

**The Materials Research Society (MRS)**  
**XXIII INTERNATIONAL MATERIALS  
RESEARCH CONGRESS 2014**  
**NACE International Congress-Mexican Section**

carlos.garay@cimav.edu.mx

**L. González-Rodelas**

Universidad Autónoma de Chihuahua,  
Facultad de ingeniería, Circuito No. 1,  
Nuevo campus universitario 2 Apdo.  
postal 1552, C.P. 31240, Chihuahua,  
Chih., México  
Tel. 6144429500  
lesliegonzalezrodelas@gmail.com

**I. Estrada-Guel**

Centro de Investigación en Materiales  
Avanzados (CIMAV), Laboratorio  
Nacional de Nanotecnología, Miguel de  
Cervantes No. 120, C.P. 31109, Chih.,  
México  
Tel. 614 439 1100  
ivanovich.estrada@cimav.edu.mx

**E. Cuadros-Lugo**

Centro de Investigación en Materiales  
Avanzados (CIMAV), Laboratorio  
Nacional de Nanotecnología, Miguel de  
Cervantes No. 120, C.P. 31109, Chih.,  
México  
Tel. 614 439 1100  
eduardo.cuadros.lugo@gmail.com

**R. Martínez-Sánchez**

Centro de Investigación en Materiales  
Avanzados (CIMAV), Laboratorio  
Nacional de Nanotecnología, Miguel de  
Cervantes No. 120, C.P. 31109, Chih.,  
México  
Tel. 614 439 1100  
roberto.martinez@cimav.edu.mx

**C. G. Garay-Reyes**

Centro de Investigación en Materiales  
Avanzados (CIMAV), Laboratorio  
Nacional de Nanotecnología, Miguel de  
Cervantes No. 120, C.P. 31109, Chih.,  
México  
Tel. 614 439 1100

---

**“INFLUENCE OF SOLUTION TREATMENT  
TIME, ZN ADDITION AND COLD/HOT  
ROLLING ON THE MICROSTRUCTURE AND  
HARDNESS OF THE 2024 ALLOY”**

## ABSTRACT

The effect of Zn addition, solubilized time and thermo-mechanical treatments on the microstructure of the Al-2024 alloy are studied by Vickers microhardness (HV), Rockwell B hardness (HRB), Optic Microscopy (OM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The addition of Zn to Al-2024 alloy represents some advantages from structural point of view, because Zn and Al have a difference of 7% in their atomic radius, where the main strengthening mechanism is the strengthening by solid solution. Additionally, a second strengthening mechanism could be activated by heat treatment. In the precipitation hardening the solution time is a critical variable to obtain a satisfactory degree of solubilization of alloying elements. This degree of solution has both, a direct relationship with precipitation sequence, and in the final mechanical properties. Finally, others strengthening mechanisms as strengthening by grain size reduction and strain hardening, which have a direct relationship with precipitation sequence and mechanical properties, could be activated by thermomechanical treatments, at intermediate or at final step. From results obtained, is evident that microstructure, precipitation kinetics and hardness of the different alloys are affected by the interaction of the involved strengthening mechanisms as: solution solid, precipitation, strain and grain size reduction.

