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Art Casting in Portuguese 19th Century Industrial Foundries: A Multi-Analytical Study of an Emblematic Copper-Based Alloy Monument

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Abstract: The outdoor sculpture of the first Portuguese king, D. Afonso Henriques (c. 1109–1185 AD), placed in Guimarães (North Portugal), is one of the most emblematic national sculptures. Created in 1887 by António Soares dos Reis, it possesses a remarkable symbolic value in the presumed birthplace of the king. In addition to the artistic and heritage importance of the monument, it is one of the few sculptures cast by a Portuguese industrial foundry in the 19th century. This study obtained data on the sculpture's elemental composition and corrosion products, gathering important historical and technical information. For this purpose, a multi-analytical approach consisting of X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM-EDS) was carried out to characterise the bulk metal and corrosion layers. The data revealed a ternary alloy of Cu, Sn and Zn, with Pb, Fe, As, Bi and Mn as minor elements. The alloy matches that of other sculptures cast in that period. In terms of corrosion, it is characterised by the presence of oxides. These results represent the first step for applying an appropriate conservation strategy for bronze sculptures with similar characteristics.

Keywords: 19th century metal sculpture; art foundries; elemental characterisation; corrosion; outdoor sculpture; Afonso Henriques

1. Introduction

Outdoor metal sculptures in the 19th century were typically cast in iron or copper-based alloys, such as bronze. They were cast primarily at military and industrial foundries, but the specificity of these types of castings led, throughout time, to the appearance of foundries specialised in sculpture.

Following the tradition of metal casting in the Italian Renaissance [1], art foundries experienced a great development during the 19th century, especially France [2–4], that soon became the European centre of the art foundry industry since the 19th to the early 20th century [2,3].

As for Portugal, the first monument cast was the statue of King José I (1775), which was produced in Lisbon in a military foundry [5]. This monument, 14 m high, was the first large-scale piece of art to be cast in the country, thus constituting the beginning of the art foundry industry in Portugal.

Despite the large number of industrial foundries working in Portugal in the mid and late 19th century, artistic ones were non-existent, and the casting of pieces of art was delegated to either military foundries or industrial metalwork companies. The first Portuguese art foundry companies were only created later, in the late 19th century. In Porto, for example, the first exclusively art foundry was in the Malmerendas Street, having been established exclusively for the casting of the King Pedro V's sculpture (1863–1866).

Two decades after this first experience, the monument of King D. Afonso Henriques was the second sculpture cast in Porto. This bronze sculpture was produced in 1887 by a local industrial foundry, known as Massarelos. Created in 1852, this company had over 400 employees in 1881, being one of the largest and most important industrial foundries of the 19th century, particularly known for producing large-scale structures and decorative cast iron [6].

The history of sculpture casting in Portugal remains to be explored. Despite the significant amount of metal statuary, there are only a few limited studies on the history of industrial foundries, but not on art foundries [7,8]. Unfortunately, regarding this topic, historical archives have not survived to the present day. These were lost for unknown reasons, and information about production processes, materials, alloys and patinas recipes are virtually unknown.

In order to fill these gaps, this paper adopts a multi-analytical approach based on in situ and laboratorial techniques: X-ray fluorescence (XRF) was used for the chemical characterisation of the bulk metal, X-ray diffraction (XRD) was performed for the identification of the corrosion products and optical (OM) and electron microscopy (SEM-EDS) were employed for the observation and characterisation of the microstructure of the alloy and corrosion layer.

Apart from the study of the corrosion of the 1775 equestrian statue of King José I [9,10], this paper highlights, for the first time, the results of a comprehensive and multi-analytical study intended to characterise the bulk metal and corrosion of the Afonso Henriques's sculpture, located in Guimarães (North of Portugal). This work is part of a larger project that aims to study a group of 19th and 20th century metal sculptures, with the final purpose to implement appropriate conservation strategies. The importance of studying the D. Afonso Henriques' sculpture is mainly determined by two different factors: (a) the symbolic and heritage national relevance of this sculpture, and (b) the effects of weather on the sculpture conservation, atmospheric pollution and repeated vandalism acts, thus making it urgent to acquire knowledge about the elemental composition of the sculpture, and the main corrosion products present on its surface. The data will allow the creation of appropriate conservation strategies that can be applied to art pieces of similar characteristics.

2. Materials and Methods

2.1. The D. Afonso Henriques' Outdoor Sculpture

The monument dedicated to D. Afonso Henriques has an important heritage value for the city of Guimarães, where it is considered a local symbol. The historical importance of the monument equally extends to the whole nation, where it is the best known and most recognisable sculpture of the first king of Portugal. The symbolism of this sculpture is so distinguished that life-size reproductions were made and are currently on display in Lisbon and Rio de Janeiro.

The idea of honouring the first Portuguese king, D. Afonso Henriques, by erecting a memorial came about in 1882. A local committee was set up to raise the necessary funds by public subscription and was later joined by a committee based in Rio de Janeiro, Brazil. The support of Portuguese and Brazilian citizens turned this donation-based project into an international cause.

