Microstructure of Partially Remelted Thixoformable Mg–Ni Alloys

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The aim of this paper is to develop a thixoformable model alloy, Mg–Ni alloy of binary eutectic system with no range of solid solubility and to report the experimental results concerning the microstructural evolution of the alloys in the reheated semisolid state. Mg–Ni alloys of various nickel compositions were produced in the form of cylindrical billets by Rotation-Cylinder method. The results showed that the appropriate thixotropic structure, the globular solid phase with less liquid droplets entrapped inside the solid, could be obtained by the normal solidification and simple reheating procedures. Of more important feature of the thixoformable Mg–Ni alloy is that the size of the solid globules and the fraction liquid were mainly dependent on nickel composition, therefore could be controllable.

(Received September 27, 2000; Accepted January 22, 2001)

Keywords: thixoforming, thixoformable magnesium-nickel alloys, Rotation-Cylinder method, partial remelting, microstructural evolution

1. Introduction

Development of thixoforming has been largely driven by the increasing demand for high-quality aluminum and more recently magnesium net shape components as the worldwide automotive industry seeks to reduce vehicle weight and improve fuel economy and emissions. More and more frequently aluminum and magnesium components are being targeted for important structural and, in many cases, life-critical applications.^{1–4)}

A number of investigations have been reported using thixoforming processes for a variety of alloys, including aluminum, magnesium and copper alloys, steels and stainless steels. The understanding of the process is concerned primarily with the microstructure of semisolid slurries generated during either partial solidification or partial remelting, with their rheological behavior and with the modeling of this behavior for the purpose of numerical simulation about thixoforming processes.^{5–8)} Many studies have been also conducted on producing pre-materials for thixoforming using commercially available alloys. It is now well demonstrated that the MHD (magneto hydrodynamic stirring) technique induced during solidification⁹⁾ or the SIMA (strain induced, melt activated)^{9,10)} and RAP (recrystallization and partial remelting)¹¹⁾ processes before partial remelting favors globularization of the primary solid phase in the reheated semisolid state.^{11,12)} An alternative SSP (single slug production) method to the established MHD-technique is also a promising new way to produce thixoforming pre-material.¹³⁾

However, little work has so far been carried out in the development of alloy composition tailored to thixoforming processes. As it is a relatively new process, thixoforming had to establish itself by exploiting alloys that were already available.

The aim of the present study is to develop a thixoformable model alloy, Mg–Ni alloy of binary eutectic system with no range of solid solubility. The word thixoformable in the present study has a meaning that fraction liquid and fine solid globules with fewer networks among them should be simply controlled by normal solidification and simple par-

tial remelting procedures. This is based on three points of the thixoformable Mg–Ni alloy: (1) grain refinement of the primary solid phase, (2) the melting temperature difference between the first-to-freeze regions (in this case, the primary solid phase) and the later-frozen regions (in this case, the eutectic phase), and (3) the isotropy of solid-liquid interfacial energy in the semisolid state.

This approach relies on the fact that partial remelting of a dendritic microstructure should lead to globularization of the primary phase, for coarsening or ripening processes leading to the reduction in surface area will be operating whereby regions of high curvature are eliminated or reduced by diffusion of solute in the liquid.^{14–17)} The transformation, however, depends on the size of the primary dendrites^{17,18)} and on the crystallographic related surface energy.^{17,19)}

2. Experimental Procedures

2.1 Material

Pure magnesium (99.93%, Xuzhou Changhong Magnesium Co.) and nickel (99.92%, Inco Co. Ltd.) ingots were used. And nickel chips were prepared from nickel ingots by drilling without cutting oil. Then Mg–Ni alloys of various nickel compositions were manufactured by the following procedure. About 800 g of pure magnesium melt were prepared in a steel crucible in an electric resistance furnace under an SF₆-CO₂ protective atmosphere. The melt was then rotated at 953 K and the desired amounts of nickel chips were added with a feed rate of about 4 g/min under a rotation speed of 800 rev/min by Rotation-Cylinder method (RCM).²⁰⁾ Post rotation of 5 min was performed after the addition of the desired mass fraction of nickel chips, and then alloy melt was cast into a permanent metal mold with the shape of diameter 32 mm and height 180 mm. The mold was held at room temperature. To avoid large temperature change during addition, the chips were heated to 473 K prior to addition. RCM was originally developed to manufacture SiC particulate reinforced magnesium composites^{20–22)} and is being used for producing particulate reinforced alloy composites as well as for alloying low-melting-point metals with high-melting-point metal chips homogeneously in a short time. The as-cast alloys were

prepared for a metallography by polishing using a α -Al₂O₃ slurry. Etching was affected by immersion in 5% nital solution. Then the microstructures were examined using an Olympus PME3 optical microscope. Noran 217Z-1SPS electron probe microanalysis was used to identify the phases.

