

Mircowave Absorption and Corrosion Resistance Properties of FeSiAl@Al₂O₃ Coating Materials

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ABSTRACT

Mircowave absorption materials can solve the problem of electromagnetic pollution, but corrosion in harsh environments will lead to a decrease in its absorption performance, so it is important to study materials that are both mircowave absorption and corrosion-resistant. In this experiment, FeSiAl alloy was coated Al₂O₃ (noted as FeSiAl@ Al₂O₃ coating) with aluminum chloride hexahydrate as aluminum source, and its mircowave absorption and corrosion resistance properties were studied. The results show that the mircowave absorption and corrosion resistance performance of FeSiAl@ Al₂O₃ coating both are obviously improved. The minimum reflection loss of FeSiAl@Al₂O₃ is -43.4 dB, the matching thickness is 2.3 mm, and the effective bandwidth is 2.97 GHz. For the coated alloy, the corrosion current decreases from 3.538*10⁻⁴ A/cm² to 3.499*10⁻⁴ A/cm², and the corrosion resistance increases from 96.1 ohm to 225.1 ohm. This provides an effective way to develop iron aluminum silicon materials that combine microwave absorption and corrosion resistance.

KEYWORDS

FeSiAl alloy; Aluminum chloride hexahydrate; FeSiAl@Al₂O₃ coating; Mircowave absorption performance; Corrosion resistance

1. INTRODUCTION

Mircowave absorbing materials are designed to solve the problem of electromagnetic radiation which is of great significance for protecting people's health and the detection in military radars [1-3]. For example, mircowave absorbing materials can convert electromagnetic waves into electricity, heat and other forms of release, greatly reducing electromagnetic pollution [4-6]. Mircowave absorbing materials can generally be divided into two types: magnetic absorbers and dielectric absorbers. The magnetic absorbers are the main low-frequency mircowave absorption materials. Among them, FeSiAl alloy have been gradually discovered in the field of mircowave absorption materials [7-9]. The FeSiAl alloy has the potential of anisotropy, high saturation magnetization, low coercivity, excellent permeability and good machining performance [10-12]. However, the poor corrosion resistance of FeSiAl directly affects its reliability and life in actual use [13]. Therefore, it is necessary

to design a kind of dual-function material with both microwave absorption and corrosion resistance [14, 15].

The combination of FeSiAl alloy and Al₂O₃ can improve the microwave absorption and corrosion resistance [16]. At present, the commonly used aluminum salt raw materials for packaging FeSiAl include α - Al₂O₃ powder, aluminum sulfate, aluminum nitrate and so on. Zhang et al. prepared FeSiAl@Al₂O₃ composite structures by annealing for 2 h at 400 °C using aluminum sulfate as aluminum source [17]. By adjusting the aluminum sulfate content, it is found that at 6.8 GHz and 3.0 mm thickness, the RL_{min} of FeSiAl@Al₂O₃ is -24.7 dB, and the effective absorption bandwidth can reach 2.8 GHz. The corrosion resistance of pure FeSiAl is 1.39×10⁵ Ω/cm², the corrosion resistance of FeSiAl@Al₂O₃ is 2.46×10⁵ Ω/cm², indicating that the microwave absorption and corrosion resistance of FeSiAl@Al₂O₃ are improved.

In practical applications, we need to consider the decomposition temperature of aluminum salt raw materials. Aluminum nitrate decomposes into aluminum oxide at temperatures above 200 °C, but it is expensive[18]. Aluminum sulfate decomposes into aluminum oxide at 500-700 °C, and the high decomposition temperature causes damage to the FeSiAl alloy[19]. This experiment considers that the cheap hexahydrate aluminum chloride is an inorganic compound with a low decomposition temperature, which can decompose into amorphous aluminum oxide at 200 °C[20]. The coating process will not cause damage to the FeSiAl alloy matrix itself. Therefore, hexahydrate aluminum chloride was selected as the aluminum source, and Al₂O₃ was coated on the surface of FeSiAl alloy to improve the absorption and corrosion resistance of FeSiAl alloy.

2. EXPERIMENTAL CONTENT

2.1. Experiment Reagent

Sheet ferrosilicon aluminum alloy (purchased from Changsha Hualiu Metallurgical Powder Co., LTD.), deionized water, anhydrous ethanol, aluminum chloride hexahydrate (AlCl₃H₂O, aluminum source), polyvinylidene fluoride (C₂H₂F₂, binder), acetylene black (conductive agent), N-methylpyrrolidone (C₅H₉NO, solvent).

