

CORROSION OF ARCHAEOLOGICAL ARTEFACT MADE OF FORGED IRON

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Abstract

One artefact of the archaeological cultural heritage from Roman period (IV century) that was found near Šabac in Serbia, was analysed. In corrosion products of the artefact (knife), dominant phases were goethite (α -FeOOH) and magnetite (Fe_3O_4). Presence of these types of corrosion products explains a good preservation of the base metal (iron) over the centuries and stability after excavation. Also, the less stable lepidocrocite (γ -FeOOH) and the phases that come from rocks and land surrounding environment (like SiO_2) were identified in the corrosion products. Phases containing chloride ions (i.e. akaganéite) have not been detected in the corrosion products. This indirectly indicates that the amount chloride ions were rather low in underground exploitation conditions.

Key words: archaeology, iron, corrosion stability, radiography, XRD.

Introduction

Iron is a relatively reactive metal and its corrosion rate in a large number of underground environments is much higher comparing to other ancient metals. The degree of preservation of iron artefacts depends on the type of underground environment. In the aggressive environments, objects made of iron can be mineralized into hard lump of corrosion products, with little or no rest metal. On the other hand, objects of iron buried in the conditions with slow access of oxygen and humidity, can survive in well-maintained condition for thousand years, if the activity of bacteria reducing sulphate is lesser [1].

In soil environments where the access of oxygen is enabled, the iron corrosion products are iron (III) compounds (Table 1), red-brown colour, mainly goethite, α -FeOOH, and other iron oxyhydroxides and magnetite Fe_3O_4 , the black iron oxide (II, III) [1-15]. Hematite, α - Fe_2O_3 , the red iron (III) oxide, is not usually formed as a

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corrosion product of underground conditions, but it can be sometimes identified on the archaeological artefacts made of iron. Since the hematite has been formed when oxyhydroxides of iron is heated (above about 250°C), its presence is usually associated with the fact that the artefact was subjected to thermal treatment before buried [1,16]. The surface of layer of corrosion products is often impregnated with particles of the ground where the object was buried.

Table 1. Some corrosion products identified in archaeological iron [1].

Chemical name	Mineral name	Chemical formula	Color
Iron oxide	Magnetite	Fe_3O_4	Black
Iron oxyhydroxide	Goethite	$\alpha\text{-FeOOH}$	Yellow-brown
Iron oxyhydroxide	Akaganeite	$\beta\text{-FeOOH}$	Red-brown
Iron oxyhydroxide	Lepidocrocite	$\gamma\text{-FeOOH}$	Orange
Iron sulphate tetrahydrate	Rozenite	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	Green
Iron sulphate pentahydrate	Siderotil	$\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$	White
Iron sulphate heptahydrate	Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Blue-green
Iron hydroxide sulphate dihydrate	Butlerite	$\text{Fe}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Orange
Iron potassium hydroxide sulphate	Jarosite	$\text{Fe}_3\text{K}(\text{OH})_6(\text{SO}_4)_2$	Yellow-brown
Iron sodium hydroxide sulphate	Natrojarosite	$\text{Fe}_3\text{Na}(\text{OH})_6(\text{SO}_4)_2$	Yellow-brown

During corrosion of iron, buried in a wet ground in the presence of dissolved oxygen, its surface can be gradually transformed into a massive layer of corrosion products rust-colored, cemented with particles of small rocks, sand, clay and soil minerals. Corrosion products, which are usually layered with compounds of lower oxidation state, are formed directly on the metal surface, while the layers of compounds with higher oxidation states are formed in external layer [1-3]. The most common iron compound, which can be identified in external layer of corrosion products, is mostly goethite ($\alpha\text{-FeOOH}$) and lepidocrocite ($\gamma\text{-FeOOH}$) [1-5,7,8]. Magnetite (Fe_3O_4) is the most common iron oxide identified on the archaeological iron and it is usually located next to the metal surface [1-3], although it may be also present in other layers of corrosion products [4,5,8]. It is important to mention that these corrosion products can reduce the corrosion rate of iron comparing to the initial corrosion rate, immediately after the burial of objects.

