International Journal Of
Recent Scientific Research
ISSN: 0976-3031
Volume: 6(12) December -2015

TYPICAL MORPHOLOGIES OF IRON CARBIDES IN PIECES OF PREROMANS STEEL SUBMITTED TO RITES OF INCINERATION IN THE IBERIAN PENINSULA

Laura García Sánchez, A.J. Criado Martín, A.J. Criado Portal and J.Mª Gómez de Salazar y Caso de los Cobos

THE OFFICIAL PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH (IJRSR)
http://www.recentscientific.com/ recentscientific@gmail.com

Available Online at http://www.recentscientific.com

ISSN: 0976-3031

International Journal of Recent Scientific Research
Vol. 6, Issue, 12, pp. 7844-7848, December, 2015

International Journal of Recent Scientific Research

RESEARCH ARTICLE

TYPICAL MORPHOLOGIES OF IRON CARBIDES IN PIECES OF PREROMANS STEEL SUBMITTED TO RITES OF INCINERATION IN THE IBERIAN PENINSULA

Laura García Sánchez*, A.J. Criado Martín, A.J. Criado Portal and J.Mª Gómez de Salazar y Caso de los Cobos

Department of Material Science and Metallurgic Engineering. Faculty of Chemistry, Complutense University of Madrid. 28040 Madrid. Spain

ARTICLE INFO

Article History:

Received 05th September, 2015
Received in revised form 08th October, 2015
Accepted 10th November, 2015
Published online 28st December, 2015

Key words:

Archaeological steel, cremation rites, metallographic structures, iron carbides, SEM.

ABSTRACT

It is the study of very typical microstructures that appear in steel parts with their corpse cremated, between Roman peoples of the Iberian Peninsula. Through analysis we can deduce like the temperatures reached in these funeral rites, the cooling rates of the funeral pyre and thermodynamic processes operating in steel parts during the rite and which these structures result.

INTRODUCTION

The metallographic study of incinerated steel parts in pre-Roman cultures of the Iberian Peninsula, it has been a real challenge its begining. The first studies were performed by Criado *et al.* in the years 1999-2003, in a research proposal by ENRESA (National Company for Nuclear Waste Spain) in order to check to behavior the long-term steel containers for waste of Nuclear High Level (RNAA) , which should be confined Deep Geological Storage (AGP) (Criado *et al,* (2000); Criado *et al,* (2003); Criado *et al,* (2004); Criado *et al,* (2004); Criado *et al,* (2005)). It would consist in use pieces of metal archaeological , mainly carbon steel, such as proposed Spanish model by ENRESA (Astudillo *et al,* (2001)) and the Nuclear Security Council of Spain (CSN). This model steel waste container is also proposed by the US and Japan, and other European countries such as France, Britain, etc. (Astudillo *et al,* (2001)). transfer the behavior of metal pieces against corrosion in soil of the burial and the microstructural changes suffered over long periods, is what is known as archaeological analogues (AA) (Criado *et al,* (2000); Criado *et al,* (2003); Criado *et al,* (2004); Criado *et al,* (2004); Criado *et al,* (2005); Criado *et al,* (2006); Criado *et al,* (2009); García *et al,* (2010). During the study of analogues archaeological Pre Roman, Roman, medieval and modern, it was found, by Criado *et al,* the emergence of some very peculiar morphologies at that AA which has prerromans chronologies, ie, Celtic, Celtiberian and Iberian, and that appeared in necropolis with graves with remains subject to incineration rites. Other authors, in a timely manner, had approached this and made the identification of these crystal structures of iron carbide present in burned pieces, with varying success. Discussion o f whether they were iron carbides or nitrides was elucidated from Liu and Criado studies (Liu *et al,* (1984); Criado *et al,* (2011)). The controversy over whether nitrides were caused by the dissolution of nitrogen from the bodies incinerated or, on the contrary, it was morphologies of iron carbides, was certified for such carbides, by the above authors.

