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Preparation and microwave absorbency of Fe/epoxy and $FeNi_3$/epoxy composites

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ABSTRACT

The focus of this study was placed on the lightness of microwave absorbing effective metal/epoxy composites. For such a focus, high aspect ratio of flake iron powder and high absorbing $FeNi_3$ were prepared. The iron powder particle size was reduced significantly through wet milling, comparing to dry milling. The $FeNi_3$ alloy powders were synthesized by mechanical alloying (MA); then, the particle size was reduced through wet milling. The iron powder and $FeNi_3$ alloy were characterized by scanning electron microscopy (SEM) and X-ray diffraction. SEM of the metal particles showed the flake and small structure by wet milling. The microwave absorbing effectiveness of metal/epoxy composite was affected by the structure, loading and dispersion of metal materials. The polyvinylpyrrolidone (PVP) plays an important role in suspending metal powders in wet milling to reduce powder size. Besides, the PVP will be a coupling agent in inhibiting the aggregation and enhancing the interfacial interaction between metal and epoxy. Results suggested that after the above manufacturing process, the microwave absorbency was enhanced substantially. Composite films of Fe/epoxy and $FeNi_3$/epoxy 1.6 mm in thickness possessed a microwave absorbency above 10 dB at 9.2–15.2 GHz and 13.1–16.2 GHz, respectively.

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1. Introduction

In addition to military applications, microwave absorbers play an important role in civilian applications, since it could reduce microwave interference of PCs' (Personal Computer), cell phones electronic instruments, and so on [1,2].

The previous study has shown that some metal alloys possess good magnetic and special properties [3–9]. It is known that Fe–Ni alloys are important magnetic materials, which have been widely applied to the electronic equipment and electrical industry.

The mechanical alloying (MA) [10–12] process has been considered an innovative method to prepare different types of powdered alloys [13–16]. The technique provides high energy to secure granular powders. The solid-state powder processing technique involves repeated welding, fracturing, and re-welding of powder particles in a high-energy ball mill. The MA process can produce over-saturated alloys, which could not be done by high-temperature melting methods.

The metal magnetic materials used for microwave absorbency should be bound within a matrix such as epoxies, elastomers, or silicones. Due to their flexibility, lightness and easiness in manufacturing. However, the composites cannot contain too many metal absorbents since the conductivity will be increased very quickly and microwaves will be reflected; moreover, the composites may become too brittle. The other key point is to disperse the metallic magnetic materials well within the matrix; otherwise the microwave absorbency may be reduced because of the aggregating absorbent.

Some polymer dispersing agents are good surfactants between metals and epoxies. They also can be absorbed onto the surfaces of particles in order to prevent oxidization and extend the life span of these microwave absorbers much longer when exposed to the elements. In this study, some polymer dispersing agents were compared and one of them was chosen for wet milling experiments.

2. Experimental

2.1. Materials

The reagent grade PVP (polyvinylpyrrolidone), ABS (alkylbenzene sulfonate), oleic acid and alcohol used in this study were obtained from the Echo Chemical Co., Ltd., Taiwan. The DGEBA-diethanolamine dispersing agent was obtained from Nano-Tech Longhai Chemical Co., Ltd., Zhang Zhou, Fujian, China, and their chemical structures are shown in Fig. 1. The iron powder (trade name: S-3700) with a high purity (>99%) and a 1–3 μm average particle size was obtained from the Maxwave Co., Ltd, Taiwan. The nickel powder (trade name: 255 Nickel Powder), with a high purity (>99%) and a 2.2–2.8 μm average particle size, was obtained from the Vale Inco company, Sudbury, Ontario, Canada. Two-component type epoxies DER-732 and D-230 (weight ratio = 10:3.5) were used to be bound with metal powders. The

