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Metallographic Interpretation of the Morphology of the Very Old Pearlite

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ABSTRACT

Metallographically, hot forged hypoeutectoid steels from archaeological artifacts more than 2000 years old have been observed. They show the microstructural evolution of pearlite over time. The structures observed for this old pearlite differ from those observed in forged and normalized hypo-eutectoid steels at present. This means that the thermodynamic equilibrium of pearlitic morphology is for very long periods of time.

Keywords: Old pearlite, Metallographic, Morphology, Steel, Archaeometallurgy.

INTRODUCTION

Archaeometallurgy aims to study and explain reasonably the ancient metallurgical techniques. It is dedicated both to the study of archaeological metal pieces (artifacts) and to metallurgical manufacturing techniques and their extractive metallurgy. The knowledge of these facts not only contributes to the knowledge of history but in many cases can contribute to the progress of current science; as is the case of archaeological and industrial analogues for their application to high level nuclear waste and to the design and study of the durability of underground industrial installations or large public works installations [1-7]. In all cases, archaeometallurgy has served to study the historical evolution of humanity and contributes to scientific progress, since it studies a sample of thousands of years in which such a long period of time reveals singular metallurgical events. Knowledge is not only provided in the field of corrosion in burial soils but also in very slow diffusion processes over very long periods of time, hundreds of thousands of years. It is in the provision of diffusion data at room temperature, over very long periods of time, where this research is inscribed. By studying metallographically carbon steels of Roman high-imperial origin from the 1st century BC and the 2nd century AD, we have been able to observe very surprising pearlite structures [5]. These metallic steel materials consist of nails, armament parts, tools, etc., which were hot forged with mild hypo-eutectoid steels. Its manufacturing process consisted of the hot forging of steel pieces with very variable carbon content. Sometimes it is even the case of welding different metals to obtain a larger piece composed of several elements. In all cases, the parts were cooled to air. The final result is steeled with grains deformed by the forge, with a typical structure of hypo-eutectoid steels of different carbon content. Structures of perlitic crystals are observed in a ferrite matrix.

The metallographic observation of these ancient steels of medieval and ancient times, allows us to contemplate structures with morphologies very different from those that can be observed in contemporary steels [5,8,9-27].

The difference between ancient and modern steel structures lies in the time when they have been exposed to very slow diffusion processes over very long periods of time. This diffusion, although slow, has been sufficient to change the microstructure towards more equilibrium morphologies.

In this investigation, the metallographic structures of a steel nail, from the Roman High Imperial period, found inside a concrete wall, belonging to a cistern of the archaeological site of Cerro de La Coja in Cerro Muriano (Córdoba, Spain), from the 1st century B.C. and 1st century A.D., are exhibited (Figures1-3) [28].

Figure 1: Staggered cyclopean concrete wall of the Roman cistern of Cerro de La Coja.

Figure 2: A sample of cyclopean concrete where the steel nail was found inside.

Figure 3: Steel nail found with traces of metalcore.

The metallographic study has been carried out using Scanning Electron Microscopy (SEM).

Experimental Technique

The steel nail was found in a sample taken from the concrete wall of a Roman cistern. This nail belonged in complete safety to the wooden formwork used in the construction of the wall (Figures 1 and 2). The piece of steel nail was embedded in epoxy resin and prepared metallographically. The attack was carried out with Nital at 4%. The micrographic observation revealed that the corrosion had respected a good part of the metal core (Figure 3).

For observation by Scanning Electron Microscopy (SEM), gold sputtering was performed. The microscope used is a Jeol 6400 JSM with thermionic cathode electron gun with tungsten filament, secondary electron detector, image resolution at 25 KV, retrodispersed electron detector and built-in EDS analysis.

Optical microscopy proved that there were almost completely ferritic zones (Figure 4) and others with an abundance of perlitic colonies (Figure 5). This shows that it is a very heterogeneous piece of steel, possibly from the hot forging of steels of very different carbon composition. Our metallographic study is directed to the perlitic zone to check the evolution of these structures.

