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Research Article

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Softening and Loss of Mechanical Strength of Carbon Steels for Extended Periods of Time at Room Temperature. Application to the Specific Case of the Santa María de la Asunción de Laredo Steel Chain

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Abstract
Carbon steels are aged for long periods at room temperature. This ageing is caused by the diffusion of carbon through the ferrite towards locations that make the system more stable according to its total free energy. The slow diffusion does not stop and in long periods of time it changes the morphology of the structure of the initial steel phases. These morphological changes imply a change in the mechanical properties of hardness, resistance, etc.

In this publication we deal with one more case of those studied by our team: the Laredo steel chain (Laredo, Cantabria (Spain)). This steel has been studied and its 13th century chronology has been certified, thanks to these microstructural changes and its implication in mechanical properties. The ageing of this steel is important, which validates that its resistance is more than 700 years.

The research has been carried out by means of optical microscopy and scanning electronics, complemented with a study of the variation of the hardness of the ferrite against a current standardised carbon steel (DIN CK15). This has also been corroborated using X-Ray diffraction, applied to the current steel and to the steel of the Laredo chain.

Keywords: carbon steel, mechanical properties, microscopy, hardness, microstructures.

Introduction
Since the year 2000 we have been researching and publishing papers about the softening and loss of mechanical resistance in archeological pieces of carbon steels. We have concluded that steel in long periods of time, hundreds and thousands of years, undergoes very evident morphological changes in its microstructure. This results in a variation in the basic mechanical properties, such as: mechanical resistance, hardness, brittleness, etc. This means that steel undergoes structural ageing processes over long periods of time. It can be of vital importance in engineering structures, which are designed for long durations of time and which cannot be easily replaced even when exhaustively controlled. See the cases of structures that are made of carbon steels: the Eifel tower, the S.Francisco bridge, underground silos and tunnels, etc. Changes in the microstructure of carbon steel have consequences on mechanical properties. The binomial microstructure-properties in Materials Science is universal. The mechanical properties depend on the size, shape, distribution and nature of the phases present in its microstructure. Any change in these variables will have a greater or lesser influence on the mechanical properties of the whole [1-9].

In our research we have applied this acquired knowledge to the topic of High Activity Nuclear Waste, which must be confined in hermetically sealed carbon steel containers, which are then controlled in Centralized Temporary Storage (ATC) and Deep Geological Storage (AGP). In these warehouses designed for this purpose, spent nuclear fuel waste is stored in Nuclear Thermal Power Plants [10-18].

Variations in mechanical properties have so far been measured with Vickers microhardness. We have been able to verify how the passage of long periods of time produces, among other microstructural changes, a relaxation and softening of the ferrite [19-36]. By experimenting with archaeological pieces of different chronologies (Roman Empire, Spanish Islam, Middle Ages, Modern Ages and present day) we have been able to see how ferrite softens linearly with time measured in centuries at room temperature [3,6,8].

In this paper we present the study carried out with a steel chain from the Almohad (medieval) period in Spain whose historical chronology dates back to the 13th century. During the Almohad period of Al Andalus (Spain), the caliph Abu Yacub Yusuf ordered the construction of a boat bridge over the Guadalquivir River in Seville (Spain) in 1171. This bridge of boats was secured with a steel chain that crossed the river from side to side. The breakage of this steel chain was essential for the conquest by Ferdinand III the Saint of Castile and Leon. The fact that it broke was the result of a ship belonging to the Castile and Leon navy, which was piloted by sailors from the town of Laredo (Cantabria, Spain). The conquest took place in May 1248. The steel chain that secured the bridge of boats was brought as a trophy to Laredo by the crew of the boats that managed to break it during the battle. Since then it has been on display in the Bethlehem Ship of the Church of Santa María de la Asunción in the Villa de Laredo (Cantabria, Spain) (Figures 1 and 2) [37].

Figure 1: Location of the iron chain under study in the church of Santa María de la Asunción in Laredo (Santander, Cantabria, Spain).

