Mechanical Alloying of Cu-Ni-Fe Powders

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Mechanical alloying method is considered to be applied to Cu-Ni-Fe system because Cu-Ni binary system is soluble at any composition and diffusion coefficient of Ni in Cu is large. Planetary ball mill with different rotational speed was used to investigate energy effects on mechanical alloying of Cu-Ni-Fe. The authors found that (1)Cu-Ni-Fe can be alloyed by ball milling with high energy, (2)milled powders with low energy can be alloyed by heat treatment, (3)the Cu-Ni-Fe mechanically alloyed powder consists of a single phase of fcc (γ) similar to those of gas atomized powders and melt spun ribbon, and (4)spinodal decomposition temperature of Cu-Ni-Fe mechanically alloyed powders was 773K. Some properties of mechanically alloyed powders and mechanism of mechanical alloying were investigated in this work.

Keywords: mechanical alloying, powder metallurgy, hard magnetic material, spinodal reaction, gas atomize, diffusion coefficient

I . Introduction

Mechanical alloying process has been developed by J.S.Benjamin in 1970's to produce oxides dispersion strengthened superalloy (ODS) powders.⁽¹⁾⁽²⁾ Main objective of this ODS process is to alloy each element with no-solubility and to produce fine grain powders. Recently, it has been found that amorphous materials can be produced by the mechanical alloying process. Many researchers have been much interested in mechanical alloying technique as one of new processes to generate new materials.⁽³⁾

The Cu-Ni-Fe alloy is a practical hard magnetic material with the nominal composition of 60%Cu, 20%Ni and 20%Fe(mass%), which has been used in magnetic scales.⁽⁴⁾⁽⁵⁾ The alloy consists of a single phase of fcc (γ) at elevated temperatures and is dissolved into two phases of non-magnetic Cu rich(γ_1) phase and magnetic Ni-Fe rich(γ_2) phase by spinodal decomposition at around 800K. The alloy for magnetic scales is conventionally produced by casting and hot extrusion followed by cold deformation such as drawing and by aging to improve magnetic properties.

We considered that the magnetic properties of the Cu-Ni-Fe alloy can be improved by using finer particles produced by mechanical alloying method and that the alloy system can be alloyed by ball milling because the Cu-Ni binary system is soluble at any composition⁽⁶⁾ and Ni diffusion coefficients in Cu matrix is large.⁽⁷⁾ Mechanism of mechanical alloying of the Cu-Ni-Fe and the magnetic

properties of the alloy powders compared with those of atomized powders and melt spun ribbon are discussed.

II . Experimental

Planetary ball mill with agate vials of 500ml and agate balls of 10mm was used. Composition of Cu-Ni-Fe alloy is shown in Table 1. Figure 1 shows electron micrographs of raw materials (Cu, Ni and Fe powders). The purity of raw material is over 3N.

Table 1 Composition of Cu-Ni-Fe alloy.(mass%)

Cu	Ni	Fe
72	20	8

Milling condition is shown in Table 2. Vials were filled with Ar gas.

Table 2 Milling condition of Cu-Ni-Fe.

Vials 500ml, Balls 10mm in dia. 360rpm,200rpm Ar gas atmosphere

Characteristics of mechanically alloyed powders were compared with those of gas atomized powders and melt spun ribbons. Microstructure of milled powders was observed using scanning electron microscope (SEM). X-ray diffractometer (XRD) with Cu radiation was used to

evaluate consisting phases of powders. Compositional analysis was done by electron probe microanalyzer (EPMA). Magnetic properties were measured by vibrating sample magnetometer.

Fig.1. Scanning electron micrographs of raw materials for production of Cu-Ni-Fe alloy.

III . Results

1. Microstructure

Scanning electron micrographs and cross-sectional microstructure of powders milled at 360 rpm for 1.8ks, 3.6ks, 10.8ks, 18.0ks and 54.0ks are shown in Figure 2 and Figure 3, respectively.

Fig.2. Scanning electron micrographs of milled powders.

The shape of powders changed from spherical to flat with high aspect ratio as the milling time increased. Lamellar structure resulted in Kneading action was observed in

powders milled for 1.8ks, 3.6ks, 10.8ks and 18.0ks. Lamellar structure disappeared when milling time was extended to 54.0ks. Microstructure of lamellar structure became finer as the milling time has been increased up to 18.0ks.

Fig.3. Cross-sectional microstructure of milled powders for various time.

The change of average particle size as the function of milling time is shown in Figure 4. Powders became smaller as the milling time increased. A linear relationship can be seen between particle size and logarithm of milling time.

Fig.4. Effect of milling time on average particle size.

2. Chemical analysis of milled powder

Figure 5 shows the distribution of each element in ball milled powders measured by EPMA. Ni diffused more uniformly as the milling time increased. It was found that Cu, Ni and Fe were alloyed very uniformly in powders milled at 360rpm for 54.0ks.

