

Synthesis and Performance of KH-560 Modified SiO₂ Insulation Coating

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Abstract: Soft magnetic alloy is the core material of the proton/heavy ion accelerator. To reduce the eddy current loss at high frequencies, the insulating coating needs to be coated on the surface of soft magnetic alloy, and to be followed-up heat treatment (~600 °C) to lower the residual stress from defects and dislocations produced in the cold forming process of soft magnetic alloys. Therefore, the insulation coating for soft magnetic alloy should meet the requirement of high-temperature resistance. SiO₂ is one of the most common inorganic coating materials, which has good insulation performance and temperature resistance, so it is especially suitable for high-temperature insulation coating. In this work, fabrication process of SiO₂ insulating coating was systematically studied. The silane coupling agent 3-glycidyloxypropyltrimethoxysilane (KH-560) was added to the phytic acid-catalyzed tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTES) sol to improve the film-forming property. Effect of KH-560 on structure and property of SiO₂ coating was analyzed in detail. The results showed that the stability and the film-forming property were improved effectively *via* adding a reasonable amount of KH-560. When adding amount of KH-560 is 0.04 mol, the as-prepared SiO₂ coating exhibits excellent film-forming characteristics, corrosion resistance and electrical insulation with sheet resistance of $2.97 \times 10^{11} \Omega/\square$ at 100 V.

Key words: soft magnetic alloy; SiO₂ coating; sheet resistance; Sol-Gel method

In recent years, with the increasing demand for spallation neutron sources, particle therapy, space effect irradiation, and other devices, the use of synchrotron has never been more extensive, which results in the continuous demand for high-grade soft magnetic alloys^[1]. The optimized goal of the soft magnetic alloy includes mainly reducing energy losses and increasing saturation inductions at high operating frequencies^[2-3].

The energy loss of soft magnetic alloys consists of hysteresis loss, eddy current loss, and excess loss. Under the high frequency operating current, the eddy current loss dominates^[4], which can be effectively reduced by applying an insulating coating on the surface of the soft magnetic alloy. The hysteresis loss arises from the internal residual stress caused by the increased density of defects and dislocations generated in the cold compaction process of the soft magnetic alloys. The subsequent heat-treatment (above 500 °C) is an effective method to release residual stress by reducing imperfections, which

results in a reduction in hysteresis loss. Therefore, the high-temperature resistance and insulating coating can significantly improve the soft magnetic alloy's performance.

Normally, the organic coatings, such as silicone and phenolic resins, have thermal resistance below 200 °C, while the inorganic coating, such as Al₂O₃^[5-6], SiO₂^[7-9], TiO₂^[10], offers an advantage of tolerating high temperature (above 500 °C). However, most of the reports are about the preparation of insulation on the surface of the powder, which remains a need for an efficient method to prepare the insulating films on the surface of the soft magnetic alloy. SiO₂ exhibits excellent insulation properties due to its large bandgap of 8.9 eV and dielectric constant of 3.9. There are many methods for preparing SiO₂ coating, such as the self-assembly method, Sol-Gel method, spraying method, impregnation method, brush coating method, and so on. And the use of the Sol-Gel method to prepare SiO₂ coating on the surface of soft magnetic alloy has

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advantages including: 1) low synthesis temperature; 2) convenience for large-area preparation; 3) uniform and controllable thickness; 4) low raw material costs; 5) simple preparation process.

When small molecular acids such as hydrochloric acid and sulfuric acid are used as catalysts, the film-forming property of SiO₂ coating is not good, due to the weak bonding force between the SiO₂ coating and the substrate. The phytic acid (C₆H₁₈O₂₄P₆), a natural and innocuous organic big molecule compound, consists of 24 oxygen atoms, 12 hydroxyl groups, and 6 phosphate groups, which makes phytic acid have powerful chelating capability with many metal ions^[11].