In 1884, the monument, consisting of a sculpture and a marble base, was commissioned to sculptor António Soares dos Reis (1847–1889) and architect José António Gaspar (1842–1909), respectively. Soares dos Reis is considered one of the leading Portuguese sculptors of the 19th century. Due to personal circumstances, only two sculptures by the artist were cast during his lifetime, of which this is one.

In 1887, the sculpture was cast in the Massarelos Foundry with bronze donated by the Portuguese government and inaugurated in the same year. The sculpture, that is 2.65 m high (Figure 1), was produced by the sand-casting technique. This casting was a great technical challenge at the time, as it has a shield attached to the hand and separated from the body, and a detachable sword. Over time, the sculpture has suffered several acts of vandalism that have affected its integrity. The piece most affected by these acts is the sword, which has been broken and restored on more than one occasion.

Figure 1. Frontal view of the monument to King Afonso Henriques.

The sculpture was built up by joining different sections produced by sand-casting. Following the casting, these sections were probably screwed together on the inside to constitute the sculpture (Figure 2). This technique does not require welding. For this typical technique, the exterior is left with slight indentations, which are later smoothed by hammering. This process allows to connect the several sections and provides the surface with a homogeneous appearance. Nevertheless, some areas of the sculpture do present signs of being welded, presumably due to the extraction or deterioration of parts during the removal of the sculpture in 1940, when it was placed in its current location.

Since its production, in the late 19th century, the sculpture has been constantly exposed in an outdoor environment, in the historical centre of Guimarães. This is a small town in the northwest of the Iberian Peninsula, located in a valley surrounded by low hills, at about 40 km as the crow flies from the Atlantic coast. Guimarães lies in a temperate climatic zone characterised by an average annual temperature of 15 °C (minimum average 10 °C, maximum average 20 °C) (data refer to the period between 1971 and 2000), with an average monthly precipitation of 300 mm [11]. Even though located within a highly anthropised region (North of Portugal), Guimarães is scarcely populated, the traffic volume is relatively low and there are no heavy industries in the surrounding areas, due to which the atmospheric pollution may be considered generally low.

Figure 2. Detail of the sculpture showing the separation lines (identified by arrows) between the different sections.

2.2. Experimental

Since the main objective of this study was to gather data concerning the metal bulk, its elemental composition, and corrosion products, a multi-analytical strategy was devised. For this purpose, different techniques were used, namely in-situ X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS).

2.2.1. XRF

In situ XRF analyses were performed using a Bruker Tracer III-SD handheld spectrometer equipped with an Rh anode tube and a Silicon Drift Detector (SDD). The operating conditions were set up at 40 kV, 3 µA current, with an Al/Ti filter (304.8 µm Al/25.4 µm Ti), and 60 s acquisition.

Five points were analysed in total. The instrument was positioned by hand in front of the sculpture, using benchtop configuration for the analysis procedure. The equipment was placed in direct contact with the sculpture surface, minimising any atmospheric interference. To evaluate the consistency of the bulk composition, XRF analyses were performed on different sections of the back of the sculpture (Figure 3).