## INTRODUCTION

Aluminium alloys are selected as materials for construction because of their low weight to volume ratio, high strength and stiffness, ability to resist corrosion and of undergoing age hardening [1]. Aluminium is alloyed with copper, manganese, magnesium, zinc, nickel and silicon as major alloying elements to meet the various demands during service [2]. Recent demand for weight reduction in structural component calls for further enhancement in strength of commercial structural alloys. In this context, it may be of interest to examine the possibility of enhancing the hardness of age hardenable alloys. In this regard, the addition of Zn to Al-2024 alloy represents some advantages from structural point of view, because Zn and Al have a difference of 7% in their atomic radius, where the main strengthening mechanism is the strengthening by solid solution [3, 4]. Additionally, a second strengthening mechanism could be activated by heat treatment. In the precipitation hardening the solution treatment time is a critical variable to obtain a satisfactory degree of solubilization of alloying elements. This degree of solution has both, a direct relationship with precipitation sequence, and in the final mechanical properties [5]. Finally, it is noteworthy that cold working prior to aging is a known technique applied industrially to increase the aging response particularly for wear resistant applications. Traditional heat treatment procedure of a precipitation-hardened alloy comprises an initial solution treatment, quench (usually to room temperature), and a final aging treatment. It is well known that the reactions associated with aging can be strongly influenced by prior plastic deformation [6]. The main objectives of the present investigation are to evaluate solution treatment time, Zn addition, and cold/hot rolling on hardness, micro-hardness, microstructure, and precipitation kinetics of 2024 alloy.

## EXPERIMENTAL PROCEDURE

The raw materials were commercial 2024 aluminum alloy and Zn (99.9999% pure). The commercial 2024 alloy is melted on a LINDBERG BLUE electric furnace at 740 °C. The Zn (99.9999% pure) was added in different proportions to obtain 2024 alloys with 0.25, 0.50 and 0.75% wt. Zn. Thereafter, each alloy was degassed for 5 minutes with argon gas (20 psi), using a graphite propeller at 490 rpm and finally Al-5Ti-1B grain refiner was added. The alloys were cast into steel molds preheated at 260 °C. Immediately, it was preceded the hot rolling at ≈460 °C to reduce the thickness of the sample 50%. Subsequently, solution treatments at 495 °C for 3, 5 and 7h were done in LINDBERG-BLUE electric furnace followed by a quenching in water at 60 °C. Thereafter, it was carried out the cold rolling to reduce the thickness of the sample 5 and 15%. Finally, aging treatments were done in a FELISA furnace at 195°C for different period of time (30, 60, 300, 600, 3000 and 6000 min.), followed by quenching in water at room temperature.

The microstructure of was characterized by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For OM and SEM samples

were prepared by conventional metallographic techniques. For TEM samples, disc-shaped specimens were used, which were ground to a thickness of 0.10 mm and then punched to obtain disc-shaped samples of 3 mm in diameter. The resulting specimens were thinned by the twin-jet electropolishing method at  $-50^{\circ}\text{C}$  into an electrolyte composed by 30 % of  $\text{HNO}_3$  and 70 % of methanol. Observations by OM were done in Olympus PGM-3 optical metallographic microscope. Analyses by SEM and TEM were carried out in a JEOL JSM6510-LV (operated at 20 kV) and PHILIPS CM-200 (operated at 200 kV), respectively. Hardness tests were carried out in a Wilson Rockwell device using Rockwell B scale. Vickers micro-hardness (HV) test were done in a Future Tech FM-7 Micro-hardness Tester. The HV measurements were performed using a 100 g load with 15 s dwell time and 20 indentations were made on each sample.

## RESULTS AND DISCUSSION

The mechanical properties of cast aluminium alloys depend mainly on the alloy composition and the parameters of the casting process. In order to further improve the mechanical properties of cast components these alloys can be heat treated. Various heat treatment cycles, e.g. different combinations of temperatures and times, are used depending on the casting process, the alloy composition and the desired mechanical properties. Solution treatment is carried out at a high temperature, close to the eutectic temperature of the alloy. The time needed for dissolution and homogenization of the alloy depends on the composition, morphology, size and distribution of the phases present after solidification, as well as on the solution treatment temperature [5]. The effect of solution treatment time (3, 5 and 7h) in 2024 alloy and in 2024 alloys with Zn additions on microstructure is shown by means of a micrograph (i) and elemental mapping (ii) obtained by scanning electron microscopy (SEM) in Fig. 1.