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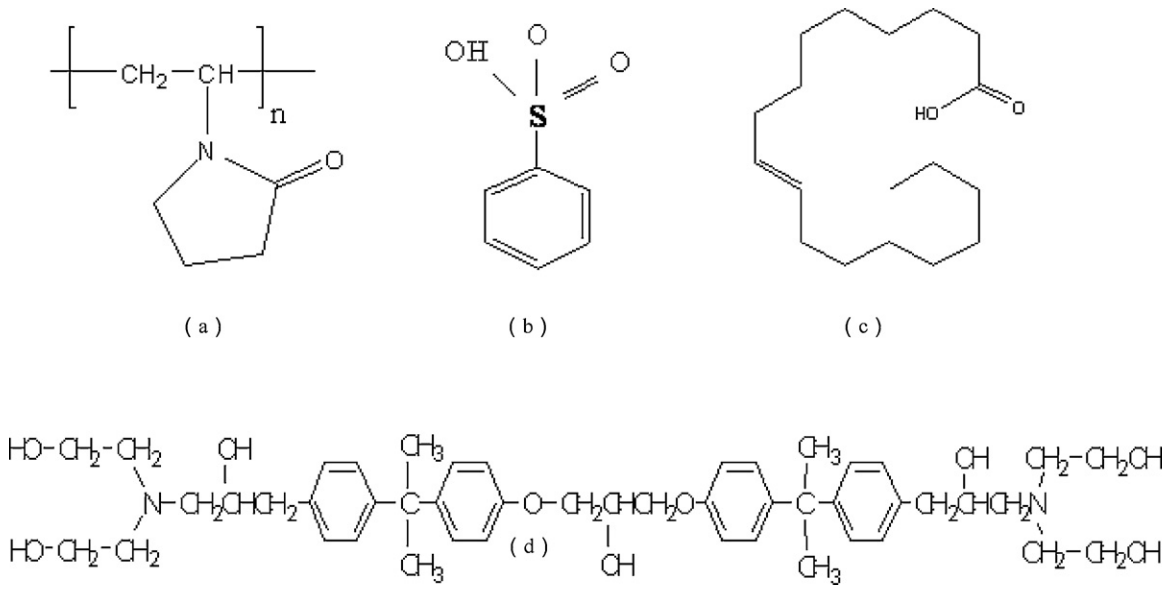

Fig. 1. Four dispersing agents (a) PVP (polyvinylpyrrolidone), (b) ABS (alkylbenzene sulfonate), (c) Oleic acid and (d) DGEBA-diethanolamine used in this study.

DER-732 was obtained from San Teh Chemical & Instruments Co., Taiwan and the D-230 was obtained from Huntsman Advanced Materials Americas Inc., Los Angeles, CA, USA.

2.2. Preparation of the microwave absorbing Fe material

The metal powders were placed in 500 ml stainless steel mixing jars which contained stainless steel milling balls of 10 mm in diameter. The weight ratio of ball to powder was 3:1 and fixed in dry or wet milling. The jars were filled with argon and were then agitated by a planetary ball mill (Fargo Co. Planet 6) at 380 rpm for 100 h [17].

The wet milling process was utilized and 1 wt% PVP alcohol solution was used to reduce the particle size and to disperse the steel into the solution. The contrast experiment, without PVP, was the same as wet milling process. The particle size and shape of the milled alloy were investigated by a scanning electron microscope (Hitachi. S-3500). After wet milling, the powders were dried at 80 °C for 4 h. Epoxy was used as a matrix to prepare films of 15 cm × 15 cm × 1.6 mm and be bound with 70 wt% iron or alloy powders. The microwave return loss of this film was then measured at 2–18 GHz, as shown in Fig. 2.

2.3. Preparation of the microwave absorbing $FeNi_3$ material

According to the literature [17], the molar ratio of iron to nickel is 1:3.58 (=1:3.72 by weight) which should be used to prepare $FeNi_3$. The metal powders were placed in a jar and milled at 380 rpm for 100 h. After dry mechanical milling, Fe–Ni alloy powders had been annealed at 650 °C in a nitrogen rich atmosphere for 1 h. The Fe–Ni alloy applied to prepared for sample was analyzed by X-ray diffraction (Shimadzu. XD-5). Then the wet milling process was utilized and 1 wt% PVP alcohol solution was used to reduce the particle size and to disperse it into the solution; besides, the microwave absorbing material $FeNi_3$ was prepared. After wet milling, the powders were dried at 80 °C for 4 h. The particle size and shape of the milled alloy were examined by a scanning electron microscope (Hitachi. S-3500). Epoxy was used as a matrix to prepare films of 15 cm × 15cm × 1.6 mm and be bound with 70 wt% iron or alloy powders.

