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CHARACTERIZATION OF TWO IRON BULLETS FROM THE ROYAL AMMUNITION FACTORY OF EUGI (SPAIN)

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Abstract

In this work, a comparative analysis of two iron bullets found in The Royal Ammunition Factory of Eugi in Navarra (Spain) was performed. Both bullets presented a spherical shape with a relatively good state of preservation, belonging to the last years of the factory production (1766-1850). Several techniques such as microhardness, X-ray fluorescence (XRF), light (LM) and scanning electron microscopy (SEM), optical mission spectroscopy (OES) and energy dispersive X-ray spectroscopy (EDX) analysis were used in order to identify the manufacturing process of the two bullets. The analyses of the microstructures carried out by LM and SEM showed that one bullet was composed of white cast iron with a pearlitic matrix, steadite and graphite; while the other was composed of grey cast iron with a pearlitic matrix, graphite and a low amount of steadite. The chemical analysis of the bullets carried out by OES indicated significant differences in the amount of silicon and phosphorous. The variation in silicon content could suggest that the foundry temperature under oxidizing environment varied during the casting. The SEM and EDX analyses showed both bullets had manganese sulphide inclusions but only one of the bullets exhibited titanium and vanadium inclusions. The microhardness analyses carried out revealed Vickers hardness differences along the diameter. This variation could be explained by the differences in cooling rate along the diameter. Based on the physical characteristics of the bullets and on the obtained results, it can be concluded that one of the bullets could have been used as a grapeshot projectile and the other one as a bullet for ribauldequins. In addition, calcined ore and slag found in this factory were also analysed. The variation found in their chemical composition corroborated that the foundry temperature employed during the manufacturing process was low, the slag being enriched in Si, Al and Mn elements.

Keywords: *Archaeometallurgy; Cast iron; Ledeburite; Phosphorous; Projectiles; Steadite*

1. Introduction

1.1 Historical background

During the 16th century, Spain, as a leading world power, had to maintain its supremacy by intensifying the safety of the sea routes. Artillery played an important role in supporting the naval war and therefore, Spain carried out important investments to obtain high quality artillery pieces [1]. It was in this period, when artillery acquired importance as an effective weapon for sieges, and above all, for naval combat, gradually replacing traditional boarding [1-2]. The production of ammunition from cast iron was of strategic importance for the Spanish monarchy, but its production was scarce. In the middle of the 16th century, foundries were established for the production of iron cannonballs for the royal artillery, among other places in Ezcurra and in Eugi, Navarra (map of Spain indicating the Eugi location is shown in Fig. 1). However, as these foundries did not use blast furnaces, they were not able to meet the growing demands of the monarchy. In the 18th century, as a result of the Bourbon industrial policy, the royal state factories were created. Among them, they were the Royal factories created to improve product quality, introduce new industries, etc. One of the fields of action of Bourbon industrial policy was the military factories and it was precisely in the 18th century when the network of military factories was created. The state enhanced the manufacturing of cannons and ammunition for artillery. The Royal Bronze Foundries of Seville and Barcelona were modernized and

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expanded and the most important private companies of cannons and ammunition of cast iron were nationalized, such as that of Liérganes and Cavada (Cantabria) in 1769 and that of Eugi (Navarra) in 1766 [2-5].

Eugi is located at the north of Navarra, Spain, on the border with France (Fig. 1). Its location is close to the Pyrenees, in the Esteribar valley, close to one of the largest beech and fir forests in Europe. The Royal ammunition factory of Eugi was one of the most productive in the state, reaching a production of 1,000,000 Kg per year. The munitions produced in this factory were highly valued for their high quality and reliability. However, the operating of this factory was abruptly ended when in 1794, during the Convention War, it was attacked and burned by the French troops. There were several attempts to re-establish the factory (the last in 1850), but a few years later, it was definitively closed due to its high cost and the danger ascribed to its location, in proximity with France. The fire that the factory suffered in 1794 and its subsequent abandonment allowed the materials used in this study to be protected by a layer of coal, stones and mortar from the demolished walls. Moreover, in 1975 a leveling of the land was made, covering the bullets with soil. This leveling work allowed further protection of this area [5].