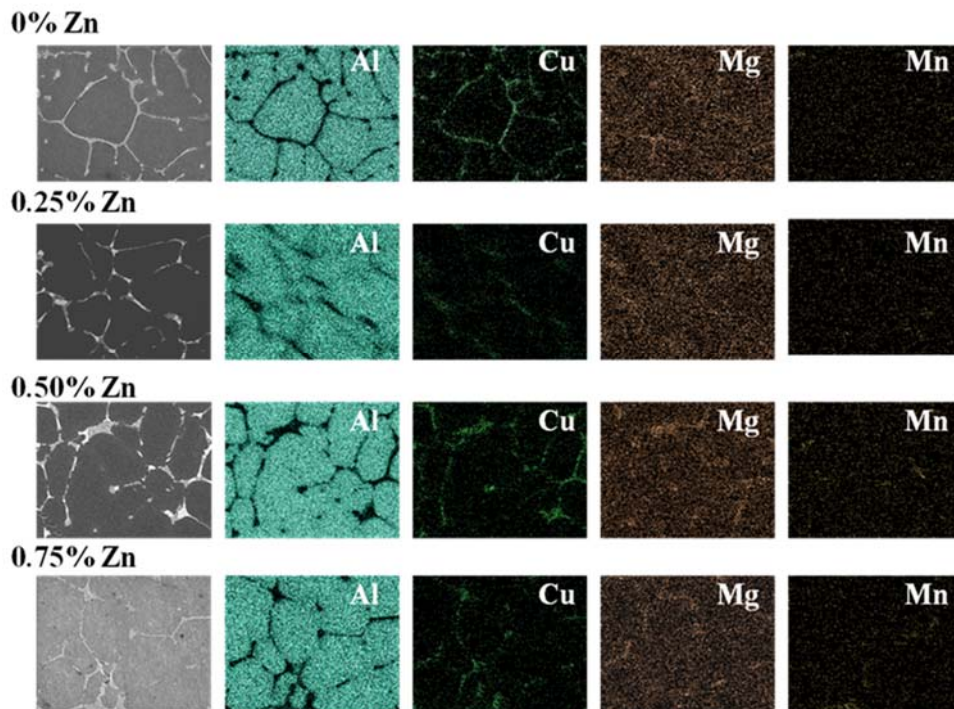
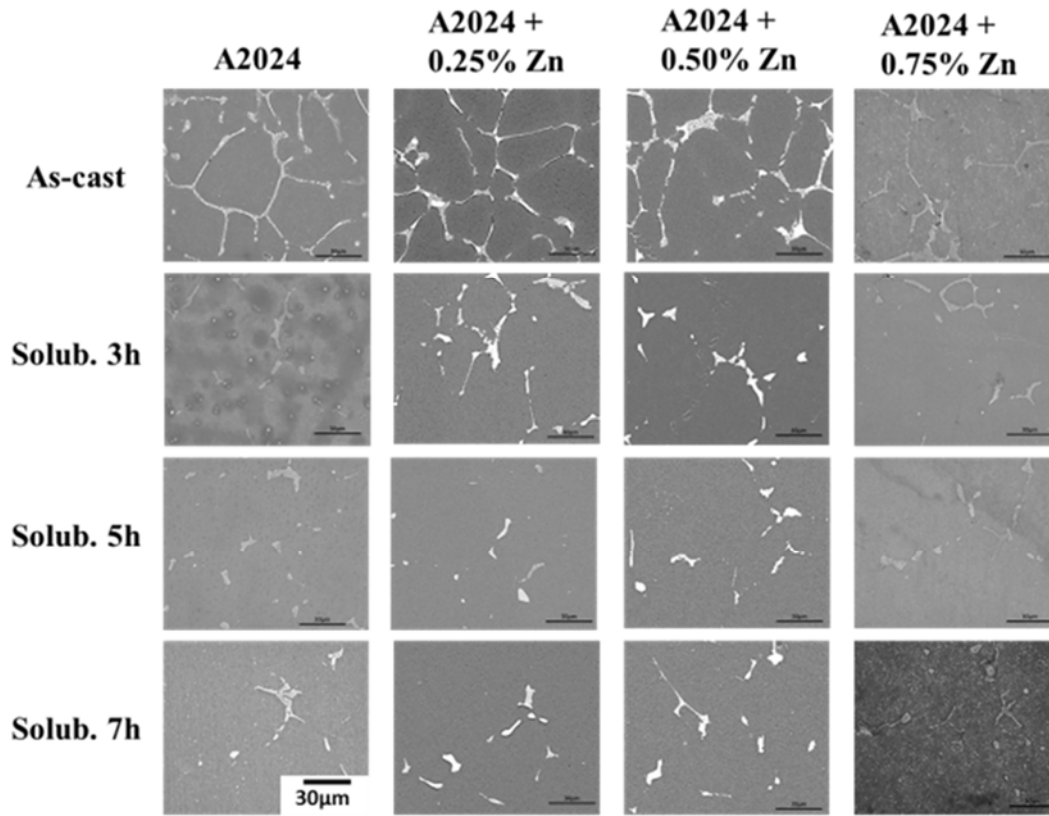