Figure 2: Detail of the Laredo chain.

The study was conducted metallographically using conventional optical microscopy and scanning electron microscopy. Vickers microhardness and X-ray diffraction were also tested.

Experimental Technique

To carry out the metallographic, hardness and X-ray diffraction tests, a link in the chain was taken (Figure.1 and 2). From this link, pieces were cut that were embedded in Buheler's EpoMetG resin (Figure.3 and 4), for its metallographic preparation.

Figure 3: Sample cut from one of the links in the Laredo chain

Figure 4: Sample embedded in resin, prepared metallographically and attacked with Nital at 4%

The specimen thus obtained is prepared metallographically in a conventional way. Wet grinding with different grit sizes of abrasive paper, Buheler Carbinet, and subsequent wet polishing with Buheler Masterpolish alumina 0.05 μm. The chemical attack carried out to reveal the microstructure of the specimen is carried out with Nital at 4%. For scanning electron microscopy, a gold sputtering was deposited.

The techniques used to carry out the study have been:

- Conventional Optical Microscopy with a built-in digital camera system for image acquisition. The microscope used is a REICHERT MEF A/M.
- Scanning Electron Microscopy with a JEOL JSM 6400 microscope with built-in EDS- EDX analysis system, operated at 20KeV.
- Vickers microhardness tests with a Vickers FUTURE_TECH microhardness meter model FM-700 of load between 10 and 100 grams. In this case the load of 10g was used.
- For X-Ray diffraction, a diffractometer EQ0434520310300 Multi-Purpose PANalytical model Philips X'PERT PRO MPD was used to perform the residual stress analysis. X'Pert Stress, Version 2.0 was used to interpret the results.

Results

The metallographic examination shows that this is a steel, manufactured in medieval times, very heterogeneous with slag typical of silicates and manganese sulphide, as shown in the micrographs of figures 5 to 10. As can be seen, this is a very heterogeneous piece of steel, with perlitic areas of carbon content between 0.15% and 0.25% (figures 5 to 8) and other areas, with total absence of carbon (figures 9 and 10).

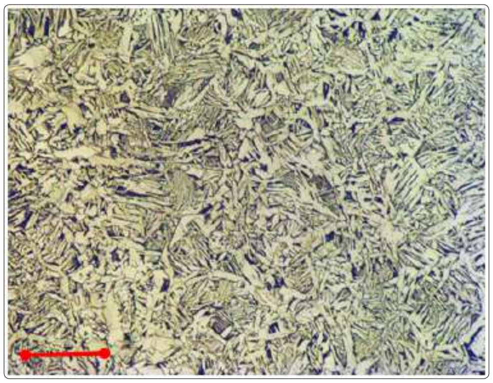

Figure 5: Image obtained by conventional optical microscopy of the steel structure of the Laredo chain, in which acicular ferrite and very fine perlite colonies are observed

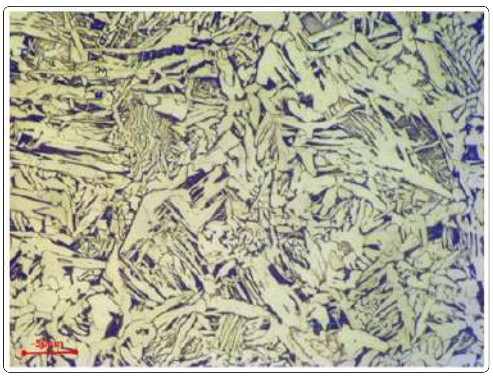

Figure 6: Detail, at higher magnifications, of the structure of the micrograph of the previous figure

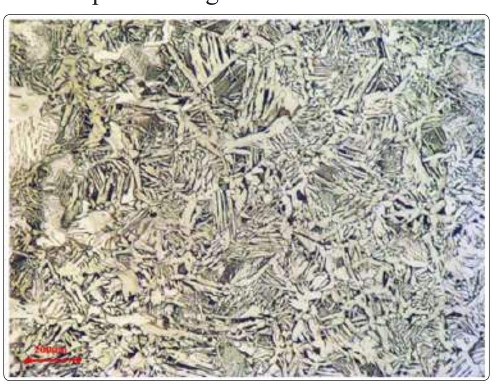

Figure 7: Image obtained by conventional optical microscopy of the steel structure of the Laredo chain, in another area of the sample. The acicular structure shows that the steel was heated to a very high temperature for forging.