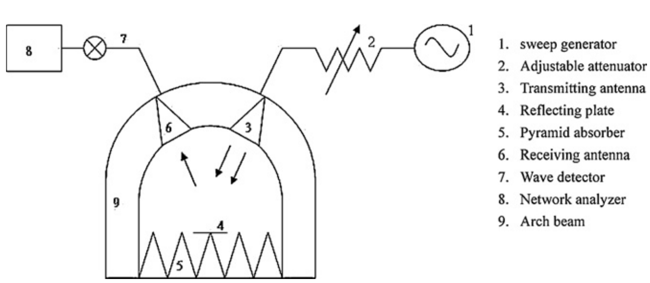

Fig. 2. Free space microwave return loss measurement.

2.4. Characterization and instruments

The microwave return loss of the samples in this study was measured by the free space method, as shown in Fig. 2 (HP 8722ES network analyzer, Damaskos Free Space Equipments). The microwave incident angle was 5° and the reflecting plate was aluminum. The return loss (R.L.) was defined and obtained by the following equation [18]:

$$\text{R.L.} = 20\log_{10}\left|\frac{Z_{in}-Z_0}{Z_{in}-Z_0}\right| = 10\ \log_{10}\frac{\text{Pr}}{\text{Pi}} \qquad (1)$$

where Z_{in} was the absorbents impedance, Z_0 was the air impedance, Pi was the microwave incident power, and Pr was the microwave reflected power.

Morphological properties of samples were investigated with a Hitachi S-3500 Scanning Electron Microscope (SEM), Japan.

X-ray diffraction (XRD) was employed to study the components of alloy particles. An X-ray diffractometer with Cu Kα (λ = 0.154 nm) radiation scanned its topside, and was parallel to the applied magnetic field from 30° to 90° at a rate of 50 min^{-1}. The X-ray source was generated at a voltage of 20 kV and a current of 40 mA.

3. Results and discussion

3.1. Dispersing agent choosing by settling method

The dispersing agents, PVP [19], ABS, oleic acid and DGEBA-diethanolamine were dissolved in alcohol to prepare 1 wt% solutions; 1 g of iron powder was put into the solutions. After ultrasonic vibrating for 5 min, the mixture was exposed to the settling

Fig. 3. The settling experiment of 1 g with iron powder dispersing agent in alcohol solution (a) PVP (polyvinylpyrrolidone), (b) ABS (alkylbenzene sulfonate), (c) Oleic acid and (d) DGEBA-diethanolamine.

