Mechanical Properties of Mg–Al–Ca Alloy Recycled by Solid–State Recycling

Yasumasa Chino¹, Lee Jae-Seol¹, Yusuke Nakaura², Koichi Ohori² and Mamoru Mabuchi³

¹Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology, Nagoya 463-8560, Japan

²Technical Development & Administration Department, Mitsubishi Aluminum Co., Susono 410-1127, Japan

³Department of Energy Science & Technology, Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan

Solid-state recycling for runner scraps of Mg–Al–Ca alloy was carried out by extrusion at 673 K and mechanical properties of the recycled Mg alloy were investigated by tensile tests. At room temperature, the recycled specimen showed a good combination of high ultimate tensile strength (348 MPa), high 0.2% proof stress (305 MPa) and large elongation (9%). Additionally, the recycled specimen exhibited superplastic behavior at 573 and 673 K. The excellent mechanical properties of the recycled specimen result most likely from fine dispersion of precipitates which is attained by hot extrusion.

(Received May 6, 2005; Accepted June 14, 2005; Published December 15, 2005)

Keywords: magnesium alloy, solid–state recycling, hot extrusion, mechanical properties, superplasticity

1. Introduction

Mg alloys are currently the lightest alloys used as structural metals and Mg products have been applied for structural uses such as automobile parts and electric appliance cases.^{1,2)} In order to obtain further demands of Mg alloys, it is necessary not only to attain good characteristics (high strength, high corrosion resistance, etc.), but also to develop useful recycling processes. To date, some recycling processes such as remelting^{3,4)} have been proposed and applied.

Recently, “solid–state recycling”, in which metal scraps are recycled by hot extrusion and so on without remelting, has been proposed as a new recycling method for Mg alloy scraps.^{5–11)} In the previous researches, machined chips of commercial Mg alloy such as AZ91⁵⁾ and AZ31^{9,10)} were recycled by hot extrusion. The recycled Mg alloys showed high strength because grain refinement was attained by hot extrusion.⁵⁾ Thus, mechanical properties can be improved due to microstructural control for the solid–state recycling.

An aim of this study is to investigate mechanical properties of Mg–Al–Ca alloy recycled by the solid–state recycling method. It is known that Al₂Ca is precipitated in Mg–Al–Ca alloy.^{12,13)} Hence, improvement of mechanical properties may be attained due to not only grain refinement, but also fine dispersion of the precipitates in Mg–Al–Ca alloy recycled by the solid–state recycling method.

2. Experimental Procedure

Runner scraps of a Mg–Al–Ca alloy with 5 mass%Al, 1.8 mass%Ca, 0.5 mass%Mn and 0.2 mass%Sr¹⁴⁾ were used as as-received scraps, as shown in Fig. 1(a). Microstructure of the as-received scraps are shown in Fig. 1(b). Equiaxed grains with 7.0 μm in grain size were observed, and the grains were covered with precipitates which corresponded to Al₂Ca and Al₂Sr as a result of XRD analysis. The scraps, which were cut into three equal parts and degreased by using acetone, were recycled into an extrusion with 6 mm in diameter by directly extruding the scraps under the condition of 673 K with an extrusion ratio of 45 : 1 in air.

Tensile specimens with 5 mm in gage length and 2.5 mm in gage diameter were machined from the recycled extrusion and the as-received scraps. Tensile tests were carried out at room temperature to 673 K with an initial strain rate of 5×10^{-4} to $5 \times 10^{-2} \text{ s}^{-1}$.

Microstructures of the specimens were observed by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Oxygen concentration in the specimens was measured by Glow Discharge Mass Spectrometry (GDMS), and concentrations of the other contaminations were detected by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

3. Results and Discussion

Figure 2(a) shows microstructure in the horizontal section to an extrusion direction of the recycled specimen observed by OM. It is found that the precipitations were dispersed parallel to the extrusion direction in the as-received specimen. The grain size of the recycle specimen was 4.7 μm. This value is smaller than that of the as-received specimen, indicating that the grains were refined by dynamic recrystallization¹⁵⁾ during hot extrusion. Observation of TEM revealed that fine precipitates with sub-micronmeter size were located at grain boundaries, as shown in Fig. 2(b). It is suggested that the fine precipitates suppress grain growth during hot extrusion.

Table 1 shows the concentration of contaminants in the Mg–Al–Ca alloy specimens. The concentrations of detrimental elements for corrosion properties such as Fe, Cu and Ni were almost the same as those of the as-received specimen. On the other hand, the oxygen concentration of the recycled specimen was higher than that of the as-received specimen. The increase in oxygen level is due to oxide layers on the scraps.¹⁰⁾ However, the oxygen concentration in the specimen made of the runner scraps in the present research was much smaller than that in the specimen made of machined chips (=0.3 mass%) in the previous work,¹⁰⁾ because a total surface area of runner scraps was much smaller than that of machined chips.

