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Heat Treatment Simulation of the Formation of Idiomorphic Iron Carbides with Widmanstätten Structure Observed in Archaeological Steel Pieces more than 2000 Years Old Subjected to Incineration Processes

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Abstract

Archaeometallurgy has shown that the passage of long periods of time - centuries and millennia - produces very characteristic structures and morphologies in hypo-eutectoid steels. It is the evolution of contemporary steel structures that over time evolve into thermodynamic equilibrium at room temperature. These morphologies have been studied by us over a long period of time. In this research we present a thermal treatment of simulation of the structures related to the incineration of pre-Roman archaeological pieces from the 3rd to the 1st century BC. With this long-lasting thermal treatment of up to 10,000 hours of heating to 300°C, prior heating to 950°C and abrupt cooling, we intend to obtain iron carbide structures of similar morphology to those observed in pre-Roman archaeological pieces.

Keywords: Iron carbides; Heat treatment; Incineration; Widmanstätten structure; Archaeometallurgy

Introduction

Time and temperature are two fundamental thermodynamic variables for all physicochemical transformations. Temperature always favours reactions, sometimes becoming an exponential factor. This variable is currently controlled by technology in a total way for certain temperature ranges. However, the time variable is more subtle and, when it comes to long periods of time, it is beyond our reach. Archaeology again provides some samples subjected to the passage of long periods of time of hundreds and thousands of years. It is as if our ancestors had left samples of steels, bronzes, copper, ceramics,..., buried in the geological soil, in geochemical and physical conditions, over centuries and millennia. This is referred to in international literature as "archaeological analogues". These "archaeological analogues" are pieces of various materials that were manipulated by humans centuries and millennia ago, and that have remained in a special geochemical environment until today. Much information can be extracted from these analogues, as the thermodynamic variable time has been of very long duration [1-6].

In the case of the Archaeological Analogues, the temperature practically does not vary in the geological soil, what is fundamental is the manipulation that was done before its burial. Therefore, these are heat treatments at room temperature with very long periods of time.

In this research we have gathered a series of micrographies obtained with SEM, from steel artefacts extracted from archaeological sites well dated from pre-Roman times in the Iberian Peninsula. All these sites have a clear chronology that places them in the 3rd century BC. These are artifacts that were incinerated with the corpse of the warrior, in rites followed by the Iberian, Celtic and Celtiberian peoples. The formation of a typical iron carbide structure with Widmanstätten structure is already explained by our research team [7-9]. Their formation and growth morphology depends on the heating temperature and cooling cycle followed by very prolonged aging over time periods ranging from centuries to millennia [1-9]. Other scientific works have been carried out by other authors trying to explain the appearance of these morphologies of iron carbides in archaeological pieces (artefacts) [10-13].

In this research we have tried to obtain the same morphologies of iron carbides, carrying out very long-lasting thermal treatments of up to more than 10,000 hours. We have tried to see the beginning of the formation of these morphologies of iron carbides with a thermal treatment of heating of a steel DIN CK10 (AISI 1010), very similar for its content in carbon and impurities with the archeological steels of the centuries III to I a.C. The treatment tries to simulate the incineration process and then the passage of a very long period of time. For the incineration process we have based ourselves on international literature [10-13] and, above all, on that of our research team [1-9]. The thermal treatment consists of heating to 900°C, followed by water quenching and subsequent reselling of long periods of time, weeks, months and years at 300°C, in order to accelerate the process and be able to visualize the beginning of the formation of these iron carbides observed in archaeological pieces (artefacts), in slow aging processes, at room temperature, during thousands of years.

We believe that the formation of these iron carbides begins at the interface of the acicular ferrite obtained during the abrupt cooling of steel DIN CK10 (AISI 1010) heated to 900°C [12-23].

In this publication we are going to show micrographics of iron carbides that have been formed in archaeological artefacts more than two thousand years old, together with micrographics of iron carbides generated in steel specimens DIN CK10 (AISI 1010), obtained by cooling in water from 900°C and tempering to 300°C during a prolonged time (hundreds and thousands of hours).

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Experimental Technique

The archaeological samples that have been studied belong to different archaeological sites and different chronologies, located in the Iberian Peninsula (Spain) (Table 1).

These artefacts can be seen in Figures 1-4.

A low carbon hypo-eutectoid steel, DIN CK10 (AISI/SAE 1010) (Table 2), was selected for the simulation heat treatment, which was used to see the origin of these carbides.

