

Article Effects of Mg Content on the Microstructural and Mechanical Properties of Al-4Cu-*x*Mg-0.3Ag Alloys

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Abstract: The aim of the present research is to manipulate the amenability between composition-microstructure-property relationships in two kinds of Al-4Cu-*x*Mg-0.3Ag alloys (where x = 0.4 and 1.4) having different Cu/Mg ratios (~9.54 and ~2.87). The effect of artificial ageing (T6) on the precipitation hardening behavior and resulting mechanical properties were also assessed and compared to two different scenarios of composition. Experimental results revealed that the modification in Magnesium concentration from 0.4 to 1.4 wt.% has a marked effect in increasing the micro hardness, ultimate tensile stress, and elongation of the alloy. Based on the microstructural analysis, the enhancement in mechanical properties was explained and addressed by considering the dual role of Mg content in the base alloy. On one hand, a large size of Mg atom produces a solid solution hardening effect, while on the other hand, a high content of Mg further promotes the formation of second phase S-type precipitate (Al₂CuMg) with various mixed morphologies. This unraveling co-precipitation phases within the matrix provide an obstacle for the dislocation glide thereby increasing mechanical strength and strain hardenability.

Keywords: Al-Cu-Mg-Ag alloy; mechanical properties; precipitation strengthening; solid solution strengthening

1. Introduction

As-cast Al and its alloys are widely used in the automotive industry due to their good castability, good corrosion resistance, and high strength to weight ratio [1,2]. However, owing to various casting defects, the as cast Al-alloys suffer from poor yield strength and hardness values when subjected to specific loading or temperature conditions. To alleviate these issues, a new generation of wrought alloys such as the Al-Cu-based 2xxx standard system with distinct compositional design and/or thermo-mechanical processing routes have been developed to date [1–3]. Since the most common strategy to enhance the mechanical strength of these kind of alloys is to add micro alloying elements that facilitate both precipitation and solution hardening phenomenon simultaneously [4]. Over recent decades, the artificially aged (T6) Al-Cu-based binary, ternary, and quaternary-based alloys containing small contents of Mg, Mn, Si, and Sn alloying elements have been the most pervasive when compared to traditional Al-based alloys [5–10]. Indeed, the coherency, size, interparticle spacing, and distribution of the precipitates plays a pivotal role in manipulating the strength of the Al-Cu-Mg-based alloys at elevated temperatures [11]. In light of this, many previous studies demonstrated that the formation of stable precipitates is mainly linked with the adjustment of Cu/Mg

ratios in the compositional design of the Al-Cu-Mg base systems. For alloys having low Cu/Mg ratios, the equilibrium precipitation phase which develops at approximately 190 °C is found to be the S (Al₂CuMg) phase [9,12]. Nevertheless, this equilibrium precipitate phase is usually preceded by various intermediate transformations, including Guinier–Preston–Bagaryatsky (GPB) zone, S", and S' (i.e., the sequence is SSS \rightarrow GPB \rightarrow S" \rightarrow S' \rightarrow S) [13]. On the contrary, for Al-Cu-Mg alloys having high Cu/Mg ratios, the equilibrium precipitation phase which develops at approximately 190 °C, is found to be the θ (Al₂Cu) phase having precursors of GPB, θ ", and θ ' (SSS \rightarrow GPB \rightarrow θ " \rightarrow θ ' \rightarrow θ) [9,11,13–15].

Correspondingly, from previous studies, it is already proven that the small addition of a quaternary element such as Ag in ternary Al-Cu-Mg alloys accelerates the nucleation of the desirable Ω phase on the {111}_{α} of the parent phase [16]. The Ω phase is chemically equivalent to the θ phase with an extra Mg-Ag co-segregation layer at the α/Ω interface and has a high potential of precipitation hardening at an elevated temperature of approximately 200 °C [16].