Fig. 1 Photographs of an as-received Mg–Al–Ca alloy runner scrap (a) and its microstructure (b).

Fig. 2 Micrographs of a recycled Mg–Al–Ca alloy specimen at the extrusion temperature of 673 K and at the extrusion ratio of 45, (a) OM micrograph, (b) TEM micrograph.

Table 1 Concentration of contaminants in Mg–Al–Ca alloy specimens.

	Unit: mass%				
	Fe	Cu	Ni	Si	O
Solid recycled specimen	0.0052	0.0005	0.0003	0.011	0.047
As-received specimen	0.0046	0.0005	0.0003	0.0091	0.011

Table 2 Tensile properties at room temperature and grain size of Mg–Al–Ca alloys.

Alloy	Ultimate tensile strength (MPa)	0.2% Proof stress (MPa)	Elongation to failure (%)	Grain size (μm)
Solid recycled specimen	348	305	9.0	4.7
As-received specimen	207	166	4.1	7.0

Table 2 shows tensile properties at room temperature of the recycled specimens and the as-received specimens. The recycled specimens showed a good combination of high ultimate tensile strength, high 0.2% proof stress and high elongation to failure. It should be noted that the mechanical properties of the recycled specimen were superior to those of the as-received specimen.

A large difference of about 140 MPa in strength between the recycled specimen and the as-received specimen cannot

be explained only by grain refinement from 7.0 to 4.7 μm. The previous work,¹⁶⁾ which described mechanical properties of the extruded Mg alloy containing dispersed Mg₂Si particles, showed that high strength was attained by some strengthening mechanisms such as Orowan strengthening and dislocation generation strengthening due to a difference in thermal expansion between a matrix and a particle. In the present work, fine particles with sub-micronmeter size were precipitated, as shown in Fig. 2(b). Therefore, an increase in

strength for the recycled specimen is likely to be attributed to not only grain refinement, but also the fine precipitates. Besides, the texture effects may contribute to strengthening in the recycled specimen because it is well known that a texture change strongly affects 0.2% yield stress of extruded Mg alloy specimens.¹⁷⁾

Variations in stress and elongation at 573 and 673 K as a function of strain rate for the recycled specimens and the as-received specimens are shown in Fig. 3. It should be noted that the recycled specimens showed larger elongation,

Fig. 3 Variation in stress (top figure) and elongation (bottom figure) as a function of strain rate for Mg–Al–Ca alloy specimens.

compared with the as-received specimen. In particular, large elongation of 359% was obtained at 673 K and at $5 \times 10^{-4} \text{ s}^{-1}$ in the recycled specimen. Also, the recycled specimen exhibited a high strain rate sensitivity of 0.5 at a low strain rate range of 5×10^{-4} – $5 \times 10^{-3} \text{ s}^{-1}$ at 573 and 673 K [Fig. 3]. Thus, the recycled specimen exhibited superplastic behavior. However, the as-received specimens did not show superplastic behavior.

Figure 4 shows the side surfaces of the recycled specimen and the as-received specimen deformed to fracture at $5 \times 10^{-3} \text{ s}^{-1}$ and at 673 K. A bumpy surface was observed for the recycled specimen, indicating that grain boundary sliding occurred. However, no evidence for grain boundary sliding was found for the as-received specimen.

Tensile specimens deformed to fracture at $5 \times 10^{-3} \text{ s}^{-1}$ and at 673 K are shown in Fig. 5. The recycled specimen showed diffusional necking, not premature fracture. However, the as-received specimen exhibited premature fracture.

The above experimental results showed the deformation and fracture mechanisms at elevated temperature for the recycled specimen were different from those for the as-received specimen, though the difference in grain size was minor between the recycled specimen and the as-received specimen. It is of interest to note that the precipitates covered grains in the as-received specimen, however, the network of precipitates was destructed by hot extrusion and fine precipitates was dispersed in the recycled specimen. The fractured surface of the as-received specimen deformed to fracture at $5 \times 10^{-3} \text{ s}^{-1}$ and at 673 K is shown in Fig. 6. The un-deformed grains were observed in a part of the fracture

Fig. 5 The specimens deformed to fracture at $5.0 \times 10^{-3} \text{ s}^{-1}$ and 673 K, (a) recycled specimen, (b) as-received specimen.

