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Environmental Friendly Modification of the Superhydrophobic Surface for Iron-Based Amorphous Alloy Films and Their Magnetic Surface Effect

Rongyu Liu, Zhifen Yuan, Zhenghou Zhu,* Sangmin Park, Hui Zhao, and Jia Zhou

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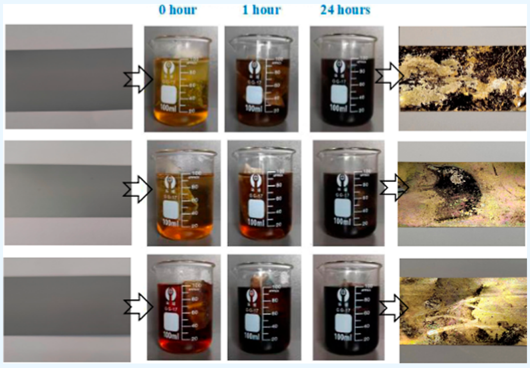
ABSTRACT: It is challenging to convert the superhydrophobic surfaces of iron-based amorphous films into hydrophilic surfaces through surface treatment. In this study, a novel, environmentally friendly method is used to change the superhydrophobic surfaces of $Fe_{78}Si_{13}B_9$ amorphous alloy films, which include their rougher and smoother surfaces. The boron element in the films reacted with the flavonoids and anthocyanins in the solution to create organic conversion membranes and organic boronizing naphthoquinone derivatives on the surfaces of the films when they were dipped in tea polyphenol aqueous solution at 80 °C for 60 min. On the rougher surface and the smoother surface, the organic conversion membranes had thicknesses of about 10 and 3 μm, respectively. When iron-based amorphous alloy films were employed as soft magnetic materials to create electronic and electrical devices, the packaging issue caused by low wettability with epoxy resin had been resolved because both the side surfaces of modified films had good wettability with epoxy resin. In addition, the magnetic surface effect of modified films was significant. After surface treatment, the inductance value of the film decreased by more than 25%. The magnetic surface effect of iron-based amorphous films can be applied to the preparation of tea sensors, and the sensor can achieve the "one to one" high precision test of "one tea curve". The magnetic surface effect of the film provides a quick, simple, lower cost, and strong anti-interference idea for the rapid detection of tea polyphenols.



1. INTRODUCTION

Because of their unique microstructure, excellent mechanical properties, and soft magnetic properties and having the advantages of high magnetic conductivity, high saturation magnetic sensitivity, low coercivity, low iron-loss value, and good thermal stability and corrosion resistance, iron-based amorphous alloy films are widely used as soft magnetic materials in the manufacture of transformers,[1] sensors,[2,3] and other devices.[4−6] When iron-based amorphous alloy films are used as soft magnetic materials to make electronic and electrical devices, they need to be encapsulated with organic resin (such as epoxy resin). Therefore, it is very important to modify the surface of the films to improve their wettability to resin.[7,8]

On the other hand, using the sensitive characteristics of the amorphous structure combined with the characteristics of film toughness,[9,10] high strength, and good magnetic performance, iron-based amorphous alloy films can be used as flexible film sensors to measure changes in magnetic signals, which has attracted great attention in wearable electronic devices,[11] electronic skin, food, clinical medicine, and industrial fields (such as complex surfaces).[12−16] Based on sensor domain applications, the study of the magnetic surface effects of films is a key problem.

During the preparation of iron-based amorphous alloy films, two kinds of surfaces with different characteristics are formed. One is the rougher surface with larger surface roughness and many defects, such as pores, which present weaker superhydrophobic characteristics than the other surface. The other is the smoother surface with lower surface roughness, fewer impurities, and stronger superhydrophobic characteristics than the rough surface.[7,8,17,18] The surface of iron-based amorphous films is not only hydrophobic but also oleophobic.[17]

At present, the surface modification of iron-based amorphous alloy films is based on the rougher surface with weaker superhydrophobic characteristics, and the chemical conversion membranes are mainly prepared by the oxidation method. An endogenous transformation film composed of

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$Cu_{0.86}Fe_{2.14}O_4$ and $Cu_{0.86}Fe_{2.14}O_4$ was generated through the transformation reaction on the surface of the catalyst, which improved the wettability between the amorphous alloy band and the epoxy resin.[17] A kind of film on the surface of an iron-based amorphous alloy with a thickness of about 1 μm was formed by reacting in a mixed weak acid environment at 85 °C for 2 h. These surface treatment technologies, however, are all aimed at the rougher surface. It is difficult to modify the smoother surface with strong superhydrophobic characteristics.

