PRELIMINARY INVESTIGATION OF A METALLURGICAL SLAG (1ST CENT. BC – 1ST CENT. AD) FROM GRUMENTUM, BASILICATA (ITALY)

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Abstract: *The present investigation focuses on the determination of the morphological, chemical and mineralogical characteristics of an ancient metallurgical iron slag, in order to obtain information about the metallurgical processes that might have taken place and level earned by local smiths. The slag comes from the* forum *of the ancient roman city of* Grumentum *(Basilicata, Italy), on an excavation near the* Cesareo *temple (1st cent. BC-1st cent. AD). The analysis have showed a different composition and mineralogical structure between the inner matrix, that contains in major percentage maghemite (γ-Fe_2O_3), wuestite (FeO) and iron fragments, and the surface, made up mainly of goethite (FeOOH) and alumino-silicates of iron. The application of ESEM revealed percentages of Cl in the inner regions and the presence of a crystalline agglomerate identified as monazite (Ce, La, Nd, Th) PO_4.*

INTRODUCTION

The slag is the archeological find no. 51, and comes from the most recent archaeological campaigns (2009-2010) in the *Forum* of *Grumentum*; to be more precise it has been found together with 25 similar pieces in the east area of the Temple Cesareo, and in a stratum dated between the middle of the 1st cent BC and the 1st cent AD. The discovery in the previus archeaological campaigns and in more recent stratigraphic units (end of the 3rd sec. AD, beginning of the 4th sec. AD), of similar archeological finds has lead at the beginning to believe that the slags cames from a melting activity of finished products so as to get back iron material reusable (very common even in more outstanding urban contests during the late middle ages), but the last archaeological campaigns have called this reconstruction into question. This study has tried to investigate the production activity in order to understand if the slags are the result of the melting of finished products and other slags, or the reduction of mineral, or the forging of a iron bloom, so as to advance theories about the level of metallurgical processes in *Grumentum* during the imperial age.

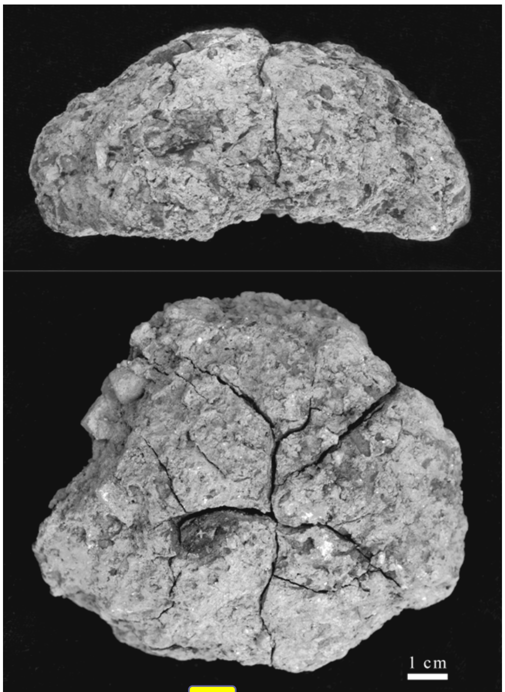

Fig. 1. Archeological find no. 51, profile and convex side

1. ANALYTICAL METHODS

The sample was preliminary analyzed for macroscopic features (color, texture, porosity, weight, magnetism). The soil near the slag was investigated with qualitative chemical tests. Mineralogy was determined by both optical microscopy (polarizing petrographic microscope) and XRD. The chemical elements of particular regions was determined by SEM/EDS.

2. RESULTS

The sample's size range between approximately 12 x 12 cm, and it has a flat-convex profile (Fig. 1). The surface is characterized by an evident textural heterogeneity, with many mineralogical inclusions and alterations ascribed to oxidation (distributed mainly in the convex area). The weight is nearly 700 g and the measured density is about di 3,8 g/cm^3.

An empirical experiment of magnetism has shown a high intensity in the inner regions and a lower intensity on the surface.

