Retraction

Retraction: Self-Healing Performance of Protective Coating with Inhibitor Loaded Nanoparticles of Mesoporous Silica on Copper Alloy (IOP Conf. Ser.: Mater. Sci. Eng. 772 012024)

Published 27 April 2022

This article has been retracted by IOP Publishing following an allegation that this work contains significant similarities to another article [1,2].

IOP Publishing has investigated in line with the COPE guidelines, and agree this article should be retracted.

The authors have admitted this is not their own work. We welcome receiving more information on this matter.

IOP Publishing wishes to credit the anonymous whistleblower for bringing the issue to our attention.

The authors agree to this retraction.

[1] Ma X, Xu L, Lin Z, Li X, and Feng C. ‘Self-Healing Performance of Protective Coating with Inhibitor Loaded Nanoparticles of Mesoporous Silica on Copper Alloy’, (Unpublished manuscript, [Corrosion Science/2017]).

[2] Ma X, Xu L, Wei W, Lin Z, Li X. (2017) ‘Synthesis and characterisation of composite nanoparticles of mesoporous silica loaded with inhibitor for corrosion protection of Cu-Zn alloy’. Corrosion Science. 120. 139-147.

Retraction published: 27 April 2022

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Self-Healing Performance of Protective Coating with Inhibitor Loaded Nanoparticles of Mesoporous Silica on Copper Alloy

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Abstract. The self-healing coating on the copper alloy surface was prepared by adding inhibitor loaded composite nanoparticles into alkyd varnish coating with a content of 4 wt.%. The self-healing performance of the scratched coating immersed in 3.5% NaCl solution was evaluated by morphology observation, Fourier transform infrared spectroscopy, electrochemical impedance spectroscopy and scanning Kelvin probe. It has been proved that the scratched coating containing the composite nanoparticles can be self-healed with the formation of the inhibitive film at the coating crevice during the immersion.

Key words: A. copper; A. organic coating; B. EIS.

1. Introduction
Copper and its alloy are widely used in such industries as electrical engineering, electronic industry, marine and offshore engineering and so on. Although they have good performance in applications, the corrosion resistance of copper and its alloy still needs to be further improved in some hostile environment, such as sea water or coastal atmosphere [1-5].

Coating is an effective means for corrosion protection of metallic structures [6-9]. However, when coating is damaged, the exposed metal surface at the defects will be prone to suffer from corrosion. To solve this problem, smart coatings with self-healing ability have attracted much attention and shown bright prospect of development [2, 10]. One of the routes to achieve self-healing is to add corrosion inhibitor into the coating. If the corrosion inhibitor is directly added to the coating, the protective performance of the coating will be reinforced but with a low efficiency. And tiny pores will be left on the coating once the corrosion inhibitor dissolves, which speeds up coating failure. In addition, the corrosion inhibitor may react with the ingredients of the coating. So adding the inhibitor-loaded nanocontainers into the coating becomes a promising and effective way to realize self-healing and enhance coating performance [10]. When the coating is broken, the corrosion inhibitor will release from the nanocontainers into the defects, making the exposed metallic surface inactivated or forming a layer of protective film to inhibit the corrosion. Since the corrosion inhibitor is stored inside the nanocontainers, its period of validity for corrosion prevention can be prolonged.

With focus on the corrosion protection of copper alloy, we prepared a new type of composite nanoparticles by loading a typical inhibitor 1-hydroxybenzotriazole (HOBT) in mesoporous silica nanocontainers. The structures of the mesoporous silica were characterised; the release kinetics of
HOBT from the nanoparticles in 3.5% NaCl solution was investigated, and the corrosion inhibition process of the composite nanoparticles on a Cu-Zn alloy was analysed. In this article, we present the self-healing performance of the coating on the Cu-Zn alloy surface containing the composite nanoparticles in the alkyd varnish, and discuss the mechanism of corrosion protection with self-healing effect.