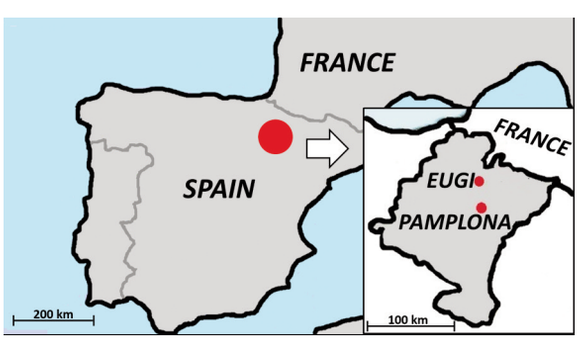

***Figure 1**. Map of Spain indicating Eugi location*

In spite of the huge advances that archaeometallurgy has experienced in recent years, there are few reports related to antique projectiles [7-15]. The majority of the analyzed projectiles belong to the 18th and 19th centuries. They are made of cast iron and present slight differences in composition and microstructures as a function of their origin and the raw materials employed in their preparation. Cvikel et al. analyzed a 12-pdr wrought iron cannonball from the Akko 1 shipwreck, Israel [9]. They analyzed the manufacturing technology employed in the fabrication of this cannonball which was dated to the first half of the 19th century. The 12-pdr cannonball was composed of relatively pure iron manufactured by the indirect smelting method and fabricated by hammering. These results were unusual due to the fact that the material usually employed to manufacture the projectiles in this century was cast iron. The same authors also reported an investigation regarding two other cannonballs (9-pdr and 24-pdr) found in the same shipwreck [10]. The 9-pdr and 24-pdr cannonballs were made of sand molding but used two different processes. Both cannonballs were made of white cast iron but in one of them, in order to compensate for the shrinkage suffered by the metal during the solidification process, grey cast iron was added. Based on the characterization results and on the manufacturing process of the cannonballs, they concluded that the projectiles were manufactured at the end of the first half of the 19th century. Kahanov et al. also analyzed a 32-pdr cannonball found in the wall of Akko [11]. This cannonball was discovered inside the wall of a mosque close to the sea. The research carried out showed that the cannonball was composed of grey cast iron. The high quality of the 32-pdr ball, which did not show any evidence of porosity or defects ascribed to the sand-casting manufacturing process, is due to the high concentration of manganese (>0.5wt% Mn). More than 0.5 wt% Mn was also detected in the 9-pdr and 24-pdr cannonballs retrieved form the Akko 1 shipwreck. The use of such manganese concentration in cast iron to avoid gas holes and porosity, indicated a post-1839 manufacturing date. Hernández et al. characterized cannonballs found in the Fortress from San Juan de Ulúa, México [12]. The analyzed specimens were composed of grey cast iron with steadite. They also characterized the corrosion layer produced by the ocean water on these samples. They concluded that the cannonballs could have been manufactured in the 18th and 19th centuries, employing cupola furnaces. They suggested the cannonballs could be manufactured in Spain, in all probability in the factories located in Sevilla or Orbaiceta, very close to the Eugi factory. Moreover, Ciarlo et al. characterized different iron projectiles from different origins: British, Spanish and French [15]. They compared a fragment of a round cannonball, three grapeshot projectiles and a canister shot within a time range from 1770 to 1813. They observed that all cannon projectiles were made of cast iron with slight differences according to the state of metallurgical technology of the time. However, they concluded that these slight variations between the projectiles seemed not to have presented any advantage for their functionality.

In order to add further more insight to the research carried out on antique projectiles from 18th and 19th century, in this work, two bullets found in an Ammunition Factory in Spain were analyzed. Both bullets were found in the factory workshop under a mass of coal and lime plaster from the walls, which protected the bullets against full corrosion. The small

size of the bullets and the information found in bibliography [5] suggests that they could have had two different uses. One could have been used as grapeshot and the other as bullets for ribauldequins. Grapeshot are the projectiles which spread out with a broad scope of action after being fired. The ribauldequins are one kind of cannon with several smooth and thin guns disposed in parallel on a platform. Each gun was loaded with one of this kind of bullets [14]. Moreover, calcined ore and slag, found close to the factory, were also analyzed. The ore were calcined to remove most of the impurities, employing better raw material in the blast furnace. The slag is the part which is separated from the molten metal during the manufacturing process. Usually, impurities and other elements are found in the slag. The comparison of the results obtained for the calcined ore and slag, with the results obtained for the bullet allow the establishing of the efficiency of the process employed in this factory.

1.2 Objectives

The main objective of this paper is to characterize two different bullets, as well as samples of calcined ore and slag coming from the Royal Ammunition Factory of Eugi in Navarra (Spain). LM, SEM and EDX will be employed to analyze the microstructures of the bullets and the inclusions and to identify their chemical composition. Its homogeneity along their diameter will be examined by analyzing the graphite content and the variation of the hardness. Finally, the chemical composition of calcined ore and slag will be identified. These results will allow us to determine the foundry efficiency. Moreover, these results will allow to establish the bullet manufacturing method employed in one of the most productive ammunition factories in Spain.

2. Experimental section

2.1 Experimental techniques

In order to analyze the metallographic structure of the bullets, the samples were prepared according to the following steps. Firstly, they were cut in half to determine their surface. Surface preparations were carried out mounting the specimens in an epoxy resin and grinding them with 180-1200 grit alumina papers, followed by polishing using 10-1 µm diamond suspensions. Secondly, the samples were vigorously cleaned with water and ethanol to remove any contamination impurities. Finally, a chemical attack was carried out by etching with Nital acid (97 mL ethyl alcohol and 3 mL nitric acid). Before etching, the graphite quantity was measured by means of a metallographic image statistical analysis program known as analySIS software.

The resultant chemical composition of the bullets was analyzed using an S-OES ARL-FISONS 2460 spectrometer and LECO CS200 carbon/sulfur elemental analyzer, respectively.

