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Precipitation of Iron Carbides in Heterogeneously Shaped Steel with Widmanstätten Structure

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ABSTRACT

We have been able to obtain by means of scanning electron microscopy, structural morphologies of iron carbide that being so singular become a definitive witness of the existence or not of incineration in the archaeological pieces of steel that present them. They present a very peculiar image, which proves their origin.

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Received: May 08, 2022; **Accepted:** May 09, 2023; **Published:** May 22, 2023

Keywords: Precipitation, Heterogeneous, Iron Carbides, Archeometallurgy.

Introduction

The aim of this research is to obtain a heterogeneous precipitation of iron carbides with a precipitate that grows semi-coherently in a planar form with growth steps and very low mobility.

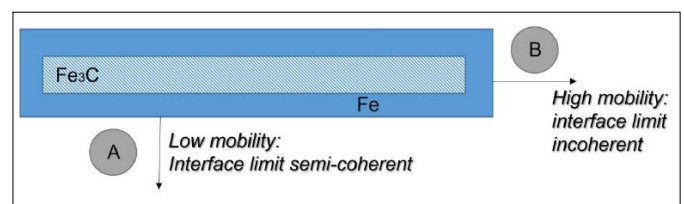
The majority phase is ferrite and the one that forms the precipitate is iron carbide. The nature of this precipitate is different from ferrite, being a phase with very complex crystals and belonging to a non-metallic phase. Ferrite crystallizes in the cubic system centered on the body while cementite crystallizes in the orthorhombic system of ceramic character. It is therefore a metal-nonmetal system with very well defined characteristics. Its growth in the solid state, as well as in the liquid state, has non-metallic characteristics as opposed to ferrite, which is a characteristic cubic centered metal.

Iron carbide is characterized by a growth with a planar character, therefore, with incoherent and semi-coherent interfaces. The structure we present is very difficult to observe outside the world of steels. These specimens come from the area of archaeometallurgy. The conditions are very special because they have undergone a process of incineration. Therefore, having undergone a strong heating followed by a severe cooling. To which must be added a very slow diffusion process over more than 2,000 years, the consequences of which we are now seeing. This is something that is observed in almost all artifacts from these incineration events. These are hot-forged, air-cooled hypoeutectoid steels that then, at the end of their life, undergo a process as unconventional as incineration.

In our case, we are dealing with an Iberian footwear of the soldier and a pilum, both with a chronology of the 3rd-2nd century BC.

They have been studied by scanning electron microscopy with EDS analysis incorporated, transmission microscopy (FEG) and electron microprobe.

The final model can be schematized as follows:



Our criterion is that it grows after a very strong subcooling from a temperature higher than the ferritic field temperature and then precipitates with time throughout the ferritic mass with priority for the planes that were more stressed during cooling, and that is why they originally have a splintered morphology. This morphology has been unraveling as the precipitates grow by mechanisms like the one we have explained in the previous model: with a high mobility interface (B) and a slower one (A). Therefore, they give rise to elongated morphologies in special planes with Widmanstätten structure [1-10].

These are limitations imposed by the characteristics of the iron carbide and the temperature, and their limitations in that the times are very long and the temperature, the environmental.

These structures have been observed from archaeological samples more than 2,000 years old, subjected to incineration processes, in which these structures are characteristic. They have thus undergone a cycle of high temperature heating followed by severe cooling.

And then, they were deposited in a place at room temperature and have remained for more than 2,000 years until their disinterment. The temperature at which they have remained in the burial is practically the same, without large oscillations.

This is yet another example of how archaeometallurgy can be used to see processes that would otherwise be impossible to detect [3-4].

Experimental Technique

The archaeological samples for this research were selected from hundreds of archaeological pieces, as the most representative. An Iberian pilum (an Iberian offensive weapon consisting of a very long pointed shape with a relatively short crimp on the handle) and a soldier's tack (an iron nail used to attach the sole to the rest of the footwear) were chosen; both had undergone a cycle of incineration of the corpses, with chronologies ranging from the third to the second century BC. The selection criterion was that they should retain a metallic core (Figures 1 and 2).

