Journal of Material Sciences & Engineering

Research Article Open Access

Appearance of Recrystallization Maclas in an Archaeological Piece of Steel from the Northern Necropolis of Cordoba (Spain) (1st Century)

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Abstract

Slow diffusion at room temperature over long periods of time (centuries and millennia) rewrites the different heat treatments suffered by a steel. With the precipitation of iron carbides, it redraws all those places in the steel where there have been some kind of marks of the thermal treatments suffered: twins, grain limits, etc. These iron carbides draw perfectly these places. In this work this fact has been visualized in one of the iron nails that appeared in a tomb from the 1st century A.D. in the Northern Necropolis of Cordoba in the Roman Baetica. It is one of the many steel artifacts that allow us to see these metallurgical phenomena that we could not easily reproduce today. The metallographic techniques used have been the Conventional Optical Microscopy and the Scanning Electron Microscope.

Keywords: Recrystallization; Archaeometry; Metallography; Steels; Twin

Introduction

This is once again a description of a metallurgical phenomenon occurring in a piece of carbon steel more than 2000 years old. This time archaeology offers a sample that underwent a specific heat treatment and then remained at room temperature for a very long period of time in the archaeological site where it was found.

Once again we are going to observe the influence of historical, very long periods of time on the diffusion of carbon in ferrite. This would be very difficult to observe by designing simulation tests, although they would not be real, so the archaeometallurgy in these cases is insurmountable.

In this publication, a phenomenon produced by the diffusion of carbon in ferrite over 2000 years at room temperature is presented. The metallographic observation of very old steel pieces visualizes metallurgical phenomena invisible in current technology. We are going to observe recrystallization twins in steel, which without a very prolonged aging process at room temperature would be impossible to observe [1-5].

An important mechanism in the deformation of metals is the twin. This twinning can occur during mechanical deformation or by subsequent annealing (recrystallization twinning).

Twining occurs when a portion of crystal (grain) takes an orientation, which is related in a symmetrical way defined, with that of the rest of the crystal without deforming. The deformed part of the crystal is a mirror image of the original crystal. The plane of symmetry between the two parts is called the plane of twin. The twin is visible on the polished surface thanks to the depth produced by the deformation and by the different orientation between the deformed and undeformed zone. The twin boundaries are attacked at the same speed as the grain boundaries, as a consequence of which they have approximately the same energy. Annealing twins are usually wider than mechanical deformation twins. Most of the cubic centered in the body metals form annealing twins. The appearance of annealing or recrystallizing twins is a good indication of mechanical deformation prior to annealing [6-17].

The high-imperial Roman iron nail (1st century A.D.), the object of study, demonstrates all these theoretical conclusions. The very slow diffusion of carbon through the ferrite, over 2,000 years marks, by precipitation of iron carbide, those places of the crystals with greater energy for having been deformed in the austenitic field. Although the twinning took place hot in the austenitic field, it leaves an indelible mark in its transformation from austenite to ferrite. Possibly, the existence of twining nuclei, produced during the deformation, are the cause that a trace of the twin remains, in the ferrite, that is marked by the carbon in its slow diffusion, by the formation of iron carbides. It is also clearly observed the choice of grain limits for the precipitation of these iron carbides, product of the slow diffusion of carbon in ferrite. All these markers have been observed in a multitude of archaeological artifacts, made of steel from the Roman and pre-Roman periods, which suffered cremation rites. The high temperatures of the cremation process and the coolings, more or less rapid, saturates of carbon the ferrite, whose solubility in this phase, to 720°C is of 0.028% in mass of carbon. However, the ferrite can only dissolve 0.008% by mass of carbon at room temperature, which is 3`5 times less. This instability of the carbon in ferrite and the changes in shape that occur in steel with the passage of long periods of time, thousands of years, are the cause of the presence of carbon atoms circulating by diffusion through the ferrite. The unique places in the structure act as markers when receiving the carbon produced by diffusion [1-5,18].

