Effect of minor Sc and Zr on recrystallization behavior and mechanical properties of novel Al–Zn–Mg–Cu alloys

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**A B S T R A C T**

Effect of trace amount of Sc and Zr on microstructure and mechanical properties of novel Al–Zn–Mg–Cu–Sc–Zr alloys are investigated. The samples were subjected to different annealing temperatures and various aging times. Analysis of microstructure and mechanical properties were carried out on TEM, EBSD technique, Vickers hardness test and tensile test. The results showed that abundant nanometer-sized Al3(Sc, Zr) particles effectively pinned dislocations and subgrain boundaries, exhibiting excellent antirecrystallization behavior and precipitates strengthening effect. Al–Zn–Mg–Cu–Sc–Zr alloys exhibited completely recrystallized structure after annealing at 470 °C for 1 h. However, the two Al–Zn–Mg–Cu–Sc–Zr alloys exhibited equiaxed grains at 600 °C. Besides, with the additions of Sc and Zr increased, a higher density of precipitates was detected obviously with excellent refinement effect. After solution-aging treatment, the maximum values of hardness, tensile strength and yield strength were 240 HV, 668 MPa, 628 MPa respectively, which were obtained by Al–Zn–Mg–Cu–0.22Sc–0.40Zr alloy at 120 °C for 24 h. The grain refinement strengthening and precipitation strengthening play a dominant role in the additional strength of the Al–Zn–Mg–Cu–Sc–Zr alloys.

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**1. Introduction**

Al–Zn–Mg–Cu alloys (7xxx series alloys) have been widely applied in aerospace and military industries due to their excellent mechanical characteristics, such as high specific strength and low density [1,2]. Addition of rare-earth element effectively improves the microstructure and mechanical performance of aluminum based alloys. Scandium (Sc) is a potential element in grain refinement, strength augment and thermal stability due to the formation of abundant Al3Sc particles. It suggests that the lattice diameter size of L12-type Al3Sc particles and α-Al are 0.4104 nm and 0.4040 nm, respectively. The small difference between them exhibits a little lattice mismatch about 1.5% [3,4]. Nucleation of Al3Sc in Al–Zn–Mg–Cu–Sc–Zr alloys occurs in Al matrix effortlessly due to small difference in lattice parameter, which exhibits grain refinement, strength increment and recrystallization resistance [5,6]. According to the aluminum-rich end of the Al–Sc binary phase diagram, a eutectic reaction among the liquid, Al matrix, and Al3Sc precipitates reacts in the Al-rich region as follows: Liquid → α-Al + Al3Sc. The eutectic reaction requires the content of Sc reaches about 0.55%–0.60% (wt.%) [4,7]. Nevertheless, considering the high price of Sc, it is expected to introduce other rare-earth elements with lower price to decrease the addition of Sc, thereby the more economic aluminum alloys with outstanding mechanical properties can be achieved. In order to balance the expensive cost, zirconium (Zr), another effective and cheaper rare-earth element is a suitable selection to replace partial Sc for its grain refinement and strength augment because of the formation of Al3Zr particles. However, alloys containing Sc exhibit better grain refinement than alloys containing Zr with the same content, which is due to the faster diffusion rate of Sc atoms than that of Zr atoms in melted alloys [8–10]. Besides, Al–Sc binary alloy provides a relative better refinement effect and mechanical properties than Al–Zr binary alloys. In order to acquire relatively inexpensive Al–Zn–Mg–Cu–Sc–Zr alloys with excellent mechanical properties, such as high specific strength and excellent recrystallization behavior.
properties, co-addition of Sc and Zr is applied in aluminum alloys. Fine coherent Al₃(Sc, Zr) particles have smaller average diameter size than that of Al₃Sc or Al₃Zr particles. The Al₃(Sc, Zr) precipitates exhibit stronger zener drag to inhibit migration of dislocations and subgrain boundaries during different annealing procedures [11–13]. In addition, aluminum alloys containing Sc require higher recrystallization temperature and effectively inhibit recrystallization. Besides, higher strength and hardness can be gained in Al–Zn–Mg–Cu–Sc–Zr alloys after different heat treatments because of precipitate strengthening effect of Al₃(Sc, Zr) particles [14–17]. Therefore, aluminum alloys containing Sc and Zr have drawn great attention to their outstanding mechanical performances, which resulted in increasing investigations of Al–Zn–Mg–Cu–Sc–Zr alloys in recent times.

