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Influences of Cu Content on the Microstructure and Strengthening Mechanisms of Al-Mg-Si- x Cu Alloys

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Abstract: The effects of the Cu content on the microstructure and strengthening mechanisms of the Al-Mg-Si- x Cu alloys were systematically investigated using scanning electron microscopy (SEM), electron probe microanalysis (EPMA), transmission electron microscopy (TEM), and mechanical tensile tests. The results show that, the strengthening mechanisms change with the Cu content. For as-quenched alloys, solution strengthening (σ_{SS}) is predominant when the Cu content ≥ 2.5 wt.%, and of equivalent importance as grain size strengthening (σ_{H-P}) when the Cu content ≤ 1.0 wt.%. With respect to peak-aged alloys, precipitation strengthening (σ_{ppt}) is predominant when the Cu content ≥ 2.5 wt.%, but σ_{SS} becomes predominant when the Cu content is 4.5 wt.%. As the Cu content increases from 0.5 to 4.5 wt.%, the main type of precipitates in alloy tends to change from a β'' phase to Q' phase, and then to a θ' phase. Among the three types of precipitates, θ' -precipitate causes the largest increase in yield strength ($\sigma_{0.2}$) and the largest decrease rate in elongation. β'' -precipitate leads to the smallest increase in $\sigma_{0.2}$ and the smallest decrease rate in elongation. The increase of Cu content reduces Si solubility in the Al matrix and thus decreases the nucleation rate of β'' phase during subsequent aging.

Keywords: Al-Mg-Si-Cu Alloy; Cu Content; microstructure; mechanical properties; high-resolution transmission electron microscopy

1. Introduction

Al-Mg-Si- x Cu alloys have been widely used in the fields of aviation, rail transportation, and the automobile industry, due to the combination of good formability and excellent corrosion resistance [1,2]; however, the relatively low strength has restricted their applications, due to the increasing requirements for larger, faster vehicles. Thus, it is necessary to develop Al-Mg-Si- x Cu alloys with better mechanical properties [3,4].

Cu is known to have a significant strengthening effect on Al-Mg-Si-Cu alloys [5]. Many studies [6,7] show that the strength of such an alloy can be enhanced by Cu additions as low as 0.1 wt.%. Jin et al. [5] indicated that additions of 0.3 wt.% Cu increased the tensile strength of Al-Mg-Si-Cu alloys from approximately 390 to 430 MPa. Shabestari et al. [8] found that an increase in Cu content from 0.2 to 1.5 wt.% could lead to an increase of around 25% in the tensile strength of such alloys. Zheng et al. [9] discovered that, when the addition of Cu increased to 4.0 wt.%, the strength of the alloy was increased by more than 37.5%. On account of the increasing demand for high-strength alloys, the recent

interest in Al-Mg-Si-Cu alloys has been switched to alloys with a wider range of Cu contents; however, as research continues, issues concerning the Cu effect on the microstructure and mechanical properties of Al-Mg-Si-Cu alloys have gradually emerged, as discussed below.

(i) In many research projects [10–12], it has been found that, with the increase in Cu content, the tensile strength of the alloy increases, while the ductility of the alloy decreases. However, in some studies, it has been shown that Cu additions can increase the strength of an alloy without an accompanying loss of ductility. Jin et al. [5] and Zhong et al. [13] even found that 0.3 and 0.6 wt.% additions of Cu increase both the strength and elongation of such an alloy. Besides, some researchers found that the strength of the alloys does not always monotonically increase with Cu content. For instance, Lu et al. [14] found that the tensile strength of such an alloy decreases when the Cu content increases from 1.48 to 1.86 wt.%.

(ii) It is known that, Cu additions can produce grain size strengthening (σ_{H-P}), solid solution strengthening (σ_{SS}), and precipitation strengthening (σ_{ppt}) effects on Al-Mg-Si-Cu alloys, but it remains unclear which effect is predominant, especially in alloys with different Cu contents. Watanabe et al. [15] and Sauvage et al. [16] investigated the strengthening behavior of Al-Mg-Si-Cu alloys with 0.2–0.7 Cu wt.% contents, and attributed the strengthening effect of Cu to the significant grain refinement therein. However, Salleh et al. [17] stated that Cu addition has no significant effect on grain refinement, and indicated that σ_{ppt} plays a major role in the increase of hardness and tensile strength. Although many studies [11] support the view of Salleh et al., others [18] have stated that the significant increase in maximum hardness during ageing, with the increase in Cu content, is mainly the results of σ_{SS} .

(iii) It is known that different types of precipitates (e.g., β'' [15], Q' ($Al_{3.8}Mg_{8.6}Si_7Cu_1$) [5,16], σ ($Al_5Cu_6Mg_2$) [19], θ' (Al_2Cu) [9], etc.) might be present, and often coexist, in Al-Mg-Si-Cu alloys during artificial aging, but their strengthening effects on such alloys were still widely debated. Esmaeili et al. [20] found that both β'' and Q' precipitates occurred in the peak-aged alloy, but only the β'' precipitate was the main cause of age-hardening. Wang et al. [18], and Lu et al. [14], support Esmaeili et al. Miao et al. [21], and Saito et al. [7] stated that the Q' precipitates were mostly formed in over-aged conditions rather than peak-aged conditions. However, some other studies find that both β'' and Q' precipitates contributed to the strength increase of the alloy. Moreover, Jin et al. [5] and Farkoosh et al. [10] found that the Q' precipitate plays the major role in improving the age-hardening of alloys with Cu addition.

In short, quaternary Al-Mg-Si-Cu alloys, straddling the compositions of 2xxx (Al-Cu(-Mg)) and 6xxx (Al-Mg-Si) alloy, are more widely used in applications, due to their excellent comprehensive performance. The Cu content is known to have a pronounced effect on both microstructure and the properties of Al-Mg-Si-Cu alloys, but details thereof remain unknown. Therefore, uncovering the effect of Cu content on the microstructure and strengthening mechanisms of Al-Mg-Si-Cu alloys is important for alloy designers. Here, Al-Mg-Si-Cu alloys with four different Cu contents (0.5 wt.%, 1.0 wt.%, 2.5 wt.%, and 4.5 wt.%) were designed, and SEM, EPMA, TEM, and mechanical tensile tests were used to study the effects of the Cu content on the microstructure, aging precipitation, and mechanical properties of the Al-Mg-Si-Cu alloys.

2. Experimental Methods

2.1. Materials

Four Al-Mg-Si-Cu alloys with different Cu contents were produced using high purity aluminium (>99.97 wt.%), oxygen-free copper (>99.95 wt.%), an Al-20% Si master alloy, industrially-pure magnesium (>98 wt.%) and an Al-5% Ti-1% B grain refiner. The specific compositions of these alloys (Alloy 1, 2, 3, and 4) are listed in Table 1.