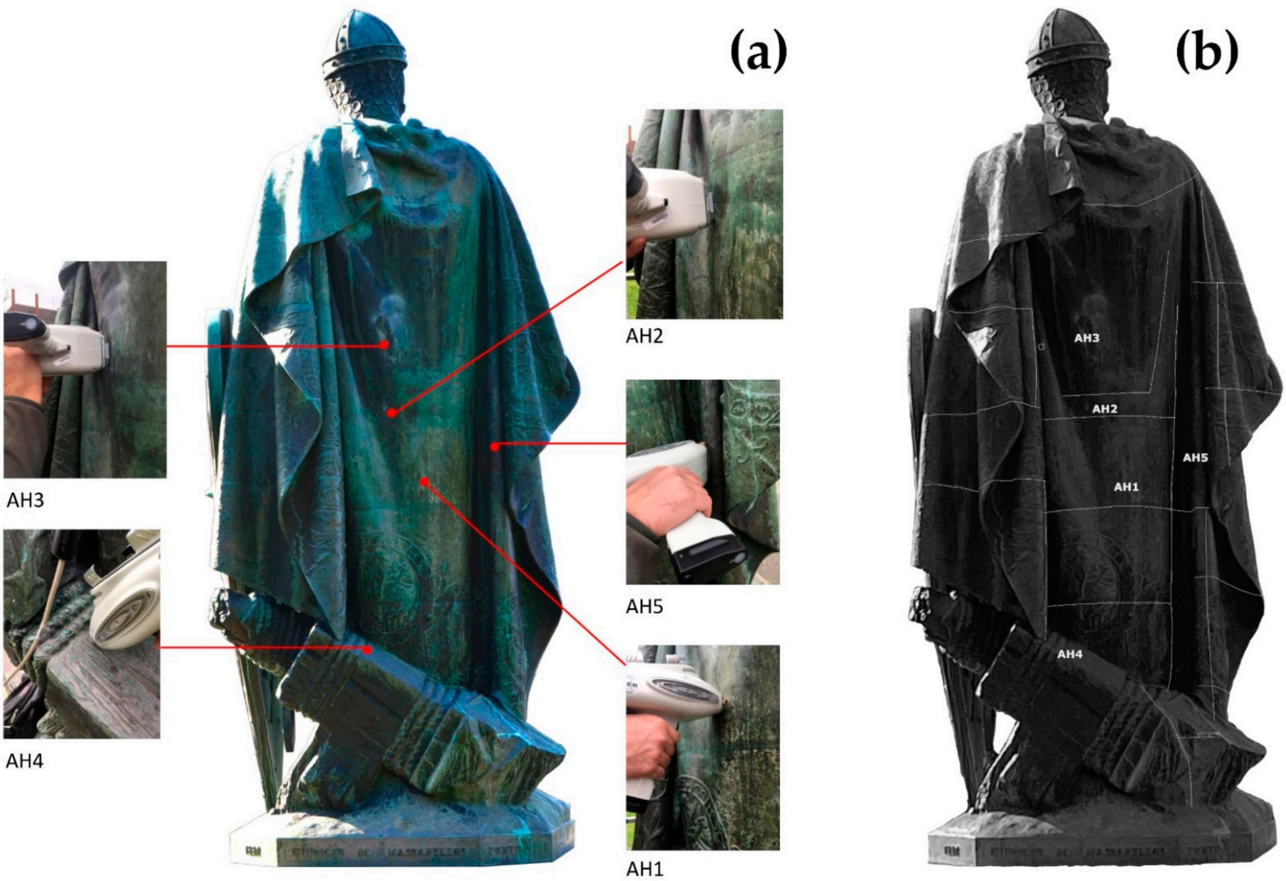

Figure 3. Areas analysed by hand-held XRF (**a**). Each analysis has been performed on a different section of the back of the sculpture. Here, all the joining areas between the sculpture's sections are also visible (**b**).

The XRF analyses were performed without any previous removal of the corrosion layers covering the sculpture. Accordingly, in order to obtain the composition of the bulk metal underlying the corrosion layers, data were processed through a Monte Carlo (MC) simulation algorithm, named X-ray Monte Carlo (XRMC) [12]. The XRF/MC protocol is a well-established non-destructive methodology that combines XRF for the spectrum acquisition and XRMC for data processing. The protocol has proven to be fully reliable for the characterisation of both the structure and the elemental composition of each layer from a multi-layered artefact, such as archaeological and historical metals [13–15], becoming a very powerful tool for determining the elemental composition of a metal object when the removal of the external corrosion layers is not permitted.

To obtain reliable data on the alloy of the sculpture analysed in this paper, the sample was modelled as being composed by two layers, i.e., the patina/corrosion layer and the bulk. After an initial estimation of the type of corrosion and composition of the alloy, a first simulation was run. The X-ray spectrum obtained following this simulation was compared to the measured one. If the simulated and experimental spectra showed noticeable differences, the procedure was further replicated modifying parameters such as the composition and the thickness of each layer, until a match between the two spectra was obtained. The model able to generate the reproduction of the experimental spectrum as perfectly as possible was considered as the real structure of the sample [16–19].

2.2.2. Microscopy

The possibility to obtain a sample from a casting defect area in the front of the sculpture allowed for performing scanning electron and optical microscopy. The location of the sample is shown in Figure 4, point E2.

Figure 4. Sample collection on the sculpture of D. Afonso Henriques, corresponding to distinctive areas with varying patina types that were analysed by XRD.

Scanning electron microscopy was carried out using a HITACHI S3700N interfaced with a Quanta EDS microanalysis system equipped with a Bruker AXS Flash silicon drift detector (129 eV spectral resolution at FWHM/Mn Kα). The following operating conditions were set up: secondary electron mode (SE), accelerating voltage of 20 kV, working distance of ~10 mm and emission current of 90 µm.

Optical microscopy was performed with a Leica DM2500P, equipped with a digital camera Leica MC170HD, coupled to a computer with the LAS V 4.4.0 software. The structure of the metal was revealed after the sample was mounted in the epoxy resin, and properly grounded, polished and etched with $FeCl_3$ and HCl in a solution of ethanol, following the methodology described by Scott [20].

2.2.3. XRD

The corrosion products were characterised with a µ-XRD BRUKER D8 Discover System with the DAVINCI design with a Cu Kα source operating at 40 kV and 40 mA, and a LINXEYE™ one-dimensional detector was used. The sample scraped from the oxidised corrosion patina of 16 points of the sculpture was deposited onto a flat zero-background sample holder and irradiated through a 0.6 mm slit. The micro-beam was achieved using a Göbel mirror and a 1 mm collimator. The angular range (2θ) was scanned from 3° to 70° at a step size of 0.02°, with a counting time of 3 s/step. Evaluation of X-ray diffractograms was performed by using the routines of the Diffrac. EVA software package and the PDF-2 database files. These sampled areas were selected according to the distinct surface colours, which indicate the likely variability in terms of corrosion compounds. The sampled areas are shown in Figure 4.

3. Results and Discussion

3.1. Metal Alloy

Data on the elemental composition and patina thickness are reported in Table 1. Regarding the latter, it is an estimation based on both the background shape and the relative attenuation of the fluorescence peak [18,19]. As for the alloy used to produce the D. Afonso Henriques' sculpture, it corresponds to a ternary alloy (Cu + Sn + Zn), in which Cu was alloyed with Sn and Zn. In addition to major elements, Pb, As and Bi also occur as impurities, although they are not able to significantly affect the mechanical properties of the alloy.