Fig. 1 SEM images (i) of 2024 alloy as a function of the Zn addition and solubilization time, and elemental mapping (ii) of as-cast sample.

For all solution treatment time, the segregation of solute elements decreased compared with as-cast. The volume fraction of segregated solute decreases as a function of time of solubilized. From the elemental mapping in as-cast samples can be seen as the segregation is mainly composed of Cu and Mg, and also lower percentage of Mn.

It is observed from the results that improved solubilization of the Al<sub>2</sub>Cu phase takes place after solubilization for 5 and 7h.

The effect of addition of Zn (0.25, 0.50 and 0.75% wt.) on the Vickers micro-hardness (HV) in 2024 alloy after solubilized for 3, 5 and 7h and 5 and 15% cold working of is shown in Fig. 2, additionally, the value of without deformation sample (reference sample) is included. Generally, there is no improvement in the HV values after adding Zn to 2024 alloy at any time of solubilized. Of the above it can be concluded that Zn is quite neutral, it neither enhances nor detracts properties of alloy. The samples solubilized for 5h presents the best values of HV after 5 and 15% cold working, the highest value was for 2024 alloy added with 0.5% wt. Zn, so this sample is taken as reference to explain the effect of hot/cold rolling for all alloys on microstructure by optical microscopy (OM).

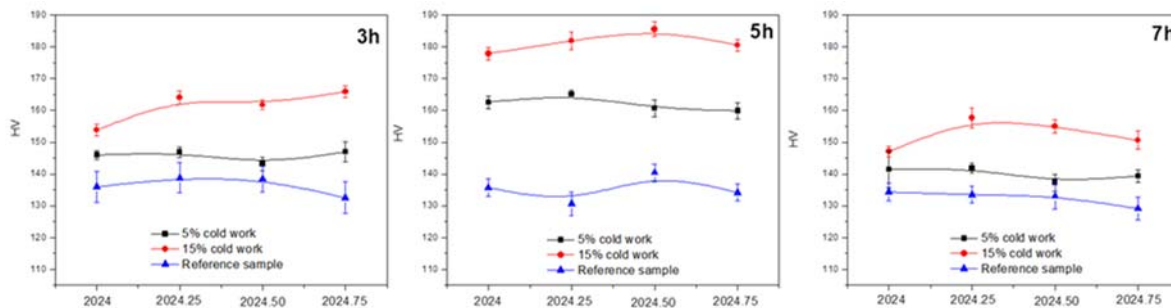


Fig. 2 HV of 2024 alloy and of 2024 alloys with Zn additions solubilized for 3, 5 and 7h, samples were 50 % hot working before solution treatment and after were 5 and 15% cold working, additionally, the sample reference is included.