These publications try to find microstructural morphology by scanning electron microscopy with a microscope of thermionic cathode with tungsten filament (FEG). This has been selected a number of pre-Roman archaeological from different sites in the Iberian Peninsula that had a very high stratigraphic chronology and reliability, which have been subjected to processes of cremation. The metallographic preparation

Corresponding author:* **Laura García Sánchez
Department of Material Science and Metallurgic Engineering. Faculty of Chemistry, Complutense University of Madrid. 28040 Madrid. Spain

adjusted to the necessary observations and the use of scanning electron microscopy (FEG) have allowed interesting images of microstructural morphology of these iron carbide crystals.

Experimental Technique

- ❖ Falcata Iberian. Museum of Armory in Vitoria (Alava) (Figure. 2 and 3).
- ❖ Pilum Iberian. Museum of Copper in Cerro Muriano (Córdoba) (Figure. 4 and 5).
- ❖ Tack celtiberic. Necropolis of Villanueva de Teba (Burgos) (Figure. 6 and 7). Fragment of arrow celtiberic.Numancia (Soria) (Figure. 8 and9).
- ❖ Fragment of arrow celtic. Castrejón de Capote (Badajoz) (Figure. 10 and 11).

Figure 1 Schematic map of the Iberian Peninsula in which are located deposits where the pieces were found under study.

Figure 2 Iberian Falcata Armory Museum of Vitoria-Gasteiz (Álava).

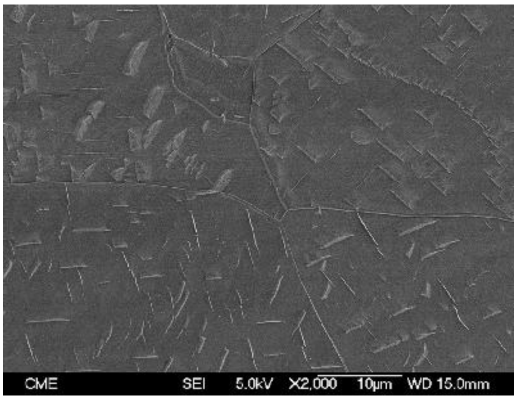

Figure 3 Micrograph of Iberian Falcata in which observed a matrix of ferritic grains with iron carbides precipitated inside.

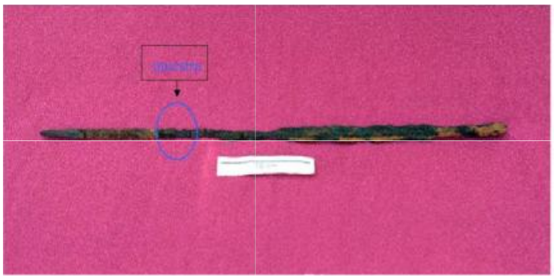

Figure 4 Iberian Pilum in Museum of Copper in Cerro Muriano (Córdoba).

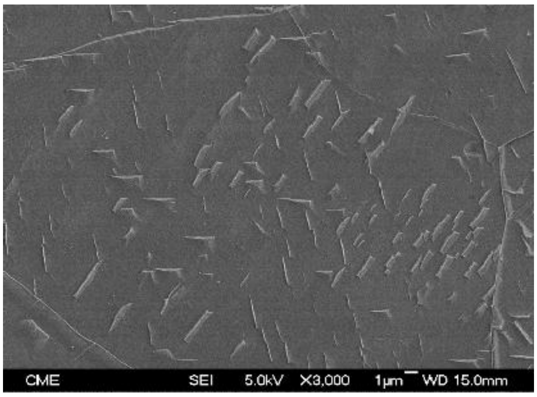

Figure 5 Micrograph of Iberian pilum which shows a matrix of ferritic grains with iron carbides precipitate inside with Widmann stätten type structure.