The samples were examined in a metallographic light microscope (LM) (Leica DMI5000) and a scanning electron microscope (JEOL JSM 5900LV). Different areas were analyzed to ensure good homogeneity and to determine the presence of different phases in the samples. In addition, EDX analysis was used to determine the elemental composition. Moreover, Vickers microhardness measurements of the projectiles were carried out with a load of 0.98 N (100 gF) using a Mitutoyo microhardness tester. The microhardness tests were performed to examine the homogeneity of the samples, to establish a correlation between microhardness measurements and the final microstructure. X-ray fluorescence was employed for a semi-quantitative chemical analysis of calcined ore and slag. A Thermo electron X-ray sequential fluorescence, ARL series and ADVANT´XP model, was used. Finally, in order to identify the structural microconstituents in both samples, X-ray diffraction was employed using a Rigaku powder diffractometer with Cu Kα radiation.

3. Results

3.1 Macroscopic characterization

Initially, a physical examination of the bullets was carried out. Eugi bullet 1 (E1) had a diameter of 40 mm and a weight of 379 g, whereas Eugi bullet 2 (E2) showed a dimension of 30 mm and 190 g. The dimensions and weight of the bullets have been measured with the encrustation layer. The two bullets of this work showed a spherical shape as it can be observed in Fig. 2. The metal presence in the union due to the two parts of the mold during the casting process indicated that they were made by sand molding. The circular seam suggested that both projectiles had to be mechanized to obtain good homogeneity and a smooth surface. Optical examination showed a corrosion layer in both bullets. Once the samples were cut, some imperfections could be observed in bullet E1. The inner surface displayed a porous structure and a hole was found in the central

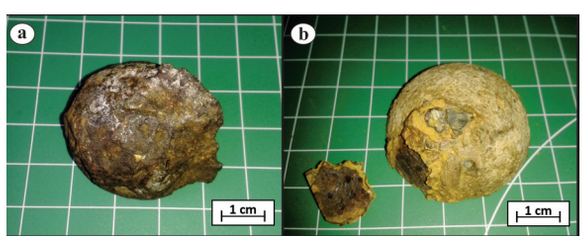

***Figure 2**. Images of E1 (a) and E2 (b) aspect without removing the corrosion layer*

part, as can be observed in Fig. 3a. In Fig. 3b, it is possible to observe these defects with a better resolution by means of LM. Several dark regions corresponding to the porous formed during the manufacturing process can be observed. The bullet showed a large hole and several small spots. On the other hand, the E2 bullet did not display any porous surface.

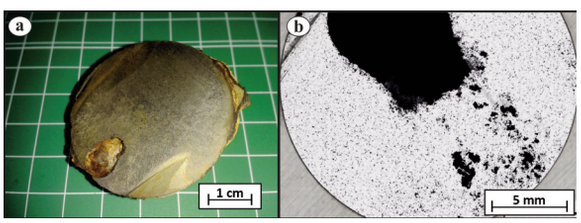

***Figure 3**. E1 bullet image showing (a) a porous surface; and (b) its magnification by using a light microscopy*

3.2 Chemical and microstructural characterization

In order to establish a relationship with the resultant microstructures, the chemical analysis of both bullets was carried out. The obtained results for the chemical composition analyzed by OES are shown in Table 1.

Table 1. Chemical composition for E1 and E2, respectively analyzed by OES

Chemical composition (wt%)										
	C	Si	Mn	P	S	V	Ti	Ni	As	Fe
E1 BULLET	3.59	-	0.18	1.53	0.03	0.08	0.01	0.01	0.02	94.54
E2 BULLET	3.53	1.63	0.58	0.11	0.66	0.06	0.01	0.01	0.02	93.38

The carbon amount was 3.59 wt% and 3.53 wt% for E1 and E2 bullets, respectively. According to these values, both bullets can be classified as hypoeutectic cast irons. Both bullets showed important differences in the content of the other chemical elements. The most significant differences between both bullets were related to the silicon and phosphorus contents. In literature, most works showed that projectiles presented a phosphorus content in the range of 0.07 – 0.7 wt% P, and silicon content from 0.53 wt% to 1.6 wt% Si [9-10,15-17], except the cannonball analyzed by M. Hernández et al. [12] which showed a higher amount of phosphorus (1.4 wt%). In this work, for E1 bullet the content in phosphorus and silicon was 0.113 wt% and 1.63 wt%, respectively. These values could indicate that this bullet is formed by grey cast iron. For E2 bullet an unusual phosphorus amount was observed, a 1.526 wt% and no silicon was detected. Other chemical elements were detected in both bullets such as Mn, Ti and V but in lower amounts.

3.3 Microstructure analysis

3.3.1 Analysis of graphite

The LM examination of E1 bullet (Fig. 4a) and E2 bullet (Fig. 4b) revealed the presence of graphite flakes which seem to form a rosette-like pattern. The final microstructure of the cast iron depends mainly on two important factors, namely the presence of graphitizer elements and the corresponding cooling rate during the solidification process [9-10]. In the case of E1, even if no silicon was observed in its composition, the phosphorous amount in E1 was high enough to induce graphite formation. The resultant graphitic structure is typical of graphite flakes, which is usually found in hypereutectic irons. However, taking into consideration the resultant carbon equivalent (CE) of E1 with a value of 4.10, this sample is considered to be hypoeutectic cast iron.