Inspired by the strong anti-oxidant effect of tea polyphenols in tea, this paper attempts to use environmentally friendly tea polyphenol treatment technology to solve simultaneously the surface modification problem of the rougher surface and the smoother surface of iron-based amorphous alloy films, which will improve the hydrophilicity of both sides of the film to epoxy resin. The results will effectively solve the epoxy resin packaging problem of iron-based amorphous alloy films used as soft magnetic materials for electronic and electrical devices. At the same time, it will provide a quick and simple, low-cost, and strong anti-interference scheme for the rapid detection of tea polyphenols sensor through magnetic surface effect research.

2. MATERIALS AND METHODS

In this paper, $Fe_{78}Si_{13}B_9$ amorphous alloy films were prepared by the rapid solidification method (Figure 1). The thickness of the film is about 16 μm (Figure 3a), the Young's modulus is about 130 GPa, and the tensile strength is about 2 GPa (Figure 2). It has good soft magnetic properties.

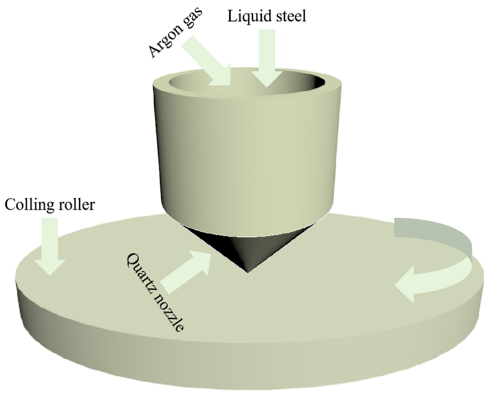

Figure 1. Preparation process of the $Fe_{78}Si_9B_{13}$ amorphous film.

First of all, a surface treatment was applied to the films. The sample was placed in an anhydrous ethanol/acetone mixture for ultrasonic shock to remove the excess oil on the film surface, and then, deionized water was used several times to remove the inorganic impurities so that the amorphous surface of the alloy was completely bare. The amorphous alloy film was then reacted in an aqueous solution of tea polyphenols at 80 °C and a pH of 5−6, and the transformation film was formed on the surface. Three different concentrations of tea polyphenol solutions were selected for the comparison test: green tea solution (tea polyphenol concentration of 350 mg/g), jasmine tea solution (tea polyphenol concentration of 230 mg/g), and oolong tea solution (tea polyphenol concentration of 100 mg/g).

The phase structure of the films was measured by the RIGAKU X-ray diffraction instrument. The micromorphology of films was observed by cold field emission scanning electron microscopy (FESEM), JSM-7500F (JEOL, Japan), and the elements in films were further detected by EDS. Raman spectroscopy was used to further analyze the surface material of the film.

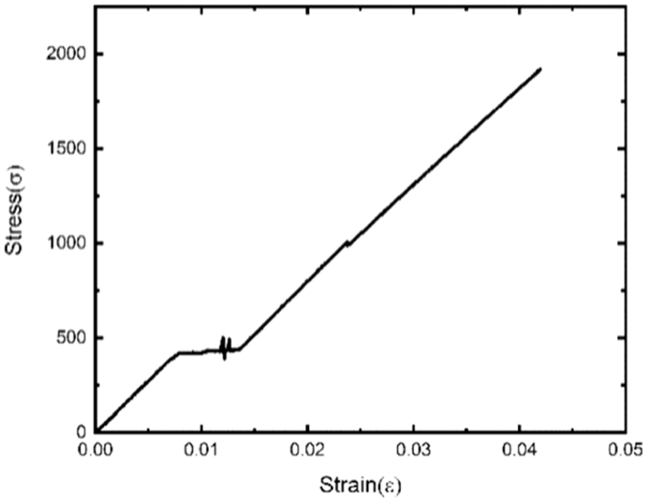

Figure 2. Stress−strain curve of the $Fe_{78}Si_9B_{13}$ amorphous film.

The magnetic surface effect is characterized by the inductance of the amorphous alloy film. The real-time inductance value, Ls, was tested by the TH2816LCR digital bridge. The test frequency was 1 kHz and the test voltage, V, was 0.3 V.

3. EXPERIMENTAL RESULTS

There is no sharp diffraction peak corresponding to the crystal in the XRD spectrum of the $Fe_{78}Si_9B_{13}$ amorphous alloy film, but there is a diffuse diffraction peak for 2θ being about 45°, which indicates that the $Fe_{78}Si_9B_{13}$ amorphous alloy film is amorphous (Figure 4).

During the preparation process of the $Fe_{78}Si_9B_{13}$ amorphous alloy film, two kinds of surfaces with different characteristics are formed. The surface directly contacting the substrate is called the "rough surface" (Figures 3c and 5a). This surface replicates the surface morphology of the substrate with greater surface roughness and has a lot of porosities and other defects. The surface color is dark. The rough surface is a super-hydrophobic surface; the other surface is the smooth surface, which has lower roughness, fewer impurities such as pores, and a brighter color. The smooth surface is a more powerful superhydrophobic surface (Figures 3b and 5b).