Forbord et al. [18] suggested that Al₃(Sc, Zr) particle presented excellent inhibition in the movement of dislocations and subgrain boundaries with increasing annealing temperatures due to the considerable thermal stability. Deng et al. [19] studied recrystallization mechanism and mechanical properties of Al–Zn–Mg–Cu–Sc–Zr alloys. The rare-earth elements were added as 0.105Sc/0.10Zr and 0.25Sc/0.10Zr (wt.%) in his study. The results showed that the antirecrystallized effect and mechanical performances were promoted with the increasing microalloying content of scandium. Wang et al. [20] analyzed that the nucleation mechanism of recrystallization in Al–Mg–Mn–Sc–Zr alloys was subgrain coalescence and subgrain growth. Moreover, it indicated that the recrystallization temperature was increased to 450 °C due to the high density of Al₃Sc precipitates with strongly pinning effect in dislocations and subgrain boundaries.

In spite of the various studies above, investigations in comparison of Al–Zn–Mg–Cu–Sc–Zr alloys with the similar Sc/Zr ratio but different content are insufficient. In this work, the co-addition value of Sc and Zr of Al–Zn–Mg–Cu–0.22Sc–0.40Zr (wt.%) approximated the eutectic point. Meanwhile, in order to analyze the effect of half content of Sc and Zr in Al-0.22Sc-0.40Zr (wt.%) alloy on the microstructure and mechanical properties, Al–0.10Sc–0.16Zr (wt.%), Al–0.3Sc–0.40Zr (wt.%), Al–0.5Sc–0.6Zr (wt.%), and Al–0.6Sc–0.7Zr (wt.%) alloy was investigated. Static recrystallization effectiveness and mechanical performances with the same Sc/Zr ratio (1:2 wt.%) in the novel Al–Zn–Mg–Cu–Sc–Zr alloys were investigated.

2. Experimental procedures

2.1. Materials preparation

Three kinds of Al–Zn–Mg–Cu alloys with similar Sc/Zr ratio (1:2 wt.%) and different content of Sc and Zr were investigated in this experiment, which were prepared by Hunan Rare-Earth Metal Research Institute. The chemical compositions of the three alloys are provided in Table 1. The three alloys are described as Al-6.80Zn-2.46Mg-0.22Cu (wt.%), Al-6.72Zn-2.49Mg-0.19Cu-0.10Sc-0.16Zr (wt.%), and Al-7.11Zn-2.49Mg-0.22Cu-0.22Sc-0.40Zr (wt.%). Moreover, Al–Zn–Mg–Cu–Al–0.3(Sc + Zr) and Al–0.6(Sc + Zr) (wt.%) stand for the above alloys in the following text for simplification, respectively.

Briefly, samples with a thickness of 20 mm were subjected to homogenization treatment at 470 °C for 12 h according to simultaneous thermal analysis. Before hot rolling to 6 mm plates, they were pre-annealed at 450 °C for 2 h. After that the hot rolled 6 mm thick plates were inter-annealed at 400 °C for 2 h, and cold rolled to 4 mm. The samples were subjected to annealing treatment at 350 °C, 470 °C, 520 °C, 560 °C and 600 °C for 1 h, respectively, and the sheets were cooled by water quenching. Finally, cold rolled sheets of the three alloys were subjected to artificial aging treatment at 120 °C for various times after solution treatment at 470 °C for 1 h followed by water quenching.

2.2. Materials characterization

In order to study the effects of different microalloying contents of Sc and Zr on microstructure and mechanical properties, investigations of microstructure were conducted utilizing transmission electron microscope (TEM) and electron back scattered diffraction (EBSD) technique. Vickers hardness test and tensile test were carried out to study the mechanical properties.

Thin sheets for observations of TEM were subjected to double-jet electro-polishing at 20 KV with electrolyte (30% nitric acid and 70% methanol) cooled to ~30 °C and observed on a TecnaiG G2 F20 transmission electron microscope operating at 200 KV. The EBSD studies were conducted using a field-emission scanning electron microscope (SEM, FEI Nanosem430) equipped with an EBSD detector (EDAX, TSL) operating at 20 KV, scanning with a step size arranged from 0.1 μm to 0.8 μm. In addition, mechanical polishing and electro-polishing were performed to acquire a strain-free surface. EBSD data was analyzed by the TSL OIM Analysis 7 software subsequently. In order to investigate the difference in recrystallization behavior between the two alloys, misorientation angles range from 2° to 15° were defined as low angle grain boundaries (LAGBs) and misorientation angles that above 15° as high angle grain boundaries (HAGBs). The hardness tests were carried out on an EveroneMH-6 machine. The tensile tests were performed on CSS-44100 electronic universal testing machine with 1 mm/min loading speed along the rolling direction. The yield strength of the samples was identified at 0.2% plastic strain.