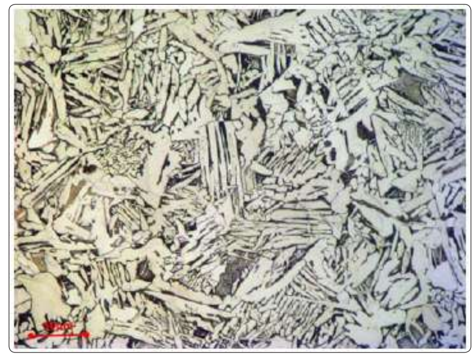

Figure 8: Detail, at higher magnifications, of the structure of the micrograph of the previous figure

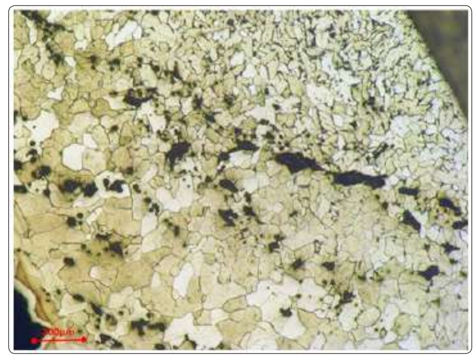

Figure 9: Image obtained by conventional optical microscopy of a detail of the steel structure of the Laredo chain, showing a clear ferritic zone. Silicate slag is abundant

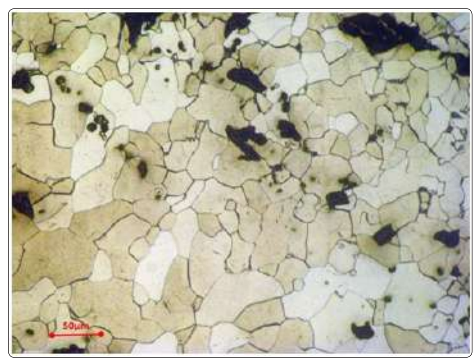

Figure 10: Detail, at higher magnifications, of the structure of the micrograph of the previous figure

The acicular structure of the ferrite shows that the steel link, very heterogeneous in carbon content, was forged hot at very high temperature and then rapidly cooled. There are large areas of the sample studied that present a massively ferritic structure. This would demonstrate, its medieval origin, in which it was quite normal to contribute with steel pieces by hot forging of metallic pieces (remnants) of steels of different origin. It was a question of taking advantage of all the steels that were available. Likewise, the ingot from the reduction furnace was very heterogeneous. This ferritic zone shows the presence of abundant silicate slag, typical of the medieval steels used in this type of manufacture: chains, tools, etc. The heterogeneity of links made by hot forging, with steels of different carbon content and presence of slag indicates their medieval origin.

Scanning electron microscopy is essential in this type of parts, to see the microstructural morphological traces resulting from the aging process over the centuries. These microstructural traces are most visible in the cementite crystals of perlitic colonies. The vain perlite crystals change their morphology over time and this is visualized with the passage of long periods of time [1-9]. These shape changes are caused by the tendency of cementite crystals to very linear geometries and by carbon redisolution and diffusion through ferrite to more convenient deposition sites, such as grain boundaries [8,9]. There is a great mobility of carbon in the ferritic matrix to try to reduce the free energy of the system. And it is this decrease in the total energy of the system that is triggered by the slow diffusion of carbon at room temperature over very long periods of time (centuries). In figures 11 to 15, several phenomena can be observed as a result of the microstructural ageing suffered by the steel under study with the passage of time. These ageing phenomena are translated into very clear morphologies and, to a certain extent, can be assessed with some precision.