The E2 bullet showed a similar structure, but with a high content of graphite flakes, as can be observed in Fig. 4b. In this case, the graphite formation was more favorable due the presence of a high silicon level in its chemical composition (see Table 1). Silicon possesses a higher graphitization capability than phosphorous. Considering the form and distribution of the graphite, this E2 sample belongs to a B type or rosette pattern, such as E1 sample [17]. The CE value for this bullet was 4.11 and it is also considered to be hypoeutectic cast iron.

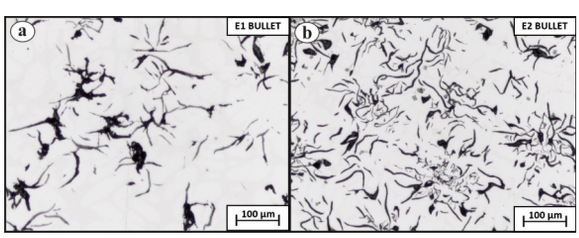

***Figure 4**. E1 (a) and E2 (b) bullets surface images showing the graphitic distribution. Magnifications 100x*

An important aspect is that the samples displayed different graphite amounts as a function of the analyzed region. More specifically, the external region of the samples showed a lower amount of graphite than in the internal part. This amount gradually is increment towards the inner region in both samples. The graphitic quantification carried out by LM in different areas of the samples (see Table 2) confirmed the observed results. This can be ascribed to the cooling rate during the solidification process of the foundry. Usually, the sand molding process induces a cooling rate gradient along the liquid metal in the mold, so the temperature was not uniform along the entire piece. This difference causes the liquid

decomposition to produce graphite or cementite. The inside of the bullet remained hotter at longer exposure times than the external surface and thus a major graphite formation was induced [18-19].

Table 2. Graphite compositions found in three different areas for E1 and E2 bullets analyzed by S-OES ARL-FISONS 2460 spectrometer and LECO CS2000 carbon/sulfur elemental analyser

Graphitic surface % per areas			
	Outside	Middle	Inside
E1 BULLET	0.8	2.5	3.9
E2 BULLET	6	7.6	7.8

3.3.2 Microstructure characterization by SEM-EDX and Light Microscopy

After samples etching, the metallographic examination revealed a white cast iron appearance with great variety of microstructures. The LM examination of E1 bullet (Fig. 5a and 5b) revealed a microstructure mainly composed of a eutectic matrix of ledeburite with cementite, thin sheets of graphite and high amount of steadite. The presence of steadite has a great influence in the final properties, making the cast iron brittle. The steadite is a ternary eutectic composed of austenite, cementite and iron phosphide (Fe_3P) with at least 10 wt% of phosphorous. Eutectic grains surrounded by a cellular phosphide network have been observed in previous works [12, 20-21].of different phases in the sinters. That means that only the proportion of the phases in the samples changed. Pseudowollastonite is an exception but, as mentioned earlier, it did not create any diffraction peak in the sample A.

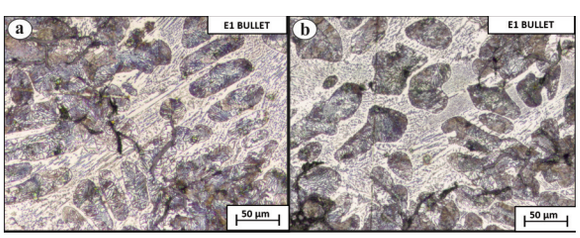

***Figure 5**. LM images of E1 bullet in two different zones (a, b) after etching with 50x magnification*

SEM and EDX techniques were used in order to identify the chemical nature of the matrix and inclusions (Fig. 6). For E1 bullet, the EDX spectrum of matrix (Fig. 6b) reveals the presence of Fe, Mn and P. Moreover, SEM micrograph (Fig. 6a) confirmed that the matrix was composed of ledeburite phase with a high content of iron phosphide. This specific result showed the presence of steadite in the E1 sample. In addition, the EDX analysis of several polygonal inclusions showed the presence of Mn, P, S and Fe elements (Fig. 6c). The analyzed area was bigger than inclusion size and in consequence iron and phosphorous were also detected. Taking into consideration these results, it is most likely that the precipitates were composed of manganese and sulphur. In cast irons, these elements can usually be combined as manganese suphide particles [22-24]. However, neither titanium nor vanadium containing particles have been found in the surface analysis.

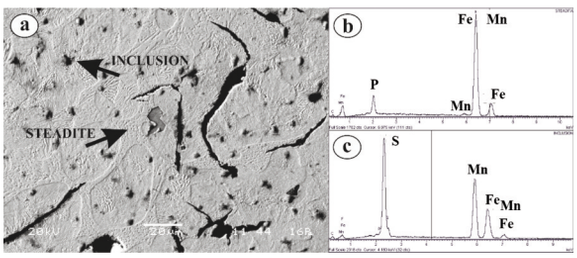

***Figure 6**. SEM micrograph (a) and EDX spectrum of matrix (b) and inclusion (c) in E1 bullet*

Metallographic images of E2 bullet show a different structure. The LM images revealed grey cast iron with a microstructure composed of pearlite matrix with several white areas of steadite and graphite sheets inclusions (Fig. 7a and 7b). E2 bullet shows higher content of pearlite and graphite phases than E1 bullet but a lower steadite amount. In these micrographies, it is possible to observe that the pearlite phases are surrounded by steadite because this phase is solidified after the matrix during the cooling process.