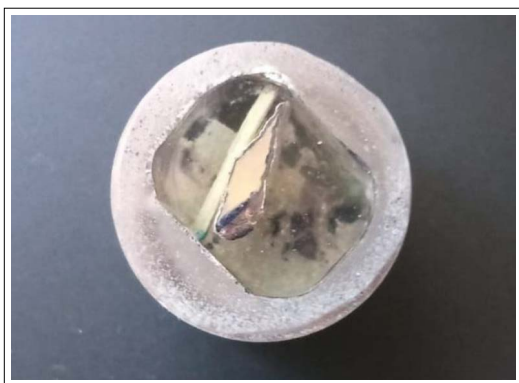


Figure 1: Macrograph Showing the Iberian Pilum under Study



Figure 2: Macrograph Showing the Stud of the Footwear of the Soldier under Study

A small sample of the set was embedded in epoxy resin in order not to spoil the archaeological piece and they were roughened with papers of different grains, from 180 to 2000, in a conventional way. Subsequently, they began by polishing with water in 0.3 μ m Micropolish II alumina and finished with 0.05 μ m Micropolish II alumina, both from Buehler. Finally, after cleaning with distilled water, they were attacked with 2% Nital.

For their metallographic observation, they were sputtered with gold and observed metallographically in a scanning electron microscope JSM 6400 is particularly suitable for the observation of the surface of materials (geological, chemical-physical...) and biological, with the possibility of performing semi-quantitative analyses to obtain an approximation of the composition of the materials. It is possible to obtain, by using backscattered electrons, the distribution of elements and phases in the study of materials.

Results

In Figures 3 and 4, the typical microstructure of tack steel can be observed. In it appear dispersed carbides, with acicular morphologies, filling the grain boundaries and the interior with Widmanstätten structure. The matrix is ferritic, and its polyhedral grain boundaries are perfectly drawn with a very clear polygonal shape. Some points of the grain boundary show coarsening due to cementite. The morphology of these carbides resembles needles but they are very narrow prisms, as seen in Figures 4, 5 and 6. In these figures it can be seen that they are elongated prisms with a uniform angle.

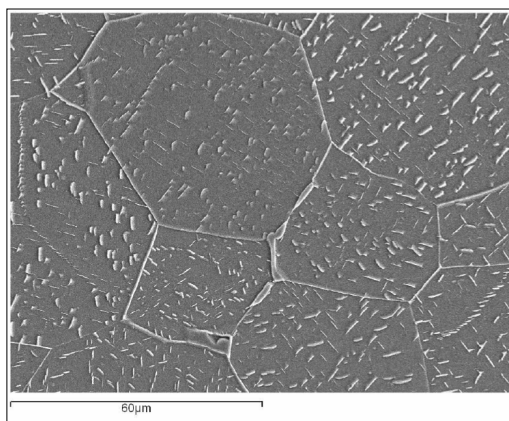


Figure 3: Micrograph, obtained by scanning electron microscopy, showing a microstructure of ferritic polyhedral grains and a precipitate of iron carbides

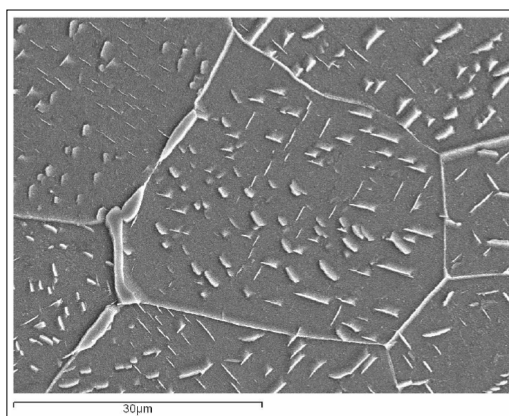


Figure 4: Micrograph, obtained by scanning electron microscopy, of the structure in Figure 3, at higher magnification. The grain boundaries appear thickened at some points; they are filled with cementite and, in the interior, the precipitate of acicular crystals of iron carbides

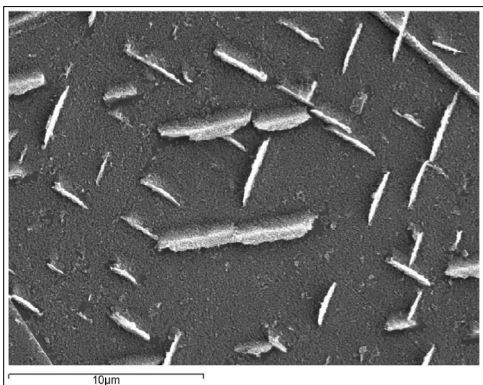


Figure 5: Micrograph, obtained by scanning electron microscopy, of the structure in Figure 4, at higher magnification. It clearly shows the morphology of these precipitated iron carbides, which resemble needles but are very narrow prisms, with Widmanstätten orientation

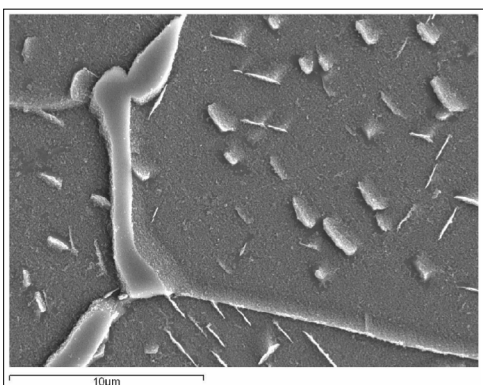


Figure 6: Micrograph, obtained by scanning electron microscopy, of the structure in Figure 4, at higher magnification. It shows the thickening of the grain boundary due to cementite

The microstructure in Figure 7 shows the prism-shaped iron carbides fused into the ferritic matrix with perfect orientations in Widmanstätten structure. The vertex orientations of the small prisms and their elongated morphologies are responsible for the typical morphology of these steels.