The simulation heat treatment consisted of heating the CK10 steel (Table 2) to 900°C for 30 minutes and cooling in water. These conditions simulate the incineration of the archaeological artefacts, together with the corpse. To obtain the starting steel structure for the simulation treatment, it was obtained by cooling in water from 900°C (Figures 5 and 6).

Artefact	Deposit/Provenance	Archaeological context	Culture/ Chronology
Iberian Pillum	Museo del Cobre (Cerro Muriano, Córdoba)	out of context	Ibérica/S. III-II a.C.
Falcata	Museo de la Armería (Álava)	out of context	Ibérica/S. III-II a.C.
Studs	Villanueva de Teba (Burgos)	Necrópolis	Celtibérica/S. III-I a.C.
Protection buckle	Villanueva de Teba (Burgos)	Necrópolis	Celtibérica/S. III-I a.C.

Table 1: Archaeological artifacts of the Iberian Peninsula [23].

Figure 1: Iberian pillum from Cerro Muriano (Córdoba, Spain) which is conserved in the Copper Museum of that locality (III-II century BC).

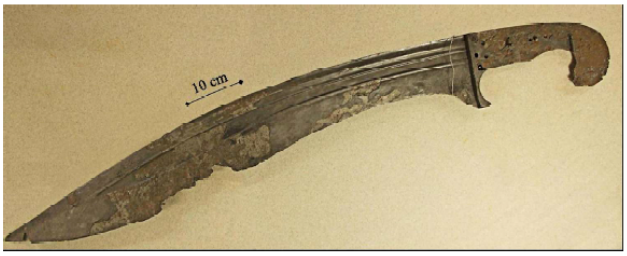

Figure 2: Iberian Falcata from Cerro Muriano (Córdoba, Spain) which is preserved in the Copper Museum in that locality (III-II century BC).

Figure 3: Studs from Villanueva de Teba (Burgos, Spain) (3rd century-1st century BC).

%C	%Si	%Mn	%S	%P
0.10	0.40	0.45	<0.04	<0.04

Table 2: Chemical composition (%) of steel DIN CK10.

Figure 4: Protection buckle from Villanueva de Teba (Burgos, Spain) (3rd century BC-1st century BC).

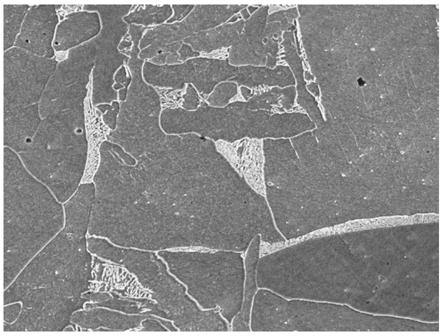

Figure 5: Steel structure DIN CK10 (AISI/SAE 1010). Small and minority colonies of perlite are observed in a ferritic matrix.

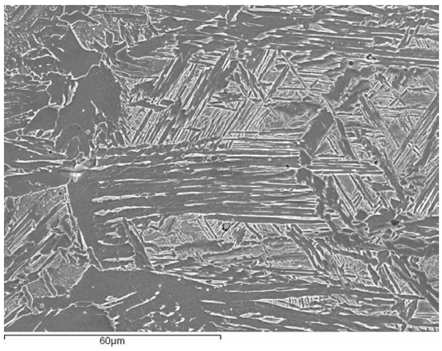

Figure 6: Steel structure DIN CK10, heated to 900°C and abruptly cooled in water. Ferritic acicular structure with iron carbides at the needle interfaces.

The steel cooled in water from 900°C was placed in a large quartz ampoule and hermetically sealed by pre-vacuuming it to prevent oxidation during simulated aging periods at 300°C, in a muffle furnace, for long periods of up to 10,000 hours (Figures 7-9).

Another temperature was also chosen for aging, as were 350°C; but the results were worse since the increase in temperature favored a process of globalization of cementite.

All samples were subjected to conventional metallographic preparation and then observed by Scanning Electron Microscopy (SEM), using the scanning electron microscope with thermionic tungsten filament cathode (FEG) used is the JEOL JSM 6400 model which provides images and physical-chemical data of the sample surface. It has three sensors: secondary electron detector, the image resolution is 35 KV, detector to work at 8 mm distance with an image resolution of 3.5 nm and detector to work at 39mm with an image resolution of 10nm. It provides backscattered electron images with an image resolution of 10 nm, a working distance of 8 mm. In addition, it can perform qualitative elemental analysis (EDS) with a resolution of 133eV.

Figure 7: Vacuum-closed ampoules with the sample inside.

