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Research Article

STUDY OF A 12th -CENTURY FRAGMENT OF HAUBERK WITH BLACK MAGNETITE PATINA

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ABSTRACT

This is the study of a fragment of hauberk from an excavation carried out on a plot of land next to the church of S. Vicente in Vitoria-Gasteiz (Álava, Basque Country, Spain).
The steel rings have a patina of matt black artificial magnetite. This patina with evident decorative effect, while protective of the corrosion and the rust, was obtained artificially to high temperature as it is deduced of the microstructure resulting from the steel of the rings. The research was carried out by Scanning Electron Microscopy (M.E.B.) and X-ray diffraction.

INTRODUCTION

The hauberk has been for 2,000 years the most important body defense. The military man and Roman literary Marco Terencio Varrón thought that the Gauls invented it (century V to 1 a.C.) [1]. Other types of protections, such as leather and fabrics, coexisted with this type of interlaced steel ring fabric. This type of protection consists of hundreds or thousands of rings interlaced with each other, forming a flexible metallic fabric. These steel rings are interlocked in a warp of four rings joined with another, and the motif is repeated indefinitely. Other types of warp can be found, such as six to one, but less used [1-3].

Our study has focused on a fragment of hauberk, found in an excavation in 1968 on a plot of housing in Vitoria-Gasteiz (Álava, Basque Country, Spain), next to the church of San Vicente and which is deposited in The Armory Museum of Álava (Figure 1). In addition to providing data on its manufacture, it provides valuable information about its decoration with a patina of magnetite, giving it a blackish appearance with semi-metallic matt shine. This finish was also presented by the arms and protections of the pre-Roman Celtic and Iberian peoples (6th to 2nd century BC) [4-7].

Figure 1 Fragment of hauberk of the Armory Museum of Álava

What is unique with regards to other findings is the presence of this artificial magnetite, adhered firmly to the steel substrate, and of continuous and uniform thickness. Also, it has been found that magnetite was produced by heat at elevated temperatures [8].

The scientific importance of the study of this hauberk lies in the fact that these are materials, hitherto little known; Although, some of them have been studied in archaeological

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contexts of the second iron age in Europe and in Roman and medieval times, as well as European [9-14]. In all cases, in no publication, references are made to the existence of magnetite patinas. It is evident that the purchasing power of certain individuals made them distinguish themselves from the rest by wearing a satin-black hauberk. This beautification, shows that the armament also personalized everything that could be. This layer of magnetite had added value to behave as a protective coating against corrosion, which also achieved a clean and rust-free effect.

The study was carried out by scanning electron microscopy metallography (M.E.B.); Using the EDS-EDX chemical identification and analysis technique, incorporated in the scanning electron microscope. X-ray diffraction has been used for the identification of the magnetite coating.

Experimental Technique

From the fragment of the hauberk (Museum of Armory of Álava) a ring was extracted and the area of the rivet was cut. The rivet and the rest of the ring were embedded in two-component epoxy resin. The metallographic preparation was performed in a conventional manner and the chemical attack to reveal the structure was done with 4% Nital (Figure 2). For the observation in scanning electron microscopy, a cathodic sputtering of gold was made to make it conductive and perform the EDS-EDX analysis correctly.

Figure 2 Macrography of one of the mesh dimension rings sectioned by a longitudinal plane

X-ray diffraction for the identification of the magnetite coating was performed with a PANalytical Multi-Purpose Diffractometer model X'Pert MPD, equipped with Cu-ray tube and two goniometers in vertical configuration th-2th, with Bragg- Brentano.

RESULTS AND DISCUSSION

This fragment of hauberk was made with a warp of four steel rings attached to another. And this motive was repeated until the necessary fabric was obtained to dress and protect the warrior.

The rings have crushed ends and riveted, as seen in Figures 3 and 4. In this way, the hauberk is secured against any tear or blow of a cutting weapon or arrow or spear impact.

The mesh fragment is well preserved thanks to the existence of the patina of magnetite, which, in addition to beautifying the satin black color, has protected it from corrosion (Figures 1, 5 and 6).