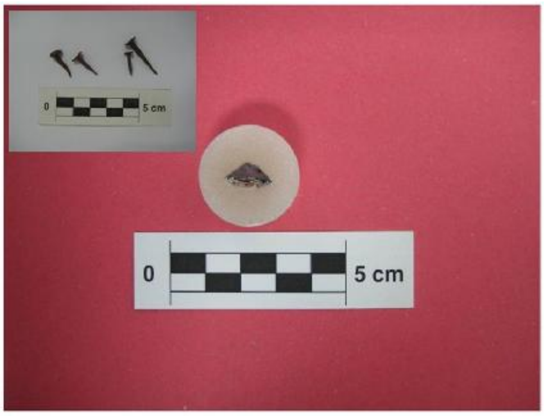

Figure 6 Tack celtiberic of the necropolis of Villanueva de Teba (Burgos).

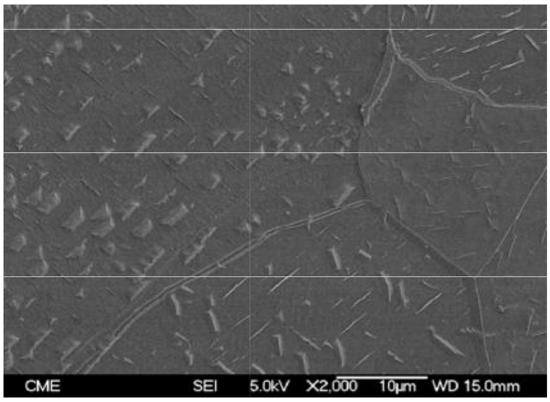

Figure 7 Micrograph of celtiberic tack which shows a matrix of ferritic grains with iron carbides precipitate inside with Widmannstätten type structure.

Figure 8 Fragment of arrow celtiberic. Numancia (Soria).

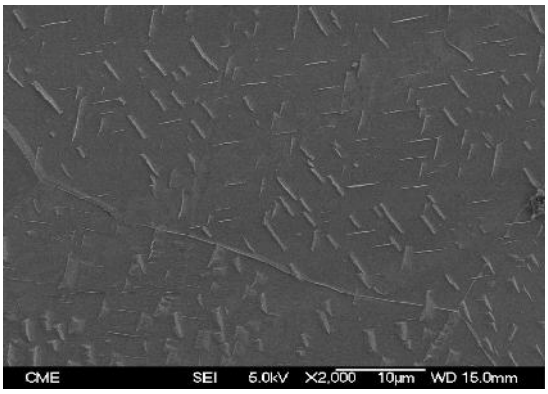

Figure 9 Micrograph of fragment of arrow of Numancia (Soria), in which there is a precipitate of idiomorphic iron carbides with structure Widmannstätten type in the interior of the ferritic grains.

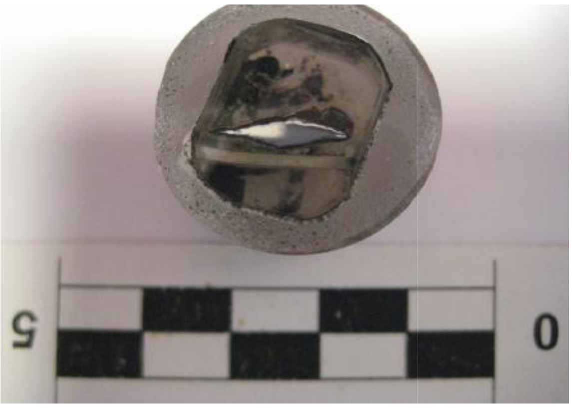

Figure 10 Fragment of arrow celtic. Castrejón de Capote (Badajoz).

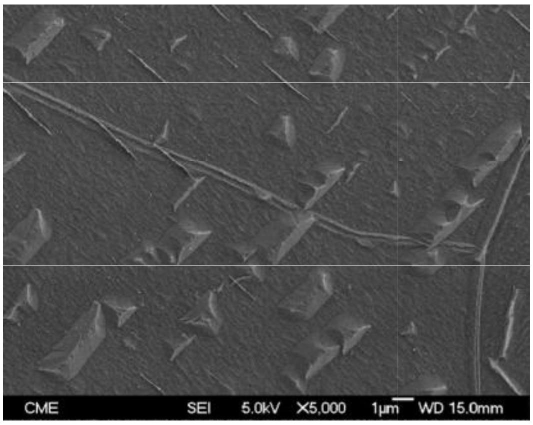

Figure 11 Micrograph of fragment of arrow of Castrejón de Capote (Badajoz), in which there is a precipitate of idiomorphic iron carbides with structure Widmann stätten type in the interior of the ferritic grains.