Fig.5. Distribution of each element in ball milled powders measured by EPMA.

3. Structure of milled powders

Figure 6 shows the X-ray diffraction patterns of powders milled at 200rpm for various time between 1.8ks and 54.0ks. Cu(111) peak and Ni(111) peak can be observed. No drastic pattern change was observed as the milling time increased. The microstructure of milled powders was very fine but each element was not alloyed completely.

Figure 7 shows the X-ray diffraction patterns of powders milled at 360rpm for various time between 1.8ks and 54.0ks compared with that of gas atomized powder. When Ni fuses into Cu, lattice parameter decreases and the resultant Cu(111) peak shifted to higher angle. In the powders milled at 360rpm for 54.0ks, Cu(111) peak which shows 43.28 deg. shifted to higher angle and intensity of the Ni(111) peak decreased. The Cu(111) peak and Ni(111) peak become close and they finally merged into one broaden peak at 43.49 deg. The diffraction angle of mechanically alloyed powder is close that of gas atomized powder. From the results, Cu-Ni-Fe can be alloyed by high energy ball milling.

Fig.6. X-ray diffraction patterns of powders milled at 200rpm.

Fig.7. X-ray diffraction patterns of powders milled at 360rpm.

The size of crystal structure was calculated from the broadening of X-ray diffraction patterns using Scherrer's formula(1). This formula is applicable to crystal structure the size of which is finer than 100nm. Figure 7 shows that the crystal structure size of powder milled at 360rpm for 54.0ks is as half as gas atomized powder structure.

$$D = \frac{k \lambda}{B \cos \theta} \quad (1)$$

where D: Size of crystal structure(nm),

k: Scherrer's constant,

λ : Wave length of X-ray(nm),

B: Broadening of diffraction patterns(radian),

θ : Bragg's angle(degree),

Figure 8 shows thermomagnetic curves of powders milled at 200rpm, 360rpm compared with annealed gas atomize powders. In the figure of 200rpm milled powders, Curie points of Ni and Fe were observed besides Cu-Ni-Fe Curie point while only Cu-Ni-Fe Curie point was observed in 360rpm milled powders.

Fig.8 Thermomagnetic curves of Cu-Ni-Fe powders.

4. Spinodal decomposition

Figure 9 shows $4\pi I_s$ of powders which was milled at 360rpm for 54.0 ks compared with gas atomized powder and melt spun ribbon which were heat treated at various temperatures such as 573K, 673K, 773K, 873K, 973K, 1073K and 1173K. While $4\pi I_s$ of samples heat treated at 573K and 673K was very small, it became higher after heat treated over 773K. Spinodal decomposition of milled powders occurred at around 773K which was close to those of gas atomized powders and melt spun ribbons. $4\pi I_s$ of powders milled at 360rpm for 54.0ks was smaller than those of gas atomized powders and melt spun ribbons after heat treatment over 773K, presumably because milled powders were contaminated from vials, balls and atmosphere during milling.

Fig.9. Effect of heat treatment temperature on $4\pi I_s$ for Cu-Ni-Fe alloy.

5. Heat treatment of milled powders

Cu-Ni binary alloy system⁽⁶⁾ indicates that Ni is soluble at any content. Diffusion coefficients of Ni in Cu matrix is large; $D=D_0\exp(-Q/RT)$, $D_0=2.7\times 10^{-4}$ [m²/s], $Q=236$ kJ/mol(1019~1349K)⁽⁷⁾.

We considered that milled powders can be alloyed by heat treatment. Characteristics of milled and heat treated powders were investigated in comparison with those of gas atomized powder. Heat treatment temperatures are 873K, 973K, 1073K and 1173K for 7.2ks in Ar gas atmosphere. Figure 10 shows the X-ray diffraction patterns of 200rpm milled and heat treated powders and gas atomized powders. The Cu(111) peak and Ni(111) peak become close and they finally mixed to diffraction peak of 43.60 deg. Figure 11 shows the effect of heat treatment temperature on diffraction angle for Cu-Ni-Fe alloy. The diffraction angle of milled and heat treated powder is consistent with that of gas atomized powder. It has been found that Cu-Ni-Fe ball milled powders can be alloyed by heat treatment.

Fig.10 X-ray diffraction patterns of ball milled powders followed by heat treatment.

Fig.11 Effect of heat treatment temperature on diffraction angle.

IV . Conclusion

Cu-Ni-Fe was mechanically alloyed from pure Cu,Ni and Fe powders by high energy ball milling. Resultant phase by milling was γ phase. Spinodal reaction of Cu-Ni-Fe milled powders occurred at around 773K which was close to those of gas atomized powders and melt spun ribbons. It was found that partially alloyed powder with low energy milling was completely alloyed by heat treatment.

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