The effect of hot/cold rolling on microstructure in 2024 alloy added with 0.5% wt. Zn after solubilized treatment for 3, 5 and 7h is shown by means of a micrograph obtained by optical microscopy (OM) in Fig. 3. To evaluate low and high deformations in this study is evaluated 5 and 15% cold working. The microstructure of as-cast sample consists of grain of dendritic morphology, classic of this stage. For 50 % hot working sample, the microstructure consists of deformed grains of elongated morphology. For the samples 5 % cold working and solubilized for 3h, the microstructure consists of small-size grains with equiaxed morphology, which suggest that grain recrystallization took place. For the samples 5 % cold working and solubilized for 5h, the microstructure consists of medium-size grains with elongated-slightly morphology. Finally, for the samples 5 % cold working and solubilized for 7h, the microstructure consists of large-size grains with elongated morphology, which suggest that the recrystallization and grain growth steps are conducted. For 15% cold

working samples and solution treatment for 3, 5 and 7h, the microstructure consists of grains with elongated morphology, which is attributed to the large applied deformation, therefore, it is not possible to make a precise comparison. Respect to cold working only few of thermo-mechanical treatments have been practically applied to aluminum alloys, like heat treatment T8 of 2024 and T9 of 2A12 alloys, in which the applied deformation is relatively small. The deformation in T851 and T87 treatments is only 5 and 7 %, respectively. The reason is to avoid the introduction of the non-uniform distribution of dislocation cell structures which may act as nucleation sites of heterogeneous precipitation. However, a significant increase of the strength is achieved by relatively large cold working after solution treatment [7]. Based on previously reported results is attributable to the greater HV value in sample solubilized for 5h to combination of deformation and recrystallization of grain.

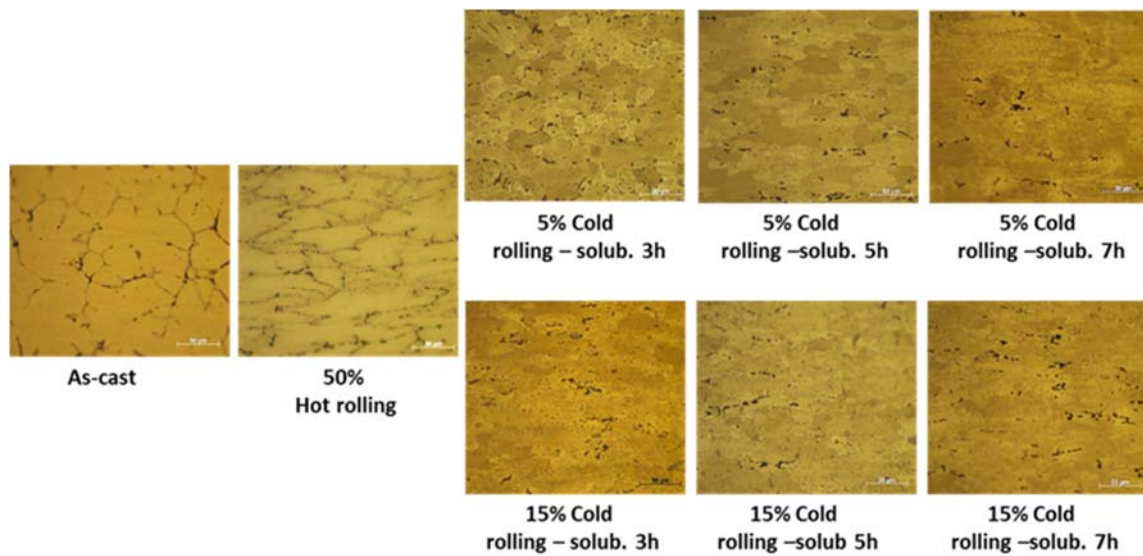


Fig. 3 OM micrographs of 2024 alloy added with 0.5% wt. Zn after solubilized treatment for 3, 5 and in as-cast conditions, 50% hot rolling and 5 and 15% cold rolling.