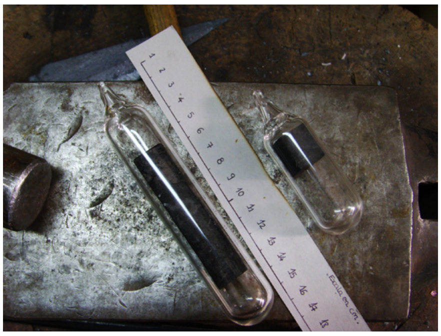

Figure 8: Appearance of ampoules after heat treatment at 300°C for 948 hours.

Figure 9: Breakage of the ampoule to remove the pre-treated steel simple.

For X-Ray diffraction a PANalytical Multi-purpose Diffractometer model X'Pert MPD was used, equipped with Cu X-ray tube and two goniometers in vertical th-2th configuration, with Bragg-Brentano optics.

Results

The archaeological steel pieces studied for this investigation are Figures 1-4; however, it can be generalized that all the archaeological pieces found in the Iberian Peninsula, with chronologies ranging from the 6th century BC to the 1st century AD and which were subjected to a process of incineration with the corpse, present the typical morphologies of idiomorphic iron carbides with a Widmanstätten structure.

Figures 5 and 6 show the morphology of the steel selected for heat treatment simulation. It is a DIN CK10 steel (AISI 1010); hypo-eutectoid steel, low carbon content, hot-rolled and normalized (Figure 5). A ferritic matrix with few perlite colonies is mostly observed. After tempering in water from 900°C, the structure is mostly acicular ferrite type Widmanstätten with iron carbides precipitated at the interfaces of acicular ferrite crystals (Figure 6). This location in the interface of the ferrite is what will condition that the nucleation and growth of the carbides, from the carbon retained in the ferrite during the temple is segregated in the interface of the acicular ferrite.

Figures 10-12 show the idiomorphic crystalline structures of the precipitated carbides with Widmanstätten structure, belonging to the archeological steel pieces of Figures 1-4. These archeological pieces were incinerated at very high temperatures and cooled very quickly. Acquired the perfect thermodynamic equilibrium over more than 2,000 years of time, that the structures observed (Figures 10-12), correspond to perfect polyhedral crystals, of an idiomorphism consistent with the crystalline network of cementite that is orthorhombic.

The cementite crystals obtained by us in the simulation treatment, trying to produce the structures of Figures 10-12, despite having lasted the tests up to 10,000 hours, are only at the beginning of their growth, but already present similar initial idiomorphic morphologies, although not as perfect as those produced in more than 2,000 years of time (Figures 13 and 14). These structures observed in Figures 13 and 14 are obtained in simulation heat treatment after hundreds of hours

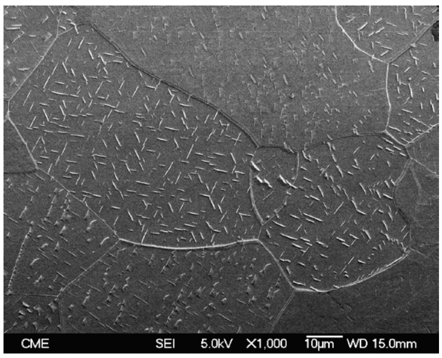

Figure 10: Micrography of archaeological steel aged for more than 2,000 years belonging to the archaeological pieces of Figures 1-4.

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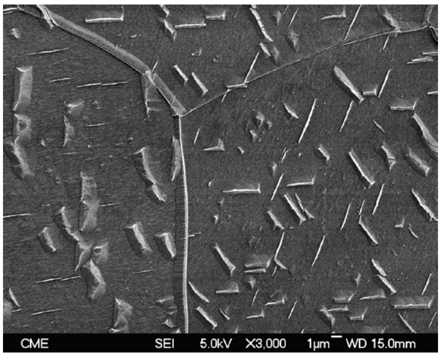


Figure 11: Micrography, at higher magnifications, of the microstructure of the Figure 10, presenting idiomorphic polyhedral carbides of iron carbur in a ferritic matrix.

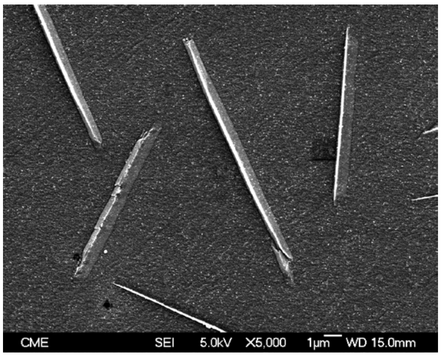


Figure 12: Detail of idiomorphic iron carbides aged for more than 2,000 years belonging to the archaeological pieces of the Figures 1-4. These carbides are very elongated.