3. Results and discussion

3.1. Effect of different combined addition of Sc and Zr on recrystallization behavior

3.1.1. Microstructure

EBSD orientation images of the aluminum alloys with and without Sc and Zr under different conditions are shown in Figs. 1–3. The color of the grains are marked by the crystal orientation built on [001] inverse pole figure.

From Fig. 1(a), a considerable coarse fiber-like structure can be detected in cold rolled Al–Zn–Mg–Cu alloy. The elongated grains are measured about 50 μm in width. After annealing at 350 °C for 1 h, the incomplete recrystallization can be observed obviously. Further increasing annealing temperature to 470 °C, the alloy exhibits plenty of equiaxed grains, indicating that the alloy exhibits full recrystallization.

Compared with Al–Zn–Mg–Cu alloy, Al–Zn–Mg–Cu–Sc–Zr alloys retain their fiber-like structure from 25 °C to 350 °C during the annealing procedure (Figs. 2(a)–(c) and 3(a)–(c)). The fraction of recrystallized grains of Al–Zn–Mg–Cu–ScZr alloys increases with the increasing annealing temperatures (Figs. 2 and 3). Furthermore, grain structure in Al-0.6(Sc + Zr) is more slender than Al-0.3(Sc + Zr) during different heat treatments. Meanwhile, partial recrystallization occurs in Al–Zn–Mg–Cu–Sc–Zr alloys when the annealing temperature reaches 560 °C, which exhibits equiaxed grains after annealing at 600 °C for 1 h.

Table 1

<table>
<thead>
<tr>
<th>Alloys no.</th>
<th>Al</th>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Sc</th>
<th>Zr</th>
<th>Sc + Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–Zn–Mg–Cu</td>
<td>90.52</td>
<td>6.80</td>
<td>2.46</td>
<td>0.22</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al-0.3(Sc + Zr)</td>
<td>90.34</td>
<td>6.72</td>
<td>2.49</td>
<td>0.19</td>
<td>0.10</td>
<td>0.16</td>
<td>0.3(1:2)</td>
</tr>
<tr>
<td>Al-0.6(Sc + Zr)</td>
<td>89.56</td>
<td>7.11</td>
<td>2.49</td>
<td>0.22</td>
<td>0.22</td>
<td>0.40</td>
<td>0.6(1:2)</td>
</tr>
</tbody>
</table>
The results signify that minor Sc and Zr effectively inhibit recrystallization in aluminum alloys during the different annealing procedures. From the comparison of the two different Al–Zn–Mg–Cu alloys, fibrous grains in Al–0.3(Sc + Zr) alloy are wider than those of Al–0.6(Sc + Zr) alloy. Moreover, the more co-addition of Sc and Zr is added, the finer elongated structure is obtained in Al–Zn–Mg–Cu–Sc–Zr alloys. The orientation maps (Figs. 2 and 3) indicate that minor Sc and Zr content significantly promote the recrystallization temperature of Al–Zn–Mg–Cu based alloys. The increasing addition of Sc and Zr results in much slender
The grain structure, which might result from the formation of ultra fine Al₃(Sc, Zr) precipitates during homogeneously solid solution procedure. Moreover, Al₃(Sc, Zr) particles exhibit excellent thermal stability and recrystallization resistance.

3.1.2. Grain boundary

The distribution of the different misorientation angles is displayed in Fig. 4. The LAGBs and HAGBs are tagged by red and black lines, respectively. Previous studies have demonstrated that the variations of the high angle grain boundaries (HAGBs 15°–180°) and low angle grain boundaries (LAGBs 2°–15°) are associated with recrystallization nature of aluminum alloys [21,22]. As shown in Fig. 4, all the misorientation angle curves exhibit similar tendency. The results indicate that LAGBs fraction increases firstly and then decreases with increasing annealing temperatures, while the HAGBs fraction presents the contrary curves. It is obvious that the initial LAGBs fraction increases with increasing content of Sc and Zr. As seen from Fig. 4(a), the LAGBs and HAGBs fraction values of Al–Zn–Mg–Cu alloy exhibit their maximum and minimum after annealing at 350 °C for 1 h, respectively. Moreover, the minimum of LAGBs and maximum of HAGBs are acquired after annealed at 470 °C for 1 h. The results suggest that the increase of LAGBs between 25 °C and 350 °C is attributed to the formation of subgrains in great amount. The sharp decrease in curve of LAGBs from 350 °C to 470 °C results from the formation of lots of recrystallized grains.

