

Article

Enhancing the Corrosion Resistance and Mechanical Properties of a High-Alloying Al-Zn-Mg-Cu-Zr Alloy by Ce Addition and Aging Treatment

Xinxiang Yu^{1,2,*}, Zhiguo Zhao³, Dandan Shi³, Xiaoyan Dong¹, Xianli Shi³, Caiqiong Li¹, Junfeng Zhao^{1,2} and Han Dai^{1,2}

- ¹ Laboratory of Advanced Light Alloy Materials and Devices, Postdoctoral Workstation of Nanshan Group Co., Ltd., Yantai Nanshan University, Longkou 265713, China; pigeon929@126.com (X.D.); Licaiqiong666@163.com (C.L.); zhaojunfengcc@163.com (J.Z.); daihan1985@189.cn (H.D.)
- ² School of Materials & Engineering, Shandong University, Jinan 250100, China
- ³ Hang Xin Material Technology Co. Ltd., Longkou 264006, China; zhaozhiguo@nanshan.com.cn (Z.Z.); shidandan@nanshan.com.cn (D.S.); shixianli@nanshan.com.cn (X.S.)
- * Correspondence: yuxinxiangcn@163.com; Tel.: +86-0535-859-0938

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Abstract: The corrosion resistance (exfoliation corrosion and inter-granular corrosion) and mechanical properties (strength and hardness) of a high-alloying Al-Zn-Mg-Cu-Zr alloy were improved by the synergistic effect of Ce addition and aging treatment. Ce addition promotes the morphology change of grain boundary precipitates from continuous form to discontinuous form at T6 temper. But the Cu content in grain boundary precipitates became much lower than that in Ce-free alloy, owing to a large amount of Cu being trapped in AlCuCe phase. Hence retrogression and re-aging (RRA) treatment were then adopted. The Cu content in grain boundary precipitates was improved, which can be attributed to the removal of Cu from solid solution during high temperature aging and its subsequent incorporation into grain boundary precipitates. In addition, the size and the distribution discontinuity of the grain boundary precipitates can be further increased and the main intra-grain phases of RRA alloy are still fine η' phase similar to T6 temper. Therefore, the alloy at RRA temper obtains the optimal corrosion resistance without loss of high strength.

Keywords: Al-Zn-Mg-Cu alloy; Ce; corrosion; microstructure

1. Introduction

Al-Zn-Mg-Cu alloy have been extensively used in aerospace applications due to its excellent specific strength [1,2]. With the increasing demands for superior strength, development of these alloys tends to high-alloying for the enrichment of precipitations [3]. However, increased Zn and Mg content would greatly reduce the corrosion resistance of these alloys [4,5]. For instance, high strength can be easily obtained in T6 peak-aged temper, but the corrosion performance is greatly weakened [6]. Even though the corrosion resistance can be increased on T7x over-aged temper, the trade-off is to sacrifice 10–15% strength [7].

At present, extensive attempts have been made to obtain the combination of high strength and favorable corrosion resistance of Al-Zn-Mg-Cu alloys [8–16]. Based on breaking the continuity and increasing the inter-precipitate distance along grain boundaries, and maintaining microstructures consisted of fine precipitates within the grains at the same time, a series of aging treatment are being conducted, such as the retrogression and re-aging (RRA) [11], non-isothermal ageing (NIA) [12], and high temperature pre-precipitation heat treatments (HTPP) [13] etc. Inhibiting recrystallization is also beneficial to improve the corrosion resistance and strength of the Al-Zn-Mg-Cu alloys by



increasing the proportion of low angle grain boundaries, as there is no obvious precipitates free zone (PFZ) formed at sub-grain boundaries and fine-grain strengthening, etc. [14,15]. In addition, higher copper content in the grain boundary phase can also contribute to the improvement of corrosion resistance of Al-Zn-Mg-Cu alloys [16]. In particular, the chemical composition of precipitates can affect the anodic polarization behavior because the alloy element Cu can shift the corrosion potential to the noble direction [17]. Therefore, we can consider using the synergistic effect of microalloying and heat treatment to achieve the effective control of the microstructures mentioned above.