It was observed that after the treatment of tea polyphenol aqueous solution, the color of the tea polyphenol aqueous solution gradually changed from clear and transparent to cloudy and black within 60 min (Figure 6). Meanwhile, it was observed that the color of the film changed from silver to gold, and there were black appendages on the surface. The higher the concentration of tea polyphenol, the blacker the appendage on the surface (Figure 7). The microstructure observation shows that a uniform and dense surface conversion membrane is formed on the surface of an amorphous alloy film, and the average thickness of the conversion membrane on the rougher surface is about 10 μm, and the average thickness of the conversion membrane on the smoother surface is about 3 μm (Figure 8). EDS energy spectroscopy analysis of the film surface shows that the main components of the amorphous alloy film are the Fe, Si, and B elements, while the main components of the conversion membrane are the C, O, B, Fe,

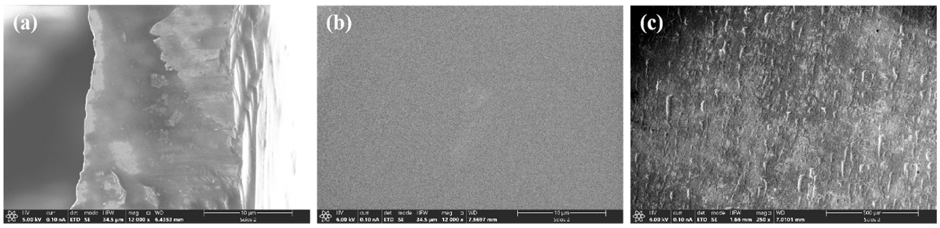

Figure 3. Surface morphology of the $Fe_{78}Si_9B_{13}$ alloy film: (a) micromorphology of the side surface, (b) micromorphology of the smooth surface, and (c) micromorphology of the rough surface.

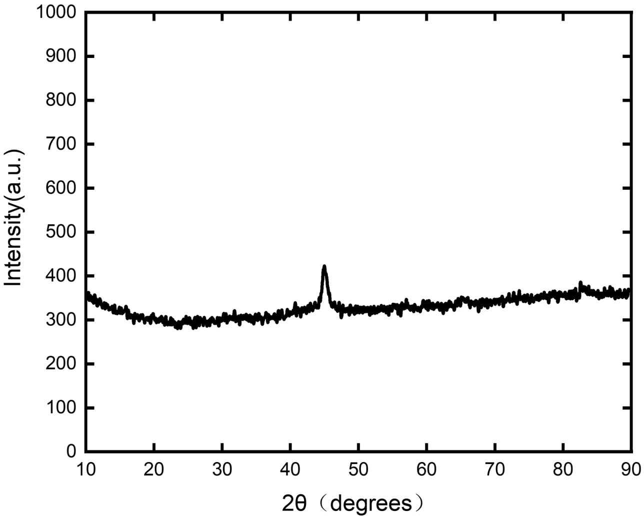

Figure 4. XRD patterns of the $Fe_{78}Si_9B_{13}$ amorphous film.

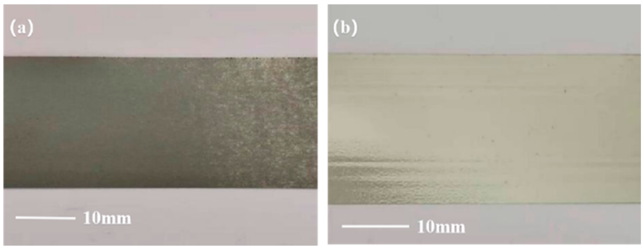

Figure 5. Surface morphology of the $Fe_{78}Si_9B_{13}$ alloy film: (a) macroscopic morphology of the rough surface and (b) macroscopic morphology of the smooth surface.

and Si elements. The EDS element analysis also revealed that the conversion membranes were also generated in the defects of the amorphous alloy film (Figure 9). The XRD spectra show that the treated films have broader peaks than those before treatment, indicating a stronger diffuse reflectance, a more short-range disordered film surface structure, and the generation of new organic phases of amorphous matter (Figure 10). The Raman spectrum analysis of the surface conversion membrane showed that there were two strong peaks near 1250 and 1650 cm^{-1}, corresponding to the Raman lines of naphthalene derivatives (Figure 11). In the air, tea polyphenols were easily oxidized to quinones. Combined with EDS analysis, the surface conversion membrane was an organic boronizing naphthoquinone derivative.