The Figs. 4 and 5 show Rockwell B hardness (HRB) as a function of aging time in the 2024 alloy and in the 2024 alloys with additions of Zn, after 5 and 15% cold working, respectively, additionally, the value of reference sample is included. In general, is observed an increase in hardness up to a maximum and then comes a softening of the material. The hardening effect is associated to the interaction between precipitates generated during the treatment of aged and dislocations. The softening effect is associated to coarsening and loss of coherency of precipitates [8].

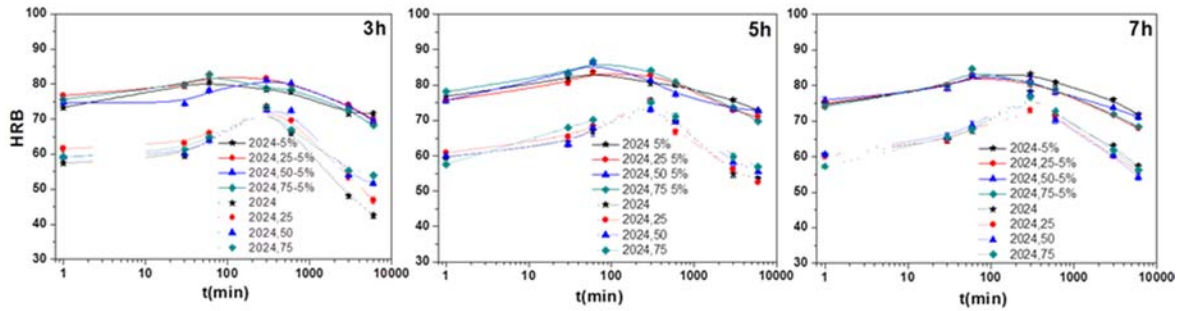


Fig. 4 HRB of 2024 alloy and of 2024 alloys with Zn additions after 5 % cold rolling and reference sample as a function of aging time, solubilization time: a) 3h, b) 5h and c) 7h.

It is observed as the HRB in cold working samples is greater than reference samples. The value obtained in peak hardening of the reference samples is between 73.72 and 78.25 HRB depending on the time of solubilized, which is close to the value obtained (79 HRB) in solubilized samples for 6h at the same temperature [9].

Additionally, it is observed, as the hardness is higher in the 15 % cold working samples compared to 5 % cold working and sample reference, finally, the time required to reach peak hardness in deformed samples is 60 min, in the sample reference the time required is 300 min, which suggest precipitation kinetics more rapid in the deformed samples.

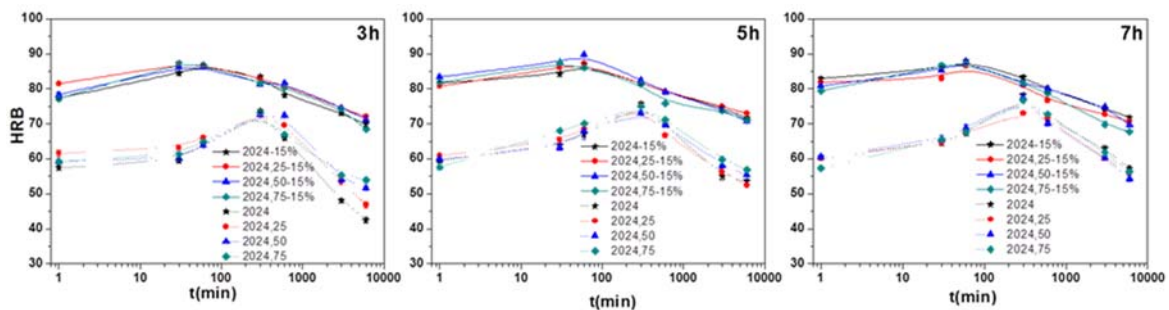


Fig. 5 HRB of 2024 alloy and of alloys with Zn additions after 15 % of cold rolling and reference sample as a function of aging time, solubilization time: a) 3h, b) 5h and c) 7h.