Beside goethite, lepidocrocite and magnetite, which are mostly crystalline and can be identified by X-ray diffraction (XRD), there are the corrosion products in the form of an amorphous substance that cannot be determined by XRD method. It is believed that the amorphous substance is another type of oxyhydroxide ($\delta\text{-FeOOH}$), feroxyhyte [8,13,17] discovered by Misawa et al. [4,5] and is often called by his name (misavit). In addition to $\delta\text{-FeOOH}$, $\alpha\text{-FeOOH}$ sometimes is present in corrosion products in the form of very fine particles, which are not possible to determine with XRD method, also [4,5,8]. The presence of these fine particles is identified on the surface of specially developed steel, resistant to atmospheric corrosion (weathering steels). During time on the surface of these steels a compact layer of corrosion products is formed slowing down further corrosion. The ancient stud in Delhi resists to corrosion over 1600 years, due to the presence of a compact layer, which consists mostly of the previously mentioned amorphous corrosion products [8].

If the surroundings environment in which the artefact was buried contains sufficient amounts of chloride ions, another iron oxyhydroxide can be formed named akaganéite, β -FeOOH. Akaganéite formation is an indication of active corrosion of iron under a layer of corrosion products. Chloride ions can be implanted into the tunnels of the crystal lattice of akaganéite, stabilizing its structure. Thus, the formula of akaganéite can be expressed as: β -FeO_{0.833}(OH)_{1.167}Cl_{0.167} [16].

Goethite is thermodynamically stable compound and shows good protective properties, especially if it is in the form of fine particles, while lepidocrocite is a semiconductor compound, which is electrochemically active and it is considered that it has no protective properties. Several formulas have been proposed for determining the index of protective ability of layer corrosion products. Hoerle et al. [11] proposed a mass ratio of α -FeOOH/ γ -FeOOH, Kamimura et al. [12] mass ratio of α -FeOOH/(γ -FeOOH+ β -FeOOH+Fe₃O₄), and Dillmann et al. [10] proposed ratio of (α -FeOOH+Fe₃O₄)/(γ -FeOOH+ β -FeOOH).

By visual inspection of the artefact, covered with a layer of corrosion products, it is not possible to estimate in what extent metal is left without corrosion. One of the procedures of such evaluation was proposed by Watkinson et al. [18] based on the measurement of ratio mass and volume of artefacts. The ratio less than 2.9 indicates that the object was fully mineralized. Another method, proposed by Thickett et al. [19] is based on measuring the amount of oxygen consumed over time. The oxygen consumption is associated with the development of process of metal corrosion under a layer of corrosion products. Radiographic method [18-20] is the most reliable method to estimate the amount of core iron without corrosion products, and the types and forms of its damage. Multiple radiographs give the most trusted results [19]. This method was used in this paper.

The aim of this paper was to explain the corrosion stability of one artefact during a time spent in the soil and after its excavation, on the basis of the composition of corrosion products and their mass proportions. The artefact from Roman period (IV century), was found in locality Duge njive, community Bogatić near Šabac in Serbia.

Experimental

Ultrasound and radiographic examinations

Before radiographic examination approximate thickness measurement of non-corroded and undamaged metal of archaeological artefact was carried out by ultrasound method. Ultrasound measurements of artefact thickness enable the choice of optimal parameters for performing radiographic examinations. Ultrasonic tests are one of the most used non-damaged techniques (NDT), which are applied to determine the size of cracks or other defects in metal, as well as for local determination of wall thickness of metal objects. Ultrasonic tests were performed using devices that generate ultrasonic waves spreading in the tested object with frequencies from 0.1 to 25 MHz. Rejected signal was analyzed. The method consists of measuring the time elapsed until returning signal and analyzing the form and intensity of the reflected signal [21, 22]. Ultrasonic tests were performed using the device USM-XS Lemo Krautkramer.

Radiographic testing was carried out by using γ -rays on defectoscope SU 50 with radioactive isotope Iridium 192. Radiograph was analysed by placing it on an intensive source of light, which is a standard procedure. In this paper, the original radiographic image was scanned and displayed in the form of image.

X-ray Diffraction (XRD) analysis

Samples of corrosion products, in the form of powder, were tested by diffractometer PHILIPS PW 1710 under the following conditions: operating voltage $U = 40$ kV, current $I = 30$ mA, X-ray radiation from anticathode copper (Cu), the wavelength of $\text{CuK}\alpha = 1.54178$ Å, graphite monochromator, the range of testing $4 - 70^\circ 2\theta$, 2θ step of 0.02, 0.5 s time constant (per step).