In this paper, we summarize the results showing the metallographic obtained images by pilum Iberian of Cerro Muriano (Córdoba) and tack celtibérica Villanueva de Teba (Burgos). Both had, like the rest of the studied typical pieces, idiomorphic iron carbides being incinerated. These pieces are from necropolis of incineration, highly reliable chronological and contextual. Samples taken from the pieces were embedded in resin Mecaprex KM-U. Roughed by abrasive discs of Buehler grain 240, 320, 600 and 2000 in water; and subsequent polishing α alumina (0.3 microns) and alumina γ (0.03 microns) in Buehler polishing cloth. Chemical etching for metallographic observation by FEG should be very careful and free from residues of attack deposited on the target surface. The high quality of the microscopic observation of this instrument may be affected with a defective metallographic preparation and chemical attack. The etching was performed with 4% Nital, and washed with distilled water in an ultrasonic bath.

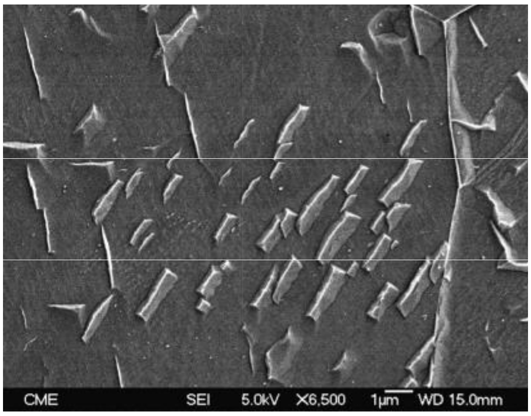

Figure 12 Micrograph of Iberian pilum of the archaeological site Cerro Muriano (Córdoba) in which seen ferrite grains with cementite prismatic crystals (orthorhombic) in Widmanstätten structure.

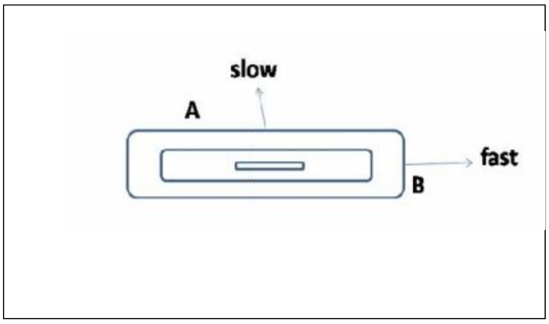

Figure 13 Interface model.

For the observation of the samples after preparation roughing, polishing and chemical etching, they were metallized with gold for 30 seconds with a current of 20 mA, and thickness of 3 nm gold. The scanning electron microscope with thermionic cathode of tungsten filament (FEG) used is JEOL model JSM 6400 that provides images and physic-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 3,5nm and detector to work to 39 mm with an image resolution 10nm. It provides backscattered electron images with an image resolution of 10 nm, a 8 mm working distance. In addition, you can perform qualitative elemental analysis (EDS) with a resolution of 133eV. (Criado *et al*, (2004); Böke *et al*, (2009)).