To acquire a homogeneous microstructure, the alloy ingots (ϕ 400 mm $\times$ L 200 mm) were subjected to homogenization annealing (Alloy 1 and Alloy 2 were homogenized at 560 °C for 12 h, and Alloy 3 and 4 were homogenized at 520 °C for 12 h) in an air furnace. Then, the ingots were extruded into a bar with a diameter of 10 mm at 440 °C and cut into 10 mm long cylindrical samples. Post solution

heat treatment of the alloys was conducted in an SG-12-10 salt-bath furnace at 520 °C for 1 h, followed by water quenching, and then, an artificial aging treatment was undertaken at 165 °C for different times immediately after quenching with a room-temperature storage time less than 30 s.

Table 1. Chemical compositions of the alloys (wt.%).

No.	Mg	Si	Cu	Mn	Cr	Zn	Ti	Fe	Al
1	0.42	0.50	0.50	0.20	0.10	0.20	0.02	<0.10	Bal.
2	0.42	0.50	1.00	0.20	0.10	0.20	0.02	<0.10	Bal.
3	0.42	0.50	2.50	0.20	0.10	0.20	0.02	<0.10	Bal.
4	0.42	0.50	4.50	0.20	0.10	0.20	0.02	<0.10	Bal.

2.2. Performance Test

The mechanical tensile tests were performed on a DDL 100 electronic universal testing machine (Changchun Research Institute for Mechanical Science Ltd., Changchun, China) with a tensile speed of 2 mm/min. The size of the tensile samples is illustrated in Figure 1. The hardness testing of each alloy sample was performed using a load of 30 N and a dwell time of 15 s.

Figure 1. Sample size for tensile testing (unit: mm).

2.3. Microstructure Analysis

Metallographic specimens were prepared using a standard procedure and were etched in a solution containing HF (2 mL), HCl (3 mL), HNO₃ (5 mL), and H₂O (200 mL). The grain size was determined by a line intersection method, according to ASTM E112-96, which involves an actual count of the number of grains intercepted by a test line. For each testing sample, at least 200 grains were considered.

The distribution characteristics of second-phase particles were obtained by the use of a JXA-8230 electron probe microanalyzer (EPMA, JEOL Ltd., Tokyo, Japan). The wavelength dispersion spectrometer (WDS, JEOL Ltd., Tokyo, Japan) was used to quantify the composition of the second-phase particles in the alloy and to observe the distribution of the main elements of the alloy.

The TEM, high-resolution transmission electron microscopy (HRTEM), and high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images were carried out on a Tecnai G² F20 (FEI Ltd., Hillsboro, OR, USA) and Titan G² 60-300 TEM (FEI Ltd., Hillsboro, OR, USA), and the accelerating voltage of both the instruments was 200 kV. Thin foils for the TEM analyse were prepared in a twin-jet electro-polishing unit using a solution of nitric acid: methanol (1:3 by volume) at −25 °C, 20 V, and a current of about 80 mA.

3. Results

3.1. Effect of Cu Content on the Metallographic Structures of the Alloys

Figure 2 shows the metallographic structures of the four alloy samples in both as-extruded, and as-quenched, states. The average grain size (AGZ) and grain aspect ratio (GAR) of these alloys

were calculated, and the results are listed in Table 2. In the as-extruded state, the grains of all four alloys were elongated along the extrusion direction (ED), and AGZs were measured to be 765, 538, 475, and 190 μm , respectively. The grains in Alloys 1 and 2 generally take on pancake shapes with GARs of 6.47 and 8.27, respectively, but the grains in Alloys 3 and 4, exhibiting remarkably fibrous characteristics, show apparently larger GARs.

Figure 2. Optical micrographs of alloys at different states: (a) as-extruded Alloy 1, (b) as-quenched Alloy 1, (c) as-extruded alloy 2, (d) as-quenched Alloy 2, (e) as-extruded Alloy 3, (f) as-quenched Alloy 3, (g) as-extruded alloy 4, (h) as-quenched Alloy 4.

Table 2. Average grain size (AGZs) and grain aspect ratio (GARs) of four Al-Mg-Si-Cu alloys at different states.

Sample State	As-Extruded State				As-Quenched			
Sample No.	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 1	Alloy 2	Alloy 3	Alloy 4
AGZ (μm)	765	538	475	190	482	351	211	108
GAR	6.47	8.27	9.67	11.23	2.35	2.97	3.56	4.12

In as-quenched states, the AGZs of all four alloys were measured to be 482, 351, 211, and 108 μm , respectively, which decreased compared with those of the as-extruded alloys. Besides, the AGZs of alloys significantly decrease, while the GARs of alloys increase as the Cu content increases. As seen, compared with Alloy 1, the AGZ of Alloy 4 decreases by 75.2% and its GAR increases by 75.4%. This indicates that the Cu addition plays an important role in both grain refinement and increasing GAR.

Figure 3 shows the $\{200\}$ pole figures of four as-quenched alloys, respectively. A texture with a pole of high intensity is seen in the center of the $\{200\}$ pole figure for all four alloys, which implies an evident fiber texture developed on the $\{200\}$ planes after quenching. Besides, this $\{200\}$ fiber texture is sharper with the increase of Cu content, which confirms that the recrystallisation is more pronounced in the alloy with a higher Cu content, since the $\{200\}$ fiber texture is known to be a typical recrystallisation texture in aluminium alloys [22].

Figure 3. The $\{200\}$ pole figures of four as-quenched alloys: (a) Alloy 1 (b) Alloy 2 (c) Alloy 3 (d) Alloy 4.

3.2. Influence of Cu Content on the Coarse Second-phase of the Alloys

Figure 4 shows the back-scattered electron (BSE) images of the four alloys in both the as-extruded, and as-quenched, states. A large number of coarse second-phase particles, arranged along ED, were observed in all four as-extruded alloys (Figure 4a,c,e,g), and their number increases with the

increase of Cu content. After solution heat treatment, the number of coarse second-phase particles decreases, but many of them are still reserved especially for the alloys with high Cu contents (Figure 4h).

Figure 4. Back-scattered electron (BSE) images of the alloys at different states: (a) as-extruded Alloy 1, (b) as-quenched Alloy 1, (c) as-extruded Alloy 2, (d) as-quenched Alloy 2, (e) as-extruded Alloy 3, (f) as-quenched Alloy 3, (g) as-extruded Alloy 4, (h) as-quenched Alloy 4.