In this work, the phytic acid is used as a catalyst to prepare a silicon sol, and different amounts of KH-560 are used as a silicone coupled agent to modify the SiO₂ coating on the surface of the soft magnetic alloy *via* the Sol-Gel method. The microstructure and electrical properties of the SiO₂ insulating coating were investigated in detail. The coating has good high-temperature resistance and excellent insulation performance, which can be used on the surface of the soft magnetic alloy.

1 Experimental

1.1 Materials and chemical reagents

The MTES, KH-560, TEOS, and 70% (weight percent) aqueous phytic acid solution were purchased from the Aladdin Reagent Co., Ltd. (China).

1.2 Preparation of SiO₂ coating

In a typical process, different additions of KH-560 (0.01–0.04 mol), 0.0012 mol of phytic acid, and 0.4 mol of ethanol were poured into a 150 mL beaker and reacted at 70 °C for 1 h under magnetic stirring. Then, 0.15 mol of MTES, 0.03 mol of TEOS, 0.6 mol of deionized water, and 0.2 mol of ethanol were poured into the above-mentioned beaker. Finally, the mixture was continued to react at 70 °C for 1 h to obtain the silicon sol.

The SiO₂ coating was prepared by dip-coating method. In a typical process, the soft magnetic alloy was dipped into silicon sol for 1 min at a constant rate of 4×10³ mm/s. Then, the coatings were air-dried at room temperature for 12 h. The soft magnetic alloy with SiO₂ coating was thermal treatment at 570 °C for 80 min under a nitrogen atmosphere. The obtained different coating was named as SiO₂-0.01 KH, SiO₂-0.02 KH, SiO₂-0.03 KH, SiO₂-0.04 KH, respectively.

1.3 Characterizations

Phase identification of the soft magnetic alloys before and after the coating process was performed using X-ray diffraction (XRD, Rigaku MiniFlex600X, Japan) with Cu

Kα radiation. Microstructures and element composition of the SiO₂ coating were measured through S3400 scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) with 15 kV acceleration voltages. Fourier transforms infrared (FT-TR) spectra were recorded by spectrophotometer (Magna-IR 560, Nicolet Co.) in the spectral range 500–4000 cm⁻¹ to investigate the composition of the insulating coating. The sheet resistance was measured by using a high resistance analyzer MCP-HT800. The electrochemical measurements were implemented by the Solartron SI1287 Advanced Electrochemical Interface instrument & Solartron SI1260 Impedance/Gain-Phase Analyzer.

2 Results and discussions

2.1 Characterization and chemical composition

The chemical composition of the coating was elucidated through the EDS method. Fig. 1 shows the elemental compositions of the soft magnetic alloy before and after the coating process. In Fig. 1(a), the soft magnetic alloy coated with SiO₂ coating contains the C, O, P, and Si elements. The P element comes from phytic acid. Besides, the EDS profiles indicated that the O and Si signals on the soft magnetic alloy surface were enhanced after coated with SiO₂ coating compared to the raw soft magnetic alloy. The mass fraction of the O element increases from 1.72% to 22.85%, and that of the Si element increases from 8.03% to 26.23%,

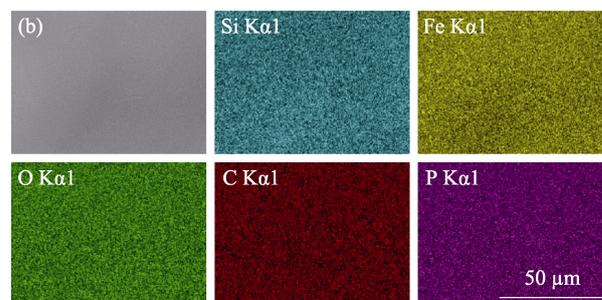
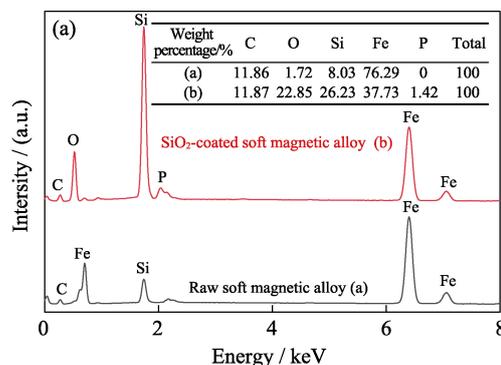


Fig. 1 (a) EDS spectra of the soft magnetic alloy before and after the coating process, and (b) EDS mapping of SiO₂ coating on the soft magnetic alloy

respectively. These results imply that the coating is SiO₂. In Fig. 1(b), it is observed that C, O, Si, and P atoms are uniformly distributed on the surface of the soft magnetic alloy.

