Revista de metalurgia

Deterioration of ancient metallic elements taken from Toledo cathedral(•)

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Abstract The construction of Toledo Cathedral spanned a period of more than 200 years and was influenced by many different trends and criteria, reflected in the wide range of styles it accommodates (basically Mudejar and Gothic, with Flemish, baroque and renaissance elements). Over the centuries it has undergone numerous restorations, also according to different criteria. The cathedral is situated in an environment of low aggressivity, in terms of atmospheric contamination, but the passage of time has taken its toll on many structural, architectural and artistic elements. During recent restoration work several metallic elements, which have been exposed for many years or even centuries to the inclemencies of the Toledo climate, were taken in order to analyse their composition and deterioration. The techniques used have been Scanning Electron Microscopy with X-Ray Microprobe (SEM/EDAX), X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD). The elements considered are a piece of roofing lead, a lead slate clamp, a piece of stained glass window leading, and an iron nail.

Keywords Atmospheric corrosion. Toledo cathedral. Lead. Iron. Architectural heritage.

Estudio del deterioro de algunos elementos antiguos de la catedral de Toledo

Resumen La Catedral de Toledo se edificó en un período de más de 200 años, bajo numerosos criterios de construcción que se reflejan en la multiplicidad de estilos que alberga (entre mudéjar y gótico, con aportaciones flamencas, barrocas y renacentistas). A través de los siglos, ha sido objeto de numerosas restauraciones, también bajo distintos criterios. La catedral esta ubicada en un ambiente poco agresivo, en cuanto a corrosión atmosférica se refiere. Sin embargo, el discurrir de tantos años no deja de hacer mella en los diversos elementos estructurales, arquitectónicos y artísticos que la componen. En recientes restauraciones se obtuvieron algunos elementos metálicos que han estado expuestos, por muchos años, siglos inclusive, a las inclemencias del clima toledano, con el propósito de analizar su composición y deterioro, empleando las técnicas de Microscopio Electrónico de Barrido con Microsonda de Rayos-X (SEM/EDAX), Espectroscopía Fotoelectrónica de Rayos X (XPS) y Difracción de Rayos-X (XRD). Dichos elementos son: una cubierta, una grapa de sujeción, un clavo y un elemento para sujetar vidrieras.

Palabras clave Corrosión atmosférica. Catedral de Toledo. Plomo. Hierro. Patrimonio arquitectónico.

1. INTRODUCTION

1.1. The cathedral

The cathedral is considered to be the most outstanding architectural element of Toledo's historic-artistic heritage. Building work began in 1227 and lasted for 266 years, and was inevitably subject to numerous projects and different cultural and architectural criteria. The cathedral is located in the urban centre, on the southern slopes of the city, and its site was previously occupied by the mosque, the Jewish market, and an old church. It was declared a national monument in 1909.

When building work began it was the largest of its kind in Gothic style and the first with 5 aisles

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(•) Trabajo recibido el día 19 de enero de 2.001 y aceptado, en su forma final, el día 25 de septiembre de 2.001.

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to be built in Castile, though the Muslim foundations upon which it was raised and the topography of the site itself made it necessary to vary its spatial proportions, which were thus different from the French cathedrals upon which it was modelled (Bourges, Paris and Le Mans). It would subsequently be surpassed in size only by Seville and Milan cathedrals.

Restoration work in the cathedral may possibly have started in the 13th century, and was a parallel activity to building and extension work between the 14th and 18th centuries. From the outset restoration work was subject to different criteria, as is reflected in the external appearance of the building, and this situation was subsequently exacerbated with the use of partial repairs that transferred problems from one point to another without achieving global solutions. The current approach is more conservative, and contemplates the removal of added elements that disfigure the controversial image of a great Gothic temple in the Mudejar structure that the city still conserves. Recent restoration work has focused on restoring roofs and triforia as close as possible to their original state, completed with a geometrically coherent modern designs when this is not feasible[1 and 2].