Figures 5 and 6 show elemental mapping of as-extruded and as-quenched samples of Alloy 1. There are two types of coarse second-phase particles: Ellipsoidal second-phase particles and white rod-shaped second-phase particles. The grey second-phase particles are rich in Fe, Si, and Mn, but the white ones are mainly rich in Cu and Si. According to the literature, the grey phase is determined to be an $\text{Al}(\text{Fe,Mn})_x\text{Si}_y$ phase [23] and the white phase is identified as an AlCu_xSi_y phase [5], which are the common inclusions in Al-Mg-Si-Cu alloys. As can be also noticed, the number density of $\text{Al}(\text{Fe,Mn})_x\text{Si}_y$ particles is significantly larger than that of the AlCu_xSi_y phase in Alloy 1 in both as-extruded, and as-quenched, states.

Figure 5. Elemental mapping of the as-extruded Alloy 1 examined by EPMA.

Figure 6. Elemental mapping of the as-quenched Alloy 1 examined by EPMA.

By comparing the maximum intensity values ($I_{\max}$) of each element in the EPMA mapping, the element distribution can be obtained. Among the tested elements, Mg and Si have quite low $I_{\max}$ values in Alloy 1 in both as-extruded and as-quenched states, implying that they are distributed relatively evenly. This is probably due to the high solubility and diffusion coefficient of Mg and Si in Al [24]. Although the Cu content is similar to the contents of Mg and Si in Alloy 1, $I_{\max, \text{Cu}}$ is much larger than $I_{\max, \text{Mg}}$ and $I_{\max, \text{Si}}$ which indicates that the Cu distribution is less uniform. In addition, it is shown that, after solution heat treatment, $I_{\max, \text{Cu}}$, $I_{\max, \text{Mg}}$, and $I_{\max, \text{Si}}$ decrease slightly but $I_{\max, \text{Mn}}$ and $I_{\max, \text{Fe}}$ increase. This means that the elements of Cu, Mg, and Si in the coarse second-phase particles gradually dissolve into the matrix while an enrichment of Mn and Fe elements in the coarse second-phase particles takes place.

Figures 7 and 8 show elemental mappings of as-extruded and as-quenched samples of Alloy 4. Differing from Alloy 1, almost all the coarse second-phase particles display a significant increase in the amount of Cu. The AlCu_xSi_y phase was transformed into a θ (Al_2Cu) phase [25], which was depleted in Si. $I_{\max, \text{Cu}}$ and $I_{\max, \text{Mg}}$ decrease, while $I_{\max, \text{Fe}}$ and $I_{\max, \text{Mn}}$ increase after solution heat treatment. In contrast to that of Alloy 1, $I_{\max, \text{Si}}$ increases from 11.0% to 57.1%, suggesting that the Si content in the second-phase particles increases after solution heat treatment.

Figure 7. Elemental mapping of the as-extruded Alloy 4 examined by EPMA.

Figure 8. Elemental mapping of the as-quenched Alloy 4 examined by EPMA.

3.3. Influence of the Cu Content on the Mechanical Properties of the Alloys

3.3.1. Age-Hardening Curves

The artificial age-hardening of as-quenched alloys (at 165 °C) was studied in our previous work [4], and here is also shown in Figure 9. It is shown that the hardness of alloys and the peak-aging time increase with the Cu content. After peak aging, the hardness of all four alloys decreases. When the alloys are aged for 14,400 min, the hardness values for Alloys 1, 2, 3, and 4 have decreased by 36, 29, 37, and 85 HV, respectively, relative to their peak-aging hardness values. This indicates that the over-aging softening phenomenon is more obvious in Alloy 4 than in the other three alloys.

Here, we continue our previous work by evaluating the tensile mechanical properties and their relationship with precipitation in alloys with different Cu contents.

Figure 9. Hardness versus aging time at 165 °C of Al-Mg-Si alloys with different Cu contents.

3.3.2. Mechanical Properties

Figure 10a shows the tensile curves of the four as-quenched alloys. The strengths of Alloys 1–4 are enhanced with increasing Cu content, in particular, the tensile strengths of Alloys 3 and 4 are enhanced by 54.8%, and 104.1%, respectively, compared with that of Alloy 1. The elongations of Alloys 1 and 2 are 29.7%, and 28.1% respectively, illustrating that the decrease in elongation is quite limited when the Cu content increases from 0.5% to 1.0%, but when the Cu content increases to 2.5%, the elongation of alloy decreases with the increase of Cu content. The elongations of Alloys 3 and 4 decrease to 20.6%, and 18.5%, respectively. This suggests that the elongations of Alloys 3 and 4 decrease by 30.6%, and 37.7%, respectively, compared to that of Alloy 1.

Figure 10. Tensile curves of the alloys in different heat-treatment states: (a) as-quenched, (b) peak-aged.

Figure 10b illustrates the tensile curves of the four alloys in peak-aged state. The strength of all four alloys are enhanced to a certain extent compared with those of as-quenched alloys, and are measured to be 261.3, 270.9, 346.2, and 442.5 MPa, respectively. Meanwhile, the elongations of Alloy 1–4 are 19.3%, 17.9%, 11.6%, and 10.0%, respectively. This indicates that the strength of the alloys significantly increases while their elongation decreases when the Cu content increases to 2.5%. Besides, in our study, it shows that either the Cu content or the aging treatment has little influence on the elastic modulus of aluminium alloy, which is in accordance with the results of previous studies [6,7].

3.4. Influence of the Cu Content on the Precipitates of the Alloys

Figure 11 shows TEM and corresponding selected area diffraction pattern (SADP) images of the four alloys in peak-aged state. In all four alloy samples, there are many precipitate particles distributed uniformly in the Al matrix. The shapes of precipitates in Alloys 1 and 2 (Figure 11a,d) are similar and are of acicular or granular form. Among these precipitates, the acicular ones were arranged along the $\langle 010 \rangle_{\text{Al}}$ directions. In addition, the number density of granular precipitates is larger and the number density of acicular precipitates is smaller than those in Alloy 1. The SADP image of Alloy 1 (Figure 11b,c) shows faint cruciform diffraction spots in the central positions of the (000) and $(202)_{\text{Al}}$ spots, but an break can be observed in the middle position of the cruciform diffraction spots for Alloy 2 (Figure 11e,f). This implies that the precipitates in Alloy 1 and 2 may be not the same.

Figure 11. TEM and SADP images of the four peak-aged Al-Mg-Si-Cu alloys observed in the $\langle 010 \rangle_{\text{Al}}$ projection: (a,b,c) Alloy 1, (d,e,f) Alloy 2, (g,h,i) Alloy 3, (j,k,l) Alloy 4.