Table 1. Results of elemental composition (wt.%). N.D.: not detected.

Area	Cu	Sn	Zn	Pb	As	Bi	Patina Thickness (µm)
AH1	67.5	17.5	12.2	1.0	1.3	0.5	120
AH2	84.1	10.9	3.0	1.0	0.9	0.1	60
AH3	90.75	6.3	2.0	0.6	0.3	0.05	60
AH4	75.3	13.5	6.6	2.1	2.4	0.1	130
AH5	89.9	7.9	0.7	1.2	0.3	N.D.	80

According to the data, Cu ranges from 67.5 to 90.75 wt.%. Although copper content in sculptural bronze is generally higher than 80%, some recipes claim that its concentration may vary between 60% and 90% [21–26], as also confirmed by the results of analyses carried out on sculptures cast in the 19th and early 20th centuries [2,25–31].

As for Sn and Zn, both show a great variability, ranging respectively from 6.3 to 17.5 wt.%, and 0.7 to 12.2 wt.%. In each of the points, Sn shows a higher concentration than Zn. Regarding Zn, based on the analyses of a large group of 20th century bronze sculptures from Parisian foundries, it has been recently speculated that its concentration in the final alloy could likely depend on the casting process technique. In fact, it has been reported that the sand-casting technique would lead to Zn values lower than 5%, while lost-wax casting would allow for attaining higher Zn levels [2]. Even though the reasons for that are still unknown (i.e., tradition vs. practical casting limitations), the variability of Zn (and to a different extent of Sn as well) in the Afonso Henriques' sculpture could be related to two possible hypotheses.

On one hand, the variability of the main elements could be related to the technique employed to produce this sculpture. In fact, the sand-casting technique has been commonly used for large sculptures since it allows to produce the different sections of the sculpture separately, to be later attached. This means that the Afonso Henriques's sculpture might have been cast on different days, thus explaining the variability in terms of its composition. This variation in the composition of the bronze in diverse areas is not unusual in large outdoor sculptures [25,26].

On the other hand, however, bearing in mind that the Massarelos Industrial foundry was specialised in casting iron, the lack of experience in producing copper-based alloy sculptures also cannot be discarded. Therefore, the variability of Zn and Sn could be explained as an indicator of the little control over the production process by the workers of the foundry.

Figure 5 shows experimental and MC-simulated spectra of the point H1. MC detected a film of organic coating likely due to a protective agent. As shown in Figure 5, in the upper layer, barium was also identified. The presence of Ba, along with Fe, on the surface may be related to the chemical composition of the mixture used in the patination of the sculpture, as the original artificial patina is dark brown [32,33]. Iron, in particular, has been detected both in the corrosion layer and in the bulk, where it appears to not be distributed in high concentrations (<0.1%).

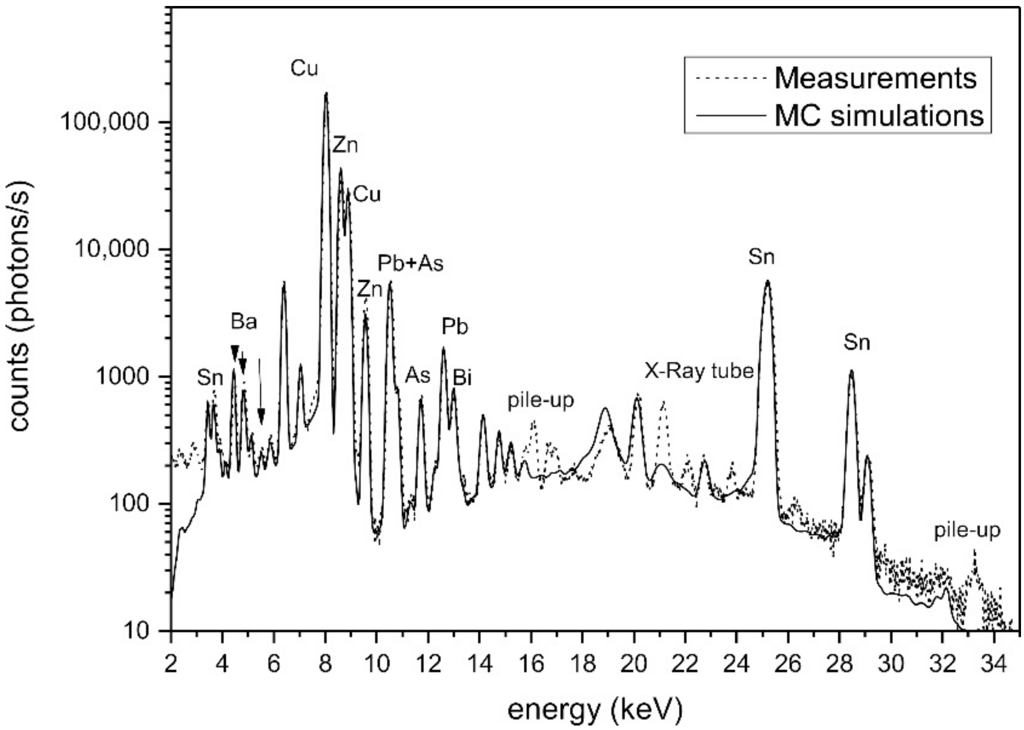

Figure 5. Analysis of the area H1, with an optimised Monte Carlo XRF spectra. Several peaks have not fitted because they do not correspond to any real chemical element, but they are the effect of the so-called pile-up phenomenon.