1.2. The Toledo climate

The city of Toledo presents a continental climate with a mean temperature of 14 °C and extremes of –14 °C and 42 °C, annual average precipitation of 377.5 litres per square metre, and around 2800 hours of sunshine per year. The average relative humidity value is 60%[3 and 4]. The time of wetness of metallic surfaces, estimated in ISO standard 9223[5] as the number of hours in which the relative humidity is greater than 80% and the temperature above 0 °C (the time during which corrosion processes can take place on metallic surfaces), is 2000 hours per year[6]. The average values of SO_2, NO_2 and O_3 in the atmosphere, according to measurements made between 1987 and 1995, are 6, 16 and 77 $\mu g/m^3$, respectively[3]. In the period between June 1984 and July 1990 atmospheric SO_2 values were measured in the cathedral, giving an average of 15.54 $\mu g/m^3$, with a maximum of 30.42 $\mu g/m^3$ and a minimum of 9.16 $\mu g/m^3$. Atmospheric NO_2 values were also measured, giving an average of 21.67 $\mu g/m^3$, with a maximum of 41.31 $\mu g/m^3$ and a minimum of 3.05 $\mu g/m^3$ [7].

In conclusion, the Toledo atmosphere can be considered to be urban and of low aggressivity[8].

1.3. Elements analysed

Taking advantage of recent restoration work in the cathedral, several metallic elements were taken in order to investigate their chemical composition and establish the influence on their deterioration of the environment in which they had been exposed for many years (even centuries). These metallic elements are a piece of roofing lead from the Clock Tower, a lead clamp for anchoring roof slates, a piece of leading from a stained glass window, and a nail used to support gypsum rendering.

The roofing lead was taken from the spire of the Clock Tower. This tower is conceptually Mudejar,. though its decoration is Gothic, and it is comprised by two parts. The lower part is square and was built in the late 14th century and 15th century. The upper part is octagonal and was built in the 18th century to support a spire constructed of wood, slate and lead. The total height of the tower surpasses 92 metres. The roofing lead was obtained in 1991 during restoration of the spire, when the lead roofs were repaired or replaced with identical materials.

The slate clamp is also of lead. It was used to fasten roofing slates on the roof of the "Transparente" and was exposed to the outdoor environment behind the high altar. It consists of a piece of lead bent double, with a hole in the fold where a nail would have been inserted to secure it in place. The "Transparente" was built in the 18th century and was a controversial project, as well as being highly risky from a construction viewpoint. It was also the last major addition to the cathedral. Its purpose was to introduce light in the retrochoir behind the tabernacle, through a circular window in the centre of the eastern facade, and gave rise to the construction of a new baroque reredos. For the light to reach this point it was necessary to make an enormous opening in the vault of the intermediate ambulatory, above which a great lantern was built to gather light from the east through a vertical circular window, and all of this construction was supported on the vault's arches and covered with a slate roof. The clamp in question was removed during the restoration of the "Transparente" and its slate roof.

The stained glass windows and triforia vary between ogival and Mudejar styles. The first stained glass windows were constructed in the 14th century, but despite the large number of master glaziers who have worked in the cathedral since then, up to the middle of the 20th century when destruction caused by the Civil War was repaired, there are very few references to the methods that they employed. Recently it was found that much of the window leading was missing and problems began to occur with falling pieces of glass, and so the latest restorations have included a general review of the stained glass windows and the repair of most of their leading. All of the cathedral's stained glass is now perfectly leaded and secured in iron frames with crossbars in order to prevent it from bulging[9]. The window lead considered in this study was installed during the restoration work carried out in the 1940's after the Civil War.

The iron nail dates from the 18th century. It was used to support gypsum rendering on the limestone walls of the lower triforium. It was taken from the cathedral in 1993.

2. MATERIALS AND METHODS

The roof is made of high purity lead in which only traces of Sn, Fe and Sb (above 0.005%) are detected. It shows a monophasic microstructure with approximately equiaxial grains. It was exposed to outdoor environment. Lead roofs was frequently used in the past because its facility of obtention (low melting point and good casting properties) and its permanence. Today, lead sheet for roofing is made from pure lead in some cases[10].