2.2. Preparation of FeSiAl@Al₂O₃ Coating

Add 25ml of deionized water, 1g of FeSiAl alloy, and 0.4354g of hexahydrate aluminum chloride to a beaker. Mechanical stirring at 200rpm for 10 hours. The samples were centrifuged with anhydrous ethanol at a rotational speed of 7000 r/min. After centrifugation twice, dry the precipitate in an 80 °C oven for 12 hours. Heat treat the sample with a muffle furnace at 200 °C without holding. The heating rate of the muffle furnace is set to 2 °C/min.

2.3. Characterization

The crystal phase composition of the samples was analyzed by X-ray diffractometer D/MAX2500PC made by Rigaku Co., LTD., Japan, and the morphology and energy spectrum of the samples after coating were analyzed by scanning electron microscope made by Hitachi Regulus 8100, Japan. The samples were mixed with paraffin wax according to mass fraction 40 wt.%. The coaxial loop was made and tested with AV3656D series microwave network analyzer produced by CLP 41. After the electromagnetic data was obtained, the reflection loss (RL) was obtained to further characterize the microwave absorbing performance of the composite structure.

The corrosion open circuit voltage, tafel curve and impedance spectrum of the sample were measured by CHI 660E electrochemical workstation. Weigh 0.06g of heat-treated sample, 0.03g of PVDF, and 0.01g of acetylene black, place them in a mortar, and add 0.3ml of N-methylpyrrolidone. Grind for

10-15 minutes, then apply with a brush onto the copper foil and dry in an 80 degree oven for 24 hours. Afterwards, a tablet press was used for tablet pressing (at 10MPa for 30 seconds), and a hole punching machine with a diameter of 16.8mm was selected for punching. Finally, a three electrode system was used to conduct corrosion resistance testing in a 5wt% sodium chloride solution, and the samples were labeled as FeSiAl@Al₂O₃.

3. RESULTS AND DISCUSSION

Figure 1. shows the XRD of FeSiAl alloy and FeSiAl@Al₂O₃ coating. From the XRD patterns, it can be seen that aluminum chloride hexahydrate was transformed into amorphous alumina after heat treatment at 200°C, which showed that Al₂O₃ coating was successfully wrapped on the surface of FeSiAl alloy [20].

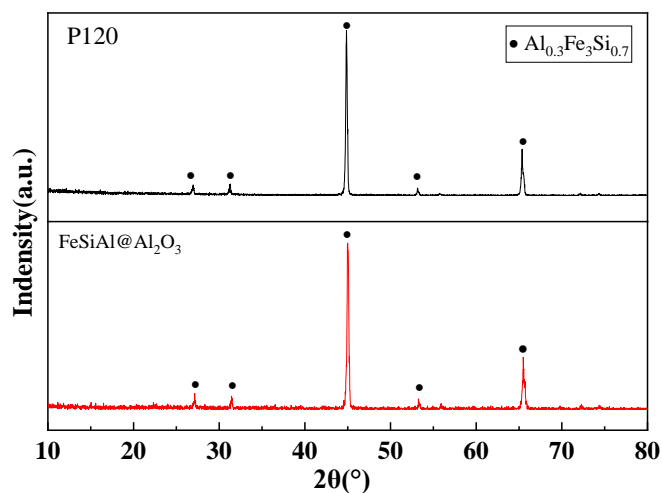


Figure 1. XRD of FeSiAl alloy and FeSiAl@Al₂O₃ coating

Figure 2(a-b) shows the SEM of flake FeSiAl, which shows that the surface is smooth and flat, with almost no graininess. **Figure 2(d-f)** shows the SEM of FeSiAl@Al₂O₃ coating. It can be seen that after the coating of Al₂O₃, the surface of the sample becomes rough and a large number of irregular particles appear, which indicates that the surface coating is Al₂O₃. **Figure 2(g)** shows the energy spectrum of FeSiAl@Al₂O₃. It can be seen from the figure that the characteristic peaks of Fe, Si, Al and O elements are the main elements in the sample, namely Fe, Si, Al and O elements. Among them, Fe was the most abundant, reaching 63.6wt%, Al 6.9wt%, and O 8.1wt%. And the mass percentage of Cl element is almost 0, which proves that aluminum chloride hexahydrate is almost oxidized to Al₂O₃. which may be Al₂O₃ generated on the surface, proving that aluminum chloride hexahydrate is mostly converted to Al₂O₃ after heat treatment at 200 °C and wrapped on the sample surface [20].