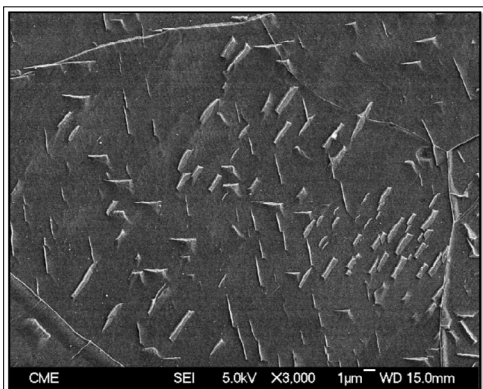


Figure 7: Micrograph showing in detail the precipitate of iron carbides. They are fine small idiomorphic prisms of iron carbide, not with acicular form as it could seem

In the microstructure of figure 8, taken at higher magnification than the previous figure, it is clearly seen that the precipitate is small elongated prisms, showing very homogeneous profiles.

It is the emergence of prismatic dihedral angles all aligned and oriented in the same orientation that causes the appearance of acicular structure at low magnification. The ferritic grain boundaries thickened with iron carbide are equally prismatic at higher magnifications, as shown in Figure 8.

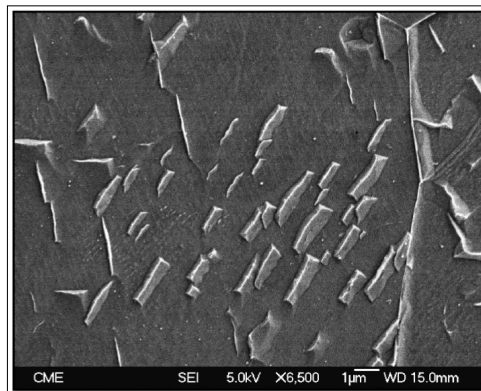


Figure 8: Micrograph, at higher magnification, of the figure

Figure 9, of the tack, shows the thinness of these laminae or prisms many times and the predominance of the length. Figure 10, at higher magnifications of the previous one, on the left side of the figure, shows some lateral steps characteristic of the growth of the prisms.

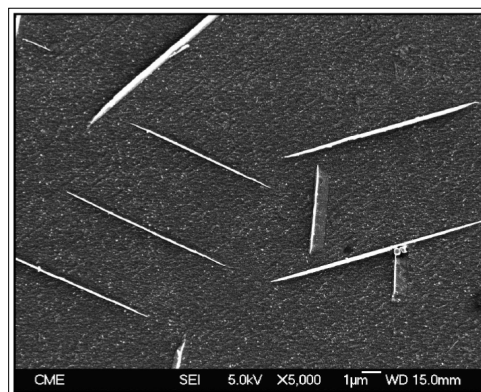


Figure 9: Micrograph, showing the true morphology of the prisms of the precipitate

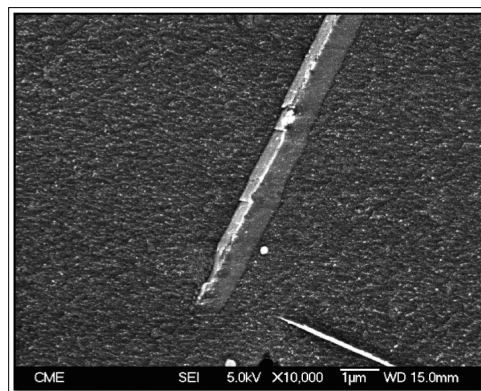


Figure 10: Micrograph, obtained by scanning electron microscopy, of the structure in Figure 9, at higher magnification, showing how the precipitate has developed greatly in length

Finally, Figure 10, shows these very elongated and thin prisms, in Widmanstätten structure.

From figures 11 to 14, obtained from the tack sample, we can see how the morphologies are not very different. All these archaeological materials show the same images, if they come from cremations. Therefore, they become a good detail to recognize incinerations: elongated iron carbide crystals distributed in a ferrite matrix with Widmanstätten structure. There may or may not be more iron carbides, but when they appear they are very easy to recognize and, therefore, to obtain the relation incineration - elongated iron carbides.

