The Morphology, Phase Composition and Effect of Corrosion Product on Simulated Archaeological Iron^{*}

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Abstract The immersion corrosion of archaeological iron in solution $(0.06\text{mol}\cdot\text{L}^{-1} \text{NaCl}+0.03\text{mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_4 + 0.01\text{mol}\cdot\text{L}^{-1} \text{NaHCO}_3)$ simulating soil water composition was presented. The evolution of archaeological iron from iron to iron oxide and to iron oxy-hydroxides compounds was investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. According to the morphology, phase composition, and transformation process, the contributions of each corrosion product to archaeological iron were discussed. **Keywords** archaeological iron, corrosion, scanning electron microscope, X-ray diffraction

1 INTRODUCTION

The deterioration of archaeological iron due to corrosion is a well-known problem. A variety of corrosion products can be formed depending on the species present in their environment (soil, sea water, atmosphere, etc.). To find out the evolution of iron rust is a real challenge since it is difficult to clearly identify the contributions of each corrosion product[1]. Although the evolution of iron oxides and oxy-hydroxides in different aeration conditions and pH have already been tested[2], their effects on the stability of archaeological iron have not been systematically studied. In addition, at present the most serious problem during restoration of iron artifacts is to find a suitable chemical treatment for their preservation[3]. Thus, the elucidation of the phase composition of the corrosion layers appears to be very important from the viewpoint of choosing proper chemical reagents to treat archaeological iron objects for their preservation.

The main phases constituting the rust layers formed on iron antiquities exposed to soil corrosion are magnetite(Fe₃O₄), goethite(α -FeOOH), lepidocrocite(γ -FeOOH), and akaganeite (β -FeOOH). Generally, iron rusts can be classified into harmful and harmless ones according to the effects on the corrosion of iron[4,5]. Harmless rusts usually do not develop on the iron matrix in the normal environment and do not need to be removed from the iron antiquities. Harmful rusts, on the contrary, are able to accelerate the further corrosion of the metal core in the normal environment and considered to be the main trouble for the iron relics.

In this article, scanning electron microscope (SEM) and X-ray diffraction (XRD) will be utilized to investigate the morphology and structure of corrosion product on archaeological iron. Aqueous solution whose composition is mostly the same as that in Chinese soil will be adopted. An attempt was made to distinguish the effects of different kinds of corrosion products on the corrosion evolution of archaeological

iron by analyzing the transforming process.

2 EXPERIMENTAL

Cast iron, with the mass composition (%) C 3.00, Si 1.84, S 0.089, P 0.098, Mn 0.82, Fe balance, was used to simulate archaeological iron. The samples were processed to be $15mm \times 15mm \times 3mm$ coupon. The surfaces of these samples were polished with emery papers up to 1000 grade followed by thorough rinsing in acetone and de-ionized water.

The corrosion media were $0.06 \text{mol} \cdot \text{L}^{-1} \text{ Cl}^{-+} + 0.03 \text{mol} \cdot \text{L}^{-1} \text{ SO}_4^{2-} + 0.01 \text{mol} \cdot \text{L}^{-1} \text{ HCO}_3^{--} \text{ solutions}$ diluted from AR grade NaCl, Na₂SO₄, NaHCO₃ with de-ionized water. H₂SO₄ and NaOH having 20% volume ratio were used to adjust pH to 7 in order to eliminate the effects of pH on the experiment.

The solution was de-oxygenated with purified nitrogen for 30min previously to each immersion to simulate the state of soil that lacked oxygen in deep earth. The specimens were fixed on the brackets at the bottom of beaker and the beaker was made to be airproof. After immersion for a certain period, the specimens were dried in nitrogen for SEM observation and XRD test. X-ray diffraction (Model DMAX) was set up as follows: scan speed $10(^{\circ}) \cdot min^{-1}$, from 3° to 90°, with Cu K_a as its radiation source operated at 50kV and 200mA.

3 RESULTS AND DISSCUSION

3.1 Corrosion products on the archaeological iron after immersion for 48 days

Figure 1 showed the images of corrosion products on the upper surface of the specimen after immersion for 48 days. It seems that corrosion products are distributed loosely on the upper surface of the specimen with grain-like shape, and the grain diameter are in the order of $1.0-1.5\mu$ m. Because of the loose distribution of corrosion product, a lot of cavities or gaps are left, even iron matrix is exposed on the local surface.