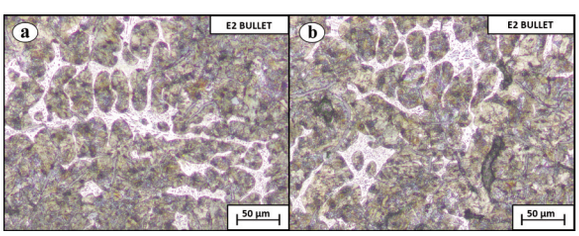

***Figure** 7. LM images of E2 bullet in two different zones (a, b) after etching with 50x magnification*

The E2 bullet surface was also analyzed by SEM and EDX in order to identify the corresponding inclusions and the white areas, as can be appreciated in Fig. 8a. The analysis of the spherical inclusions showed elements of manganese and sulphur (Figs. 8 b) and c)), indicating that these inclusions can be formed by MnS particles. The white areas showed a significant amount of phosphorous, being indicative of the presence of steadite as also occurred with the E1 bullet.

The E2 bullet showed other types of inclusions with a different geometry to the inclusions in E1(Fig. 9a). These inclusions were found in the outer surface of the sample. According to the EDX spectrum shown in Fig. 9b, these inclusions were composed of

titanium and vanadium. These elements can combine with nitrogen forming particles of carbonitride titanium or carbonitride vanadium [13, 25-26].

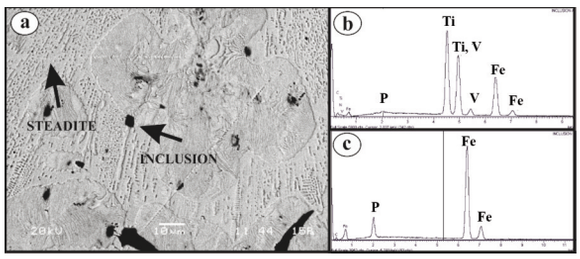

***Figure 8**. SEM micrograph (a) and EDX spectrum of matrix (b) and inclusion (c) for the E2 bullet*

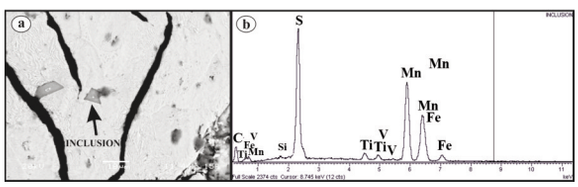

***Figure 9**. New inclusions with a characteristic geometric shape in E2 bullet analyzed by SEM micrograph and EDX spectrum*

The analyzed microstructures of the bullet play a crucial importance in the efficiency of the projectiles. The cast irons with a pearlitic or ferritic-pearlitic matrix with a graphite phase (mostly grey cast iron) make possible an improvement in the toughness of the bullets, avoiding brittle failures at the time of the final explosion. However, the bullets with a ledeburitic matrix and cementite (mostly white cast iron) were simultaneously hard and brittle. The choice of the type of cast iron strongly depends on their final utilization. Consequently, considering the E1 microstructure, probably this bullet could be used as a grapeshot projectile. On the other hand, the E2 bullet showed a pearlitic matrix with a lower amount of steadite. This bullet will be tough and its utility could be as a projectile for ribauldequins.

3.4 Microhardness measurements

The microhardness tests were carried out in both samples in order to analyze their homogeneity along the diameter by means of micro-Vickers measurements. The tests were performed, beginning from the external regions towards the internal ones. Three measurements were performed in each region. The resultant microhardness values are listed in Table 3 as a function of different positions.

Table 3. Vickers microhardness measurements (100 gF) at different positions in depth

	Hardness values (HV)	
	Internal regions	External regions
E1 BULLET	529 ± 23	498 ± 10
E2 BULLET	370 ± 18	330 ± 15

The obtained values are in strong concordance with the resultant microstructure since the E1 bullet had a higher hardness value of around 500 HV. In the literature, it can be observed that the average hardness of this phosphide eutectic was around 482 HV and the pearlite 252 HV [12]. Therefore, the E1 bullet hardness values can be associated with a cast iron with high steadite content. The hardness values corresponding to the E2 bullet were lower than for the E1 bullet. The E2 bullet exhibited a microstructure composed of a pearlitic matrix with steadite and graphite. The obtained values, around 350 HV, were the consequence of the hardening effect of steadite and graphite in pearlite matrix.

On the other hand, both bullets showed different hardness values depending on the measured regions, as was expected. In both bullets, the external regions were harder than the internal ones. These results could suggest that the different regions of bullets had different cooling rates.

3.5 Calcined ores and slag

XRD analyses were carried out in order to identify the compositions of calcined ores and slag. It is worth mentioning that it is not clear to which bullet correspond exactly the calcined ores and the slag. The chemical variations between the calcined ore and slag could explain the precedence of the elements found in the bullets.