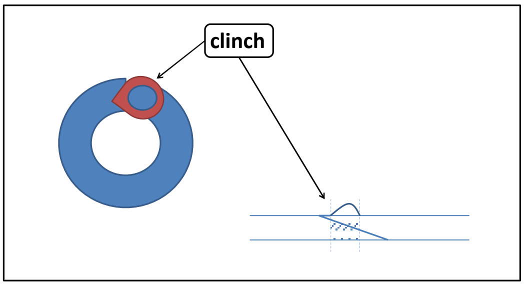


Figure 3 Schematic drawing of one of the rings of the mesh fragment with the crushing of the ends and the rivet

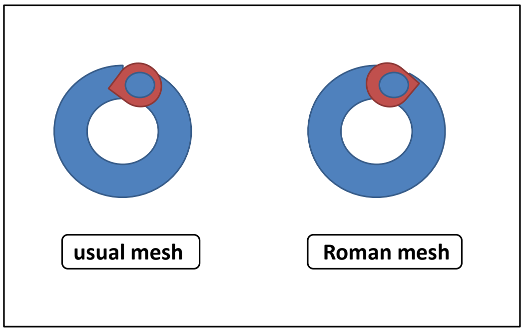


Figure 4 Schematic drawing of chain mail rings according to the Roman model and the usual one. In our fragment of mesh dimension the model presented is the usual one.

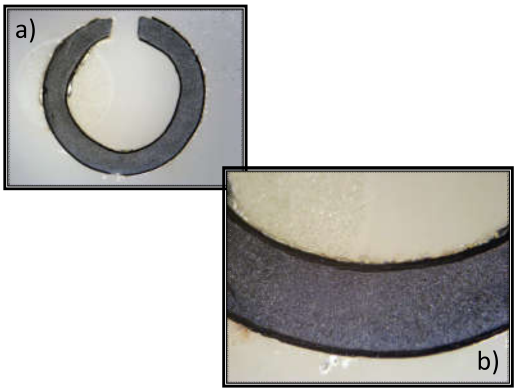


Figure 5 a) Ring belonging to the fragment of mesh with the segment of the rivet cut, protected by the patina of magnetite. b) Detail of figure 5a.

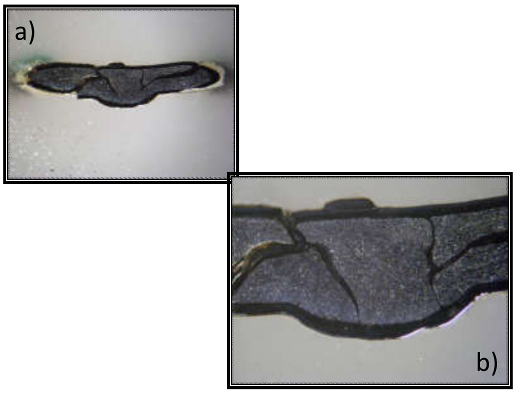
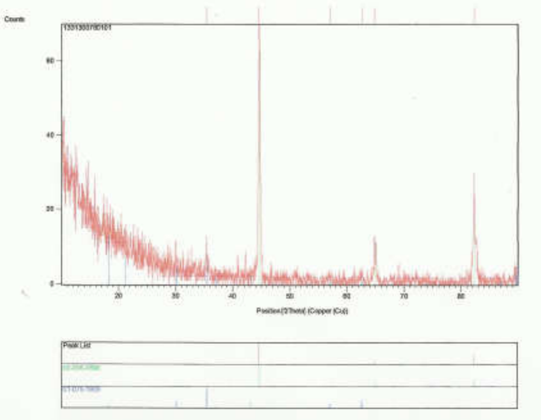


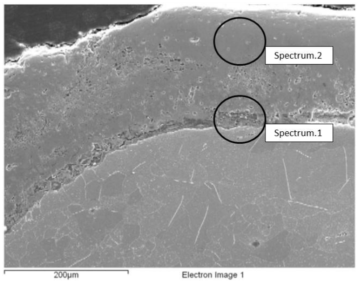
Figure 6 a) Segment of the rivet cut by a longitudinal plane, protected by the patina of magnetite. b) Detail of figure.6a

The magnetite layer has been identified by X-ray diffraction (Figure 7) and by EDS-EDX analysis (Figure 8). It is a compact film of Fe_3O_4, well adhered to the steel substrate of the ring (Figures 9-10). The magnetite patina is homogeneous and of constant thickness (Figure 5b and 9).



