Improved Combination of Strength and Ductility in Zirconium-Added Al-Zn-Mg-Cu Alloy Processed with High-Pressure Torsion

Hiroyuki Kawabata1,*, Ichiro Aoi1, Keiichiro Oh-ishi1, Takenori Nakagaki1, Yoshihiro Shimizu1 and Shigeru Kuramoto2

1Toyota Central R&D Labs., Inc., Nagakute 480-1192, Japan
2Department of Mechanical Engineering, Ibaraki University, Hitachi 316–8511, Japan

To realize high-strength and high-ductility aluminum alloys, an Al-Zn-Mg-Cu-based alloy was produced by high-pressure torsion (HPT) processing. The chromium in the alloy was replaced with zirconium, and the iron content of the alloy was decreased to avoid ductility loss due to iron-containing intermetallic compounds formed during crystallization. The microstructures and mechanical properties of the processed alloy were investigated. The grains were elongated perpendicular to the rotation axis. The elongation of the alloy containing chromium decreased with increasing number of turns. In the case of the alloy in which chromium was replaced with zirconium, the strength increased with increasing number of turns, without reducing the elongation. The alloy exhibited an ultimate tensile strength of 929 MPa and an elongation of 6.4%.

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1. Introduction

To reduce the weight of automobiles, it is necessary to increase the use of aluminum alloys. It is well known that grain refinement is extremely effective for achieving alloys with both high strength and high ductility.1 High-pressure torsion (HPT) is one of the methods of grain refinement. It has been reported that the grains of Al-Zn-Mg-Cu alloys, which are the basic systems of 7xxx series aluminum alloys, processed by HPT were refined to the nanoorder and the strength of the alloys increased to up to 1 GPa.2–5) Thus, HPT processing is effective for increasing the strength and ductility of aluminum alloys.

On the other hand, it has been reported that dynamic recrystallization occurs during HPT processing. Therefore, it is important to suppress the coarsening of recrystallized grains. For example, in the case of 7075 aluminum alloy, chromium is usually added to suppress stress corrosion cracking and grain coarsening during recrystallization.6–8) Zirconium is also effective for suppressing the coarsening of recrystallized grains and is thus added to aluminum alloys.9–11) Many reports have compared the effects of chromium and zirconium.12–15) Zirconium has been recognized to be more effective for the grain refinement and strengthening of aluminum alloys. However, there have been no reports on the effect of zirconium on the HPT processing of aluminum alloys. It is thus worthwhile investigating the effect of zirconium on the microstructure and strength of aluminum alloys fabricated by HPT processing compared that of chromium.

In addition, iron is well known to be an unavoidable impurity in commercial aluminum alloys, and up to 0.5 mass% of iron is allowed in 7075 aluminum alloy.16–18) It is considered that reducing the iron content improves the ductility of aluminum alloys.

In the present study, with the aim of achieving high strength and high ductility aluminum alloys, an Al-Zn-Mg-Cu-based alloy equivalent to a 7xxx series aluminum alloy was produced by HPT processing. Generally speaking, 7xxx series aluminum alloys contain chromium. As mentioned above, it has been well established that zirconium is more effective than chromium for suppressing the recovery and recrystallization during solution treatment and hot deformation processes such as extrusion, rolling, and forging. It is expected that zirconium will have a stronger effect than chromium on grain refinement and increase the strength and ductility of aluminum alloys subjected to HPT processing. In this study, chromium was replaced with zirconium, and the iron content of the alloy was decreased to avoid ductility loss due to iron-containing intermetallic compounds formed during crystallization. The microstructure of the alloy was observed and its mechanical properties were recorded. Finally, the effect of zirconium on the tensile strength and ductility of the alloys was investigated.

