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ARTICLE

Interface Design and Wave Absorbing Properties of FeCuNbSiB Amorphous Alloy Strips/Epoxy Resin Composites

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Abstract: To solve the problem of non-infiltration between FeCuNbSiB amorphous alloy strips and epoxy resin matrix, the interface layer of $Cu_{0.75}Fe_{2.25}O_4$ and Fe_3O_4 phases, whose thickness was 5~10 μm, was obtained on both sides of FeCuNbSiB amorphous alloy strips by surface chemical modification. The results show that the interface layer has high bonding strength with FeCuNbSiB amorphous alloy strips, and good infiltration with epoxy resin matrix. The epoxy resin matrix composites using the amorphous alloy strips as reinforcing materials were prepared according to FSS grid design, and the electromagnetic wave absorption peaks of composite board appear in the frequency range of 13~18 GHz while the value of reflectivity R is -5 ~ -10 dB. The value of absorption peaks keeps constant but absorption peak frequency bands shift to lower frequency along with increasing the layer number of FeCuNbSiB strips. This kind of character can be used to modify radar absorbing properties of other composites and to broaden absorption band.

Key words: FeCuNbSiB amorphous alloy strips; interface; surface chemical modification; wave absorbing properties

Fe based amorphous alloy strip is an ideal reinforcing material for structural composites due to its excellent properties such as high tensile strength and elastic modulus that are better than those of T700 carbon fiber. A mature preparation method can obtain thin strip thickness smaller than 35 μm, good corrosion resistance and toughness. On the other hand, Fe based amorphous alloy strip shows superior comprehensive soft magnetic properties including high frequency soft magnetic property[1-8]. Therefore, amorphous alloy strips/epoxy resin composites with Fe based amorphous alloy strips as reinforcing materials can obtain good mechanical properties as well as excellent soft magnetic properties, which indicates a broad prospect for structural function integration composites.

$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (hereinafter short for FeCuNbSiB) amorphous alloy strip as the most outstanding representative of Fe based amorphous alloy strips is the ideal reinforcing material for preparing structural function integration composites[9-15]. However, FeCuNbSiB amorphous alloy strip shows a low surface activity and strong water-oil repellency, which lead to the non-infiltration phenomenon between strip and epoxy resin. There are some bubbles on the interface of FeCuNbSiB amorphous alloy strips/epoxy resin composites. It becomes a main difficulty to solve the interface problem of FeCuNbSiB amorphous alloy strips/epoxy resin composites[16-20].

In recent years, higher performance requirements for wave absorbing materials have been put forward due to the development of the electronics and military industries over the past few decades. Absorbing materials with multiple structures are being explored to achieve better wave absorbing properties by both dielectric loss and magnetic loss[21]. Meanwhile, some researches show that frequency selective surface absorbing materials with resistive patches can modify and improve the absorbing performance of radar wave. Recently, the frequency selective surface absorbing materials with magnetic film attract a lot of attention because of their unique properties[22,23].

In this paper, an interface layer was introduced by re-

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peated experiments, which effectively solved the problem of the non-infiltration between FeCuNbSiB strip and epoxy resin. The epoxy resin matrix composites using the magnetic amorphous alloy strips as reinforcing materials were prepared according to FSS grid design, and the radar wave-absorption properties were investigated.

1 Experiment

An interface of FeCuNbSiB amorphous alloy strips was obtained by surface chemical modification design. The FeCuNbSiB amorphous alloy strips with a width of around 4.5 mm and a thickness of around 30 μm were selected in this experiment. First of all, a degreasing process was applied to the FeCuNbSiB amorphous alloy strips. Some adsorbates on the surface of strips were removed after repeated cleaning with absolute ethyl alcohol. After that, the strips were rinsed repeatedly with deionized water, and dried for later use. Then we put the clean strips into the reaction solution whose composition was 0.8 mol/L$NaNO_3$ and 12.5 mol/L NaOH, and the reaction time was 15 min at 85 °C. These strips were dried at room temperature after the surface was rinsed with deionized water.