The archaeological piece chosen among many others, in which the carbon is located at the limits of the recrystallization twins is a very soft steel nail, forged hot and cooled in the air, which later underwent a process of incineration [19].

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Received September 16, 2019; **Accepted** October 15, 2019; **Published** October 21, 2019

Citation: García SL, Queirós GW, Criado AJ, Fernando P, de Salazar JMG (2019) Appearance of Recrystallization Maclas in an Archaeological Piece of Steel from the Northern Necropolis of Cordoba (Spain) (1st Century). J Material Sci Eng 8: 543.

This is a piece extracted in an archaeological intervention in Cordoba (Spain), which was carried out in the northern Roman high-imperial necropolis located in the city Colonia Patricia (Cordoba, Spain), belonging to the Roman province called Bética, whose chronology of the tomb is located in the reign of Emperor Tiberius (1st century AD) (Figure 1-4).

It is an incineration burial, so the nail was subjected to a very high heating and very fast cooling process during this process. It is common to find the incineration urn surrounded by some iron nails. The meaning of this fact is not yet known [19-23].

The complete heat treatment of this nail, which was the object of study, was hot forging and air cooling during the manufacturing process, and then, when it was incinerated, it was reheated to high temperatures and cooled very quickly.

The archaeological piece underwent a metallographic study using Conventional Optical Microscopy (C.O.M.) and Scanning Electron Microscopy (S.E.M.).

Figure 1: Map of the Roman provinces Hispania in the Roman High Imperial period. (www.beticaromana.org). This study archaeological site belongs to the Baetica.

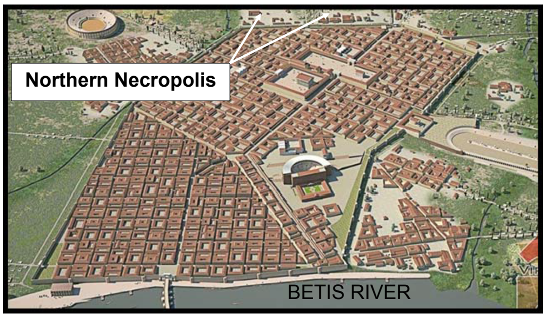

Figure 2: Schematic drawing of the Roman Corduba with the location of the excavated northern necropolis.

Figure 3: View of the tomb excavated next to the layout of a roadway.

Experimental Technique

The steel nail that has been studied was chosen for its good conservation among several found in the excavated incineration tomb. It was washed with distilled water in an ultrasonic bath and, once dried, embedded in a black phenolic resin.

It was then roughened with Buehler SiC Carbimet abrasive paper and polished with 0.05 µm aqueous suspension alumina of Buehler Masterpolish. Finally, it was chemically attacked with 2% Nital by mass (Figure 5).

For metallography by conventional optical microscopy, the test tube with the chemical attack described above was used. When observed by scanning electron microscopy, a gold sputtering was previously deposited.

Conventional optical microscopy was performed with a Reichert MEF4 A/M microscope and a confounded 3D Infinite Focus SL Alicona Gmbh magnifier for macrographs. The scanning electron microscopy was performed with a JEOL JSM-6400 operating at 20KeV.

Figure 4: Image of the iron nail studied in a remarkable state of conservation.

Figure 5: Macrography of sectioned iron nail subjected to deep drawing, grinding, polishing and chemical attack with 2% Nital.

Results and Discussion

The studied iron nail was hot forged and air cooled. Therefore, it has a structure according to a very intense deformation. During the subsequent incineration, the nail is reheated to a high temperature for a period of time that we cannot confirm. In this period of time, which we thought might not have been very long, the steel structure partly recrystallizes. This is very clearly seen in the macrographies made to the iron nail in Figures 5 and 6.