The microstructure of peaks aged-hardening and after solution treatment(3, 5 and 7h) in the 2024 alloy and in the 2024 alloys with additions of Zn, 5 and 15% cold working and reference sample, is shown by means of a micrograph obtained by transmission electron microscopy (TEM) in Fig. 6.



The rod-shaped particles presented in as-solution and each peak aged-hardening (60 and 300 min) are identified as T-phase dispersoids ( $\text{Al}_2\text{Cu}_2\text{Mn}_3$ ) by EDXS (not shown). Rod-shaped T-phase dispersoids are distributed randomly in the Al matrix. Additionally, these precipitates grow in function of aging time for all conditions and in cold work samples at 15% are smaller in size compared with cold work samples at 5% and as-solution condition. Finally, the morphology of the T-phase in the cold work sample is different to that of the reference sample, at the first samples is observed a rod-shaped morphology and the second needle morphology is observed. The first peak aged-hardening (60 min) is attributed to the morphology and distribution of this phase as well as to high density of dislocation introduced by cold working and strengthening of GP zones or nanometer-sized  $S'$  particles and its relation to the dislocations generated by cold work. On the other hand, the precipitates that can be observed in second peak age-hardening (300min) with morphology of needles are identified as  $S'$  ( $\text{Al}_2\text{CuMg}$ ) by EDXS (not shown).

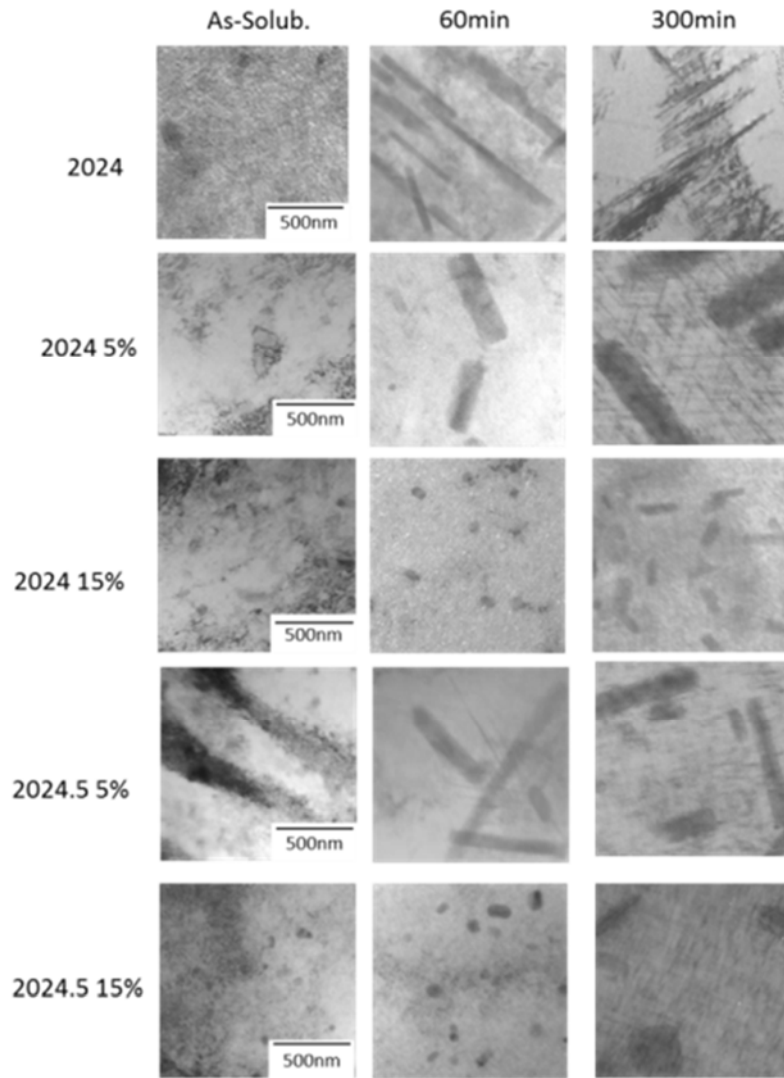


Fig. 6 TEM images of 2024 alloy and 2024-0.5 Zn alloy in each peak aged-hardening and as-cast.

