Influence of Added Fourth Elements on Precipitation in Heat-Resistant Al–Mg–Zn Ternary Alloys

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In the present study, we investigated the effects of Cu or Ni additions on the precipitation of intermetallic phases in the heat-resistant aluminum alloy with a ternary composition of Al–5Mg–3.5Zn (mol%). The quaternary alloys with 1 mol%Cu or 1 mol%Ni content were solution-treated at 480°C and subsequently aged at 300°C for different periods. Both Cu and Ni additions have a slight effect on the age-hardening of these alloys at 300°C. The added Cu element partitioned into not only the T-Al12Mg0.7Zn0.3 phase but γ-Zn0Mg phase precipitated in the α-Al matrix. The observed Cu enrichment in the precipitates of the T phase indicated high stability of the T phase in the Al–Mg–Zn–Cu quaternary system, which was different from the results of thermodynamic calculations using the existing database. The added Ni element enhanced the formation of fine Al1Ni phase located at grain boundaries and slightly influenced the precipitation of T phase in the grain interior. These results provided new insights to design novel heat-resistant Al alloys using the Al–Mg–Zn–Cu–Ni system.

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1. Introduction

The installation of turbochargers has been proposed as an approach for improving fuel efficiency in automobile engines. Although this approach can realize high output with high-efficiency combustion, which allows downsizing the engine and improving fuel efficiency, it has gained considerable attention in terms of environmental concerns. A further increase in engine output can be achieved effectively via improvements in the compression ratio of compressed air. This can be achieved by increasing the speed of the impeller inside the compressor. However, this requires high temperatures and pressures inside the compressor intake, and improvements in the high-temperature strength of impeller members are needed.

Casting aluminum (Al) alloy AC4D (Al–5Si–1Cu–0.5Mg (mass%)) and wrought Al alloy 2618 (Al–2.3Cu–1.2Mg–1.1Fe–1.0Ni (mass%)) are currently utilized for impellers in turbochargers for automobile engines. Both alloys show significant decreases in strength in temperature ranges not less than 200°C. Therefore, their applicable temperatures are limited to values not exceeding 200°C. These Al alloys are T6-treated (artificial aging treatment temperature below 200°C). For example, the 2618 alloy is strengthened using the S-Al2CuMg phase, which is precipitated by the aging treatment; however, its equilibrium volume fraction does not exceed 5% based on thermodynamic calculations. In addition, the 2618 alloy precipitates the metastable S' phase in aging treatment at 200°C. It is believed that the metastable phase undergoes a phase change into a stable phase (S phase) after long-term use at not less than 200°C, and the precipitation morphology becomes remarkably coarse with this change, which can lead to a significant weakening of the material. Thus, the limited volume fraction of the strengthened phase and the thermal stability of the strengthened phase (use of the metastable phase) are cited as problematic issues when using existing Al alloys in high-temperature environments.

Like wrought Al alloys, nickel (Ni)-based superalloys precipitate the γ'-Ni3M phase (intermetallic phase with the L12 structure; M indicates metal elements such as Al and Ti), which equilibrates with the parent γ-phase with the aging treatment following the solution treatment (single γ-Ni (fcc) phase). The wrought-type Ni-based alloy contains an intermetallic phase with a high-volume fraction above 10%, and it maintains a stable microstructure morphology at high temperatures. Therefore, it exhibits high-temperature strength. This research group was inspired by the structural morphology of wrought-type Ni-based alloys that can achieve superior high-temperature strength, and a new heat-resistant wrought-type Al alloy strengthened by a thermodynamically stable intermetallic compound phase (equilibrium phase) with a volume fraction of not less than 10%, where the assumed operating temperature is not less than 200°C, was designed in this study. This study explored the alloy composition and improvements in the thermodynamic stability of the α-Al phase (extended α-Al phase solubility limit) of an Al–Mg–Zn ternary alloy. Based on the phase diagram calculated using an existing thermodynamic database, we designed an alloy composition of Al–5Mg–3.5Zn (mol%); this alloy sets the T-Al12Mg0.7Zn0.3 phase in the Al–Mg–Zn system. Figure 1(a) and Fig. 1(b) show the isothermal cross-section (300°C) in the Al–Mg–Zn ternary calculated phase diagram and the crystal structure of the T phase, which is the strengthening phase of the designed alloy, respectively. The T phase precipitated in the α-Al matrix exhibits a fine morphology and is relatively stable even at high temperatures not less than 200°C. In addition, the designed alloy (heat-treated by artificial aging at 200°C for 1 h) demonstrates superior yield and tensile strengths.