In comparative terms, the kind of alloy used to produce the Afonso Henriques' sculpture has been frequently used since the 18th century sculptures, although with differences in the abundance of Zn, Sn and Pb. Ganio et al. [31], for example, have recently analysed a group of 23 copper-based sculptures from the Smart Museum of Art at the University of Chicago by Antoine Bourdelle, Félix Charpentier, Édgar Degas, André Derain, Jacques Lipchitz, Aristide Maillol, Henri Matisse, Mahmoud Makhtar and August Rodin, cast in art foundries active in the first half of the 20th century in the USA and France. Although cast more recently with respect to the Afonso Henriques' monument, XRF analyses performed on these sculptures also show a great variability of Zn (from 1.2 to 29.2 wt.%) and Sn (from 0.6 to 10.0 wt.%), that the authors ascribe to the different art foundries where they were produced. Similar conclusions were drawn by Pouyet et al. [2], commenting on the XRF analysis carried out on a vast group of 20th century bronze sculptures from Parisian foundries.

Finally, it should also be stressed that XRF data are consistent with the analysis performed by EDS in the cleaned sample (Figure 6), containing 90.75 wt.% Cu, 5.2 wt.% Zn, 2.9 wt.% Sn and 1.15 wt.% Pb.

Optical and scanning electron microscopy allowed to observe the microstructure of the sample. OM shows a dendritic structure typical of as-cast metal (Figure 7).

The SEM image presents a homogeneous alloy in which Pb stands out in the microstructure of the alloy as globular bright spots scattered across the sample. These spots are inter-dendritic micro-porosities that remain in the metal when the high melting point elements of the alloy have solidified. These micro-porosities are filled by lead, which is in a liquid state within the solid metal but still at elevated temperatures [34,35]. EDS detected Si, Zn, S and Al due to the occurrence of grains of quartz placed close to the outside of the metal and patina. Due to their composition, they may correspond to particles of the sand used as a mould for casting the different sections of the sculpture (Figure 8).

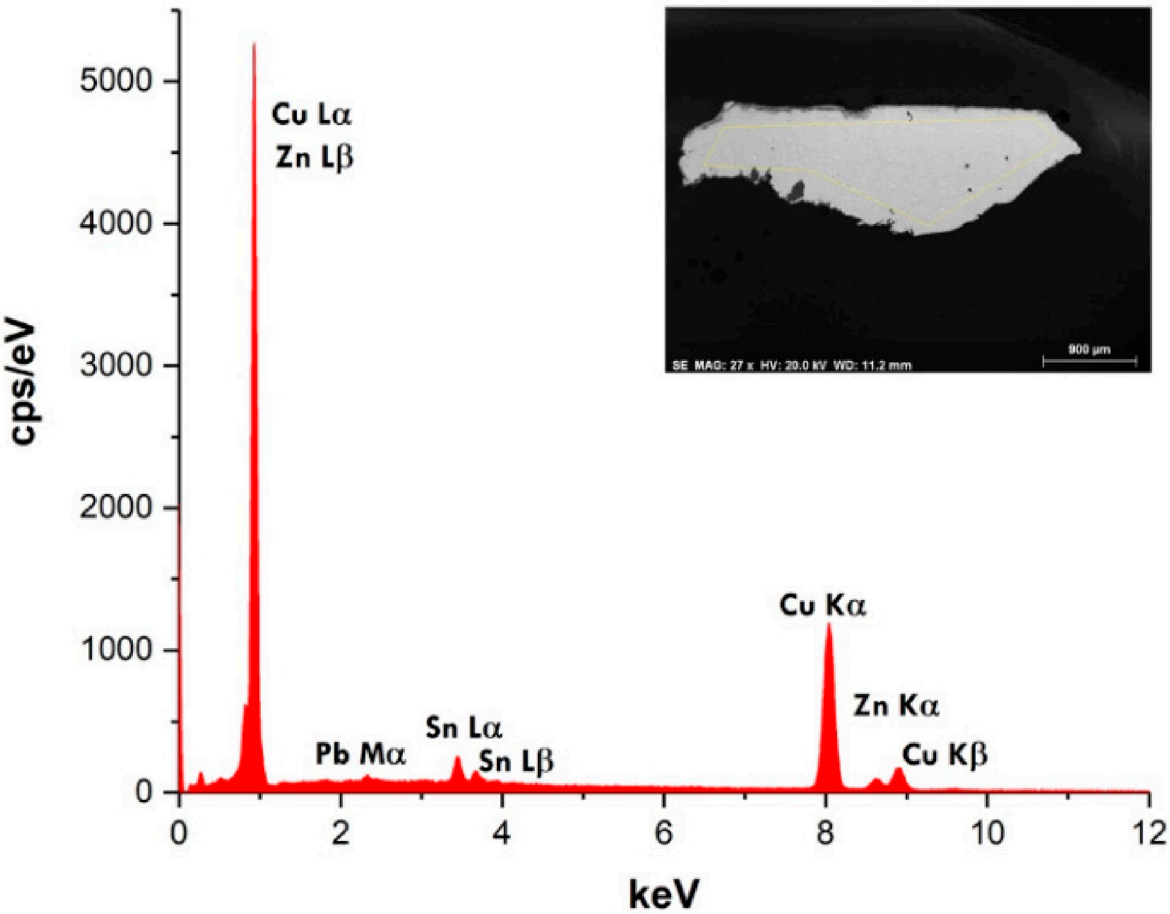

Figure 6. EDS spectrum and SEM microphotography of the sample from the bulk metal.