2. Experimental

2.1 Samples

Two different Al-8%Zn-2%Mg-2%Cu (mass%)–based alloys were prepared. One of these alloys contained 0.25% chromium (hereafter, “Cr-added alloy”), while the other contained 0.15% zirconium (hereafter, “Zr-added alloy”). To ensure that their strengths exceeded that of 7075 aluminum alloy (Al-5.6%Zn-2.5%Mg-1.6%Cu-0.23%Cr), the zinc content of the two alloys was adjusted to be higher than that of 7075 aluminum alloy. The chemical compositions of the two alloys are shown in Table 1. In addition to the elements listed in Table 1, the two alloys also contained 0.07% iron and 0.04% silicon. The iron content of the two alloys was lower than that of commercial 7075 aluminum alloy.

The two molten alloys were poured into a mold whose cavity thickness was 60 mm. The castings were heat treated at 723 K for 12 h for homogenization. The surface of the castings after homogenization treatment was scraped to a depth of 5 mm on both sides. After scraping, the alloys were heat

*Corresponding author, E-mail: h-kawabuta@mosk.tytlabs.co.jp
treated at 683 K for 1 h, then hot rolling at a reduction rate of 80% was performed at the same high temperature. Upon hot rolling, the thickness of the alloys was reduced to 10 mm. Disk-shaped test pieces, which were 10 mm in diameter and 1 mm in thickness, were machined from the alloys after hot rolling. These test pieces were solution heat treated at 753 K for 5 h in an argon atmosphere with ice water used as the quenchant. The surface of the test pieces was scraped to remove the native oxide layer. The final thickness of the test pieces was 0.92 mm.

These test pieces were subjected to HPT processing. Figure 1 illustrates the HPT setup. The rotational anvil was turned once or 10 times at a speed of 1 rpm under a compressive stress of 2 GPa. The specimens were subjected to considerable distortion during HPT processing.

The test pieces after solution treatment (and before HPT processing) will hereafter be referred to as solution-treated samples, those after HPT processing with one turn as HPT-1turn samples, and those after HPT processing with 10 turns as HPT-10turn samples.

2.2 Evaluation

2.2.1 Microstructures

The microstructures of the solution-treated samples of the two alloys were observed by optical microscopy. The planes observed were the L-ST (longitudinal - short transverse) and LT-ST (long transverse - short transverse) planes, which were parallel and perpendicular to the rolling direction, respectively. The samples were etched with Keller’s reagent for 15 s before observation.

Thin-film specimens were fabricated by ion milling from the solution-treated samples and by the focused ion beam (FIB) technique from HPT-1turn and HPT-10turn samples. All samples were characterized by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The TEM and STEM observations were conducted using a JEM-2100F microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) analysis system. Selected area electron diffraction (SAED) patterns were obtained by TEM and annular dark field (ADF) images were obtained by STEM. Moreover, the elemental distributions of magnesium, zinc, chromium, and zirconium were obtained by EDS analysis.

2.2.2 Tensile testing

Small tensile test pieces were machined from the HPT-1turn and HPT-10turn samples. They had a gage length of 3 mm and a cross section of 1.2 mm width and 0.6 mm thickness. Tensile testing was performed at room temperature under an initial strain rate of \(5 \times 10^{-4} \text{s}^{-1}\). The number of test pieces used for each condition was \(n = 2\). Fracture surfaces of the samples after tensile testing were examined by scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Microstructures before and after HPT processing

3.1.1 Microstructures (grains, secondary phases)

Figure 2 shows the microstructures of solution-treated samples of the Cr-added alloy and Zr-added alloy, as observed by optical microscopy. The grains of both alloys were elongated along the rolling direction rather than being equiaxial. The measured minor axis of the grains in the Cr-added alloy was about 45 \(\mu\text{m}\), and that of the grains in the Zr-added alloy was 56 \(\mu\text{m}\). It is considered that secondary phase inclusions containing chromium or zirconium prevented grain boundary motion, which in turn prevented recrystallization. The measured minor axis of the grains in the Cr-added alloy was about 45 \(\mu\text{m}\), and that of the grains in the Zr-added alloy was 56 \(\mu\text{m}\). It is considered that secondary phase inclusions containing chromium or zirconium prevented grain boundary motion, which in turn prevented recrystallization.

