Hydrogenation Properties of Partially Remelted Mg–Ni Alloys

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Thixotropic Mg alloys have been focused only on the aspect of semi liquid forming until now. In the present study, with the aim of improving hydrogen storage capacity, we kept an eye on the microstructural evolutions and chemical properties of thixotropic microstructure in Mg-(3, 6, 9, 12 mass%) Ni alloys by using a partial remelting process. According to the results of pressure-composition-isotherm (PCT) measurements and image analysis, Mg rich solid phases were regarded as the hydrogen absorbing phases and eutectic regions (quenched liquid phase) were considered as the catalyst to improve hydrogenation kinetics. Especially, the hydrogenation properties depended on the properties of globules and liquid fractions.

(Received March 14, 2002; Accepted May 22, 2002)

Keywords: thixotropic, magnesium alloys, hydrogen absorbing phases, hydrogenation, catalyst

1. Introduction

In the early 1970s, it was discovered that by stirring an alloy during solidification, the dendrite structure was disintegrated, allowing the metal to flow like a liquid containing up to 60% non-dendritic solid particles.1) The metal showed thixotropic behavior meaning that the viscosity is shear and time dependent. On the basis of this phenomenon, the fluid like behavior of thixotropic metals has resulted in several suggestions for new casting processes or modifications of conventional methods like die-casting. Thixotropic microstructure, which is very different from that obtained during conventional solidification, can be produced either during solidification or partial remelting of the material after prior solidification. A shearing action (mainly by mechanical or electromagnetic stirring) during solidification of alloys destroyed the forming dendrites thus leading to globules of the primary solid phase suspended in the liquid. The resulting slurry can then be shaped directly by forming or fully solidified for subsequent forming after partial remelting in the semi-solid state.2–6)

In the present study, with the aim of improving hydrogen capacity, we kept an eye on the microstructural evolutions and chemical properties of thixotropic microstructure on Mg–Ni alloys by using a partial remelting process. In order to understand the effect of thixotropic microstructures on the hydrogenation properties of Mg–Ni alloys, a study of automatic pressure-composition-isotherm was performed.

2. Experimental Procedures

2.1 Preparations of specimen by RCM

Mg–Ni alloys of various nickel compositions were synthesized by using rotation-cylinder method (RCM). RCM was utilized to alloy homogeneously two metals of large melting point difference in a short time. High-melting-point metal chips instead of reinforcement particles were incorporated into pure low-melting-point melt and dispersed and alloyed simultaneously by RCM. Pure magnesium (99.93 mass% purity) and nickel (99.92 mass% purity) ingots were used. Nickel chips were prepared from nickel ingots by drilling without cutting oil. About 600 g of the molten magnesium were prepared in a steel crucible in an electric resistance furnace. Oxidation-inhibiting sulfur hexafluoride gas diluted to about 1% in carbon dioxide gas was used to prevent burning of molten magnesium during the process. The melt was then rotated by a steel hollow cylinder at 953 K and the desired amounts of nickel chips were added with a feed rate of about 5 g·min⁻¹ under a rotation speed of 13.3 rev·s⁻¹. Post rotation of 5 minutes was conducted after the addition of the desired mass fraction of nickel chips. After that, the molten alloy was cast into a permanent metal mold with the shape of diameter 32 mm and height 180 mm. The mold was at room temperature. The chips were preheated to 473 K in order to avoid local temperature change during the addition. The illustration of the RCM apparatus with the detailed explanation of the parts is given in Fig. 1. For each experiment, the same procedure was applied only by changing the nickel mass fraction of 3, 6, 9 and 12 mass%. Based on the previous studies7,8) about the effects of blade depth and rotation speed for incorporation and dispersion of particles, experimental conditions were fixed (blade depth: 70 mm, rotation speed: 13.3 rev·s⁻¹).

Figure 1 shows the illustration of RCM apparatus.

2.2 Preparations of thixotropic Mg–Ni alloys

Partial remelting experiments were carried out in an electric resistance heating apparatus under protective gas atmosphere. The specimen was held in a steel tube in order to avoid deformation of the specimen by its own weight as the microstructure was coarsening. The rate of heating was ∼0.5 Ks⁻¹ in the solid state and ∼0.08 Ks⁻¹ within the solidification range, and the temperature change was monitored using a thermocouple placed in the center of the specimen. After holding at predetermined temperature (913, 898, 883 and 863 K for 3, 6, 9 and 12 mass%Ni, respectively), the specimen was withdrawn out of the tube and quenched into water. The predetermined temperature was calculated by Scheil's equation.9,10) Figure 2 shows the illustration of the resistance heating apparatus and the schematic process of superheating for grain refining.