Figure 11g–l illustrates the TEM images and corresponding SADP results for the peak-aged Alloys 3 and 4. In Alloys 3 and 4, the acicular precipitates are replaced by lamellar-shaped ones. Besides, the number of granulate-shaped precipitates decrease compared to that of the other three alloys. The SADP images of Alloy 3 and 4 are similar: Distinct cruciform diffraction spots, due to the precipitates are observed between (000) and $(002)_{\text{Al}}$, (000) and $(200)_{\text{Al}}$, $(200)_{\text{Al}}$ and $(202)_{\text{Al}}$, and $(002)_{\text{Al}}$ and $(202)_{\text{Al}}$, but the diffraction spots of the precipitates are brighter in Alloy 4, which may be related to its more numerous and thicker lamellar-shaped precipitates, compared with those in Alloy 3.

To further determine the type of precipitate in these alloys, HRTEM and HAADF-STEM were used. Figure 12 shows the HRTEM results for the typical granular-shaped precipitate in the peak-aged Alloy 1. As shown in Figure 12a, this precipitate has a monoclinic structure with lattice parameters of $a = 1.51$ nm and $c = 0.67$ nm. According to Figure 12b,c, the orientation relationships of $(200)_{\text{precipitate}} \parallel (301)_{\text{Al}}$ and $[010]_{\text{precipitate}} \parallel [010]_{\text{Al}}$ can be detected. Therefore, the granular-shaped precipitate is determined to be the β'' phase [4,15].

Figure 13a shows the HRTEM results for the typical acicular precipitates in the peak-aged Alloy 1 which is approximately four Al atom layers in width but over 100 Al atom layers in length. Due to its acicular shape feature, the precipitate usually overlaps with the Al matrix, and it is thus difficult to observe its lattice structure viewed in the edge-on direction [26], but the corresponding FFT (Figure 13b,c) reveals that these precipitates are a β'' phase. Therefore, both the acicular, and granular-shaped, precipitates are of the β'' phase. Their different shapes are only caused by differences in viewing direction, namely, viewed edge-on (acicular) or end-on (granulate shape). Since no other precipitate is observed, the β'' phase should be the predominant precipitate in peak-aged Alloy 1.

The β'' phase and Al matrix are known to have a coherent interface with a large interface strain energy, which exerts a favourable effect on the alloy in terms of strength [27]. For the alloys with a low Cu content (Alloy 1), the β'' phase is the main strengthening phase in the peak-aged condition.

Compared with those in Alloy 1, the acicular precipitates in the peak-aged Alloy 2 are relatively coarser. Figure 14a shows the HRTEM image of a typical acicular precipitate particle in Alloy 2 whose width exceeds seven Al atom layers. As shown in Figure 14b,c, this precipitate has the same FFT pattern with that of acicular precipitates in Alloy 1, and is also determined to be the β'' phase.

Figure 12. Granular-shaped precipitate in the peak-aged Alloy 1 (165 °C/360 min) observed via the $\langle 010 \rangle_{\text{Al}}$ direction: (a) HRTEM image; (b) corresponding fast Fourier transform (FFT); (c) simulated pattern.

Figure 13. Acicular precipitate in the peak-aged Alloy 1 (165 °C/360 min) observed via the $\langle 010 \rangle_{Al}$ direction: (a) HRTEM image; (b) corresponding FFT; (c) simulated pattern.

Figure 14. Acicular precipitate in the peak-aged Alloy 2 (165 °C/480 min) observed via the $\langle 010 \rangle_{Al}$ direction: (a) HRTEM image; (b) corresponding FFT; (c) simulated pattern.

The HRTEM image and corresponding FFT pattern of the granulated precipitate in the peak-aged Alloy 2 are shown in Figure 15. This precipitate has a polygonal (hexagonal) shape with a typical HCP crystal structure which is different from the shape of the β'' phase. Its lattice parameters are determined to be $a = 1.032$ nm and $c = 0.405$ nm, besides, its interface is largely parallel to the three crystal faces of the Al matrix, i.e., $(501)_{Al}$, $(103)_{Al}$ and $(506)_{Al}$ (Figure 15). Moreover, its orientation relationships with the Al matrix are found to be $(2110)_{precipitate} \parallel (501)_{Al}$ and $[0001]_{precipitate} \parallel [010]_{Al}$, i.e., the angle between

$(2110)_{\text{precipitate}}$ and $(200)_{\text{Al}}$ is approximately 9.5° . These results are consistent with previous reports concerning a Q' phase [4,5,25].

Figure 16 shows the HAADF-STEM image and corresponding energy-dispersive X-ray spectroscopy (EDS) mapping results for the peak-aged Alloy 3, viewed along $\langle 010 \rangle_{\text{Al}}$ axis. As can be seen, all the granulate-shaped precipitates (shown by broken circles) are enriched in Cu, Mg, and Si, consistent with the ingredients of a Q' phase; however, the lamellar-shaped precipitates without Mg and Si in Alloy 3 are only enriched in Cu, indicating that these precipitates are not the β'' phase. According to the HRTEM and corresponding FFT images shown in Figure 17, these lamellar precipitates, elongated along $\{200\}_{\text{Al}}$, exhibit a tetragonal structure with lattice parameters of $a = 0.404$ nm and $c = 0.58$ nm. Their orientation relationships with Al matrix are determined to be $(200)_{\text{precipitate}} \parallel (200)_{\text{Al}}$ and $[010]_{\text{precipitate}} \parallel [010]_{\text{Al}}$. From the literature [25], it can be concluded that these precipitates are a θ' phase, and so the predominant precipitates in the peak-aged Alloy 3 are θ' and Q' phases.

Figure 15. Granular-shaped, Q' -phase precipitate in the peak-aged Alloy 2 ($165^\circ\text{C}/480$ min) observed via the $\langle 010 \rangle_{\text{Al}}$ direction: (a) HRTEM image; (b) corresponding FFT; (c) simulated pattern.

Figure 16. HAADF-STEM images and corresponding EDS mapping of peak-aged Alloy 3 (165 °C/540 min) observed via the $\langle 010 \rangle_{\text{Al}}$ direction.

Figure 17. HRTEM image and corresponding FFT of lamellar precipitates in the peak-aged Alloy 3 (165 °C/540 min) observed via the $\langle 010 \rangle_{\text{Al}}$ direction.

The HAADF-STEM images of Alloy 4 viewed along $\langle 010 \rangle_{\text{Al}}$ are shown in Figure 18a: similar to Alloy 3, a large quantity of lamellar precipitates and fine granular precipitates are distributed in Alloy 4. Figure 18b shows the Z-contrast image of the lamellar precipitated phases. This precipitate has an orientation relationship of $(200)_{\text{precipitate}} \parallel (200)_{\text{Al}}$ and $[010]_{\text{precipitate}} \parallel [010]_{\text{Al}}$ with the matrix. So, this precipitate is considered to be a θ' phase (see Figure 19). Since this imaging mode is dominated by atomic number, the brightest dots can be identified as atomic columns of Cu ($Z_{\text{Cu}} = 29$). Also imaged, but with a lower intensity, are the Al atomic columns ($Z_{\text{Al}} = 13$) within the precipitates and the surrounding matrix. This reveals that the Cu atoms inside these lamellar precipitates have a regular, periodic, distribution.