The advantages of this method are reliable and rapid identification of material, simple preparation of sample, equipment availability and relatively rapid interpretation of data. Limitations of method consist in the fact that homogeneous sample must be available for more reliable identification of present phases; the amount of a few grams of the material is needed for analysis [23].

Results

From photographic image of the archaeological artefact shown in Figure 1, it can be seen that the artefact (knife) is covered with thick layer of corrosion products (rust), characteristic for iron. Length of the artefact is 23.5 cm, and width 3.5 cm. The artefact have flat blade, with blunted part that ends with squared grip.



Figure 1. Photographic image of the archaeological artefact (Museum Šabac).

Radiograph of the archaeological artefact is shown in Figure 2. Dark places of radiograph represent corroded areas or areas that are mechanically damaged, while the bright places show an undamaged base metal (iron). Cracks or other internal defects in the material were not observed in the radiograph. The edges of artefact are of irregular shape, due to the mechanical and corrosion damage.

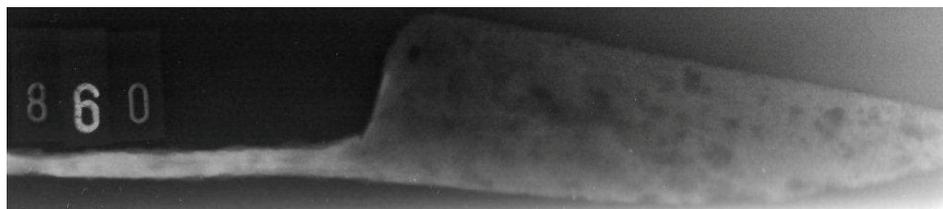


Figure 2. Radiograph of the archaeological artefact.

There is a visible roughness on the surfaces of artefact, a consequence of the mechanical damage and corrosion (possible pitting or some other form of localized corrosion). In general, it may be concluded that artefact is in fairly well-maintained condition.

From the surface of archaeological artefact (knife, Fig. 1) corrosion products were taken for XRD analysis. The analysed corrosion products of iron were partially impregnated with particles of the surrounding environment. Crystalline phases detected in the corrosion products, value of Bragg's angle (2θ), Miller's indexes of the corresponding crystal plane (hkl), interface distance (d) and X-ray intensity ratio (I/I_{\max}) are given in Table 2. It may be seen that iron oxyhydroxide, goethite, and magnetite are mostly present. Some amount of lepidocrocite was also detected.

Table 2. Values of Bragg's angle (2θ), Miller indexes of crystallographic plane (hkl), interface distance (d) and X-ray intensity ratio (I/I_{\max}) obtained during the examination of corrosion products by XRD method.

	2θ (°)	Crystallographic plane (hkl)	d_{hkl} (Å)	I/I_{\max} (%)
α -FeOOH	21.185	110	4.191	40.00
	26.705	120	3.336	60.00
	35.490	101	2.527	100.00
	36.655	111	2.450	40.00
Fe ₃ O ₄	30.190	220	2.958	33.33
	35.490	311	2.527	100.00
	36.655	222	2.450	40.00
γ -FeOOH	26.705	210	3.336	60.00
	36.655	410	2.450	40.00
	53.285	511	1.718	33.33
SiO ₂	21.185	100	4.191	40.00
	26.705	011	3.336	60.00
	36.655	110	2.450	40.00

In Figure 3 is shown XRD diagram of crystalline phases identified in the corrosion products taken from the surface of this archaeological artefact.

Four crystalline phases are present in the sample. Three of them belong to the iron corrosion products. All crystalline phases exhibit the low level of crystallinity. Corrosion products from the most common (50%) crystalline phase is poorly crystallized iron oxyhydroxide, goethite α -FeOOH (JCPDS 290713). Approximately 30% of magnetite Fe₃O₄, was detected (JCPDS 19-0629). Iron oxyhydroxide, lepidocrocite γ -FeOOH (JCPDS 44-1415) is present in a lesser amount (10%), whereas silica, quartz SiO₂, (JCPDS 89-8935) originates from surrounding rocks.