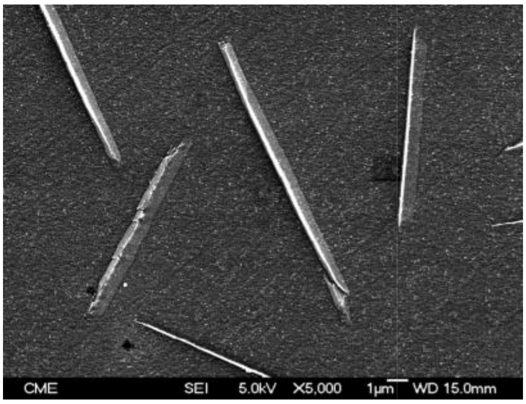

Figure 14 Micrograph of thumbtack of Teba Villanueva (Burgos), in which seen elongated prismatic morphologies of iron carbides.

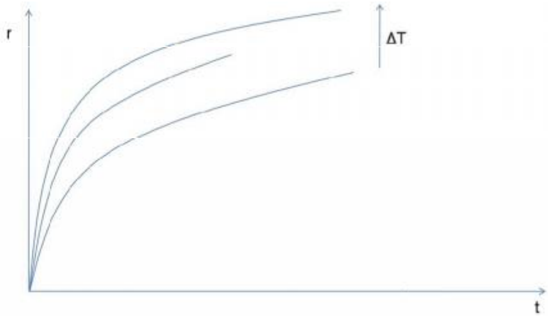

Figure 15 Schematic diagram of the variation of the crystal growth of cementite with time at different temperatures.

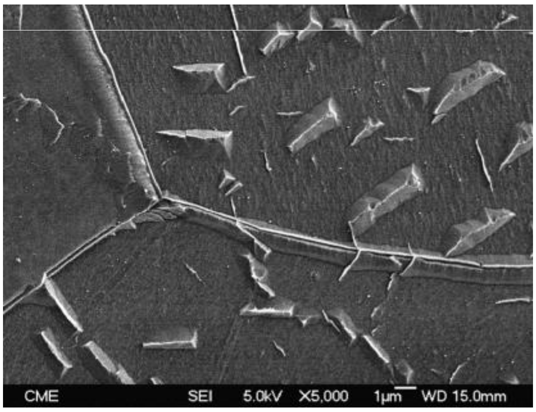

Figure 16 Micrograph of Iberian pilum of the archaeological site Cerro Muriano (Córdoba) in which seen the precipitation of cementite in grain boundaries ferritic.

RESULTS AND DISCUSSION

Images of iron carbide crystals obtained by FEG show a very marked idiomophic character, due to the slow precipitation within the ferrite, caused by carbon diffusion along thousands of years (Figure 12 and 13). This slow diffusion produces a clear idiomorfismo, characterized by prismatic forms of idiomorphic cementite crystals (Chadwick, (1972); Porter *et al,* (1981); Rostoker *et al,* (1977)).

These crystals are the result of segregation of carbon dissolved in the ferrite during thermal process of incineration (heating to high temperatures followed by sudden cooling)

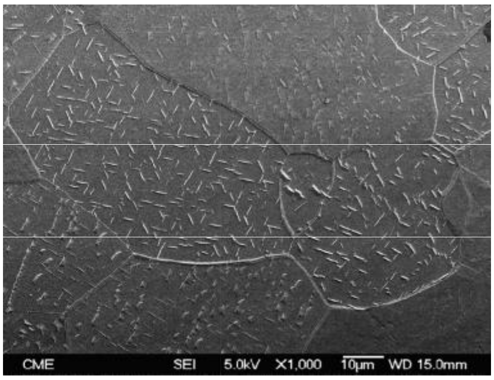

Figure 17 Micrograph of Iberian pilum of the archaeological site Cerro Muriano (Córdoba) in which seen the cortex of cementite continuous in grain boundaries ferritic in the steel.

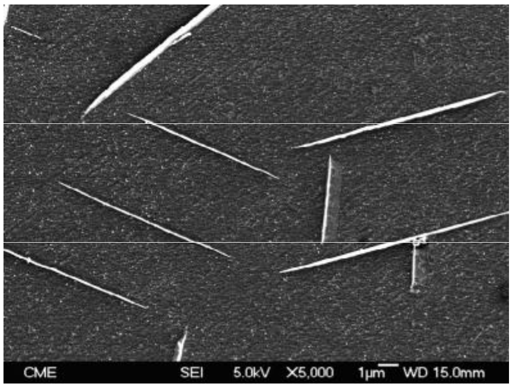

Figure 18 Micrograph of thumbtack of Teba Villanueva (Burgos), in which seen acicular morphologies in the iron carbide crystals with Widmanstätten structure.