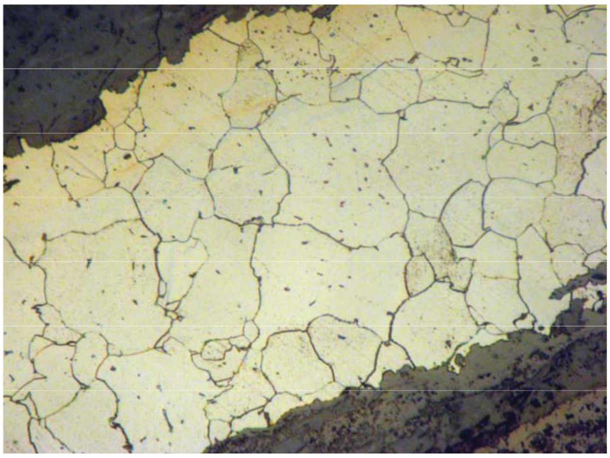

Figure 4: Ferritic zone of the Roman nail object of study.

Figure 5: Nail zone with ferritic-perlitic structure.

RESULTS

The formation of pearlite colonies in carbon steels is a subject widely studied in international literature [11-27]. However, these structures, obtained for certain temperature gradients, are not in equilibrium, as demonstrated by their natural evolution over very long periods of time, such as hundreds of years or millennia.

The possibility of contemplating steel structures, which have remained buried for one or two millennia, shows us that perlitic structures continue to evolve, due to the very slow diffusion of carbon at ambient temperatures without appreciable variations, in archaeological sites. This means that the perlitic structures obtained in conventional metallurgical processes are a consequence of them, but they are still far from what we call equilibrium.

It is this real equilibrium that causes these structures to change over long periods of time. The linearity and parallelism of the cementite sheets (Figures 6-8) is something that immediately attracts attention and alerts us to the presence of ancient pearlite structures.

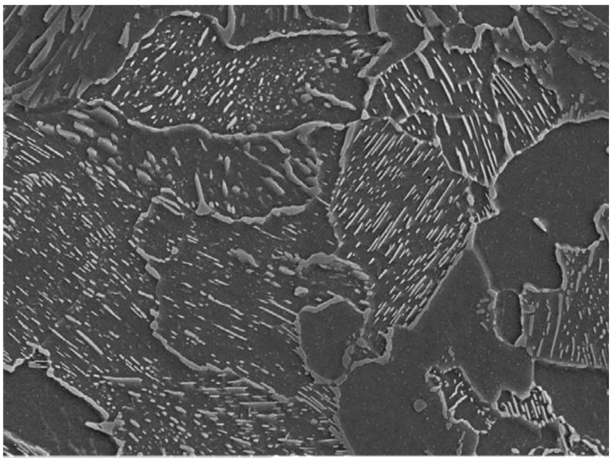

Figure 6: The typical structure of the old pearlite showing a linear laminar geometry with cementite at ferritic grain limits. Excessive interlaminar spacing in favor of ferrite.

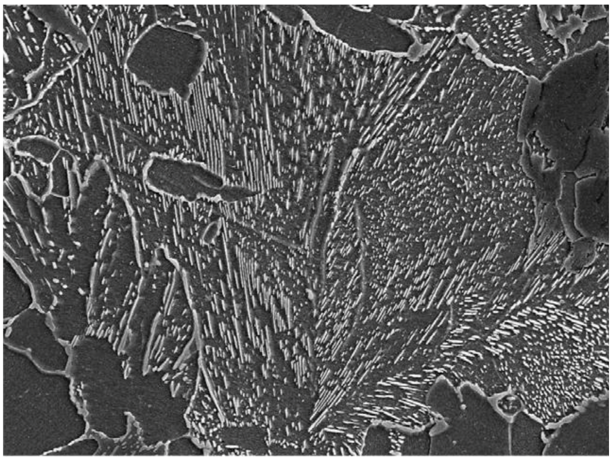

Figure 7: Typical old pearlite structure with discontinuous and segmented cementite sheets.

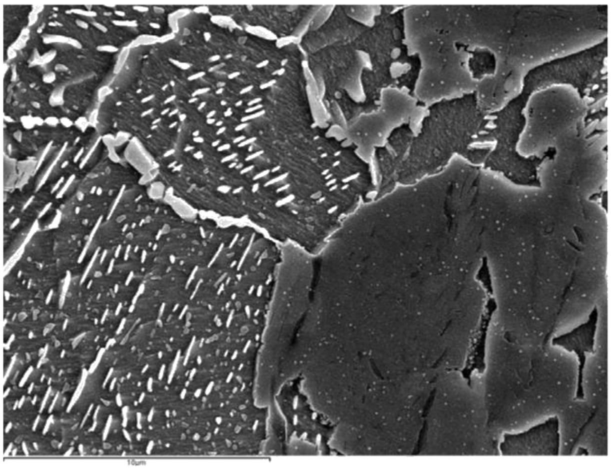

Figure 8: Old pearlite showing a high segmentation of cementite and cementite sheets at grain limit. Iron oxide (magnetite) is observed in the lower right corner of the nail corrosion.