In this stage, recrystallization of twin is produced in the austenitic phase that would not be visible at room temperature. The carbon that overwhelms the ferrite, since this phase dissolves only 0.008% by mass, is segregated and diffused through the ferritic matrix over a very long period of time, 2.000 years, at room temperature. This diffusing carbon is secreted in the form of Fe_3C in those places where it has the most free energy, such as grain limits and twin planes. These iron carbides located in these privileged places, make visible the grain limits and the twin planes; presenting a surprising structure of twins in the ferrite at room temperature (Figures 7-16). This effect of recrystallization twins visible in the ferrite at room temperature is a consequence of the recrystallization twins leaving a memory of their maceration planes, in the form of many with some free energy, which are remarked a posteriori by the diffusion of carbon over time of two millennia at room temperature. Carbon serves to mark with its precipitation the places with more free energy. This carbon has a lot of time to act as a tracer and be located and placed in places of privilege.

In the Figures 7-10, it is observed how the recrystallization twins are exclusively located in the recrystallized and re-grown grains. In

Figure 6: Macrograph with confocal magnifying glass showing one grain growth zone and another small grain zone. The twins are only in the grains that have grown.

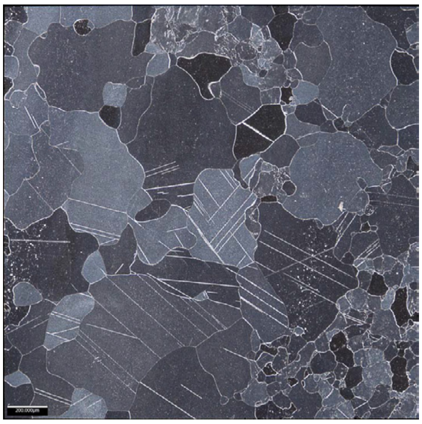

Figure 7: Macrograph with confocal magnifying glass that shows the existence of macles in those grains that have grown during recrystallization.

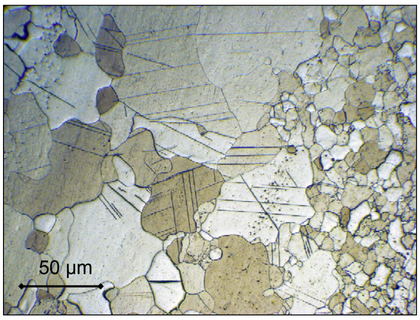

Figure 8: Micrograph obtained by optical microscopy where the existence of twins in the coarse grains is appreciated.

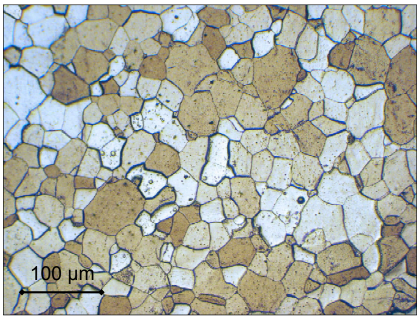

Figure 9: Micrograph obtained by optical microscopy, showing a fine-grated area with no twins.

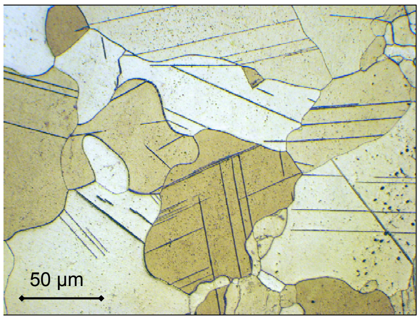

Figure 10: Micrograph obtained by optical microscopy, showing the twinning in grains of great growth.

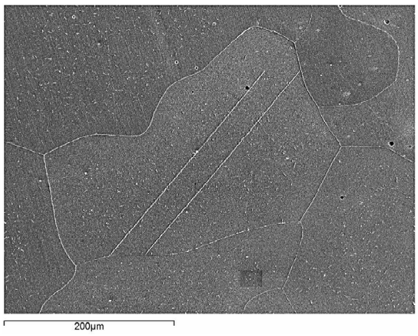

Figure 11: Micrograph obtained by scanning electron microscopy, showing the twins and grain limits marked with iron carbides.