Many studies have also simultaneously correlated the effect of Cu/Mg ratio on the possible precipitation scenarios and the mechanical properties of Al-Cu-Mg alloys. For example, Liu et al., [17] investigated the effect of the Cu/Mg ratio on two commercial aluminum alloys (2519 and 2024) with high and low Cu/Mg ratios, respectively. It has been claimed that when the Cu/Mg ratio decreases, the tensile strength and yield strength of the Al-Cu-Mg alloy increase [17]. The hardness of the 2024 alloy (Cu/Mg ratio ~3.41) and 2519 alloy (Cu/Mg ratio ~16.29) was found to be 152 and 141 HV, respectively. The aforementioned research team claimed that the improvement in the mechanical properties of the newly designed alloy called HM is by virtue of varying the Cu/Mg ratio, which has resulted in the substitution of the θ' phase by the S phase [17]. Thus, the contribution of the S phase could be beneficial for improving the mechanical properties of Al-Cu-based alloys.

This paper intends to explore more systematically the effect of high and low Cu/Mg ratios on the evolution of microstructural and mechanical properties of Al-Cu-Mg-Ag alloys after T6 heat treating parameters. Two Al-4Cu-*x*Mg-0.3Ag-based alloys with different Mg contents and separate Cu/Mg ratios were designed based on the fundamental thermodynamic phase diagram [15]. Microstructural and mechanical results were correlated as a function of compositions (i.e., high and low Cu/Mg ratios, respectively). The experimental results demonstrated that the dual structure-composition strategy is useful for achieving outstanding strength-ductility combination in Al-Cu-Mg-Ag alloys. For instance, by adjusting the Cu/Mg ratio and optimizing the microstructure, the high mechanical strength of about 440 MPa was observed in the Al-4Cu-1.4Mg-0.3Ag alloy which makes it alluring for continuous commercial applications.

2. Materials and Methods

In the present study, two Al-4Cu-*x*Mg-0.3Ag alloys (x = 0.4, 1.4) were designed. The design criterion for the present alloys with different Mg contents can be classified with respect to high and low Cu/Mg ratios. The Cu/Mg ratios were determined to be ~9.54 and ~2.87 for each composition, respectively. Hereafter, Al-4Cu-0.4Mg-0.3Ag (wt.%) and Al-4Cu-1.4Mg-0.3Ag (wt.%) will be designated as H-0.4Mg and L-1.4Mg, respectively. The designed compositions ingots were synthesized by high-purity Al (99.99%), pure Cu, pure Mg, and pure Ag. The raw materials were melted in an electric resistance furnace at 730 °C and then cast into a preheated steel mold to obtain an ingot with a dimension of 16 (thickness) × 40 (width) × 100 mm (length). The composition of the prepared alloys was determined from five measurements using an Optical Emission Spectrometry (OES, SPECTROMAXX from SPECTRO, Kleve, Germany). The mass loss after the melting procedure were negligible and impurities were only a few percent. Thus, the actual composition was considered the same as the nominal composition. The chemical composition of the experimental alloys corresponding to their respective high and low Cu/Mg ratio are listed in Table 1.

Allovs	Cu/Mg Ratio		Chemical Composition (wt.%)					
- J -		Al	Cu	Mg	Ag			
H-0.4Mg	~9.54	95.34	3.91 ± 0.158	0.41 ± 0.005	0.34 ± 0.008			
L-1.4Mg	~2.87	93.99	4.19 ± 0.046	1.46 ± 0.024	0.36 ± 0.003			

Table 1. Average chemical composition (wt.%) of the experimental alloys.

The as-cast ingots were then homogenized in an air furnace at 520 °C for 24 h to reduce the segregation of the solute elements and dissolve the primary precipitated phases. After homogenization, a thin layer of oxides was removed from each side of the ingot (about 0.5 mm) to ensure the ingot quality. Following homogenization step, the ingots were subjected to hot rolling operation. The ingots were hot-rolled from 15 to 2.5 mm to obtain an approximately 84% reduction in thickness. The hot-rolled sheets of the respective alloys were then solution heat-treated (SHT) at 520 °C for 2 h in the furnace, followed by water quenching. After the supersaturated solid solution (SSSS) treatment, the artificial aging process was performed for each alloy specimens in a salt bath. Several specimens were prepared and aged at 180 °C in a salt bath and then quenched in water at room temperature after several intervals of time—10, 30, 60, 120, 240, 480, 600, 720, 960, 1920, and 2880 min.