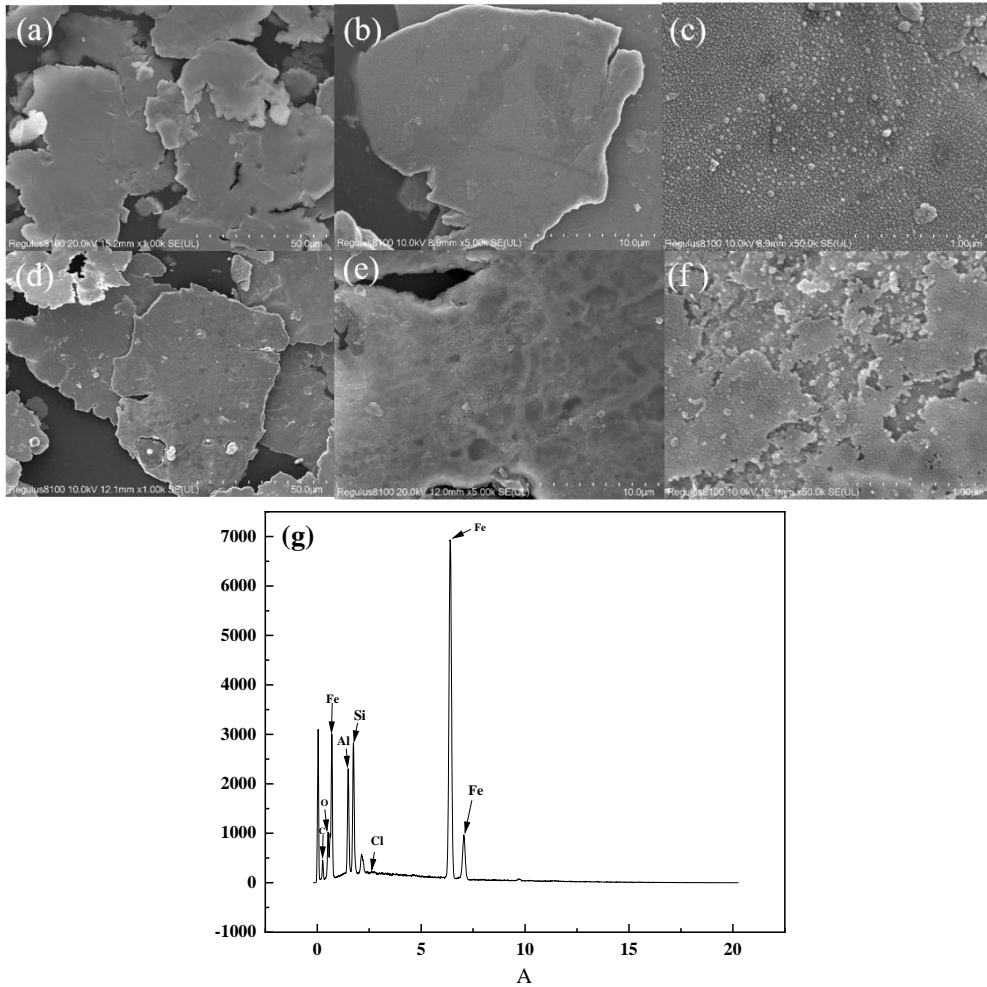


Figure 2. SEM of (a-c) Flake FeSiAl; (d-f) FeSiAl@Al₂O₃; (g) Energy spectrum of FeSiAl@Al₂O₃ coating

Figure 3.(a) shows the the real and imaginary parts of dielectric and permeability constant of FeSiAl alloy and FeSiAl@Al₂O₃ coating. The ϵ' and μ' represent the storage capacity of electric energy and magnetic energy respectively, and the ϵ'' and μ'' represent the loss of electric energy and magnetic energy respectively [21]. It can be found that the ϵ' of FeSiAl@Al₂O₃ coating is higher than that of FeSiAl alloy, and the ϵ'' of FeSiAl alloy and FeSiAl@Al₂O₃ coating is stable around 0 at 0~10 GHz, with small fluctuations in the high frequency region. In the low-frequency range, both the μ' and μ'' of the two samples show a decreasing trend with increasing frequency, and the final μ' is stable at about 1, and the μ'' is stable at about 0.