Figure 3 shows TEM and DF-STEM images of the solution-treated samples. The Cr-added alloy exhibited lumpy secondary-phase inclusions with a size of about 50 nm and platelike precipitates dispersed uniformly in the grains (Fig. 3(a)). In the Zr-added alloy, globular inclusions with a size of about 30 nm and platelike precipitates were observed (Fig. 3(b)). The precipitates observed in the Zr-added alloy were finer than those in the Cr-added alloy.

Figure 4 shows TEM images of HPT-1turn and HPT-10turn samples of the two alloys. The grains of the HPT-1turn sample of the Cr-added alloy were elongated perpendicular to the rotation axis (Fig. 4(a)). The major and minor axes of the
As mentioned above, the grains became extremely small and elongated upon HPT processing, regardless of whether the additional element was chromium or zirconium. In addition, there was no difference between the Cr-added alloy and Zr-added alloy in terms of grain orientation.

### 3.1.2 Composition of secondary phases

Figure 5 shows the elemental distribution maps obtained by EDS analysis for solution-treated, HPT-1turn, and HPT-10turn samples of the Cr-added alloy and Zr-added alloy.

#### 3.1.2.1 Cr-added alloy

In the solution-treated samples of the Cr-added alloy, aluminum, magnesium, and chromium were detected in the secondary-phase inclusions with a size of roughly 50 nm. These inclusions are considered to be Al18Mg2Cr3 (the E phase). This phase is known to precipitate during homogenization.7) Magnesium and zinc were detected in the platelike precipitates. Given that the matrix plane observed was the (110) plane, as determined from the diffraction pattern, these precipitates were considered to be dispersed parallel to the {111} plane of the matrix. These results suggest that the precipitates belonged to the MgZn2-family (η, η'). The inclusions observed along the grain boundaries are also considered to be MgZn2.

In the HPT-1turn sample of the Cr-added alloy, lumpy Al18Mg2Cr3 inclusions were observed. These had the same shape and size as those in the solution-treated sample. This suggests that the shape and size of the Al18Mg2Cr3 phase were unchanged by HPT processing. Nanosize inclusions were scattered along the grain boundaries. EDS analysis revealed that these inclusions contained Mg and Zn, suggesting that they were MgZn2-family precipitates formed dynamically during HPT processing. In addition, the platelike precipitates observed in the grains of the solution-treated sample were absent in the HPT-1turn sample. It was concluded that they dissolved during HPT processing.

In the HPT-10turn sample of the Cr-added alloy, lumpy Al18Mg2Cr3 and MgZn2 inclusions were observed at the grain boundaries. Even when the number of turns was increased to 10, the Al18Mg2Cr3 inclusions did not decrease in size. The MgZn2 inclusions on the grain boundaries were formed during HPT processing by dynamic precipitation. However, their size also did not change with the number of turns. It is believed that the formation and dissolution of MgZn2 occur continuously during HPT processing.

#### 3.1.2.2 Zr-added alloy

In the solution-treated sample of the Zr-added alloy, zirconium was detected in spherical particles with a size of about 30 nm. These particles are considered to be Al3Zr. The fine platelike precipitates dispersed uniformly in the grains are presumably MgZn2, as observed in the solution-treated sample of the Cr-added alloy.

In the HPT-1turn sample of the Zr-added alloy, MgZn2 inclusions were scattered along the grain boundaries, rather than in the grains as in the HPT-1turn sample of the Cr-added alloy. The MgZn2 behavior of the HPT-10turn sample was similar to that of the HPT-1turn sample. On the other hand, the spherical Al3Zr particles observed in the solution-treated sample were not observed in the HPT-1turn sample but were observed in the HPT-10turn sample. It is considered that Al3Zr did not dissolve during HPT processing with one turn of the dielectric tensor.
and that it precipitated with increasing number of turns. It was presumably not by chance that Al$_3$Zr particles were seen within the observation area of the HPT-1turn sample.