To establish the effect of composition and to evaluate the peak hardening condition the hardness testing was performed after the artificial ageing treatment process. The average Vickers hardness number (VHN) of each H-0.4Mg and L-1.4Mg specimen aged for a different time was calculated from five indents using a Vickers hardness tester (WOLPERT UH930, Wilson Hardness, Shanghai, China). Each indentation was performed by imposing a load of 10 KgF for 15 s. Error bars for the Vickers Pyramid Number (HV) plots were constructed with one standard error of the mean.

To observe the microstructural features such as the average grain size, the optical microscopy observation was made for each specimen. The surface of the specimens for optical observation was prepared by grinding from 500 to 1200 grit and mirror polishing while using 0.05 μ m alumina particles. The etching of the specimens was performed in accordance to ASTM E 407-99 standard (2 mL HF, 3 mL HCl, 5 mL HNO₃, and 200 mL H₂O). The etching was used not only to delineate grain boundaries but also to allow the different phases to appear by differences in brightness, shape, and color. After etching, the optical microstructures were observed with an optical microscope (Olympus BX51M, Tokyo, Japan).

Furthermore, to gain an insight into the in-depth microstructural features at peak-aged state the microstructural characterization was undertaken while using the scanning electron microscopy (SEM, JEOL FE-SEM Model 7600, Tokyo, Japan), which was operated at 15 kV. SEM image analysis was carried out to accomplish mainly two purposes. First, to analyze different precipitates and grain structure at the higher resolution. Secondly, an energy-dispersive X-ray analysis (EDX) was also employed to obtain the elemental analysis of the precipitate via an energy dispersive X-ray (EDX) unit (JEOL, Tokyo, Japan) coupled to the SEM instrument.

In order to acquaint with the various phases, present in the alloy after ageing treatment. X-ray diffraction (XRD) analysis was carried out while using X-ray diffractometer (Model: D-8 Discover, Bruker, Berlin, Germany) machine with CuK α monochromatic X-ray radiation and a tube current of 15 mA and voltage of 30 kV.

Furthermore, in order to distinguish the effect of the composition (i.e., high and low Mg content) on the mechanical properties the tensile testing was performed. Each set of specimens for the alloys described in Table 1 was subjected to uniaxial tension at room temperature after peak ageing treatment. The uniaxial tensile testing was performed on a computer-controlled tensile testing machine (Instron, University Ave, Norwood, USA). Dog bone tensile test samples were used for the measurement in tensile tests. Whilst, the dimensions of the dog bone shaped specimens were 2.5 mm in thickness and 6 mm in width, with a gauge length of 12.5 mm. The shape and size of the tensile specimens were in compliance with the ASTM/E 606 standard. The strain was measured by the axial extensometer epsilon

3542-0125M. The samples were tested at an initial strain rate of about 10^{-3} s⁻¹. The detailed mechanical properties including the yield stress (YS), ultimate tensile stress (UTS), elongation (ductility), and work hardenability of the prepared alloy specimens at peak-aged state condition were measured and were plotted w.r.t to compositions. At least five sets of specimens for each composition were tested to check the reproducibility of the measured data. Finally, the stress–strain curves of each H-0.4Mg and L-1.4Mg alloys were also drawn.