The soil in which lied the slag has been resulted rich in carbonates and sulfates, as well as rich in Fe ions.

The X-Ray diffractograms revealed the minerals wuestite (FeO), maghemite (γ-Fe_2O_3) and goethite (FeOOH). The mineralogical analysis clearly shows that the sample no. 51 is a slag.

The presence of wuestite might indicate relatively weak reduction conditions, as those dominating during the refining stage, subsequent to the production of the iron bloom[1].

Goethite appears to be a corrosion product, as the material had been handled in the atmosphere for a long time. This could be either from the slag (wuestite being later converted to ghoetite) or the oxidation of the metallic matrix [2]. The absence of fayalite (Fe_2SiO_4), iron silicate, could indicate a not optimized process. Indeed the fayalite forms at temperature over 1100°C.

The study of the thin section at the polarizing petrographic microscope has given the possibility to understand the XRD results and especially to identify the mineral phase positions. The inner matrix, appearing mat at the cross polarized light, is probably composed by high percentage of wuestite e maghemite (ferromagnetic mineral), whereas the surface appear to be an earthy/argillaceous facing composed by a matrix of goethite e alumino-silicates, in which are immersed quartz crystals.

The SEM provided information on the microstructure of the sample and combined with the X-ray analysis helped us in the elemental identification across different areas and in the identification of particles in the matrix. The main structure is the one of iron oxides(the white rounded shapes) and the allumino-silicata groundmass in grey (Fig. 2).

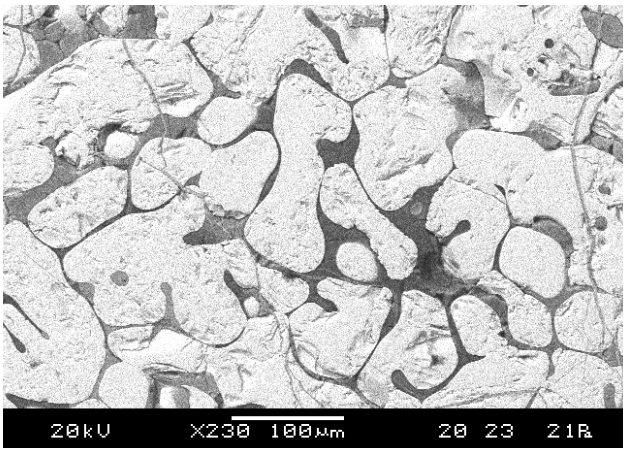

Fig. 2. ESEM microphotograph. Iron oxides (wuestite) and allumino-silicata groundmass

The outer layer, supposed to be an earthy/argillaceous facing, is mostly composed by Si, O, C and K (C e K probably as a result of organic compounds used as combustible), as well as Fe. In particular the SEM revealed in this area a crystal with high atomic weight elements, for which the EDS identified Ce, Th, La, P and O. The phosphate which contains lanthanide and thorium is monazite [(Ce, La, Nd, Th) PO_4], coming most likely from sands used during the ironmaking process as antioxidant, rather than from the iron ore (Fig. 3).

