Preparation and Corrosion Behavior of Bulk Mg_{75}Ni_{15}Si_{10} Amorphous Alloy by Mechanical Alloying and Pulsed Current Sintering

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Amorphous Mg_{75}Ni_{15}Si_{10} powders synthesized by mechanical alloying were consolidated into bulk pieces by pulsed current sintering. An investigation was also done on the corrosion behavior of the pieces by measuring the corrosion rate and the polarization curve. The mechanically alloyed powder was examined by X-ray diffraction and TEM with selected area electron diffraction and differential scanning calorimetry. The amorphous powder could be made by milling for 2520 ks. However, the powder included Si particles and nano-crystals in addition to the amorphous phase. The composition of the amorphous phase has been determined to be Mg_{27.3}Ni_{13.5}Si_{13.5} by TEM-EDS. The crystallization temperature was 571 K. The bulk alloys sintered at 473 K and 523 K kept the amorphous phase, but Mg crystals grew in the alloy. The sintering density increased with increasing die pressure and reached to at 94% under 500 MPa at 473 K. The real density was calculated to be 2588 kg/m^3. No corrosion of the bulk amorphous alloy could be observed when exposed to 5 mass%NaCl solution for a period of 86.4 ks (24h) because of the passive film formed on the surface of the amorphous alloy. It was confirmed by the measurement of the polarization curve in 5 mass%NaCl solution that the corrosion rate of the amorphous alloy was a quarter or one-fifth that of AZ91D alloy.

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1. Introduction

Magnesium based alloys have an advantage of high specific strength, but have a disadvantage of low corrosion resistance. Therefore, amorphous Mg alloys have been developed to improve the corrosion resistance. Generally, Mg amorphous alloys are produced by rapid quenching methods such as single roll: e.g. Mg-Ca, Mg-Ni, Mg-Cu, Mg-Y binary alloys and their ternary alloys. In general the Mg amorphous alloys made by the single roll method have the shape of ribbon. On the other hand, bulk Mg amorphous materials are prepared by high-pressure die-casting and by extrusion of atomized powders in a closed system. It is necessary to melt magnesium materials before these processings. As the molten magnesium reacts with oxygen explosively, a complicated device is required to control the atmosphere and to regulate SF6 gas against global warming. However, there is the advantage that solid Mg does not react easily with oxygen as compared with the liquid Mg. Then, solid-state reactions such as mechanical alloying (MA) are effective to make an amorphous alloy. Mg-Y-Cu, Mg-Ni, Mg-Ni-Sn, Mg-Ni-Y and Mg-Y-Ni-Al amorphous powders have been prepared by MA. The compositions of the MA powders has been scarcely reported.

The purpose of this study is to prepare bulk Mg amorphous materials from MA powders and to evaluate their corrosion resistance. Therefore, Mg_{75}Ni_{15}Si_{10} amorphous alloy powders were synthesized by MA, and a bulk amorphous alloy was prepared by pulsed current sintering. The corrosion behavior of the bulk Mg_{75}Ni_{15}Si_{10} amorphous alloy was evaluated for characterization of the properties.

2. Experimental Procedure

Mg_{75}Ni_{15}Si_{10} ternary alloy was prepared from 99.9% purity Mg, 99.9% purity Ni and 99.9% purity Si powders. This powder was milled in a planetary ball mill (Ito Seisakusyo Ltd., Fritsch type), in which the rotation turned against the revolution in reverse and cold air was blown for controlling the rise in the temperature of the Cr steel pot. The pot was sealed in purified Ar gas atmosphere at 100 kPa. In the pot, a total weight of 400 g of stainless steel balls with 10mm in diameter was put with 20 g powders. The revolution speed was set at 2.8 s^{-1} (170 min^{-1}). The maximum milling time was 2520 ks (700 h). The changes in structure of the milled powders were characterized by X-ray diffraction (XRD, Shimadzu DP-D1) measurements using CuKα radiation. Thermal stability was evaluated by differential scanning calorimetry (DSC, Shimadzu DSC-50). The microstructures of the powders were determined by transmission electron microscopy (TEM, JEOL JEM-2010) coupled with selected area electron diffraction and energy dispersion spectrometry (EDS). The specimen used for TEM observation was prepared by focused ion beam (FIB, FEI FIB-200), and cross-section of the powder was observed by TEM. The compositions of the powders were determined by fluorescence X-ray analysis.