3. Results and Discussion

3.1. Effect of Composition on the Age Hardening Behavior

In order to explore and compare the age hardening behavior the hardness measurements were plotted as a function of ageing time. Figure 1, shows the age hardening behavior of the H-0.4Mg and L-1.4Mg alloys, respectively, after the artificially ageing process at 180 °C with varying time. The age-hardening curve showed a strong dependence on the overall Cu/Mg ratios of the designed alloys. While comparing the age hardening behavior of the studied alloys, it is evident that the L-1.4Mg revealed higher hardness even in the solution treated state i.e., at 0 h when compared to the H-0.4Mg alloy. The increase in the hardness value in the solution treated state could be attributed to the higher lattice distortion (solid solution strengthening) associated with the Mg atoms in the Al-matrix, as the atomic radius of Mg (0.160 nm) is larger when compared to Ag (0.144 nm) and Cu (0.128 nm). It is well known that the increase in lattice distortion makes the movement of dislocation very difficult which consequently increases the hardness value [18]. Hence, an alloy with a smaller Cu/Mg ratio is found to give a considerably higher strengthening effect per atom in the Al matrix. Beyond, the initial Cu/Mg ratio effect, it was observed that since from the beginning of the artificial aging process there was a progressive increase in the hardness value trend for both of the alloys which is consistent with the previously reported literature [6,19,20]. The monotonic increase in hardness values can be related to the formation of several precipitation phases from the metastable Al matrix during the ageing process [6,19,20]. In general, the hardness increases with the increase in ageing time, reaching a maximum value (peak ageing point T6) and then progressively decreases with further ageing leading to so-called overaged point (T7). The decrease in the hardness value at over age state could be related to the coarsening of solute-rich particles and/or precipitates [21,22].



Figure 1. Evolution of microhardness of L-1.4Mg and H-0.4Mg alloys as a function of ageing time after solution treatment at 180 °C followed by quenching at room temperature (RT).

It is important to mention that the total time for achieving the peak ageing state for the H-0.4Mg is 5 h, and for L-1.4Mg alloy, the time required for reaching peak ageing state is 6 h. Indeed, the average

value of Vickers Pyramid Number (HV) hardness at the peak-aged condition was determined to be 150 HV at 5 h for L-1.4Mg and 135 HV for the H-0.4Mg alloy as shown in Figure 1. The higher value of hardness at the peak ageing state in the L-1.4Mg alloy specimen, when compared to H-0.4Mg alloy specimen, could be explained with respect to our current scenario of compositional design that is related to the variation of Cu/Mg ratio resulting from difference Mg content. It is well established that addition of Mg content in Al-Cu base alloying systems could affect the precipitation sequence and results in the formation of additional phases such as the S (Al₂CuMg) phase. The reported precipitation sequence for this S-phase is usually transited the Guinier-Preston-Bagaryatsky zones, coherent S", semicoherent S', and equilibrium S phase. Thus, the increase in hardness for the L-1.4Mg alloy specimen is attributable to the synergistic effect of co-precipitation phases, namely Al-Cu- and Al-Cu-Mg-based phases. Particularly, it is reasonable to assume that the age-hardening behavior of our studied alloy is strongly dependent on two microstructural parameters: the precipitates size and their distribution in the matrix [19]. From the viewpoint of precipitation hardening, it is well known that the peak ageing state is controlled neither from very fine nor very coarse precipitate distributions but by the virtue of the intermediate precipitate size which is distributed at the grain boundary and in the matrix. This is because the dislocations generally require a large amount of energy to cut through the precipitate when compared to circumvent the precipitate. Nonetheless, the S-phase can promote a significant precipitation hardening effect due to their semi-coherent nature. Furthermore, the semi-coherent precipitates can effectively generate a high strain field when compared to coherent or non-coherent precipitate [19–23]. Nevertheless, for the higher hardness values of the L-1.4 Mg alloy (as seen in Figure 1), the role of multiple precipitation phases at peak-aged state along with initial solid solution strengthening effect could be a key factor. The quantification of the precipitation hardening behavior in multicomponent Al alloys is a daunting subject, and it demands combined knowledge of the precipitation strengthening mechanism and reliable measurement of precipitates size and volume fraction.