The FeCuNbSiB amorphous alloy strips after surface chemical modification were used as reinforcing materials, and the E-51 epoxy resin was used as matrix material. FeCuNbSiB amorphous alloy strips ply was put on the surface of E-51 epoxy resin according to FSS grid design. Square plates were prepared after the curing of FeCuNbSiB amorphous alloy strips ply. The length and width were both 180 mm, while the thickness was 2 mm.

The true phase state identification of FeCuNbSiB amorphous alloy strips was tested by X-ray diffraction (XRD) on a Bruker D8 Focus X-ray diffractometer with Cu Kα radiation. Surface morphologies of strips were investigated by VHX-100 3D high depth field microscope. Microstructure of the conversion coat was observed by scanning electron microscope (SEM) image, and elemental composition was characterized by energy dispersive spectrometer (EDS). Hysteresis loop was studied by physical property measurement system (PPMS) Quantum Design.

2 Results and Analysis

2.1 Interface design of amorphous alloy strips/epoxy resin composites

It is confirmed that FeCuNbSiB amorphous alloy strip exhibits amorphous structure from the XRD results shown in Fig.1. Sides of amorphous alloy strip were divided into free side and roll side. Free side refers to the contact surface between hot metal and air. The surface can shrink partially but freely on account of a lower cooling rate compared to roll side, so the free side exhibits a smooth and defect free surface. In contrast, as the roll side is in direct contact with rotating Cu wheel, the hot metal can not shrink freely because of a high cooling rate. As a result, the roll side exhibits a rough and dark surface.

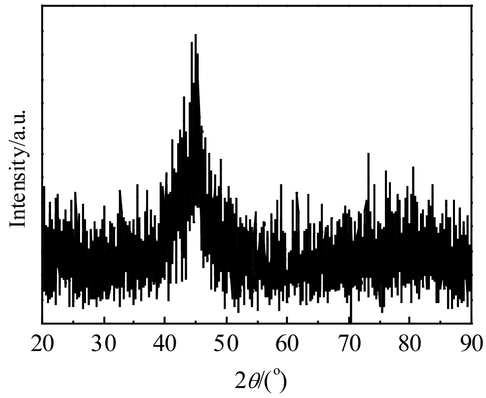

Fig.1 XRD pattern of FeCuNbSiB amorphous alloy strip

Fig.2 shows the contrast photos of FeCuNbSiB amorphous alloy strips before and after surface chemical modification. Under the natural state, the strip has a smooth, silvery-white and metallic luster surface. After surface chemical modification, a kind of stable black conversion coat is successfully formed. The surface morphologies of the strips before and after surface chemical modification are shown in Fig.3, which are observed through high depth field microscope. The stable black conversion coats are formed on both free side and roll side of strip shown in Fig.3c and Fig.3d. The conversion coat of roll side is more compact than the free side, which is owing to the roll side with rough surface having strong forming film property.

The conversion coats on the free side and roll side are uniform and the thickness is about 10 μm, which are shown in Fig.4. There is no obvious air gap between conversion coat and the strip, implying conversion coat combines closely with the strip. The bonding strength is very strong through hand scraping and fine emery paper friction test.