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compared to those of existing alloys in the high-temperature range above 150°C. The effectiveness of the proposed alloy as a strengthening phase of the T phase is verified in cast-type alloys where the volume fraction of the T phase is increased to not less than 50%.16,17,18

The addition of a fourth element is presented as a method to further strengthen the proposed design alloy. For example, considerable research has been conducted on identifying how Cu addition affects the precipitation (age hardening) of existing Al–Mg–Zn alloys (7000 series alloys) with aging.19–21 Cu addition promotes precipitation during the aging treatment, and it is effective for strengthening the alloy. In addition, the T-(Al,Cu)Mg(Zn) phase exists in a ternary Al–Mg–Cu system,22 and therefore, the Cu would partition into the T phase23 and makes it thermodynamically stable. Meanwhile, Ni has been discussed as an alloy element that improves heat resistance in Al alloys. Ni addition in Al alloys promotes the formation of the Al3Ni phase (orthorhombic oP16)24 and contributes to the higher strength and creep resistance at high temperatures.25 Ni addition to the proposed alloy forms a stable intermetallic compound phase different from the T phase, and it is expected to improve high-temperature strength.

In this study, we investigated the effect of adding a fourth element (Cu and Ni) predicted to play different roles in the microstructural development of the ternary base alloy with a composition of Al–Mg–3.5Zn (mol%). Further, we explored how the addition of a fourth element affects the constituent phase and precipitation morphology associated with solution treatment and artificial aging treatment from the viewpoint of the precipitation of the intermetallic compound phase equilibrated with the parent α-Al phase.

2. Design of Improved Alloys by Thermodynamic Calculations

Figures 2(a) and 2(c) present the respective cross-sectional views of the Al–Mg–Zn–Cu and Al–Mg–Zn–Ni quaternary systems created based on the commercially available thermodynamic database PanAluminum26 and multidimensional phase diagram calculation software Pandat (CompuTherm LLC). The appropriate alloy composition range for thermodynamic calculations using PanAluminum is within 6% Mg, 3.3% Zn, 2.3% Cu, and 0.3% Ni (mol%),26 and the assessments are conducted within this composition range. The origin of the horizontal axis in both cross-sectional views is Al–5Mg–3.5Zn (mol%). The addition of the Cu element to the Al–Mg–3.5Zn alloy changes the two-phase region of α-Al/T in the temperature range not less than 200°C to the two-phase region of α-Al/η-Zn3Mg (Fig. 2(a) and Fig. 2(b)). This change in the phase region suggests that the added Cu element would partition into the η phase rather than the T phase, and it promotes the precipitation of the former phase. Further, the addition of the Ni element generates an extensive three-phase region of α-Al/T/Al3Ni (Fig. 2(d)). This phase region does not change in the temperature range of 200–400°C regardless of the Ni concentration (Fig. 2(c)). This calculation result indicates that the Ni element would not be distributed to the T phase for strengthening and it independently generates the Al3Ni phase in the parent α-Al phase. Based on the above quaternary phase diagram, we designed an alloy in this study wherein 1 mol% of Cu and Ni were added to the alloy composition of Al–5Mg–3.5Zn (mol%), which is the base alloy of the ternary system.