The above results for the microstructures of the Cr-added alloy and Zr-added alloy before and after HPT processing can be summarized as follows:

(i) The grains were elongated perpendicular to the rotation axis as a result of HPT processing. No preferential orientation was observed.

(ii) In the solution-treated samples, both Al$_{18}$Mg$_2$Cr$_3$ and Al$_3$Zr were observed. The Al$_3$Zr particles were smaller than the Al$_{18}$Mg$_2$Cr$_3$ particles. The size of these inclusions did not change upon HPT processing.

(iii) The $\eta'$ phase, which was observed in the matrix of the solution-treated specimen, dissolved, although the $\eta'$ phase precipitated along the grain boundaries during HPT processing.

3.2 Tensile properties of alloys subjected to HPT processing

Figure 6 shows the relationship between the tensile strength and elongation for the HPT-1turn and HPT-10turn samples. In this figure, two samples were used for each condition. The measured tensile properties were different for each test piece. The tensile test pieces were machined from small (10-mm-diameter) disk-shaped test samples and thus were very small. Therefore, the tensile data were easily affected by the inclusions and cracks introduced irregularly into the test pieces.

Fig. 5  Elemental distribution maps obtained by EDS analysis for specimens before and after HPT processing with ADF image ($N$: number of turns).
during HPT processing. In the following, the larger of the two elongation values is taken as the representative value. In addition, the smaller data are defined as reference data and are displayed with parentheses in Fig. 6. For the HPT-1turn samples, the Cr-added alloy and Zr-added alloy exhibited nearly the same tensile strength and elongation (Fig. 6(a)). As the number of turns was increased to 10, the elongation of the Cr-added alloy decreased sharply (Fig. 6(b)). On the other hand, the elongation of the HPT-10turn sample of the Zr-added alloy was the same as that of the HPT-1turn sample, while the tensile strength increased by about 100 MPa from one turn to 10 turns. Finally, the HPT-10turn sample of the Zr-added alloy exhibited a tensile strength as high as 929 MPa and an elongation to failure of 6.4% (Fig. 6(b)). Liddicoat et al.\textsuperscript{2} recorded an ultimate tensile strength of nearly 1 GPa and an elongation to failure of 6.4% (Fig. 6(b)). Liddicoat et al.\textsuperscript{2} reported a 7075 aluminum alloy with a yield strength of 276 MPa and an elongation to failure of 9%. Liddicoat et al.\textsuperscript{2} reported a 7075 aluminum alloy with a yield strength of 276 MPa and an elongation to failure of 9%. Liddicoat et al.\textsuperscript{2} reported a 7075 aluminum alloy with a yield strength of 276 MPa and an elongation to failure of 9%. Liddicoat et al.\textsuperscript{2} recorded an ultimate tensile strength of 830 MPa and 1% elongation in a 7075 aluminum alloy subjected to HPT processing. The tensile strength and elongation obtained in this study were between the value of Liddicoat et al.\textsuperscript{2} and Horita et al.,\textsuperscript{3} which were obtained in studies on the severe plastic deformation of a 7075 aluminum alloy. Our alloys are also superior to alloys subjected to rapid solidification in terms of the balance between tensile strength and elongation.\textsuperscript{19}

Figure 7 shows fractographs of the tensile test specimens of the HPT-10turn samples of the two alloys. At the lower magnification, the fracture surfaces appear smooth and flat. However, very small dimples are revealed in both alloys at the higher magnification.

We now discuss the structure of the HPT-1turn and HPT-10turn samples. The minor axis of the grains of the specimens before HPT processing was about 50 μm. After HPT processing, the grains were elongated perpendicular to the rotation axis in both the Cr- and Zr-added alloy samples. The minor axis of the grains of the two alloys in the case of the HPT-1turn sample was about 80 nm, while that of the HPT-10turn sample was about 40 nm. As the number of turns was increased from one to 10, the size of the Al\textsubscript{13}Mg\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{3}Zr particles did not decrease.