The slate clamp is made with the same material of the roof lead (high purity lead with traces of Sn, Fe and Sb) and exhibits a similar microstructure. It was used to support roofing slates on the roof of the "Transparente" and was exposed to the outdoor environment. Its facility of obtention and malleability can be important reasons for made this element with lead.

The window lead is a Pb-Sn alloy with the following composition: 97.97% Pb, 2% Sn, 0.02% Sb and traces of Fe (< 0.005%). It shows a heterogeneous microstructure with light and dark gray zones. This element provides support to stained glass windows, for which it must be have enough strength. Adding tin to lead or lead alloys increases hardness and strength while melting and casting properties are still good.

The composition of nail is the following: 99.65% Fe, 0.21% C, 0.11% Si and < 0.02% P. The microstructure of this element is heterogeneous, formed by ferrite (as major constituent) and perlite. Nail of this material are commonly used to support gypsum rendering on the limestome walls of the cathedral, due to its good mechanical strength.

The methods for analysis of these elements include SEM/EDX, XPS and XRD techniques.

For observation with the scanning electron microscope (SEM), a thin layer was cut perpendicularly from each specimen. A JEOL JXA-840 unit equipped with a LINK SYSTEM electron microprobe was used to analyse the morphology of the materials and of the exterior layers. Semiquantitative EDX analysis of the composition of the specimens was also made.

The corrosion products films on the lead specimens were subjected to surface analysis using the X-Ray Photoelectron Spectroscopy (XPS) technique. Square specimens of 1 cm^2 were prepared and analysed using a VG Microtech MT500 multitechnique surface analysis equipment with pumping unit, with a Mg/Al double anode X-ray source operating at 15 kV and 20 mA.

The corrosion products layer on the nail was examined by X-Ray Diffraction (XRD). A semiquantitative analysis of the composition of this layer was made using a SIEMENS D5000 unit with graphite filter monochromatised copper anode radiation.

3. RESULTS

3.1. SEM / EDX analysis

3.1.1. Roofing lead

The surface is highly homogeneous, it being possible to observe grains of large size and irregular shape. Some grains present a parallel "fibrous" texture associated with slip lines (fig. 1a). Slip lines can appear because low melting point and low creep strength of lead. The general spectrum of the specimen indicates that it is lead of high purity (close to 100%).

A very thin and uniform corrosion products layer is observed at the edges, with a thickness of approx. 15 μm (fig. 1b). EDX analysis of this layer reveals the following composition: lead (44.73%),

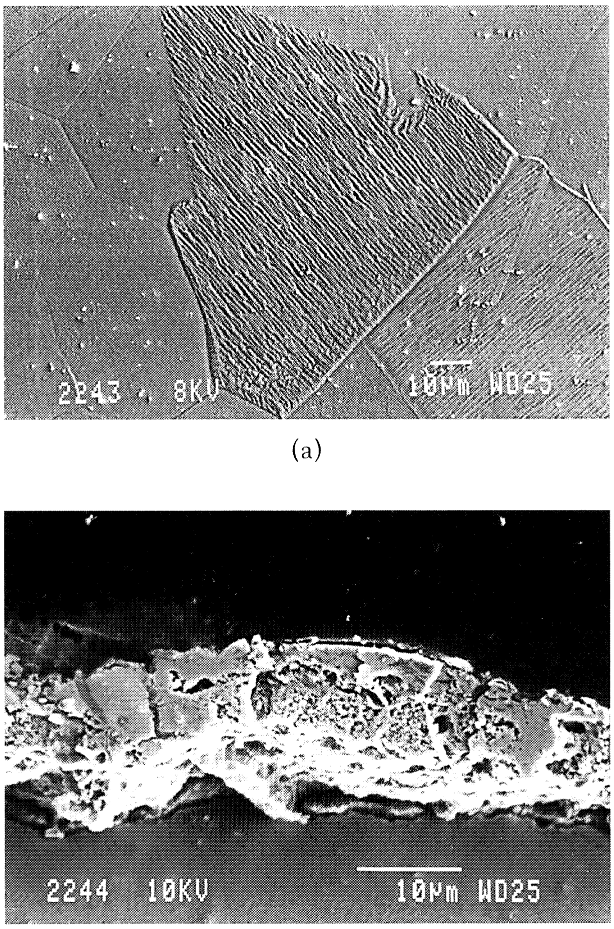


Figure 1. SEM images of the roofing lead, (a) Photograph in which grains of a fibrous appearance can be observed, (b) Corrosion products film, whose thickness is approximately 15 µm.