Ce addition in Al alloy can promote the surface Al₂O₃ film to be transformed to Ce oxide film in corrosive environments, which has better corrosion inhibition effect than other rare earth oxides such as La₂O₃, Nd₂O₃, Pr₂O₃, Y₂O₃, etc. [18]. Besides, Ce addition also modifies the intra-grain precipitate shape from spherical to needle-like in Al-Zn-Mg-Cu alloys and improves the tensile strength by about 10% [19]. Moreover, improved recrystallization resistance of Al-Cu-Li-Zr alloy through Ce addition has been observed [20]. Ce easily interacts with other elements in the alloy to form intermetallic species [21], which would change the chemical composition and morphology of grain boundary precipitates, thus affecting the corrosion properties of the alloy. Therefore, the addition of small amounts of Ce in a high-alloying Al-Zn-Mg-Cu alloy can be used as a method to improve the corrosion resistance and strength simultaneously.

Nevertheless, so far there is little information available in the literature about the corrosion performance and mechanical properties of a high-alloying Al-Zn-Mg-Cu-Zr-Ce alloy. The purpose of the article is to investigate the effect of Ce addition and aging treatment on the microstructure, inter-granular corrosion, exfoliation corrosion and strength of a high-alloying Al-Zn-Mg-Cu-Zr alloy.

2. Materials and Methods

Al-Zn-Mg-Cu-Zr (Ce-free alloy) and Al-Zn-Mg-Cu-Zr-Ce (Ce-containing alloy) alloys were prepared by a casting metallurgy method. Industrial high purity Al (99.87 wt%), Mg (99.92 wt%) and Zn (99.94 wt%), and Al-Cu (51.51 wt%), Al-Zr (3.29 wt%), and Al-Ce (10.01 wt%) master alloys were taken as the starting raw materials. The experimental alloys were melted by induction heating, and then cast into Cu moulds to produce billets with 190 mm in length, 130 mm in width and 24 mm in thickness. The composition measured by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) method using a BAIRD PS-6 instrument (Thermo Nicolet, Madison, WI, USA) is shown in Table 1.

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|--------------------------|--------------|--------------|--------------|--------------|--------------|---------------------------------------|-----------|--------------|
| Alloy | Zn | Mg | Cu | Zr | Fe | Si | Ce | Al |
| Ce-free Ce-containing | 3.91 3.90 | 2.43 2.41 | 0.97 0.98 | 0.03 0.03 | 0.03 0.03 | 0.04 0.09 | - 0.02 | Bal. Bal. |

Table 1. Chemical composition of investigated alloys (at%).

The as-cast ingots were homogenized at 435 °C for 8 h and 470 °C for 32 h (H), followed by air cooling to room temperature. The ingots were converted into plates of 4.5 mm in thickness by hot rolling at 400–450 °C. The hot-rolled plates were held at 430 °C for 1.5 h and then cooled to room in the furnace. Finally, these plates were cold rolled to a thickness of approximately 2.2 mm. The solid solution treatments were performed at 450 °C for 50 min and subsequently 485 °C for 30 min (SS) in a salt bath furnace with an accuracy of ± 2 °C. The samples were water-quenched at room temperature. At last, the experimental alloy went through a series of aging treatment: the peak-aging which means being artificially aged at 120 °C for 24 h (T6); the over-aging, which means being artificially aged at 120 °C for 24 h, followed by retrogression process at 190 °C for 1 h, and then being artificially aged at 120 °C for 24 h. The heat treatment procedures applied in this study have been separately given in the Table 2.

| Heat | Freatment Condition | Procedures | | | |
|------|----------------------------|--|--|--|--|
| Н | Homogenization | 435 °C/8 h + 470 °C/32 h | | | |
| SS | Solid solution | 450 °C/50 min + 485 °C/30 min | | | |
| T6 | | 120 °C/24 h | | | |
| T7 | Aging | 120 °C/24 h + 160°C/8 h | | | |
| RRA | | 120 °C/24 h + 190 °C/1 h + 120 °C/24 h | | | |

Table 2. Heat treatment procedure of experimental alloy.

Tensile tests were performed at a loading speed of 2 mm/min with an Instron3369 machine (INSTRON, Boston, MA, USA). The accelerated intergranular corrosion (IGC) testing was performed in an aqueous solution consisting of 30 g/L NaCl and 10 mL/L HCl (PH:0.85) at 35 ± 1 °C, according to the IGC test standard of GB7998-2005 [22]. Exfoliation corrosion testing (EXCO-testing) was carried out in an aqueous solution consisting of 234 g/L NaCl, 50 g/L KNO₃ and 6.5 mL/L HNO₃ (PH:0.4) at 25 ± 2 °C, according to the Chinese HB5455-90 specification [22].