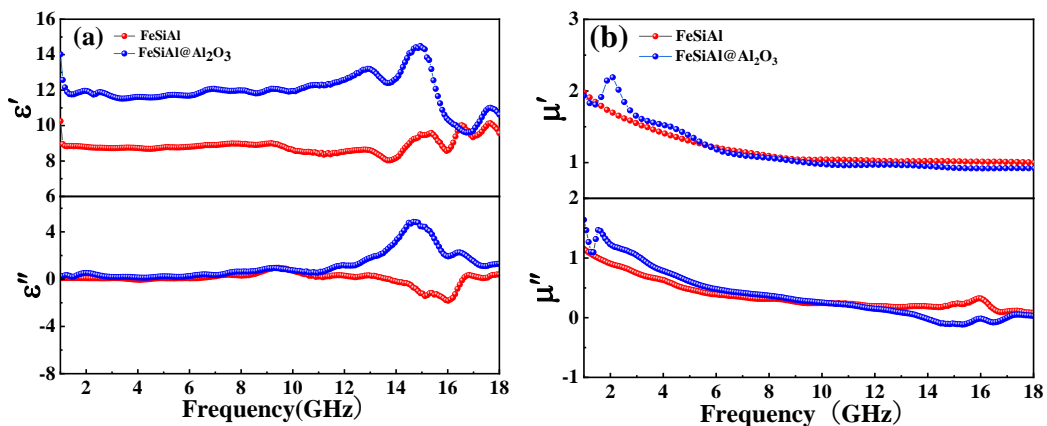


Figure 3. (a) permittivity curve and (b) permeability curve of FeSiAl and FeSiAl@Al₂O₃ coating

Figure 4. (a) shows the attenuation constant curves of FeSiAl alloy and FeSiAl@Al₂O₃ coating. It can be seen from equation (1) that the value of α is closely related to μ'' and ε'' , and it can be found that the attenuation constant fluctuates in the range of 0~150, and the attenuation constant of FeSiAl@Al₂O₃ coating is always higher than that of FeSiAl alloy. **Figure 4.** (b) shows the Cole-Cole semicircle of FeSiAl alloy and FeSiAl@Al₂O₃ coating, which is an important index reflecting the loss mechanism. The relationship between ε' and ε'' can be derived from the Debye model, equation (2). The Cole-Cole semicircle curves of both FeSiAl alloy and FeSiAl@Al₂O₃ coating contain multiple arcs, so it can be proved that the sample relaxation process exists before and after encapsulation [22].

$$\alpha = \frac{\sqrt{2}\pi f}{c} \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu''\varepsilon' + \mu'\varepsilon'')^2}} \quad (1)$$

$$(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_s - \varepsilon_\infty}{2})^2 \quad (2)$$

ε_s —Static permittivity at the high frequency limit

ε_∞ —Relative permittivity at high frequency limit

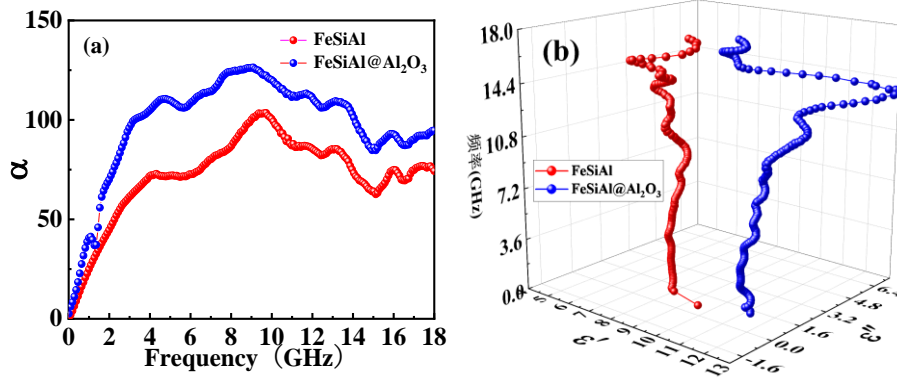


Figure 4. (a) decay constant curve (b) Cole-Cole semicircle curve for FeSiAl and FeSiAl@Al₂O₃

Figure 5. shows the tangent curves of dielectric loss and permeability loss of FeSiAl alloy and FeSiAl@Al₂O₃ coating, respectively. The dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) is used to evaluate the dielectric loss capacity of the material, and the magnetic loss tangent ($\tan\delta = \mu''/\mu'$) is used to evaluate the magnetic loss capacity of the material. In the tangent curve of dielectric loss, the value tends to 0 at the beginning, but as the frequency increases, the value fluctuates in the high frequency region. However, in the tangent curve of the permeability loss, there is a small fluctuation in the low frequency region, and the final value tends to 0. In the range of 0~10 GHz, the tangent value of the permeability loss of the two samples is higher than the tangent value of the dielectric loss, indicating that the magnetic loss is the main value of the two samples.