Figura 1. Imágenes de la cubierta obtenidas mediante SEM, (a) Micrografía en la que se aprecian algunos granos de aspecto fibroso, (b) Capa de productos de corrosión cuyo espesor es de unos 15 µm.

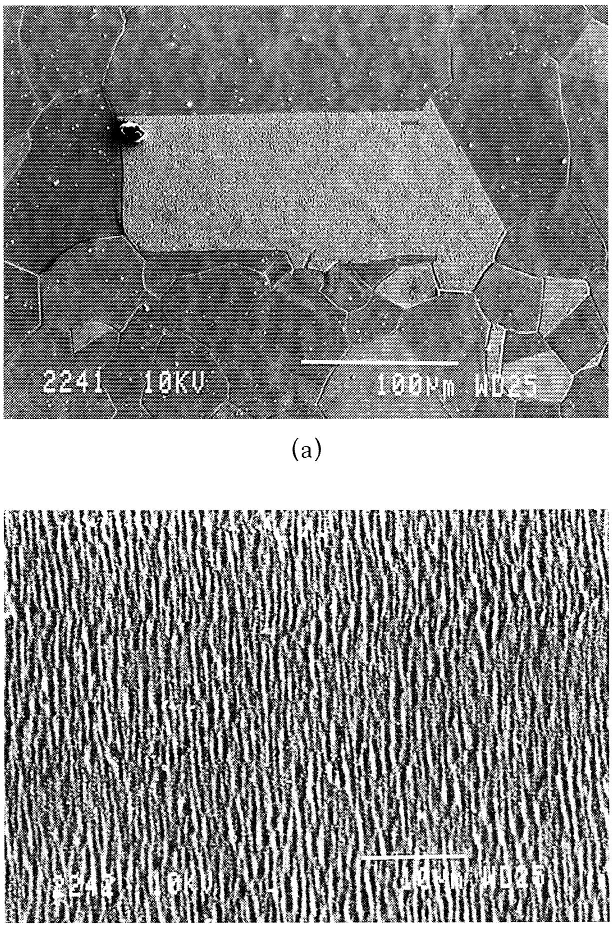


Figure 2. SEM images of the lead clamp, (a) Photograph in which the grains can be observed, (b) Detail of the central grain with a fibrous appearance.

Figura 2. Imágenes de la grapa de plomo obtenidas mediante SEM, (a) Micrografía en la que se aprecian los granos del material, (b) Detalle del grano central con una textura fibrosa.

carbon (35.17%), oxygen (16.37%) and traces of phosphorus and calcium. Probably, lead carbonates are the principal corrosion product formed in this layer. Carbonates are typical compounds found in atmospheric corrosion of lead.