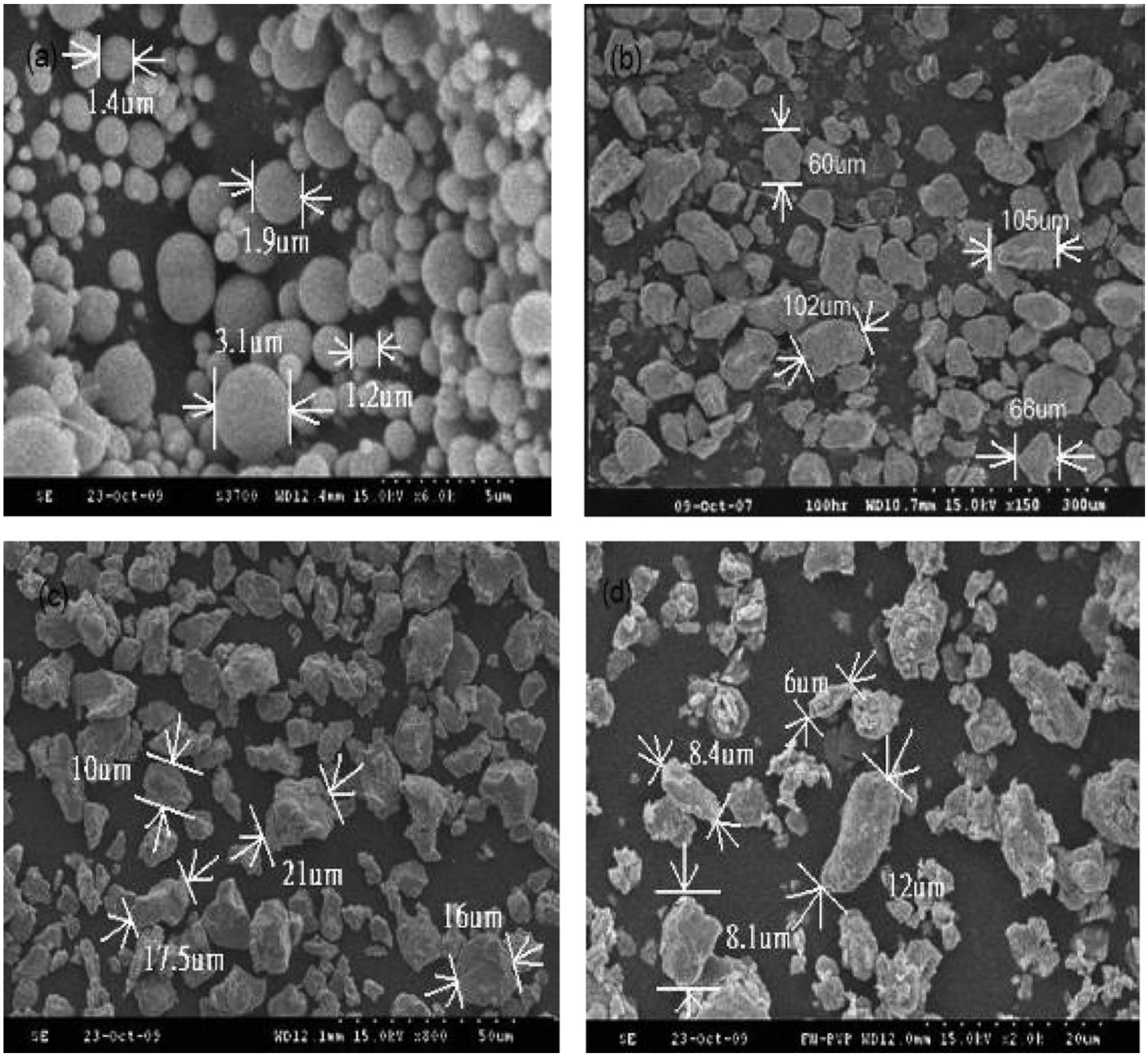

Fig. 4. The SEM microphotographs of iron powders: (a) before mechanical milling (×6000), (b) after dry mechanical milling for 100 h (×150), (c) after wet milling for 20 h in alcohol solution without PVP (×800) and (d) after wet milling for 20 h in alcohol solution with 1 wt% PVP (×2000).

rate for 30 min. Fig. 3 shows that the alcohol solution with 1 wt% PVP and 1 g iron powder was better than the other agents for dispersing the iron powders. Because PVP was widely used as a metal protective agent [20], it was suitable to be the dispersing agent in this study.

3.2. *Morphology of the iron powder by the different grinding methods*

Specific investigation was put on the different morphology of iron powders, which were prepared by dry and wet milling (in alcohol solution with 1 wt% PVP). On the basis of Fig. 4(a) and (b), the SEM microphotographs show that the particle size of the iron powders, which were treated by dry milling at 380 rpm for 100 h, was not reduced significantly. Before milling, the iron powder particle size was about 1–3 μm and spheroid. After dry milling for 100 h, the iron powder particle size was increased to 20–120 μm and became disk-like. Fig. 4(c) presents the iron powder exposed to wet milling for 20 h in an alcohol solution without PVP; the iron powders treated by wet milling for 20 h in alcohol solution with 1 wt% PVP. The figure shows that the particle size was reduced from 5–20 μm to 800 nm to 15 μm, when a 1 wt% PVP dispersing agent in alcohol solution was used.

Either dry or wet milling, the iron powders were deformed and looked like spheres, due to the hit of numerous milling balls, as illustrated in Fig. 5.

