Solid Recycling of an AZ31 Mg Alloy with a Vapor Deposition Coating Layer of High Purity Mg

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Solid recycling of AZ31 Mg alloy with vapor deposition coating layer of high purity Mg was evaluated. In the open die forging experiments, two AZ31 Mg alloy specimens with the pure Mg deposition coating layer of the 30 μm in thickness were forged. The specimens were sufficiently bonded by forging at 673 K. Furthermore, the elements (Al and Zn) of the AZ31 substrate diffused up to the center of the pure Mg deposition coating layer. The theoretical analysis in which only the lattice diffusion was considered showed that the elements in the AZ31 substrate cannot diffuse to the center of the pure Mg deposition coating layer. The grain boundary diffusion coefficient of Mg at 673 K is about 25 times larger than the lattice diffusion coefficient. Therefore, it is suggested that the grain boundary diffusion enhanced by grain refinement due to hot forging largely contributes to the solid state bonding of the forged specimens. Also, the solid recycled specimen was fabricated from the AZ31 Mg substrate with pure Mg deposition coating layer by hot extrusion at 673 K. The solid recycled specimen showed almost the same tensile properties as the virgin extruded specimen. This is probably related not only to the grain boundary diffusion enhanced due to grain refinement, but also severe plastic deformation by hot extrusion.

(Received October 18, 2002; Accepted January 20, 2003)

Keywords: magnesium alloy, deposition coating, solid recycling process, hot extrusion, grain refinement, grain boundary diffusion

1. Introduction

Mg alloys are currently the lightest alloys used as structural metals and some 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 ductility, high corrosion resistance, creep resistance and so on), but also to develop useful recycling processes.³⁾ Some recycling processes for Mg alloys, for example, remelting,^{4,5)} electrorefining in molten salt⁶⁾ and vacuum distillation,⁷⁾ have been proposed. The “in-house scraps” have been recycled by the remelting processes.^{4,5)} However, when the scraps coated with nickel, copper and so on are recycled, contamination of nickel, copper and iron causes a significant increase in corrosion rate in recycled Mg products.^{4,8)} Therefore, it is important to avoid the contamination for recycling of Mg alloys.

Recently, the “solid recycling” process has been proposed as a new recycling method for metal scraps.^{9–11)} In the process, metal scraps are recycled by hot consolidation using hot working such as hot extrusion. It should be noted that remelting is not required in the solid recycling process. Furthermore, the solid recycled Mg alloy shows high strength due to grain refinement and homogeneous dispersion of the oxide film on the surface of scraps.⁹⁾ However, for the solid recycling as well as the above recycling processes, application of the recycling process to Mg scraps is limited to the clean scraps such as “in-house scraps”. When the surface treated Mg scraps are recycled by solid recycling process, complicated pretreatments such as elaborate scrubbing are needed for elimination of the surface coating.

Recently, Yamamoto *et al.*^{12,13)} developed a new method for surface treatment of Mg alloys by deposition coating of

high purity Mg which shows high corrosion resistance.¹⁴⁾ Mg products with the Mg deposition coating will show high recycling ability because of no contamination.

In the present study, the conditions for solid recycling of AZ31 Mg products with the pure Mg deposition coating layer are investigated from the viewpoint of diffusion of the elements of AZ31 to the pure Mg deposition coating layer. In addition, mechanical properties of the solid recycled specimens are evaluated by tensile tests.

2. Experimental Procedure

An AZ31 (Mg–3 mass%Al–1 mass%Zn–0.15 mass%Mn) Mg alloy specimen with the dimension of 10 mm $\times$ 10 mm $\times$ 6 mm was used as a substrate plate. Also, pure Mg with three nine purity was used as an evaporation source. A horizontal vacuum furnace which had two heating zones was used for deposition of pure Mg. Pure Mg was heated at about 973 K in the higher temperature zone, while the substrate plate was held at about 623 K in the lower temperature zone. Evaporation and deposition coating were carried out on the substrate plate for 7.2 ks under about 1×10^{-3} Pa in vacuum. Then, the deposition coated specimen was turned over and the evaporation and the deposition coating were carried out again to homogenize the thickness of the deposition coating. The cross section of the deposition coated specimen is shown in Fig. 1. The average thickness of the coating was 30 μm .