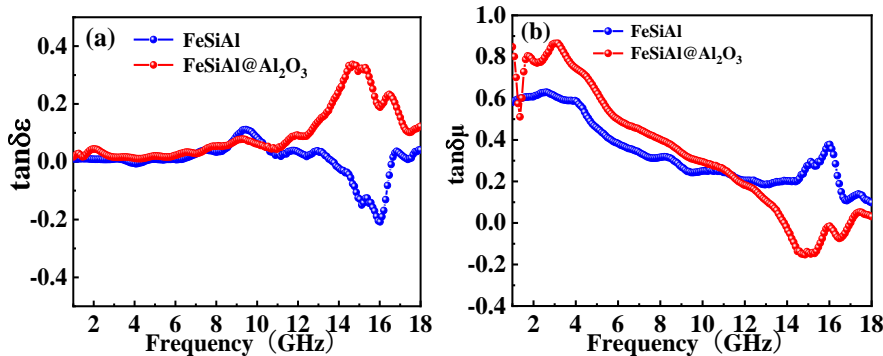


Figure 5. (a) dielectric loss tangent curve and (b) permeability loss tangent curve of FeSiAl and FeSiAl@Al₂O₃ coating

Figure 6. shows the reflection loss curves of FeSiAl alloy and FeSiAl@Al₂O₃ coating respectively. The reflection loss is related to the microwave absorption performance of the sample. The vector network analyzer is used to test the sample coaxial, and its electromagnetic parameters are obtained. Then the reflection loss is calculated according to the reflectivity formula. The formula required for reflection loss is as follows (3), (4) and (5). It can be seen from the figure that when the filler volume is 40 wt%, the FeSiAl is 4.4 GHz, the matching thickness is 5.1 mm, the effective bandwidth (RL< -10 dB) is 1.9 GHz, and the reflection loss is -41.3 dB. The minimum reflection loss of FeSiAl@Al₂O₃ coating at 9.7 GHz is -43.4 dB, and when the thickness is 2.3 mm, the effective absorption bandwidth (<-10 dB) is 2.97 GHz. FeSiAl@Al₂O₃ coating has good absorption performance and can absorb most microwave, which improves the absorption performance of FeSiAl alloy. Compared with FeSiAl alloy, the minimum microwave loss RL_{min} and effective bandwidth of FeSiAl@Al₂O₃ coating synthesized by coating Al₂O₃ are significantly improved, and the matching thickness is also obtained, which enhances the microwave absorbing performance of the material.

$$RL = 20 \log \left| \frac{Z_1 - Z_0}{Z_1 + Z_0} \right| \quad (3)$$

$$Z_0 = (\mu_0 / \varepsilon_0)^{1/2} \quad (4)$$

$$Z_{in} = Z_0 \sqrt{\mu / \varepsilon} \tanh \left(i \left(\frac{2\pi f d}{c} \right) \sqrt{\mu \varepsilon} \right) \quad (5)$$

i —imaginary unit, $i^2=1$;

d —set thickness;

c —speed of light;

Z_0 —Free space characteristic impedance;

Z_{in} —input resistance;

RL —Return Loss.

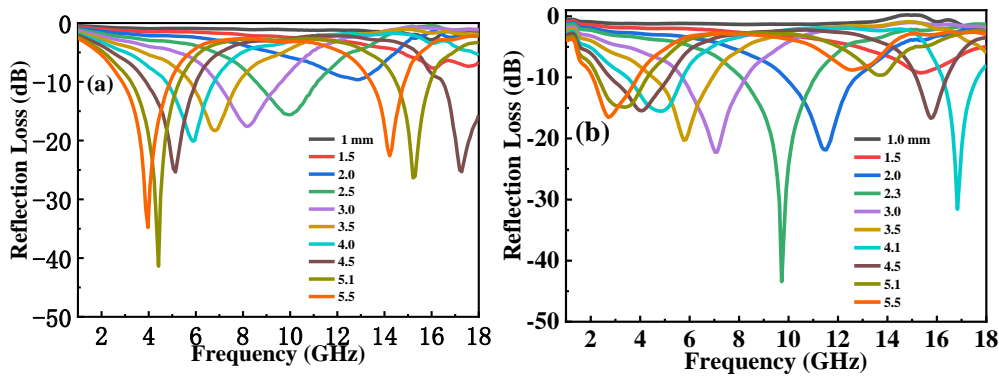


Figure 6. Reflection loss curve (a) FeSiAl(b) FeSiAl@Al₂O₃ coating

Table 1. Reflection loss of FeSiAl and FeSiAl@Al₂O₃ coating

Materials	RL/(dB)	Thickness /(mm)	Frequency (GHz)	Effective bandwidth /(GHz)
FeSiAl	-41.3	5.1	4.4	1.9
FeSiAl@Al ₂ O ₃ coating	-43.4	2.3	9.7	2.97