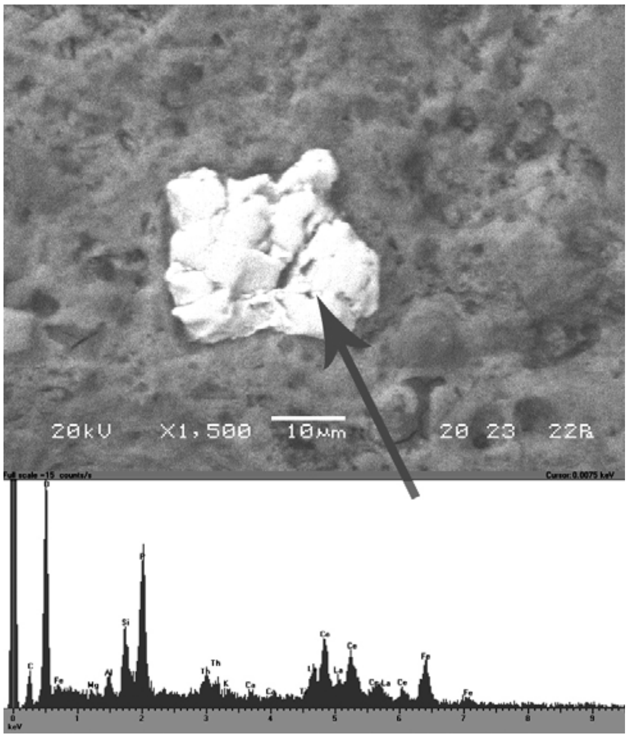

Fig. 3. ESEM microphotograph and EDS spectra of monazite [(Ce, La, Nd, Th) PO_4]

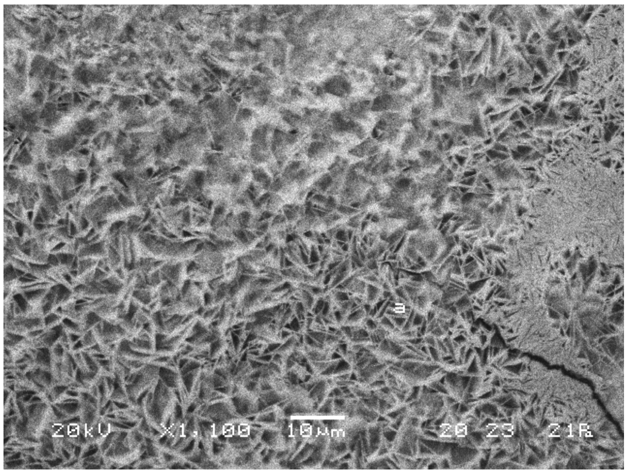

Fig. 4. ESEM microphotograph of inner region with Cl crystals

In the inner zone of the slag the ESEM revealed broad areas with needle-shaped and inter-penetrated crystals. The EDS revealed high percentage of Cl (17%). Shape of crystals and composition make us think it could be some hydrate of iron (II) chloride (Fig. 4).

3. CONCLUSIONS

The sample, having a flat/convex profile, a high weight, an earthy/argillaceous facing outer layer probably resulting from the contact with the walls of the furnace, a high magnetism (not present in casting slags), a considerable amount of iron fragments and a high percentage of wuestite, can be identified as slag coming from the forging of an iron bloom, certainly not a reduction of mineral. The crystal attrib suggest a slow cooling. The absence of fayalite could indicate a not optimized process or a final stage during the processing. Since the Fe is present like oxide (maghemite and wuestite), instead of silicate (fayalite), the slag could be a product of a final stage (the case in which the smith had enough material), in which will not be necessary to purify the iron bloom remaining. The slag still rich in iron could be in fact reused eventually in the future.

The amount of archeological finds even in geological layers with different dating means a manufacture continuous during the time. The stratum, in which the slag under consideration was found, was dated on the first imperial age (from the end of 1st cent. BC to the beginning of 1st cent. AD) and, even if some documentation is provisional, it seems the temple C (the older of the forum) was built at the beginning of the Tiberian age. Since the the period of the forging agree about the bulding of the temple, we can suppose the local foundry produced metallic elements to use in the bulding of the temple. The hypothesis seems more truthful if we consider in the same stratum, and close to it layers, were found a lot of ceramic and zooarchaeological samples with fire trace. All these things make us think it could be a religious ritual with the purpose of consecrate the temple: it was usual in the roman regions of South-Italy, like a pagan ceremony, to lighting a fire in votive funds (in Greek language: *bothroi*) which contained the remains of instruments used during the building and the slags (remains of the iron production) [4].

Chloride and monazite could coming from the sand used as antioxidant and to increase the melting of the iron bloom. The rare-earth elements which contains the mineral monazite are very difficult to find and not usual in Italy, but we have confirmation of limited local concentrations on Calabria and Basilicata (Lucania) coasts, especially in coastal sands [5].

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