Fig. 10 shows the diffractogram and percentage of components in the calcined ore. As was expected, the results showed that the calcined ore was mainly composed of magnetite (Fe_3O_4), hematite (Fe_2O_3) and cristobalite (SiO_2). The main objective of calcinating the ore was to purify the ore in ferrous components and to remove the impurities as much as possible. According to these results, it was observed that the obtained product was rich in ferritic and silicon oxides.

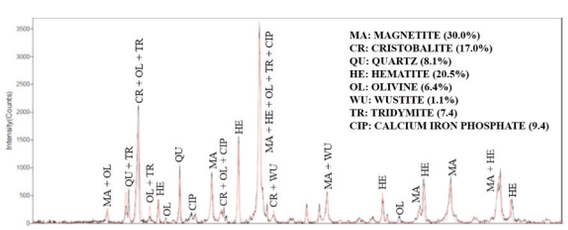

***Figure 10.** The diffractogram and percentage of components in the calcined ore*

The XRD results of the calcined ore, collected in Table 4, revealed the presence of a high amount of iron and silicon. In addition, different elements such as P, Mn, K, V and S were found. In the chemical analysis of bullets those elements were also found. Therefore, the calcined ore could be the origin of these elements in bullets. The XRD diffractogram of the slag is shown in Fig. 11.

Table 4. The atomic composition of calcined ore obtained by XRD

Chemical composition (wt%)										
Fe	Si	Al	P	Ca	Mg	Mn	Ti	K	V	S
34.2	16.2	3.9	1.6	2.2	0.7	0.4	0.1	0.1	0.1	0.02

Table 5. Chemical composition of the analyzed slag (SEM-EDS)

Chemical composition (wt%)									
Fe	Si	Al	P	Ca	Mg	Mn	Ti	K	S
3.4	18.6	11.8	0.1	19.5	1.3	0.6	0.3	0.1	0.2

The analysis showed that the slag had a ceramic nature. It was mainly composed of aluminosilicates and quartz. There was not any evidence of ferritic compounds. Table 5 shows the chemical composition of the slag.

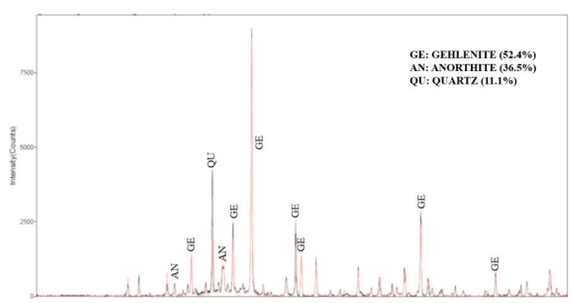

***Figure 11**. The diffractogram and percentage of components in the slag*

These results indicate that the slag was mainly composed by calcium, aluminum and silicon, and that it was low in iron. This is indicative that the process for obtaining cast iron in blast furnaces had a high level of efficiency. The high amount of phosphorous presented in the calcined mineral and its absence in the slag could indicate that most of P was not removed in the casting process and that it was kept in the cast iron. Regarding the other elements such as Si, Al or Mn, it can be observed that their amounts were higher in the slag than in the calcined ore. The presence of those elements could indicate that the casting temperature was low. These elements would be oxidized at low temperature, being transferred to the slag. Therefore, the melting metal would contain low amounts of those elements.

4. Discussion

In this work, two different bullets, as well as samples of calcined ore and slag coming from the Royal Ammunition Factory of Eugi in Navarra (Spain) have been analyzed. From the physical examination of the bullets, it can be concluded that the E1 bullet was not significantly affected by the surrounding environment during its lifetime, showing a slight superficial corrosion layer, while the E2 bullet showed a uniform thicker corrosion layer. Despite these layers, both bullets remained spherical in shape. Their relatively good state of preservation could be due to the fact that they were covered by several materials which acted as a protective layer. A deeper examination of the bullets showed in the E1 bullet the presence of porosity, a significant defect in cast iron products that is generated in the cooling stage. This porous surface could be produced by several factors such as an excessive carbon content, gas generation or absorption during the elaboration process, an inappropriate metal degasification or a defective mold construction. These kinds of problems are of great importance in small caliber bullets because their corresponding cooling rates during their manufacturing is relatively fast [10-11, 27].

The EDX analysis revealed differences in chemical composition between these two bullets concerning mainly C, Si, Mn, P, S, V and Ti contents. This result could be ascribed to the employment of different kinds of minerals and flux during foundry process. A typical modern grey cast iron normally contains 1-3 wt% silicon and 0.002-1.0 wt% phosphorous [28]. This is the case of the E2 bullet, that which displayed the usual silicon and phosphorous amount. Surprisingly, the E1 bullet showed the absence of silicon and the phosphorous amount was higher than usual. Silicon and phosphorous play a key role in the final microstructure of the samples and, therefore, in the final properties of the bullets. The differences observed in silicon content between the two bullets could indicate that they were obtained in different casting conditions. When the blast furnace is ignited under oxidizing environment, the temperature is not optima. Under these conditions the silicon is usually oxidized, being trapped on the slag, and consequently the silicon amount in cast iron would be low [28]. The E1 bullet could have been manufactured under these conditions. However, the E2 bullet showed a significant silicon amount (1.63 wt%), suggesting that the temperature of the blast furnaces was higher than for the obtaining of the E1 bullet. Therefore, both bullets could have been obtained during different phases of the casting. The low temperature of the blast furnace could also explain the chemical composition of the calcined ore and slag. The differences in Si, Mn and Al contents between calcined ore and slag suggest that these elements were oxidized during the casting process. To sum up, the EDX analysis of the bullets, the calcined ore and the slag, could indicate that the bullets did not belong to the same phase of the casting or that they were manufactured employing different

kinds of raw materials.