3.1.2. Slate clamp

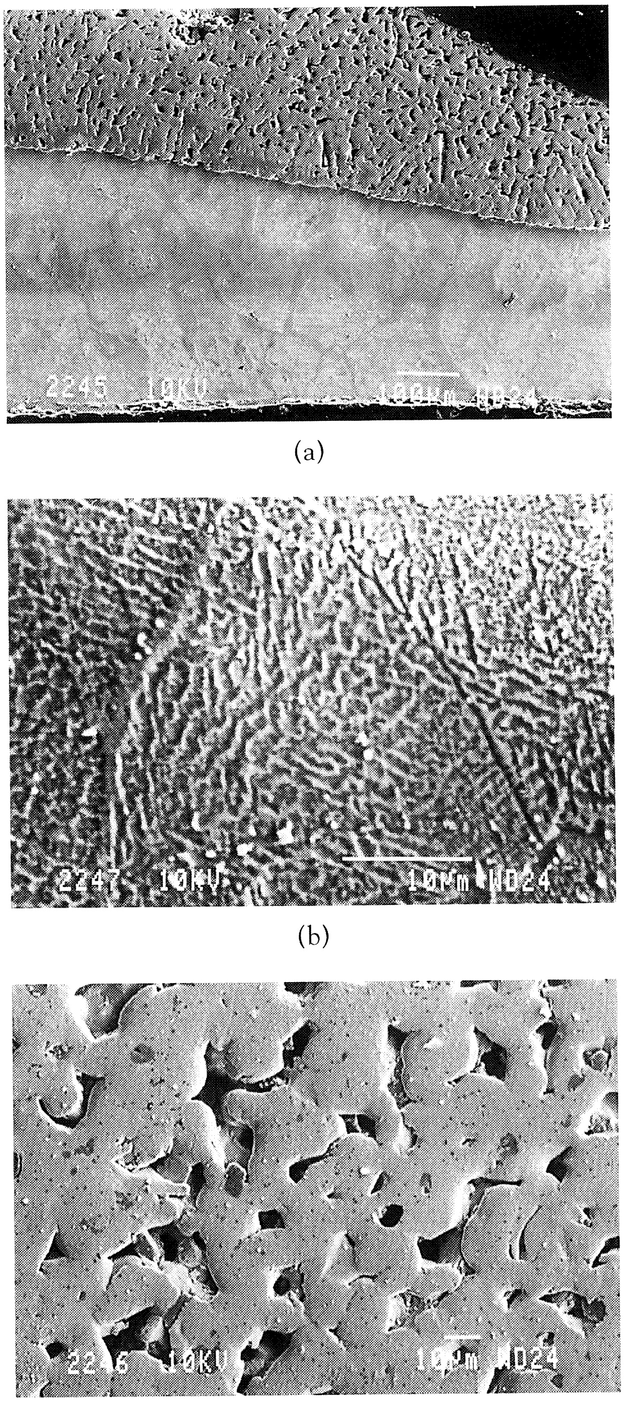
This presents similar characteristics to the roofing lead, with a highly homogenous surface that is comprised almost entirely of lead and a thin corrosion products layer consisting mostly of lead, carbon and oxygen.

The large size of the grains permits their differentiation even with the naked eye. Some appear darker than others due to greater oxidation of the surface (fig. 2a). At 2000 magnifications the slip lines texture described in the previous case can clearly be seen (fig. 2b). In this case, slip lines appear in major extent, probably due to fatigue phenomenon.

Roofing lead and slate clamp show similar composition and microstructure, and probably they were made directly from sheets obtained by cast process, cold-worked with little deformation.

3.1.3. Window lead

EDX analysis shows that this is a lead alloy with approximately 3% tin. Two clearly differentiated types of zones are observed on the surface: the



(a)

(b)

(c)

Figure 3. SEM images of the window lead, (a) There is a clear differentiation between lead-rich regions (light grey) and tin-rich regions (darker), (b) Detail of the lead-rich region, showing its very fine arborescent morphology, (c) Detail of the tin-rich region, with a porous morphology similar to a cheese.

Figura 3. Imágenes del plomo de vidriera obtenidas mediante SEM, (a) En esta Micrografía se diferencian claramente las regiones ricas en plomo (gris claro) y las regiones ricas en estaño (oscuras), (b) Detalle de la zona rica en plomo, con una morfología arborescente muy fina, (c) Detalle de la zona rica en estaño, con una morfología porosa, similar a un queso.

first is light and uniform (more extensive), while the second is darker and appears in fewer places (fig. 3a).

The more uniform zones are comprised almost totally by lead, and when observed at sufficient magnification (2500 X) a dendritic or arborescent texture is appreciated. The grain size is very small (fig. 3b). In the darker zones the main component is tin. The surface has the appearance of being full of holes, like a cheese (fig. 3c).

A lead alloy with approx. 3% Sn, at steady state, must shows a monophasic microstructure with equiaxial grains. The appearance of darker zones is possible due to segregation process during solidification. This segregation allow to the formation of Sn-Pb lamellar eutectic phase, which remains in the material during conformation process. For other hand, it is possible that porosity appears during solidification process.