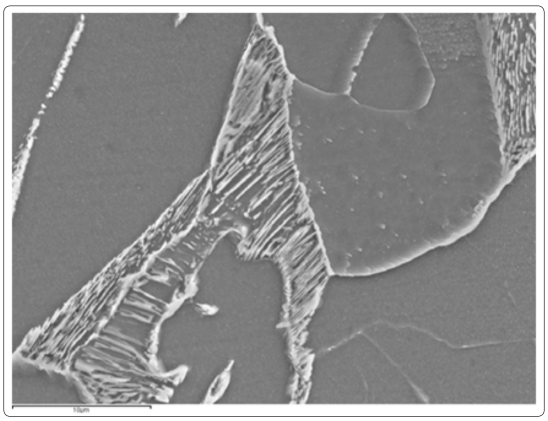

Figure 11: Scanning electron microscopy image of the Laredo chain steel sample showing an aged perlite colony

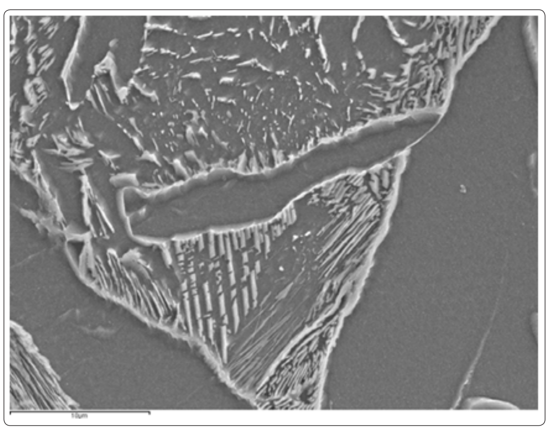

Figure 12: Scanning electron microscopy image showing an aged perlite colony wrapped in a cementite crust

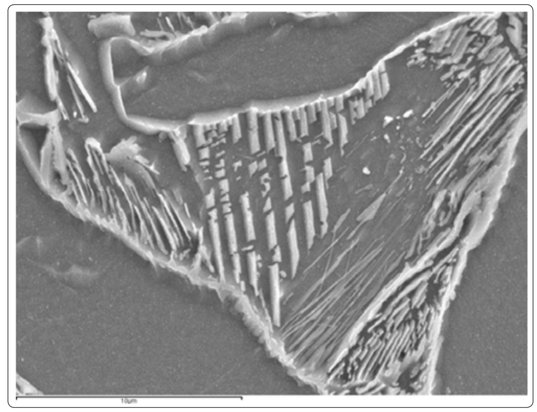

Figure 13: Detail, at higher magnifications, of the micrograph structure of the previous figure, showing the redisolution of the cementite sheets of perlite and the supply of this carbon for the formation of an outer cortex in the perlitic colonies

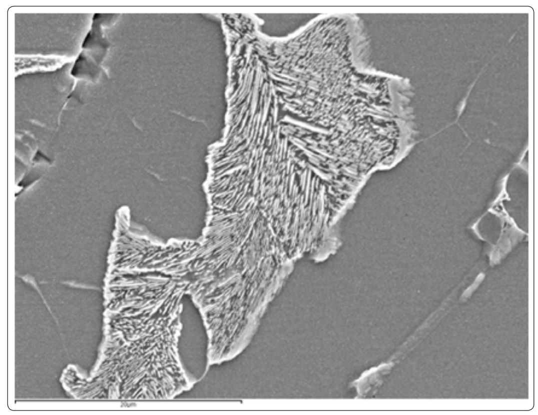

Figure 14: Scanning electron microscopy image of the Laredo chain steel

sample showing continuous cementite at grain limits and small iron carbides in the perlitic matrix.