Fig. 2(a) displays the XRD patterns of the soft magnetic alloy before and after the coating process. The diffraction peak of Fe(110) at around $2\theta=45^\circ$ can be observed, and the XRD patterns of the soft magnetic alloy before and after the chemical coating process are similar. Based on the XRD patterns and EDS data, it can be confirmed that an amorphous SiO₂ phase is formed on the surface of the soft magnetic alloy.

To further confirm the presence of SiO₂ coating on the soft magnetic alloy, the FT-IR spectra of the soft magnetic alloy before and after the coating process were measured. As shown in Fig. 2(b), compared with the soft magnetic alloy, some characteristic absorption peaks are observed after coating. The peak at around 1030 cm^{-1} is attributed to the asymmetric stretching vibration of Si–O–Si, and the symmetric stretching vibration of Si–O–Si gives rise to the peak at around 775 cm^{-1} [12]. The peak with the center located at around 1273 cm^{-1} was associated with the stretching vibration of Si–CH₃ groups. Moreover, the peak with the center located at around 3202 cm^{-1} was associated with the stretching vibration of the –OH bond, which can be contributed to the excessive amounts of the hydroxyl groups during the hydrolysis and condensation processes[5]. Therefore, the appearances

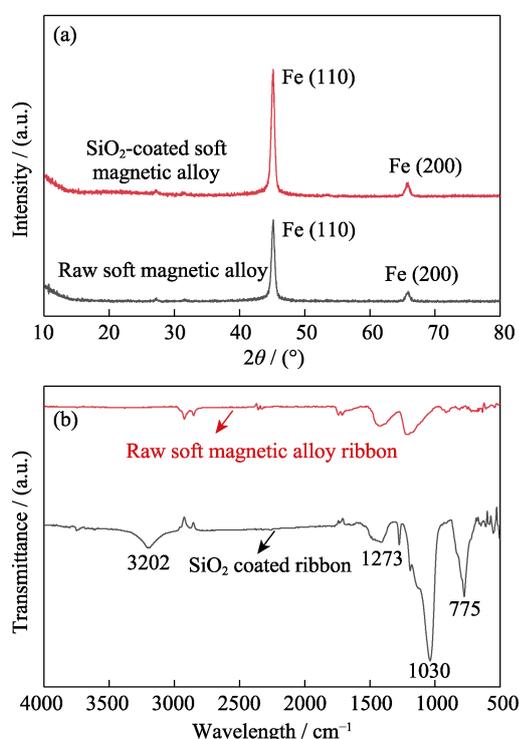


Fig. 2 (a) XRD patterns of the soft magnetic alloy before and after coating process, and (b) FT-IR spectra of the soft magnetic alloy before and after coating process

of those characteristic peaks further verify that the obtained coating on the surface of the soft magnetic alloy is SiO₂ coating.

The microstructures of the different SiO₂ coating are shown in Fig. 3. As shown in Fig. 3(a1), the SiO₂-0.01 KH coating contains some obvious cracks, which may be formed because of the higher inner stress. It could not completely cover the soft magnetic alloy surface. In Fig. 3(a2), the thickness of SiO₂-0.01 KH coating is about $1.93\text{ }\mu\text{m}$, and there are several holes in the coating section. With the increase of KH-560, the alloy surface is covered by a complete coating as shown in Fig. 3(b1, b2). But the SiO₂-0.02 KH coating still has some defects as shown in the coating section. For the SiO₂-0.03 KH coating and SiO₂-0.04 KH coating, their surfaces are more smooth and uniform. The SiO₂-0.04 KH coating possesses the most complete section and uniform thickness as shown in Fig. 3(d2).