Open die forging tests were carried out to investigate diffusion to the pure Mg deposition coating layer. The deposition coated specimen was put on the other and the two specimens with a total thickness of 12 mm was forged to a total thickness of 5 mm at a cross head speed of 1.2×10^{-2} mm/s, that is, the draft was set to be 0.6 and the forging time was set to be 600 s. The forging temperature was

Fig. 1 The cross section of the deposition coated AZ31 Mg alloy specimen.

set to be 503 K and 673 K because the machined chips of AZ31 Mg alloy could be consolidated by hot extrusion at more than 503 K in the previous work.¹¹⁾

Distributions of Mg, Al and Zn concentration at the interface of the forged two specimens were investigated by EPMA analysis. At the analysis, the line profiles perpendicular to the bonded interface of the forged specimen were measured.

Furthermore, hot extrusion of the deposition coated specimens was carried out. The deposited specimens were filled into a container with a diameter of 40 mm and then extruded at 673 K with an extrusion ratio of 5 : 1 in air. A cross head speed of ram was set to be 10^{-2} mm/s. For comparison, extrusions were processed from the AZ31 substrate plates without deposition coating under the same extrusion conditions. In the present study, extrusions from the deposition coated specimens are called the solid recycled specimens and those from substrate plates without deposition coating are called the virgin extruded specimens.

Tensile tests at room temperature were carried out at a strain rate of $1.7 \times 10^{-3} \text{ s}^{-1}$. The tested specimens had a gauge length of 10 mm and a gauge diameter of 2.5 mm. The tensile axis was parallel to the extrusion direction. A metallographic investigation was carried out by optical and scanning electron microscopies. The grain size of the specimens was measured by optical microscopy using the linear intercept method.

3. Results and Discussion

3.1 Solid recycling by open die forging

Figure 2 shows the distributions of Mg, Al and Zn concentration at the interface of the two specimens forged at 503 K. The deposition coating layer, whose initial thickness was about 60 μm, was compressed to about 30 μm by the open die forging. At the center of the deposition coating layer, the concentration of Mg suddenly decreased. This indicates that the bonding between the specimens forged at 503 K is not sufficient. Besides, an abrupt increase in Mg concentration and a decrease in Al and Zn concentrations were observed at the interface between the deposition coating layer and the AZ31 substrate. Clearly, the elements of Al and Zn in AZ31 scarcely diffused into the deposition coating

Fig. 2 Distributions of Mg, Al and Zn concentration at the interface of AZ31 Mg alloy with Mg deposition coating layer forged at 503 K (a) and schematic view of the open die forging test (b).

Fig. 3 Distributions of Mg, Al and Zn concentration at the interface of AZ31 Mg alloy with Mg deposition coating layer forged at 673 K.

layer of pure Mg in the case of forging at 503 K.

Distributions of Mg, Al and Zn concentration at the interface of the two specimens forged at 673 K are shown in Fig. 3, respectively. The thickness of the deposition coating layer was compressed to about 30 μm by forging. It can be seen that the elements of Al and Zn in AZ31 diffused into the deposition coating layer of pure Mg by forging at 673 K, although the concentration gradient of Al was observed, suggesting that the bonding between the specimens forged at 673 K is relatively sufficient.

Fukumoto *et al.*¹⁵⁾ proposed the utilization of hot pressing method for improvement of bonding between high purity Mg deposition coating layer and Mg alloy. They estimated the concentration distribution of Mg between the deposition coating layer and the substrate from one-dimensional self-diffusion in two semi-infinite slabs¹⁶⁾ given by

$$C = C_0 + \frac{C_1 - C_0}{2} \left[1 + \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (1)$$

where C is the concentration of each element in the pure Mg layer, C_0 is the initial concentration of each element in the substrate, C_1 is the initial concentration in the deposition coating layer and D is the diffusion coefficient of each element. In order to understand the concentration gradient