The corrosion products film was extremely thin and its analysis with this technique was not possible.

3.1.4. Nail

Figure 4 clearly shows an outer layer of corrosion products and a more or less homogenous inner layer.

The general spectrum for the nail indicates that it is comprised essentially by iron, with some silicon (0.32%). It is a carbon steel.

The spectrum of the outer layer shows that its main component is iron, also detecting oxygen and sulphur. This is a very compact and relatively

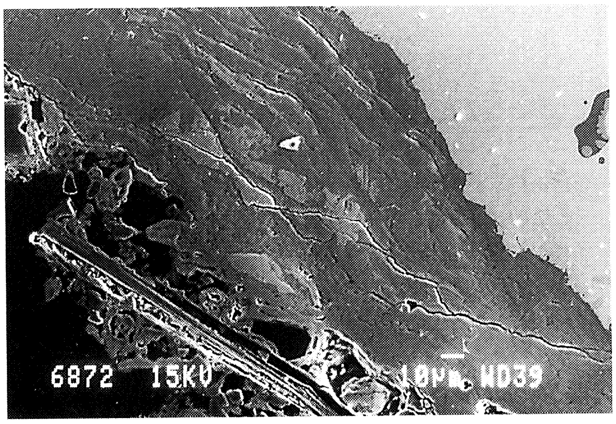


Figure 4. Corrosion products layer of the iron nail, with a thickness of between 120 and 160 µm.

thick layer, with a thickness of between 120 and 160 µm. Deterioration of nail is slight. According to this information, although nail is placed in an aggressive environment, the corrosion products (mainly Fe hydroxides) exhibit protective characteristics.

3.2. XPS analysis

Figure 5 shows the general spectrum for the lead specimens, which is representative for all three specimens analysed. There is little difference between the original specimen and after one minute of argon sputtering.

According to the information given by the different peaks in the general spectrum, the outermost surface of the specimens is formed mainly by lead oxides and carbonates.

Lead sulphates have also been found on the roofing lead. Figure 6 shows a high resolution spectrum of the S2p peak, which indicates the presence of this compound.

3.3. X-ray diffraction analysis

XRD analysis was carried out on the nail's corrosion products layer (Fig. 7), indicating that this is comprised mainly by Goethite (γ-FeOOH) and, to a lesser extent, Lepidocrocite (γ-FeOOH). Some gypsum ($CaSO_4 \cdot 2H_2O$) is being detected, but this compound is originating from the rendering that the nail supported

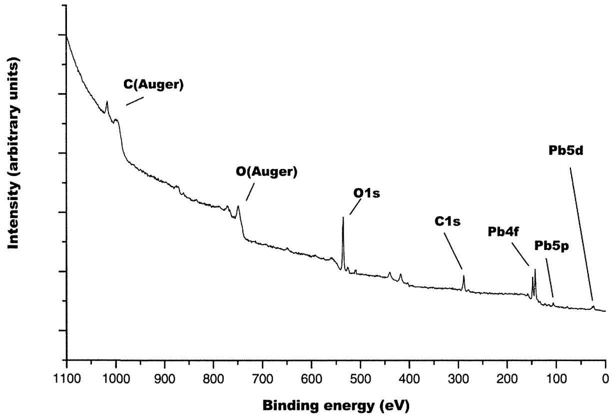


Figure 5. General XPS spectrum characteristic of the lead specimens, indicating the main elements found (carbon, oxygen and lead). The spectrum of the roofing lead only differs in that sulphur is detected (S2p).

Figura 5. Espectro general XPS característico de las muestras de plomo, en la que se señalan los principales elementos encontrados (carbono, oxígeno y plomo). El espectro de la cubierta solamente difiere en que se detecta azufre (S2p).