Figure 3 shows temperature-dependence of the mole fraction of the constituent phases in the equilibrium state of the ternary base alloy and quaternary modified alloy. The base alloy with the composition Al–5Mg–3.5Zn (mol%) (Fig. 3(a)) exhibits a single α-Al phase in the temperature range 450–500°C. In addition, the mole fraction of the strengthening T phase is not less than 6% at low temperatures not exceeding 300°C. This change in the phase region shows that the T phase is precipitated from the parent α-Al phase by subjecting it to an aging treatment after solution treatment at temperatures not less than 450°C. The two phases of α-Al and η phases exist up to the high-temperature region just..
In this study, we used Al (purity 99.99%), Mg (purity 99.9%), Zn (purity 99.9%), Cu (purity 99.99%), and Ni (purity 99.9%) provided by Kojundo Chemical Laboratory Co., Ltd. as the raw alloy materials. They were weighed into an iron mold to produce a rod-shaped alloy ingot with a 1 cm diameter.

A sample obtained by cutting the rod-shaped ingot into a thickness of approximately 3 mm was used for heat treatment. The three alloy types underwent solution treatment at 480°C for 24 h in an electric furnace (DDR-3000, Isekyu Co., Ltd.), after which it was quenched with water. The water-quenched material underwent artificial aging treatment at 300°C for 60 s to 1000 h using a salt bath (electric crucible furnace BK-3, Yamada Denki Co., Ltd.) and electric furnace (KDF-S8, Denken-Highdental, Co., Ltd.). In this study, the aging temperature was set to 300°C based on previous research(15) for obtaining basic knowledge regarding the precipitation of the intermetallic compound phase in equilibrium with the parent α-Al phase. The samples that were water-quenched after solution treatment were placed in the furnace within 60 s and this was followed by aging treatment to eliminate the effect of alloy hardening from natural aging.

 Samples that underwent solution and aging treatments were wet polished with SiC paper (#320, #2400) and then mirror finished with colloidal silica (Chemical Liquid 0.05 μm PH9.8, Musashino Denshi, Inc.). A Vickers hardness test was conducted on this sample using a microhardness tester (FM-700e, Future-Tech Corp.) with a test load of 9.8 N and load time of 15 s. The test was conducted over five times with the same sample, and the test position was set within the crystal grains. The Vickers hardness test was conducted after solution treatment and within 0.5 h after aging treatment to minimize the effect of hardening from natural aging of the sample. In this experiment, the Vickers hardness test was conducted at room temperature using samples held at the temperature for each time point to obtain basic knowledge on the change in strength because of the precipitation and coarsening of the equilibrium phase at 300°C.

After the prepared sample was embedded in the resin, it was mechanically wet polished using SiC paper (#8320, #800, #1200, #2400). Afterwards, it was buffed with a diamond slurry (3 μm, 1 μm) and mirror finished with colloidal silica. The structural observations of these samples were performed using a scanning electron microscope (SEM, JSM-5510 and JSM-6010A, JEOL Ltd.) at an acceleration voltage of 15 kV. Elemental analysis was conducted using energy dispersive X-ray spectrometry (EDS).

A test piece with a smooth surface was prepared from the heat-treated sample, after which it underwent wet polishing using SiC paper (#800). Next, the sample was placed on a sample table for an X-ray diffractometer (goniometer: Rigaku ULTIMA IV). Each slit has a divergence-limiting slit (DHL) of 10 mm and divergence slit (DS) of 1°. The scattering slit (ss) was set as 1°, and the receiving slit (RS) as 8 mm. The measurement conditions were an X-ray output of 40 kV and step width of 0.02°. The observed diffraction peaks were compared with those created by calculations using the database for phase identification. Measurements of the solution-treated material considered the effects of natural aging, and samples that were taken out of the furnace within 1 h were used.

Three alloy samples aged at 300°C for 1 h were used as test materials for transmission electron microscope (TEM) observation samples. The test materials were cut into a

![Fig. 3 Changes in calculated mole fractions of constituent phases in (a) base alloy, (b) Cu added alloy and (c) Ni added alloy as a function of temperature.](image-url)
plate shape using a low-speed precision cutting machine (IsmetTM LS, BUEHLER Ltd.), after which it was fixed to a slide glass with solid wax (Adfix, Nikka Seiko Co., Ltd.), wet polished using SiC paper (#320, #2400), and prepared as a flaky sample with a thickness of approximately 0.1 mm. The surface of the sample was washed and dehydrated using acetone. This thin-plate sample underwent argon-polishing at 6.0 kV using an Ion Slicer TM (EM-09100IS, JEOL, Ltd.), after which it was finished for 300 s at an acceleration voltage of 2.0 kV to prepare a TEM observation sample.

