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CHARACTERIZATION OF ARCHAEOLOGICAL OBJECTS COMING FROM MOLDOVIAN SETTLEMENTS IN THE XIVTH CENTURY

Mihaela POTECAȘU, Marian BORDEI
"Dunarea de Jos" University of Galati
e-mail: mbordei@ugal.ro

ABSTRACT

This paper presents the characterization, from the materials science point of view, of an object found in an archaeological vestige of the 14th century.

The object studied (an iron nail used in constructions) proves that the inhabitants of those lands were very good craftsmen, capable of performing useful products for everyday life, who worked with precision, ingenuity and ability.

The analysis of the archaeological relic led to the conclusion that plastic deformation was achieved by successive cycles of hammering (driving) applied after repeated heating meant to enable the material to regain its deformability so that, through low repeated deformation, it could finally reach the requested shape.

The process is revealed by microstructural analysis and by the value obtained for hardness.

KEYWORDS: nail, plastic deformation, strings oxides, archaeology

1. Introduction

Despite the fact that the processing of raw materials was complex and difficult, the craft of iron processing originated in the earliest times of human existence and continuously improved with the development of human society. In what regards the exploitation of iron and brass, the written documents of the fourteenth and fifteenth centuries contain little information, but supplemented by archaeological testimonies. Archaeological excavations have revealed man-made tools: hammers, anvils, pliers, chisels, household items (knives, locks, keys), objects for construction (nails, chisels), or parts of weapons and harness.

The techniques used in the production of iron tools and objects in the 14th-15th centuries were: casting, hot and cold processing, heat treatments.

The ore rock was taken to pieces using crowbars, and the pieces were broken with hammers (later hydraulically); the ore was previously crushed, washed and sorted, then, before being introduced into the furnace, it was roasted to remove water and ferrous components. From the mineral thus prepared, the iron reduction followed using the procedures documented in the 9th-13th centuries in an oval oven-furnace built partially in the ground, the inner walls being coated with clay "with a siliceous refractory facing". After placing the ore and charcoal in layers, and sometimes adding pieces of limestone (lime), the preparatory operations were over and the burning process that followed was maintained by air currents using bellows. In the oven, temperatures were between 1300 and 1450 °C. This type of furnace, as evidenced by the findings at Ghelar (9th-10th centuries), Hlincea (11th century), partly to Bucov (10th century) and Barlad (11th-12th centuries), similar to that discovered in other European countries about the same time, continued to be used in the Romanian countries in the 14th and 15th centuries [1, 2].

If, in early feudalism, extractive metallurgy was not separated from processing metallurgy (e.g. Bucov, 10th-11th centuries), starting with the 14th century the process of separation emerges, certified by the workshops where the iron objects were made (e.g. Zimnicea), but which do not contain any trace (pieces of ore, slag) resulting from the reduction of mining operations. The object processing was done at a temperature of about 1000 °C, as the craftsmen of that period knew how to make steel (research revealed the existence of a 0.370 carbon steel in the metal paste with a rather homogeneous structure) for steel blades (swords, knives) [1, 3].

Cold working operations that include modeling by "hammering", cutting, stamping, drilling, incision, bending, twisting, cold riveted joint are used in particular for working bands, bars, thin sheet and wire. Hot working operations include: bonding, bending, twisting, drilling. These techniques are used, in particular, for heavy parts so that, together with the cold working techniques, they form an assembly which allows obtaining multiple types of objects made of iron or its alloys with carbon. The different hardening procedures ensured the hardness and resistance of the processed iron objects. The skill of the autochthonous craftsmen regarding hardness is demonstrated by the fact that all the pieces found are hardened; moreover, the hardness is not uniform but it is differently executed only on the active parts of the piece.

There are some cases considered extraordinary for the technologies in that period or at least incompletely elucidated scientifically. One such example is the "dacian nail" found in the Dacian sanctuary at Racoş (Romania). According to the analysis carried out by the physicist Andrei Vartic at the Institute of Metallurgy in Balti (Rep. of Moldova), this one dates back over 2,000 years and is assigned to the Dacian culture. The Nail, considered an "ancient miracle" consists of 99.97% pure alpha iron without traces of impurities (carbon compounds remaining from processing), which leads to the conclusion that it could have been done by techniques and under conditions inexistent during that period.