In order to further investigate the microwave absorbing properties of FeSiAl alloy and FeSiAl@Al₂O₃ coating, the impedance matching of FeSiAl alloy and FeSiAl@Al₂O₃ coating is further described. Generally speaking, when the impedance matching value is close to 1 ($Z_{in} = Z_0$), the microwave completely penetrates the absorber. Figure 7 shows the impedance matching of the FeSiAl alloy and the FeSiAl@Al₂O₃ coating. After encapsulating Al₂O₃, the impedance matching value is closest to 1 at 9.7 GHz, which significantly improves the impedance matching of the sample. This means that more microwaves enter the absorber than the FeSiAl alloy before the wrapping.

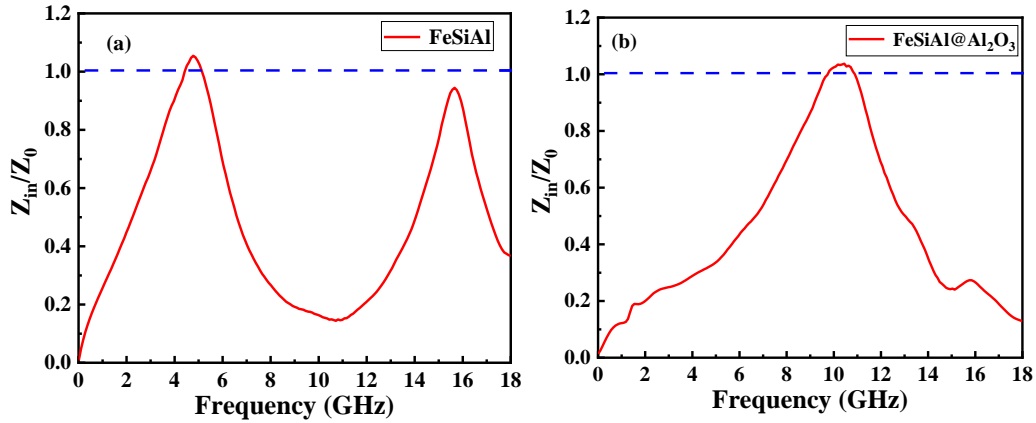


Figure 7. Impedance matching (a) FeSiAl (b) FeSiAl@Al₂O₃ coating

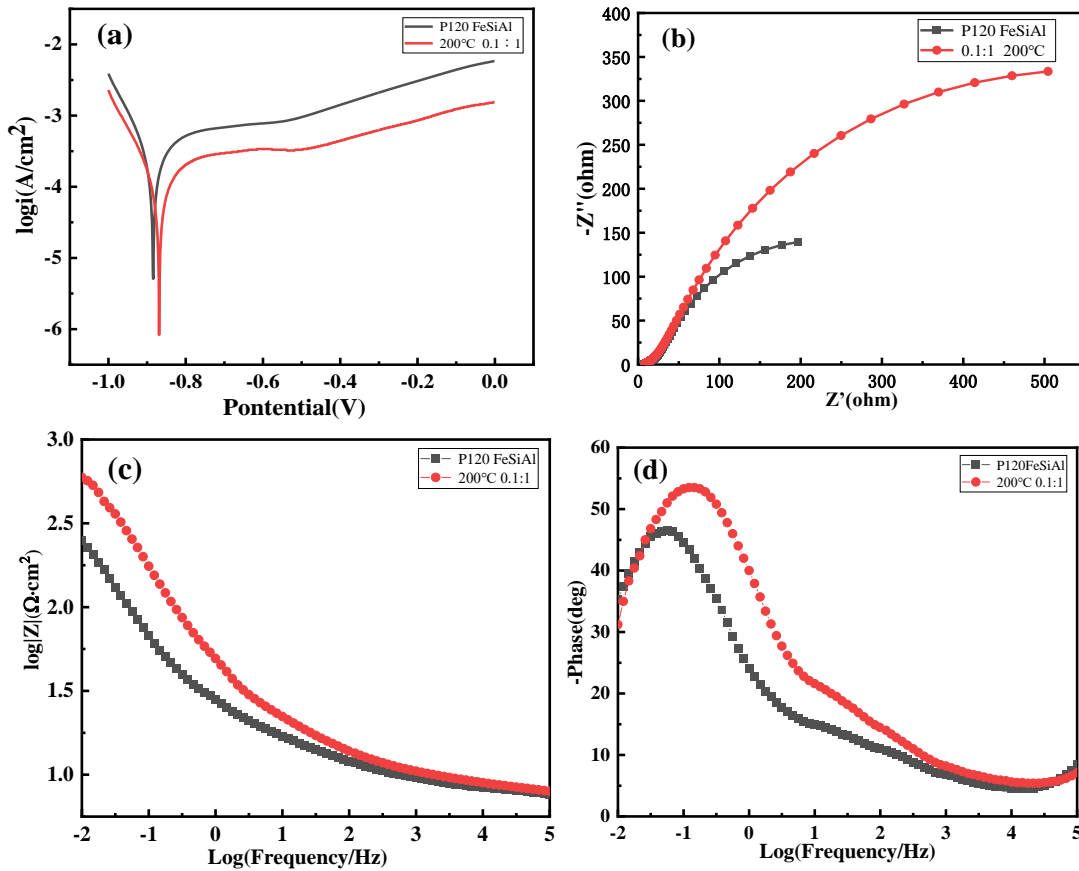


Figure 8. Corrosion resistance test of FeSiAl alloy and FeSiAl@Al₂O₃ coating (a) Tafel curve (b) Nyquist diagram (c-d) Bode diagram fitted

Figure 8. shows a comparison of corrosion resistance tests of FeSiAl alloy and FeSiAl@Al₂O₃ coating. It can be seen from the Tafel curve that, compared with unwrapped FeSiAl alloy, the self-corrosion potential of FeSiAl@Al₂O₃ coating is positively shifted from -0.884 V to -0.869 V. The

corrosion tendency of the sample coated with Al₂O₃ is reduced, and the corrosion resistance is improved. The corrosion current density of the sample coated with Al₂O₃ decreased from 3.538*10⁻⁴ A/cm² to 3.499*10⁻⁴ A/cm², and the polarization resistance increased from 96.1 ohm to 225.1 ohm. Compared with the unwrapped FeSiAl alloy, the sample coated with Al₂O₃ has better corrosion resistance.

Table 2. Electrochemical corrosion parameters of the sample

Materials	E _{corr} /(V)	I _{corr} /(A/cm ²)	R _p /(ohm)
FeSiAl	-0.884	3.538*10 ⁻⁴	96.1
FeSiAl@Al ₂ O ₃ coating	-0.869	3.499*10 ⁻⁴	225.1

4. SUMMARY