The microstructural observations of the prepared sample were conducted using TEM (JEM 2100plus and JEM-2100F/HK, JEOL, Ltd.) at 200 kV to capture bright-field image, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed to obtain a scanning transmission electron microscope (STEM) image. Elemental analysis was conducted using EDS.

4. Experimental Results

4.1 Solution treatment

Figure 4 shows the backscattered electron image of the sample wherein each alloy underwent solution treatment at 480°C for 24 h. The base alloy that underwent solution treatment was entirely composed of the $\alpha$-Al phase (Fig. 4(a)). The T phase (bright contrast) that formed during casting was entirely decomposed. Meanwhile, the Cu-added alloy (Fig. 4(b)) and Ni-added alloy (Fig. 4(c)) had masses of an intermetallic compound phase with a bright contrast on the grain boundaries. The intermetallic phase observed in the Ni-added alloy was more finely distributed than that of the Cu-added alloy. A thermodynamic calculation showed the formation of a trace amount of liquid phase at the solution-treatment temperature of 480°C in the Cu-added alloy composition, whereas there was no fine solidified region that indicated the presence of a liquid phase at 480°C.

Figure 5 shows the XRD profile obtained from each alloy that has undergone solution treatment. A large diffraction intensity is observed from the base alloy because of the $\alpha$-Al phase, and minute diffraction intensities are detected as derived from the locally remaining T phase (Fig. 5(a)). The diffraction results are almost the same as the SEM observation results (Fig. 4(a)). The diffraction of the $\eta$ and T phases were detected from the Cu-added alloy (Fig. 5(b)), and the intermetallic phase observed in the backscattered electron image (Fig. 4(b)) corresponds to the $\eta$ and T phases. A relatively strong diffractions intensity derived from the Al$_3$Ni phase were observed from the Ni-added alloy. This result indicates that the compound phase observed in the backscattered electron image (Fig. 4(c)) is the Al$_3$Ni phase. The above-mentioned experimental results are mostly in agreement with the prediction of the equilibrium phase of the design alloy by thermodynamic calculations (Fig. 3), whereas the existence of the T phase in the Cu-added alloy differs from the calculation results.

4.2 Microstructural changes by aging treatment

Figure 6 shows changes in Vickers hardness of each alloy with aging treatment at 300°C (after the solution treatment at 480°C). The base alloy (Al–5Mg–3.5Zn) showed a maximum hardness of approximately 130 HV not exceeding 0.1 h of the aging treatment, after which the hardness decreased with subsequent aging. The hardness after 1000 h was approximately 60 HV. The solution-treated base alloy had a higher hardness than the Cu-added (Al–5Mg–3.5Zn–1Cu) and Ni-added alloys (Al–5Mg–3.5Zn–1Ni), however, the hardness of the Cu-added alloy showed a maximum hardness of approximately 150 HV after the aging below 0.1 h, and it was higher than that of the base alloy. The hardness then decreased with subsequent aging. The Ni-added alloy showed
a maximum hardness of approximately 130 HV not exceeding 0.1 h of aging treatment, whereas the value does not change with the hardness of the base alloy. The hardness then gradually decreased with a subsequent aging treatment, and the hardness value at not less than 10 h was similar to that of the base alloy.