(Liu *et al,* (1984); Criado *et al,* (2011); Criado Martín (2012)). Quenching since high temperature causes that the ferrite is satured in carbon at room temperature (% C≈ 0'028 to 720 ° C). As the solubility of carbon in ferrite at room temperature is C≈0'008%, this carbon will segregate over time within the ferritic matrix in the form of idiomorphic crystals with Widmanstätten structure. The diffusion of carbon atoms in ferrite, is slow at room temperature, but time is very long (≥ 2000 years). The equation governing the growth of crystals is: (Porter *et al* (1981):

$$(r)^{3} - r_{O}^{3} = k.t \quad (1)$$

where ro is the mean radius of the crystal to t = 0; being, therefore, the growth of carbides is a linear relationship with time. K for the above equation is:

$$k \approx D \bullet \gamma \bullet Xe \quad (2)$$

Where, ro is the mean radius of the crystal to t = 0; D is the diffusion coefficient of carbon in ferrite; γ is the interfacial energy; Xe is the equilibrium solubility for very large iron carbide crystals. Substituting the value of k, (1) (2), the equation is:

$$(r)^{3} - ro^{3} = D \bullet \gamma \bullet Xe \bullet t$$

The growth model of these cementite particles is adjusted kinetically to the model (Porter *et al,* (1981) (Fig.13 Fig.14): This kinetic behavior model leads to the formation of elongated prisms cementite with Widmanstätten structure (Figure14). The graphical representation of the variation of the crystal growth of cementite with respect to temperature is as follows (Porter *et al,* (1981) (Fig.15): The crystal growth of cementite in the ferrite matrix is slowed to room temperature; but as the extremely long time, it continues, causing the appearance of idiomorphic crystals with Widmanstätten structure; untilex haustion of the carbon that supersaturated the ferrite. The precipitation of iron carbide or cementite, occurs not only inside the grains of carbon supersaturation in ferrite but also in ferritic grain boundaries (Figure.16). This means that in many of these ancient steels, subjected to processes of cremation, the ferritic grains present a continuous bark of cementite (Figure.17).

So far, the optical and scanning electron microscopy have provided image allowing assimilate the structure of these crystals of iron carbide to crystals like needle (Liu *et al*, (1984); Criado *et al*, (2011); Criado Martín, (2012); however, scanning electron microscopy with a thermionic cathode with tungsten filament (FEG), has allowed us to make clear that its structure is prismatic. The acicular image gives the reflection of light or electrons, according to the technique, which occurs in the slim mesetas produced on the dihedral angles of the prisms during the roughing and polishing (Fig. 18).

SUMMARY AND CONCLUSIONS

The use of scanning electron microscopy with a microscope of thermionic cathode with tungsten filament (FEG), has been essential to observe the crystal morphology of iron carbide precipitates in the ferritic matrix in those steels under went cremation rites. Heat treatment suffered by a steel during the rite of cremation (incineration) is essentially a more or less prolonged heating at high temperatures - 800 ° C to 1100ºC-, followed by air cooling (strong thermal gradient) or by turning off the funeral pyre with any liquid such as water, wine, beer, etc., according to the ritual culture of each people or nation. In all cases the ferrite is supersaturated with carbon, at least 0'028 mass%, which is the solubility of carbon in ferrite to 720°C, approximately.