In this experiment, the FeSiAl@ Al₂O₃ coating composite structure was successfully designed. The microstructure, microwave and corrosion resistance of FeSiAl@Al₂O₃ coating composite structure were studied. The test results show that the impedance matching ability and microwave absorption performance can be improved by reasonable alumina coating. The reflection loss of FeSiAl@Al₂O₃ coating at 9.7 GHz is -43.4 dB, and when the thickness is 2.3 mm, the effective absorption bandwidth (<-10 dB) is 2.97 GHz. Electrochemical analysis was used to study the corrosion resistance of the FeSiAl@Al₂O₃ coating composite structure in 5 wt% NaCl solution. Through open-circuit corrosion potential method, electrochemical impedance spectroscopy and Tafel polarization curve tests, it is found that the corrosion current of the FeSiAl@Al₂O₃ coating decreased, and the corrosion resistance increased. This proves that the Al₂O₃ layer helps to improve the corrosion resistance of the sheet FeSiAl. FeSiAl@Al₂O₃ coating is an ideal material with improved microwave absorption and corrosion resistance.

CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest or any competing interest.

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REFERENCES

- [1] DUAN Y, LIU W, SONG L, et al. A discrete structure: FeSiAl/carbon black composite absorption coatings [J]. *Materials Research Bulletin*, 2017, 88: 41-8.
- [2] CAI X-D, JIANG X-J, XIE W, et al. Effect of particle size on the preparation and microwave absorption properties of FeSiAl magnetically soft alloy hollow microspheres [J]. *Defence Technology*, 2018, 14(5): 477-83.
- [3] MA G, DUAN Y, LIU Y, et al. Effect of surface modified SiO₂ powders on microwave absorbing properties of flaky FeSiAl coatings [J]. *Journal of Materials Science: Materials in Electronics*, 2018, 29(20): 17405-15.
- [4] XU H, BIE S, JIANG J, et al. Electromagnetic and microwave absorbing properties of the composites containing flaky FeSiAl powders mixed with MnO₂ in 1–18 GHz [J]. *Journal of Magnetism and Magnetic Materials*, 2016, 401: 567-71.
- [5] ZHOU L, YU J, WANG Z, et al. Electromagnetic and microwave absorption properties of FeSiAl and flaky graphite filled Al₂O₃ composites with different FeSiAl particle size [J]. *Ceramics International*, 2020, 46(4): 4329-34.
- [6] ZHU Y, XIE G, XIE N, et al. Electromagnetic properties of Sm-doped FeSiAl alloy absorbing materials prepared by melt spinning [J]. *Materials Science and Technology*, 2022, 38(7): 419-24.