2.2 Partial remelting experiments

The as-cast alloy billets were cut to approximately 20 mm thick slugs and partial remelting experiments were carried out in an electric resistance furnace for 1800 s at the temperatures just below the liquidus temperatures of the alloys. The isothermal holding temperatures were 918 K, 907 K, 898 K, 883 K, and 863 K for Mg–3, 4, 6, 9, and 12 mass%Ni alloys.

The reheating rate was controlled to be about 0.5 K/s, and the temperature change was monitored using a thermocouple placed in the center of the slug. The slug was held in a steel tube in order to avoid deformation of the slug under its own weight as the microstructure was coarsening in the semisolid state. After a predetermined isothermal holding time, the slug was withdrawn with the tube and quenched in water. The specimens were prepared for a metallography by the same procedure applied to the as-cast alloys. In the semisolid state, a portion of the liquid appeared as islands within the solid. This structural feature is referred to as “liquid droplets” in this paper.

3. Results and Discussion

3.1 Microstructure of the as-cast alloys

The solidification microstructures of Mg–Ni alloys in comparison with the microstructure of pure magnesium are shown in Fig. 1. It is important to note that Mg–Ni alloys with various nickel compositions were manufactured well by a new alloying method, RCM, whereby high-melting point nickel chips were incorporated into low-melting point molten pure magnesium and dispersed and alloyed simultaneously. A typical hypoeutectic structure consisting of primary α dendrites

plus an interdendritic filling of eutectic phase is seen except for pure magnesium. The fine primary phases of Mg–Ni alloys can be clearly seen. The grain size of Mg–1 mass%Ni alloy decreases by a factor of approximately 4 as compared to that of pure magnesium. And much finer primary phases are obtained with increasing nickel composition. Although there is not yet agreement on what that basic mechanism is for the grain refinement of Mg–Ni alloys with increasing nickel composition, the result is important in terms of microstructural evolution in the semisolid state. This is because the critical time for microstructure evolution in the semisolid state is proportional to the cube of the dendritic arm spacing,^{17,18)} which indicates that rapid microstructure evolution can take place only for a fine dendrite structure, and because the initial grain size also determines the initial size of the solid globules generated in the reheated semisolid state.^{17,23,24)}

Figures 2(a) and (b) are the SEM backscattered images of magnesium and nickel line profiles of Mg–5 mass%Ni alloy, respectively. The nominal composition of the alloy is 94.38 mass%Mg and 5.62 mass%Ni (Fig. 2(c)), and the composition of the later-frozen region is 79.00 mass%Mg and 21.00 mass%Ni (Fig. 2(d)), which corresponds to the eutectic composition of binary Mg–Ni alloy system. It is also seen that the magnesium composition across the solid phase does not vary and is measured to be constant close to 100 mass%, which is the value of the equilibrium magnesium composition, as predicted well by the binary Mg–Ni alloy phase diagram.

Almost all techniques to produce pre-materials for thixo-forming, except the SIMA method and the chemical grain refining treatments, use shear forces at the solid-liquid interface in order to shear off the dendrites and to reshape them to a globular microstructure.^{5–8)} The processing variables, such as fraction solid, shear rate, stirring time, and initial preparation conditions, have great influence on the resultant microstructure, the effect of which has been well confirmed.^{11,12)} However, it should be noted that continuous stirring and quenching

Fig. 1 The morphology of the as-cast microstructures of Mg–Ni alloys (a) pure magnesium, (b) Mg–1 mass%Ni alloy, (c) Mg–3 mass%Ni alloy, (d) Mg–4 mass%Ni alloy, (e) Mg–6 mass%Ni alloy, (f) Mg–9 mass%Ni alloy.

Fig. 2 EPMA result of Mg-5 mass%Ni alloy (a) SEM backscattered image with magnesium line profile, (b) SEM backscattered image with nickel line profile, (c) the nominal composition of the alloy, (d) the composition of the later-frozen region.

the slurry through the eutectic temperature are very important for microstructural control in the semisolid state. For the epitaxial solidification of the liquid on the solid grains can be minimized and partial remelting can be easier and controllable if the liquid to be quenched is of eutectic composition. It is clear that the later-frozen regions on Mg-Ni alloys may well be of eutectic composition, which is very promising feature for microstructure control in the semisolid state, based on the previous discussion.

