CORROSION STABILITY OF CORROSION PRODUCTS ON AN ARCHAEOLOGICAL IRON ARTEFACT

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Abstract

A spearhead of archaeological and cultural significance has been found and analysed in Serbia. In the corrosion products of the artefact, the dominant phases were goethite (α-FeO(OH)) and magnetite (Fe₃O₄) whose presence explains a good preservation of the base metal, iron, over the centuries and the artefact stability after excavation. Besides goethite and magnetite, the corrosion products were identified to contain, to a lesser extent, less stable lepidocrocite (γ-FeO(OH)) and the phases that come from the rocks and soil from the surrounding environment (plagioclase). The phases containing chloride ions were not detected in the corrosion products (akaganéite, β-Fe₈O₈(OH)₈Cl₁.₃₅), which indirectly indicates that the content of chloride ions was not significant in the underground exploitation conditions. The lack of chloride ions also contributed to the corrosion stability of the artefact during the period after excavation.

Keywords: corrosion; iron; radiography; XRD; archaeology.

Introduction

The corrosion products of iron are red and brown iron (III) compounds, usually goethite and other iron oxy-hydroxides and black iron magnetite (II,III) oxide [1-16]. Hematite (α-Fe_2O_3), a red iron oxide, is not usually formed as a corrosion product in underground conditions, but can sometimes be identified on archaeological iron. Since hematite is formed when oxy-hydroxides of iron are heated (over $250^{\circ}C$), its presence can be related to the fact that the object was exposed to fire before burial [1, 17]. The surface layer of corrosion products is often impregnated with particles of the ground where the object was buried.

When iron corrodes, buried in the moist ground in the presence of dissolved oxygen, its surface can be gradually transformed into a massive layer of rust-coloured corrosion products, cemented with particles of small rocks, sand, clay and soil minerals. Corrosion products, usually layered with compounds of a lower oxidation state, form directly on the metal surface while the layers of compounds with higher oxidation states form in the external layer [1-5]. The most common iron compound which can be identified in the external layer of corrosion

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products is an iron oxy-hydroxide, mostly goethite (α-FeO(OH)) and lepidocrocite (γ-FeO(OH)) [1-7, 9, 10, 18]. Formed corrosion products can reduce the corrosion rate of iron compared to the initial corrosion rate immediately after the burial of objects. Magnetite (Fe_3O_4) is the most common iron oxide identified on the archaeological iron, usually located next to the metal surface [1-5], although it can be also present in other layers of corrosion products [6, 7, 10].

Beside these compounds, which are mostly crystalline and can be identified by X-ray diffraction (XRD), there are also corrosion products in the form of an amorphous substance that cannot be determined by the XRD method. It is believed that the amorphous substance is another type of oxy-hydroxide (δ-FeO(OH)), feroxyhyte [10,15,19] discovered by Misawa et al. [6, 7] and often called misavit in his honour. In addition to δ-FeO(OH), sometimes α-FeO(OH) is present in the corrosion products in a form of very fine particles, which are also not possible to be determined with the XRD method [6, 7, 10]. The presence of these fine particles is identified on the surface of specially developed steel, resistant to atmospheric corrosion (weathering steels), in which the surface, with time, forms a compact layer of corrosion products that greatly slows down further corrosion. An ancient stud in Delhi has been resisting corrosion for over 1600 years, due to the presence of a compact layer consisting mostly of the previously mentioned amorphous corrosion products [10]. The presence of such a layer of corrosion products is the result of the applied metallurgical manufacturing process of iron objects at that time [10].

Another iron oxy-hydroxide can be formed, if the surrounding environment in which the artefact was buried contains a sufficient amount of chloride ions. It forms akaganéite (β-FeO(OH)), particularly in the period after excavation, when the access to oxygen is increased; while objects get dry, the concentration of chloride ions in the corrosion products increases [1-7, 9, 11, 17, 20-27]. The 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, so that the formula of akaganéite can be β-FeO$_{0.833}$(OH)$_{1.167}$Cl$_{0.167}$ [9, 17].

The relative ratio of individual compounds in the layer of corrosion products is also very important because the protective ability of the compound depends on the relative ratio. Lepidocrocite is a semiconductor compound, electrochemically active and considered not to have protective properties. Goethite is a thermodynamically stable compound showing good protective properties, especially if it is in a form of fine particles. Magnetite is a good electrical conductor; it is considered to have protective properties due to its thermodynamic stability [13]. Several formulas were proposed for determining the index of the protective ability of corrosion product layers. Hoerle et al. [13] proposed a mass ratio of α-FeO(OH)/γ-FeO(OH), Kamimura et al. [14] a mass ratio of α-FeO(OH)/(γ-FeO(OH) + β-FeO(OH) + Fe$_3$O$_4$), and Dillmann et al. [12] proposed a ratio of (α-FeO(OH) + Fe$_3$O$_4$)/(γ-FeO(OH) + β-FeO(OH)).

