AMORPHIZATION OF Mg-BASED ALLOYS BY MECHANICAL ALLOYING

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ABSTRACT

The negative heat of mixing of Mg-Zn and Mg-Ni alloy systems are very small. It was considered that the amorphization of the alloys by mechanical alloying of the pure elements was very difficult. In this experiment we chose Mg-Zn and Mg-Ni alloy systems, treated in a self designed vibrating ball mill. Amorphization of $\text{Mg}_{50}\text{Zn}_{50}$ alloy finished within 50 hours. So Mg-based binary alloys could realize amorphization even when their negative heat of mixing was very small. The amorphization reaction was both chemically and mechanically driven. $\Delta H_{\text{mix}}$ had some effect on the alloy’s amorphization ability. When $\Delta H_{\text{mix}}$ of the system was very small its influence on the amorphization ability would be critical.

1. INTRODUCTION

Mechanical alloying(MA) has become a well-known technique in powder metallurgy since it was established[1]. In 1983 Ni-Nb amorphous alloy powder was synthesized by MA of pure crystalline elemental nickel and niobium powder[2]. Subsequently amorphous alloys have been synthesized by MA of elemental powder in many binary metal systems[2,3,4]. From the experiment results it has been concluded that amorphous alloys formation during mechanical alloying is closely related to the formation by solid-state interdiffusion reaction in metallic composites[3,4,5]. Recent years some researchers[6] argued that amorphization of MA is quite different from solid-state interdiffusion reaction and the conditions $\Delta H_{\text{mix}}<0$ and $D_0\rightarrow D_A$ are not needed. Some researchers[7,8,9] have synthesized successfully MA amorphous alloy powder even when $\Delta H_{\text{mix}}=0$ or $\Delta H_{\text{mix}}>0$.

A. Calka and A.P. Radlinski[10] first studied MA amorphization of Mg-based binary metal system. They synthesized $\text{Mg}_{70}\text{Zn}_{30}$ amorphous alloy powder successfully by mechanical grinding, using $\text{Mg}_{70}\text{Zn}_{30}$ master alloy powder. The attempt to synthesize amorphous powder by MA of pure crystalline elemental magnesium and zinc was unsuccessful. It was considered that the negative heat of mixing was too small and the reaction in MA would not be very effective. To continue the study of MA amorphization of Mg-based alloy, we chose Mg-Zn and Mg-Ni binary metal system for the experiment in order to investigate if they could realize MA amorphization when $\Delta H_{\text{mix}}$ is small and the influence the variation of composition on the system’s amorphization.
2. EXPERIMENTAL PROCEDURE

The MA experiment was performed in a self-designed vibrating ball mill. The device was driven by an electric motor. The cylinder material was stainless steel. According to the enthalpy of formation\[^{11}\], we chose Mg\(_{50}\)Zn\(_{50}\) (\(\Delta H_{\text{mix}} = -3.47\) \(\text{kJ/mol}\)), Mg\(_{50}\)Ni\(_{40}\) (\(\Delta H_{\text{mix}} = -3.24\) \(\text{kJ/mol}\)), Mg\(_{50}\)Zn\(_{20}\) (\(\Delta H_{\text{mix}} = -2.05\) \(\text{kJ/mol}\)), Mg\(_{60}\)Ni\(_{40}\) (\(\Delta H_{\text{mix}} = -5.17\) \(\text{kJ/mol}\)) and Mg\(_{60}\)Ni\(_{20}\) (\(\Delta H_{\text{mix}} = -3.15\) \(\text{kJ/mol}\)). Pure magnesium powder (60 mesh 99.9 wt%), zinc powder (200 mesh 99.9 wt%), nickel powder (200 mesh 99.9 wt%) were mixed according to the alloy composition and sealed into the cylinder of the mill. Ball to powder weight ratio was \(W_{\text{ball}} : W_{\text{powder}} = 100:1\). Vibrating frequency was over 2000 rpm. During the process of milling the powder was protected in argon atmosphere. The samples of the powder were analysed at various stages of milling, using X-ray diffraction (\(D_{\text{max}}\) = 0.03R, Cu \(K\alpha = 1.54\)\(\AA\)). Scanning electron microscopy (S250MK3), transmission electron microscopy (H800). For the SEM samples, the powder were inlaid with epoxy resin in a small mould. Then the samples were ground, polished and sprayed with carbon. For the TEM samples, the powders were immersed into alcohol then the powder could be dispersed. One drop of this liquid was put onto a micro-holey carbon replica until alcohol evaporated.

3. RESULTS

3.1 X-ray analysis

Progress of the MA process was monitored by performing X-ray diffraction on small amounts of powder at different stage taken from milling cylinder. Figure 1 shows Mg\(_{50}\)Zn\(_{50}\), Mg\(_{60}\)Ni\(_{40}\) and Mg\(_{60}\)Zn\(_{20}\) MA alloy powder X-ray diffraction patterns. As Mg\(_{50}\)Zn\(_{50}\) alloy powder the structure of initial mixture of powder was determined as crystalline magnesium and zinc. Due to the particle size difference of magnesium and zinc powder (fine Mg powder was easy to be oxidized) the initial sample was not evenly mixed. It could be observed obviously on the X-ray diffraction pattern. The intensity of the crystalline diffraction lines were gradually reduced with increasing processing time. The crystalline line were broadened due to the decreasing crystallite size and the severe deformation during milling. After 15h the clearly visible maximum of the amorphous showed up at about \(2\theta = 41^\circ\) along with some crystalline diffraction peaks of unreacted Zn and only little amount of Mg. Milling for 50h finally leaded to full amorphous powder. From the X-ray diffraction pattern we can see that the amorphous phase formed directly from crystalline magnesium and zinc. No other phase formed during the process of mechanical alloying.

As for Mg\(_{50}\)Zn\(_{40}\) alloy the situation was to some extent similar to that of Mg\(_{50}\)Zn\(_{50}\). But the progress of amorphization became a little slower. Milling to 50h there was still very small amount of crystalline Mg and Zn.

As for Mg\(_{60}\)Zn\(_{20}\) alloy the progress of amorphization became much slower. Milling to 15h although amorphous phase was obviously visible, there was much more amount of crystalline Mg and some Zn. It was very difficult for Mg\(_{60}\)Zn\(_{20}\) alloy powder to realize full amorphization in this condition.

Figure 2 shows X-ray diffraction patterns of Mg\(_{60}\)Ni\(_{40}\) and Mg\(_{60}\)Ni\(_{20}\) MA alloy powder. Both Mg\(_{60}\)Ni\(_{40}\) and Mg\(_{60}\)Ni\(_{20}\) MA alloy powder couldn’t finish amorphization in this stage. Especially for Mg\(_{60}\)Ni\(_{20}\) alloy milling to 50 hours there was still a large amount of crystalline nickel. From the patterns we can see that amorphization speed of Mg\(_{60}\)Ni\(_{40}\) alloy powder was faster than that of Mg\(_{60}\)Ni\(_{20}\). This was correspond with their \(H_{\text{mix}}\). However it appeared the Mg-Ni system amorphization ability was lower than Mg-Zn system.