Figure 18c,d show the HAADF-STEM images of the granulated precipitate. All these precipitates have the same orientation relationship with the Al matrix, i.e., $(\bar{2}\bar{1}10)_{\text{precipitate}} \parallel (501)_{\text{Al}}$ and $[0001]_{\text{precipitate}} \parallel [010]_{\text{Al}}$. Thus, this precipitate is determined to be the Q' phase. Since Q' phase is made up of Mg ($Z_{\text{Mg}} = 12$), Si ($Z_{\text{Si}} = 14$) and Cu, and Cu has a much larger atomic number than Mg and Si, the brightest dots in the Q' lattice can also be identified as atomic columns of Cu. As can be seen, the Cu atoms are periodically arranged in this precipitate when viewed along $\langle 010 \rangle_{\text{Al}}$.

Figure 18. High-resolution HAADF-STEM images of Alloy 4 (165 °C/960 min) observed via the $\langle 010 \rangle_{\text{Al}}$ zone axis. (a) The lamellar θ' precipitates; (b) Z-contrast image of the θ' phase; (c) the granulated Q' precipitate; (d) Z-contrast image of the Q' phase.

Figure 19a shows the Z-contrast image of the θ' phase/Al matrix interface obtained via HAADF-STEM. The lattice constants of the θ' phase are $a_{\theta'} = 0.404$ nm, $c_{\theta'} = 0.574$ nm, and $\beta = 90^\circ$. At the Al matrix/ θ' phase interface, $(200)_{\text{Al}}$ and $(200)_{\theta'}$ have a favorable, one-to-one corresponding relationship. This indicates that the θ' phase exhibits a completely coherent interface structure with the matrix. Besides, a change in structure is evident at the coherent interfaces between the θ' precipitates and the matrix, as additional Cu atoms appear at the interfaces of θ' precipitates. This agrees with the results reported elsewhere [28,29].

Image intensity profiles taken along (002) planes across the broad interfaces (B1-B2) confirm that the Cu occupancy of the interstitial sites at the interface is almost full for the precipitate in Figure 19b. The interstitial site occupancy was estimated by measuring the interstitial atom column intensities in

the experimental HAADF-STEM images and comparing them with intensities for non-interstitial Cu columns. The intensity profiles of the C1-C2 profile illustrates an interstitial site between every two Cu atoms, which is consistent with the θ' phase atom positioning model proposed by other studies [30,31]. Bourgeois et al. [32] noted that the Cu occupancy of the interstitial sites at the θ' phase/Al matrix interface change with the thickness of the θ' phase: Thicker θ' precipitates exhibit a lower occupancy of interstitial sites at the interface and the interstitial site occupancy rate of Cu is quite low when the thickness of the θ' phase exceeds $8C_{\theta'}$. In the present study, the thickness of the θ' phase observed in Figure 18 reaches $12.5C_{\theta'}$, but the interstitial sites at the interface are still fully occupied by Cu atoms. This is probably due to the different Mg contents in alloys between the present study and Bourgeois et al. [32]. The materials studied by Bourgeois et al. are Al-Cu-Si ternary alloys in which the Cu content was similar to that of Alloy 4 but did not contain Mg. It is known that, the atom radii of Al, Mg, Si, and Cu are 0.143, 0.160, 0.138, and 0.128 nm [33], respectively. The greater atom radii of Mg might play a role in balancing the negative strain produced by the occupied Cu atoms at the interface which increases the interstitial site occupancy rate of Cu.

Figure 19. The interface of the θ' phase in Figure 18b. (a) Z-contrast image; (b) image intensity profiles; (c) schematic diagram of the atomic positions.

Figure 20 illustrates the HRTEM image of the granulated precipitates in Alloy 4. According to the lattice measurement and the FFT analysis, it is confirmed that these precipitates are of the Q' phase.

Figure 20. Granular-shaped Q' precipitate in peak-aged Alloy 4 (165°C/960 min) observed via the $\langle 010 \rangle_{Al}$ direction: (a) HRTEM image, (b) corresponding FFT, and (c) simulated pattern.

According to the above analyses, Alloy 4 has the same types of precipitates with alloys which are θ' and Q' phases; however, the θ' phase is dominant in Alloy 4, and the number and size of Q' phase particles are also smaller than those of Alloy 3.

4. Discussion

4.1. Influence of Cu Content on Alloy Microstructure

4.1.1. Coarse Second-Phase Particles

In Alloy 1, the coarse second-phase particles include the Cu-depleted $\text{Al}(\text{Fe}, \text{Mn})_x\text{Si}_y$ phase and Cu-riched AlCu_xSi_y phase. With increasing Cu content, the amount of Cu in the coarse second-phase particles gradually increases. When the Cu content increases to 4.5 wt.% (Alloy 4), almost all the coarse second-phases show some certain enrichment of Cu and the AlCu_xSi_y phase in Alloy 1 as it transforms into a θ -phase.

As Alloy 1 has a low Cu content (0.5 wt.%), its element distribution changes during solution heat treatment, which is similar to that of Al-Mg-Si alloy in which Mg and Si in the coarse second-phase have been sufficiently dissolved. This is consistent with our observation showing that Mg and Si elements are distributed more uniformly and $I_{\text{max}, \text{Mg}}$ and $I_{\text{max}, \text{Si}}$ decrease significantly after solution heat treatment. Cu also has a higher solubility in the Al matrix at elevated temperatures, therefore, the Cu element in the coarse second-phase particle gradually dissolves into the Al matrix during solution heat treatment, causing a decrease in $I_{\text{max}, \text{Cu}}$, while, Mn and Fe have limited solubilities in Al, both at room temperature and high temperature, different from Cu, Mg, and Si. Therefore, after solution heat treatment, the Mn and Fe elements still remain in the coarse second-phase, but, since other elements (e.g., Cu, Mg, and Si) dissolve back into the Al matrix, the relative concentrations of Mn and Fe in the coarse second-phase particle increase which leads to an increase in $I_{\text{max}, \text{Mn}}$ and $I_{\text{max}, \text{Fe}}$ (Figures 5 and 6).