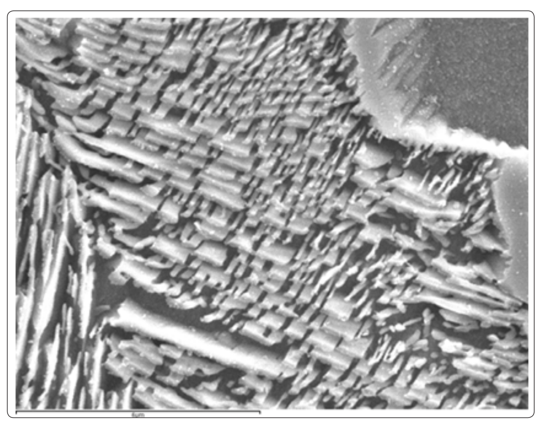

Figure 15: Detail, at higher magnifications, of the structure of the micrograph of the previous figure.

An effect of carbon diffusion through the ferritic matrix is a redistribution of carbon from the cementite sheets. Perlite cementite partially redisolves over time at room temperature and, with this origin, carbon is directed to grain boundaries and to the perlite crystal boundary forming a continuous cementite crust at both locations (Figures 8, 12, 13 and 16). Both the formation of continuous cementite at the borders of the perlitic colonies and at the grain boundaries are very clearly observed in Figures 17 and 18. All these morphological changes are produced by the carbon redisolution of perlite cementite and its diffusion through the ferrite matrix over time at room temperature.

This effect is more evident the older the steel artefacts [3,8,9]. This has been proven over time in our research of Roman, medieval and modern pieces [1-9].

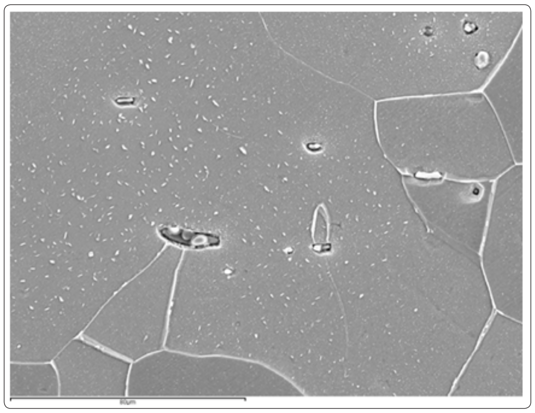

Figure 16: Scanning electron microscopy image showing continuous at grain limit

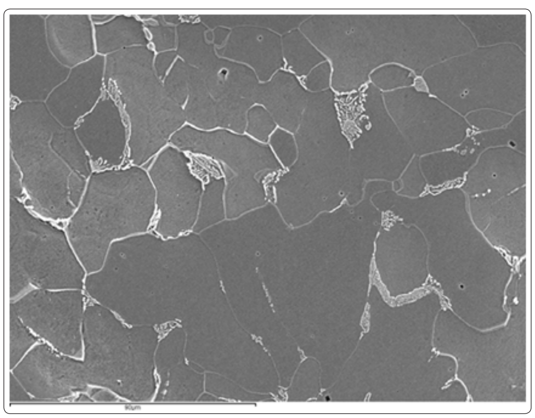

Figure 17: Image obtained by scanning electron microscopy of the steel sample of the Laredo chain, showing a ferritic matrix without small carbides precipitated in it. Grain limits appear with continuous cementite and lagoons of aged perlite

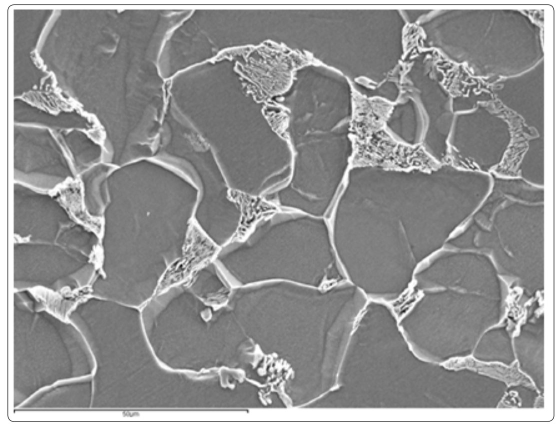

Figure 18: Scanning electron microscopy image of the Laredo chain steel sample clearly showing continuous cementite at grain boundaries and colonies of very aged perlite.