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2.3 Characterizations and evaluations of pressure-composition-isotherm

After quenching, the specimen was prepared for metallographic observation by polishing with α-Al₂O₃ and etching using 5% citric acid solution, and examined with an optical microscopy. The specimen was carefully prepared so that good contrast between the primary Mg rich phase (i.e. globules) and the eutectic constituent (i.e. quenched liquid) was obtained. An image analysis system (Image-Pro® Plus) was used to determine the liquid fraction, average globule size, the number of globules per unit area and roundness of the globules. At least five fields were randomly chosen for each specimen to ensure an uncertainty less than 5%. The evolution of phase and the distribution of composition were observed by backscattered electron imaging (BEI) and energy dispersive X-ray spectrometry (EDS).

To examine the hydrogenation properties, alloy chips were prepared from the as-cast alloys by drilling without cutting oil and mechanically ground to granules under 2 MPa hydrogen atmosphere for 1 or 4 h. The mechanically ground Mg–Ni granules were characterized by X-ray diffraction pattern analysis.

The hydriding and dehydriding properties were examined with a Sieverts-type automatic pressure-composition-isotherm (PCT) apparatus at 523, 573 and 623 K. Before the PCT examination, activation treatments were performed for 3 cycles at 523 K. The van’t Hoff plots were formed based on the PCT profiles of dehydriding mean plateau pressure.

3. Results and Discussion

Figure 3 shows the microstructure of partially remelted specimen with respect to the amount of Ni addition. Typi-
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Fig. 3 Optical micrographs of partial-remelting specimen: (a) Mg–3 mass%Ni (b) Mg–6 mass%Ni (c) Mg–9 mass%Ni, and (d) Mg–12 mass%Ni.

cal microstructures of thixotropic alloy were observed in Fig. 3(a), (b), (c) and (d). It is clear from Fig. 3 that Mg–Ni alloys with various nickel compositions were manufactured properly by RCM and that the grain size of the primary phase decreased with increasing nickel composition. The white areas in Fig. 3 correspond to the first-to-freeze regions (in this case, the primary magnesium phase) while the darker areas are the later-frozen regions (the eutectic regions). The \( \alpha \)-Mg phase and eutectic region were distinguished clearly as like-island type, because the non-eutectic compositions of Mg-(3, 6, 9 mass%)Ni proceed as follows; namely, the single solid phase (\( \alpha \)-Mg) that forms preferentially before the eutectic point is reached is described as primary phase and the solidification of the remaining liquid then proceeds by the normal eutectic mechanism. The domain of \( \alpha \)-Mg phase decreased according to the appearance of the skewed coupled zone\(^1\)\(^,\)\(^2\) with increased nickel composition. From the results of image analysis, the volume fractions of the eutectic regions increased as 27 → 55 → 58 and 67% with nickel contents of 3, 6, 9, 12 mass%, respectively, and the size of \( \alpha \)-Mg changed as 20–273 \( \mu \)m (Mg–3 mass%Ni), 17–148 \( \mu \)m (Mg–6 mass%Ni), 16–117 \( \mu \)m (Mg–9 mass%Ni) and 14–95 \( \mu \)m (Mg–12 mass%Ni).

Figure 4 shows the BEI and the line profiles (Mg, Ni) of Mg-(3, 6, 9, 12 mass%)Ni specimens. The large difference of linear absorption coefficient between Mg and Ni helped to affirm the BEI observation. By the line scanning analysis of BEI, the dark gray color region was confirmed as \( \alpha \)-Mg phase and the white gray region was ascertained as nickel-rich eutectic regions. According to the results of EDS, the nominal composition of partially remelted specimen was consistent with that of the cast alloy, and the composition of the white gray region was consistent with that of the eutectic structure, Mg–Mg\(_2\)Ni (see Fig. 5).

Figure 5 shows the results of XRD after 1 or 4 h crushing under 2 MPa hydrogen atmosphere. The Mg–3 mass%Ni alloy revealed that the magnesium peaks were detected mainly. However, in the cases of Mg–6 mass%Ni and Mg–9, 12 mass%Ni alloys, the patterns consisted of Mg, Ni, and Mg\(_2\)Ni hydride peaks. Especially, the formation of beta phase hydride, Mg\(_2\)NiH\(_4\), in Mg–9, 12 mass%Ni alloy proved the existence of the Mg–Mg\(_2\)Ni eutectic structure in later-frozen regions. In addition, the transition of hydrde phases (Mg\(_2\)NiH\(_{0.3}\) → Mg\(_2\)NiH\(_4\)) revealed that the formation of hydride was affected by the amount of Ni addition. This result appears to be due to the effect of Ni as a catalysis for hydrogen dissociation.