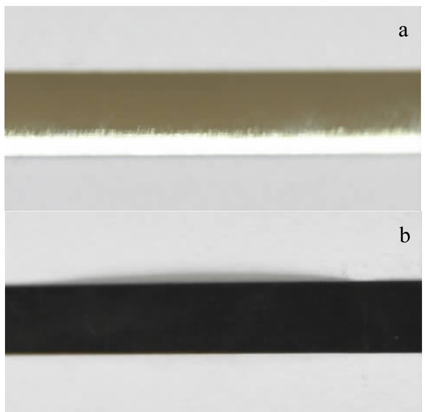

Fig.2 Photos of strips before (a) and after (b) surface chemical modification

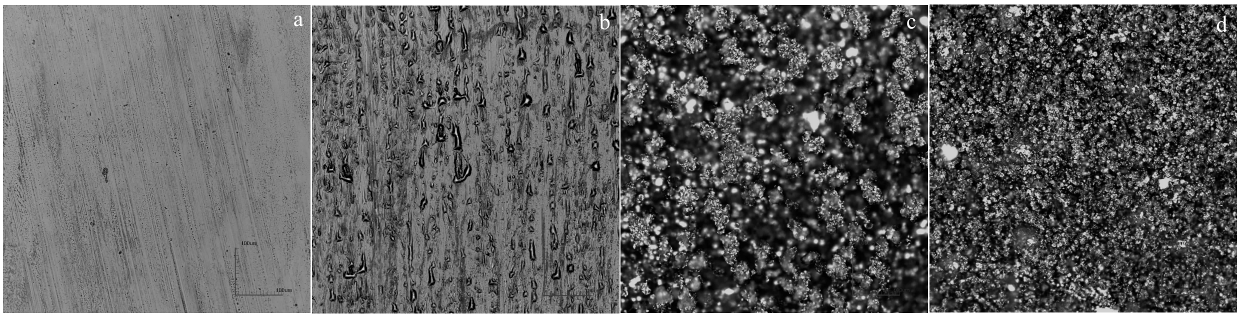

Fig.3 Surface morphologies of the strips before and after surface chemical modification: (a) free side of untreated strip; (b) roll side of untreated strip; (c) free side of modification strip; (d) roll side of modification strip

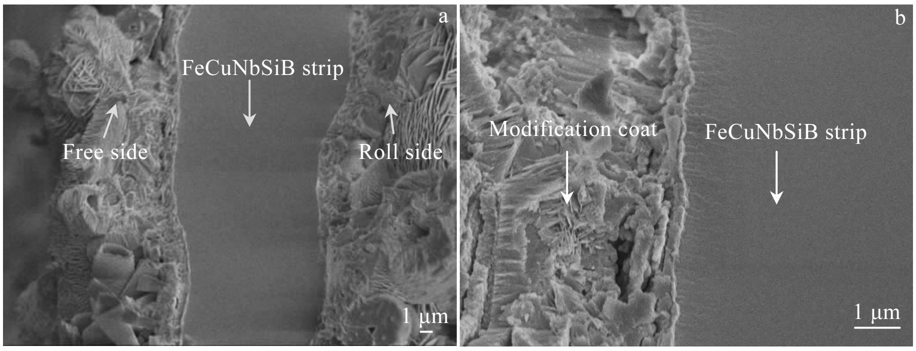

Fig.4 Microstructures of the strips before (a) and after (b) surface chemical modification

Elemental composition of conversion coat was characterized by SEM-EDS (Fig.5). It demonstrates that the conversion coat is composed of $Cu_{0.75}Fe_{2.25}O_4$ and Fe_3O_4 combined with XRD patterns analysis (Fig.6). Fe_3O_4 is formed through the reaction between FeCuNbSiB amorphous alloy strip and $NaNO_3$ as well as NaOH solution. The main experimental reactions are as follows:

$$4Fe+NaNO_3+7NaOH=4Na_2FeO_2+2H_2O+NH_3 \quad (1)$$

$$6Na_2FeO_2+NaNO_2+5H_2O=3Na_2Fe_2O_4+7NaOH+NH_3 \quad (2)$$

$$Fe+NaNO_3+2NaOH=Na_2FeO_2+NaNO_2+H_2O \quad (3)$$

$$8Na_2FeO_2+NaNO_3+6H_2O=4Na_2Fe_2O_4+9NaOH+NH_3 \quad (4)$$

$$Na_2Fe_2O_4+Na_2FeO_2+2H_2O=Fe_3O_4+4NaOH \quad (5)$$

Meanwhile, part of Fe ions are replaced by Cu ions for the phase composition of the conversion coat during the reaction process, which leads to the formation of $Cu_{0.75}Fe_{2.25}O_4$.