3.2 Microstructures of the partially remelted Mg-Ni alloys

Partial remelting of a dendritic structure should lead to globularization of the primary phase, for coarsening or ripening processes leading to the reduction in surface area will be operating whereby regions of high curvature are eliminated or reduced by diffusion of solute in the liquid.¹⁴⁻¹⁷ The transformation, however, depends on the size of the primary dendritic phase, as mentioned previously.^{17,18,23,24} This discussion is clearly demonstrated in Fig. 3, which shows the change of the microstructure of Mg-3, 4, 6, and 9 mass%Ni alloys after isothermal holding for 1800 s at the given temperatures. The microstructures of partially remelted Mg-Ni alloys in Fig. 3 reveal that the appropriate thixotropic structure, the non-dendritic globular solid phase separated and enclosed by the liquid, could be attained even through such simple reheating within a length of time suitable for commercial production.

A further important aspect of the result is that the fully globular solid phase with less liquid droplets entrapped inside the solid can be obtained. When the interfacial energy is a function of orientation, as it will be in general when one of the phases in contact is a crystalline solid, equilibrium shape departs from sphericity in such a fashion as to preferentially expose crystallographic orientation of low energy.^{19,25,26} It is reported the anisotropy of the liquid-solid interface energies in certain zinc and cadmium alloys of hexagonal lattice structure is very large and this leads to the surprisingly ir-

Fig. 3 The as-quenched microstructures of Mg-Ni alloys after isothermal coarsening for 1800 s at the given temperatures in the semisolid state (a) Mg-3 mass%Ni alloy at 918 K, (b) Mg-4 mass%Ni alloy at 907 K, (c) Mg-6 mass%Ni alloy at 898 K, (d) Mg-9 mass%Ni alloy at 883 K.

regular shapes of the solid phase and the liquid droplets in the semisolid state.¹⁹ In marked contrast to the results obtained for zinc and cadmium, the previous experiment for the microstructure of partially remelted AZ91D magnesium alloy shows that the shapes of the solid phase and the liquid droplets are globular and the solid globules also coarsen keeping its globular shape.^{27,28} That the anisotropy of the solid-liquid interfacial energies of AZ91D and Mg-Ni alloys are near zero, which is presumably due in part to the near-ideal axial ratio of magnesium and its alloys,²⁹ may be responsible for the observed results.

A more important feature of thixoformable Mg-Ni alloys is that the composition of the liquid phase does not vary and is constant close to the eutectic composition in the semisolid state. If thermal fluctuation is induced during isothermal holding in the semisolid state, the epitaxial solidification of the liquid on the solid and the fine equiaxed dendrite are easy to be generated in alloys of eutectic systems with a range of solid solubility. They are difficult to be remelted because the melting point of them is relatively high and the small fraction of them causes a change of the flow behavior of the semisolid slurry, which has detrimental effect on thixoformability. So the reheating system for partial remelting of semisolid billets requires a high accuracy of the equipment. And the careful transportation of slugs should also be made not to drop off the temperature of the slug during transportation. In the present Mg-Ni alloy system, however, the equiaxed dendrite and the epitaxial growth cannot be generated even with thermal fluctuation induced during isothermal holding and during transportation of the slug. That is a very promising point for microstructural control for thixoforming.

4. Conclusion

The Mg-Ni alloys of various nickel compositions can be manufactured well by Rotation-Cylinder method whereby high-melting point nickel chips were incorporated into low melting point molten pure magnesium and dispersed and alloyed simultaneously. Even through such simple reheating

within a timescale suitable for commercial production, Mg–Ni alloys can attain the appropriate thixotropic structure, the fully globular fine solid phase with less liquid droplets entrapped inside the solid. It is seen that the size of the solid globules and the fraction liquid in the semisolid state are mainly dependent on nickel composition in Mg–Ni alloys, therefore could be controllable. The liquid composition in the semisolid state does not vary and is measured to be of the eutectic composition of Mg–Ni alloy system over a range of nickel compositions, which implies that the equiaxed dendrite and the epitaxial growth cannot be generated upon thermal fluctuations in the present alloy system.

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