On the other hand, the ferrite, with the passage of time, undergoes a process of structural relaxation, which we have been able to verify in our exhaustive study of steel artefacts of the different cultural stages of humanity, from antiquity to modern times [1- 18]. This has been verified using Vickers microhardness and X-ray diffraction [8, 12, 13, 16, 19, 20, 30, 36].

In figure 16, there is a continuous cementite sheet at the boundary of the ferritic grains and a precipitation inside the ferrite of small crystals with a Widmanstätten structure. This is due to the fact that the cooling of the steel piece was very fast from a very high forging temperature of around 900ºC. This rapid cooling results in some of the carbon remaining in the ferrite. Aging over time, at room temperature, causes this carbon to be segregated into small iron carbide crystals within the ferrite. In this way the ferrite relaxes into a more stable structure [1, 3, 5, 7, 38].

Another detectable and measurable consequence of aged ferrite is its relaxation, which depends on the time elapsed. This relaxation is quantifiable with the microhardness test [2, 3, 6, 26, 31, 33]. For this investigation we have used a Vickers microhardness tester with a load between 10 and 100 grams. The selected load was 10 grams. As we have observed metallographically, different ferritic grains appear in the ferritic zone of the sample. Some have small iron carbide crystals, as described in figure 16. On the other hand, others appear clean of iron carbides in their matrix (figures 17 and 18). The microhardness obtained in some grains is different, having detected microhardness from 121 to 115 HV10, for ferritic grains with presence of iron carbides in their matrix (Figure 16) and, from 112 to 85 HV10, in those ferritic grains with absence of iron carbides in their matrix (Figures 17 and 18).

If these values are compared to the Vickers microhardness of the ferrite, from a current standardized carbon steel DIN CK15 (Figure 19), it has an average microhardness of 137 HV10. This gives us an idea of the softening suffered by ferrite in carbon steels aged for several centuries. The hardness of the ferrite in the steel of the Laredo chain therefore has a relative hardness that varies between 80% and 70% of the hardness of the ferrite of a current steel. This confirms the age of the chain according to our quantitative and comparative evaluation with archaeological pieces studied by us, with chronologies from the 1st century A.D. to the 20th century A.D. [1-8].

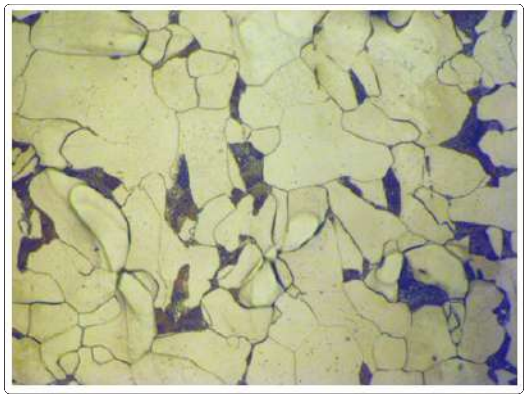

Figure 19: Image obtained by conventional optical microscopy of the current standardised carbon steel DIN CK15. This steel has been a reference for the microhardness of the ferrite of a current steel and for X- Ray diffraction.

These results are very conditioning for the carbon steel metallic structures that are built thinking about a duration of several hundred years. The loss of mechanical strength of the steels has been demonstrated by the study of these archeological steel pieces. Moreover, the appearance of a continuous sheet of cementite at the grain limits and at the edges of the perlite crystals can lead to very severe brittleness (figures 11, 12, 13, 14, 16, 17 and 18). Therefore, the time of use of these large metallic structures is very limiting, with the passage of centuries: bridges, silos, reinforced concrete structures, etc.; as we have also been able to verify with the application of archaeological analogues to the safety of Deep Geological Storage (DGS) of carbon steel containers of High Activity Nuclear Waste [10-18].