To further distinguish the possible mechanism of strengthening of the presently prepared H-0.4Mg and L-1.4Mg alloys in detail, the post microstructural analysis was carried out and mechanical properties were evaluated in the peak age hardened state specimens.

3.2. Effect of Composition on the Microstructures Evolution of H-0.4Mg and L-1.4Mg Alloys

Figure 2a,b show the optical microstructure of the H-0.4Mg and L-1.4Mg alloys at peak-aged state, respectively. It can be observed that for the H-0.4Mg alloy that the overall grains are mostly equiaxed with an average grain size of approximately 121 µm (as seen in Figure 2a). Additionally, solute-rich particles and/or precipitates, which are few in number, are also visible in the black color, and their average sizes are around 4 μ m. On the contrary, the L-1.4Mg alloy specimen at peak-aged state revealed an average grain size of 204 µm with quasi-equiaxed grain distribution (as seen in Figure 2b). It should be noted that here that the solute-rich aggregate (precipitates) distribution is random, and their average size is around 23 μ m. In an overall view, the L-1.4Mg alloy specimen exhibited a very complex evolution of second-phase particles and precipitation formation of the precipitate. For example, firstly, these intermetallic precipitates are distributed randomly in both the matrix and along the grain boundaries. Secondly, unlike the H-0.4Mg alloy counterpart, the solute-rich particles and/or precipitates are distributed along the grain boundaries and are mostly spherical and large in size for the L-1.4Mg alloy. It can be further seen that these solute-rich precipitates within the matrix are relatively irregular and are smaller in size (Figure 2b). Interestingly, huge differences in the size, growth, and dispersion of precipitates were observed when the microstructural features of both the alloys were compared simultaneously. In summary, the prominent distinguishing feature of precipitation processes in our developed alloys is that for the H-0.4Mg alloy specimen in which the precipitates are smaller in size. On the other hand, for L-1.4Mg alloy specimens, the precipitates continued to grow while maintaining the same high density which revealed the diverse evolution of precipitates both at grain boundaries (GBs) and in the matrix. Noticeably, the mixed precipitation

structure found in the L-1.4Mg alloy at peak-aged state can provide a vital contribution in increasing the mechanical properties of the alloys.



Figure 2. Optical microstructure of (a) H-0.4Mg and (b) L-1.4Mg alloys at peak-aged state.

To further clarify the optical microscopy observations, detailed SEM analyses were also performed and are discussed in the next section.

3.3. SEM and XRD Analysis of H-0.4Mg and L-1.4Mg Alloys

Figure 3a,b, shows scanning electron images of H-0.4Mg and L-1.4Mg alloys revealing the morphology, size, and distribution of precipitates at the peak aging condition. SEM analysis was carried out in a back-scattered electron (BSE) mode to distinguish different phases. Broadly speaking, the presently studied alloys (H-0.4Mg and L-1.4Mg) compositions are designed with respect to a low and high Cu/Mg ratio. Consequently, according to the isothermal phase diagram of Al-Cu-Mg alloys [12,15], these microscaled solute precipitates are presumed to be enriched in Cu and/or Mg elements. On the SEM image of both the H-0.4Mg and L-1.4Mg alloy specimens, the visible secondary phase can be seen in the form of white precipitates in the dark grey matrix. The H-0.4Mg alloy reveals a relative volume fraction of 0.57% as seen in the figure (Figure 3a). In contrast, with the L-1.4Mg alloy specimen, the white precipitated phase revealed the relative volume fraction of 0.65% (Figure 3b). This observation, in conjunction with the size and distribution of the white precipitate after aging treatment, reveals strong information about the difference in the cluster formation, nucleation, and the precipitation-hardening process. Owing to the chemical composition of our designed alloy, the sequence of the formation of precipitates could be either GPI + GPII zones $\rightarrow \theta' \rightarrow \theta$ (Al₂Cu) or GPII zones \rightarrow S' \rightarrow S' \rightarrow S1 and S2 (Al₂CuMg). Indeed, precipitation nucleation is a kind of diffusion transformation, which strongly relies on the diffusion of Mg atoms in our alloys.