Fig. 4 The side surfaces of Mg–Al–Ca alloy specimens deformed to fracture at $5.0 \times 10^{-3} \text{ s}^{-1}$ and at 673 K, (a) recycled specimen, (b) as-received specimen.

Fig. 6 The fractured surfaces of the as-received specimen deformed to failure at $5.0 \times 10^{-3} \text{ s}^{-1}$ and 673 K.

surface. Figure 6 might suggest that the network of precipitates at grain boundaries suppresses grain boundary sliding and enhances crack formation. The crack formation at grain boundaries might lead to premature fracture in the as-received specimen. Therefore, it is likely that superplastic behavior was not obtained and the premature fracture occurred due to the network of precipitates in the as-received specimen, however, because the network of precipitates was destructed by hot extrusion, the recycled specimen showed superplastic behavior.

4. Conclusions

Mechanical properties of Mg–Al–Ca alloy recycled by the solid–state recycling have been investigated. The results are summarized as follows.

- (1) As a result of tensile tests at room temperature, the recycled specimens showed a good combination of high ultimate tensile strength, high 0.2% proof stress and high elongation to failure. The mechanical properties of the recycled specimen were superior to those of the as-received specimen.

- (2) As a result of tensile tests at 573 and 673 K, the recycled specimens showed larger elongation and high strain rate sensitivity, compared with the as-received specimen. In particular, large elongation of 359% was obtained at 673 K and at $5 \times 10^{-4} \text{ s}^{-1}$ in the recycled specimen. Thus, the recycled specimen exhibited superplastic behavior. However, the as-received specimens did not show superplastic behavior.
- (3) Precipitates covered grains in the as-received specimen, however, the network of precipitates was destructed by hot extrusion and fine precipitates was dispersed in the recycled specimen. The excellent mechanical properties of the recycled specimen are likely to result from fine dispersion of precipitates which is attained by hot extrusion.

REFERENCES

- 1) T. Ebert and B. L. Mordike: *Mater. Sci. Eng. A* **302** (2001) 37–45.
- 2) Y. Nishikawa and A. Takara: *Mater. Sci. Forum* **426–432** (2003) 569–574.
- 3) M. Inoue, M. Iwai, S. Kamado, Y. Kojima, T. Itoh and M. Sudama: *J. Jpn. Inst. Light Met.* **49** (1999) 277–281.
- 4) T. Itoh: *KINZOKU* **71** (2001) 554–560.
- 5) M. Mabuchi, K. Kubota and K. Higashi: *Mater. Trans., JIM* **36** (1995) 1249–1254.
- 6) Y. Chino, K. Kishihara, K. Shimojima, Y. Yamada, C. E. Wen, H. Iwasaki and M. Mabuchi: *J. Jpn. Inst. Met.* **65** (2001) 621–626.
- 7) H. Watanabe, K. Moriwaki, T. Mukai, K. Ishikawa, M. Kohzu and K. Higashi: *J. Mater. Sci.* **36** (2001) 5007–5011.
- 8) K. Kondoh, T. Luangvaranunt and T. Aizawa: *J. Jpn. Inst. Light Met.* **51** (2001) 516–520.
- 9) Y. Chino, K. Kishihara, K. Shimojima, H. Hosokawa, Y. Yamada, C. E. Wen, H. Iwasaki and M. Mabuchi: *Mater. Trans.* **43** (2002) 2437–2442.
- 10) Y. Chino, M. Kobata, K. Shimojima, H. Hosokawa, Y. Yamada, H. Iwasaki and M. Mabuchi: *Mater. Trans.* **45** (2004) 361–364.
- 11) T. Aida, N. Takatsuji, K. Matsuki, S. Kamado and Y. Kojima: *J. Jpn. Inst. Light Met.* **54** (2004) 532–537.
- 12) R. Ninomiya, T. Ojio and K. Kubota: *Acta Mater.* **43** (1995) 669–674.
- 13) M. O. Pekguleryuz and E. Baril: *Mater. Trans.* **42** (2001) 1258–1267.
- 14) K. Ohori and Y. Nakaura: *ALUTOPIA* **31** (No. 11) (2001) 9–16.
- 15) T. Mohri, M. Mabuchi, M. Nakamura, T. Asahina, H. Iwasaki, T. Aizawa and K. Higashi: *Mater. Sci. Eng. A* **290** (2000) 139–144.
- 16) M. Mabuchi and K. Higashi: *Acta Mater.* **44** (1996) 4611–4618.
- 17) D. V. Wilson and J. A. Chapman: *Philos. Mag.* **8** (1963) 1543–1551.