Tafel polarization curves can characterize the corrosion resistance. Fig. 4 shows the Tafel polarization curves of SiO₂ coating with different adding amounts of KH-560. Compared with the soft magnetic alloy without coating, the corrosion current density decreases after coating, and the corrosion potential of different SiO₂-xKH samples shifts to the positive electrode region, which

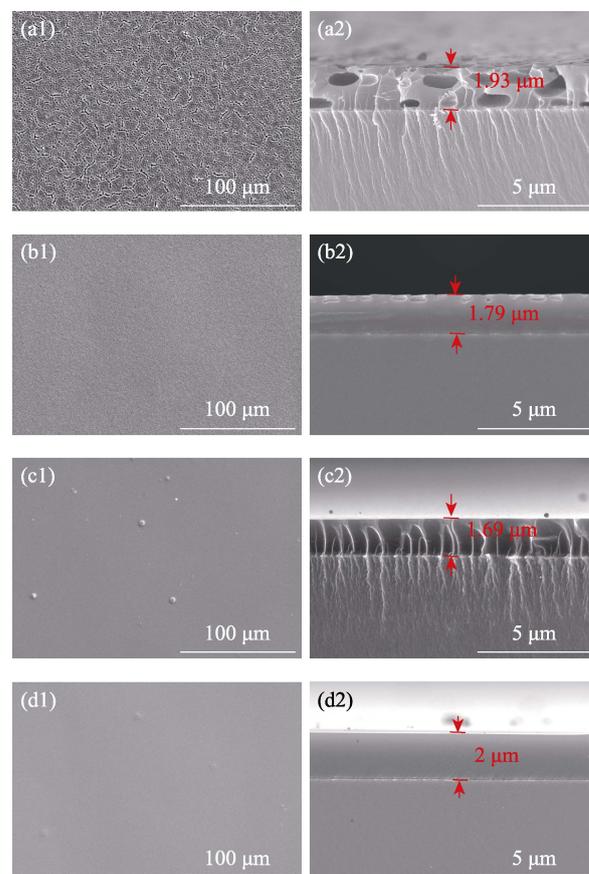


Fig. 3 SEM images of (a) SiO₂-0.01 KH, (b) SiO₂-0.02 KH, (c) SiO₂-0.03 KH, and (d) SiO₂-0.04 KH

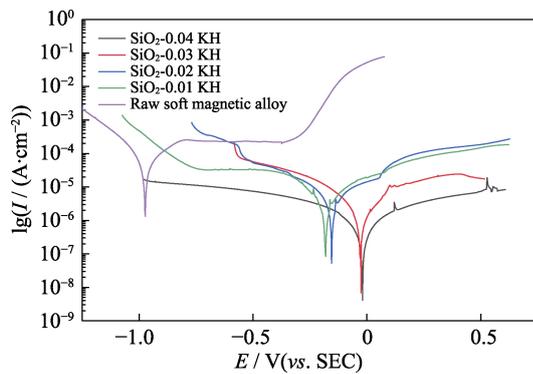


Fig. 4 Tafel polarization curves of the soft magnetic alloy with different SiO₂ coating

indicates that the corrosion resistance of the soft magnetic alloy is improved obviously after coating. The reason is that SiO₂ coating on the surface of the soft magnetic alloy slows down the corrosion rate.

In Table 1, the corrosion potential (E_{corr}), corrosion current (I_{corr}), and polarization resistance (R_p) are obtained by the Tafel epitaxial method. The corrosion current of the raw soft magnetic alloy is 4.0982×10^{-5} A/cm². Compared with the performance of 4 coating samples, the SiO₂-0.04 KH coating has the lowest corrosion current of 2.9071×10^{-7} A/cm² and the highest polarization resistance of 76910 Ω·cm². The corrosion current of SiO₂-0.04 KH coating is less than 1/10 of that of SiO₂-0.01 KH coating. The protective efficiency (PE) of the coating is calculated as follows:

$$PE = (I_c^0 - I_c) / I_c^0 \times 100\% \quad (1)$$

where, I_c^0 and I_c are the corrosion current without coating and the corrosion current of SiO₂ coating, respectively. From Table 1, the protection efficiency of SiO₂-0.01 KH coating is 81.95%, and that is up to 99.29% of SiO₂-0.04 KH coating. This indicates that the SiO₂-0.04 KH coating has the best corrosion resistance due to its good film-forming properties.