The aim of this paper was to explain the corrosion stability of one artefact during the time it spent in the soil and after its excavation on the basis of the composition of its corrosion products and their mass proportions. The spearhead (hasta) made from wrought iron, dating from the Roman period, I/IV century, was found in the location Duge njive, Banovo polje (Sabac, Serbia).

Experimental part

An ultrasonic testing was performed using devices that generate ultrasonic waves, frequencies from 0.1 to 25MHz, which exceed in the tested object. The ultrasonic tests were performed using the device USM-XS Lemo Krautkramer.

The radiographic examinations were performed using X-ray on an industrial X-ray Baltpost 200kVA, with 135kV voltage and the electric current of 5mA. The radiographs were analyzed with a strong light source which is a usual procedure. Since the original radiographic images were scanned and displayed in the form of digital images in this paper, many important details cannot be visible in them.

The sample was tested by the X-ray Diffraction (XRD) method on a diffractometer PHILIPS PW 1710 for powder, under the following conditions: operating voltage: $U = 40$kV, current $I = 30$mA, X-rays from anticathode copper (Cu), wavelength CuKα = 1.54178Å, graphite monochromator, test range: 4 - 90º 2θ, step: 0.02° 2θ, time constant: 0.5s (per step).

Results

From the photographic image of the archaeological artefact shown in figure 1, it can be seen that the artefact (spearhead) is covered with a thick layer of corrosion products (rust), characteristic for iron. The length of the artefact is 14cm, and the width is 3.5cm. The top of the spearhead is in a shape of a leaf and a socket for planting.

Fig. 1. Photographic image of the archaeological artefact-spearhead

Figure 2 shows the archaeological object (spearhead) recorded by the radiographic method. The brighter areas on the radiographs indicate thicker parts of the artefact. It can be seen that the base metal (iron) is slightly damaged by the corrosion process. At the narrow part of the spearhead, a longitudinal crack can be seen, probably due to mechanical damage of the artefact. Additional internal defects in the material were not observed on the radiograph. The spearhead is generally in a well-maintained condition.

Fig. 2. Radiograph of the archaeological artefact-spearhead.

The corrosion products from the surface of the artefact are carefully taken for the XRD analysis. The analysed iron corrosion products were impregnated with a compact layer testing. Table 1 shows that crystalline phases are detected in the corrosion products. The table also includes: the value of Bragg's angle (2θ), the Miller indices of the suitable crystal plane (hkl), the interface distance (d) and the X-ray intensity ratio (I/I_{max}) obtained during the examination of the corrosion products. It can be seen that goethite, an iron oxy-hydroxide, is mainly present, although lepidocrocite is also present to some extent.

Four crystalline phases are present, two of which belong to the iron corrosion products, and two probably come from the surrounding rocks in this sample. All present crystalline phases are at a very low level of crystallization. The most common (60%) crystalline phase of the corrosion products is a poorly crystallized iron oxide-hydroxide, goethite, α-FeO(OH) (JCPDS 29-0713). The second most common phase (20%) is a mineral from the feldspar mineral families, a group of plagioclase. In the plagioclase, there are a number of minerals, from albite, $NaAlSi_3O_8$ to anorthite, $CaAl_2Si_2O_8$, with different amounts of sodium, calcium, aluminium and silicon, and they are often the ingredients of rocks.

Table 1. 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 the corrosion products by the XRD method.

	2θ (°)	Crystallographic plane (hkl)	d (Å)	I/I_{max} (%)
	21.315	110	4.165	100.00
	26.735	120	3.332	58.33
α-FeO(OH)	36.760	111	2.443	62.50
	53.190	221	1.721	41.67
	61.545	002	1.506	41.67
	14.230	200	6.219	45.83
γ-FeO(OH)	36.760	410	2.443	62.50
	53.190	511	1.721	41.67
	28.055	004	3.178	75.00
plagioclase	33.395	-134	2.681	41.67
	67.020	190	1.395	41.67
	29.565	104	3.019	45.83
$CaCO_3$	36.760	110	2.443	62.50
	39.930	202	2.256	41.67

Due to their very low level of crystallinity and relatively low content in the sample, it is not possible to claim which mineral is in question, but the diffraction maximum leads to the conclusion that it is approaching $CaAl_2Si_2O_8$ to anorthite (JCPDS 41-1486). Lepidocrocite, an iron oxide-hydroxide, γ-FeO(OH) (JCPDS 44-1415), can be found in a small amount (about 10%) as well as the product of corrosion, calcium carbonate, calcite, $CaCO_3$, (JCPDS47-1743), as an integral part of the surrounding rocks. The very weak diffraction maximums, at small angles, indicate a possible presence of some silicates, but it has not been possible to identify them due to their low content.