Compared with Al–Zn–Mg–Cu alloy, the maximum LAGBs fraction of Al–0.3(Sc + Zr) alloy arises at 520 °C, which suggests that the recrystallized grains occur above 520 °C. The curves of aluminum alloys with Sc and Zr vary little from cold rolled condition to annealing at 560 °C. Furthermore, the minimum of LAGBs and maximum of HAGBs are acquired at 600 °C synchronously. From the results of misorientation angles of Al-0.6(Sc + Zr),

![Fig. 3. Orientation maps of cold rolled Al-0.6(Sc + Zr) alloy annealed at different temperatures for 1 h: (a) cold rolled; (b) 350 °C; (c) 470 °C; (d) 520 °C; (e) 560 °C; (f) 600 °C.](image)

![Fig. 4. Misorientation angle fraction of the alloys with different annealing temperatures: (a) Al–Zn–Mg–Cu alloy; (b) Al-0.3(Sc + Zr) alloy; (c) Al-0.6(Sc + Zr) alloy.](image)
the maximum and minimum fractions of LAGBs appear at 560 °C and 600 °C severally, while the maximum and minimum values of HAGBs fraction exhibit at 600 °C and 470 °C, respectively. The consequences demonstrate that lots of subgrain boundaries form from dislocations and deformation during the elevate temperature until 520 °C. With the increasing temperatures, the rise of HAGBs curve at 520 °C is attributed to occurrence of HAGBs and decrease of dislocations in density. In summary, subgrains appear in Al−Zn−Mg−Sc−Zr alloys at 470 °C and recrystallized grains occur above 560 °C in large quantities. In addition, a large number of HAGBs can be evidently observed at 600 °C.

3.1.3. Al3(Sc, Zr) particles

To analyze the antirecrystallization mechanism during different annealing procedures, samples annealed at 470 °C and 560 °C for 1 h are selected for further investigation of the microstructure by TEM. The effects of second-phase particles on the recrystallization behavior may derive from two factors: on the first place, the particles may act as nucleation sites for recrystallization in aluminum alloys. On the second place, they may exhibit significant pinning effect on grain boundaries. Particles can either promote or suppress recrystallization depending on their size, shape, and volume fraction. Lefebvre [23] indicated that the formation procedure of Al3(Sc, Zr) particles during heat treatment was described as follows: Sc-rich region → Al3Sc particles → Al3Sc enriched in Zr at the interface → Al3Sc core + Al3(Sc,Zr1.3) shell. Thus the Al3Sc particles are hence unambiguously identified as the precursors of Al3(Sc, Zr) dispersoids.

From Fig. 5, fine coherent Al3(Sc, Zr) dispersoid precipitates from Al matrix during annealing treatment are distributed as well as in subgrain interiors or on subgrain boundaries. Moreover, the secondary bean-like Al3(Sc, Zr) particles in aluminum alloys containing Sc and Zr exhibit approximate average diameter after the same heat treatments, and the average size of Al3(Sc, Zr) increases with the increasing annealing temperatures. Compared with Al-0.3(Sc + Zr) alloys, the density of fine secondary Al3(Sc, Zr) particles are double in Al-0.6(Sc + Zr) approximately. Besides, after annealing at 470 °C for 1 h, nanometer-sized secondary Al3(Sc, Zr) particles formed from the two Al−Zn−Mg−Cu−Sc−Zr alloys have the same average diameter about 25 nm. Moreover, as the annealing temperature increases to 560 °C, the average size of Al3(Sc, Zr) particles grows up to about 50 nm. Ashby-Brown strain contrast in bright-field images as well as the superstructure reflection demonstrates that the precipitates are Al3Sc or Al3(Sc, Zr) particles. Moreover, the particles are coherent with Al matrix with a cubic L12 structure (Fig. 5(b)) [17,24]. Secondary Al3(Sc, Zr) particles dispersoids exhibit an excellent thermal stability with the increasing annealing temperatures, which contributes significantly to recrystallization resistance in Al−Zn−Mg−Cu−Sc−Zr alloys. It is noted that the high density of Al3Sc particles plays an important role in pinning the dislocations and subgrain boundaries. The precipitates provide better antirecrystallized effect in Al−Zn−Mg−Cu alloy, which increases the recrystallization temperature. Deng [21] observed the average size of Al3(Sc, Zr) particles reached a maximum of 110 nm at 600 °C, which exhibited equiaxed crystal structure, remaining coherent with Al matrix [23,24]. Fig. 4(b) also shows that Al3(Sc, Zr) precipitates strongly pin the dislocations and subgrain boundaries, which inhibit recrystallization and increase strength of alloys.