A set of powders was consolidated by pulsed current sintering (PCS, Izumitech SPS-510L). The sintering conditions were an atmospheric pressure of 13.3 Pa, a maximum axial pressure of 500 MPa, a sintering rate of 0.25 K/s and a sintering temperature identical to or less than that of the crystallization temperature. The sintering was done by holding the powders at a constant temperature for a period of 300 s. Hard metal (WC-Co) die set was used for sintering the powders at a high die pressure. The bulk material structure was characterized by XRD, and the thermal stability was investigated by
Corrosion resistance of the sintered alloys was evaluated by weight loss measurement and by anodic and cathodic potentiodynamic polarization. The corrosion rate was determined by measuring the weight loss in a 5 mass% NaCl solution at 296 K. The measurement of the weight loss was done within an accuracy of 0.01%. Anodic and cathodic potentiodynamic polarization was performed with potentiostat field machine in a 5 mass% NaCl electrolyte at 298 K. A conventional three-electrode technique consisted of a silver-silver chloride reference electrode (SSCE), platinum counter electrode and a working electrode of the sample was used for the electrochemical tests. The tests were conducted at 298 K with a scan rate of 0.33 mV/s. All potentials were referenced to the SSCE. The working electrode was made by sticking Cu wire in a sintered specimen of 10 mm in diameter and sealing into polyester resin. The total surface area of the specimen exposed to the solution was 78.5 mm².

3. Results and Discussion

3.1 Synthesis of Mg_{75}Ni_{15}Si_{10} powder by MA

Figure 1 shows the changes of XRD patterns for the milled composite of Mg_{75}Ni_{15}Si_{10} with milling time. When milling was done for a period of less than 1440 ks (400 h), no amorphous powder could be obtained, and flakes of 1 or 2 mm in diameter were formed instead. The sharp peaks of Mg, Ni and Si crystal observed by XRD show that the flakes were only mixed with Mg, Ni and Si. The diffraction peaks broadened by milling for 1440 ks except for that of Si peaks. The intensity of the broad and Si peaks decreased with increasing milling time. Si peaks was observed even for the milling times of up to 2520 ks (700 h).

The powders milled for a period of 2520 ks were by TEM for characterization of their microstructures. The TEM image and the selected area electron diffraction pattern are shown in Fig. 2. In the TEM image a relatively large crystal of about 1 μm in size, a small (nano size) particle and a gray matrix can be observed. The large crystal was confirmed to be Si by EDS, but the small particle remained to be unknown. The gray matrix is an amorphous phase, because its selected area electron diffraction pattern in Fig. 2 indicated a halo ring of amorphous structure. Therefore it can be said that this powder consists of Si crystals, unknown nano-crystals and amorphous phases. The amorphous phase was recognized to be Mg_{71.5}Ni_{13.5}Si_{13.0} alloy according to the EDS analysis. It was then suggested that the nano-crystals shown in the TEM image consisted of Mg and Ni, due to the fact that the composition of the start material was Mg_{75}Ni_{15}Si_{10}. As a contamination from the pot and the balls, less than 0.3 at%Fe was found.

The thermal stability of the milled powders was evaluated by DSC. The changes in DSC curves of the milled powders with milling time are shown in Fig. 3. After 1440 ks (400 h) of milling an exothermic reaction occurred at 475 K. The exothermic reaction peak and the exothermic temperature increased with increasing milling time. The highest peak and temperature were observed after 2520 ks milling, and the crystallization temperature T_c was 571 K. Considering the XRD analysis and the TEM observation discussed above, it was confirmed that the exothermic reaction has occurred by crystallization of the amorphous phase. The crystallization enthalpy \( \Delta H_k \) was 2.69 kJ/mol. The powder milled for 2520 ks was used for the sintering and the corrosion experiments. This powder had the characteristic that its crystallization temperature was higher than that of other Mg amorphous alloys. Figure 4 shows the relationship between the Mg content and the crystallization temperature. The previous results are also shown in the figure. These results indicated that the crystallization temperature depended on Mg content. The crystallization temperature decreased with in-
increasing Mg content. However, this Mg$_{75}$Ni$_{15}$Si$_{10}$ amorphous alloy had a higher crystallization temperature than other alloys. It was considered that Si has played a role in increasing the crystallization temperature, because the other alloys did not include Si. It was concluded that the Mg amorphous alloy with high crystallization temperature was easy for consolidation of the powders and was available higher temperature use.