Similar to Alloy 1, the Cu and Mg in the second-phase of Alloy 4 gradually dissolve, and Mn and Fe remain in the coarse second-phase particle during solution heat treatment, but, because Alloy 4 has a much higher Cu content (4.5 wt.%) than that in Alloy 1, the surplus Cu atoms remain in the coarse second-phases, inducing Alloy 4 to have a larger number of coarse second-phase particles after solution heat treatment (Figure 21). Besides, different from Alloy 1, $I_{\text{max}, \text{Si}}$ increases from 11.0% for the as-extruded Alloy 4 to 57.1% for as-quenched Alloy 4, which indicates that Si content in second-phase particles after solution heat treatment increases significantly. It should be noted that the difference in the chemical compositions between Alloy 1 and Alloy 4 lies only in the Cu content; however, the Si content in second-phase particles of alloy 4 is higher than that in Alloy 1, especially under the solution heat treatment state. This indicates that a significant increase of the Cu content would decrease Si solubility in Al, contributing to the Si element being preserved in the coarse second-phase particle.

4.1.2. Grain Size

The AGZs of alloy significantly decrease as the Cu content increases, especially for the as-quenched alloys. The Cu content of Alloy 2 is twice that of Alloy 1, and its AGZ in as-quenched state decreases by only 27.1%, compared with as-quenched Alloy 1. The Cu content of Alloy 4 is eight times larger than that of Alloy 1, but its AGZ significantly decreases by 76.1% compared with Alloy 1. This indicates that, when the content of Cu is between 0.5 wt.% and 4.5 wt.%, the grain refinement effect is gradually enhanced with the increase of Cu content.

In Salleh et al. [17] and Zeren et al.'s [11] work on as-cast Al-Mg-Si-Cu alloys, it is shown that the effect of Cu addition on grain refinement is small. This indicates that Cu addition has no significant effect on either growth restriction or enhancing nucleation during $\alpha(\text{Al})$ solidification. In the studies on hot-worked and as-quenched alloys, Cu addition always shows a strong grain-refinement effect. This agrees with our observation, which is probably due to the particle-stimulated nucleation of recrystallisation (PSN) caused by Cu addition [34–36]. As shown in Figure 4, the coarse second-phase

particles increase with the increase in Cu content. On the one hand, during hot working, these coarse second-phase particles would produce a strong local strain field, which induces dynamic recrystallisation. On the other hand, during solution heat treatment, these coarse second-phase particles can also act as nucleation sites for the recrystallized grains, finally refining the grain sizes. Therefore, Cu addition causes the decreases in grain size of alloys in both hot-worked, and as-quenched, states. This pronounced PSN effect of coarse second-phase particles on Al alloys is consistent with results from Chakrabarti et al. [37], which shows that the increase in amount of coarse θ -phase particles leads to an increase in recrystallisation nucleation of alloys and grain size refinement. Besides, these coarse second-phase particles can also exert a pinning force on the grain boundaries, and thus limit the grain growth and refine the grain size.

4.1.3. Precipitates

With the increase in Cu content, the main precipitates of the peak-aged alloys change from an acicular β'' phase in 0.5 wt.% Cu alloy (Figure 21a) to an acicular β'' phase and granulated Q' phase in 1.0 wt.% Cu alloy (Figure 21b), a granulated Q' phase and lamellar θ' phase in 2.5 wt.% Cu alloy (Figure 21c), and a lamellar θ' phase with a small amount of Q' phase in 4.5 wt.% Cu alloy (Figure 21d).

In Al-Mg-Si-Cu alloys, with a Cu content less than or equal to 1.0 wt.%, β'' precipitates are observed and the amount thereof decreases with the increase of Cu content, owing to the formation of Q' precipitates. The Q' precipitate is found in Alloys 2, 3, and 4, and its number density decreases with the increase of Cu content. This is probably attributed to the precipitation of lamellar θ' -phase.

It is known that the β'' phase is the main strengthening phase in Al-Mg-Si alloys [38]. At the initial aging stage of β'' precipitate formation, Mg and Si atomic clusters are formed almost simultaneously, but Mg atomic clusters gradually dissolve into the Si atomic clusters during subsequent aging [39,40], therefore, the Si atomic cluster should be the nucleus for the β'' precipitate. As shown in Figure 7, the increase of Cu content could reduce the Si solubility in the Al matrix. Since Alloy 2 has a higher Cu content than that of Alloy 1, the concentration of Si in Alloy 2 should be lower than that in Alloy 1, which suppresses nucleation of β'' precipitates and finally leads to the relatively lower number density of β'' precipitates. Besides, in Al-Mg-Si alloys with $Mg/Si < 1$ (in wt.% terms), it is usually observed that Si-particles form after aging because of the excess of Si [24], but in Alloys 1–4 in which Mg/Si is equal to 0.84, Si-particles are not seen. This could be also due to the decrease in Si solubility in Al, caused by the addition of Cu, since it suppresses the dissolution of Si atoms in the Al matrix during solution heat treatment and thus reduces the supersaturation of Si during aging.

Due to the increase in Cu content in Alloy 2, the major strengthening phase changes to the Q' phase [37,41,42]. Previous studies have shown that, at a low Cu content (≤ 1.0 wt.%), the Q' phase only precipitates in alloy with a small Mg/Si ratio, which usually coexists with β'' phase. Perovic [43] and Chakrabarti et al. [37] found that, when $Mg/Si < 1.73$, the Q' phase and β'' phase are the main strengthening phases in the peak-aged Al-Mg-Si-Cu alloy with 1.0 wt.% Cu content. This is consistent with our observation in Alloy 2. For a high Cu content (≥ 2.0 wt.%), the formation of Q' phase depends on Cu/Mg ratio of alloy which decreases with the increase of Cu content. This is also found in Alloys 3 and 4 where the Q' precipitates continue decreasing in amount when the Cu content increases from 1.0 to 4.5 wt.%. In many studies [37,44] of Al-Mg-Si-Cu alloys with Cu contents ranging from 0.1 to 1.0 wt.%, some other types of precipitates (e.g., U1, U2, etc.) were observed. Saito et al. [7] indicated that U1- and U2-precipitates were mainly formed in the over-aging stage. This is consistent with our observation showing that these types of precipitates are not present in peak-aged alloys.

The θ' phase usually forms in Al alloys with a relatively high Cu content [45,46]. Liu et al. [47] found that the formation of a θ' phase depends on both the Mg content and Cu/Mg ratio. When the Mg content is less than 1.0 wt.% and Cu/Mg ratio is greater than 2.6, the θ' phase forms, otherwise, an S phase will form. In both Alloys 3 and 4, the Mg content is equal to 0.42 wt.%, and their Cu/Mg ratios are calculated to be 5.95, and 10.71, respectively, which are much larger than 2.6. Therefore, the θ' phase precipitates in the alloy and S-phase is not observed. Since both Q' and θ' phases contain

Cu, the formation of a θ' phase will significantly reduce the extent of supersaturation of the Cu in solid solution and thus suppress the precipitation of the Q' phase, therefore, with the increasing formation of θ' precipitates in Alloy 4, its number density of Q' precipitates apparently decreases compared to Alloy 3.