Fig. 5. The bright field images of Al-Zn-Mg-Cu-Sc-Zr alloys annealed at different temperatures for 1 h: (a) Al-0.3(Sc + Zr)/470 °C; (b) Al-0.6(Sc + Zr)/470 °C; (c) Al-0.3(Sc + Zr)/560 °C; (d) Al-0.6(Sc + Zr)/560 °C.
According to Fig. 4, the range from 470 °C to 560 °C exhibits a sharper variation rate than the range from 350 °C to 470 °C. Previous papers \[18,25\] demonstrated that the ultrafine coherent Al\(_3\)(Sc, Zr) particles were regarded as grain boundary pinners and grain structure stabilizers during the heat treatment with high temperatures. The results indicate that a faster migration rate is obtained by dislocations with the increasing annealing temperatures, suggesting the occurrence of static recrystallization of the Al–Zn–Mg–Mg–Cu–Sc–Zr alloys. The phenomenon may result from the weaker pinning effect of the larger Al\(_3\)(Sc, Zr) particles. Broadly speaking, recrystallized effect is attributed to the dislocation migration and growth of Al\(_3\)(Sc, Zr) particles.

Compared with Al–Zn–Mg–Cu alloy, Al–Zn–Mg–Cu–Sc–Zr alloys exhibit finer fibrous microstructure during the same annealing procedures (Figs. 1–3), which is due to numbers of nanoscale Al\(_3\)(Sc, Zr) particles. Al\(_3\)(Sc, Zr) particles effectively pin the subboundaries and dislocations for their tiny average size and high quantity. In addition, with the growth of Al\(_3\)(Sc, Zr) particles, these precipitates with larger size exhibit weaker pinning effect.

### 3.1.4. Hardness

Effect of different additions of Sc and Zr on the hardness of the three alloys under different conditions is shown in Fig. 6. It can be seen clearly that the variation of hardness curves varies with the same regular in Al–Zn–Mg–Cu and Al–Zn–Mg–Cu–Sc–Zr alloys. The curves are divided into three sections: slightly decrease (25 °C–350 °C), sharp increase (350 °C–470 °C), stable decrease (470 °C–600 °C). Compared with Al–Zn–Mg–Cu alloy, the hardness value is much higher in other two Sc-enriched alloys. Moreover, the hardness value increases with the increasing co-additions of Sc and Zr. According to Fig. 6(b) and (c), initially slight decrease appears in the low temperature recovery stage, and then a sharp increase occurs between 350 °C and 470 °C, a stable decline and rapid reduction arise at 470 °C–560 °C and 560 °C–600 °C, respectively.

The hardening behavior is usually associated with the grain size and precipitates. Wu [25] argued that a great many of incoherent interface and HAGBs were formed with the increasing recrystallized grains, thus the heterogeneous precipitation was promoted. Moreover, precipitate hardening and strength decreased due to the decline of solute supersaturation in the aluminum matrix.

Among the three alloys, the primary decrease between 25 °C and 350 °C (recovery procedure during low temperature) results from migration of dislocations and defects. The second increase between 350 °C and 470 °C of Al–Zn–Mg–Cu is due to the formation of substantial recrystallized grains. Above 470 °C, the hardness of Al–Zn–Mg–Cu alloy continues to decrease because of the growth of recrystallized grains. However, the hardness value of aluminum alloys containing Sc and Zr increases between 350 °C and 470 °C for formation of subgrains. Meanwhile, the range from 470 °C to 560 °C of Al-0.3(Sc + Zr) alloy is due to the lack in recrystallization driving force and the decrease of restoring driving force as well. Finally, formation and growth of a great many recrystallized grains result in sharp decrease in hardness value of Al-0.3(Sc + Zr) alloy from 560 °C to 600 °C. Different from the above alloys, the relatively stable stage of Al-0.6(Sc + Zr) ranges from 470 °C to 560 °C is mainly due to the small variations in dislocations density. Besides, the release of deformation of stored energy contributes to a rapid decline between 560 °C and 600 °C, which derives from the transformation from internal stored energy to recrystallization driving force. After annealed at 470 °C for 1 h, lots of nanometer-sized Al\(_3\)(Sc, Zr) particles effectively pin the dislocations and subgrains (Figs. 1–5). Moreover, a mass of LAGBs form fine recrystallized grains than Al–Zn–Mg–Cu alloy. The migration rate of dislocations accelerates to form more recrystallized grains above 470 °C. Meanwhile, the grain size increases with the evaluated temperatures, which results in decrease of hardness. Furthermore, the hardening effect gets better with larger additions of Sc and Zr due to more Al\(_3\)(Sc, Zr) precipitates.