An iron-based amorphous alloy is a short-range ordered and long-range disordered material composed of Fe, Si, and B atoms. Its unique atomic arrangement makes it extremely high specific surface energy and in a metastable state, which gives the material many special properties, including its special extremely disordered atomic arrangement and numerous surface defects that give it high coordination unsaturation and many reactive active sites, so it is an excellent catalytic degradation, adsorption, reaction and other materials.[19−21] When the tea polyphenols molecules contact the amorphous alloy film surface, the O atoms of the organic molecules directly reduce the electrons, while the zero-valent Fe atoms on the film surface lose the electrons and enter into the solution as divalent iron ions to form a complex transformation film on the film surface, the color of tea polyphenol solution turns black. The tea infusions brewed in water with higher pH and total dissolved solids (TDS) generally had a darker color and lower overall sensory acceptability. Moreover, those infusions had less catechins, particularly galloylated-catechins, and lower antioxidant capacity.[22] The boron element in the iron-based amorphous film reacts with flavonoids and anthocyanins in the polyphenol solution to generate naphthoquinone derivatives of organic boride. The polyphenols in the solution decrease and the color becomes darker, and the pH value increases from 5.5 to 6.5 within 50 min. Referring to the iron-based amorphous alloy film, the reaction rate of AOII is 1000 times that of nano-zero valent ferropowder, and its reaction activation energy

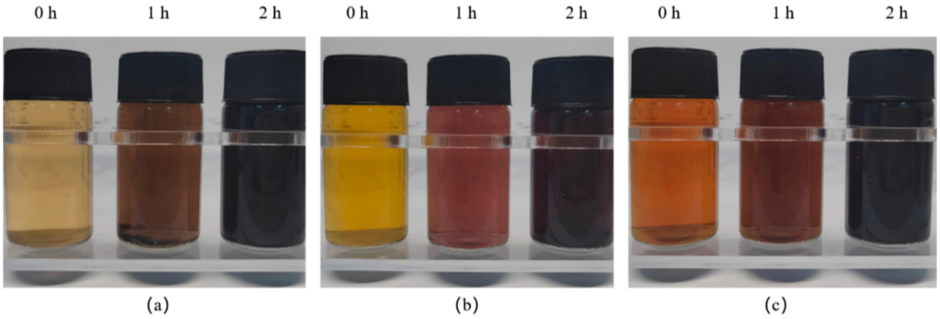

Figure 6. Color change of tea polyphenol solution treated for 24 h: (a) green tea solution, (b) jasmine tea solution, and (c) oolong tea solution.

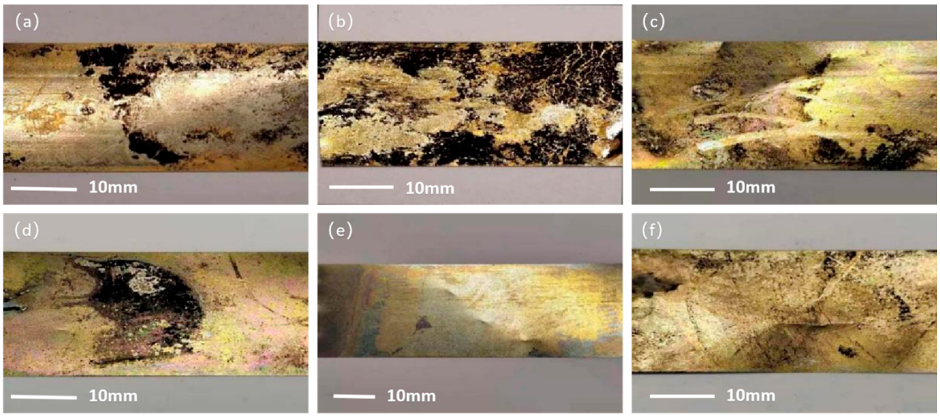

Figure 7. Macroscopic surface morphology of treated $Fe_{78}Si_9B_{13}$ alloy films: (a) smooth surface after green tea solution treatment, (b) rough surface after green tea solution treatment, (c) smooth surface after jasmine tea solution treatment, (d) rough surface after jasmine tea solution treatment, (e) smooth surface after oolong tea solution, and (f) rough surface after oolong tea solution.