According to Fig. 6(a), it can be seen that the metal powders were stuck to the wall of the jar and the surface of the milling balls by dry milling. Fig. 6(b) reveals that metal powders were dispersed in the solution by wet milling. Furthermore, through dry milling,

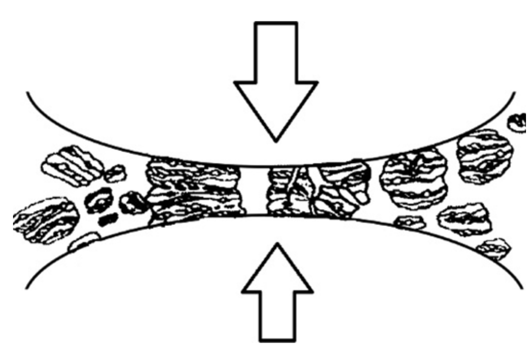

Fig. 5. The iron powders were deformed sphere to disk-like due to milling balls hitting.

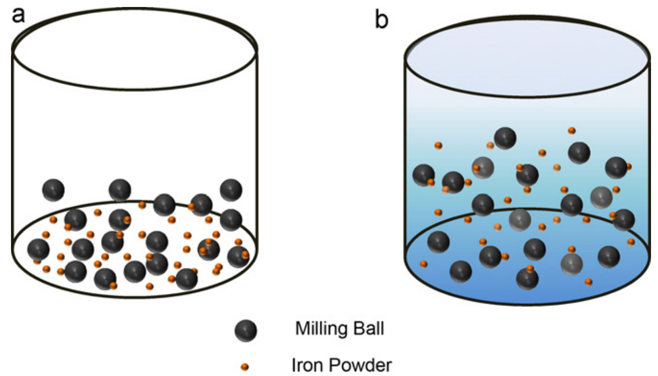

Fig. 6. The schematic diagram of metal powders milled by (a) dry milling (b) wet milling.

metal powders were drawn to the bottom by gravity. Through wet milling, metal powders could be suspended in the solution with high speed milling. Consequently, the particle sizes can be reduced by wet milling.

3.3. Microwave absorbency of iron powder/epoxy composites

Fig. 7 shows the comparison of the three microwave absorbencies. Specifically, one is pristine Fe (all 70 wt%/epoxy), another is Fe treated by wet milling with 1 wt% PVP, and the other is Fe treated by wet milling without PVP. It could be seen the 10 dB (90% power was absorbed) loss range of iron powder, after wet milling with 1 wt% PVP was from 9.2 to 15.2 GHz. Furthermore, the 10 dB bandwidth was enhanced substantially from 3.8 to 6 GHz. The 10 dB bandwidth of Fe treated by wet milling without PVP was about 4 GHz. The maximum of R.L. were 16.5, 26.2 and 20.2 dB, also demonstrating the enhancement of microwave absorbency by wet milling process. The particle size and shape of metal powders are important factors which affect the microwave absorbency of magnetic materials [21]. In the iron powder/epoxy composites, the micron degree and flatter particles can disperse well and construct a network structure. When the microwave gets into the composites, it will be absorbed greatly by the larger interactive area. Thus, smaller and flatter metal particles will be better for microwave absorbing. In addition, the dispersing aging PVP played a vital role in this study, because it could help metal powders suspend in alcohol solution, which reduced the metal powder size. Besides, the PVP became a coupling agent between metal powder and epoxy, which facilitated the dispersing of the metal powders in metal/epoxy composites.

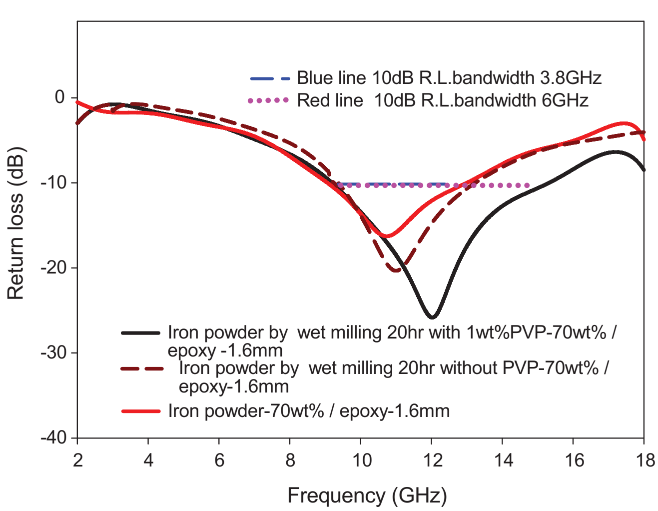

Fig. 7. The return loss of composites containing 70 wt% iron powder/30 wt% epoxy measured at 2–18 GHz.