Fig. 4 Calculated distributions of Mg, Al and Zn concentration at the interface of AZ31 Mg alloy with Mg deposition coating layer at 673 K; (a) Mg, (b) Al, (c) Zn.

shown in Fig. 3, distributions of Mg, Al and Zn concentration in the deposition coating layer were estimated using the eq. (1), in which diffusions of Al and Zn in Mg and Mg in Mg (self-lattice diffusion) were evaluated. Figure 4 shows the calculated concentration distributions of each element in the pure Mg deposition coating layer at 673 K after 600 s, where the diffusion coefficients of Al and Zn in Mg at 673 K are $3.01 \times 10^{-15} \text{ m}^2/\text{s}$ and $1.96 \times 10^{-14} \text{ m}^2/\text{s}$, respectively¹⁷⁾ and the self-diffusion coefficient in Mg at 673 K is $3.28 \times 10^{-15} \text{ m}^2/\text{s}$.¹⁸⁾ Concerning to Mg and Al, the concentration gradient distributes within only 5 μm from the interface. This indicates that the lattice diffusion is not a dominant factor which affects the concentration distribution in the deposition coating layer during open die forging at 673 K.

It is well known that for wrought alloys with high dislocation density, the dislocation core diffusion accelerates solid state bonding.¹⁹⁾ Besides, the grain boundary diffusion accelerates solid state bonding, in particular, for fine-grained metals.²⁰⁾ Hence, the dominant diffusion process of solid state bonding in the solid recycling may be the dislocation core diffusion or the grain boundary diffusion. The contribution of each diffusion process may be estimated using the effective diffusion concept. When both the lattice diffusion and the dislocation core diffusion of Mg are considered, the effective diffusion coefficient may be given by

$$D_{\text{eff(c)}} = D_0 \exp(-Q_v/RT) + a\rho D_{\text{co}} \exp(-Q_c/RT) \quad (2)$$

Fig. 5 The variation in calculated diffusion coefficients of magnesium at 673 K as a function of dislocation density.

where $D_{\text{eff(c)}}$ is the effective diffusion coefficient concerning to the lattice diffusion and the dislocation core diffusion, D_0 is the pre-exponential of the lattice diffusion coefficient ($= 1.8 \times 10^{-4} \text{ m}^2/\text{s}$), Q_v is the activation energy of the lattice diffusion ($= 135 \text{ kJ/mol}$), a is the cross sectional area of the dislocation core, ρ is the dislocation density, D_{co} is the pre-exponential of the dislocation core diffusion coefficient ($aD_{\text{co}} = 3 \times 10^{-23} \text{ m}^4/\text{s}$), Q_c is the activation energy of the dislocation core diffusion ($= 92 \text{ kJ/mol}$) and R is a gas constant ($= 8.314 \text{ J/molK}$).^{18,19)} Figure 5 shows the variation in diffusion coefficients of Mg at 673 K as a function of dislocation density. In general, the dislocation density of wrought metals is from 10^{12} to $10^{15}/\text{m}^2$.²¹⁾ Inspection of Fig. 5 shows that the dislocation core diffusion is not effective even at the high dislocation density of 10^{15} m^{-2} .

On the other hand, the effective diffusion coefficient concerning to the lattice diffusion and the grain boundary diffusion of Mg may be given by

$$D_{\text{eff(b)}} = D_0 \exp(-Q_v/RT) + (\pi\delta/d)D_{\text{bo}} \exp(-Q_b/RT) \quad (3)$$

where $D_{\text{eff(b)}}$ is the effective diffusion coefficient concerning to the lattice diffusion and the grain boundary diffusion, δ is the effective thickness of the boundary, d is the grain size, D_{bo} is the pre-exponential of the grain boundary diffusion coefficient ($\delta D_{\text{bo}} = 5 \times 10^{-12} \text{ m}^3/\text{s}$) and Q_b is the activation energy of the grain boundary diffusion ($= 92 \text{ kJ/mol}$).^{18,19)} Figure 6 shows the variation in calculated diffusion coefficients of Mg at 673 K as a function of grain size. It should be noted that the grain boundary diffusion is dominant when the grain size is less than 300 μm . The grain size of the specimens forged at 673 K was 14 μm , which was almost the same as that of the solid recycled specimen shown in Fig. 8. The grain boundary diffusion coefficient at the grain size of 14 μm is $8.2 \times 10^{-14} \text{ m}^2/\text{s}$. This value is about 25 times larger than the

Fig. 6 The variation in calculated diffusion coefficients of magnesium at 673 K as a function of grain size.