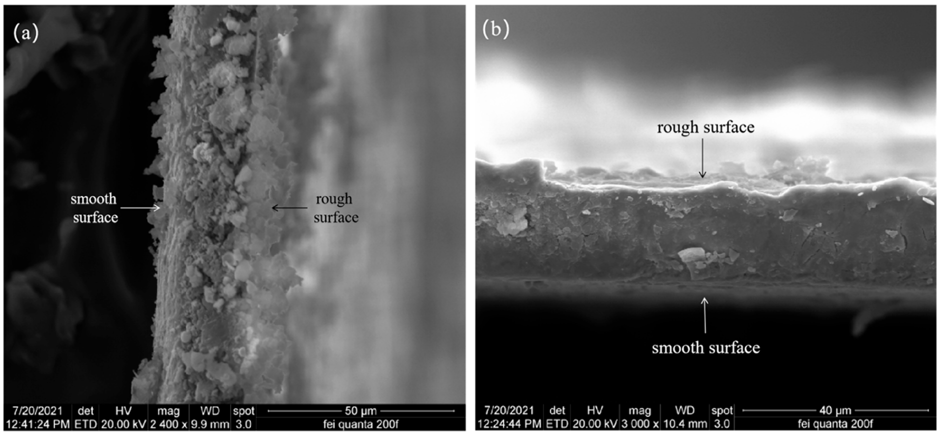

Figure 8. Microscopic surface morphology of treated $Fe_{78}Si_9B_{13}$ alloy films: (a) smooth facing outside and (b) rough facing outside.

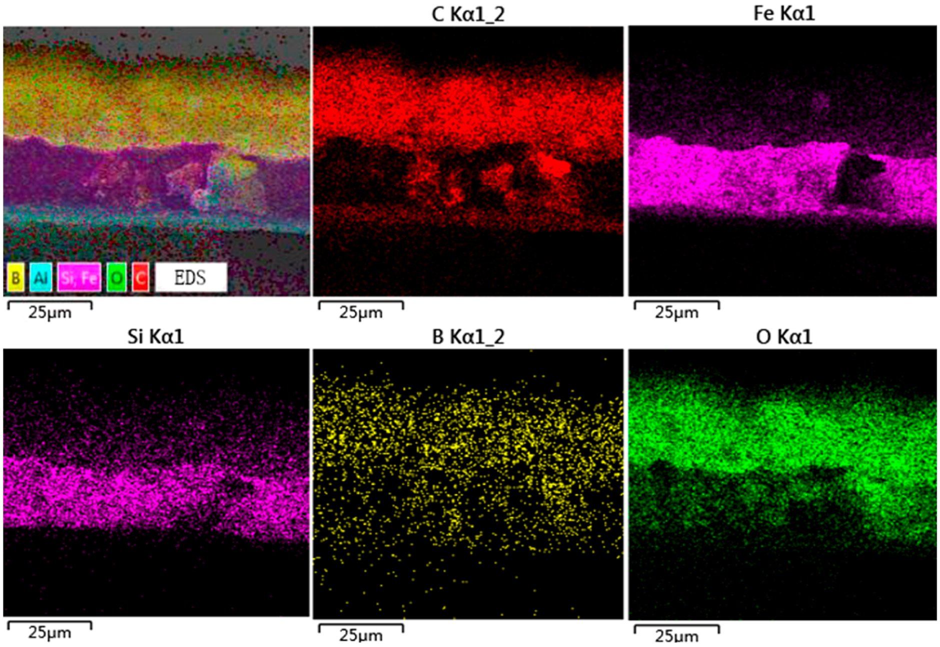

Figure 9. Elemental mapping images of treated $Fe_{78}Si_9B_{13}$ alloy films.

(27.9 KJ/mol) is much lower than that of the ordinary thermochemical reaction (60−250 KJ/mol), indicating that the amorphous alloy has high catalytic properties[23] in degraded dye wastewater.

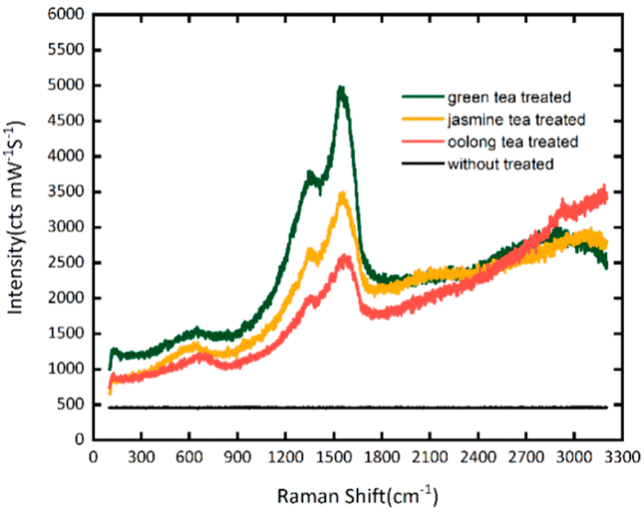

Figure 10. XRD patterns of surface transformation films.