We next focus on the change in the grain size that occurs from one to 10 turns during HPT processing. According to simple geometry, if an equivalent strain increases tenfold upon uniaxial tensile deformation, the length increases by much more than tenfold and the cross-sectional area decreases by much more than tenfold (the radius or side length decreases by a factor of the square root of more than tenfold).

It is well known that the increase and disappearance of dislocations balance each other by the dynamic recovery and dynamic recrystallization occurring during HPT processing when the equivalent strain exceeds 10 in the case of pure aluminum (99.99%).\textsuperscript{20}

In this study, the equivalent strain after HPT processing with one turn was about 9. Thus, in the HPT-1turn and HPT-10turn samples, the increase and disappearance of dislocations balanced each other, and the grain refinement induced by the increase in strain became less significant. Therefore, the cross-sectional area did not decrease more than tenfold. On the other hand, the minor axis was halved with increasing number of turns (the cross-sectional area decreased by a factor of four). Thus, dynamic recovery and dynamic recrystallization were, to a certain extent, limited. As mentioned above, the η’ phase dispersed along the grain boundaries, and the Al\textsubscript{13}Mg\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{3}Zr phases prevented dislocation motion.

Let us now turn to the sizes of the inclusions and the grains. In both alloys, the sizes of the secondary phase inclusions and grains of the HPT-1turn sample were the same as those of the HPT-10turn sample. However, there was a difference in the balance between the inclusion size and the grain size. In the Zr-added alloy, the Al\textsubscript{3}Zr particles were smaller than the grains in both the HPT-1turn and HPT-10turn samples. On the other hand, in the Cr-added alloy, the Al\textsubscript{13}Mg\textsubscript{2}Cr\textsubscript{3} particles were smaller than the grains in the case of the HPT-1turn sample but larger in the case of the HPT-10turn sample.

As a result of the prevention of dynamic recovery and dynamic recrystallization by Al\textsubscript{13}Mg\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{3}Zr, and the balance between the size of these inclusions and the grain size, the ductility of the Cr-added alloy decreased with increasing number of turns, while that of the Zr-added alloy did not change. A more detailed analysis is necessary to verify the above findings.

4. Conclusion

The microstructure and tensile properties of Al-8%Zn-2%Mg-2%Cu alloys containing chromium or zirconium were investigated. The results obtained can be summarized as fol-
(1) The grains of the HPT-1turn sample of both the Cr-added and Zr-added alloys were elongated perpendicular to the rotation axis. The minor axis was about 80 nm. The minor axis decreased to about 40 nm as the number of turns was increased to 10. No preferential orientation was observed. There was no difference between the Cr-added and Zr-added alloys.

(2) In the Cr-added alloy, after solution heat treatment, lumpy $\text{Al}_{18}\text{Mg}_2\text{Cr}_3$ inclusions with a size of about 50 nm were observed. In the Zr-added alloy, after solution heat treatment, spherical $\text{Al}_2\text{Zr}$ particles with a size of nanoorder were observed. The size of these inclusions did not change upon HPT processing.

(3) The $\eta'$ phase, which was observed in the matrix of the solution-treated specimen, dissolved to precipitate along the grain boundaries after HPT processing.

(4) In the case of the HPT-1turn samples, the Cr- and Zr-added alloys exhibited nearly the same tensile strength and elongation. As the number of turns was increased to 10, the elongation of the Cr-added alloy decreased sharply. In contrast, in the case of the Zr-added alloy, the elongation of the HPT-10turn sample was the same as that of the HPT-1turn sample, and the tensile strength increased by about 100 MPa from one to 10 turns. Finally, the HPT-10turn Zr-added alloy sample had a tensile strength of 929 MPa and an elongation to failure of 6.4%. As a result of the prevention of dynamic recovery and dynamic recrystallization by $\text{Al}_{18}\text{Mg}_2\text{Cr}_3$ and $\text{Al}_2\text{Zr}$, and the balance between the size of these inclusions and the grain size, the ductility of the Cr-added alloy decreased with increasing number of turns, while that of the Zr-added alloy did not change.

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