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula	Chemical Name	Empirical Formula	Matched Lines	Quality
*	00-006-0696	62	ferrite	0,000	0,883	Fe		Fe	3	"S"
*	01-075-1609	36	Iron diiron(III) oxide - LT	0,000	0,095	Fe3 O4		Fe3 O4	9	"C"

Figure 7 Diffractogram of the magnetite patina



Spectrum	O	Fe	Total
1	17,65	82,35	100,00
2	23,15	76,85	100,00

Figure 8 EDS-EDX analysis of the magnetite patina

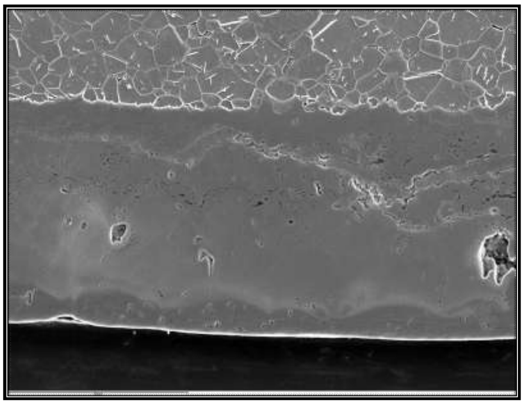


Figure 9 SEM image showing the fairly compact and homogeneous and continuous thickness of magnetite patina

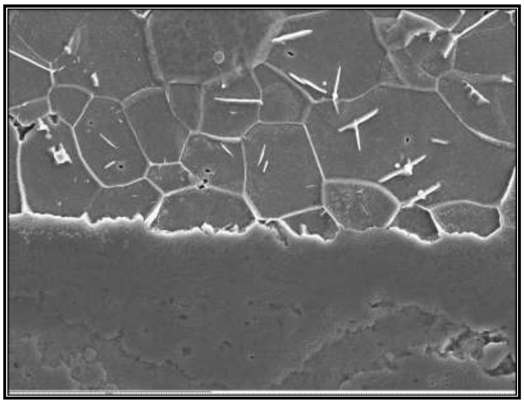


Figure 10 SEM image showing the good adhesion of the magnetite patina with the steel substrate

This dimensional detail serves to confirm the artificial creation of the layer. This layer of magnetite, in its zone of contact with the steel, is richer in iron than the outer zone, as can be seen by the EDS-EDX analysis carried out at two different points of the patina (Figure 8). This higher iron content of the magnetite layer is also observed in the diffractogram of Figure 7.

This layer of artificial magnetite is manufactured by heating to high temperature in conditions of a low oxidizing atmosphere, as it was done with the same patinas in the pre-Roman armament of the Iberian Peninsula (centuries VI to II a.C.) [4-7].

The layer remains with a remarkable adhesion and its tenacity to the blows is excellent, reason why it does not peel easily [4-7].

The magnetite gives good resistance to corrosion by having a very compact texture. Because of these good characteristics, the rings of the hauberk, analyzed in this study, are preserved acceptably, although it has remained buried several centuries in the vicinity of the church of S. Vicente de Álava. The magnetite is an iron oxide (Fe_3O_4) very compatible with the crystalline network of the ferrite, hence its good adhesion to the metallic surface of iron [15].

The black patina of magnetite was produced after the fabrication of the mesh, which is deduced from the rivet, previously made (Figure 6a and 6b). If the magnetite layer was produced before the riveting, it would have deteriorated with the blows for the forge of the rivet.

The temperature, to which the mesh dimension was subjected, to produce the patina, is deduced from the microstructure of the steel. In Figures 11 and 12 a ferritic structure with carbides of very characteristic morphologies can be observed.