Figure 21. Schematic drawings illustrating the microstructure of the peak-aged four alloys (a) Alloy 1, (b) Alloy 2; (c) Alloy 3, and (d) Alloy 4.

4.2. Influence of Cu Content on Alloy Strengthening Mechanisms

4.2.1. Strength

For the as-quenched alloys, the influence of Cu content on the strength of alloy is mainly affected by σ_{H-P} and σ_{SS} , since the precipitation has not yet taken place. Assuming that different strengthening mechanisms act independently and can be taken into account as being additive, the influence of Cu content on the mechanical properties Al-Mg-Si-Cu alloy can be expressed as follows [48]:

$$\sigma_{0.2,Q} = \sigma_{H-P} + \sigma_{SS} \quad (1)$$

where $\sigma_{0.2,Q}$ is the yield strength of as-quenched alloy.

The σ_{H-P} is generally described by the Hall-Petch equation [49]:

$$\sigma_{H-P} = \sigma_0 + Kd^{-1/2} \quad (2)$$

where σ_0 is the yield strength of single crystal, K is a parameter related to grain size that describes the relative strengthening contribution of grain boundaries, and d refers to AGZ.

It has been shown that, for Al alloys with AGZ > 50 μm , K is a constant which generally lies within the range 0.17 to 0.22 [48,50,51]. The AGZs of Alloys 1–4 are 482, 351, 211, and 108 μm , respectively. Even using the maximum value of K (0.22), the σ_{H-P} value of four alloys are only 10.0, 11.8, 15.2, and 21.2 MPa, respectively. Then, the increase of $\sigma_{0.2}$ caused by σ_{SS} for Alloys 2–4 compared with Alloy 1 can be calculated to be 5.2, 61.3, and 146.6 MPa, respectively. This indicates that the increase of $\sigma_{0.2}$ for as-quenched alloys is mainly attributed to the σ_{SS} at high Cu contents (≥ 2.5 wt.%). It is known that Cu atoms in Al-lattice replace Al atoms and form replacement solutes so as to generate a significant stress field [52] in the matrix and generate frictional resistance to dislocation slippage [53]. As can be predicted, this hindering effect on dislocation should be significantly enhanced by the addition of Cu. Thus, σ_{SS} significantly increases with the increase of Cu content and is predominant in alloys with high Cu contents.

Differed from the as-quenched alloys, the peak-aged alloys show pronounced σ_{ppt} . Thus, the effect of Cu addition on the mechanical properties of alloy can be expressed as [48]:

$$\sigma_{0.2,P} = \sigma_{H-P} + \sigma_{SS} + \sigma_{ppt} \quad (3)$$

where $\sigma_{0.2,P}$ is the yield strength of the peak-aged alloy.

Given that the decrease in the value of σ_{SS} during precipitation is quite small, σ_{ppt} can be estimated by the strength difference between the as-quenched and peak-aged alloys, which can be calculated according to the following equation:

$$\sigma_{ppt} \approx \sigma_{0.2,P} - \sigma_{0.2,Q} \quad (4)$$

According to Equation (4), the values of σ_{ppt} for Alloys 1–4 are calculated to be 96.7, 99.4, 116.1, and 122.2 MPa, respectively (Figure 22) which are greater than the corresponding values of σ_{H-P} and σ_{SS} , except for that of σ_{SS} in Alloy 4, besides, the σ_{ppt} values in θ' -precipitates-contained alloys (Alloys 3 and 4) are greater than those of alloys without θ' precipitates (Alloys 1 and 2). In particular, Alloy 4 has the largest amount of θ' precipitation and has the largest increase in the value of σ_{ppt} . This implies that the θ' phase exerts the greatest effect on the increase in strength of the alloy. β'' precipitate is the predominant precipitate in Alloy 1, but the strength change of Alloy 1 is the smallest. Besides, with the number density of β'' precipitates decreasing and that of the Q' precipitates increasing (Alloy 2), there is an increase in the strength of the alloy. This indicates that the Q' precipitate has a more pronounced strengthening effect than that of the β'' precipitate.

It should be pointed out that, the value of σ_{SS} is calculated to be larger than the value of σ_{ppt} in Alloy 4, which means σ_{SS} is predominant when the Cu content increases to 4.5 wt.%. This agrees with the findings of Zeren et al. [11] and Wang et al. [18] show that the strengths of as-quenched alloys (without σ_{ppt}), with a relatively high Cu contents (≥ 4.0 wt.%) are almost equal to, or even higher than, those of peak-aged alloys with relatively low Cu contents (≤ 1.0 wt.%)

Figure 22. Influence of precipitation on the strength of the alloy.

To sum up, the θ' phase confers the best strengthening effect on alloys, followed by the Q' phase and the β'' phase. As shown in Figure 19, the θ' precipitate has a coherency interface with Al matrix, which can produce an apparent strain and significantly hinder dislocation movement. In addition, the lamellar θ' phases are densely distributed in the alloy on $\{200\}$ planes of the Al matrix (Figure 23a). It is known that the main slip system of fcc Al is $\{111\}\langle 110\rangle$, in section on a $\{111\}_{Al}$ slip plane and the lamellar θ' precipitates will form a triangular array in the manner shown in Figure 23b. This could also trap the dislocation therein [54], therefore, θ' precipitates have a remarkable strengthening effect on Al alloy. Other than θ' precipitate, the projection shapes of β'' and Q' precipitates in the $\{111\}_{Al}$ plane are roughly circular and hexagonal respectively, (Figure 23c–f), which have a weak effect on trapping dislocations. This might account for the remarkably smaller increase in the σ_{ppt} values for Alloys 1,2 than those for Alloys 3,4.

For such small precipitates in the peak-aged alloys, the increment in the strength can be estimated using the Orowan cutting mechanism [20].

$$\sigma_{ppt} \propto r \quad (5)$$

where r is the radius of an average equivalent circular cross section of precipitates. Under peak-aging condition, the Q' precipitate (Figure 15a) is obviously larger than β'' precipitate (Figure 12a) which might explain the more significant strengthening effect of Q' precipitate.

The rates of increase in strength caused by precipitation can be described by $\sigma_{ppt}/\sigma_{0.2, Q}$, as shown in Figure 22, Alloy 1 has the largest value of $\sigma_{ppt}/\sigma_{0.2, Q}$ (58.7%), but Alloy 4 has the smallest value of σ_{ppt}/σ_Q (38.1%). This indicates that the rate of increase of strength caused by precipitation of the θ' phase is the smallest, while that caused by precipitation of the β'' phase is the largest.