Effect of Ce addition on recrystallization inhibition during solid solution treatment was observed by optical microscopy under polarized light and electron backscatter diffraction (EBSD, FEI-Nova Nano SEM 450, FEI Company, Hillsboro, OR, USA). The gathered EBSD data were analyzed using TSL OIM Analysis 7 software (EDAX Inc., Mahwah, NJ, USA). In order to clarify the dissolution of intermetallic phases during solid solution, the sample before solid solution was performed by using differential scanning calorimeter (DSC, DSC1/700, Mettler Toledo, Columbus, OH, USA) at a heating rate of 10 °C/min. Electron probe micro-analysis (EPMA, JXA-8230, JEOL Corp., Tokyo, Japan) and/or scanning electron microscopy (SEM, FEI-Nova-Nano SEM450, Hillsboro, OR, USA) was used to characterize the segregation of the main element in Ce-enrichment phase after homogenization and solid solution respectively. The phases of the Ce-containing alloy after homogenization and solid solution were investigated by X-ray diffraction (XRD; Rigaku D/max-2400, Ultima IV, Rigaku Corp., Tokyo, Japan). Conductivity test was carried out on a SIGMATEST 2069 eddy current conductivity meter (Institut Dr. Foerster GmbH & Co. KG, Reutlingen, Germany). The samples were processed into 30 mm × 30 mm × 2 mm blocks. The conductivity of the alloy was characterized by international annealed copper standard (IACS). The experimental results were converted into % IACS value. The distribution of precipitates along grain/sub-grain boundaries and in grain was analyzed on a JEOL-2100F transmission electron microscopy (STEM) system (JEOL Corp., Tokyo, Japan). In order to study the change in chemical composition of grain boundary phase, elemental mapping was also conducted by using energy-dispersive X-ray spectroscopy (EDS) measurements (FEI Company, Hillsboro, OR, USA).

3. Results and Discussion

The existing form of Ce and its influence on the segregation of other main elements after homogenization (H) and solid solution treatment (SS) in Ce-containing alloy are shown in Figure 1. The elements mappings of Al, Cu, Ce, Zn and Mg are observed after homogenization (Figure 1a). Cu segregates with Zn, Ce or Mg at dendrite boundaries. The Cu atoms fixed in the insoluble Ce-containing phase or CuMg phase in dendritic interface after homogenization are seriously deficient in dendritic matrix according to the Cu mapping. On the contrary, more Zn and Mg atoms solubilize in dendritic matrix. To be more specific, the chemical composition of the bright phase marked as A, dark phase marked as B and matrix Al marked as C in Figure 1a are presented in Table 3 by using quantitative X-ray wavelength dispersive spectroscopy (WDS) analysis. According to the XRD analysis results in Figure 2, the main phases after homogenization are Al₈Cu₄Ce and Al₂CuMg, so the bright phase enrichment with Cu, Ce and Zn is an insoluble Al₈Cu₄Ce phase with some Zn dissolved in it [23,24]. The dark intermetallic phases enrichment with Cu and Mg are thought to be the Al₂CuMg phase because the Cu to Mg ratio is close to 1:1 in this phase [25]. Cu is mainly locked by Al₈Cu₄Ce and Al₂CuMg phases which are insoluble during homogenization with the upper temperature of

470 °C, while only the fine residual phase distributing along rolling streamline is observed after rolling and solid solution treatment (Figure 1b). These fine residual phases are only Al_8Cu_4Ce without Zn in it according to EDS (Figure 1a) and XRD results (Figure 2). Therefore, it can be inferred that Zn originally trapped in crushed Al_8Cu_4Ce phase is also diffused into the matrix and the Al_2CuMg particles are almost completely dissolved due to the ultrahigh solid solution temperature at 485 °C and being smashed during the severe rolling process. These results are also well confirmed by DSC plots before and after solid solution treatment in Figure 3. Two endothermic peaks, sited at 477.9 °C and 498.4 °C respectively, are observed before solid solution. The endothermic peak at 477.9 °C is mainly attributed to the melting of T(Mg₃₂(Al,Zn)₄₉) phase [26]. The endothermic peak at 498.4 °C attributed to the dissolution of Al_2CuMg phase [25] is nearly eliminated after solid solution treatment. Yet some Cu atoms are still locked by the insoluble Al_8Cu_4Ce phase, so it is difficult for them to get into the super-saturated solid solution, let alone subsequently precipitate from it and then diffuse to the precipitates in the grain and grain boundaries during aging.