2. Experimental Process

2.1. Material
The Cu-Zn alloy of H68 brass used as substrate was manufactured by Shandong Qingteng Metallic Materials Co., Ltd. with the composition, wt. %: 67.59 Cu, 0.10 Fe, 0.03 Pb, and balance Zn. SiC sandpaper (600#, 800#, 1000#, 1200#) was purchased from Shanghai Yihe Grinding Materials Co., Ltd.. Alkyd varnish was acquired from Lehua Inc. China. Ethanol and sodium chloride (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd.. The water utilised in all of the experiments was produced with the Millipore Milli-Q Plus 185 purification system having a resistivity higher than 18.1 MΩ cm.

2.2. Preparation of self-healing coatings
The Cu-Zn alloy plate of 3 mm thick was used as the coating substrate, which was abraded using the SiC sandpaper in the order from 600 to 1200 mesh, then washed with purified water and ethanol successively, and finally, air-dried at room temperature.

The detailed descriptions on the synthesis and characterisation of the composite nanoparticles were given in the previous paper. The prepared mesoporous silica nanoparticles had an average diameter of about 60 nm and pore size distributed between 2 nm and 8 nm with most pores of around 3 nm. The silica nanocontainer had a high surface area of 951.6 m²/g and a large pore volume of 1.045 mL/g, loaded with about 40 wt.% of the corrosion inhibitor HOBT.

The composite nanoparticles were added into the alkyd varnish with a content of 4 wt.%. The mixture was stirred vigorously for 20 min to obtain the paint. Then the paint was coated on the surface of the prepared copper alloy substrate by brushing. Finally, the samples were heated at 30 oC for 72h. As a comparison, the alkyd varnish coating without nanoparticles was also prepared on the copper alloy samples using the same procedure. The coatings for the tests had a dry film thickness of 100±5 μm. The scratches of 5mm long were made with a sharp blade through the coating to the substrate.

2.3. Characterisation
The morphologies of the coatings after immersion testing in 3.5% NaCl solution were observed with KH-8700 digital microscope (HIROX).

The measurement of electrochemical impedance spectroscopy (EIS) was conducted with Princeton PARSTAT 2273 electrochemical workstation at the open circuit potential in 3.5% NaCl solution. A three-electrode cell was used in the electrochemical measurement with the coated copper alloy sample served as the working electrode, the saturated calomel electrode (SCE) as the reference electrode and the platinum sheet as the counter electrode. The working electrode was insulated using epoxy resin with an exposed testing area of 1 cm². The amplitude and frequency range of the applied disturbing signal were 10 mV and 10² - 10⁵ Hz respectively with 49 points recorded. The EIS data simulation based on the equivalent circuit were conducted using the software ZsimpWin.

Volta potentials of the coated samples with scratches were recorded using VERSA SCAN scanning Kelvin probe (SKP, Princeton). The SKP measurement was carried out in the air atmosphere with about 65% relative humidity. The tungsten probe with a diameter of 500 μm was utilised and lifted up from the surface to a constant distance of 100 μm. The scanning area was a square of 2000μm × 2000μm with the scratches in the middle of the scanning area (at X=1.0 mm). The scanning step both in X axis and Y axis direction was 100 μm. The measurement sensitivity was 50 μV.
The infrared spectra were measured with Thermo Scientific Nicolet iS 10 spectrometer (Thermo Fisher Scientific Inc.) with a FT-IR scanning range of 2000 cm$^{-1}$~ 550 cm$^{-1}$ and a resolution of 2 cm$^{-1}$.

3. Results And Discussion

3.1. Morphology observation
Fig. 1 (a) shows the appearance of the blank alkyd varnish coating with a scratch after 150h immersion in the NaCl solution. The coating is transparent, therefore, the condition at the interface between the coating and the substrate can be observed. The solution spread into the interior along the interface between the coating and the substrate from the crevice. The failed area of the blank coating was large after 150h immersion. The copper alloy substrate corroded evidently under the coating around the scratch. While at the scratched region of the self-healing coating with composite nanoparticles (Fig.1(b)), a protective film was formed to retard the development of the coating defect and the corrosion of the substrate at the defect was hindered.