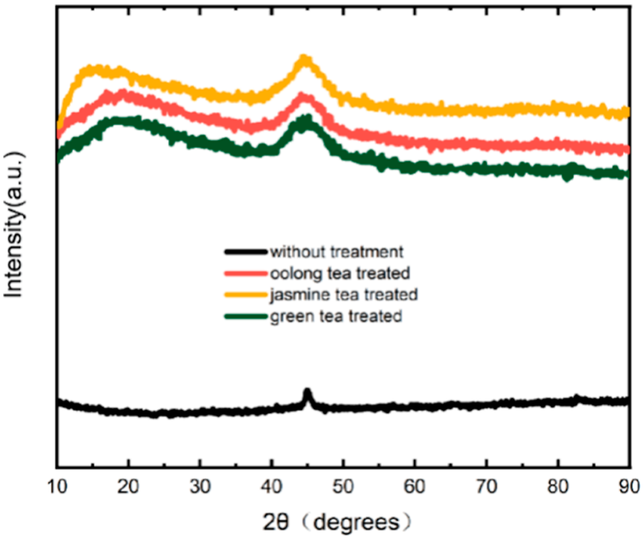

Figure 11. Raman spectroscopy of surface transformation films.

Analysis of amorphous alloy film micromorphology and structure and elements of the surface transformation film, combined with the surface structural characteristics of iron-based amorphous alloy thin films, it can be speculated that the formation process of the surface transformation membrane includes two processes: adsorption and diffusion reaction. First of all, the large number of defects on the surface of the film have a strong adsorption effect on tea polyphenols molecules in solution. Tea polyphenols molecules in solution were adsorbed to the surface of the film. Then, the oxidation of zero-valent iron atoms inside the film produces atomic hydrogen in the water, so that the C−O bond adsorbed in the tea polyphenols molecules on the surface is produced by the atomic hydrogen reduction lysis. Meanwhile, the zero-valent B atoms and Si atoms inside the membrane react with active O atoms to form class C−O−B polymer materials that eventually form complex structures. The reactant is adsorbed to the film surface and produces a diffusion reaction of Fe and B atoms. The binding interface layer of the transformed membrane and the membrane matrix changes from a simple adsorption interface (physical binding) to a diffusion reaction interface (chemical bond bonding), so the interface binds well.

4. SURFACE INFILTRATION AND MAGNETIC SURFACE EFFECTS

The film before and after treatment is immersed into E51 epoxy resin, slowly pulled out after the film surface is in full contact with the resin, and pulled up to observe the shrinkage phenomenon of epoxy resin on the surface of film to evaluate the infiltration of the iron-based amorphous film to epoxy resin (Figure 12).The surface resin without treatment with tea polyphenols water solution contracted rapidly, gradually unable to cover the surface of the film, and only a small amount of resin remained after 6 h, while the film lifting after treatment with tea polyphenols water solution showed good coating of epoxy resin, the resin evenly spread on the film surface and still showed no loss after 6 h. The contact angle between the film and the epoxy resin before treatment was 101°, while the contact angle between the film and the epoxy resin after treatment with tea polyphenol solution was only 25.6°, proving that the wettability was significantly improved (Figure 13). Experiments show that the transformed film generated on the film surface after tea polyphenols solution treatment can significantly improve the infiltration of iron-based amorphous film and epoxy resin and solve the problem of non-infiltration with epoxy resin matrix during the film packaging.

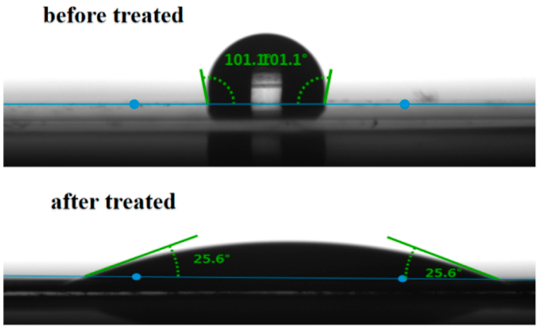

Figure 13. Contact angle of film and epoxy resin treated with tea polyphenol aqueous solution.

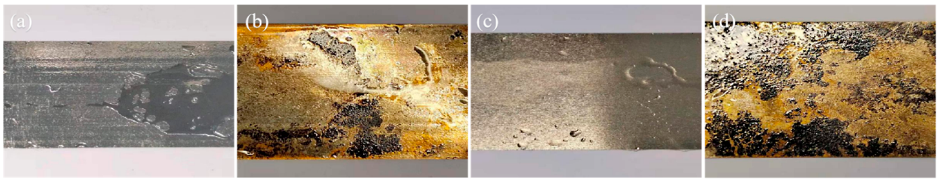

Figure 12. Wettability of film and epoxy resin treated with tea polyphenol aqueous solution: (a) smooth surface with epoxy resin infiltration before treatment, (b) smooth surface with epoxy resin infiltration after treatment, (c) rough surface with epoxy resin infiltration before treatment, and (d) rough surface with epoxy resin infiltration after treatment.