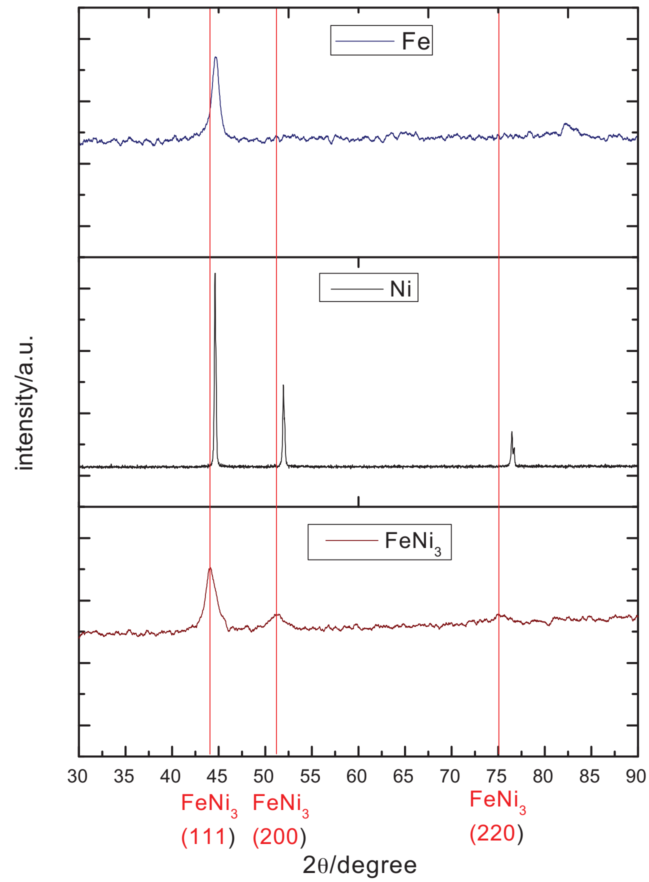

Fig. 8. The X-ray spectrum of Fe, Ni and $FeNi_3$ powders.

3.4. X-ray scattering and morphology of iron and nickel alloy ($FeNi_3$)

Fe, Co and Ni are magnetic materials and good microwave absorbers. The previous study has reported that Fe/Ni, Fe/Co and Fe/Ni/Co alloys have special properties in magnetism and wave absorbing [22–25]. The Fe/Ni alloys still have pretty good anti-oxidant properties [26]. This study utilizes MA method to prepare alloys.

Reported by Lu et al. [27], three characteristic peaks of $FeNi_3$ ($2\theta = 44.3°$, $51.5°$, $75.9°$), corresponding to Miller indices (1 1 1), (2 0 0), (2 2 0), were observed. Fig. 8 presents the X-ray spectrum of Fe, Ni and $FeNi_3$ (prepared by MA method) powders. We ensured that after 100 h of milling, $FeNi_3$ was produced. It was verified by three characteristic peaks ($2\theta = 44.3°$, $51.5°$, $75.9°$) that the $FeNi_3$ had formed. After dry mechanical milling, $FeNi_3$ had been annealed at 650 °C for 1 h. Then wet milling was used to reduce the particle size and to enhance dispersion. Fig. 9 illustrates the SEM of $FeNi_3$ by dry milling for 100 h and wet milling for 20 h, It also reveals that the shape of the particles was disk-like and layer-like, as indicated by the black arrows. In wet milling, it was a better dispersal method to use the alcohol solution with 1 wt% PVP. Moreover, the PVP is a metal powder protective agent which has been commonly employed, effectively preventing metal powders from oxidization.