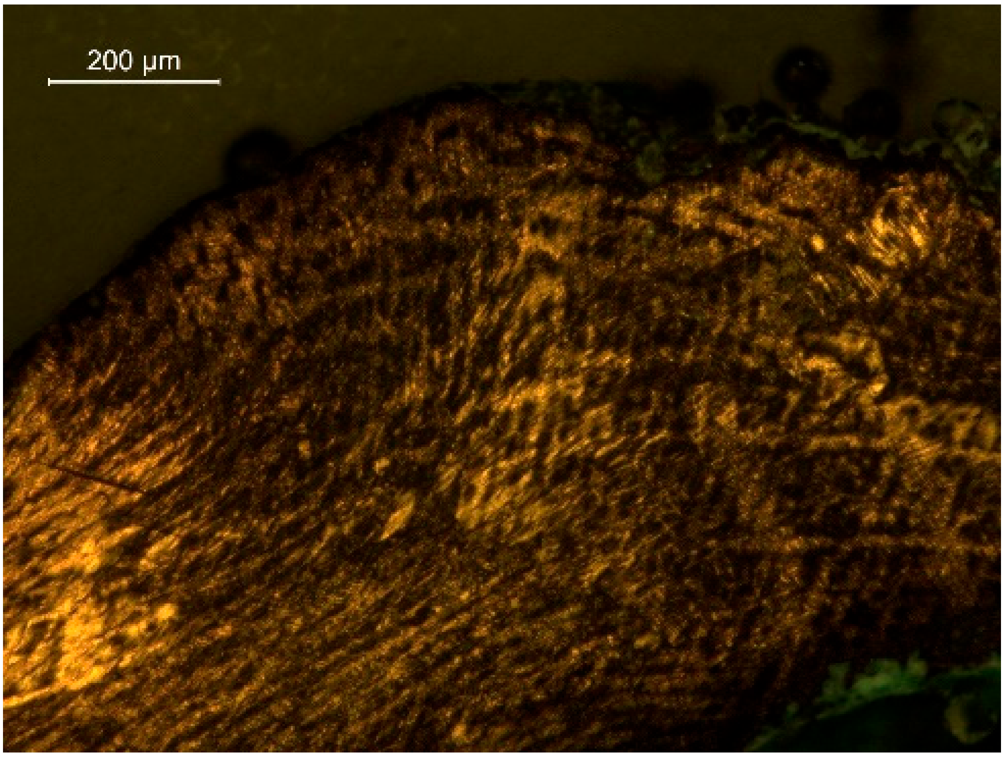

Figure 7. Metallography of the sample showing an as-cast microstructure.