### 3.2. Effect of different Sc and Zr contents on age hardening and mechanical properties

#### 3.2.1. Age hardening behavior

In order to promote the hardness, the alloys were subjected to different aging procedures after solid-solution treatment at 470 °C for 1 h. Aging hardening curves of the alloys at 120 °C for various times are shown in Fig. 7. The three curves exhibit similar tendency. Compared with Al–Zn–Mg–Cu alloy, additions of Sc and Zr significantly promote the hardness. Moreover, the hardness value is improved with the increasing content of Sc and Zr. Initially, the hardness of the alloys increases with increasing aging time sharply (under-aging state) from the starting point until reaching the highest value (peak-aging state). And then, the aging hardness varies little with the prolonged aging time. Among the alloys, the peak hardness is 240 HV, which is obtained by Al-0.6(Sc + Zr) alloy after aging at 120 °C for 24 h (peak-aging state). With the prolongation of aging time, the hardness values of the three alloys...
3.2.2. Mechanical properties

In order to investigate the effect of different microalloying additions of Sc and Zr on mechanical properties, tensile tests are conducted. The ultimate tensile strength (UTS), yield strength (YS) and elongation to failure (EI) of the three aluminum alloys under different states are presented in Fig. 8. Among all the alloys under different heat treatment procedures, Al–Zn–Mg–Cu alloy exhibits the minimum values of UTS and YS. The UTS and YS values increase with the increasing addition of Sc and Zr in Al–Zn–Mg–Cu alloys. Among the solid-solution alloys, the highest values of UTS and YS acquired by Al-0.6(Sc + Zr) alloy are 488 MPa and 318 MPa, respectively. Furthermore, the elongations of all the three alloys exceed 15%. In the aged states, the UTS and YS exhibit a significant promotion, however, the elongation decreases. There is no evident change in strength with the increasing aging times after peak-aging condition. The results indicate that the variation of the strength is in good accordance with the results of aging hardening curves (Fig. 7). From Fig. 8, Al-0.6(Sc + Zr) alloy obtains the best balance between UTS (668 MPa) and EI (9%) after aging treatment at 120 °C for 24 h (peak-aging state).

The results reveal that the combination of Sc and Zr content makes large contributions to the increment of strength. The higher strength can be obtained with more Sc and Zr contents and aging procedures as well. Therefore, the higher tensile strength and yield strength are acquired by Al-0.6(Sc + Zr) with peak-aging state, indicating that better reinforcement effect on strength results from abundant secondary Al3(Sc, Zr) particles.

3.2.3. Aging precipitates behavior

Fig. 9 shows the TEM graphs of aluminum alloys with and without Sc and Zr after aging procedure of 24 h at 120 °C (peak aging state). As seen in Fig. 9(a)–(b), large amounts of η’ precipitates are continuously distributed in grain interior and some rod-like precipitates are distributed discontinuously along grain boundary.
boundaries, respectively. The precipitation of Al–Zn–Mg–Cu 7XXX alloys is displayed as follows: over-saturated (α) → GP zones → metastable η' phase → stable η phase (MgZn2). [1,7] In general, during the initial stage of the aging procedure, the precipitation reaction occurs with the formation of GP zones which is coherent with α-Al matrix. And then the GP zones transform into the main hardening η' phase with a more thermal stability than GP zones. Lastly, the η' phase will transform into η phase which is an equilibrium phase and non-coherent with α-Al matrix with higher temperatures or longer aging times [19,26,27]. In addition, considering the strengthening factors of 7XXX series alloys such as Al 7050 and Al 7055, η' phase is considered to exist in significant amount during peak-aging condition as the main age-hardening phase [3,28]. Therefore, the η' phases play a dominant role in strengthening effect in our Al–Zn–Mg–Cu alloy.