![Figure 1](image1.png)

Figure 1. The appearance of the blank alkyd varnish coating with a scratch after 150h immersion in the NaCl solution

3.2. FT-IR Analysis
FT-IR analysis was used to detect the release of the inhibitor HOBT from the mesoporous nanoparticles and the chemical changes after self-healing process of the coating. The alkyd varnish coating contains the most functional groups of the inhibitor HOBT, such as benzene ring, hydroxyl, etc., which makes the FT-IR spectrum of the alkyd varnish covering the most characteristic bands of the inhibitor. Fig.2 shows the FT-IR spectra of the inhibitor HOBT (I), the crevice region (II), and the peripheral region (III) of the coating containing composite nanoparticles after 150h immersion in 3.5% NaCl solution. The bands at 668 cm$^{-1}$ and 1450 cm$^{-1}$ correspond to the characteristic vibration frequencies of HOBT aromatic structure and the stretching vibration frequencies of C-N respectively, with an obvious shift to the low wave number because of conjugation effect, which are the unique characteristic bands of the inhibitor HOBT (Fig.2 I) comparing with alkyd varnish coating[24, 25]. At the crevice region, the FT-IR spectrum (Fig.2 II) displayed the unique characteristic bands of the inhibitor HOBT, while there were not these bands in the peripheral region (Fig.2 III), which indicated that the inhibitor was released and the film formed at the crevice.

![Figure 2](image2.png)

Figure 2. The FT-IR spectra of the inhibitor HOBT (I), the crevice region (II), and the peripheral region (III) of the coating containing composite nanoparticles after 150h immersion in 3.5% NaCl solution
3.3. EIS Measurements

EIS measurements can be used to study the self-healing process of protective coating. The prepared self-healing coating containing composite nanoparticles with a scratch of 5 mm long was immersed in 3.5% NaCl solution. The EIS measurements were conducted at the open-circuit potential during the immersion. Fig.3 gives the evolution of the EIS spectra of the self-healing coating having scratch with immersion time.

The impedance modulus (|Z|) at the low frequency of 0.01 Hz can be used to evaluate the protective effect of the organic coatings. Fig.4 shows the change of the impedance modulus (f=0.01 Hz) of the scratched self-healing coating immersed in the NaCl solution. In the initial 2h of the immersion, the solution penetrated into the crevice and reached the copper alloy substrate, leading to the |Z| value (f=0.01 Hz) at a low level of 2.37 MΩ cm². Then the |Z| value (f=0.01 Hz) was increased sharply to 9.01 MΩ cm² at 14h and fluctuated within a range of 4.30 MΩ cm² ~ 6.67 MΩ cm² from 14h to 112h. This is because that the inhibitor HOBT can release from the mesoporous composite nanoparticles exposed in the solution at the crevice of the coating, which can be absorbed on the exposed copper alloy surface and form a film covering the coating crevice with the increase of the immersion time. Because the area of the scratched crevice is small, a small amount of inhibitor released can form a protective film healing the coating defect. On the other hand, the chloride ions in the solution can destroy the healed film. The little fluctuation of the |Z| value (f=0.01 Hz) at 14h to 112h may be attributed to the alternative growing and damage of the formed protective film in the self-healing process. The self-healing process was repeated until the released inhibitor exhausted after 112h. After that time, the |Z| value (f=0.01 Hz) of the coating began to decrease from 6.67 MΩ cm² to 1.22 MΩ cm² at the end of testing, which means the failure of protection by the coating. The EIS plots in Fig.3 revealed two time constants for the scratched coating from the beginning of immersion in the NaCl solution, corresponding to the relaxation processes of the coating and the electric double layer on the interface with the solution respectively.