Figure 23. Schematic diagrams showing (a) distribution of lamellar β'' precipitates in the Al matrix and (b) projection of the intersected β'' precipitates in a $\{111\}_{\text{Al}}$ plane (c) distribution of lamellar Q' precipitates in the Al matrix and (d) projection of the intersected Q' precipitates in a $\{111\}_{\text{Al}}$ plane (e) distribution of lamellar θ' precipitates in the Al matrix and (f) projection of the intersected θ' precipitates in a $\{111\}_{\text{Al}}$ plane.

4.2.2. Elongation

The elongation continues decreasing with the increase of Cu content, in both as-quenched, and peak-aged, alloys.

For as-quenched alloys, their elongation is mainly affected by grain size and coarse second-phase particles [54], which can be expressed as follows:

$$\delta_Q = \delta_{\text{GR}} + \delta_{\text{CS}} \quad (6)$$

where δ_Q is the elongation of as-quenched alloy, δ_{GR} is the elongation increment contributed from grain refinement, and δ_{CS} denotes the elongation increment related to the coarse second-phase.

Generally, a Cu addition can produce grain refinement, which is beneficial to the plasticity of the alloy (namely, $\delta_{GR} > 0$). However, the increase in the amount of coarse second-phase particles, led by a Cu addition, is known to be deleterious to the plasticity of alloys (namely, $\delta_{CS} < 0$), due to their brittleness and incoherent interfaces with the matrix [28]. Compared to the as-quenched Alloy 1, the changes in δ_Q for Alloys 2,3 are -1.6% , -9.1% , and -10.9% . This means that, with the increase of Cu content, the δ_{CS} effect on δ_Q is enhanced. Since coarse second-phase particles cause crack initiation and promote crack growth, the significant increase in the number of coarse second-phase particles, caused by the Cu addition, can increase the probability of crack nucleation and reduce the plasticity of alloy. Thus, δ_Q is more dominant in those alloys with high Cu contents.

For peak-age alloy, in addition to δ_{GR} and δ_{CS} , its elongation is also affected by the precipitates, which can be expressed as follows:

$$\delta_P = \delta_{GR} + \delta_{CS} + \delta_{ppt} \quad (7)$$

where δ_P is the elongation of peak-aged alloy, and δ_{ppt} represents the elongation increment arising from precipitation.

Since δ_{ppt} is independent of both δ_{GR} and δ_{CS} , it can be described by the difference between the elongation of as-quenched and peak-aged alloys, namely

$$\delta_{ppt} = \delta_P - \delta_Q \quad (8)$$

According to Equation (7), δ_{ppt} for Alloys 1–4 are -10.4% , -10.2% , -9.0% , and -8.5% , respectively (Figure 24). It is somewhat surprising to note that the lowest value of δ_{ppt} is found in Alloy 1, where β'' precipitates dominate and the maximum value of δ_{ppt} is presented in the Alloy 4, where θ' precipitates dominate.

The rate of decrease of elongation, caused by precipitation, can be described by $|\Delta\delta_{ppt}|/\delta_Q$. As shown in Figure 24, the value of $|\Delta\delta_{ppt}|/\delta_Q$ for Alloy 4 equals to 46.0% which is the greatest among these four alloys, while, the value of $|\Delta\delta_{ppt}|/\delta_Q$ for Alloy 1 is to 35.0% (the smallest thereof).

In summary, among these four alloys, the precipitation of the β'' -phase in peak-aged Alloy 1 causes the largest reduction in elongation, but the rate of reduction is the smallest compared with those of as-quenched alloy. The precipitation of θ' -phase in peak-aged Alloy 4 leads to the smallest reduction in elongation, while the rate of reduction is the largest compared with those of as-quenched alloy. The largest reduction caused by θ' -precipitation is probably related to its trapping effect on dislocations (Figure 23b), which weakens the density of mobile dislocations in alloys and makes it difficult to activate the slip systems.

It should be pointed out that, according to our study, the difference between β'' - and θ' -precipitates, in terms of their effect on elongation, is quite small. For alloys with relatively low Cu contents, it is possible to increase the elongation by increasing the Cu content if the δ_{GR} is sufficiently large. This might account for the results of Jin et al. [5] and Zhong et al. [13] showing that even a small Cu addition increases both the strength and ductility of Al-Mg-Si-Cu alloys.

Figure 24. Influence of precipitation on the elongation of the alloy.

5. Conclusions

A systematic study was performed on the evolution of the microstructural features and strengthening mechanisms of Al-Mg-Si-*x*Cu alloys with different Cu contents, and the following conclusions were drawn:

(1) The Cu content exerts a grain refinement effect on both as-extruded and as-quenched Al-Mg-Si-Cu alloys. As the Cu content increases from 0.5 to 4.5 wt.%, the grain size decreases from 765 to 190 μm in the as-extruded state and from 482 to 108 μm in as-quenched state.

(2) With the increase of Cu content, the main types of precipitates of alloys change from a β'' -phase in 0.5 wt.% Cu alloy to a β'' -phase and a Q' -phase in 1.0 wt.% Cu alloy, Q' -phase and θ' -phase in 2.5 wt.% Cu alloy, and θ' -phase with a small amount of Q' -phase in the 4.5 wt.% Cu alloy.

(3) Cu addition decreases the solubility of Si in the Al matrix, which suppresses the nucleation of β'' precipitates and leads to the relatively low density of β'' precipitates in Alloy 2.

(4) Mg influences the interfacial structure of the θ' -phase and increases occupancy of interstitial sites at the coherent interface with the Al matrix.

(5) Cu addition plays an essential role on σ_{H-P} , σ_{SS} , and σ_{ppt} of Al-Mg-Si-Cu alloys. In as-quenched state, σ_{SS} is predominant in alloys with a high Cu content (≥ 2.5 wt.%) but is of equivalent importance as σ_{H-P} in alloy with a low Cu content (≤ 1.0 wt.%). In peak-aged state, σ_{ppt} is dominant in alloys with Cu content ≤ 2.5 wt.% but σ_{SS} is predominant in alloys with 4.5 wt.% Cu content.

(6) Among the four peak-aged alloys, the precipitation of θ' -phase in Alloy 4 leads to the largest increase amplitude while the precipitation of β'' -phase in Alloy 1 causes the smallest increase amplitude in $\sigma_{0.2}$. Compared with as-quenched alloys, the rate of increase of $\sigma_{0.2}$ attributed to θ' -phase precipitation in Alloy 4 is the smallest, while the rate of increase of $\sigma_{0.2}$ induced by β'' -phase precipitation in Alloy 1 is the largest.

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