Numerous nanometer-sized Al3(Sc, Zr) particles are distributed in Al matrix and along grain boundaries (Fig. 9(c)–(f)). The precipitates are distributed homogeneously with a diameter of about 30 nm. With the increasing additions of Sc and Zr, the secondary Al3(Sc, Zr) particles exhibit a higher density and larger average particle size. The quantity of Al3(Sc, Zr) particles in Al-0.6(Sc + Zr) alloy is approximately double than that in Al-0.3(Sc + Zr) alloy. In addition, the strengthening effect of additional Sc and Zr is due to the formation of nanometer-sized secondary Al3(Sc, Zr) particles, which is independent from the strengthening effect of other aging precipitates in Al–Zn–Mg–Cu alloys [16,18]. From Fig. 9(c)–(f), coherent secondary Al3(Sc, Zr) precipitates stabilize the fine grain structure and enhance the strength by pinning the subgrain boundaries and inhibiting the motion of dislocations. According to dispersion-strengthening effect, the increment of YS in Al–Zn–Mg–Cu–Sc–Zr alloy is attributed to the shearing mechanism and Orowan dislocation bypass mechanism for smaller sizes and larger sizes, respectively. Therefore, the Al3(Sc, Zr) particles with a mean diameter of about 30 nm make contributions to strength increment due to the Orowan dislocation bypass mechanism.

The results explain that the η' phase is the major strengthening effect in Al–Zn–Mg–Cu alloy. While the η' phase and Al3(Sc, Zr) precipitates are the major strengthening effect in Al–Zn–Mg–Cu–Sc–Zr alloys. Higher volume fraction of Al3(Sc, Zr) particles is obtained with a larger addition of Sc and Zr, which drives from a higher strength enhancement in Al-0.6(Sc + Zr) alloy. Besides, the strength of Al-0.6(Sc + Zr) alloy increases sharply due to the high density of Al3(Sc, Zr) particles, which is related to the age hardening behavior and mechanical properties.

### 3.3. Strengthening mechanisms of Al–Zn–Mg–Cu–Sc–Zr alloys

According to the above experimental results, the anti-recrystallization behavior and precipitates strengthening result from nano-scale secondary Al3(Sc, Zr) particles. The yield strength is largely promoted by adding minor Sc and Zr, especially after aging treatments. The main strength mechanisms are investigated in the following text, which can be attributed to grain/subgrain boundary strengthening and Orowan strengthening.

From previous studies, the mechanical properties of metallic materials are generally related to the average grain size. The Hall–Petch equation has described the relationship of the mechanical properties and average grain size as follows [29]:

\[
\sigma = \sigma_0 + k \frac{d}{2}^{-1/2}
\]  

(1)

Where \(\sigma_0\) is the lattice friction stress to motion of dislocations and \(d\) is the average grain size, \(k\) is a material-dependent constant that represents the contribution of grain boundary to the related strengthening [19,30].

From the Hall–Petch relationship, the enhancement in YS is determined by the mean grain size, and the two variables have an inversely proportional relationship. Compared with Al–Zn–Mg–Cu alloy, the fine grain strengthening makes a large contribution to the enhancement of strength in Al–Zn–Mg–Cu–Sc–Zr alloys, which is attributed to two major factors. On the one hand, the formation of equiaxed grains during the recrystallization procedure provides a mass of fine grains with small grain size. On the other hand, the fibrous structure of Al–Zn–Mg–Cu–Sc–Zr alloy with slender grains exhibits more subgrain boundaries. Moreover, with the increasing additions of Sc and Zr, alloys exhibit more slender fiber-like structure with more subgrain boundaries (Figs. 1(c), 2(c) and 3(c)). The results can be used to analyze the strengthening effect due to the approximate grain size of the solution state and aged state [19,24,29]. In summary, Al-0.6(Sc + Zr) alloy acquires the best reinforcement effect with the smallest average grain size and most subgrain boundaries. The results successfully explain the phenomenon that Al-0.6(Sc + Zr) alloy acquires the highest strength than the other two alloys after aging at 120 °C for 24 h.