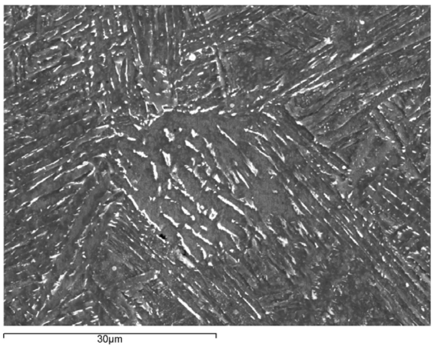


Figure 13: Steel structure CK10 (AISI/SAE 1010) subjected to a simulated ageing process at 300°C for 948 hours. Carbides with Widmanstätten structure at the acicular ferrite interfaces.

at 300°C, then cooling in water. It is a very short time despite having increased carbon diffusion with prolonged heating to 300°C. It would still be a short time to reach morphologies such as those obtained during 2,000 years of time at room temperature in its archaeological bed after incineration.

Idiomorphism and polyhedral morphologies are determined by slow growth at low temperatures, for very long periods of time, and by a very low rate of carbon diffusion in the ferrite. It is a classic aging process

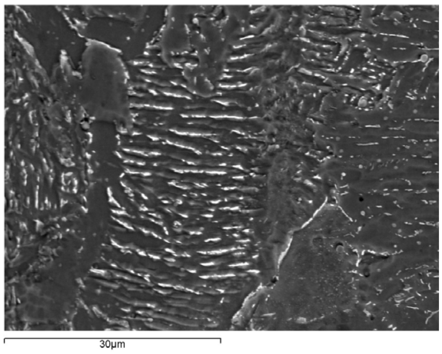
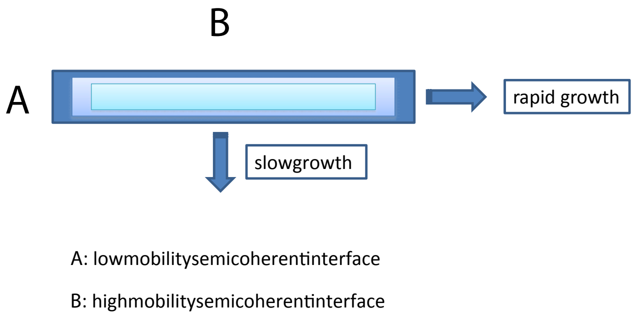


Figure 14: Another image of a CK10 steel structure (AISI/SAE 1010) subjected to an artificial ageing process at 300°C for 948 h.



Scheme 1: Mechanism of growth.

of iron carbide structures. We think that this elongated crystalline growth is due to the intermetallic compound character of Fe3C, so that some planes are still semi-coherent with the ferritic matrix, which slows its growth in that direction, while others remain incoherent with the ferritic matrix and grow faster [20,23]. This mechanism of growth can be observed in the following schematic drawing (Scheme 1).

Conclusions

Archaeometallurgy contributes to observing the evolution of carbon steel structures, with the passage of very long periods of time, at room temperature. This makes it possible to observe the consequences of time in equilibrium structures. It shows how such thermodynamic equilibrium is not a stable equilibrium, but an unstable equilibrium, if the variable time acts in long periods such as centuries or millennia.

Today, the problem of stability arises in large constructions where steel is involved and which must last for a long time: architectural constructions, bridges, underground tanks, buried high level nuclear waste containers, etc. It is necessary to shuffle the variable time, beyond the values that are taken into account today. The variation of the structural morphology of steel with very long times can affect the values of mechanical resistance calculated for these structures.

In this investigation it has been possible to observe the appearance of idiomorphic iron carbides in Widmanstätten structure, in carbon steels that have undergone a high temperature heating followed by a fast cooling, as it is the case of the incineration rites in the pre-Roman towns of the Iberian Peninsula.

We have tried to present the unique morphology of the iron carbides of the archeological carbon steels and to present a proposal for a heat treatment that simulates the incineration of these steels. This long-term treatment of up to 10,000 hours consists of heating the steel to 900°C and cooling it in water, followed by ageing at 300°C to speed up the process. The results, as can be seen, have been good, and in this period of time we can see why and how these idiomorphic morphologies with a Widmanstätten structure are created.

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