Figure 1. The existing form of Ce and its influence on the segregation of other main elements in the Ce-containing alloy: (**a**) after homogenization; (**b**) after solid solution treatment.

Table 3. Chemical composition of intermetallic phases in Figure 1a (at%).

| Point | Al | Zn | Mg | Cu | Ce | Phases |
|-------|---------|--------|---------|---------|--------|--|
| А | 56.8445 | 8.7635 | 1.2425 | 25.1083 | 6.5830 | Al ₈ Cu ₄ (Ce, Zn) |
| В | 51.1837 | 1.2160 | 25.6502 | 21.9270 | 0.0230 | Al ₂ CuMg |
| С | 94.5761 | 3.0612 | 1.9676 | 0.3801 | 0.0001 | Matrix |



Figure 2. XRD analysis of the Ce-containing alloy after homogenization and solid solution.



Figure 3. DSC curves of the Ce-containing alloy before and after solid solution treatment.

The recrystallization degree of the Ce-free and Ce-containing alloys after solid solution treatment (SS) is illustrated in Figure 4. Although almost complete recrystallization can be observed in Ce-free alloy (Figure 4a), there are still large areas of unrecrystallized or fiber grain structures in local area of the Ce-containing alloy even when the solid solution temperature is up to 485 °C (Figure 4b). In addition, grain orientation in Ce-containing can be clearly observed by using EBSD, as shown in Figure 4c,d. A considerable amount of partial recrystallization zone, which consists of subgrains with a high proportion of low-angle grain boundaries, clearly remained. Accordingly, a large number of low angle grain boundaries in fine grain are also observed by TEM (Figure 4e). Small Ce addition can inhibit recrystallization of Al-Zn-Mg-Cu alloy during solid solution and improve the proportion of low angle grain boundary. Similar results have also been found in Al-Cu-Li-Zr alloy by Ce addition [20]. Because a large number of spherical Al₈Cu₄Ce phases tend to form in the Al₃Zr dispersoid-free bands owing to the opposite microsegregation patterns of Ce and Zr in Al alloy. Even nano-scaled AlCuCe dispersoids showing high-temperature stability have been observed in Al-Zn-Mg-Cu-Zr-Ce alloy in our previous work [22]. So uniform coverage of dispersoids achieved through joint addition of Zr and Ce in Al alloy can inhibit recrystallization and improve the proportion of zr and



Figure 4. The recrystallization degree of the experimental alloys after solid solution treatment: (**a**) Optic micrography images of the Ce-free alloy; (**b**) OM images of the Ce-containing alloy; (**c**) EBSD image (**d**) grain boundary orientation angle distribution and (**e**) TEM image of the Ce-containing alloy.

The precipitates distributed along the grain and/or subgrain boundaries at different aging treatment of the experimental alloys are shown in Figure 5. Equilibrium small η (MgZn₂) phases with a hexagonal lattice [27] in Ce-free alloy at T6 temper are distributed on the grain boundaries continuously and close to each other, as shown in Figure 5a, while discontinuous grain boundary phase characteristics are observed on both grain boundaries and subgrain boundaries in Ce-containing alloy at T6 temper (Figure 5c,d). In addition, there are no obvious precipitates free zone (PFZ) formed on both grain boundaries and subgrain boundaries. Small Ce addition can lead to more obvious discontinuity of precipitates at grain boundaries. This phenomenon has also been found in other Ce additional Al alloys [19]. Then the T6 temper sample was further aged at higher temperature 160 °C for 8 h and the over aging state T7 temper was obtained. The results show that the grain boundary precipitates of the Ce-containing alloy is sparse and extremely coarsen (size: 30–40 nm), and the width of the precipitated zone (PFZ) is increased to 30–50 nm (Figure 5e). It is noted that even though sufficient element diffusion occurs at T7 temper, the Cu content of the grain boundary precipitated phase in the Ce-containing alloy is still much lower than that in the Ce-free alloy at T6 temper, as shown in Figure 5b,f.



Figure 5. The precipitates distributed along the grain boundaries and elemental mapping of Al, Cu, Zn and Mg in grain boundary phase at different aging treatment of the experimental alloys: (**a**,**b**) Ce-free alloy at T6 temper; (**c**,**d**) Ce-containing alloy at T6 temper; (**e**,**f**) Ce-containing alloy at T7 temper; (**g**,**h**) Ce-containing alloy at RRA temper.