3.2 Consolidation of Mg$_{75}$Ni$_{15}$Si$_{10}$ amorphous powder by PCS

The relationship between heating rate and crystallization temperature is shown in Fig. 5. The crystallization temperature increased with increase in the heating rate. The temperature difference reached 34 K when the heating rate increased up to one order of magnitude. This result suggested that the amorphous powder was easily crystallized by sintering at low heating rates. Therefore, the sintering at a high heating rate was required to prepare a bulk amorphous material from the amorphous powders. The powders could be heated at a high heating rate of more than 1.0 K/s by the pulsed current sintering (PCS) method. However, when the heating rate was increased, a difference was generated in the sintering density of the alloy specimen. The reason is that the PCS method increasing the heating rate leads to the increase of the temperature difference in the inside of the alloy specimen in the process of sintering. In this experiment the heating rate was set at 0.25 K/s. The crystallization temperature was calculated to be 568.7 K. It was confirmed by PCS that the Mg$_{75}$Ni$_{15}$Si$_{10}$ powder milled for 2520 ks was consolidated at a die pressure of 500 MPa. Figures 6 and 7 show the XRD patterns and DSC curves of the alloy specimens sintered at 473, 523 and 573 K. The sharp peaks observed in the XRD pattern and the absence of an exothermic peak in the DSC curve show that the specimen sintered at 573 K crystallized in a greater part compared with the others. Both the specimens sintered at 473 and 523 K had an amorphous phase. However, Mg peaks were found in the XRD patterns of these specimens. The intensity of the Mg peaks in the specimen sintered at 523 K was larger than that in the specimen of 473 K. It indicated that the amount of Mg precipitates in the specimen sintered at 523 K was more than that in the specimen at 473 K. The Mg crystal growth leads to the decrease of the amorphous phase. The enthalpies of the sintered alloy specimens were calculated on the basis of DSC measurements. Then, the residual amorphous ratio was determined by obtaining the proportion of the enthalpy of the sintered alloy to that of the MA powder. Figure 8 shows the relationship among the residual amorphous ratio, the Vickers hardness and the sintering temperature. The values of residual amorphous ratio and Vickers hardness at 300 K indicate those of the as-MAed powder. The residual amorphous ratio of the alloy sintered at 473, 523 and 573 K were 100, 98 and 0% respectively. The ratio suddenly changed between 523...
Fig. 6 XRD patterns in the as-MAed Mg75Ni15Si10 powder and the bulk alloys sintered at 473, 523 and 573 K.

Fig. 7 DSC curves of the as-MAed Mg75Ni15Si10 powder and the bulk alloys sintered at 473, 523 and 573 K.