Collectively, for identifying the composition of these white precipitates the energy-dispersive X-ray analysis (EDX) was performed. For the sake of simplicity, we will restrict ourselves to the L-1.4Mg alloy only. The nominal chemical composition by EDX analysis for the white precipitate phase is shown in Figure 4. From EDX results, it can be deduced that these white precipitates are reasonably close in composition to the Al₂CuMg (S) phase [22]. It should be noted that the two alloys investigated in this work have a significant difference in composition, as the L-1.4Mg alloy specimen contains almost three times more Mg when compared with the H-0.4Mg alloy specimen. Thus, according to literature data on the precipitation process, the above observation is something to be expected because precipitates grow at the expense of solute atoms [15,24]. Consequently, the lower precipitate density found after ageing treatment for the H-0.4Mg alloy compared to L-1.4Mg can be easily attributed to the variation of Mg contents in solid solution and vice versa. Nevertheless, the co-existence of dual intermetallic phases such as the θ phase or nano-sized precipitates (Ω phase) cannot be completely neglected. The Ω phase precipitates could not be detected easily using scanning electron microscopy

(SEM) because of their small size (~1 nm) and poor diffraction contrast when they are fully coherent with the Al-matrix. Thus, the discussion particularly related to the Ω phase falls beyond the scope of this paper.



Figure 3. Scanning electron microscopy (SEM) analysis of (**a**) H-0.4Mg and (**b**) L-1.4Mg alloys at peak-aged state.



Figure 4. Energy-dispersive X-ray analysis (EDX) analysis of precipitate in L-1.4Mg alloy at peak-aged state.

Results of the microstructural analysis are further verified and complemented by X-ray diffraction (XRD) analysis. Figure 5, shows the XRD profile of the H-0.4Mg and L-1.4Mg alloy specimens at the peak-aged state. The XRD diffractogram patterns of both the alloys display the strong characteristic peaks of a solid solution α -Al (Face centered cubic structure, FCC). The twin peaks observed in both XRD spectra are due to Cu-K-alpha doublet. From XRD profiles, beside the matrix phase (Al), the additional peaks corresponding to the intermetallic phases were also determined for H-0.4Mg and L-1.4Mg alloys, respectively (as shown in Figure 5). These additional peaks could be identified as the Al₂Cu (θ) phase (tetragonal structure, 14/mcm, a = 0.6066 nm, c = 0.4878 nm) and Al₂CuMg (S) phase (orthorhombic structure, Cmcm, a = 0.400 nm, b = 0.923 nm, c = 0.580 nm) [19,22,23]. It is evident that the Al₂Cu (θ) phase and Al₂CuMg (S) phase co-exist in both high and low Cu/Mg ratio compositional scenarios. However, it is noteworthy that the peak intensity from the S-phase became stronger as the Mg content increased from 0.4 to 1.4 wt.%. It is suggested that the low Cu/Mg ratio (i.e., higher Mg content) promotes the formation of the S-phase when compared to the θ phase. Thus, our XRD results support our compositional scenario and are consistent with the microstructural observations as well.



Figure 5. X-ray diffraction (XRD) patterns of H-0.4Mg and L-1.4Mg alloys at peak-aged state.

