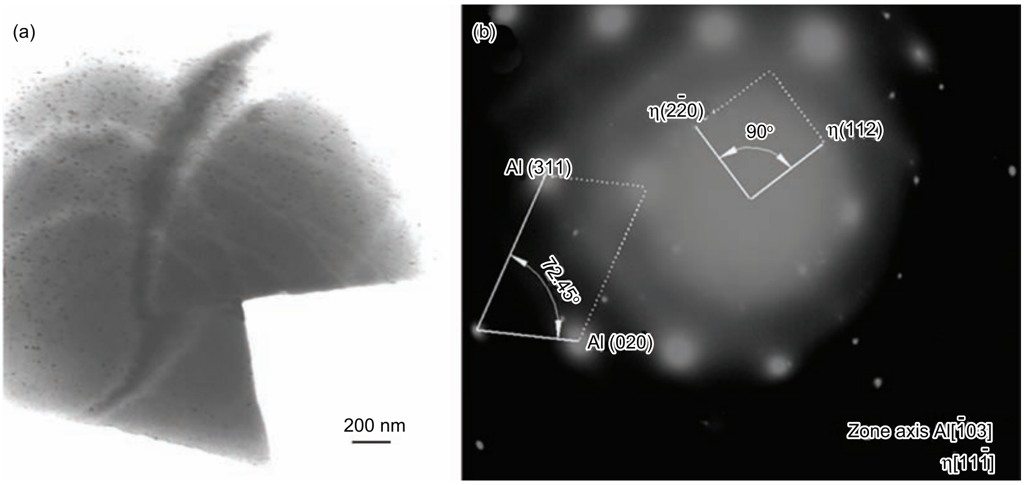

Fig. 4 (a) Bright field TEM image for C2 alloy (5.5 wt pct Zn and 2.1 wt pct Mg) aged at 180°C for 4 h (aged peak), (b) the corresponding SAED pattern

Table 2 Relation between phases and rings observed in Fig. 2

Ring	1	2	3	4	5	6
Phase	τ (134)	η (021)	η (006)	η(220)	η (232)	η (120)

Table 3 Relation between phases and rings observed in Fig. 3

Ring	1	2	3	4	5
Phase	η' (112)	η' (120)	η' (302)	η' (403)	η' (150)

alloy and the lattice parameter behavior, mainly depending on alloying elements content. The presence of η in the peak aged condition instead of η', could be explained on the basis of high concentration of vacancies, which was originated during the processes of rolling and solution heat treatment. This could kinetically modify the precipitation sequence reported in the literature [3]–[7], where η' is generally observed in the aging peak.

For the alloy C2 (5.5 wt pct Zn and 2.1 wt pct Mg), an important increase in the amount of precipitates can be observed for an aging time as short as 0.5 h (Fig. 3(a)), corresponding to η' precipitates (Fig. 3(b)). The characteristic rings of η' are shown in Table 3. The increase in Zn+Mg content for this alloy allowed the retention of higher concentrations of these elements in the supersaturated solid solution compared to that of the C1 alloy, leading to a higher

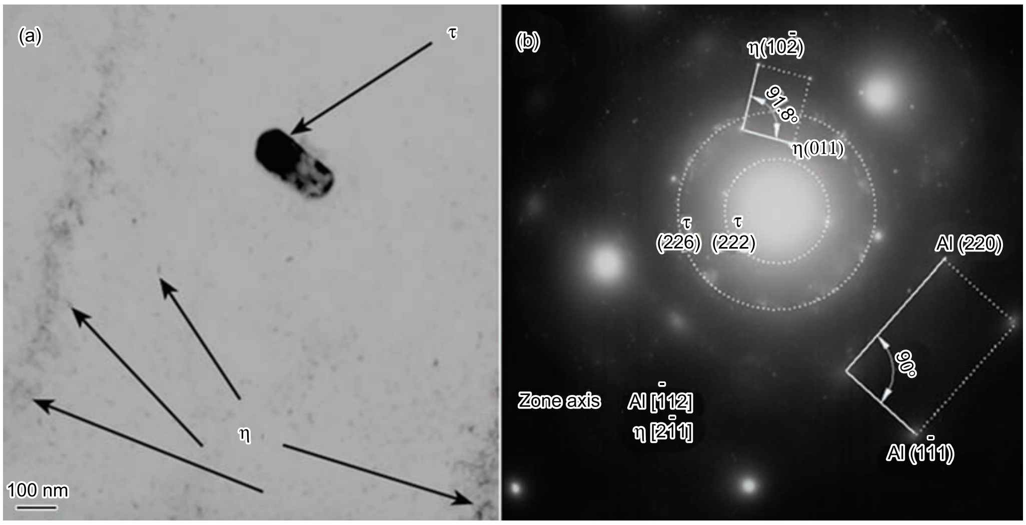

Fig. 5 (a) Bright field TEM image for C2 alloy (5.5 wt pct Zn and 2.1 wt pct Mg) aged at 180°C for 47 h (overaged), (b) the corresponding SAED pattern

precipitation response and microhardness improvement. The loss of alloying elements in the supersaturated solid solution leads to matrix relaxation, explaining the lattice parameter values observed in Fig. 1(b). Please note that no τ precipitates were found.