![Figure 3](image-url)

**Figure 3.** The evolution of the EIS spectra of the self-healing coating having scratch with immersion time.
Figure 4. The change of the impedance modulus (f=0.01 Hz) of the scratched self-healing coating immersed in the NaCl solution

3.4. SKP Measurement

SKP technique, which can measure the distribution of Volta potential of the local area around the defects of the coating, was employed to analyse the healing process of the scratched alkyd coating with composite nanoparticles. For comparison, an alkyd varnish coating with scratch was prepared as blank contrast.

Fig.5 shows the SKP measurement results of the blank alkyd varnish coating at different immersion time. At the place of X=1.0 mm in the Volta potential maps, there appeared an obvious line of peaks, which was referred to the scratched crevice, and the both sides corresponded to alkyd varnish coatings. The solution penetrated into the crevice with immersion, causing the copper alloy substrate exposed at the crevice corroded. The exposed copper alloy surface with corrosion product had higher Volta potential than that of the around alkyd coating. After immersed for 2h, the Volta potential maps showed obvious peak in the range of Y=1.0 mm ~ 2.0 mm at the crevice, while the peak was not obvious in the range of Y=0.0 mm ~ 1.0 mm (Fig.5a), showing the inconsistence of the prepared scratch. The latter may result from the drawing close of the two side walls of the scratched crevice at this part due to the inherent elasticity of alkyd varnish coating. After 22h of immersion, all of the parts of the crevice were infiltrated by solution and gradually covered by corrosion products, and the Volta potential peaks became more obvious in all the range of the crevice (Fig. 5(b), (c) and (d)).

Figure 5. The SKP measurement results of the blank alkyd varnish coating at different immersion time

With the immersion time increased, the maximum Volta potential of the alkyd varnish coating went up, to about -350mV. The range of the high Volta potential was slightly enlarged, indicating that the solution penetrated into the bottom of the crevice and began to spread slowly to both sides at the interface of the coating and the metal substrate.

Fig.6 shows the Volta potential maps of the self-healing coating containing composite nanoparticles with a scratched crevice at different immersion time, with the crevice at the X=1.0 mm. Like the blank varnish coating, some obvious Volta potential peaks can be seen at the part of the crevice after immersed for 2h. However, with the immersion time increased, the Volta potential peaks at the crevice became lower and lower. And the peaks were almost invisible after 50h of immersion. This phenomenon can be related to the self-healing effect of the coating. When the solution penetrated into the crevice, the
inhibitor could be released quickly from the mesoporous nanoparticles exposed in the coating. The dissolved inhibitor would adsorb on the surface of the exposed copper alloy substrate at the crevice and form a layer of organic film, making the Volta potential shift negatively close to that of the alkyd coating.

4. Conclusion
A self-healing coating on the Cu-Zn alloy surface was prepared by adding the composite nanoparticles with a content of 4 wt. % of mesoporous silica loaded inhibitor HOBT into the alkyd varnish. The performance of the scratched coating immersed in 3.5% NaCl solution was investigated using optical microscope, FT-IR spectroscopy, EIS and SKP. Morphology observation indicated that the coating with the composite nanoparticles presented better protective performance for the copper alloy substrate than the blank vanish coating. The FT-IR analysis proved the formation of the inhibitive film at the coating crevice with immersion. The self-healing process of the scratched coating was well characterised by EIS and SKP. In the initial period of immersion, the solution penetrated into the crevice, and the coating demonstrated low impedance and high Volta potential peaks at the scratch. With the increase of immersion time, the coating resistance and the charge transfer resistance presented a trend of fast increasing first, then maintaining for a period of time and finally decreasing, while the coating capacitance and the double layer capacitance showed an opposite trend, which indicated that the scratched crevice was self-healed with inhibitive film formation and then failed after the inhibitor was exhausted. The Volta potential peaks of the scratched alkyd coating containing composite nanoparticles decreased continuously with immersion time increased, and became not obvious, indicating the crevice was well self-healed.

Figure 6. The Volta potential maps of the self-healing coating containing composite nanoparticles with a scratched crevice at different immersion time, with the crevice at the X=1.0 mm.

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