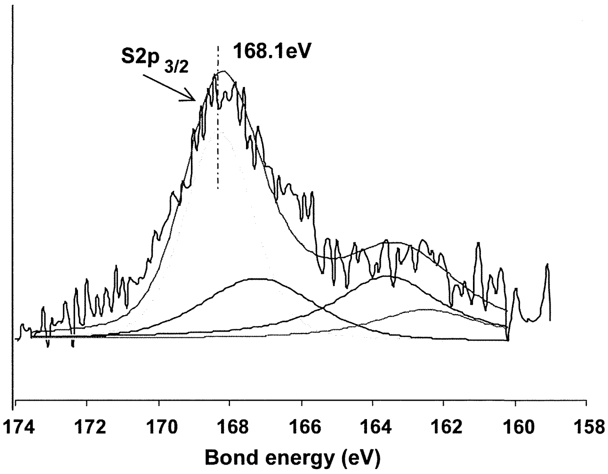


Figure 6. High resolution spectrum of S2p obtained in the XPS analysis of the roofing lead.

Figura 6. Espectro de alta resolución del S2p obtenido en el análisis XPS de la cubierta de plomo.

4. DISCUSSION

4.1. Lead elements

It is well known that lead was widely used as a building material in the Middle Ages. Many great buildings of the 15th and 16th centuries still conserve their original lead roofs[10]. Though lead was often used in the past on the grounds of supposed properties that do not actually exist, it was most often used for its malleability, its appearance and its permanence.

Because lead is very soft and malleable, it is probably that lead elements were made by cold conformation of sheets obtained by cast processes.

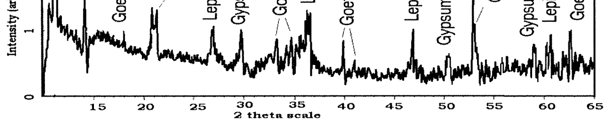


Figure 7. XRD spectrum of the nail corrosion products layer, in which lepidocrocite, goethite and gypsum have been detected.

Figura 7. Espectro XRD de la capa de productos de corrosión del clavo, en la que se han detectado lepidocrocita, goethita y yeso.

Lead was frequently used unalloyed, as in the case of the slate clamp and the roofing lead. The large grain size corroborates the high purity of the lead used and indicates that casting were made with high pouring temperatures and low cooling rates, which promote the formation of large sized grains. A coarse structure weakens its mechanical properties[10].

Later, in applications where mechanical demands were greater (as in the case of the window lead, which is subject to greater stresses in supporting the stained glass), other elements such as tin were incorporated in the lead, and by helping to reduce its grain size thus improved its mechanical properties. The incorporation of these elements can also decrease lead's corrosion resistance[11]. Homogeneous alloys (it is the case of roofing lead and slate clamp) are usually more corrosion resistant than heterogeneous alloys (window lead). In the window lead, tin addition produces a second phase, which in presence of humidity can produce galvanic coupling effects. Then, corrosion resistance of the alloy decreases. It is possible that porosity appears because high solidification rate, which do not allow the leaking of dissolve gases.

The atmospheric corrosion rate of lead depends on a complex combination of electrochemical and physical-chemical parameters, such as the nature and level of environmental contaminants, the relative humidity of the air, and the composition and morphology of the material.

In general, lead shows good resistance to atmospheric corrosion, due to the formation of a highly adherent and relatively thin corrosion products layer. The composition of this protective film depends on the atmosphere in which the material is exposed, but in most cases is highly effective in protecting the metal. During its initial stages, the film is formed by lead oxides. Subsequently basic lead carbonate forms (poorly adherent), due to the reaction with CO_2, and this can give rise to a highly adherent lead carbonate. In the presence of SO_2, the carbonate can transform into lead sulphite, which in a subsequent stage becomes converted into lead sulphate[12 and 13].

According to SEM and XPS analyses, the corrosion products found on the lead elements are basically lead carbonates. Lead sulphates have been detected on the roofing lead (in a lesser proportion) in addition to the carbonates. These results correspond well with the low aggressivity of the Toledo atmosphere. The film is highly adherent and provides good protection to the material for an indefinite time, unless it is physically damaged or altered. The phosphorus and calcium found on the roofing lead may be considered to be impurities.