Figure 7 shows the XRD measurement results of each alloy subject to an aging treatment at 300°C for different periods. Diffraction was detected from the aged base alloy (Al–5Mg–3.5Zn) derived from the α-Al and T phases (Fig. 7(a), (b)); the diffraction intensity of the T phase increased after long aging times (1000 h) (Fig. 7(b)), which implies the T phase was precipitated from the parent α-Al phase at an aging treatment of 300°C. Diffraction not only from the α-Al and T phases but also from the η phase was detected from the Cu-added alloy (Al–5Mg–3.5Zn–1Cu) (Fig. 7(c)). After aging for 1000 h, the number of lattice planes corresponding to diffraction from the η phase increased, and their diffraction intensities increased (Fig. 7(d)), which suggests that many precipitation phases of the Cu-added alloy at 300°C are η phases. The diffraction peaks detected from the Ni-added alloy (Al–5Mg–3.5Zn–1Ni) correspond to that derived from the α-Al, T, and AlNi phases (Fig. 7(e)). The increase in diffraction intensity derived from the T phase in the sample subjected to long-term aging indicates the precipitation of the T phase during the aging at 300°C.

Figure 8 shows microstructural changes in each alloy with an aging treatment at 300°C (after the solution treatment at 480°C). In the base alloy (Al–5Mg–3.5Zn), the T phase preferentially precipitated at the grain boundaries of the parent Al phase and covered most of the grain boundaries (Fig. 8(a)–(d)). Further, the granular T phase was finely and uniformly distributed in the grains, and the T phase became coarse with long-term aging. This coarsening of the precipitated phase is related to the decrease in the hardness with aging after 1 h. Preferential precipitation on the grain boundaries was confirmed in the Cu-added alloy (Al–5Mg–3.5Zn–1Cu) (Fig. 8(e)–(h)), and the precipitated phase covered most grain boundaries. Granular precipitates are observed as well as in the base alloy, whereas precipitation free zones were clearly observed near the grain boundaries and coarse compound phases (T phase and η phase) (Fig. 8(h)). Preferential precipitation on the grain boundaries
is similarly observed in the Ni-added alloy (Al–5Mg–3.5Zn–1Ni) (Fig. 8(i), (j)), whereas there is no significant covering of the grain boundaries by the precipitated phase after long-term aging (Fig. 8(k), (l)). The T phase coarsened in the grains of the α-Al matrix after long-term aging treatment, whereas precipitation free zones were not observed. Note that voids (dark contrast) were locally observed in some parts of the Ni-added alloy (Fig. 8(i)–(l)). This tendency was observed regardless of the aging time, and it is believed that the fine T phase or Al3Ni phase would fall off when the sample surface is being polished.

Figure 9 shows the backscattered electron images of the Cu-added and Ni-added alloys after aging treatment at 300°C for 100h, and the elemental distribution diagram by EDS analysis. In the Cu-added alloy, not only the coarse intermetallic phases exist on the grain boundaries (solidified in casting and remained after the solution treatment) but Mg, Zn, and Cu element concentrations were detected on the grain boundaries and precipitation phase (Fig. 9(a)–(d)). The η and T phases were identified by X-ray diffraction (Fig. 7(d)). Therefore, the Cu alloy element partitions into both the η and T phases. In the Ni-added alloy, as shown by the arrow in Fig. 9(e)–(h), two different intermetallic phases were observed. The phase where Mg and Zn elements are concentrated, and one where the Ni element is enriched. Based on the X-ray diffraction results (Fig. 7(f)), the region where Mg and Zn elements are concentrated is the T phase, and the phase where the Ni element is concentrated is the Al3Ni phase. Thus, the Ni alloy element does not partition into the T phase and it independently forms the Al3Ni phase. These results are in good agreement with thermodynamic calculations (Fig. 3(c)).

Figure 10 shows the TEM bright-field image of alloy samples that underwent aging treatment at 300°C for 1 h. In the base alloy (Fig. 10(a)), a fine T phase with a diameter not exceeding 200 nm is uniformly dispersed in the grains of the α-Al matrix. The T phase has a crystallographic relationship of (1-11)α // (1-21)T, [011]α // [111]T with the α-Al matrix. Further, a similar precipitation morphology is observed in the Ni-added alloy (Fig. 10(c)), which corresponds with the phase identification result of the precipitated phase wherein the Ni-added alloy is the T phase (Fig. 7(e), (f)). The precipitated phase observed in the Cu-added alloy (Fig. 10(b)) has a plate-like and spherical morphology with a size of approximately 100 nm. A number of finer ones were observed relative to those of the base alloy. This difference in precipitation morphology would be attributed to the promotion of the η phase precipitation by Cu addition (Fig. 7(c), (d)).