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Figure 1 SEM image of corrosion products on the upper surface of the specimen after immersion for 48 days

The composition of surface corrosion products was identified by means of X-ray diffraction; the result was shown in Fig.2. Obviously, the spectra are mainly of goethite and some iron matrix. Accordingly, the grain-like corrosion product formed on the upper surface of the specimen after immersion for 48 days mainly consisted of goethite. But goethite didn't cover the iron surface; its loose distribution can be proved by the appearance of spectra of iron matrix. Here the composition of grain-like substance, not confirmed in Dillmann's study on atmospheric corrosion of iron[6], proved to be goethite. Zhu et al.[7] observed that goethite was stalactite-like on the surface of iron artifacts. Possibly, the difference is because of the shorter immersion period (48d) in this experiment than the buried period (several thousand years) of genuine iron artifacts in the soil. The grain of goethite was tiny since it formed in the initial corrosion stages on the iron surface.



Figure 2 XRD spectrum of corrosion products on the upper surface of the specimen after immersion for 48 days

Figure 3 showed the images of corrosion product on the undersurface of the specimen after immersion for 48 days. The corrosion product was tiny scale-like shape with loose distribution and some petal-like morphology was also present in partial corrosion product. Fig.4 revealed the result of XRD test to this scale-like rust; it was proved to be primarily lepidocrocite, which coincides with author's former study[8] on the corrosion products of archaeological iron.

3.2 Corrosion products on the simulated archaeological iron after immersion for 138 days

After immersion for 138 days, the surface of specimen was covered with a thick layer of corrosion product, the outer one of which was brown, and the



100um

40um

Figure 3 SEM image of corrosion products on the undersurface of the specimen after immersion for 48 days



Figure 4 XRD spectrum of corrosion product on the undersurface of the specimen after immersion for 48 days

grain was coarse to naked eyes. After the outer layer of the rust removed by needle, there were two other layers below. The inner one adhering to the metal core was orange in color, while the middle one was little dark green. The layers can be easily peeled off from each other.

Figure 5 showed the images of corrosion products on the undersurface of the specimen after immersion for 138 days. It can be observed that the inner layer is covered with lots of acicular substance or square acicular substance; while the middle layer is leprose, similar to Fig.3(a); the outer layer also shows leprose shape, but the scales have become thicker than that found in the inner layer. Moreover, from the magnified image Fig.5(d) some scales covered with granular substance are observed and the corrosion product becomes stalactitic.

From the XRD analysis on the thick layer of corrosion product in Fig.6, it seems that there are several diffraction peaks of goethite, a few diffraction peaks of lepidocrocite, and some separate diffraction peaks of hematite or magnetite. It was confirmed earlier in this article that the stalactite-like corrosion product was goethite (Fig.2), and the scale-like one



(a) The inner layer



(b) The middle layer



(c) The outer layer



(d) The magnified image of the small frame on (c) Figure 5 SEM images of corrosion products on the undersurface of the specimen after immersion for 138 days



Figure 6 XRD spectrum of corrosion product on the undersurface of the specimen after immersion for 138 days

was lepidocrocite (Fig.4). Consequently, together with the SEM images in Fig.5 and the above-mentioned XRD spectrum, it can be concluded that the leprose middle layer on the undersurface of the specimen after immersion for 138 days consists of lepidocrocite, and stalactitic outer layer consists of goethite. But in Fig.6 the diffraction peaks of lepidocrocite are less than that of goethite; this is probably because X-ray hardly penetrates through the thick and compact stalactitic goethite into the middle layer of lepidocrocite resulting in the few diffraction peaks of lepidocrocite. In addition, the corrosion products on the upper surface of the specimen after immersion for 138 days were consisted mainly of goethite, as was shown in Fig.7.