Further research conducted in Leningrad and Moscow can lead to the conclusion that the protection is given by three molecular layers: first layer (surface) - Magnetic "Fe_3O_4"; second layer - Iron Oxide "FeO"; third layer - alumo silicates [4]. The Dacian nail is found at the cedar doors of St. Catherine's Monastery in Sinai.

The study of this work was done on a metal nail originating in an archaeological vestige from the 14th century and pursued its characterization: determination of chemical composition, metallographic analysis and hardness determination.

2. Results and discussions

The chemical composition of the sample was determined using a portable metal analyzer (X-ray fluorescence spectrometer Innov-X Systems brand) and is presented in Table 1.

Table 1. *Chemical composition of the studied object*

Object	*Chemical composition* **(%)**			
	C	**Mn**	**Si**	**Al**
Nail	0.10	0.13	0.084	0.026

A first finding of the macrostructural analysis carried out on the studied object is the advanced state of degradation of the object and the penetration of oxide films in the thickness of the product as seen in the microstructural analysis performed in the longitudinal section of the object (Figure 1).

In Figure 1, using the 100X microscope increase, uncontested evidence is found regarding the degradation mechanism and damage on the analyzed object under the action of chemical agents in the external environment from chemical (especially electrochemical) reactions which started from the nail surface to its core (process known as rust of iron).

The areas analyzed showed that object-environment interaction in time evolved unevenly and non-simultaneously.

Thus, after the appearance of destruction, highly complex phenomena of corrosion are observable, i.e. corrosion both continuous (because the entire metal-environment interface showed destructive action of aggressive environment) and local (because the destruction occurs in depth pin, mostly in certain areas with greater instability).

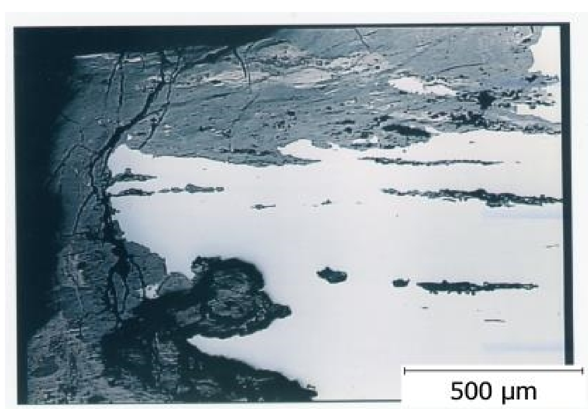

Fig. 1. *Nail microstructure in longitudinal section in the end section (no metallographic attack) magnification x100*

The macrostructural analysis of the studied object shows that the continuous corrosion process evolved over the centuries and the nail oxidation in the atmosphere led to its dressing in layers of brown and black iron oxide (the so-called iron rust).

According to the literature [5, 6], it is known that, in the first stage of iron oxidation, FeO is formed, ferrous oxide, which is stable only in the absence of oxygen. When the atmospheric oxygen appears, the iron oxide is converted into iron hydroxide ($Fe_2O_3H_2O$) and FeO (OH), in two phases:

- phase 1, corresponding to a large excess of oxygen;

- phase 2, characterized by an amount of insufficient oxygen that slows down the oxidation process.

Depending on the rust color, 3 type scan be distinguished:

1. White rust $Fe(OH)_2$, which is formed by the reaction

$$Fe+2H_2O \rightarrow Fe(OH)_2+H_2$$

This type of rust quickly changes through oxidation into brown rust; that is why it is so rarely observed.

2. Brown rust occurs from the reaction

$$4Fe(OH)_2+O_2 \rightarrow 4FeO\cdot OH+2H_2O$$

3. Black rust consists of ferrous and ferric oxide (also called magnetite because of its magnetic properties) and is considered the most stable form of iron oxide. It forms on the metal surface a protective layer with homogeneous and adherent structure. The reaction proceeds as follows:

$$2FeO\cdot OH+Fe(OH)_2 \rightarrow Fe_3O_4+2H_2O$$

The microstructural aspect of Figure 1 shows that local corrosion has several aspects:

• punctiform corrosion, located on small surfaces (corrosion points);

• under subsurface corrosion, starting at the surface but preferably extending below the metal surface, which causes metal swelling and peeling (corrosion bags);

• corrosion spots, distributed on relatively large areas, but of small depth;

• intercrystalline corrosion, characterized by the selective destruction of the metal on the edge of the crystals;

• transcristalline corrosion, a typical local corrosion at which the corrosive destruction of the mechanical stresses is determined by the direction of stretching.