Combination of Sc and Zr significantly contributes to the ultra-high strength of Al based alloys due to the formation of extremely fine secondary Al3(Sc, Zr) particles, the augment of yield strength via Orowan strength (\(\Delta \sigma_{or}\)) mechanism can be analyzed as follows [30]:

\[
\Delta \sigma_{or} = \frac{k_4 M b}{\sqrt{1 - v}} \ln \left( \frac{d_i}{b} \right)
\]  

(2)

\[d_i = \frac{\pi d_m}{4}
\]  

(3)

\[\lambda = \frac{1}{2} \left( \sqrt{\frac{2\pi}{3} v} - 1 \right) \frac{\pi d_m}{4}
\]  

(4)

where \(M\) is the Taylor factor, \(v\) and \(G\) is the matrix Poisson’s ratio and the shear modulus, \(b\) is the magnitude of the Al matrix Burgers vector, \(k_4\) is a constant depending on the particle size and distribution, \(d_i\) and \(\lambda\) are the mean particle diameter and an effective inter-particle spacing on the dislocation slip plane, respectively [31,32]. This theory suggests that the higher YS value is obtained with a smaller particle size and larger volume fraction of the particles.

Compared with Al–Zn–Mg–Cu alloy, ultra fine secondary Al3(Sc, Zr) precipitates can be detected obviously in Al–Zn–Mg–Cu–Sc–Zr alloys (Fig. 9(d)–(f)). With the increasing additions of Sc and Zr, Al3(Sc, Zr) particles in Al-0.6(Sc + Zr) alloy exhibit a higher density and smaller particle size, indicating that larger Orowan strength effect can be obtained during the aging treatment at 120 °C for 24 h. As is known to all, the yield strength of Al–Zn–Mg–Cu–Sc–Zr alloy mainly depends on precipitate strength, which is deriving from the inhibition of the dislocations migration by nanometer-sized Al3(Sc, Zr) precipitates [13]. From Fig. 9(c) and (e), approximate average particle sizes can be detected in the two Al–Zn–Mg–Cu–Sc–Zr alloys, which exhibit little difference of the effect on yield strength. Moreover, according to the Equations (2) and (4), \(\Delta \sigma_{or}\) and volume strength (\(f_c\)) present directly proportional relationship. The mean Al3(Sc, Zr) particle size in Al-0.3(Sc + Zr) alloy and Al-0.6(Sc + Zr) alloy are 27 nm and 31 nm, respectively. The \(f_c\) of Al3(Sc, Zr) particles can be calculated using Equation (4), which are about 3 × 10⁻³ and 8 × 10⁻³ in Al-0.3(Sc + Zr) alloy and Al-0.6(Sc + Zr) alloy, respectively. Therefore, the larger \(f_c\) value of Al3(Sc, Zr) particles results in higher yield.
strength in Al-0.6(Sc + Zr) alloy. In summary, the finer subgrains and higher density of Al3(Sc, Zr) particles in Al-0.6(Sc + Zr) alloy make larger contributions to increase the yield strength.

4. Conclusions

Al–Zn–Mg–Cu alloys with and without Sc and Zr subjected to different heat treatments have been investigated in microstructures and mechanical properties. The main results of the current study are summarized as follows:

(1) Compared with Al–Zn–Mg–Cu alloy, better anti-recrystallization behavior and thermal stability can be obtained by adding 0.10Sc/0.16Zr and 0.22Sc/0.40Zr (wt.%). With the increasing additions of Sc and Zr, the alloys exhibit more excellent recrystallization resistance by effectively inhibiting the dislocations migration and pinning subgrain boundaries. Al-0.6(Sc + Zr) alloy exhibits finer fibrous structure during different annealing procedures due to a higher density of Al3(Sc, Zr) precipitates.

(2) Additions of Sc and Zr significantly contribute to strength increment in Al–Zn–Mg–Cu–Sc–Zr alloy. The higher enhancement of strength is achieved with more additions due to larger volume fraction of Al3(Sc, Zr) precipitates. Therefore, the highest hardness and strength are obtained by Al-0.6(Sc + Zr) alloy after aging treatment at 120 °C for 24 h. The maximum hardness, ultimate tensile strength and yield strength are 240 HV, 668 MPa and 628 MPa, respectively.

(3) The strength increment of the Al–Zn–Mg–Cu–Sc–Zr alloys in aged states results from secondary Al3(Sc, Zr) precipitates, indicating that more fine subgrains and Orowan strengthening are caused by pinning effect and small particle size, respectively. The strengthening mechanisms in aged Al–Zn–Mg–Cu–Sc–Zr alloys are attributed to subgrain strengthening and precipitation strengthening.

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References