Infiltration tests between modification strips and epoxy resin show that infiltration angle is 0 degree and the infiltration property is excellent. Fig.7 shows the interface condition of FeCuNbSiB amorphous alloy strips/epoxy resin composite. There are no obvious cracks that indicates the bond between strips and epoxy resin is excellent.

2.2 Absorbing properties of amorphous alloy strips/epoxy resin composites

One prominent character of FeCuNbSiB amorphous alloy strips is superior to soft magnetic properties at high frequency.

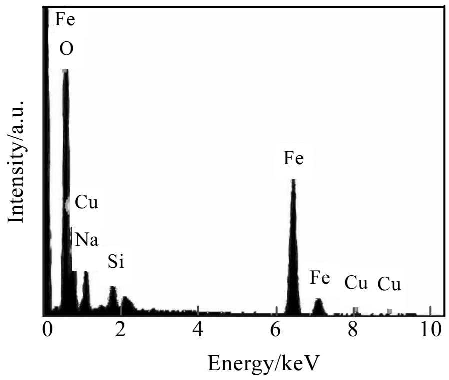

Fig.5 EDS spectrum of the strip conversion coat

Fig.8 shows magnetic properties of the amorphous alloy strips before and after surface chemical modification. It is investigated that strips under the two states both have high saturation magnetization M_s, low coercive force H_c and residual magnetization M_r. Compared with the strip before surface chemical modification, the M_s of the strip after surface chemical modification decreases from 131.04 to 83.43 $(A\cdot m^2)\cdot kg^{-1}$. This is because that two kinds of iron oxides ($Cu_{0.75}Fe_{2.25}O_4$ and Fe_3O_4) are formed on the surface of modification strip, which leads to the drop of M_s of the whole modification strip.