To obtain both high strength and good corrosion resistance at the same time, a retrogression and re-ageing (RRA) treatment was carried out. The microstructures consist of relatively coarser precipitates distributed discontinuously on the grain boundaries (size: 20–30 nm, interparticle spacing: 20–45 nm) and fine precipitates within the grains. Although the interspace and size of precipitates at grain boundaries are smaller than those of T7 state, the relative Cu content of precipitated phase in grain

boundary increases obviously (Figure 5h). These results can be attributed to the removal of Cu from solid solution during high temperature aging and its subsequent incorporation into grain boundary phase at RRA temper [17]. In addition, the chemical composition of the grain boundary phase marked as A in Figure 4a, marked as B in Figure 5e and marked as C in Figure 5g are presented in Table 4 by using STEM-EDS analysis. The Cu content of grain boundary precipitate in Ce-containing alloy at RRA temper is increased to be close to that of Ce-free alloy after short-time high-temperature aging.

| Point | Al | Cu | Zn | Mg | Phase |
|-------|------|-----|------|------|----------------------|
| А | 56.1 | 9.7 | 20.7 | 13.5 | $\eta (Mg(Zn,Cu)_2)$ |
| В | 64.3 | 4.0 | 19.0 | 12.6 | $\eta (Mg(Zn,Cu)_2)$ |
| С | 59.6 | 7.8 | 19.6 | 13.0 | $\eta (Mg(Zn,Cu)_2)$ |

Table 4. Chemical composition of grain boundary precipitates in Figure 5 (at%).

The maximum depth of attack on the experimental alloy in the IGC test for 24 h is illustrated in Figure 6. The maximum depth of attack for T6 temper is 290.82 µm in Ce-free alloy (Figure 6a). For Ce-containing alloy, it can be seen that the maximum depth of attack for T6 temper is slightly reduced to 234.69 µm (Figure 6b), while the maximum depth of attack for T7 and RRA temper is only 81.63 µm and 100.01 µm respectively (Figure 6c,d). Although the inter-granular corrosion attack was retarded due to Ce addition, the corrosion resistance property still needs, to a large extent, to be optimized through T7 and RRA aging treatment. Results of EXCO evaluations after being exposed for 12 h are showed in Figure 7. The corrosion pattern on the surface of alloy changed from the EC (Exfoliation) state (notable layering and intense penetration into the metal) in Ce-free alloy to the EA (Exfoliation) state (slight layering and penetration into the metal) in the Ce-containing alloy. Moreover, the corrosion pattern changed from EA to PC (Pitting) state (superficial pitting and slight penetration into the metal) when the Ce-containing alloy was treated at T7 and RRA temper. The corrosion resistance (exfoliation corrosion and inter-granular corrosion) of a high-alloying Al-Zn-Mg-Cu-Zr alloy was improved by the synergistic effect of Ce addition and aging treatment.



Figure 6. The maximum depth of attack on the experimental alloy in the IGC test for 24 h: (**a**) Ce-free alloy at T6 temper; (**b**) Ce-containing alloy at T6 temper; (**c**) Ce-containing alloy at T7 temper; (**d**) Ce-containing alloy at RRA temper.



Figure 7. Results of EXCO evaluations after exposed for 12 h: (a) Ce-free alloy at T6 temper; (b) Ce-containing alloy at T6 temper; (c) Ce-containing alloy at T7 temper; (d) Ce-containing alloy at RRA temper.

The mechanical properties and conductivity of the Ce-containing alloy at T6, T7 and RRA temper are shown in Figure 8. It can be seen that the ultimate strength (UTS), 0.2% yield strength (YS) and hardness of the alloy with RRA are similar to those of T6 temper, and do not decline obviously. The electrical conductivity varies with precipitate size of Al alloy, which has an effect on the chemical potential between intra-grain/grain boundary phases, and corrosion channels along grain boundaries.



Figure 8. The mechanical properties and conductivity of the Ce-containing alloy at T6T7 and RRA temper: (**a**) tensile properties; (**b**) micro hardness and conductivity.