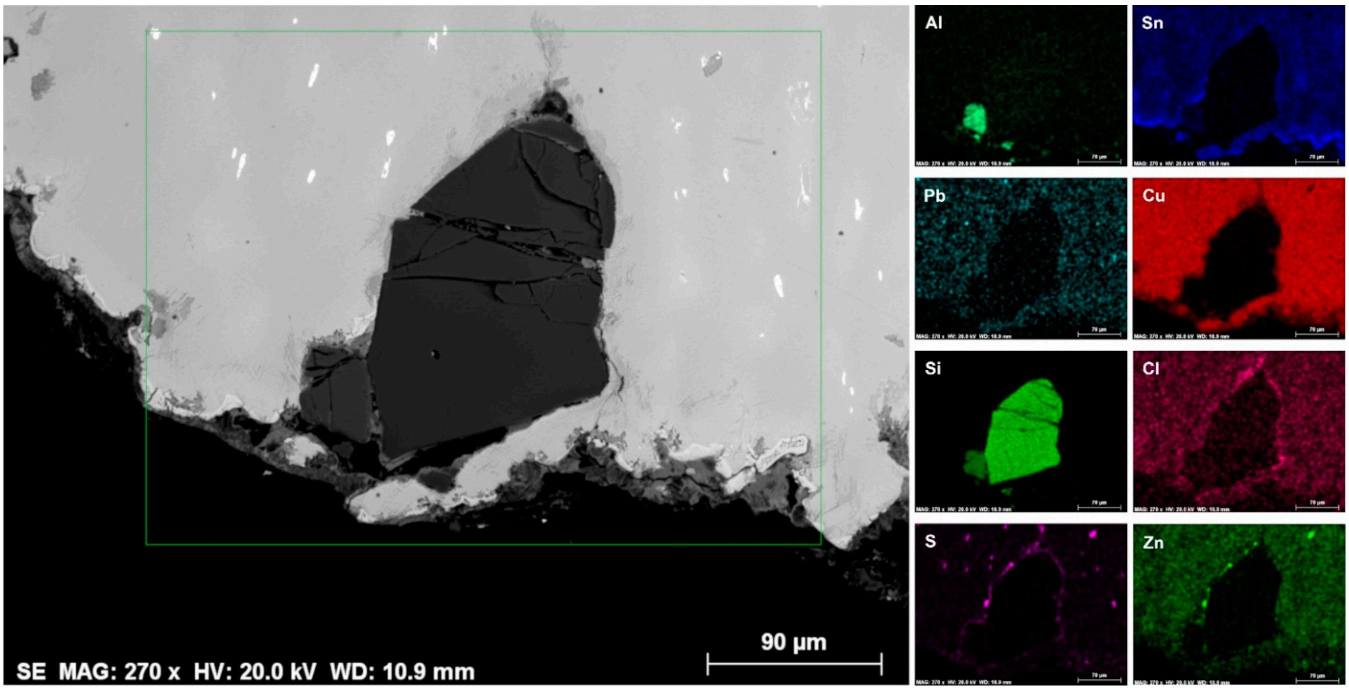

Figure 8. Detail of a sample taken from the sculpture. The EDS map shows the presence of an extensive Si encrustation and small concretions of Al, S, Zn and Pb in the interior of the metal, and Sn, particularly along the external corrosion area.

3.2. Corrosion Products

Table 2 shows the main corrosion products identified by XRD in the samples analysed. The XRD results reveal that the most abundant phase in the patina samples was brochantite ($Cu_4(SO_4)$ $(OH)_6$) in 14 of the 16 samples analysed, followed by cuprite (Cu_2O), quartz, posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$), tenorite ($CuO$) and cassiterite ($SnO_2$).

Table 2. Corrosion compounds discriminated by samples analysed on the statue (AH and E) and the sword (ESP).

Sample	Colour	Cuprite	Brochantite	Cassiterite	Posnjakite	Tenorite	Quartz
AH1	White	X	X				X
AH2	Light green/blue		X				
AH4	Pale green	X	X				X
AH6	Pale green	X					X
E1	Green/Blue	X	X		X		
E2	Green/Blue	X	X		X		
E4	Yellow/green	X	X				
E5	Dark brown		X	X			
E6	Green/Blue		X	X			
E7	Dark brown	X	X				X
ESP1	Dark brown	X				X	
ESP2	Light brown	X	X		X	X	
ESP5	Dark brown		X				
ESP6	Pale green	X	X				
ESP7	Dark brown		X		X	X	
ESP8	Brown		X				X

The absence of a black crust on the sculpture surface has been investigated as well, but no relevant clue has been found to explain this phenomenon. A realistic hypothesis is that the sculpture has been cleaned during its lifetime. However, no specific information that confirms any specific cleaning intervention has been found so far.

These results coincide with an environment far from the sea without highly polluting industrial activity in the area, which benefits the sculpture with passivating corrosion products [27]. These elements are also present in similar sculptures, with their formation usually being ascribed to the environment in which they are located [26,35,36].

The presence of cuprite and brochantite in most samples is expected given the rainy environment of Guimarães and the favourable reaction of these compounds to humid environments [37].

Cuprite and tenorite, primary corrosion products in the bronze passivation process, are located above the surface of the alloy, giving a dark-brown, brown-red or orange tone to the metal [26,38]. In the sculpture of D. Afonso Henriques, while cuprite has been detected in most of the areas analysed, tenorite was only found in the sword. This sculpture element has been the object of various interventions due to episodes of vandalism, which meant that it was subject to abrasion, welding and possibly other undocumented actions.

Posnjakite and brochantite are produced by the reaction of cuprite patina with sulphates and humidity present in the environment. The posnajkite evolves into brochantite, losing the water of its composition [26,39]. Brochantite settles as a second layer of the patina, giving the metal a bluish-green hue [40,41] (Figure 9).

Cassiterite, a natural product of tin corrosion, was only found in two samples collected from the front of the sculpture. Unidentified Sn and Cu compounds were also detected. Like cuprite and tenorite, cassiterite is placed on the alloy surface, sometimes covered by these two compounds [26,27]. The presence of quartz in the patina is generally connected to airborne particles. This mineral can increase the volume of the patina and reduce the adhesion to the metal surface [27].

Finally, SEM revealed other types of corrosion on the sample (Figure 10a). Pitting, intergranular and stress-crack corrosion are evident, both in the patina and in the bulk metal. These forms of deterioration are typical in urban and marine bronzes and are predominantly studied in archaeological objects [42–45] (Figure 10b).