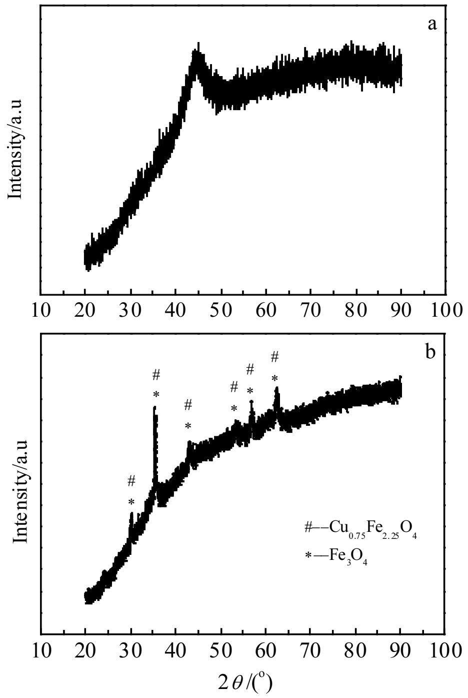

Fig.6 XRD patterns of strips before (a) and after (b) modification

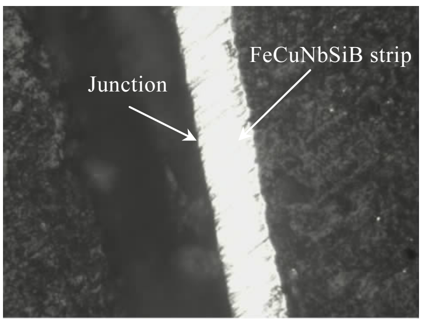

Fig.7 Microstructure of FeCuNbSiB amorphous alloy strips/ epoxy resin composite

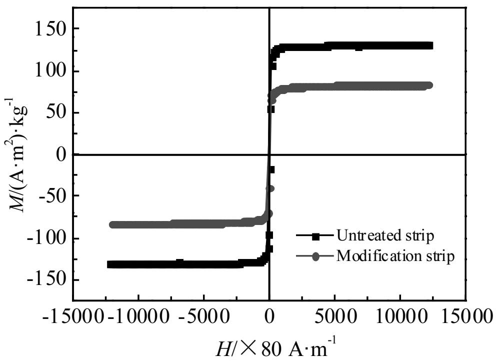

Fig.8 Hysteresis loops of amorphous alloy strips

After making FeCuNbSiB amorphous alloy strips compound to epoxy resin, the mechanical property of composite material is improved owing to FeCuNbSiB amorphous alloy strips as reinforcing materials. Furthermore, thanks to FeCuNbSiB amorphous alloy strips having excellent soft magnetic properties, the composite material achieves other special character-wave absorbing properties.

We used the E-51 epoxy resin as matrix material. FeCuNbSiB amorphous alloy strips with a width of around 4.5 mm and a thickness of around 30 μm were put on the surface of E-51 epoxy resin according to FSS grid design as shown in Fig.9. FSS means a period surface that unit structure arranges according to specific mode, FSS presents different working characteristics in electromagnetic space on the basis of unit structure and arrangement mode difference[24-26].

Magnetic loss portion (reflectivity R) is used to evaluate the wave absorption properties of FeCuNbSiB amorphous alloy strips/epoxy resin composites materials. By means of reflectivity test of composites materials, the electromagnetic wave absorption peaks of single FSS layer appear in the frequency range of 13~18 GHz and the value of reflectivity R is between -5~-10 dB (Fig.10). The value of absorption peaks remains constant but absorption peak frequency bands shift to lower frequency along with increasing FSS layer number shown in Fig.11.The research results show two encouraging messages: (1)FeCuNbSiB amorphous alloy strips according to FSS grid design exhibit such wide frequency absorption that the absorption peak frequency range reaches 5 GHz, even though absorption peak value of FSS structure is not very high. (2)Wave absorption frequency can shift through increasing FSS layer number. Hence, it illustrates that we can make use of the FeCuNbSiB amorphous alloy strips/epoxy resin composites layer to modify radar absorbing properties, such as broadening absorption band and adding the wave absorbing properties.

FeCuNbSiB amorphous alloy strips are also a kind of magnetic materials. When incident electromagnetic waves reach strip surfaces, electric current moves continuously on strips unit, and a magnetic field that surrounds the