- [7] DONG Y, LIANG X, ZHONG S, et al. A simple method for preparing flaky FeSiAl for low-frequency electromagnetic wave absorber [J]. *Journal of Magnetism and Magnetic Materials*, 2023, 574.
- [8] LI J, GUO Y, YANG R, et al. Achieving ultra-low frequency microwave absorbing properties based on anti-corrosive silica-pinned flake FeSiAl hybrid with full L band absorption - ScienceDirect. [J]. *Journal of Alloys and Compounds*, 2021.
- [9] FENG Y, TANG C, QIU T. Effect of ball milling and moderate surface oxidization on the microwave absorption properties of FeSiAl composites [J]. *Materials Science and Engineering: B*, 2013, 178(16): 1005-11.
- [10] ZHANG C, WANG X. A novel high-temperature FeSiAl-CaO-B₂O₃-SiO₂ microwave absorption coating prepared via atmospheric plasma spraying - ScienceDirect. [J]. *Ceramics International*, 2024, 50(17).
- [11] TIAN W, LI J, LIU Y, et al. Atomic-Scale Layer-by-Layer Deposition of FeSiAl@ZnO@Al₂O₃ Hybrid with Threshold Anti-Corrosion and Ultra-High Microwave Absorption Properties in Low-Frequency Bands [J]. *Nano-Micro Letters*, 2021, 13(1).
- [12] DU L, CHEN J, ZHANG Q, et al. Enhancing the Magnetic Core Properties of Ultra-Thin Flaky FeSiAl Alloy Powders Through High-Temperature Reduction Treatment [J]. *Journal of Superconductivity and Novel Magnetism*, 2024.
- [13] TAOLI L, SHUTING F, LIN L. Effect of corrosion behavior of FeSiAl electromagnetic shielding coating on wave absorption performance [J]. *Chinese Journal of Engineering Science*, 2019, 41(10): 1324-31.
- [14] YAN X, LIU F, GUO J, et al. Excellent electrically insulated, thermal-oxidation resistant and corrosion resistant flaky-FeSiAl-BN core-shell composites for high-performance microwave absorption in harsh environments - ScienceDirect. [J]. *Composites Part A: Applied Science and Manufacturing*, 2023, 175: 107778.
- [15] ZHANG X, GUO Y, ALI R, et al. Bifunctional carbon-encapsulated FeSiAl hybrid flakes for enhanced microwave absorption properties and analysis of corrosion resistance [J]. *Journal of Alloys and Compounds*, 2020, 828.
- [16] LEI C, GE C, GE X, et al. Enhanced microwave absorption of flaky FeSiAl/ZnO composites fabricated via precipitation [J]. *Materials Science and Engineering: B*, 2022, 275.
- [17] ZHANG X. Design of FeSiAl composite structure and its anti-corrosion properties [D]; University of Electronic Science and Technology of China, 2021.
- [18] EI-SHEREAFY E, ABOUSEKKINA M M, MASHALY A, et al. Mechanism of thermal decomposition and ~/-pyrolysis of aluminum nitrate nonahydrate [Al(NO₃)₃·9H₂O] [J]. *Journal of Radioanalytical & Nuclear Chemistry*, 1998, 237(1-2).
- [19] TRUEX T J, HAMMERLE R H, ARMSTRONG R A. The thermal decomposition of aluminium sulfate [J]. *Thermochimica Acta*, 1977, 19(3).
- [20] YANG Y, WANG N, PANG X, et al. Thermodynamics of the decomposition of aluminum chloride hexahydrate to prepare alumina [J]. *Journal of Materials Research and Technology*, 2021, 15: 6640-6.
- [21] SUN J, XU H, SHEN Y, et al. Enhanced microwave absorption properties of the milled flake-shaped FeSiAl/graphite composites [J]. *Journal of Alloys and Compounds*, 2013, 548: 18-22.
- [22] HUANG L, LIU X, CHUAI D, et al. Flaky FeSiAl alloy-carbon nanotube composite with tunable electromagnetic properties for microwave absorption [J]. *Scientific Reports*, 2016, 6(1).