Fig. 7 Microstructure of the pre-extruded AZ31 Mg specimen.

Table 1 Tensile properties at room temperature and the grain size of the solid recycled AZ31 Mg alloy and the virgin extruded AZ31 Mg alloy.

Alloy	Ultimate tensile strength (MPa)	0.2% Proof stress (MPa)	Elongation to failure (%)	Grain size (μm)
Solid recycled Mg alloy	268	195	14	13.5
Virgin extruded Mg alloy	279	203	18	12.4

Fig. 8 Microstructures of AZ31 Mg alloy for the solid recycled specimen (a) and the virgin extruded specimen (b).

lattice diffusion coefficient of Mg at 673 K. Therefore, it is suggested that the grain boundary diffusion largely contributes to the solid state bonding of the forged specimens and to the concentration distributions in the pure Mg deposition coating layer. The previous works^{9,22)} showed that a small grain size can be attained by hot working without any additional treatments for Mg alloy. It is noted that grain refinement due to hot deformation plays an important role in the solid recycling process because the grain boundary diffusion contributing to the solid state bonding is enhanced by grain refinement.

3.2 Solid recycling by extrusion

Solid recycling using hot extrusion was carried out on the AZ31 alloy with Mg deposition coating layer, where the extrusion temperature was 673 K and the ram speed was 10^{-2} mm/s. Microstructure of the AZ31 prior to the solid recycling process is shown in Fig. 7. The grain size was 37 μm.

Microstructures of the solid recycled specimen (b) and the virgin extruded specimen (b) are shown in Fig. 8, respectively. A small grain size of about 13 μm was obtained for

both the solid recycled specimen and the virgin extruded specimen. The grain size is almost the same as that of the specimen forged at 673 K.

Mechanical properties of the solid recycled specimen and the virgin extruded specimen by tensile tests are summarized in Table 1, respectively. The solid recycled specimen exhibited the ultimate tensile strength of 268 MPa, 0.2% proof stress of 195 MPa and elongation to failure of 14%, and the virgin extruded specimen showed the ultimate tensile strength of 279 MPa, 0.2% proof stress of 203 MPa and elongation to failure of 18%. Thus, the solid recycled specimen showed almost the same tensile properties as the virgin extruded specimen. This is probably related not only to the grain boundary diffusion enhanced due to grain refinement, but also plastic deformation by hot extrusion because severe plastic deformation is given by hot extrusion, compared to the forging. To quantitatively understand effects of plastic deformation on the solid state bonding in solid recycling process, further research is needed. Anyway, it is conclusively demonstrated that AZ31 Mg alloy scraps with pure Mg deposition coating layer can be recycled by hot extrusion at 673 K.

4. Conclusions

Solid recycling of AZ31 Mg alloy with vapor deposition coating layer of high purity Mg was conducted by hot forging and extrusion. The results are summarized as follows.

- (1) The specimens with the pure Mg deposition coating layer of 30 μm thickness were bonded by open die forging at 673 K. Elements of Al and Zn in AZ31 diffused to the center of the Mg deposition coating layer.
- (2) The theoretical analysis showed that the grain boundary diffusion coefficient at 673 K is about 25 times larger than the lattice diffusion coefficient for Mg. It is therefore suggested that the grain boundary diffusion largely contributes to the solid state bonding of the forged specimens and the concentration distributions in the pure Mg deposition coating layer.
- (3) When the solid recycling process using hot extrusion at 673 K was carried out, the recycled specimen showed almost the same tensile properties as the virgin extruded specimen.

