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XRD, SEM/EDX and micro-Raman spectroscopy for mineralogical and chemical characterization of iron slags from the Roman archaeological site of Forua (Biscay, North Spain)

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ABSTRACT

The Roman village of Forua (North Spain) was an important iron production and distribution centre during the 1st-4th centuries AD. Different metallurgical materials at the archaeological site were identified as forged slag, bog ore mineral and refractory materials used in the walls and on the floor of furnaces. The samples were studied by macroanalysis and microanalysis techniques. The mineralogical characterization was carried out via optical microscopy and X-ray powder diffraction, and the textural characteristics and the composition of individual phases were determined using scanning electron microscopy coupled with electron-dispersive spectroscopy, and by Raman microspectroscopy. Mineral associations not only reflect furnace cooling rates and temperatures but also indicate quartz was the main flux used. The microanalysis results reflect the elements that constituted the slags and other materials from the forge and the worked metallic materials. The results showed the slags originated from iron smithing, which also was confirmed by the presence of iron particles. The ore materials consisted of goethite.

1. Introduction

In the past, iron objects were produced in a process consisting of two or sometimes three steps. Iron ore, usually iron oxides, was roasted in order to lose volatiles, such as hydrogen and sulphur. Then the ore was reduced in solid state by heating in a closed furnace with charcoal. This is known as direct or bloomery smelting [1, 2]. The ore changed into a metallic state by the carbon monoxide produced in the furnace, resulting in a porous mass of iron and impurities called "bloom". As a result of the smelting process between 10 and 20% of ore mass changed into the iron bloom while the rest was transferred into the iron slag [3]. The solid iron bloom incorporates such other substances as silica, alumina and unreduced iron oxides, resulting in iron smelting slags, and charcoal.

In the next step the bloom was refined during the smithing process to remove adhered slags until it was shaped into a finished product. The smithing process was performed in two stages and consisted of heat-treating in a hearth and hammering on an anvil. In the primary smithing process, adhered slag inclusions and charcoal were removed from the bloom, thus consolidating the metal into a more compact and manageable bar. Then, in the secondary smithing process the iron was shaped into the final object [1, 4–7]. Wastes associated with both stages form the smithing slags, which are accumulations of fused residual materials at the bottom of the hearth. Thus, two main slag types are generally formed, the smelting slag, corresponding to the gangue material discarded from the ore, and smithing slag, formed by an accumulation of fused materials at the hearth [2]. Both smithing and smelting processes result in the production of numerous types of silicate slag. Smithing and smelting slags are from different pyrometallurgical stages and often are hardly distinguishable chemically and mineralogically [6]. However, the archaeological context is able to determine the type of slags due to the elements of installation found in the excavations (e.g., type of furnaces, extant equipment). Slags can also be differentiated by the type of morphological characteristics, chemical composition and phase composition and microstructure [1, 2, 6, 8]. Thus, within the by-products of the metallurgical process, slags are often the only relicts of ancient pyrometallurgy and represent a valuable source of information regarding ancient metallurgical technology and economy [7].

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Since the smithing process consists of heating and hammering not only the shape of the product is modified but also the internal structure, the chemical composition and the physical properties [5]. The phase composition and microstructure of the smithing slags provides valuable information about the conditions of slag formation, the nature of raw materials, quality of the product, efficiency of the metallurgical process, etc.

The most important process leading to the formation of smithing slags, beside grain growth, is the oxidation of iron at high temperature forming a crust of oxides at the surface of the metal [2, 9]. In addition, different kinds of waste are produced: slags at the bottom of the hearth, small flat particles during the hammering and metallic fragments during the fashioning. The most common wastes are the slags formed during the heat-treating of the bloom. During heating, the oxidized crust of the bloom expands and breaks because the specific volume of the crust is higher than that of the metal. It is more rigid and fragments fall down to the base of the hearth. The melting of these remains forms plano-convex slags [6]. During hammering, slags can also be formed when the crust, oxidized by contact with the air, is broken into small particles [4].

When the smithing slags cool off, crystallisation processes occur and certain phases are formed depending on the cooling conditions and the stages in the production process [10]. During forging, the physical nature of the metal and complexity of waste objects produced is highly variable. Nearly all ancient metallurgical slags contain ferrous silicates as the main component but other compounds such as oxides and the residues of metals can be also present [11].

To characterize the smithing slags, several analytical techniques were used, including X-ray diffraction (XRD), scanning electron microscopy coupled with electron-dispersive spectroscopy (SEM–EDX) and Raman microspectroscopy. Mineralogical composition of samples was determined by means of XRD. SEM/EDX provides compositional and microtextural information about the samples. Qualitative and semi-quantitative analyses were performed to characterize ore, slag and metal compounds of the samples from different metallurgical processes in the same site. These analyses can provide information about the efficiency of the metallurgical process [12].