Figure 11 shows the STEM-HAADF image of the Cu-added alloy that underwent aging at 300°C, and the elemental distribution maps obtained via EDS analysis. The precipitated phases with different contrast are observed in the STEM image (Fig. 11(a)). The contrast of the HAADF image depends on the atomic number of the element, with a heavier element exhibiting a higher brightness. Therefore, precipitated phases with high contrast include the high concentrations of the Zn element with a high atomic number. This is confirmed with EDS elemental analysis (Fig. 11(d)). Furthermore, the Al concentration in the precipitated phase
where the Zn element is concentrated is low compared to those of Mg and Cu (Fig. 11(b)). These results indicate that the precipitated phase with a bright contrast is the $\eta$-$\text{Zn}_2\text{Mg}$ phase. The precipitated phase that includes not only the Al element but Mg and Zn elements corresponds to the T-$\text{Al}_6\text{Mg}_{11}\text{Zn}_{11}$ phase. This analysis result is in good agreement with the phase identification result obtained via XRD measurements (Fig. 7(c), (d)). Therefore, the precipitated phases at 300°C are the $\eta$ and T phases. Furthermore, the added Cu element partitions into both the $\eta$ and T phases precipitated in the $\alpha$-Al matrix (Fig. 11(e)). This tendency can be confirmed in the SEM-EDS analysis results (Fig. 9).

Figure 12 shows the STEM-HAADF image of the Ni-added alloy that underwent aging at 300°C, and the elemental distribution maps obtained by the EDS analysis. A relatively coarse precipitated phase where the Ni element concentrated (Fig. 12(a), (c)) is observed at the grain boundaries, and a fine precipitated phase where Mg and Zn are concentrated are distributed at the grain boundaries and in the grain interior (Fig. 12(a), (c), (d), respectively. These phases corresponded with the $\text{Al}_3\text{Ni}$ and T phases, and no Ni element was detected in the $\alpha$-Al phase. Therefore, the $\text{Al}_3\text{Ni}$ phase remaining after the solution treatment was unevenly distributed at the grain boundaries with only the T phase precipitating within the grains. No Ni element was detected inside the T phase (Fig. 12(e)), indicating the Ni element hardly partition into the precipitated T phase.

5. Discussion

We used the ternary base alloy with a composition Al–5Mg–3.5Zn (mol%) designed as a heat-resistant alloy strengthened by the T-$\text{Al}_6\text{Mg}_{11}\text{Zn}_{11}$ phase. Then, we added Cu and Ni as the fourth element (1 mol%) to this base alloy as modified alloys (Fig. 3) to investigate the precipitation behavior of the molten alloy as it underwent the aging
treatment. The added Cu element partitioned into the T phase and the η-ZnMg phase (Fig. 11) precipitated in the α-Al matrix, indicating the promoted precipitation of the η phase by Cu addition. Further, the Ni element was not distributed to the T phase (strengthening phase of the base alloy), this instead formed the Al₃Ni phase (Fig. 9, Fig. 12). The Al₃Ni phase was formed on the grain boundaries and has almost no effect on the precipitation of the T phase within the grains. These experimental results correspond to the predictions from the quaternary equilibrium phase diagram obtained via thermodynamic calculations (Fig. 2, Fig. 3).

The maximum hardness of the Cu-added alloy with aging treatment at 300°C was higher than that of the base alloy (Fig. 6); therefore, the Cu element promotes precipitation (particularly the η phase) in the grain at the start of the aging treatment. However, after maintaining high temperatures for long periods of time, the alloy hardness decreased greatly with the low-strain rate conditions (grain boundary precipitation (strengthening28,29)).

This result is in good agreement with the fact that the Ni element was hardly partitioned into the precipitated phase (Fig. 12). However, the Al₃Ni phase formed on the grain boundaries maintained a relatively fine morphology even after maintaining the temperature for long periods of time (Fig. 8), whereby this is expected to play a role of creep resistance at high-temperature under low-strain rate conditions (grain boundary precipitation strengthening28,29).