2.2 Mechanism analysis

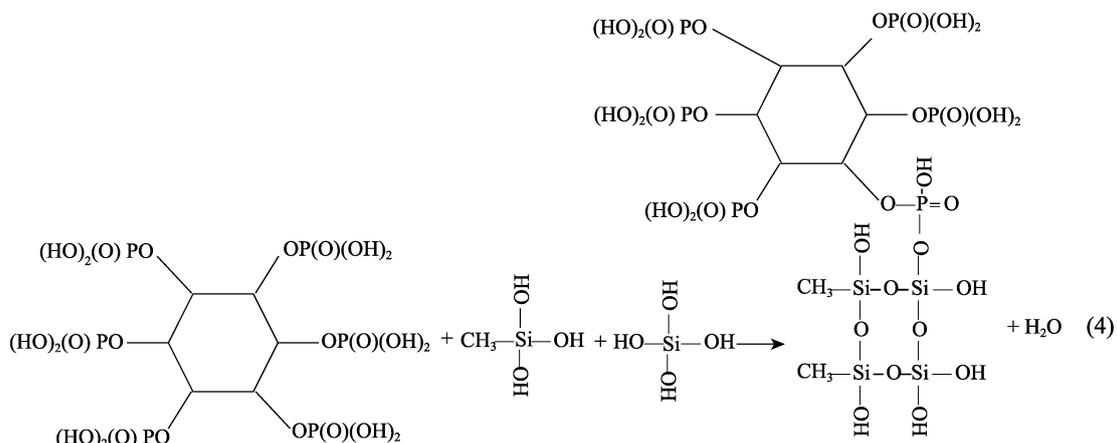
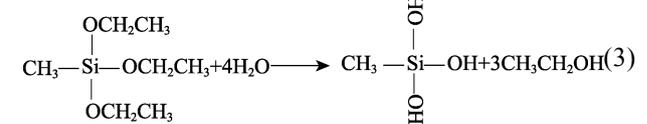
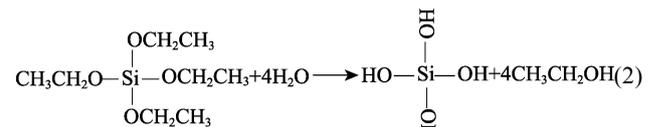
Formula (2) and (3) show the hydrolysis reactions of MTES and TEOS, which produces ethanol, Si(OH)₄, or