Figure 6 shows results of PCT behaviors of partially remelted Mg–Ni alloys. Generally, it was known that the kinetics of hydrogenation is strongly influenced by specific surface area directly. However, it is clear that the degradation problems of Mg based hydrogen absorbing materials are caused by the high surface area. Therefore, to examine the hydrogenation properties, alloy chips were prepared from as-cast alloys by drilling and thereafter mechanically ground to granules under 2 MPa hydrogen atmosphere during 1 or 4 h. The size of granules were \( \phi \) 5–12 mm (1 h crushing) and \( \phi \) 1–3 mm (4 h crushing), respectively. Figure 6(a) shows the dehydriding curves of Mg–3 mass%Ni alloy. Even though the profiles of PCT of chips were solid solution type at 523 and 573 K, the hydrogen capacity was over 2.27 mass% after 1 h crushing, and the plateau pressure approached 0.01 MPa at 573 and 623 K in granules. The reversible capacity was analyzed as 1.0–2.1 mass% with a little slope. Figure 6(b) shows the dehydriding curves of Mg–6 mass%Ni alloy. The hydrogenation properties were confirmed to increase to more
Fig. 4 Backscattered electron image with line profiles of Mg and Ni: (a) Mg–3 mass%Ni (b) Mg–6 mass%Ni (c) Mg–9 mass%Ni, and (d) Mg–12 mass%Ni.

than Mg–3 mass%Ni. However, large differences in the hydrogenation and reversible capacity values were retained depending on the measuring temperature and crushing conditions. Figure 6(c) shows the dehydriding profiles of Mg–9 mass%Ni alloy. The hydrogenation behaviors of chips specimen were similar to Mg–3, 6 mass%Ni alloys regarding the formation of hydrogen solid solution. However, after 1 h crushing, the hydrogen capacity reached to 5.5–7.0 mass%, and the plateau pressures were 0.03, 0.18 and 0.65 MPa at 523, 573 and 623 K, respectively. These hydrogen capacities closely approached to the theoretical hydrogen capacity of Mg–9 mass%Ni alloy. The reversible capacity was analyzed as 4.8–5.8 mass% with a near zero slope. These properties are almost the same for 4 h crushed samples. Figure 6(d) shows the dehydriding profiles of Mg–12 mass%Ni alloy. The alloy displayed unique hydrogenation behaviors in chips specimen. The hydrogen capacity reached to 3.4–5.4 mass% and the plateau pressure was attained at 0.016, 0.11 and 0.62 MPa at 523, 573 and 623 K, respectively. On the other hand, the hydrogenation properties (e.g. hydrogen capacity, reversible
capacity), except for the plateau pressure and dehydriding kinetics, were more decreased than other alloys subjected to 1 h or 4 h crushing. These results may be considered as a catalytic contribution of nickel as well as the effects of increased alloying composition.

Figure 7 shows the van’t Hoff plots of the dissociation plateau pressure of PCT analysis for the crushed alloys. In the case of 1 h crushing, the reaction enthalpies, \( \Delta H_{d.\text{plateau}} \), were evaluated as \(-96.2 \pm 0.9, -95.6 \pm 0.1, -88.7 \pm 0.1\) and \(-80.6 \pm 0.2\) kJ/mol-H\(_2\) for Mg-(3, 6, 9, 12 mass%)Ni alloys, respectively. In the case of 4 h crushing, \( \Delta H_{d.\text{plateau}} \) were evaluated as \(-93.1 \pm 0.3, -94.0 \pm 1.4, -81.7 \pm 0.3\) and \(-79.6 \pm 0.1\) kJ/mol-H\(_2\) for Mg-(3, 6, 9, 12 mass%)Ni alloys, respectively. Therefore, even if the value of the reaction enthalpies on partially remelted Mg-(3, 6, 9, 12 mass%) Ni alloys are poorer than mechanically milled alloys,\(^{13}\) they may be regarded as one of the best candidates of lightweight hydrogen storage materials at high service temperatures.

4. Conclusion

From the present results and discussion, we arrived at the following conclusions.

(1) Thixotropic (i.e. partially remelted) Mg-(3, 6, 9, 12 mass%)Ni alloys were found to have excellent hydrogenation properties compared with conventional casting/polycrystalline ones.

(2) The hydrogenation properties were influenced by evolution of microstructure and nickel content. In the present study, the hydrogen capacity and reversible capacity of Mg-12 mass%Ni alloy decreased in comparison with other alloys after 1 h or 4 h crushing. These results may be considered as a catalytic contribution of nickel as well as the effects of increasing alloy composition.

(3) In the case of 1 h/4 h crushed Mg-9 mass%Ni alloys, the specimen measured at 523, 573, 623 K revealed good hydrogenation properties. According to the Image analysis, the liquid fractions were analyzed to be around 55–60% and the
average size of globules were below 110 μm.

(4) Experimental results of partial remelting and PCT measurements show that the α-Mg phases contribute to hydrogen storage and the eutectic regions have a catalytic effect.

REFERENCES


Fig. 7 The van’t Hoff plots according to dehydriding mean plateau pressure: (a) after 1 h milling (b) after 4 h milling.