The bloomery method was the most usual technique to smelt iron ore in the Roman period and the slags constitute a valuable archaeological material to establish the ore type used and the conditions to obtain the metal [13]. The phase and chemical composition and microstructure of slags can supply answers to questions about the production technology, including raw material type and provenance and the efficiency of the bloomery method in this period. Therefore, the aim of this work was to study a set of smithing materials corresponding to the iron-making processes followed at the Roman archaeological site of Forua (Biscay, North Spain) in the 4th century AD. This provides useful information to further knowledge of metallurgic processes, of which little is known for the period in which Iberian culture developed.

2. Materials and methods

2.1. Materials

The studied samples were 28 ferrous samples stored in Bilbao *Arkeologi Museoa* (North Spain). These materials come from the Roman archaeological site of Forua (Biscay, North Spain) (Fig. 1). Archaeological investigations carried out at this Roman settlement were able to identify a large group of workshops corresponding to iron forges dated in the 1st–4th centuries AD. Seven buildings with a large number of smithing furnaces and auxiliary installations for metallurgical transformation were identified. Forua, close to the coast on the Urdaibai estuary, would facilitate raw material and product distribution around the Cantabrian Sea and Bay of Biscay [14].

The stereomicroscopic examination of the selected ferrous material samples was able to discriminate three different sample groups according to macroscopic features and these were named FM (ferrous material). All the studied samples were small in size, $<8 \times 5 \times 4$ cm, and were hardly weathered on the surface, covered with a yellowish patina of limonite. The first FM1 group was characterized by a plano-convex shape, with heterogeneous colours ranging from black to yellowish, vesicles ranging in size from microscopic to several mm in diameter and a light magnetism (Fig. 2a, d). The samples in FM2 group are more compact and dense with a less irregular surface than the former group and with very small pores inside. While the surface of FM2 samples is greyish in colour, the matrix ranges from grey to a reddish-yellow colour (Fig. 2b, e). Finally, FM3 group is characterized by having low density, clayey aspect, deep red colour and high magnetism (Fig. 2c, f). Macroscopically, due to their morphological characteristics, the selected samples correspond to smithing slags rather than to smelting slags.

2.2. Optical microscopy

Thin-sections of the ferrous samples were analysed by light polarized microscopy using a petrographic polarizing Nikon Eclipse LV100POL microscope equipped with a DS F-11digital camera and DS L2 camera control unit. The microscope observations were performed using both transmitted and reflected light modes.

2.3. X-ray powder diffraction

Mineralogical assemblage of the ferrous materials was established by an MDP Phillips (X'Pert Pro model) diffractrometer for polycrystalline samples. The diffractometer is equipped with two Theta 2Theta goniometers operating independently while sharing a single source of x-rays and equipped with secondary monochromators. One goniometer is used for high temperature measurements (Anton Paar HTK16 camera). The second goniometer operates with an automatic 15-position charger. The operating conditions were 40 kV and 20 mA, suitable for routine measurements of powder samples. Phase identification was made by using the quartz present in the samples as internal standard in the random orientation of the powdered material. A systematic procedure for phase identification was by ordering the d-spacings of the most intense peaks. Files of d-spacings for hundreds of thousands of inorganic compounds are available from the International Centre for Diffraction Data as the Powder Diffraction File (PDF). Commonly, this information is an integral portion of the software that comes with the instrumentation.

2.4. Scanning electron microscopy with energy dispersive X-ray spectroscopy

Sample characterization was performed using a JEOL JSM 6400 scanning electron microscope (SEM) operating with an INCA EDX detector X-sight Series Si (Li) pentaFET Oxford. Samples were carbon-coated to eliminate charging effects. Microtextural observations and elemental analysis was performed on polished thin sections of ferrous materials. Qualitative microanalysis was carried out using the ZAF method, which is based on the correction of the matrix effect in multielemental analysis that takes place in the simultaneous determination of the concentration of each element present in a multi-element material. This method provides X-ray intensity correction, absorption correction, and the fluorescence correction produced by the atomic number effect of each element, by the composition and depth of electron penetration, and by the secondary fluorescence respectively. The counting time for punctual analyses was 60 s. Concentrations were calculated by stoichiometry from elements generated by ZAF software.

2.5. Raman microspectroscopy

Raman spectra were documented with a Renishaw inVia Raman spectrometer coupled with a Leica DMLM microscope using three objectives (5×, 20×, and 50×), resulting in a spot of 1–2 μm. A+ laser