A very regular geometric formation is evident, with very wide interlaminar spacing, distant from that which occurs in the precipitation of pearlite for conventional thermal formation gradients [29] (Figures 9 and 10).

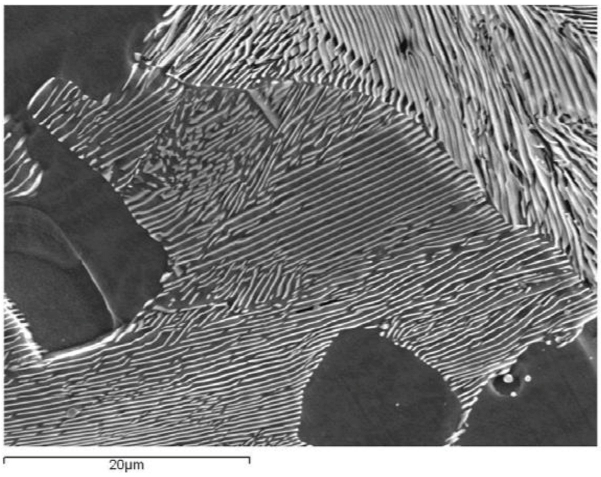

Figure 9: Conventional pearlite in a steel of current manufacture, hot-rolled and normalized. The cementite sheets are more or less continuous.

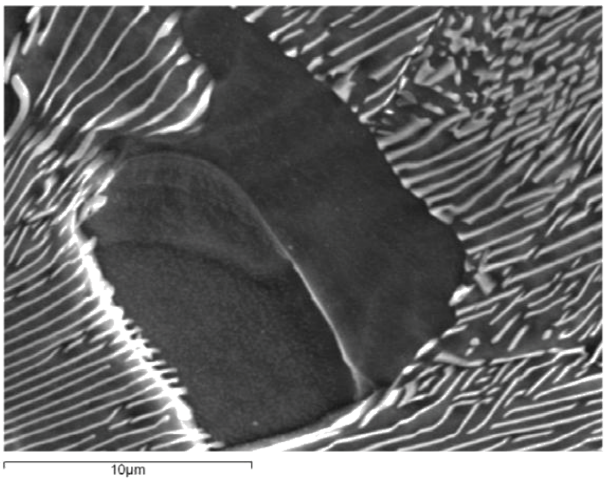

Figure 10: Conventional pearlite, hypo-eutectoid hot-rolled and normalized steel. An adequate interlaminar spacing is observed.

The ratio of ferrite to cementite in old pearlite formations is very favourable to ferrite; cementite sheets appear in large areas of ferrite. Possibly, this phenomenon can be explained by the precipitation of cementite in the limits of the pearlitic colonies (Figures 6 and 8). It is evident the redissolution of cementite in the ferrite matrix and its diffusion through it and its precipitation in the limits of these colonies. The redissolution of laminar cementite is evident by its narrowing and segmentation (Figures 7 and 8).

The slow redisolution of the cementite sheets of pearlite wave causes a strong diffusion of carbon atoms through the ferrite, making appear and disappear these cementite sheets, reprecipitating the carbon in places and forms of more equilibrium: in the limits of the colonies or pearlitic grains (Figure 6).

Thanks to the abundance of carbon circulating through the ferrite matrix, the precipitation of new carbides is carried out in the most stable ferrite planes and respecting an evident planar linear geometry (Figure 7).

This planar linear geometry is very evident in the old pearlite and also ends up building a clear Widmanstätten structure (Figures 11 and 12). This Widmanstätten structure of the cementite is very evident in all the old pearlite observed in ancient artefacts studied so far. It is a clear and defining characteristic.

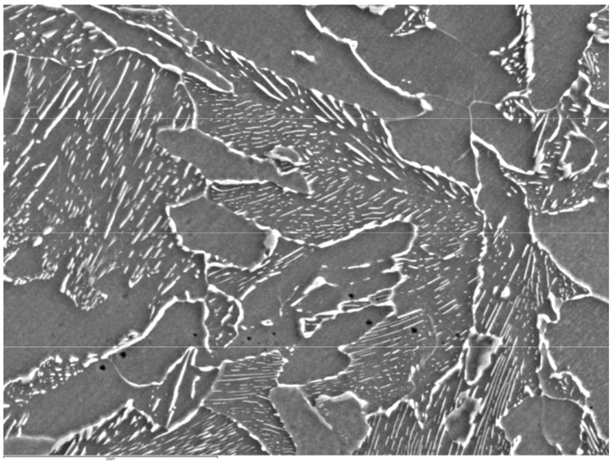

Figure 11: Old Pearlite showing in its cementite sheets a typical Widmanstätten structure. It has a lot of cementite precipitated in grain limits.