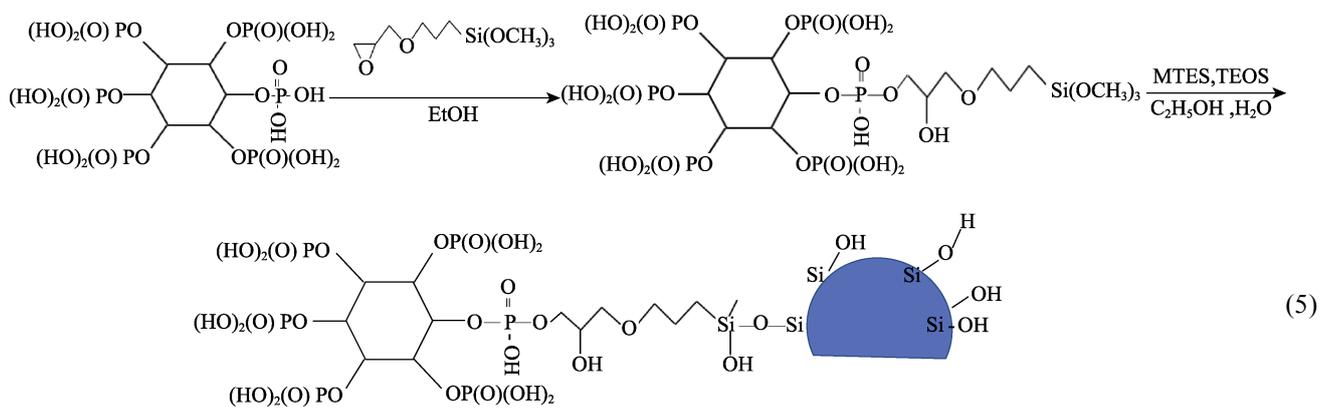
CH₃Si(OH)₃. As shown in formula (4), the P-OH groups of phytic acid react with the Si-OH group to form the Si-O-P bond that binds the phytic acid molecules with the silicon-oxygen chain. Besides, in formula (5), the P-OH in phytic acid and the epoxy bond of KH-560 can also bond in the ring-opening reaction of epoxy, which further improves the degree of cross-linking between phytic acid and Si-O-Si, and increase the P-OH groups in silica sol. Then, the product continues to undergo co-hydrolysis and condensation reactions with MTES and TEOS to form the phytic acid-bound siloxane network structure^[11].

Usually, the phosphate group, carboxyl group, and other functional groups are more easily absorbed on oxide metal surfaces. When the soft magnetic alloy is immersed in the SiO₂ solution, the surface can be slightly oxidized by the phytic acid containing 6 phosphate groups that promote adsorption of the SiO₂ molecule^[13-16]. In addition, the remaining P-OH groups in phytic acid can provide a strong chemical interaction between the substrate and the coating to improve the adhesion between them^[17].

Table 1 Sheet resistance of different SiO₂ coating

Sample	E_{corr}/V (vs. SEC)	$I_{\text{corr}}/(A \cdot \text{cm}^{-2})$	$R_p/(\Omega \cdot \text{cm}^2)$	PE/%
Raw soft magnetic alloy	-0.973	4.0982×10^{-5}	552.31	-
SiO ₂ -0.01 KH	-0.182	7.398×10^{-6}	8559.9	81.95
SiO ₂ -0.02 KH	-0.150	3.4603×10^{-7}	6519.6	99.16
SiO ₂ -0.03 KH	-0.065	3.1833×10^{-7}	22077	99.22
SiO ₂ -0.04 KH	-0.007	2.9071×10^{-7}	76910	99.29





As shown in formula (5), the 3-glycidyl ether oxypropyl group from coupling agent KH-560 are much longer than the methyl group of MTES. These long-chain organic groups were introduced into the inorganic skeleton of Si–O–Si *via* the addition of KH-560, which further improves the flexibility of the SiO₂ coating, enhances the ability of the film to resist stress, and reduces the generation of cracks.

2.3 Electrical resistance

The test results of sheet resistance of different SiO₂ coating are shown in Table 2. When the test voltage is 10 V, the sheet resistance of SiO₂-0.01 KH is only 10⁹ Ω/□, while the sheet resistance of SiO₂-0.02 KH, SiO₂-0.03 KH, SiO₂-0.04 KH is above 10¹⁰ Ω/□. When voltage increases to 50 and 100 V, the sheet resistance of SiO₂-0.02 KH, SiO₂-0.03 KH, SiO₂-0.04 KH does not reduce obviously, except that of SiO₂-0.01 KH. In particular, the SiO₂-0.04

KH sample shows the best resistance characteristics. This is because KH-560 improves the stability and film-forming property of silicone^[18]. When the addition of KH-560 increases from 0.01 mol to 0.04 mol, the sheet resistance increases significantly, and the SiO₂-0.04 KH shows the best insulating property of 2.95×10¹¹ Ω/□ at 100 V.