Characteristic of this type of corrosion is that cracks do not propagate only at the crystal’s edge but they actually transit them.

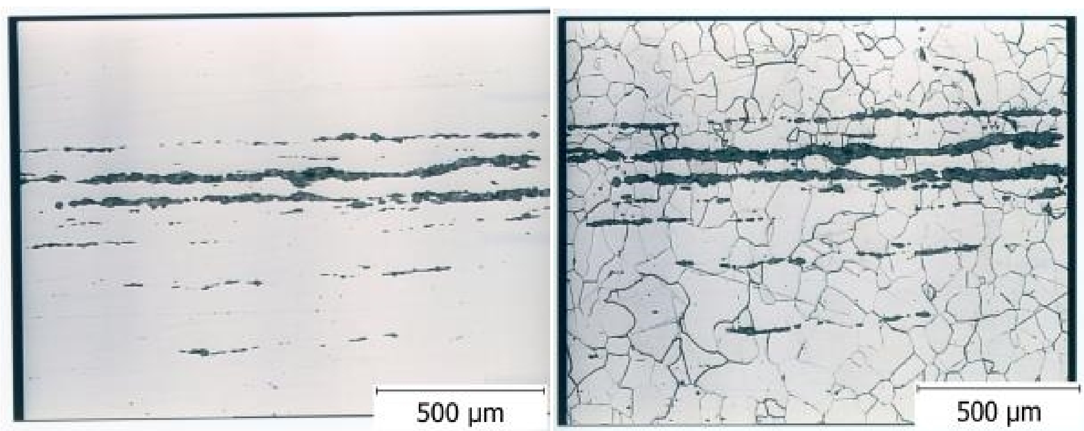

Fig. 2. *Nail microstructure in longitudinal zone in the end section (a - metallographic attack-free, b - with metallographic attack), magnification x 100*

On the metallographic sample attack (NITAL reagent 2%), the microstructural analysis carried out in longitudinal section shows a structure made of a ferritic matrix with tertiary cementite separation and small pearlite amounts (in agreement with the content of 0.1% C determined by the fluorescence spectrometer).

On the sample without metallographic attack, the microstructural analysis performed in longitudinal section shows the fibering inclusions and corrosion preferentially developed in the metallic base mass of the pin on these strings of inclusions. In Figure 2b the pin microstructure in longitudinal section towards the end (the outer edge of the nail) shows only a ferrite and tertiary cementite structure (F + Fe3CIII), indicating a low carbon content (less than 0.0218%), i.e. advanced decarburization due to successive heating cycles necessary to achieve the object by plastic deformation. Here, the crystalline grains are coarser compared to grains from the center section. This decarburization is confirmed by the very low hardness 110-120 HB, compared to values of 140-145 HB towards the center area of the nail longitudinal section with finer granulation and where pearlite grains are also present. The ferrite in the base mass of the analyzed object is a light hardened ferrite of manganese and silicon atoms dissolved by substitution in the iron network (Table 1).

3. Conclusions

• The analyzed object comes from an archaeological relic of 14th century Moldovan settlements.

• The Analysis of the object (iron nail) led to the conclusion that plastic deformation was achieved by successive cycles of hammering (driving) applied after repeated heating meant to enable the material to regain its deformability so that, by low repeated deformation, to obtain finally the desired shape.

• Repeated heating (probably in fire) had the effect of decarburization emphasized in the surface layer.

• The microstructure consists of ferrite and tertiary cementite on the surface of the object (decarburized zone) and ferrite with tertiary cementite separations and small amounts of perlite in the core of the object.

• Hardness varies according to the microstructure from 110-120 HB to the outer edge of the studied object in longitudinal section to 150-155 HB to the center.

• The studied object (iron nail) proves that people from Moldovan lands were very good craftsmen, capable of performing useful products for everyday life, who worked with precision, ingenuity and ability.

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