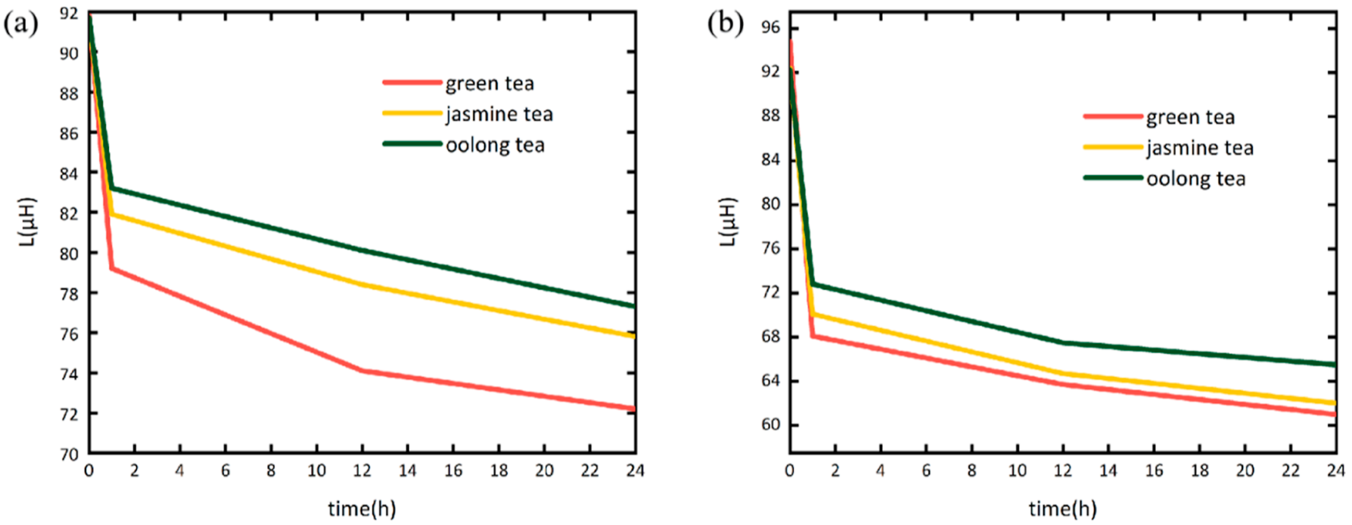

Figure 14. Inductance values after the thin-film surface treatment: (a) reaction temperature of 32 °C and (b) reaction temperature of 80 °C.

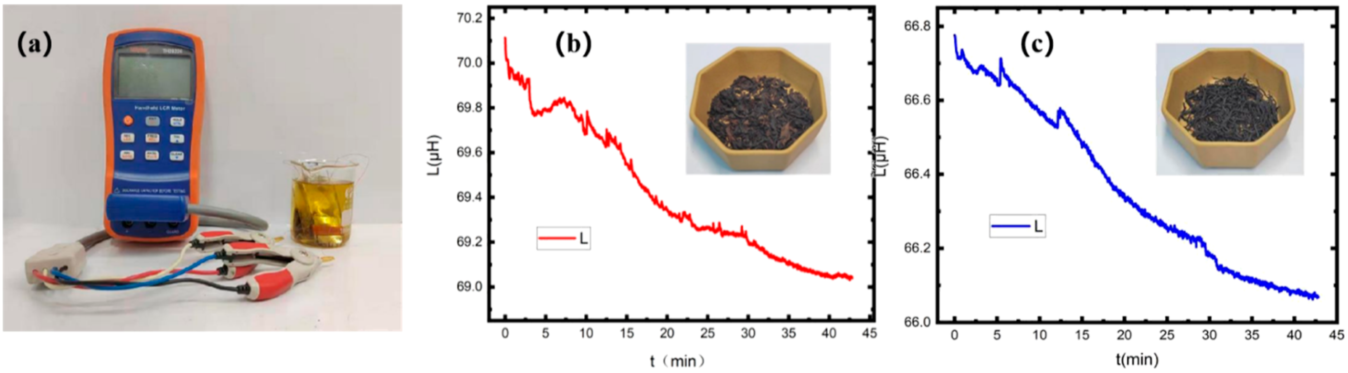

Figure 15. Tea polyphenol detection sensor and inductance change curves of Chinese famous tea: (a) tea polyphenol detection sensor, (b) inductance change curves of Da Hong Pao, and (c) inductance change curves of Pu'er.