Slip lines are detected in elements not alloyed. The low tensile strength and low creep strength of lead must always be considered when designing lead components. The principal limitation on the use of lead as structural material is not its low tensile strength but is susceptibility to creep. Lead continously deforms at low stresses, even at room temperature. The fatigue properties of lead-base alloys can be affected by creep-fatigue interaction. However, in this case, lead exhibit slight deterioration by creep due to thermal fatigue as a consequence of climatic changes of temperature.

4.2. Iron nail

This element is a carbon steel with a microstructure formed by ferrite and approx. 20% perlite. This type of elements was obtained by forging.

Carbon steels are by their nature of limited alloy content, usually less than 2% by weight for the total of all additions. These levels of addition do not generally produce any remarkable changes in general corrosion behaviour. Ferritic steels exhibit better corrosion resistance than, for example, martensitic steels, because its microstructure is more homogeneous[14].

The atmospheric corrosion products of iron and its alloys (rust) are constituted by different types of oxides, hydrated oxides and other substances originating in the substrate or in the atmosphere. The percentages in which they are found depend on the characteristics of the metal and the medium in which it is exposed, as well as on the exposure time[15 and 16]. There is a clear relationship between the protective capacity and the thickness of the layer formed after several years of exposure. In time, processes such as agglomeration, filling of pores and recrystallisation may occur in the rust layers, leading to more compact layers that impede the diffusion of the contaminants involved in the corrosive process. This means that a reduction in the corrosion rate in time may be associated with an increase in the compactness of the rust[17 and 18]. Good quality rusts have thicknesses of the order of 100-200 μm, compared with the 200-400 μm thicknesses of little protective layers[19].

According to the state of the corrosive process, the main constituent of rust can be lepidocrocite (γ-FeOOH), amorphous oxyhydroxide (AM-FeO-OH) or goethite (γ-FeOOH). In some cases magnetite (Fe_3O_4) can be a significant component[16, 19 and 20].

The compounds detected in EDX and X-ray analyses, i.e. goethite and lepidocrocite, correspond with the long exposure time of the nail. According to the layer thickness, this is a rust with protective characteristics, which once formed has impeded any subsequent deterioration of the material. It is common to find this type of rust in rural and urban atmospheres.

Some gypsum has also been found adhered to the rust, whose origin lies in the rendering that the nail supported. The presence of sulphur detected in the EDX analysis may be due to this compound. Gypsum contributes to accelerating the corrosion of iron and steel, and thus it is not recommendable to combine these materials.

In cases such as this, the high initial corrosion rates lead to a large amount of corrosion products whose outermost layers become detached due to their low adherence. For this reason only the innermost layer remains, which is more compact, adherent and protective. This layer has impeded greater deterioration of the nail.

5. CONCLUSIONS

The low aggressivity of the Toledo environment has permitted good conservation of the metallic components of its historic heritage, with regard to atmospheric corrosion.

The lead elements present a very slight degree of deterioration, from the point of view of corrosion, bearing in mind their antiquity and the low aggressive environment of Toledo. The corrosion products film that covers the material is basically comprised by lead carbonates. Their great adherence provides good protection, which is to be expected in this type of atmosphere.

The lead used for the elaboration of the oldest elements is of high purity. Probably, they were made by cold conformation with very low plastic deformation grade due to high malleability of lead. They exhibit similar composition and homogeneous microstructure with coarse grains, which is more corrosion resistant.

The lead used in the stained glass window, manufactured in the middle of the 20th century, is a lead-tin alloy. Tin provides the material with greater mechanical resistance without affecting its melting and casting properties. Probably, it was obtained by cold working and shows segregation processes during solidification and a heterogeneous microstructure that decreases corrosion resistance.

The deterioration of the iron nail is greater than that of the lead elements. It was placed in a more aggressive medium. However, the corrosion products layer presents a protective character, which has impeded greater deterioration of the material. In addition, its homogeneous microstructure helps to improve corrosion resistance.

Acknowledgements

To María del Carmen Sánchez, of the National Metallurgical Research Centre (CENIM) for her important collaboration in obtaining the specimens and historic documentation on the cathedral.

J.G. Castaño expresses his gratitude to the Colombian Institute for the Development of Science and Technology "Francisco José de Caldas" (COLCIENCIAS), for the doctoral grant awarded.

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