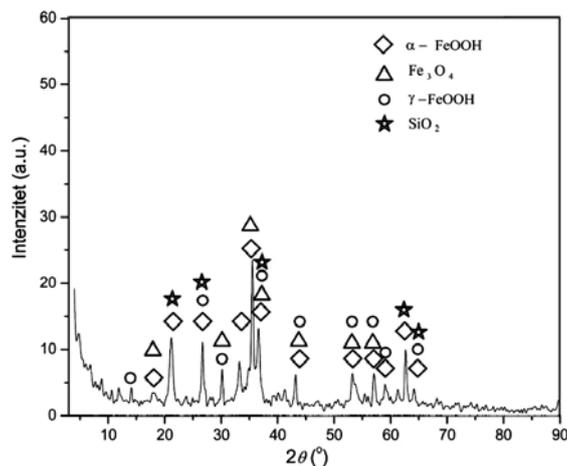


Figure 3. XRD diagram of corrosion products.

Discussion

After radiographic examination (Figure 2) of iron artefact-a knife, it could be concluded, that the artefact is in a fairly well-maintained condition, besides its burial under the ground for many centuries. Good preservation may be due to the low aggressiveness of soil in which these objects had been buried, and also as the result of composition of formed corrosion products and their structure. Weak crystallinity of corrosion products (Table 2 and Figure 3), could be attributed to the presence of very fine particles of goethite α -FeOOH and misavite (amorphous oxyhydroxides of iron, ferrihydrite) δ -FeOOH, which cannot be identified by XRD method.

It was shown experimentally [12] that the layer of corrosion products, formed on steel in different places, shows a high corrosion protection, if for example index is α -FeOOH/(γ -FeOOH + β -FeOOH + Fe_3O_4) greater than 1. There are different opinions about the role of magnetite in the corrosion products. Some authors [12] think that magnetite, because of its conductivity, enables easy operation of cathodic oxygen reduction reaction, what leads to increasing stronger corrosion of the base metal. On the contrary, other authors [10] think that magnetite, incorporated in a layer of corrosion products, increases resistance to corrosion, what is explained by a high thermodynamic stability of magnetite. We believe that the magnetite, formed in the layer of corrosion products on examined archaeological artefact has a protective role not only because of its high thermodynamic stability, but also because of its compactness and small molar volume. Volume of one mole of Fe_3O_4 is 14.9 cm^3 , and α -, β - and γ -FeOOH 20.9 cm^3 , 26.7 cm^3 and 21.7 cm^3 , respectively [3].

In the corrosion products phases containing chloride ions (i.e. akaganeite), were not detected, indirectly indicating that in underground conditions these ions were not present, or at least not present to a significant extent. This also points out the additional corrosion stability of the artefacts during the period after excavation. Although akaganeite has not been identified in the corrosion products, it still does

not mean that chloride ions are not present in small quantities [1-3]. In any case, it is still necessary to perform a preventive stabilization (desalination) of artefact in suitable solutions [1-3], before their final conservation. It will provide a long-term stability of the artefact in the circumstances that are in the museums.

Conclusions

Two methods for determination of the extent of preservation of the base metal (iron) of archaeological cultural heritage artefact were used: radiographic and ultrasonic method. The amount of core iron without corrosion products and the types and forms of its damage were determined by the radiographic method. The composition of corrosion products of the artefact (knife) under a layer was determined by the method of X-ray diffraction (XRD) analysis.

It was assumed that corrosion products were at a low-grade of crystallinity. In the corrosion products, dominant phases in the corrosion products were goethite, α -FeOOH, and magnetite, Fe₃O₄. The presence of these phases explains the preservation of the base metal over a very long time and the stability after excavation. Besides goethite and magnetite, in the corrosion products were also identified, although to a lesser extent, lepidocrocite, γ -FeOOH, and phases originating from rocks and soil surrounding environment like SiO₂. Weak crystallinity in the sample of corrosion products, could be due to the presence of very fine particles of goethite and ferrosilite (amorphous oxyhydroxides of iron, often called misavite), δ -FeOOH, that cannot be identified by XRD method.

Phases containing chloride ions were not detected in the corrosion products. That indirectly indicates that the chloride ions were not present in the exploitation conditions underground. This also points out additional corrosion stability of the artefact during the period after the excavation.

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