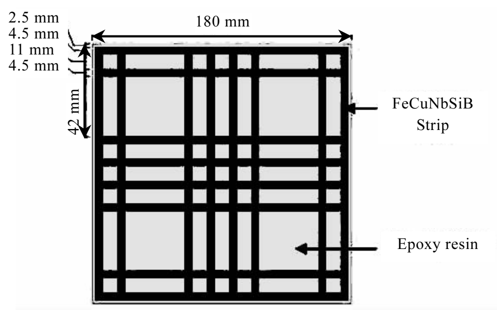

Fig.9 Sketch map of composites materials structure

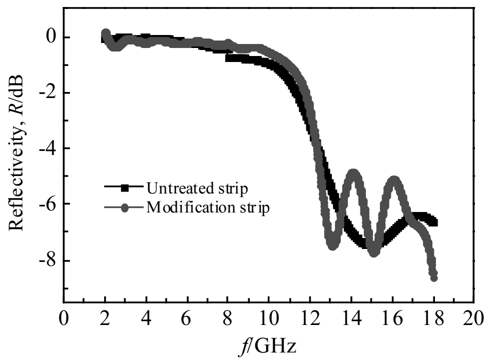

Fig.10 Reflectivity of composites materials

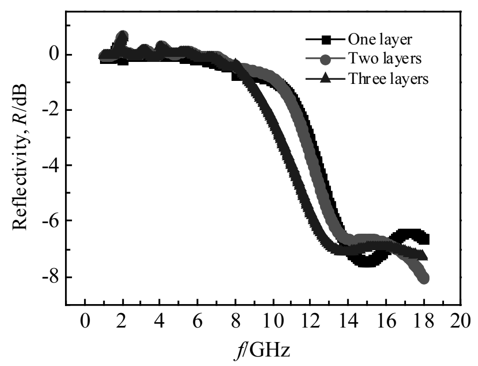

Fig.11 Effect of layer number on reflectivity of composites materials

strips is generated. The magnetic field is similar to the function of inductance. At the same time, a large number of electric charges gather on two sides of strips that makes positive and negative properties different, which leads to the capacitance among strips unit be generated. As a result, the composites materials are equivalent to series of inductance, capacitance and resistance during microwave frequency band, and the equivalent circuit is shown in Fig.12. The equivalent impedances of composites are affected by the FSS grid design of FeCuNbSiB amorphous alloy strips, and the values of equivalent impedances are equal to the sum of inductance, capacitance and resistance according to the equivalent circuit. The composites show different impedance matching from the FSS grid design and increasing ply numbers, which leads to different microwave absorption properties [27,28].

FeCuNbSiB amorphous alloy strips play a major role in the microwave absorption of the composites materials because the microwave can go through epoxy resin. Both dielectric loss and magnetic loss contribute to the absorption properties for FeCuNbSiB material. In this regard, it is the synergy of dielectric loss and magnetic loss that causes the absorption properties of composites materials. According to recent researches about the mechanism of dielectric loss

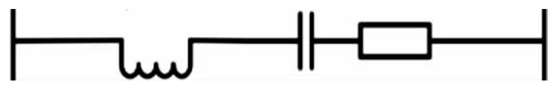

Fig.12 Sketch map of equivalent circuit

and magnetic loss, the interfacial polarizations and relaxation loss play an important role in the dielectric loss. The nature resonance and exchange resonance lead to the magnetic loss. Meanwhile, the multilayer of FSS grid and the abundant interfaces among FeCuNbSiB strips and epoxy resin have great contribution to microwave attenuation [29-31].

3 Conclusions

1) An interface layer is successfully obtained, which can be used to solve the non-infiltration problem effectively between the ribbon and epoxy resin. The interface layer is an endogeny conversion coat composed of $Cu_{0.75}Fe_{2.25}O_4$ and Fe_3O_4 phases. The bonding strength between the interface layer and strips is very strong. Infiltration between the interface layer and epoxy resin is excellent.

2) FeCuNbSiB amorphous alloy strips/epoxy resin ply is prepared according to FSS grid design, the electromagnetic wave absorption peaks of ply appears in the frequency range of 13~18 GHz and the value of reflectivity R is between -5~-10 dB. The value of absorption peaks remains constant but absorption peak frequency bands shift to lower frequency along with increasing ply number.

3) The application of FeCuNbSiB strips on absorbing composites materials demonstrates good absorbing performance without using other absorbing agent and increasing the thickness. This kind of character can be used to modify radar absorbing properties of other composites and to broaden absorption band.

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FeCuNbSiB 非晶带材/环氧树脂复合材料界面设计及其吸波性能

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摘　要：针对 FeCuNbSiB 非晶带材与环氧树脂基体不浸润的难题，通过表面化学改性，在 FeCuNbSiB 非晶带材两面分别生成一层厚度 5 ~10 μm、相结构为 $Cu_{0.75}Fe_{2.25}O_4$ 和 Fe_3O_4 的界面层。结果表明：界面层与带材结合强度高，与环氧树脂浸润性好；以 FeCuNbSiB 非晶带材为增强材料，同时按 FSS 网络设计的 FeCuNbSiB 非晶带材/环氧树脂铺层在 13~18 GHz 频带出现 R=-5 ~ -10 dB 的吸收峰。增加铺层数，吸收峰值不变，但吸收峰频带往低频率方向移动。利用此特性可以修正其它复合材料的雷达波吸波特性，拓宽吸收频带，增加吸波性能。

关键词：FeCuNbSiB非晶带材；界面；表面化学改性；吸波性能

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