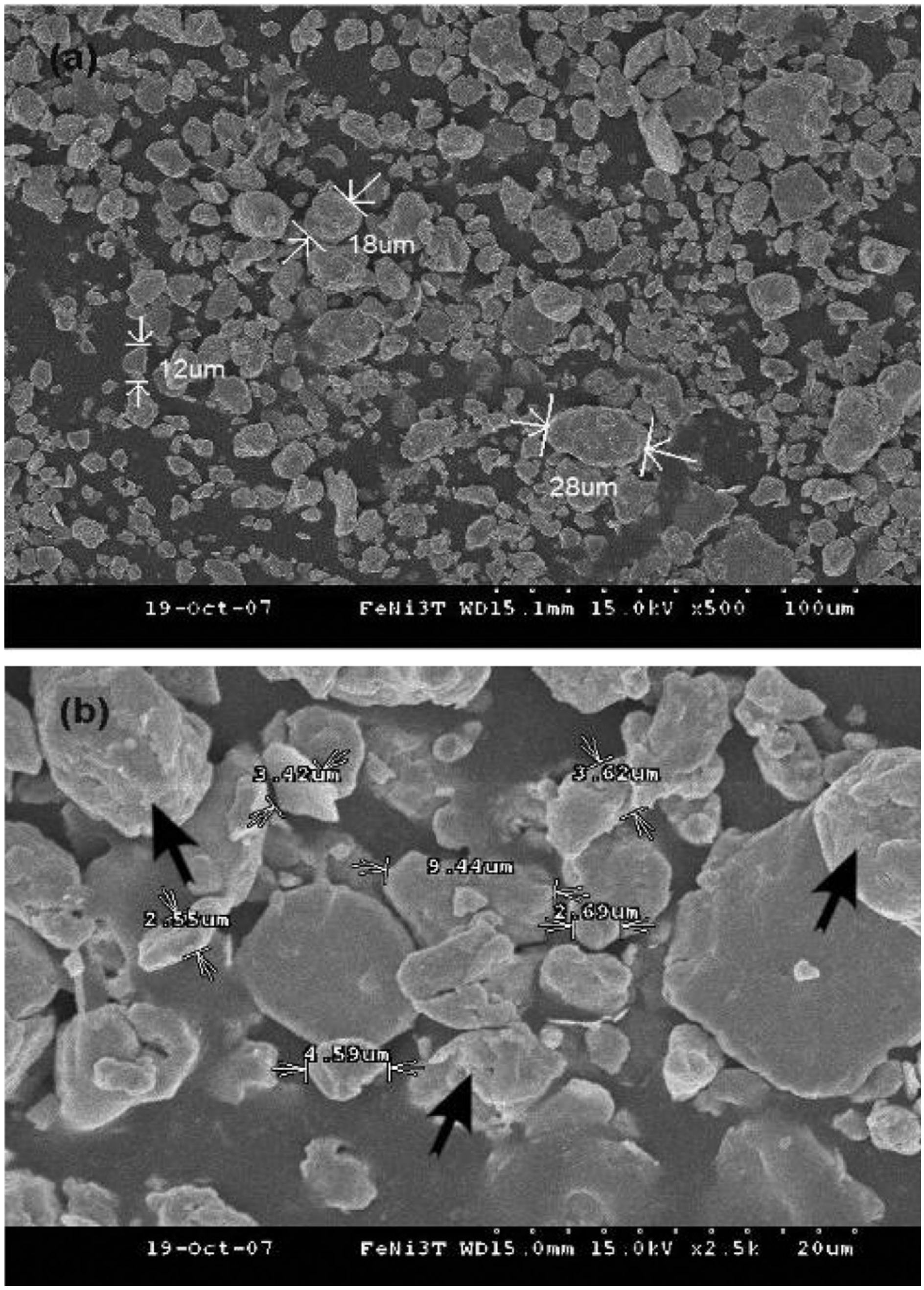

Fig. 9. The SEM microphotographs of $FeNi_3$ after wet milling for 20 h in 1 wt% PVP alcohol solution (a) ×500 (b) ×2500.