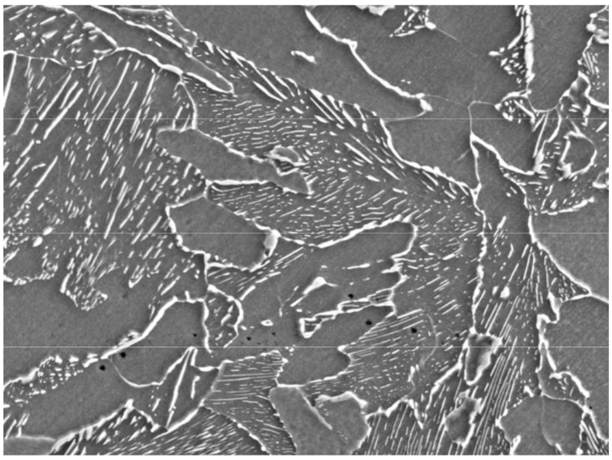

Figure 12: Old Pearlite showing laminar cementite in Widmanstätten structure. It also has a cementite bark at grain limits.

Another very evident detail of old pearlite structures is a lot segmented appearance of cementite sheets in certain areas of the structures (Figures 7, 13 and 14). The partial redisolutions of the cementite sheets cause them to emerge as an iceberg in the polishing plane of the ferrite sheet sections (Figures 13 and 15). With much more detail and greater clarity, this phenomenon is seen when the 4% Nital attack becomes deeper (Figures 16 and 17). Even in these micrographs, it is observed that old pearlite sheets are extremely thin and elastic, curving due to their height without breaking. It is also observed, clearly, in these figures, the holes made by the redissolution in the ferrite of the cementite sheets.

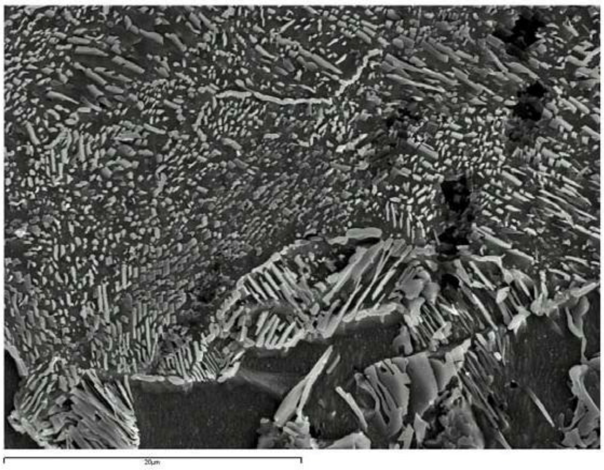

Figure 13: Old Pearlite showing a very segmented image of its cementite sheets.

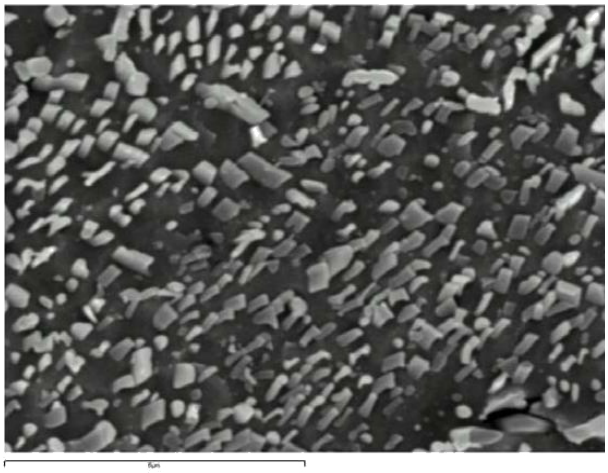

Figure 14: Detail of the image of the previous figure.