and 573 K. The Vickers hardness of the alloy sintered at 473, 523 and 573 K were 284, 348 and 278 HV, respectively. These were almost the same value as the Vickers hardness of the MA powders except for that of the alloy sintered at 523 K. However, as shown in Fig. 6, the structure of the alloy sintered at 573 K was completely different from that of the as-MAed powder and the alloy sintered at 473 K. The Vickers hardness of the alloy sintered at 523 K decreased because of the formation of Mg crystals. In the case of the alloy sintered at 523 K, nano-crystalline particles with unknown composition, as shown in Fig. 2, made the alloy specimen hard. In spite of Mg alloy, this amorphous alloy was hard because of the dispersion of Si crystals of 2 to 5 μm in size. Figure 9 shows the sintering density as a function of die pressure at 473 K. The sintering density for the sintering temperature is also shown in the figure. The density expectedly increased with increasing die pressure or sintering temperature. However, the sintering density was about 94% at an applied pressure of 500 MPa. This value was lower than that of Mg–Ni–Y type amorphous alloys13 under the same pressure condition. From these data of the sintering density at 473 K, the density of the amorphous alloy was calculated to be 2588 kg/m³. When the sintering temperature was increased, the alloy specimen sintered at 523 K became brittle because of hardening with Si element as already mentioned, and the alloy sintered at 573 K showed low corrosion resistance as will be described later. Figure 10 shows the sintered samples of bulk Mg75Ni15Si10 amorphous alloy produced by MA and PCS. The samples were a bar of 3 mm in width, 2 mm in thickness and 30 mm in length, and two thin disks of 6 and 10 mm in diameter, respectively, and 1–2 mm in thickness. These samples were sintered at 473 K.

Fig. 8 Sintering temperature dependence of residual amorphous ratio and Vickers hardness.

Fig. 9 Relationship between sintering density and die pressure.
under 500 MPa of die pressure. The surfaces of three samples were polished by a buff. It was concluded that a bigger size sample could be prepared on the basis of a theoretical prediction. It would be necessary for producing large size samples to apply a large force between the dies. As shown in Fig. 9, the sintering density increased with increasing the pressure applied between the dies. Therefore, a large force is needed to apply a high pressure between the dies.

3.3 Corrosion rate and polarization curve of bulk Mg$_{75}$Ni$_{15}$Si$_{10}$ amorphous alloy

The corrosion rates of the Mg$_{75}$Ni$_{15}$Si$_{10}$ alloy sintered at 473, 523 and 573 K are 0, 0 and 956 g/m$^2$d, respectively, as shown in Fig. 11. No mass of the specimens sintered at 473 and 523 K was lost within an accuracy of 0.01% for 86.4 ks (24 h) exposure in 5 mass%NaCl solution. The surfaces of these specimens changed to a black color without luster, but the surface structure was not identified by XRD. In 5 mass%NaCl the alloy specimen sintered at 573 K crumbled in 10.8 ks (3 h) and changed from a bulk into black powder. The black powder was identified to be Mg(OH)$_2$ by XRD. Then, it was considered that the surfaces of the alloy specimens sintered at 473 K and 523 K were covered with Mg(OH)$_2$. It was also considered that this Mg(OH)$_2$ film might be a fine film formed on amorphous phase. Therefore, the film prevented the specimens sintered at 473 K and 523 K from corrosion. On the other hand, the corrosion of the specimen sintered at 573 K revealed aggressive behavior because of the crystallization of the specimen. Generally, Ni contained in Mg crystalline alloy lowers the corrosion resistance. However, a passivity film was formed on the surface of the amorphous alloy even though it contained Ni. A commercial AZ91D ingot has a value of about 0.011 mm/d (4 mm/yr); this value equaled to about 20 g/m$^2$d. The bulk Mg$_{75}$Ni$_{15}$Si$_{10}$ amorphous alloy had better corrosion resistance than a commercial AZ91D alloy.