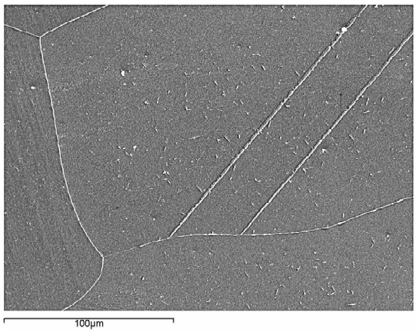

Figure 12: Detail, to greater increases, of the zone of the Figure11.

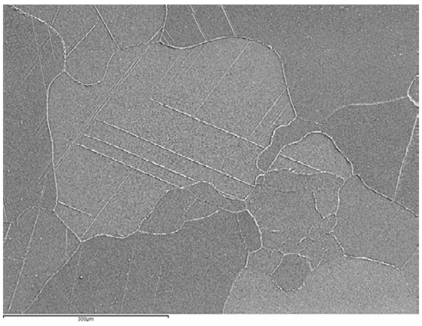

Figure 13: Micrograph obtained by scanning electron microscopy, showing the numerous grain twins and grain limits of the grain growth zone.

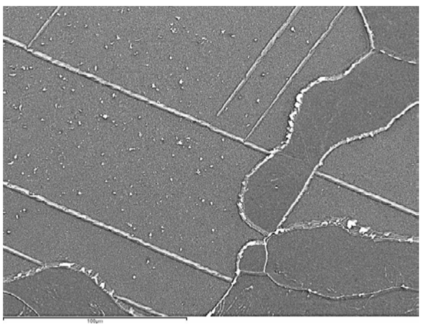

Figure 14: Detail, at higher magnifications of the area shown in Figure 13, showing how the iron carbides mark perfectly the grain boundaries and twin planes.

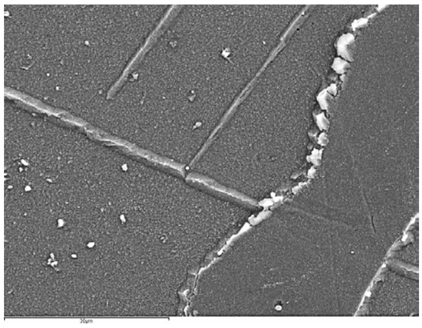

Figure 15: Detail, at higher magnifications in the area of Figure 14, showing the morphology of the iron carbides of twins and grain limits.

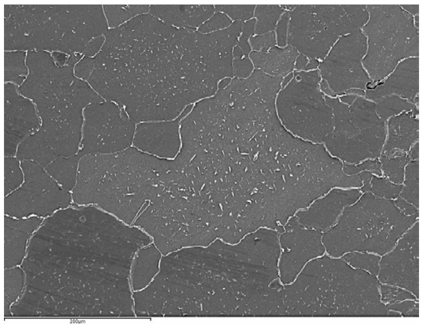

Figure 16: Micrograph obtained by scanning electron microscopy, showing an area of small grains. Carbides are observed at grain boundaries and in the ferritic matrix with Widmanstätten structure.

small grains where there has been no effective recrystallization, there is a total absence of twins (Figures 9 and 10). In Figure 10, it is observed how the diffused carbon is placed in the grain limits and in its interior in the form of small crystals of Fe3C with Widmanstätten structure.

Using archaeometallurgy it has been possible to visualize structures that have required a very slow diffusion of carbon at room temperature. It is very clear that the structures of the irons and steels evolve with long periods of time, which can only be observed in these archaeological pieces.

Conclusions

It has become evident that the possibility of observing equilibrium structures in which diffusion intervenes over long periods of time, such as two millennia, is only possible using archaeometallurgy.

In this research it has become clear that recrystallization twinning leave free energy nuclei in the twin planes. A long period of time favours that the diffusion of the carbon in ferrite allows that this carbon in form of carbide of iron marks of evident form the existence of those places with greater free energy. It is evident that the iron carbides clearly draw the grain limits, twin planes and precipite inside the ferrite crystals in the form of small crystals with Widmanstätten structure.

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