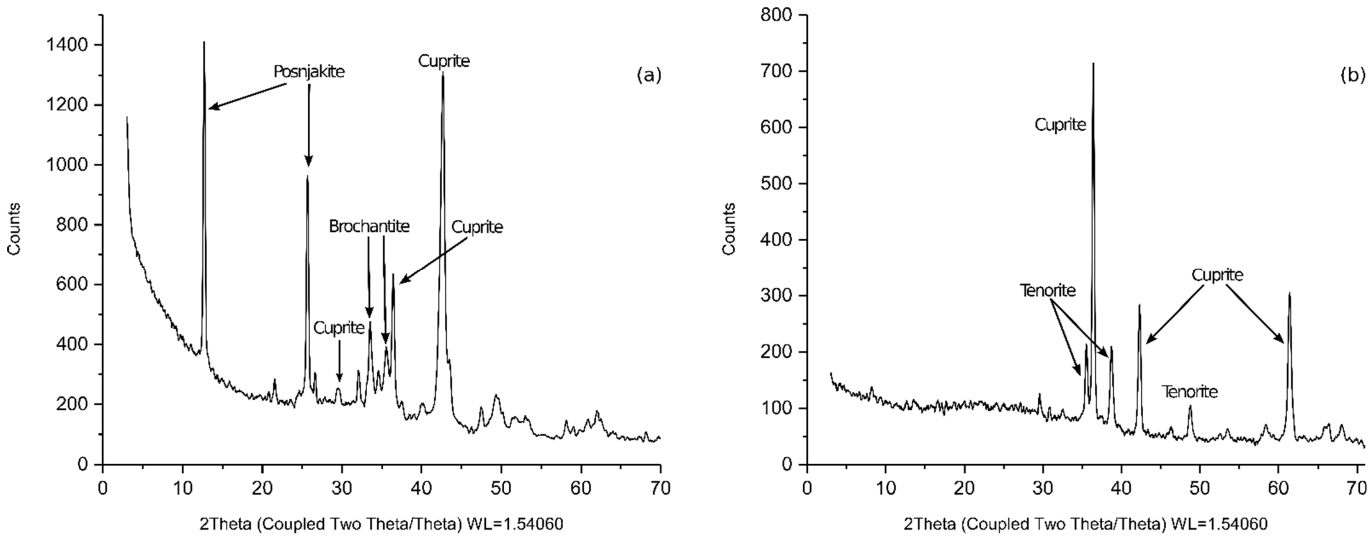

Figure 9. Diffractograms of samples E2 (**a**) and ESP1 (**b**).

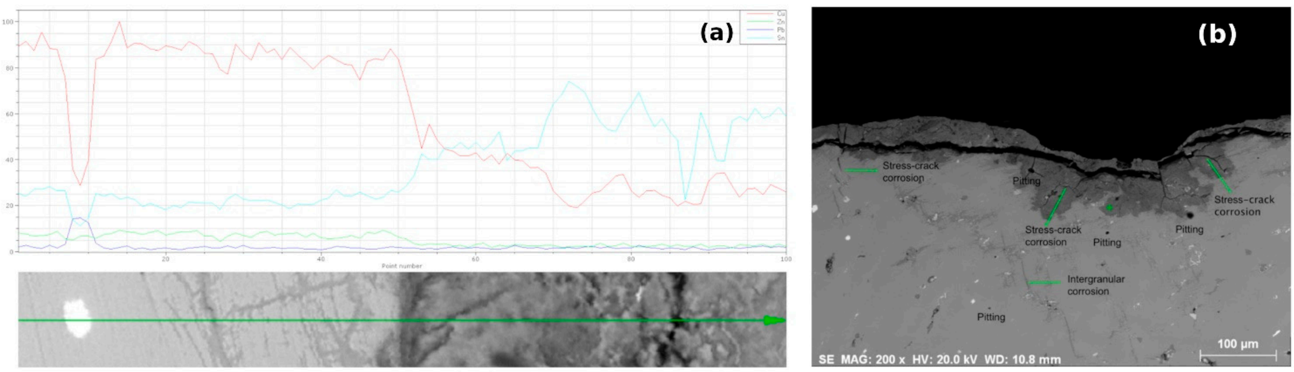

Figure 10. A SEM-EDS line scan of the bulk metal and patina showing the variability of Cu (red line), Zn (green line), Pb (blue line) and Sn (light blue line) (**a**). Types of pitting, intergranular and stress-crack corrosion that were observed on the bulk metal and patina of the sculpture (**b**).

4. Conclusions

The metal of the sculpture of D. Afonso Henriques (1887) was analysed for the first time. It is known that it was produced by the sand-casting technique, and it has now been possible to conclude that it was made of an alloy consisting of Cu, Sn and Zn, with Pb, Fe, As and Bi as impurities. This type of alloy resembles other pieces cast in Europe from the 18th to the early 20th century. The sculpture, which has been in the open air since 1887, has a patina befitting from an atmosphere with no significant polluting industries or marine environments in the vicinity.

The study of natural patinas carried out by XRD determined the presence of stable corrosion products on their surface. These products, e.g., brochantite, which appears in most of the analysed samples, provide a passive layer that protects the bulk metal from the atmosphere.

It is worth noting the increase of Sn and the reduction of Cu that gradually occur from the interior of the bulk metal towards the exterior. This alteration process has been likely produced by creating tin and copper oxides on the surface and the subsequent leaching of the latter element due to rainfall events characteristic of northern Portugal.

Although the techniques and materials used to develop the artificial patina are unknown, the presence of barium and iron on the surface may suggest that the sculpture was covered with a preparation containing these elements.

The information obtained in this study is essential for determining the state of conservation of the monument and providing preliminary data on its manufacture. It additionally provides a first insight into the initial casting techniques used in northern Portugal at the time, as this was the only bronze sculpture made by an industrial foundry in this part of the country.

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