Acknowledgements

H.T. and M.M. gratefully acknowledge Grant-in-Aid for Scientific Research on Priority Areas (B) of “The priority Group of Platform Science and Technology for Advanced Magnesium Alloys”, Ministry of Education, Culture, Sports, Science and Technology in Japan. Also, Y.C. gratefully acknowledges the financial support by Industrial Technology Research Grant Program in 2002 from the New Energy and Industrial Technology Development Organization (NEDO) in Japan.

REFERENCES

- 1) E. Aghion and B. Bronfin: *Mater. Sci. Forum* **350–351** (2000) 19–28.
- 2) B. Landkof: *Proc. Magnesium Alloys and Their Applications*, ed. by K. U. Kainer, (WILEY-VCH Verlag GmbH, Weinheim, 2000) pp. 168–172.
- 3) O. Tsukamoto: *ALUTOPIA* **32** (No. 4) (2002) 16–21.
- 4) J. F. King, A. Hopkins and S. Thistlethwaite: *Proc. the Third Int. Magnesium Conf.*, ed. by G. W. Lorimer, (The University Press Cambridge, UK, 1997) pp. 51–61.
- 5) E. Sato: *SOKEIZAI* **40** (No. 10) (1999) 1–9.
- 6) T. Takenaka, T. Fujita, S. Isazawa and M. Kawakami: *Mater. Trans.* **42** (2001) 1249–1253.
- 7) Y. Tamura, T. Haitani, N. Kono, T. Motegi and E. Sato: *J. JILM* **48** (1998) 237–241.
- 8) H. Tateishi, M. Inoue, S. Kamado, Y. Kojima, T. Itoh and M. Sugama: *J. JILM* **48** (1998) 19–24.
- 9) M. Mabuchi, K. Kubota and K. Higashi: *Mater. Trans., JIM* **36** (1995) 1249–1254.
- 10) Y. Chino, K. Kishihara, K. Shimojima, Y. Yamada, Cui’e Wen, H. Iwasaki and M. Mabuchi: *J. Japan Inst. Metals* **65** (2001) 621–626.
- 11) Y. Chino, K. Kishihara, K. Shimojima, H. Hosokawa, Y. Yamada, Cui’e Wen, H. Iwasaki and M. Mabuchi: *Mater. Trans.* **43** (2002) 2437–2442.
- 12) A. Yamamoto, A. Watanabe, K. Sugahara, H. Tsubakino and S. Fukumoto: *Scr. Mater.* **44** (2000) 1039–1042.
- 13) A. Yamamoto, A. Watanabe, K. Sugahara, S. Fukumoto and H. Tsubakino: *Mater. Trans.* **42** (2001) 1237–1242.
- 14) M. Inoue, M. Iwai, K. Matuzawa, S. Kamado and Y. Kojima: *J. JILM* **48** (1998) 257–262.
- 15) S. Fukumoto, M. Tsukamoto, A. Yamamoto and H. Tsubakino: *Collected Abstracts of the 2002 Spring Meeting of the Japan Inst. Metals* (2002) p. 69.
- 16) P. Shewmon: *Diffusion in Solid*, (The Minerals, Metals & Materials Society, Pennsylvania, 1989), p. 9.
- 17) Japan magnesium association ed.: *Handbook of Advanced Magnesium Technology*, (Kallos Publishing Co., Ltd., Tokyo, 2000) pp. 131–136.
- 18) H. J. Frost and M. F. Ashby: *Deformation-Mechanism Maps*, (Pargamon Press, Oxford, 1982) p. 44.
- 19) H. J. Frost and M. F. Ashby: *Deformation-Mechanism Maps*, (Pargamon Press, Oxford, 1982) pp. 6–16.
- 20) J. Pilling and N. Ridley: *Superplasticity in Crystalline Solids*, (The Institute of Metals, London, 1989), p. 175.
- 21) C. Kittel: *Introduction to Solid State Physics*, 7th ed., (Wiley, New York, 1996), p. 585.
- 22) T. Mohri, M. Mabuchi, H. Iwasaki, T. Aizawa and K. Higashi: *Mater. Sci. Eng.* **A290** (2000) 139–144.