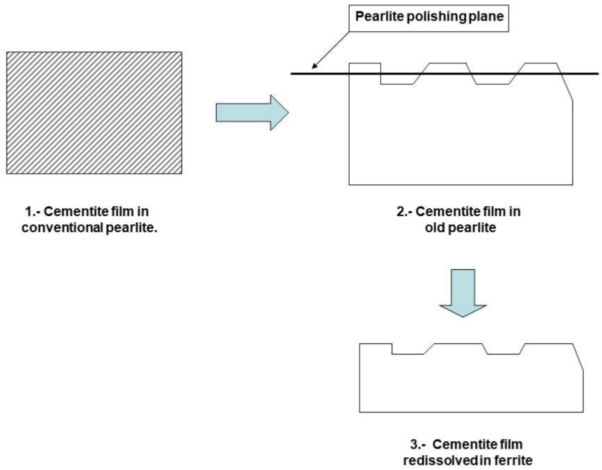

Figure 15: Schematic drawing of the partial redissolution of cementite in the ferritic phase in the old pearlite.

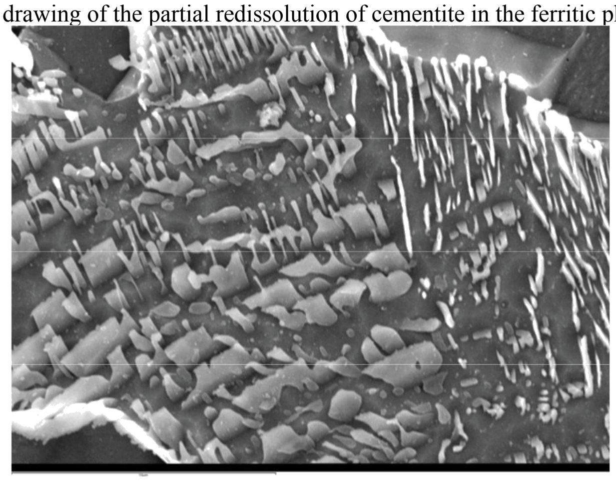

Figure 16: Image of the old pearlite showing the redissolution of the cementite sheets, very advanced. Depending on the polishing plane of the sample, it will appear more or less segmented.

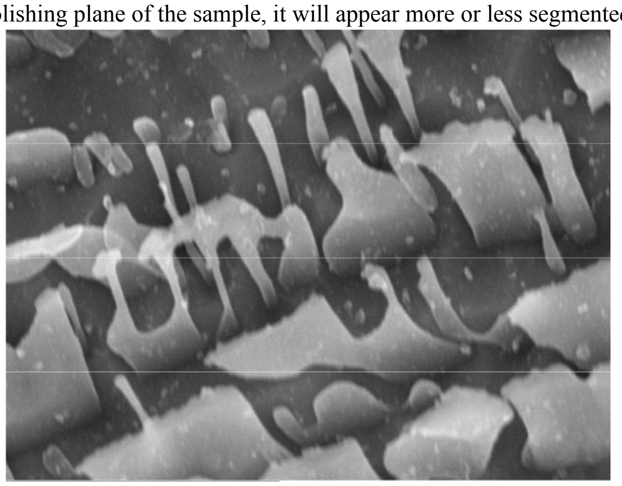

Figure 17: Old pearlite showing an image of the cementite sheets eroded by the ferrite redissolution.

CONCLUSIONS

Differences in the morphology of old pearlite colonies with respect to conventional pearlite obtained by subcooling austenite for not very severe thermal gradients are very evident. Old pearlite is the most stable morphology of pearlite, its structure is closer to thermodynamic equilibrium. It can be said that all pearlite structures would try to evolve towards more stable morphologies. The transformation depends on the diffusion of carbon through the ferritic phase, which is very slow. Long periods of time are necessary for this diffusion to be quantifiable at temperatures close to the ambient temperature. These periods of time, we have been able to verify thanks to archaeometallurgy, can be millennia, so it can be said that for conventional times is not valuable.

The evolutionary trend, shown by the old pearlite, is towards more regular and more stable geometric forms. All this is caused by the diffusion of carbon in ferrite and the source of this carbon is inexhaustible as long as there are sheets of cementite. The coarser they are at the source, the more carbon they diffuse when they are resolved. The most obvious facts, apart from the very regular geometric shapes and the tendency to form Widmanstätten-like structures, is the partial or total redissolution of the cementite sheets, depending on the time. This redissolution of cementite into ferrite feeds other carbon reservoir sinks such as ferritic grain limits.

The end of this structural evolution is not difficult to predict, but we still do not have clear evidence in archaeological samples (artifacts).

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