This thermodynamic calculation using the existing thermodynamic database suggested that the α-Al phase in the Cu-added alloy would equilibrate with only the η phase at high temperatures ranging from 300°C to 480°C (Fig. 2(a), Fig. 3(b)). Meanwhile, many T-phase precipitates were experimentally confirmed in the Cu-added alloy (Fig. 7(c), (d)). This difference between the calculation and experiment would be attributed to the underestimation of the partition coefficient of the Cu element to the T phase in the Al–Mg–Zn–Cu quaternary thermodynamic database. We prepared a 1% Cu calculated cross-sectional diagram of the Al–Mg–Zn–Cu quaternary system at 300°C to investigate this in detail. The results are shown in Fig. 13. The symbols on the cross-sectional diagram correspond to the alloy composition (Al–5Mg–3.5Zn–1Cu (mol%)). In the current thermodynamic calculation, the alloy composition at the aging treatment temperature (300°C) is positioned in the α-Al/η two-phase region. However, the experimental results indicate the alloy composition could be placed in the α-Al/η/T three-phase region. This suggests that the Gibbs energy of the T phase in the actual Al–Mg–Zn–Cu quaternary system would be lower than the calculated value, which indicates high phase stability of the T-phase. This result is in good agreement with the clear partitioning of the Cu element in the T phase (Fig. 11). The reduced Gibbs energy of the T phase expands the two-phase α-Al/T and three-phase α-Al/T/η regions, resulting in shifting the phase boundary between the two-phase α-Al/T and three-phase α-Al/T/η regions to the Al-rich and Zn-rich sides. These results indicate that the added Cu element partitions into the T phase as the strengthening phase for the heat-resistant alloy, resulting in improved stability of the T phase at high temperatures.

The results as mentioned above suggest that the combined addition of Cu and Ni to the base Al–Mg–Zn ternary alloy (i.e., modification toward quintuple alloy) would increase the stability of the T phase (and η phase) precipitated in the grains and achieve strengthening by the Al₃Ni phase on the grain boundaries in a stable manner. However, a highly reliable thermodynamic database of the quintuple Al–Mg–Zn–Cu–Ni system based on experiments is yet to be reported. The Al₃(Ni,Cu)₄ phase found in the Al–Cu–Ni ternary phase diagram24) is expected to be formed in a quintuple alloy, but the only database that has reproduced the Al₃(Ni,Cu)₂ phase is the Al–Cu–Ni ternary system.30) In the future, it will be essential to experimentally identify the phase equilibrium and construct a quintuple (Al–Mg–Zn–Cu–Ni) thermodynamic database to achieve an improved design to a quintuple alloy with superior high-temperature strength and creep properties.

6. Conclusions

We used a base alloy with a composition of Al–5Mg–3.5Zn (mol%), which was designed as a heat-resistant alloy strengthened by the T-Al₃Mg₃Zn₁₁ phase, and we added the fourth element of Cu and Ni at 1 mol% to design modified alloys. Then, we examined the precipitation behavior of this alloy after the aging treatment at 300°C. We investigated how the addition of the fourth element affected precipitation based on the above results. The findings are shown below.

1. η and T phases were formed on the grain boundaries in the solution-treated Cu-added alloy. These phases preferentially precipitated on the grain boundaries during subsequent aging treatment to cover most grain boundaries. In addition, these phases precipitated finely and uniformly in the grains. Precipitation free zones were formed around the coarsened intermetallic phases formed after the solution treatment. The Cu element...
partitioned into both the T and η phases. The T phase stabilized by the added Cu element differed from the prediction of thermodynamic calculations obtained using an existing database.

(2) The solution treatment generated relatively fine Al$_3$Ni phases on grain boundaries in the Ni-added alloy. The T phase precipitated in the grain interior after the subsequent aging treatment. The Ni element did not partition into the T phase, which was a strengthening phase, and it independently generated the Al$_3$Ni phase. These results were in good agreement with the prediction of thermodynamic calculations that used an existing database.

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