Figure 7 XRD spectrum of corrosion product on the upper surface of the specimen after immersion for 138 days

According to the previous researches on the corrosion of iron objects[9], electrochemical process occurs on the iron in the environment; the formed rusts are in fact a sort of precipitation with very fine rust grain and loose distribution. As a result, the oxygen and water are easy to approach the metal core and aggravate the corrosion.

$$Fe \longrightarrow Fe^{2+} + 2e \tag{1}$$

$$\frac{1}{2}O_2 + H_2O + 2e \longrightarrow 2OH^-$$
(2)

$$\operatorname{Fe}^{2+} + 2\operatorname{OH}^{-} \longrightarrow \operatorname{Fe}(\operatorname{OH})_2$$
 (3)

$$Fe(OH)_2 + O_2 \longrightarrow Fe_2O_3 \cdot H_2O \text{ or } 2FeOOH \qquad (4)$$

In the humid environment iron is corroded to γ -FeOOH in the beginning, then with the interaction of water and oxygen γ -FeOOH partly or entirely transforms into stable α -FeOOH. This coincides with the experimental result. The specimen was parallel to the bottom of beaker in the solution, so the diffusion of oxygen from the mouth of the beaker to the upper surface of specimen was easier than its diffusion to the undersurface. Therefore, after immersion for a long time, the undersurface of specimen was mainly covered with unstable rust y-FeOOH, and later it was transformed into more stable goethite due to the abundant supply of oxygen; thus, the rust on the upper surface was mainly goethite. Attributed to the diffusion of oxygen, the leprose γ -FeOOH, and α -FeOOH transforming to stalactitic phase were observed on the undersurface of specimen immersed for 138 days. However, what on earth were the acicular substance and square acicular substance in the inner layer?

After dried in nitrogen, it was found that the

corrosion product on the specimen immersed for 138 days cracked and became easy to be peeled off. XRD was conducted onto the inner side of the corrosion product, specifically the side clinging to the iron matrix. The result was shown in Fig.8, and the microstructure shown in Fig.5(a).



Figure 8 XRD spectrum of corrosion product on the inner layer of the specimen after immersion for 138 days

XRD analysis showed that the inner layer of the product was mainly composed of α -FeOOH and a little β -FeOOH and Fe₃O₄. This is because lepidocrocite that formed on the iron surface not only react with the oxygen and water and become goethite, but also can act on Fe²⁺ dissolved from the iron and form magnetite. At the same time, this reaction just expresses the process of cathodic depolarization for the continual eroding of iron artifacts with rusts after exhumation.

$$8\gamma - FeOOH + Fe^{2+}2e \longrightarrow 3Fe_3O_4 + 4H_2O$$
 (5)

Figure 5(a) showed the morphology of corrosion product that was closely clinging to the metal core. It seems that the surface of iron is scattered with many acicular substances; below them a lot of little cube grains are distributed. Fe_3O_4 has a cubic spinelle-like structure. From the results of XRD test it can be confirmed that the little cube grains distributed on the iron surface are Fe_3O_4 . This is consistent with Matsui *et al.*'s observation[10] to the Fe_3O_4 grains on the rusts of real iron antiquities.

The dissolution process of archaeological iron in the media containing Cl^- can be expressed[11]:

$$Fe + Cl^{-} \underbrace{\stackrel{k_{+1}}{\overleftarrow{k_{-1}}}}_{k_{-1}} FeCl_{ads} + e$$
 (6)

$$\operatorname{FeCl}_{\operatorname{ads}} \xrightarrow{k_2} \operatorname{Fe}_{\operatorname{sol}}^{2+} + \operatorname{Cl}^- + e \tag{7}$$

When the specimen is dried, the humidity on the surface of cast iron that is in dissolution state largely declines; thus, the dense FeCl₂ liquor is concentrated under the thick rusts or in the pitting cavities. This leads to the phenomenon of "weeping" that shows yellow droplets containing ferrous and ferric ions on the surface of the artifacts[12]. During burial, the porous oxide layer is filled with an aqueous electrolyte containing a large amount of ferrous ions. Hydrolysis of ferrous ions lowers the pH, and chloride ions will in most cases be the dominant counter ion due to its high mobility and availability[13]. Thus, the local high concentration of chloride combined with a low pH is

favorable for akaganeite formation and makes akaganeite of special relevance to the stability of archaeological objects. As soon as the specimen contacted with air, β -FeOOH will be produced between rusts and iron because of the existence of Cl⁻ and oxidation proceeding in acid conditions[14]:

$$\operatorname{Fe}^{2+} + O_2 + H_2O \xrightarrow{\operatorname{Cl}^*} \beta - \operatorname{FeOOH} + H^+$$
 (8)

The reason for the presence of β -FeOOH on the XRD spectrum of corrosion product on the undersurface of the specimen corroded for 48 days is also explained here.