The inductance value of ferro-based amorphous alloy films changed after surface modification and produced a magnetic surface effect. The iron-based amorphous alloy film decreased significantly after the surface treatment at room temperature (32 °C), with the maximum decrease from the treatment to 1 h, 1 h with the surface conversion membrane, and no longer significantly changed after 24 h (Figure 14a). The greater the concentration of tea polyphenols, the greater the film inductance value decreases. When the tea polyphenol concentration was 350, 230, and 100 mg/g, the film inductance decreased at 1 h by 12, 8.1, and 1%, respectively. After 24 h, the film inductance decreased by 20, 15.5, and 14.5%, respectively. Increase the surface treatment temperature, the membrane magnetic surface effect was more significant. The film surface treatment temperature is 80 °C. When the tea polyphenol concentrations were 350, 230, and 100 mg/g, after 1 h of surface treatment, the thin-film inductance decreased by 25.1, 25.8, and 20.5%, respectively. The thin-film inductance decreased by 33.8, 31, and 32.8%, respectively, after 24 h of surface treatment (Figure 14b).

The magnetic surface effect of $Fe_{78}Si_{13}B_9$ amorphous alloy films is complex and a system effect, whose mechanism can be analyzed in two aspects. On the one hand, when the surface of the film generates a conversion membrane, the loss of iron atoms objectively causes the magnetic effective thickness of the film to decrease, so the inductance value decreases; on the other hand, the anisotropic internal stress surface makes the magnetic anisotropy of the film, when the film surface conversion membrane is generated, conducive to reducing the film surface magnetic anisotropy, which makes the film inductance value increase. At the initial stage of surface conversion film generation, the higher the concentration of tea polyphenols, the more conversion units per unit time, the faster the inductance value decreases, and the surface conversion film generation gradually reaches saturation after 24 h of reaction, no more new material conversion occurs, and the inductance value decreases to the minimum value, so the percentage decrease of the inductance value of the films treated with three different concentrations of tea polyphenol solutions tends to be similar after 24 h. When the surface treatment temperature increases, it is conducive to the rapid generation of the surface transformation film, and the thickness of the transformation film is further increased, leading to a large reduction of the magnetic effective thickness of the film, which becomes the determinant of the decline of the film inductance.

Based on the fact that tea polyphenol solutions can surface treat iron-based amorphous films and change the inductance, the corresponding tea sensing device can perform one-to-one detection of different types of tea solutions. The tea polyphenol detection sensor has the advantages of high sensitivity, fast detection speed, and strong anti-interference ability, which can be widely used to detect the quality of various kinds of tea (Figure 15a). The above figure shows the inductance variation curves of the famous Chinese tea Dahongpao (Figure 15a) and Pu'er (Figure 15b). In this study, our sensor can achieve the "one to one" high precision test of "one tea curve", providing a fast, simple, low-cost, and strong anti-interference scheme for the detection of tea polyphenol content and evaluation of tea quality.

5. SUMMARY AND CONCLUSIONS

An environmentally friendly surface treatment technology, tea polyphenol treatment technology, is adopted to modify the superhydrophobic surfaces consisting of the smoother surface and the rougher surface of $Fe_{78}Si_{13}B_9$ amorphous alloy films. Organic boronizing naphthoquinone derivatives with a uniform thickness were formed on the surfaces of films. The thickness of organic conversion membranes was approximately 10 μm on the rougher surface and 3 μm on the smoother surface.

Both the side surfaces of modified films have good wettability with epoxy resin, which solves the packaging problem when $Fe_{78}Si_{13}B_9$ amorphous alloy films are adopted for electronic and electrical devices as a soft magnetic material.

After the surface cation, the modified films of $Fe_{78}Si_{13}B_9$ amorphous alloy have a significant magnetic surface effect. The magnetic surface effect increases with improving the surface treatment temperature. At the surface treatment temperature of 80 °C, the film inductance decreased by more than 25% when the tea polyphenol concentration was $\geq$230 mg/g. The magnetic surface effect of iron-based amorphous films can be applied to the preparation of tea sensors. The sensor can achieve the "one to one" high precision test of "one tea curve", providing a fast, simple, low-cost, and strong anti-interference scheme for the detection of tea polyphenol content and evaluation of tea quality.

■ AUTHOR INFORMATION

Corresponding Author

Zhenghou Zhu − *College of Physics and Materials, Nanchang University, Nanchang 330031, China;*
Email: zhuzhenghou@ncu.edu.cn

Authors

Rongyu Liu − *College of Physics and Materials, Nanchang University, Nanchang 330031, China;* orcid.org/0000-0001-6290-9082
Zhifen Yuan − *College of Physics and Materials, Nanchang University, Nanchang 330031, China*
Sangmin Park − *Korea Institute of Rare Metals, Korea Institute of Industrial Technology, Incheon 21655, Republic of Korea*
Hui Zhao − *Institute of Space Science and Technology and Jiangxi Institute of Ecological Civilization, Nanchang University, Nanchang 330031, China*
Jia Zhou − *Institute of Space Science and Technology and Jiangxi Institute of Ecological Civilization, Nanchang University, Nanchang 330031, China*

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

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