The LM, SEM and EDX analysis revealed that the E1 bullet is formed by white cast iron with graphite flakes. Although this bullet lacks silicon, the graphite formation could be explained by the high amount of phosphorous observed in the chemical analysis. The graphitizer power of phosphorous is lower than for silicon, but the high amount of this chemical element could induce the formation of graphite [29].

The E2 bullet is formed by grey cast iron with a microstructure composed of pearlite matrix with several white areas of steadite and graphite sheets inclusions. According to the quantification carried out by EDX, the E2 bullet presented a considerable Si amount, inducing higher graphitization. Several inclusions containing manganese and sulphur were detected in both bullets. In addition, the E2 bullets showed vanadium and titanium particles. These kinds of inclusions are characteristics of cast iron [12-13, 16].

In addition, in both bullets the external region of the samples showed a lower amount of graphite than the inner part. This can be ascribed to the cooling rate during the solidification process of the foundry. The differences in the cooling rates of liquid metal significantly affects the liquid decomposition, producing graphite or cementite during the solidification process. The slow cooling rate induces the graphite formation. Usually, the sand molding process induces a cooling rate gradient along the liquid metal in the mold, so the temperature was not uniform along the entire piece. This difference affects the liquid decomposition, producing graphite or cementite. Therefore, as the inside of the bullets remained hotter than the external surface, a major graphite formation was induced [10-11].

The results obtained in the metallographic analysis were confirmed by microhardness tests. The E1 bullet showed a Vickers hardness value of 529 ± 23 HV and 498 ± 10 HV in internal and external regions, respectively. The pearlite and steadite have an average hardness of 252 and 482 HV, respectively. Therefore, the obtained hardness value for the E1 bullet allows one to think that the steadite content in pearlitic matrix was high. Considering that the microstructure of the bullet was composed of a ledeburitic matrix with cementite, graphite and a high steadite content, the obtained value suggested the steadite had a strong hardening effect in this cast iron. The E2 bullet exhibited a lower hardness value, 370 ± 18 HV and 330 ± 15 HV in internal and external regions, respectively. The bullet was composed of pearlitic matrix with graphite and lower amount of steadite. Despite having a lower amount of steadite than the E1 bullet, the steadite amount was enough to contribute to the hardness value.

5. Conclusions

The analyzed two bullets were manufactured by sand casting molds employing cast iron. The E1 bullet showed a pearlitic matrix with steadite and graphite, while the E2 bullet exhibited a pearlitic matrix with graphite and a lower amount of steadite. In both cases, it was observed that the amount of graphite was higher in the external regions than in the internal ones indicating that the cooling rate of the bullets during the manufacturing process was not uniform along the diameter. The obtained chemical composition and the microstructures suggested that they were obtained during different phases of the casting or employing different ores. The differences in silicon and phosphorous content in the two bullets could indicate that the operating conditions during the casting were not the same for the two bullets. This behavior was also found in the chemical composition analysis of calcined ore and slag. The Al, Mn and Si amount in slag was higher than in the calcined ore, suggesting that those elements were oxidized during the casting process.

According to the physical characteristics of the bullets as well as the microstructure, composition and hardness, it could be suggested that the final utility of both bullets would be different. One of the bullets could have been used as grapeshot and the other one as bullets for ribauldequins.

References

[1] J. Torrejón, Rev. de Cult. Mil. 10 (1997) 291-324.

[2] J. Setién, J.A. Díez-Aja, Rev. Metal. 44(4) (2008) 299-309.

[3] J. Alcalá-Zamora, Q. De Llano, Historia de una empresa siderúrgica española: Los Altos Hornos de Liérganes y La Cavada, 1622-1834. Centro de Estudios Montañeses. Santander (1974) 49-55.

[4] I.M Carrión, Gunpowder, explosives and the state. A technological history. Ed. by Brenda J. Buchanan, Aldershot (United Kingdom), Ashgate, (2006) 266-280.

[5] A. Rabanal. Colección Marte. Madrid: Servicio de publicaciones del estado mayor del ejército (1990) 30-33.

[6] R.F. Tylecote, A history of metallurgy. 2nd ed. London: Institute of Materials, (1992) Chaps. 8-9.

[7] J. Wadsworth, Mat. Charact. 99 (2015) 1-7.

[8] D. Bourgarit, N. Thomas, J. Archaeol. Sci. 39 (2012) 3052-3070.

[9] D. Cvikel, D. Ashkenazi, A. Stern, Y. Kahanov, Mat. Charact. 83 (2013) 198-211.

[10] D. Cvikel, E.D. Mentovich, D. Ashkenazi, Y. Kahanov, J. Min. Metall. Sect. B-Metall. 49 (1) B (2013) 107-119.