This happens to thermal gradients above200ºC (Liu *et al*, (1984). The solubility of carbon in ferrite low down to 0'008 mass% at room temperature. This is equivalent to a solubility less than 3.5 times that possesses to temperatures of 720°C, approximately. This insolubility of carbon in ferrite is caused by segregation of carbon and the formation of iron carbide crystals. Segregation and diffusion of carbon in ferrite, over thousands of years, produce the appearance of prismatic and idiomorphic crystals of cementite, very characteristic in the steel pieces that have suffered incineration or cremation. The growth model for the cementite formation is very elongated prismatic crystals idiomorphic in those levels more favorable ferritic matrix; producing morphologies in carbides very characteristic with Widmanstätten structure.

References

1. ASTUDILLO, J. *et al*. (2001): Plan de Investigación y Desarrollo Tecnológico Enresa (1999-2003), IV Jornadas de Investigación y Desarrollo Tecnológico de Residuos Radioactivos, Vol.1. 9-24.
2. BÖKE, H. *et al*. (2009): Properties of Roman bricks and mortars used in Serapis temple in the city of Pergamon, Materials Characterization, 995-1000.
3. CHADWICK, G.A. (1972): Metallography of phase transformations, The Butterwhorth Group, 188-194.
4. CRIADO, A.J. *et al.* (2000): Análogos arqueológicos e industriales para almacenamientos profundos: estudio de piezas arqueológicas metálicas, Publicación Técnica de ENRESA, 204.
5. CRIADO, A.J. *et al*. (2003): Análogos arqueológicos e industriales para almacenamiento de residuos radiactivos: estudio de piezas arqueológicas metálicas (Archeo II), Publicación Técnica de ENRESA, 03/2003, 272.
6. CRIADO, A.J. *et al*. (2004): Aplicación de los análogos a la evaluación de seguridad y comunicación del almacenamiento geológico. Síntesis Ilustrativa, Colección de Documentos I+D de ENRESA y Consejo de Seguridad Nuclear, Vol.10, 189.
7. CRIADO, A.J. *et al.* (2004): Analogue application to safety assessment and communication of radiactive waste geological disposal. Ilustrative synthesis, Colección de Documentos I+D de ENRESA y Consejo de Seguridad Nuclear, Vol.11, 167.
8. CRIADO, A.J. *et al*. (2004): A new method for datation of ancient steel simples using Vickers microhandness, Materials Characterization, 145-151.
9. CRIADO, A.J. *et al*. (2005): Aplicación de los análogos a la evaluación de seguridad y comunicación del almacenamiento geológico. Catálogo de análogos más significativos, Colección de Documentos I+D de ENRESA y Consejo de Seguridad Nuclear, Vol.13,675.
10. CRIADO, A.J. *et al.* (2006): Archaeologic analogues: microstructural changes by natural ageing in carbon steels, *Journal of Nuclear Materials*, 349, 1-5.
11. CRIADO, A.J. *et al*. (2009): An archaeological analogue for a composite material of carbon steel, copper and magnetite, Praktische Metalographie,8 /2009, 377-393.
12. CRIADO, A.J. *et al*. (2011): Los carburos de hierro como testigos de los ritos de cremación entre los pueblos prerromanos de la Península Ibérica: algunos ejemplos, SPAL, Vol.18, 105-130.
13. CRIADO MARTÍN, A.J. (2012): Arqueometria: hierro y fuego. Técnicas arqueométricas aplicadas al estudio de los hierros y aceros protohistóricos y romanos de la Península Ibérica sometidos a incineración o incendio, Tesis Doctoral, Universidad Nacional de Educación a Distancia, Madrid.
14. GARCÍA, L. *et al* (2010): A contribution to the understanding of Sollingen steel in the 19th. Century, Praktische Metalographie, 6/2010, 342-353.
15. LIU, K.H. *et al* (1984): Analytical electrón microscopy of early steel from Bacqah Valley (Jordan), Microbeam Analysis, 261-264.
16. PORTER, D.A. *et al.* (1981): Phase transformation in metals and alloys, Van Nostrand Reinhold Company Ltd., 279-287.
17. ROSTOKER, W. and DVORAK, J.R. (1977): Interpretation of metallographic structures, Academia Press, 127-165.

ISSN 0976-3031

9 770976 303009 >