3.5. Microwave absorbency of $FeNi_3$/epoxy composites

Table 1 summarizes the make-up of three composites of epoxy, iron and nickel. The comparison of return loss of these three composites and pristine Fe 70 wt%/epoxy is shown in Fig. 10. It could be noticed that Ni 70 wt%/epoxy is lower than 5 dB R.L. at 2–18 GHz. The Fe + Ni 70 wt%/epoxy has an absorbing peak at 6.4 GHz. But, the return loss is only about 7 dB, after $FeNi_3$ alloy powders were formed. The sample of $FeNi_3$/epoxy, the 10 dB (90% power was absorbed) loss range of $FeNi_3$ was from 13 to 16.6 GHz, and was obviously enhanced. The pristine Fe (70 wt%/epoxy) was mentioned to be compared with $FeNi_3$. The 10 dB bandwidth of pristine iron powder and $FeNi_3$ (70 wt%/epoxy) were almost the same 3.8 GHz. The maximum return loss comparing result was that $FeNi_3$/epoxy (20 dB) was larger than iron powder/epoxy (16 dB). The absorbing peaks at different frequency depended on their intrinsic physical characters (permeability and permittivity).

Table 1
Composition of hybrid materials/epoxy composites.

Composition	$FeNi_3$ (70 wt%)	Ni (70 wt%)	Fe + Ni (70 wt%)
$FeNi_3$ (g)	70	–	–
Nickel (g)	–	70	55.3
Iron (g)	–	–	14.7
Epoxy (g)	30	30	30
Thickness (mm)	1.6	1.6	1.6

The Section 3.3 elucidates that smaller and flatter metal particles would be better for microwave absorbing. Particularly, in terms of alloys and the particle size of the alloys, the microwave absorb-

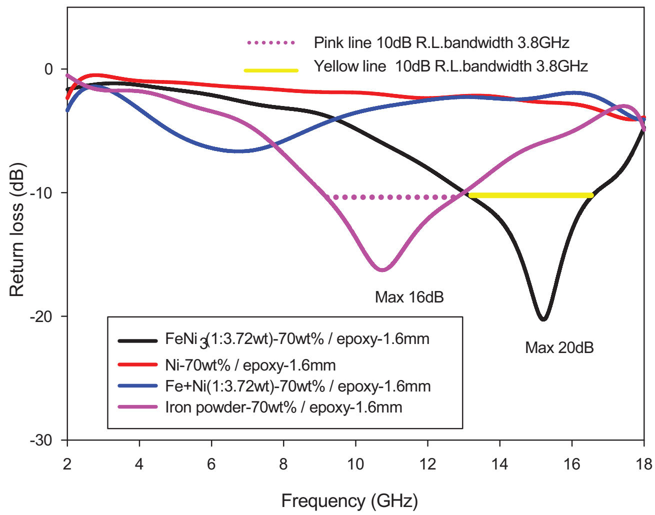

Fig. 10. The comparison of return loss of four composites.

ing performance of $FeNi_3$ was better than that of Fe, Ni or Fe + Ni powders.

4. Conclusion

The structured powders of Fe and $FeNi_3$ have been successfully prepared by mechanical alloying (MA). The structure of the $FeNi_3$ alloy was verified by X-ray. The microwave absorbing composites of iron powder/epoxy and $FeNi_3$/epoxy have been fabricated. The optimum process to reduce metal particle size should involve wet milling after mechanical alloying.

Four dispersing agents have been compared by the settling rate. PVP was selected and used in wet milling. In the Fe system, after wet milling in the alcohol solution with 1 wt% PVP dispersing agent, the particle size of iron powders was reduced and dispersed well. The iron powder/Epoxy (wet milling with 1 wt% PVP dispersing agent) composite possesses an electromagnetic absorbing characteristic of more than 10 dB (90% power was absorbed) at 9.2–15.2 GHz with 1.6 mm thickness.

In the Fe–Ni alloy system, the $FeNi_3$/Epoxy (dry milling for 100 h and wet milling for 20 h with 1 wt% PVP dispersing agent) composite possesses an electromagnetic absorbency of more than 10 dB (90% power was absorbed) at 13–16.6 GHz with 1.6 mm thickness. The microwave absorbency (return loss) was enhanced obviously after iron and nickel powders were alloyed to $FeNi_3$.

Particle size and shape of magnetic metal powders are crucial factors in relation to the microwave absorbency; particularly, smaller and flatter particles are better. The PVP alcohol solution will disperse iron and $FeNi_3$ powders greatly, being able to prevent metal or alloy powders from oxidization.

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