Briefly, in the humid environment, an active rust γ -FeOOH was formed on the archaeological cast iron in the beginning; then with the action of water and oxygen, γ -FeOOH was transformed into α -FeOOH, which is more stable than γ -FeOOH. At the same time, γ -FeOOH that was formed on the matrix of cast iron reacted with Fe²⁺ leads to the formation of Fe₃O₄. Owing to drying, FeCl₂ were concentrated on the matrix of samples so that Fe²⁺ was oxided into β -FeOOH with the action of Cl⁻. As a result, the corrosion product of cast iron in the solution for 138 days was made up of three layers: α -FeOOH, Fe₃O₄, and a little β -FeOOH in the inner layer; γ -FeOOH in the middle layer; and α -FeOOH in the outer layer.

3.3 Effects of rusts on the archaeological iron

3.3.1 Goethite (α -FeOOH)

Production free energy of goethite at 25° C is -495.748kJ·mol⁻¹, which is less than that of lepidocrocite -470.25kJ·mol⁻¹[15]. This is to say, goethite is relatively stabler than lepidocrocite in thermodynamics. Besides, from the SEM images [Fig.5(d)] it can be seen that the layer of goethite, with the crust like stalactite, has a good continuity and compactness in texture. So it is assumed to be a non-reactive phase with an important protection[16] owing to its ability to effectively prevent the iron matrix suffering from attacks of other environmental factors such as oxygen, moisture as well as polluted gases.

3.3.2 Lepidocrocite (γ -FeOOH)

Lepidocrocite has a loose structure with complicated leprose or petallike shape (Fig.3). It is porous and similar in absorbency to the skeleton of sponge. Water, electrolyte, oxygen, or other polluted gas in the environment can be absorbed and reserved. Air pollutants like SO₂ and NO₂ dissolve in the fluid film on the surface of iron objects resulting in the decrease of pH and the acceleration of γ -FeOOH dissolution. Therefore, the concentration of Fe³⁺ will be increased:

$$\gamma - \text{FeOOH} + 3\text{H}^+ \longrightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O} \tag{9}$$

Being oxidant, Fe^{3+} and its ramification, whose oxidation ability increases with concentration of H⁺, can be the catalyzer and activator to the corrosion of iron core. Fe^{3+} is able to either directly oxide the iron to be Fe^{2+} , or induce oxygen acting on Fe^{2+} and accelerate the transformation from Fe^{2+} to Fe^{3+} . As long as the medium and environment are propitious to the dissolution of lepidocrocite and production of Fe^{3+} , the process mentioned previously will be cycled, and the continual corrosion of iron will be induced below the rusts[17]. Consequently, lepidocrocite is a kind of harmful rusts to the preservation of iron antiquities. It is strongly suggested that the lepidocrocite should be removed from iron antiquities immediately after excavated, even compulsive desiccation or chemical disposal for stabilization can be used to restrain its development.

3.3.3 Akaganeite (β -FeOOH)

Formation of ferric oxy-hydroxides is associated with volume expansion, which cause cracks and exfoliation of the corrosion layers or even the whole artifact, which in turn may accelerate the deterioration. At the position of fracture, an orange powder can be observed, which has been identified as akaganeite on several artifacts[18]. Akaganeite, with the molecular formula $FeO_{0.833}(OH)_{1.167}Cl_{0.167}[13]$, is mainly acicular or virgulate in appearance. Its structure is even not as compact as lepidocrocite, and the interspaces among the acicular are relatively large. The absorption or storage ability is stronger than lepidocrocite. As a result, different kinds of polluted gas, oxygen or moisture are easy to be reserved. This supplies favorable conditions for the occurrence of local corrosion to a great extent[19].