[11] Y. Kahanov, E. Stern, A. Stern, R. Ronen, D. Cvikel, D. Ashkenazi, Hist. Metall. 46(2) (2012) 98-110.

[12] M. Hernández, M. Hernandez-Escampa, C. Abreu, J. Uruchurtu, M. Bethencourt, Archaeometry DOI: 10.1111/arcm.12194.

[13] N.C. Ciarlo, A.N. López, H.M De Rosa, M. Pianetti, Procedia Mater. Sci. 8 (2015) 712-721.

[14] I. Sagredom El castillo de Amaiur a través de la historia de Navarra, Pamiela (2009) 48-49.

[15] C. Berlanga, J.M. Erro, J.F. Carrasquilla, An. Ing. Mec. 14 (2003) 778-783.

[16] M. Bethercourt, M.A. Hernández, E.A. Martínez, C.M. Abreu, Apuntes sobre la evolución histórica de la metalurgia armamentística española, IV Congreso Latinoamericano de Conservación y Restauración de Metal (2011).

[17] International Organization for Standardization, ISO 945-1-2008.

[18] H.R. Abbasi, M. Bazdar, A. Halvaee, Mater. Sci. Eng. A 444 (2007) 314-317.

[19] L. Collini, G. Nicoletto, R. Konecna, Mater. Sci. Eng. A 488 (2008) 529-539.

[20] O. Oloyede, T.D. Bigg, R.F. Cochrane, A.M. Mullis, Mater. Sci. Eng. A 654 (2016) 143–150.

[21] I. Minkoff, The physical metallurgy of cast iron, Wiley, Chichester (1983).

[22] C. Thomas, R. Hunter, R. Gordon, J. Archaeol. Sci. 39 (2012) 2714-2721.

[23] A.A. Pereira, L. Boehs, W.L. Guesser, J. Mater. Process. Technol. 179 (2006) 165-171.

[24] O. Asi, Eng. Fail. Anal. 13 (2006) 1260–1267.

[25]L.E. Samuel, Australia´s Contribution to Archaeometallurgy. Mater. Charact. 29 (1992) 69-109.

[26] M. Medina, H. López. Caracterización microestructural de piezas de fundición de hierro de un navío mercante español del siglo XVIII, 12º Congreso Binacional de Metalurgia y Materiales CONMET/SAM. Valparaíso, Chile (2012).

[27] H. Fredriksson, J. Stjerndahl, J. Tinoco, Mater. Sci. Eng. A 413-414 (2005) 363-372.

[28] B. He, G. Xu, M. Zhou, Q. Yuan. Metals 6 (137) (2016) 1-9.

[29] J.M. Radzikowska, Metallography and Microstructures of Cast Iron, ASM International (2004) 565-566.

KARAKTERIZACIJA DVA GVOZDENA METKA IZ KRALJEVSKE FABRIKE MUNICIJE U EUGIU (ŠPANIJA)

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Apstrakt

U ovom radu je predstavljena komparativna analiza dva gvozdena metka iz Kraljevske fabrike municije iz Eugia u pokrajini Navara u Španiji. Oba metka su sferičnog oblika, relativno dobro očuvana, napravljena tokom poslednjih godina proizvodnje u fabrici (1766-1850.). Da bi se utvrdio proces proizvodnje u izradi ova dva metka korišćeno je nekoliko različitih metoda ispitivanja, kao što su merenje mikrotvrdoće, rendgenska fluorescencija (XRF), optički mikroskop (LM), skenirajući elektronski mikroskop (SEM), optička emisiona spektroskopija (OES) i energijski razlučujuća/disperzivna rendgenska spektrometrija (EDX). Analiza mikrostrukture, koja je izvršena optičkim i skenirajućim elektronskim mikroskopom, pokazala je da se jedan metak sastoji od belog livenog gvožđa sa matricom u kojoj se nalazi perlit, stedit i grafit, dok se drugi metak sastoji od sivog livenog gvožđa sa matricom koja sadrži perlit, grafit i malu količinu stedita. Hemijska analiza, (OES), pokazala je da postoje značajne razlike u prisutnim količinama silicijuma i fosfora. Razlika u količini silicijuma se može objasniti promenom temperature livenja pod oksidacionom atmosferom tokom procesa livenja. SEM i EDX analize su pokazale prisustvo mangan sulfida, ali je u samo jednom metku utvrđeno i prisustvo titanijuma i vanadijuma. Analiza mikrotvrdoće je otkrila razlike u tvrdoći po Vikersu duž prečnika. Ove razlike se mogu objasniti različitom brzinom hlađenja duž prečnika. Na osnovu fizičkih osobina metaka i dobijenih rezultata, može se doći do zaključka da je jedan metak korišćen kao topovski projektil, a drugi kao metak za srednjevekovni mitraljez (poznat i kao paklena mašina). Pored toga, analizirana je i kalcifikovana ruda i šljaka koja je tu pronađena. Razlike otkrivene u hemijskom sastvavu potvrđuju da je temperatura livenja tokom procesa proizvodnje bila niska budući da šljaka sadrži Si, Al i Mn.

Ključne reči: *Arheometalurgija, Liveno gvožđe, Ledeburit, Fosfor, Projektili, Stedit.*