Another technique applied to the steel of the Laredo chain was X-Ray diffraction. This technology has shown the relaxation of residual stresses, providing a very clear picture of the offset of the peaks of the steel diffractogram of the chain and a current carbon steel normalized DIN CK15 (figure 20). This comparison was necessary in order to verify this gap between a current standardised carbon steel and a very old standardised carbon steel. For large angles these changes in the diffractogram signal can be better visualized. In Fig. 20, you can see the peaks already treated with the X'Pert Stress program, Version 2.0; in blue, the peak corresponding to the current standard steel and, in red, the peak corresponding to the old steel of the Laredo chain.

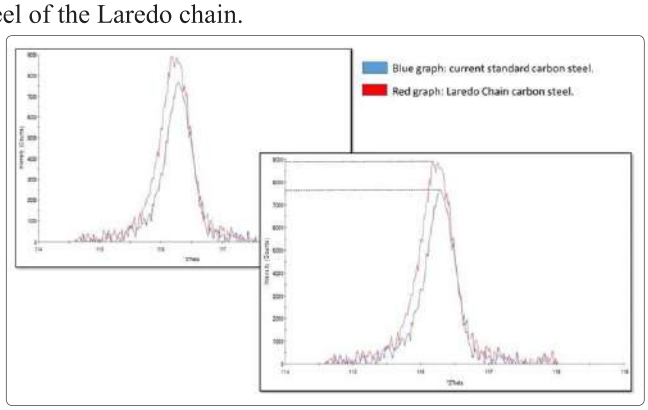

Figure 20: Figure showing the graphs representing the peaks of the diffractograms of the current normalized steel and the aged steel of the Laredo chain

A fact that also corroborates that the chain of Laredo is a chronology of the thirteenth century, is its Muslim typology and the time when it is reported that it was brought to Laredo. An archaeological excavation in Marmuyas (Málaga, Spain) has brought to light numerous iron and steel objects belonging to that ninth, twelfth and thirteenth century chronology, parallel to the Laredo chain [39]. This would demonstrate the Muslim origin of this type of chain.

Conclusions

With this study carried out with the Laredo chain, the correct dating of its steel as manufactured in the 13th century has been shown, therefore, of an antiquity of more than 700 years.

The aging of the steel of the chain is verified by the morphological changes produced in it by the passage of a long period of time, of more than 700 years, at room temperature. These morphological changes in its metallographic structure can be clearly observed in the thinning by redisolution of the cementite sheets of perlite. This redissolution of the cementite in the ferritic matrix, supplies the carbon that by diffusion moves towards the grain limits and the borders of the perlite crystals. The emigration of carbon, by diffusion through the ferrite, favoured by a long period of time, is the cause of the formation of continuous sheets of cementite at the grain limits and the formation of a crust, also continuous, at the external borders of the perlitic colonies.

The hardness measurements, by means of the microhardness test Vickers, of the ferrite, have shown a relaxation and softening of this phase adjusted to the aging produced in the structure by the passage of more than 700 years, with respect to a similar steel currently normalized (DIN CK15). This hardness obtained from the ferritic phase of the steel of the Laredo chain, with this consequent aging and relaxation, remains at 70% to 80% of the hardness of the ferrite of a current standardized carbon steel (DIN CK15).

On the other hand, the stress measurements by X-ray diffraction of the ferritic phases of the steel of the Laredo chain and a current one (DIN CK15), a notable displacement of the peaks corresponding to a certain angle is observed; although in this paper no quantified values are presented.

The typology of the Laredo chain has been studied by comparison with iron and steel objects from archaeological excavations from the Muslim period in Al Andalus (Iberian Peninsula), and its profile has been adapted to the iron chains manufactured in the period from the 9th to the 13th century in this area.

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