As is known, Cl⁻ was considered to be one of the most important factors to the preservation of archaeological iron[20], which not only involve the chloride that was formed in the environment (sea water, soil) before exhumation, but also the chloride ions trapped in the lattice of akaganeite[21]. It is obvious that there is chloride element in the molecular structure of β -FeOOH, and the mass ratio comes to 6.24%. When the iron antiquities are conserved, the dissolution of polluted acid gas will make the solution acidic, thus induce akaganeite to dissolve, and chloride element will be released in the form of ions. Simultaneously, the phase transformation like decompounding due to drying can also bring on the release of chloride element[13]:

$$2 \text{FeO}_{0.833}(\text{OH})_{1.167} \text{Cl}_{0.167} \longrightarrow Fe_2O_3 + 0.333 \text{HCl} + \text{H}_2\text{O}$$
(10)

the released chloride dissolves in the acid fluid film, together with H^+ and the oxygen which diffuses into the rust, forms a condition capable of accelerating the corrosion of iron.

The existence of akaganeite is a risk for ironwork, and chloride element carried by akaganeite is the main potential trouble. So akaganeite is another kind of harmful rusts to ironware and must be stabilized or removed in the preservation. At present, conservators have been using various treatments for removal of chlorides from artifacts including different desalination and heating treatments. Dechlorination is used to decrease or remove chloride ions by washing and immersion in alkaline solution or by electrochemical technologies.

3.3.4 Magnetite (Fe_3O_4) and hematite (Fe_2O_3)

Lepidocrocite reacted with Fe²⁺ which dissolved from iron matrix to be magnetite, or become hematite

in certain conditions, for example, desiccation. This is also the reason Fe₂O₃ and Fe₃O₄ exist in the XRD spectrum of corrosion product on the undersurface of the specimen after immersion for 138 days (Fig.6). Moreover, in dry atmosphere and dry soil, rusts formed on the iron objects are mainly oxides. As another kind of rust on ironwork, iron oxide is stabler than iron oxy-hydroxides. Fe₂O₃ and Fe₃O₄ have the production free energy $- 822.16kJ \cdot mol^{-1}$ and $-1117.13kJ \cdot mol^{-1}$, respectively, which are far less than that of γ -FeOOH and α -FeOOH. They also have very high lattice binding energy. Consequently, Fe₂O₃ and Fe₃O₄ are harmless rusts; they are able to prevent iron artifacts from farther corrosion.

Iron objects usually need to be compulsively dried immediately after exhumation. The purpose for this is transforming the unstable rusts to stable rusts like Fe_2O_3 and Fe_3O_4 to avoid the further development of harmful rust. Besides, at present there are many chemical stabilization methods for the preservation of iron antiquities. However, no matter what kinds of methods, they are all intended to accelerate the transformation of unstable, active and loose rusts into stable and compact rusts[22] so that the protection can be arrived.

4 CONCLUSIONS

(1) Corrosion products on the upper surface of the specimen after immersion for 48 days were mainly α -FeOOH, which was grain-like in appearance with loose distribution; while corrosion products on the under surface of the specimen after immersion for 48 days were mainly γ -FeOOH, with leprose or petallike shape.

(2) Corrosion product of archaeological iron in the solution for 138 days was made up of three layers: α -FeOOH, Fe₃O₄ and a little β -FeOOH in the inner layer; γ -FeOOH in the middle layer; and α -FeOOH in the outer layer.

(3) In the rust of iron antiquities, the layer of α -FeOOH, with the shape like stalactite, is able to prevent the iron matrix suffering from attacks of other environmental factors because of its good continuity and compactness. γ -FeOOH has a complicated leprose or petal-like structure; it can decompose to Fe³⁺ under acidic condition and able to accelerate the corrosion of iron matrix. The molecular structure of β -FeOOH includes chloride element which, if released, will induce the deterioration of iron core. So γ -FeOOH and β -FeOOH are harmful rusts to the preservation of iron antiquities. Moreover, iron oxide like Fe₂O₃ and Fe₃O₄, which are more stable than iron hydroxide, is harmless to iron objects.

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