Figure 4(a) and (b) show a bright field TEM image of C2 alloy aged for 4 h (peak-aged) and a SAED pattern corresponding to the precipitates. As can be observed in Fig. 4(a), a high amount of precipitates is evident, which could be associated to the high hardness improvement for this alloy. The diffraction pattern inset in Fig. 4(b) shows the spots corresponding to α-Al and η phases. The presence of a high amount of semi-coherent precipitates in the aging peak could explain the minimum value of the lattice parameter due to the matrix compression.

After aging the C2 alloy for 47 h (overaged condition), the change of precipitates is rather visible, as shown in Fig. 5(a). Certainly, not only η phase is observed but also rod of 200 nm in diameter like τ precipitates. It must be noted that the quantity of η phase decreases. SAED pattern depicted in Fig. 5(b) also shows some rings corresponding to τ phase. The presence of non-coherent τ precipitates provokes a matrix relaxation, reaching the value of pure aluminum lattice parameter (Fig. 1(b)).

4. Conclusion

The results shown in this paper demonstrate the feasibility of employing the lattice parameter for predicting aging response behavior in Al-Zn-Mg alloys. For the 2.2Zn-0.95Mg alloy, an inverse correlation has been found between microhardness and lattice parameter (the corresponding derivatives have opposite signs). At higher Zn+Mg content, *i.e.* 5.5Zn-2.1Mg, such correlation remains inverse but becomes complex. It is thought that this complexity is originated by a large amount of precipitates. The 2.2Zn-0.95Mg alloy shows low values of microhardness due to a poor precipitation response. The decreases of the lattice parameter for this alloy could be associated to the diffusion of alloying elements from the supersaturated solid solution towards the precipitates. On the other hand, when increasing the alloying elements for the 5.5Zn-2.1Mg alloy, the microhardness increases twice its original value. The large precipitation observed provokes a lattice compression, since the minimum point of the lattice parameter coincides with maximum point of the aging peak. Lastly, the main precipitates found are η' for low aging time, η for the aged peaks and τ at overaged conditions.

Acknowledgement

The authors are thankful to Gabriel Lara, Omar Novelo and Teresa Vazquez from IIM- UNAM, and Alejandro Garcia from IQ-UNAM, Mexico, for their technical support.

REFERENCES

[1] E. Hornbogen: *J. Light Metals*, 2001, **1**, 127.

[2] J.E. Hatch: *Properties and Physical Metallurgy*, American Society for Metals, USA, 1993.

[3] H.P. Degischer, W. Lacom, A. Zahra and C.Y. Zahra: *Z. Metallkd.*, 1980, **71**, 231.

[4] X.Z. Li, V. Hansen, J. Gjϕnnes and L.R. Wallenberg: *Acta Mater.*, 1999, **47**, 2651.

[5] Z. Li, B. Xiong, Y. Zhang, B. Zhu, F. Wang and H. Liu: *Mater. Charact.*, 2008, **59**, 282.

[6] L. Hadjadj, R. Amira, D. Hamana and A. Mosbah: *J. Alloy. Compd.*, 2008, **462**, 283.

[7] N.Q. Chinh, J. Lendvai, D.H. Ping and K. Hono: *J. Alloy. Compd.*, 2004, **378**, 59.

[8] J. Lendvai: *Mater. Forum,* 1996, **217-222**, 43.

[9] H. Auld and S.M. Cousland: *J. Aust. Inst. Metals,* 1974, **19**, 194.

[10] B.C. Muddle, S.P. Ringer and I.J. Polmear: *Trans. Mater. Res. Soc. Jpn.,* 1994, **19B**, 999.

[11] A. Deschamps, F. Livet and Y. Bréchet: *Acta Mater.,* 1998, **47**(1), 281.

[12] I.J. Polmear: *J. Inst. Metals,* 1957, **86**, 113.

[13] T. Engdahl, V. Hansen, P.J. Warren and K. Stiller: *Mater. Sci. Eng. A,* 2002, **327**, 59.

[14] F.H. Cocks: *J. Mater. Sci.*, 1972, **7**, 771.

[15] J.L. Cavazos and R. Colás: *Mater. Charact.,* 2001, **47**, 177.

[16] M. Tavoosi, M.H. Enayati and F. Karimzadeh: *J. Alloy. Compd.,* 2008, **464**, 108.

[17] M.J. Starink, V.M.F. Abeels and P. van Mourik: *Mater. Sci. Eng. A,* 1993, **163**, 115.