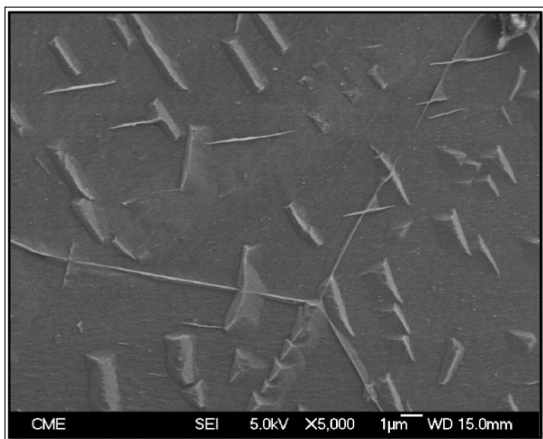


Figure 11: Micrograph showing how the precipitate of iron carbides is the same from one sample to another

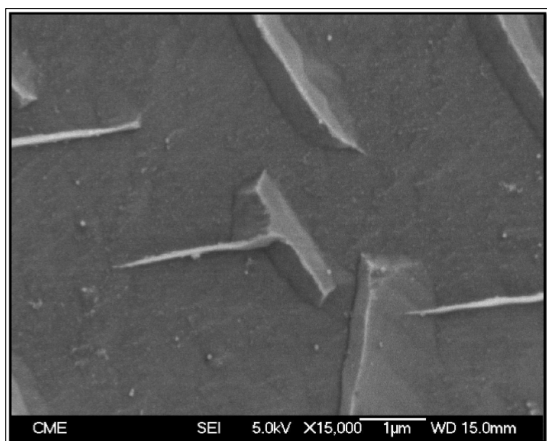


Figure 12: Micrograph showing the precipitate of iron carbides in the tack, showing a profile where the typical growth steps can be seen

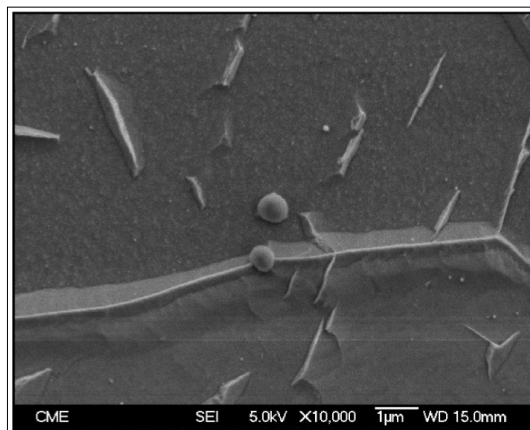


Figure 13: Micrograph showing the carbides crossed by a grain boundary filled with iron carbide

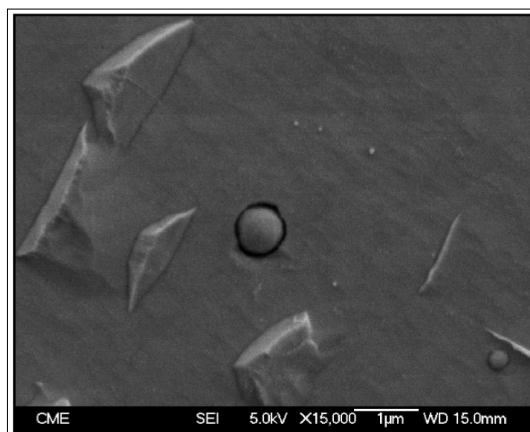


Figure 14: Micrograph showing how the carbide precipitates are macerated

We believe that we have covered the most important aspects of these characteristic structures that occur in carbon steels from archaeological pieces incinerated with the corpses of these subjects.

Discussion of Results

We have been able to observe some morphologies of the iron carbides present in steels of archaeological incinerated pieces, which are difficult to observe with such profusion in the rest of archaeological carbon steels or not, due to their rarity. They have served us to testify the heterogeneous nucleation in carbon steels. A singular structure that, due to its association with cremated corpses, serves to detect which archaeological pieces have been cremated with their corpse.

In addition, the existence of these structures is a clear example of the precipitates that appear in a heterogeneous form with a semi-coherent direction of slow growth and another of an incoherent type whose growth is fast. This is the cause of the growth of elongated crystals in a very characteristic direction. But that, after all, these anisotropic iron carbide crystals form prisms with idiomorphic forms, as corresponds to iron carbide crystals. All this on a ferritic matrix.

These structures so characteristic of incineration are very repetitive, always appearing as traces of these processes, which become a very important vector in archaeometallurgical science.

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