Figure 3 shows an XRD diagram of the crystalline phases identified in the corrosion products taken from the surface of the artefact.
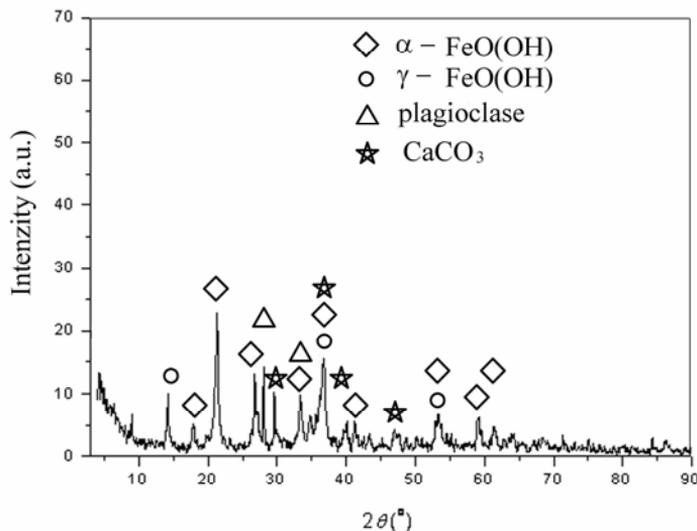
Fig. 3. XRD diagram of the corrosion products of the spearhead

Discussion

Based on the displayed radiographic image (Figure 2) of the examined iron artefact, it could be concluded that the artefact is in a fairly well-maintained condition, although it was buried under the ground for many centuries. The reason for the good preservation may be, primarily, due to the low aggressiveness of soil in which the object was buried as well as to the composition (and possibly the structure) of the formed corrosion products. The crystalline phases present in the corrosion products were determined by XRD, and shown in Table 1 and figure 3. The weak crystallinity of the sample of the corrosion products could be due to the presence of very fine particles of goethite, α-FeO(OH) and misavit (amorphous oxy-hydroxides of iron, feroxyhyte), δ-FeO(OH) which cannot be identified by the XRD method.

Long before the Bessemer's discovery of the modern process of steel production in 1856 [24], it was usually obtained from the ore by reduction, using charcoal. The spearhead dates from the Roman period, so it is clear that it was produced by the bloomery heath process; such iron contains P when it is made from bog iron ore since this ore often contains vivianite.

A favourable composition of corrosion products that can be expressed by the index of their protective ability, mentioned in the introduction of this work, was revealed. It was shown experimentally [14] that a layer of corrosion products formed on steel in different places shows high corrosion protection, if for example the index is (α-FeO(OH)/(γ-FeO(OH) + β-FeO(OH) + Fe_3O_4)) greater than 1. There are different opinions about the role of magnetite in corrosion products. Some authors [14] think that magnetite enables easier cathodic oxygen reduction reaction, which leads to the increase of corrosion of the base metal. On the contrary, other authors [12] think that magnetite, incorporated in a layer of corrosion products, increases the resistance to corrosion, which is explained by a high thermodynamic stability of magnetite. We believe that the magnetite formed in the layer of the corrosion products on the examined archaeological artefact has had a protective role, not only because of its high thermodynamic stability, but also because of its compactness and a small molar volume. The volume of one mole of Fe_3O_4 is 14.9 cm^3, and α-, β- and γ-FeO(OH) 20.9cm^3, 26.7cm^3 and 21.7cm^3, respectively [3].

In the corrosion products, phases containing chloride ions (akaganeite, β-FeO$_{0.833}$(OH)$_{1.167}$Cl$_{0.167}$) were not detected, which indirectly indicates that in the underground exploitation conditions chloride ions were not present, or at least not present to a significant extent. This also contributed to the additional corrosion stability of the artefact during the period after excavation. Although akaganeite has not been identified in the corrosion products, it does not mean that chloride ions are not present in small quantities [1-5], so that it is still necessary to perform a preventive stabilization (desalination) of the artefact in suitable solutions [1-5] before final conservation. It will provide long-term stability to the artefact in the museum conditions. The corrosion characteristics of different metals and alloys are considered in [2-5, 10-13, 25-27].

Conclusions

The extent of preservation of the base metal on the archaeological artefact made of iron under a layer of corrosion products was determined by the radiographic method, and the thickness of that undamaged and non-corroded object under the layer of corrosion products was evaluated by ultrasound. The composition of the corrosion products of iron was determined by X-ray diffraction (XRD).

The corrosion products were at a low level of crystallinity. In the corrosion products of the artefact, the dominant phases in the corrosion products were goethite (α-FeO(OH)) and magnetite (Fe$_3$O$_4$) whose presence explains the preservation of the base metal (iron) over the centuries and the stability after excavation. Besides goethite and magnetite, the corrosion products also contained, to a lesser extent, lepidocrocite, γ-FeO(OH) and the phases that come from the rocks and soil in the surrounding environment (plegioclase).

The weak crystallinity in the sample of the corrosion products could be due to the presence of very fine particles of goethite, α-FeO(OH), and feroxyhyte (amorphous oxy-hydroxides of iron, often called misavit), δ-FeO(OH), that cannot be identified by the XRD method.

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