Anodic and cathodic potentiodynamic scans in 5 mass%NaCl solution for the specimen sintered at 473, 523 and 573 K are shown in Fig. 12. The corrosion potentials, $E_c$, of the specimens sintered at 473, 523 and 573 K were evaluated as $-889$, $-902$ and $-927$ mV respectively. They shifted to negative potential with increasing the sintering temperature. For the cathodic halves of the scans, linear Tafel slopes $\beta_c$ defined as the voltage change per decade were detected for the specimens sintered at 473, 523 and 573 K with $-143.3$, $-140.5$ and $-173.9$ mV, respectively. Tafel slopes of the corrosion potentials revealed corrosion currents, $I_c$, of $6.1 \times 10^{-4}$ A/m$^2$ at 473 K, $4.9 \times 10^{-4}$ A/m$^2$ at 523 K and $2.6 \times 10^{-3}$ A/m$^2$ at 573 K. This result indicated that the corrosion rate of the specimen sintered at 573 K was 4–5 times as fast as that at 473 and 523 K. This result is different from that described above as shown in Fig. 11; the corrosion rates of the specimen sintered at 573 K by measuring the weight loss was more than 1000 times as fast as that at 473 and 523 K. The reason is that the specimen sintered at 573 K crumbled by exposing for a long time in the NaCl solution.
as described above; the actual weight loss by long period of exposure as shown in Fig. 11 became larger than the weight loss calculated by measuring the ion current by short period of exposure as shown in Fig. 12. The anodic halves of the potentiodynamic scans showed Tafel slopes $\beta_a$ with 102.2 mV at 523 K and 55.7 mV at 573 K. In the specimen sintered at 473 K, Tafel line hardly appeared due to the onset of passivation, which was indicative of the formation of a passive film of Mg(OH)$_2$. The passivation also appeared at 573 K, but it appeared in a region unrelated to the Tafel region. These passive films were unstable for potential, and the current density did not decrease. It was expected that the anodic reaction could be expressed by $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$. The anodic curve under about $-800 \text{ mV}$ showed more negative potential with increasing the sintering temperature. It suggested that the discharge amount of electron or ion depended on the amount of precipitation of Mg crystallized from the amorphous phase. In the range between $-600 \text{ mV}$ and $-800 \text{ mV}$, the potential curve of the specimen sintered at 473 K became more negative than that of the specimen sintered at 523 K, because a relatively large current was needed with the process of forming the passive film on the specimen sintered at 473 K. In the potential of more than $-600 \text{ mV}$, any potential curves showed the same behavior. The anodic and cathodic potential curves of any sintered specimen were more positive than that of a commercial AZ91D cast alloy. The corrosion potential and the corrosion current density of the AZ91D were $-1465 \text{ mV}$ and $2.5 \times 10^{-3} \text{ A/m}^2$, respectively. The corrosion current density of the AZ91D alloy was larger than that of the amorphous Mg$_{75}$Ni$_{15}$Si$_{10}$ alloys, which were sintered at 473 and 523 K. It was similar to that of the crystallized Mg$_{75}$Ni$_{15}$Si$_{10}$ alloy, which was sintered at 573 K. However, the corrosion rate of AZ91D alloy was measured to be 55.1 g/m$^2$/d, although it was previously reported to be about 20 g/m$^2$/d. The corrosion rate of the crystallized Mg$_{75}$Ni$_{15}$Si$_{10}$ alloy was 956 g/m$^2$/d, as shown in Fig. 11. As described before, the difference in corrosion rate should be due to the mass defect of crystallized Mg$_{75}$Ni$_{15}$Si$_{10}$ alloy. The corrosion rate of the amorphous alloy was a quarter or one-fifth as fast as that of AZ91D alloy according to the polarization curve.

4. Conclusions

Powder metallurgy technique is effective for making complicated shape or large-size materials. Therefore, the amorphous powder of Mg$_{75}$Ni$_{15}$Si$_{10}$ was synthesized by mechanical alloying, and a bulk amorphous alloy was prepared by pulsed current sintering. Additionally, the corrosion behavior was investigated by measuring the corrosion rate and polarization curve. The amorphous powder was obtained by milling for a period of 2520 ks. However, the powder included Si and nano-crystals in addition to the amorphous phase. The composition of the amorphous phase was evaluated to be Mg$_{75.5}$Ni$_{13.5}$Si$_{15.0}$ by TEM-EDS. The crystallization temperature was 571 K. The specimen sintered at 473 and 523 K composed of amorphous phases, and Mg crystals were partly formed. The sintering density increased with increasing die pressure and arrived at 94% under the condition of an applied pressure of 500 MPa at 473 K. The real density was calculated to be 2588 kg/m$^3$. No corrosion of the bulk amorphous alloy could be observed in 5 mass%NaCl solution for 86.4 ks (24 h) exposure, because a passive film was formed on the surface of the amorphous specimen.

It was expected that this amorphous alloy have a high strength as well as the hardness of larger than 270 Hv. However, the tensile strength of this amorphous alloy has not been measured yet. It would be necessary to increase the sintering density in the preparation of high strength materials.

REFERENCES