3.4. Effect of Composition on the Tensile Properties

To elucidate the relationship between the precipitate morphology and strengthening effectiveness, the mechanical properties of H-0.4Mg and L-1.4Mg alloys are also discussed. Figure 6a displays the tensile properties of H-0.4Mg and L-1.4Mg alloys at peak-aged state, the tensile properties were found dependent on Mg content. Among the different tensile properties, the ultimate tensile strength is typically improved upon the increase in the Mg content from 0.4 to 1.4 wt.%. All in all, it can be observed that the tensile strength increased with decreasing Cu/Mg ratio from 386 MPa for the H-0.4Mg specimen to 439 MPa for the L-1.4Mg specimen. By comparing both results, the overall increase in tensile strength is found to be 14%. The correlation between the microstructural and mechanical properties is summarized in Table 2. It is meaningful to mention that this increase in ultimate stress is ascribed mainly to the precipitation hardening effect. As it is well known that depending on the closeness of mismatch the strain field surrounding the precipitate retard the movement of dislocations and can effectively increase the strength [24]. It has been suggested that the dual precipitate structure of fine dispersive precipitates in the matrix and coarse precipitates at grain boundaries provides combined matrix and grain boundary strengthening for L-1.4Mg alloys, as shown in Figure 2a,b. Thus, based on our microstructure analysis, the main strengthening factor in the L-1.4Mg specimen is attributed to the existence and distribution of S (Al₂CuMg) precipitates formed at peak-aged state. Another factor for the increase in the mechanical strength could be due to the larger atomic size of the Mg than the Al; the Mg atom can occupy the substitutional position in the lattice and can impart an effective solid solution strengthening effect [19].



Figure 6. (a) True stress–strain curves; (b) dependence of strain hardening rate on the strain; (c) dependence of the strain hardening rate on the $(\sigma - \sigma_o)$ of H-0.4Mg and L-1.4Mg alloys at peak-aged state.

Alloys	Yield Stress (MPa)	Tensile Stress (MPa)	% Elongation	Average Hardness (HV)	Average Grain Size (µm)	Average Precipitate Size (μm)
H-0.4Mg	328 ± 12	386 ± 14	15	135	121	4
L-1.4Mg	307 ± 34	439 ± 32	17	149	204	23

Table 2. Summary of the mechanical and microstructural properties at peak-aged state.

Besides tensile strength, the percentage of fracture strain (elongation) increased from 15% for the H-0.4Mg specimen to 17% for the L-1.4Mg specimen, which could be attributable to the increase in the grain size; another reason for the higher ductility might be due to the difference in the dynamic recovery mechanisms in both of the alloys [25]. In contrast, the yield stress slightly decreased from 328 MPa for the H-0.4Mg specimen to 307 MPa for the L-1.4Mg specimen. Nonetheless, the difference in yield stress for both of the alloys is very small and, therefore, the yield strength shall be perceived as the same.

To compare the effect of different precipitation states on the plastic flow behavior during tensile testing, i.e., on the strain or work hardening rate (Θ) the L-1.4Mg and H-0.4Mg alloys were also derived from the tensile curve at peak-aged condition. The strain hardening rate (Θ) curves of L-1.4Mg and H-0.4Mg alloys were also derived from the experimental tensile curves and are shown in Figure 6b; here, the normalized Θ can be defined as [25]

$$\Theta = 1/\sigma \left(\frac{\partial \sigma}{\partial \varepsilon} \right) \tag{1}$$

where σ and ε are instantaneous values of stress and strain, and the hardening coefficient Θ is the slope of the stress–strain curve. As a matter of the fact, Equation (1) is the relationship between the incremental change in flow stress per incremental change in strain; therefore, Θ is logically termed as the strain hardening coefficient. Here, it should be mentioned that in our tensile test experiment, the strain rate was kept constant for both of the alloys. The strain hardening rate (Θ) curves of L-1.4Mg and H-0.4Mg alloys were also derived from the experimental tensile curves and are shown in Figure 6b. Although it is seen that through the test, the strain hardening rate (Θ) decreases with the increase in strain but depends on the presence of Mg content. In both cases, an initial abrupt drop in the strain hardening rate (Θ) is observed with the increasing strain which might be due to the elastic/plastic transition associated with the chemical composition of alloy material [26]. Following the elastic/plastic transition stage, the L-1.4Mg and H-0.4Mg alloys showed distinct behavior in strain hardening rate resulting due to their microstructural characteristics at peak-aged state. The Θ of the L-1.4Mg alloy remains positive until the $\varepsilon = 16\%$ when compared to H-0.4Mg where the Θ starts to be negative around $\varepsilon = 11\%$. Additionally, Figure 6c represents the dependence of the strain hardening behavior (also called work hardening) as a function of effective stress (σ - σ ₀). Here, σ is the stress at the plastic stage and σ_0 is the yield stress. It clearly shows that increasing Mg content in the Al-Cu-Mg-Ag alloy increases the value of Θ_0 . However, the Θ_0 reaches zero at 100 MPa of the effective stress for the H-0.4Mg alloy. In contrast, the L-1.4Mg alloy exhibits almost double value almost reaching 200 MPa as seen in Figure 6c.