3 Conclusions

The SiO₂ coating was fabricated on the soft magnetic alloy surface through a dip-coating process. The mechanism of KH-560 improving the SiO₂ coating performance was systematically analyzed. The reasonable KH-560 addition can enhance the stability and film-forming property of SiO₂ coating. When the addition amount of KH-560 is 0.04 mol, the protection efficiency of as-prepared SiO₂ coating is up to 99.29%, which exhibits the smoothest surface and the highest electrical insulation property of 2.97×10¹¹ Ω/□ at 100 V compared with other samples. This coating has application potential on the soft magnetic alloy of proton/heavy ion synchrotron.

Table 2 Sheet resistance of different SiO₂ coating at different voltages

Sample		Sheet resistance at 10 V/(Ω/□)	Sheet resistance at 50 V/(Ω/□)	Sheet resistance at 100 V/(Ω/□)
SiO ₂ -0.01 KH	1	2.33×10 ⁹	3.66×10 ⁸	2.92×10 ⁸
	2	8.68×10 ⁸	4.58×10 ⁸	7.56×10 ⁸
	3	1.59×10 ⁹	5.85×10 ⁸	2.61×10 ⁸
	Average	1.60×10 ⁹	4.70×10 ⁸	4.36×10 ⁸
SiO ₂ -0.02 KH	1	1.82×10 ¹⁰	4.92×10 ¹⁰	8.88×10 ⁹
	2	4.55×10 ¹⁰	3.70×10 ¹⁰	4.40×10 ⁹
	3	2.19×10 ¹⁰	2.71×10 ¹¹	1.71×10 ¹¹
	Average	2.85×10 ¹⁰	1.19×10 ¹¹	6.14×10 ¹⁰
SiO ₂ -0.03 KH	1	8.71×10 ¹⁰	1.25×10 ⁹	2.21×10 ⁹
	2	4.17×10 ¹⁰	6.55×10 ¹⁰	6.52×10 ⁹
	3	5.68×10 ¹⁰	8.58×10 ⁹	6.02×10 ⁹
	Average	6.19×10 ¹⁰	2.51×10 ¹⁰	4.92×10 ⁹
SiO ₂ -0.04 KH	1	8.62×10 ¹⁰	2.81×10 ¹¹	4.51×10 ¹⁰
	2	3.33×10 ¹¹	4.52×10 ¹⁰	2.76×10 ¹¹
	3	1.91×10 ¹¹	1.56×10 ¹⁰	5.70×10 ¹¹
	Average	2.03×10 ¹¹	1.14×10 ¹¹	2.97×10 ¹¹

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KH-560 改性 SiO₂ 绝缘薄膜的制备及性能研究

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摘要: 软磁合金是新一代质子/重离子同步加速器加速器的核心材料, 在其表面涂覆绝缘涂层可有效降低高频涡流损耗。同时, 高温热处理(~600 °C)可有效减少软磁合金冷压成形产生的缺陷和位错而引起的内部残余应力。因此, 软磁合金用绝缘涂层还需满足耐高温要求。SiO₂ 涂层是最常见的无机涂层材料, 具有良好的绝缘性能和耐高温性能。本工作在植酸催化 TEOS+MTES 制备硅溶胶的基础上, 加入硅烷偶联剂 KH-560 进一步提高硅溶胶的成膜性能, 系统研究了 KH-560 对 SiO₂ 涂层结构与性能的影响, 并系统分析了 KH-560 提高 SiO₂ 涂层性能的机理。研究表明, 添加适量的 KH-560 可有效提高薄膜的稳定性和成膜性。特别是当 KH-560 添加量为 0.04 mol 时, SiO₂ 涂层质量最好, SiO₂-0.04 KH 涂层表现出最佳的耐腐蚀性和电绝缘性。在 100 V 时, SiO₂-0.04 KH 涂层的方块电阻仍保持 2.95×10¹¹ Ω/□。综上, 本研究利用植酸催化和 KH-560 改性协同作用制备出高质量的 SiO₂ 涂层, 涂层具有良好的耐高温和优异的绝缘性能。

关键词: 软磁合金; SiO₂ 涂层; 方块电阻; 溶胶-凝胶法

中图分类号: TQ174 文献标志码: A