It is observed that the cementite is globulated, although acicular carbides with Widmanstätten structure appear. To produce the globulization, temperatures around the eutectoid temperature must be reached. If it is above or below 723 ° C, the key is in the acicular carbides (Figures 10 and 11) according to the literature, acicular carbides are generated by diffusion at room temperature for long periods of time from a carbon saturated ferrite [8, 16-17].

This occurs if the temperature reached is sufficient to dissolve the carbon in the austenite and then cool rapidly, which would occur if the eutectoid temperature was exceeded for a while.

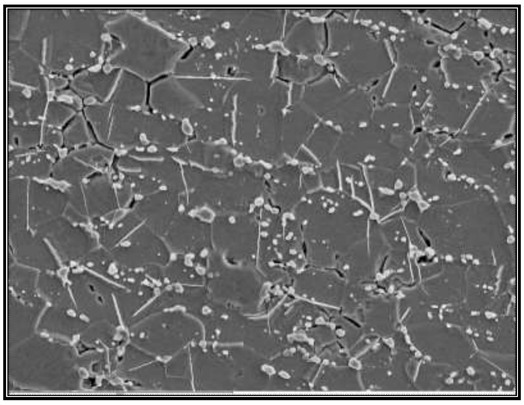


Figure 11 SEM image of the steel microstructure of the ring. Globulized iron carbides and Widmanstätten acicular cementite are observed in a ferrite matrix.

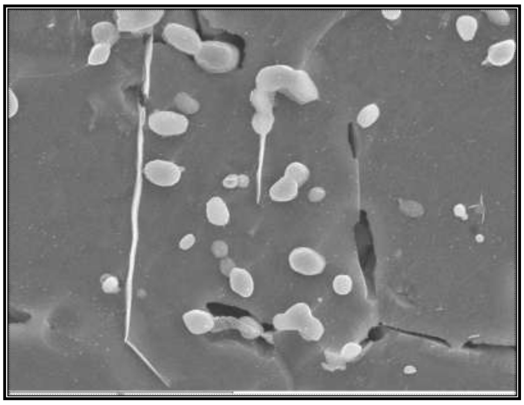


Figure 12 Detail to larger increases of the microstructure of figure

Time sufficient to dissolve one part of the cementite in austenite and to globulize another quantity. We are inclined to assume that the temperature reached was above the eutectoid isotherm [8, 16-17].

What is evident is that the temperature reached was sufficient to globulize the cementite. This implies that the magnetite patina was obtained by heating in a low oxidizing atmosphere [4-7].

The intentionality of obtaining a decorative patina in the mesh dimension is evident. This relates the pre-Roman custom of decorating with black patches of magnetite the armament, with this dimension of medieval mesh (XII century).

CONCLUSIONS

The study of this fragment of mesh dimension leads us to conclude that the layer of magnetite, which forms the black patina, has been obtained artificially for decorative purposes. This links with the patinas of artificial magnetite, existing in the pre-Roman armament of the VI-II bce centuries, of the pre-Roman peoples of the Iberian Peninsula.

The patina of magnetite at the same time that contributed a decorative effect, preserved to the mesh quota of the typical rust in these protections. The magnetite patina kept the hauberk clean and rust free, at the same time, which had a beautiful matt black satin color. His appearance was very beautiful and his touch special and delicate.

The mechanical properties of this patina are excellent, due to the tenacity of the magnetite, its perfect adhesion and its good crystalline compatibility with the iron base on which it is supported.

The formation conditions of this magnetite patina are deduced from the steel metallography of the rings. The existence of globulized cementite in a matrix of ferrite allows us to think that its obtaining was by heating to high temperature, above the eutectoid isotherm. The existence of acicular carbides indicates that part of the original cementite was dissolved in the existing austenite above the eutectoid; Although the temperature reached did not reach the total austenitic field. At this time and at that temperature the globulization of the cementite occurred. The carbon dissolved in the austenite was retained in the ferrite during cooling. This carbon was segregated by diffusion over time (several centuries) at ambient temperature forming the acicular carbides with Widmanstätten structure.

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