In general, while comprehensively considering the overall strain hardening rate (Θ), the L-1.4Mg alloy is higher with the distinct value of 500 MPa when compared with the H-0.4Mg alloy. The increase in strain hardening rate by the Mg content has also been reported in many articles [27]. It has also been claimed that work hardening of alloys hardened by precipitate heat treatments depends on the distribution of the precipitate sizes and the solute level left in the metal matrix [26].

Thus, the difference in strain hardening for both of the alloys seems to be directly associated with variety of factors including; the differences in the precipitates, their volume fraction, average size, and spatial distribution and finally with the nature of their interaction with dislocation. Indeed, the accumulation of forest dislocations near the precipitates plays a dominant role in the distinct work hardening mechanisms, as widely observed in FCC polycrystalline alloys [28,29]. To date, although several mechanisms such as chemical, stacking fault, modulus, order, and coherency hardening due to shearable precipitates have been discussed in the literature, complete understanding of these phenomena is far from complete [19,26–28]. According to the model developed by X Wang et al., [30], the drastic changes in the work hardening of AA6111 and AA7030 can be explained based on dynamic recovery which results from shear and non-shearable precipitate transition. Surprisingly, despite intriguing relevance for structural application, the data related to the work hardening behavior in aged 2xxx series alloys are very sparse in the literature. The robust mechanical properties of our investigated alloys are comparable to the earliest reported age-hardenable aluminum alloys designed for structural applications [1,22–26,29–31].

In summary, we propose to exploit the potential of precipitation strengthening with dual precipitation phases and found it to be a remarkable strategy when compared with solid-solution strengthening, grain-boundary strengthening, and work hardening methods. From this work, we demonstrated that tailoring the Cu/Mg ratio by Mg content and consequently tuning the macroscopic properties of precipitates is an effective route for the enhancement of strength in engineering structural materials.

4. Conclusions

The effect of the various amount of Mg content on the microstructure, hardness, ultimate tensile stress, percentage elongation, and work hardenability of the wrought Al-Cu-Mg-Ag alloy with different Cu/Mg ratios (~9.54 and ~2.87) was analyzed.

The following conclusions are summarized:

- Comparing the results of solution-treated and peak-aged states, the L-1.4Mg alloy had the highest hardness values, and the tendency remained the same during the entire ageing processes.
- The peak hardness value and age-hardening response were dependent on the Cu/Mg ratio which is aided by the modification in the Mg contents.
- In general, the increase in Mg content modifies the precipitate growth features. The L-1.4Mg comprises precipitate morphology in the duplex size (fine and coarse) precipitate distribution when compared to the H-0.4Mg alloy.
- A comparative study of microstructural analysis and XRD relative intensities manifests that the presence of solute consisting intermetallic precipitates—i.e., the Al₂Cu (θ) phase, Al₂CuMg (S) phases.
- Relative XRD profile data identified that the Al₂CuMg (S) phase proceeds to form, to a large extent, in the low Cu/Mg ratio of alloy.
- Heterogeneous precipitate size distribution in the matrix and at grain boundaries provides a pathway for matrix and precipitation/grain-boundary strengthening in the L-1.4Mg alloy.
- Owing to the optimal combination of solid solution strengthening and precipitation strengthening the ultimate strength increased to 14%, and the strain hardening rate was almost doubled in the L-1.4Mg alloy when compared to H-0.4Mg alloy.

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