

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(Fe_3O_4), goethite($\alpha\text{-FeOOH}$), lepidocrocite($\gamma\text{-FeOOH}$), and akaganeite ($\beta\text{-FeOOH}$). 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 $15\text{mm}\times 15\text{mm}\times 3\text{mm}$ 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 $0.06\text{mol}\cdot\text{L}^{-1}\text{Cl}^-+0.03\text{mol}\cdot\text{L}^{-1}\text{SO}_4^{2-}+0.01\text{mol}\cdot\text{L}^{-1}\text{HCO}_3^-$ solutions diluted from AR grade NaCl, Na_2SO_4 , NaHCO_3 with de-ionized water. H_2SO_4 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 air-proof. 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 $10(^{\circ})\cdot\text{min}^{-1}$, from 3° to 90° , with Cu K_{α} 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 $1.0\text{--}1.5\mu\text{m}$. 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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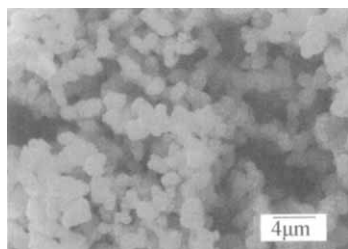


Figure 1 SEM image of corrosion products on the upper surface of the specimen after immersion for 48 days

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.

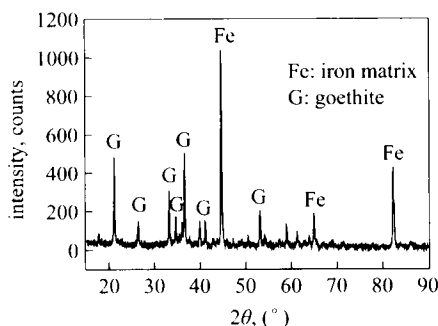
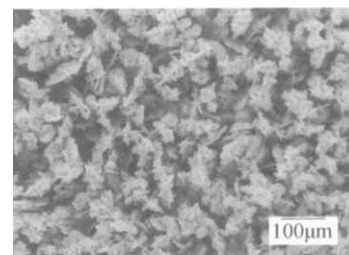


Figure 2 XRD spectrum of corrosion products on the upper surface of the specimen after immersion for 48 days

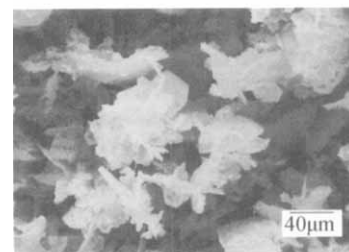
Figure 3 showed the images of corrosion product on the undersurface of the specimen after immersion for 48 days. The corrosion product was tiny scale-like shape with loose distribution and some petal-like morphology was also present in partial corrosion product. Fig.4 revealed the result of XRD test 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



(a)



(b)

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

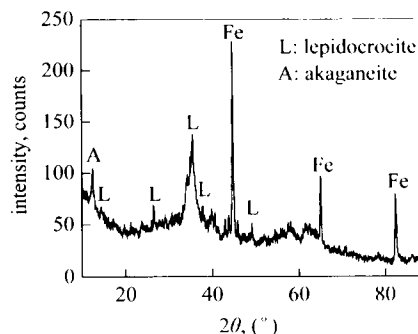


Figure 4 XRD spectrum of corrosion product on the undersurface of the specimen after immersion for 48 days

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

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