## CONCLUSION

It is observed from the results that improved solubilization of the Al<sub>2</sub>Cu phase takes place after solubilization for 5 and 7h. Of the above it can be concluded that Zn is quite neutral, it neither enhances nor detracts properties of alloy. Based on previously reported results is attributable to the greater HV value in sample solubilized for 5h to combination of deformation and recrystallization of grain. It is observed, as the hardness is higher in the 15 % cold working samples compared to 5 % cold working and sample reference, finally, the time required to reach peak hardness in deformed samples is 60 min, in the sample reference the time required is 300 min, which suggest precipitation kinetics more rapid in the deformed samples.

The first peak aged-hardening (60 min) is attributed to the morphology and distribution of this phase as well as to high density of dislocation introduced by cold working and strengthening of GP zones or nanometer-sized S' particles and its relation to the dislocations generated by cold work. On the other hand, the precipitates that can be observed in second peak age-hardening (300min) with morphology of needles are identified as S' (Al<sub>2</sub>CuMg) by EDXS (not shown). The 0.75 Zn wt% to the A2024 alloy promoted the greater hardening by solid solution mechanism, without a significant effect on the precipitation kinetics. Before cold deformation, the greater hardness values were obtained after 7h of solubilization, however, after cold-rolling, the solubilized alloys for 5 h reached the higher hardening. According to microhardness results, after aging treatments the strengthening effect is attributed to phases precipitation. The higher contribution to hardening was done by the cold deformation (strain).

## ACKNOWLEDGMENT

The authors would gratefully thank J .E. Ledezma-Sillas, K. Campos-Venegas and R. A. Ochoa-Gamboa for their valuable technical support through the study.

## REFERENCES

- [1] S.K. Ghosh. Influence of Cold Deformation on the Aging Behaviour of Al-Cu-Si-Mg Alloy. *J. Mater. Sci. Technol.*, 2011, 27, 193-198.
- [2] I.J. Polmear. *Light Alloys—From Traditional Alloys to Nanocrystals*, 4th edn, Butterworth-Heinemann, Oxford, UK, 2006
- [3] Ž. Skoko, S. Popović and G. Štefanić. Microstructure of Al-Zn and Zn-Al Alloys. *Croatica Chemica Acta*, 2009, 82, 405–420.
- [4] H. Löffler, *Structure and Structure Development in Al-Zn Alloys*, Akademie Verlag, Berlin, 1995.
- [5] Emma Sjölander and Salem Seifeddine. The heat treatment of Al–Si–Cu–Mg casting alloys. *J. Mater. Process. Technol.*, 2010,210, 1249–1259.
- [6] AL Ning, ZY Liu and SM Zeng. Effect of large cold deformation after solution treatment on precipitation characteristic and deformation strengthening of 2024 and 7A04 aluminum alloys. *Trans. Nonferr. Met. Soc. China*, 2006, 16, 1341–1347.
- [7] A. Naimi, H. Yousfi and M. Trari. Influence of cold rolling degree and ageing treatments on the precipitation hardening of 2024 and 7075 alloys. *Mech Time-Depend Mater.*, 2013, 17 and 285–296.
- [8] Zhanli Guo and Wei Sha. Quantification of Precipitation Hardening and Evolution of Precipitates. *Materials Transactions*, 2002, 43, 1273-1282.
- [9] Grigoris E. Kiourtsidis, Stefanos M. Skolianos and, George A. Litsardakis. Aging response of aluminium alloy 2024/silicon carbide particles (SiCp) composites. *Mater. Sci.*