Therefore, to some extent, the electrical conductivity can reflect corrosion resistance of the alloy in different heat treatment states [28]. The electrical conductivity of alloy at T6 temper is the lowest, which is 31.6% IACS, and its corrosion resistance is the worst. After T7 and RRA heat treatment, the electrical conductivity of the alloy increases significantly to more than 40% IACS, and the corrosion resistance is significantly improved. The degree of recrystallization and grain boundary precipitation characteristics are the main factors that affect the corrosion resistance and mechanical properties of Al-Zn-Mg-Cu alloys [2,6]. The morphology and distribution of grain boundary precipitates can be easily affected by Ce addition and aging process, and hence the corrosion properties can be changed. Compared with Ce-free alloy at T6 temper, a considerable amount of partial recrystallization zone and more discontinuous grain boundary phase characteristics on both grain and subgrain boundaries in Ce-containing alloy are observed, but the Cu content of the grain boundary precipitated phase becomes lower. Because the unique electrochemical behaviour of η phase (MgZn₂) has been determined to be such that when η phase is present in an Al alloy, η phase is polarised anodically, hence preferentially dissolving in aqueous electrolytes [29,30]. The substitution of Zn with of Cu in η phase minimises the extent of anodic polarisation of η phase, owing to a decreased electrochemical potential difference between the Cu-containing η phase and the alloy matrix [29,31]. Therefore, the enhancement of corrosion resistance such as IGC and EXCO is inadequate. After over aging and regression and re-aging treatment, the grain boundary precipitates coarsen and the spacing increases significantly. Especially, the Cu content of grain boundary precipitate is increased after short-time high-temperature aging at RRA temper. Hence the parameters of IGC (the maximum depth of attack from 290.82 µm to 100.01 µm) and EXCO (pattern changed from EC to PC) are significantly improved, which indicates the significant corrosion resistance improvement of the Ce-containing alloy at RRA.

The main strengthening mechanism of the experimental alloys was precipitates. The movement of the dislocations could be effectively blocked by the precipitates and the strain field around the precipitates.

Figure 9 shows the intragrain precipitates and selected area electron diffraction (SAED) of the Ce-containing alloy at various aging tempers. Figure 9a,b show that the main strengthening phases of the alloy at T6 temper are coherent GP zone and fine semi coherent $\eta'(MgZn_2)$ phase with a metastable hexagonal lattice [27], only 2–5 nm. At this time, the shear stress increment is positively correlated with the volume fraction and the radius of the precipitates [28], which means, the strengthening effect can be enhanced by increasing the radius of GP zone and fine η' phase until peak aging. So, the strength of the Ce-containing alloy at T6 peak-aged temper reaches its maximum at the peak aging (σ_b : 653 MPa, $\sigma_{0.2}$: 611 MPa, δ : 10% and HV_{0.5}: 207).

However, as the aging degree goes any further, the main precipitate size grows larger and more and more η' phase is transformed into extreme coarsening equilibrium η phase (size: 14–26 nm), as shown in Figure 9c,d. At this time, the interaction between dislocations and strengthening phases is dominated by bypass mechanism [28]. That is to say, the strength of the alloy will decrease rapidly with the increase of the precipitate size. Therefore, the strength (σ_b : 588 MPa, $\sigma_{0.2}$: 541 MPa, δ : 12% and HV_{0.5}:183.7) of the alloy decreases sharply to 588 MPa due to the aggregation and growth of precipitates, and the dissolution of a small amount of unstable η' phase during over aging at T7 temper. For the RRA temper, the fine precipitates (size: 5–10 nm) distributed homogenously within the matrix and the main strengthening phases of RRA alloy are fine η' phase and only a small amount of η phase (Figure 9e,f), which is basically similar to that of T6 temper alloy, and thus also has high strength (σ_b : 640 MPa, $\sigma_{0.2}$: 598 MPa, δ : 12% and HV_{0.5}:203). Therefore, the alloy at RRA temper obtains the optimal corrosion resistance without the loss of high strength.



Figure 9. Intragrain precipitates and selected area electron diffraction (SAED) of the Ce-containing alloy at various aging tempers: (**a**,**b**) T6; (**c**,**d**) T7; (**e**,**f**) RRA.

4. Conclusions

Enhancing corrosion resistance and mechanical properties in a high-alloying Al-Zn-Mg-Cu-Zr alloy by Ce addition and RRA treatment was investigated. Ce addition can enhance the proportion of low angle grain boundaries and promote the morphology of grain boundary precipitates to change from continuous to discontinuous at T6 temper. Additional aging treatment as retrogression and re-aging (RRA) was adopted, the size and the distribution discontinuity of the grain boundary precipitates were further increased, and the Cu content in grain boundary precipitates was obviously improved. In addition, the main strengthening phases of RRA alloy are fine η'phase, similar to that of T6 temper. Therefore, the optimal corrosion resistance without the loss of high strength is obtained in a high-alloying Al-Zn-Mg-Cu-Zr by Ce addition and RRA treatment.

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