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Microstructural Characterisation of Archeologic Finds Discovered at the Ironworks in Mădăraș

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Abstract

In the middle of the 16th century the ironworks of Mădăraș was one of the important centres of iron production. During its one and a half century lifespan its output provided a significant part of Transylvania's iron supply. While it operated it used up the entire raw material extracted in the iron ore mines of the Felcsík basin. This study presents the reconstructed ground-plan of the ironworks, its layout on the shores of the Mădăraș creek, and the chemical composition and microstructure of the samples discovered during exploration of the location by means of XRF analysis, EDS analysis and metallography. The analysis of the pig iron, the steel and the slag although performed on individual samples, still provides a good approach regarding the products of the ironworks, their chemical composition and microstructural characteristics.

Keywords: *ironworks, microstructure, metallography, spectrometry, use of waterpower, melting, smithy.*

1. Introduction

Documents from the time of the Principate of Transylvania contain a considerable amount of information about the mining, production and manufacturing of iron, at and around the already known as well as the more recently discovered iron sources in the Szekely land **[1]**, **[2]**. In the middle of the 16th century one of the centres of Transylvanian iron production, **[3]** the Mădăra ș ironworks was already producing iron **[4]**, **[5]**. During its lifespan of one and a half centuries its output contributed significantly to Transylvania's iron demands. Besides the fact that it was profitable, it was important also because inhabitants from ten settlements of the Csíkszék jurisdiction were employed there and therefore enjoyed tax exemption, moreover, quite a few of the employees from the Ciuc, Gheorgheni and Cașin areas received the minor nobiliar title of „lófő" (an exclusive rank among the Szekelys) from Transylvanian prince Báthory Zsigmond **[6]**.

In those times it was already known that in the Mădăraș area of Harghita county there was iron ore. It is a characteristic of the Mădăraș ironworks that basically the entire product of the mines from the upper Ciuc basin was melted there. In 1659 the Mădăraș ironworks began to decay fast and an inventory document from 1703 already tells about its deplorable condition. At that time it was rented for a mere 40 forints, when the market price of an ox was around 10-14 forints. In 1722 when it was rented again the contract doesn't even mention iron production, the object of the contract was only the land and the still functioning sawmill.

The ironworks functioned continuously between 1567 and 1725. Its demise was attributed to lack of iron ore which in fact is only one of the many shortcomings: The most important was without a doubt the owners' bad management.

2. The ironworks and its products

In the Mădăraș ironworks both the equipment and t production processes was at that time considered state of the art. The ideal conditions were provided by the large and constant water discharge of the fast flowing Mădăraș creek. Close to the ironworks there was a beech forest that provided plenty of beech wood as the raw material for charcoal burning, the iron quarry was also close by as was the limestone which is important in slag forming. The ironworks could function continuously from April to November, that is, the entire frost-free period of the year.

In 1673 there were 137 employees only one of whom was an iron stone seeker – today we would call him a Geologist. Two judges of the ironworks coordinated the activity of the miners, the melters, the smiths, the cobblers who made blowers, the smiths who sharpened pickaxes, the iron beaters and the cart handlers. It was probably a well organized venture. The quantity of the produced iron reached 19 tons a year. Comparing that with the five ironworks of Hunedoara we see that the combined yield of those only exceeded that of the Mădăraș ironworks by 118 kg a week.

The product was at the disposal of the prince's court. It was sent to Iernut, Gurghiu, Dumbrăveni or Făgăraș for further processing. In Mădăraș iron rods, cannon balls, horseshoes, horseshoe nails and agricultural tools were made. Looking back 280 years from the present, the truth is that as a consequence of nature's transformative powers and of human negligence, today only professionals can realize the true size of this once thriving ironworks. Based on an inventory made in 1677 a ground plan was realized that is the first one to present a probable picture of what it must have looked like (**Figure 1.**).

According to the ground plan the ironworks was on the right shore of the Mădăraș creek. From the creek a mill race ran into a water reservoir which still can be found today (C in **Figure 1**.) the purpose of which was to provide a constant water discharge under a constant pressure to the three water wheels. The propulsion of a fourth water wheel was provided by the Mădăraș creek itself. There were two iron melting stoves (3 and 7) the outputs of which was taken for further processing to the smithies (4 and 6).

On the site the iron stone sifter and roaster (2) the iron ore was prepared for processing, melting. The building marked 5 was the deposit for the finished products. The coal barn (9) received the loads of the carts, the charcoal. Carts entered the site through the gate (A). Besides these, some of the buildings had multiple functions such as lodgings, leather processing workshop etc.

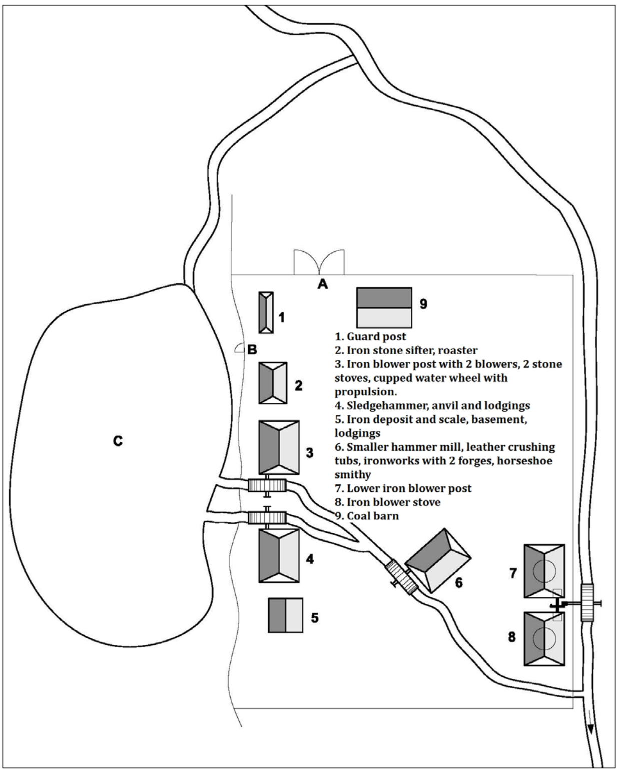


Figure 1. *The ground plan of the Mădăraș ironworks*

3. Analyses of the residues from the ironworks

As a result of several searches on the site different residues were found: slag, pig iron and steel residues.

From these materials we cut samples for research. The chemical analysis was done by Thermo Niton XL3T type X-ray fluorescence spectrometer (XRF), SPECTROTEST TXC25 type optical emission spectrometer (EDS) and the spectrometer of the Zeiss EVO10 scanning electron microscope. We used an iqualitrol iMet-400 and an Olympus PMG3 metallographic microscope, also a stereo-microscope (macroscope) and a scanning electron microscope to analyse the surface of the sample pieces and on metallographic samples also their inner structure. **Table 1.** shows the results of this chemical analysis

Analysing the three rows of data in **Table 1**, the following conclusions can be drawn:

- The iron content of the residues is between 38,3–74%. The only remarkable aspect of this data compared to information regarding the composition of modern iron forging residues is that the iron content of the slag is 38.3 %, which is the result of poor extraction. In the slag there is a significant quantity of rare and expensive metals, such as Zn, Ni, Sb, extracting those from the mountain of slag that was produced during the lifespan of the ironworks could be an opportune task.
- Naturally the pig iron samples contain more iron, around 32.1 %. It should be noted that the cast iron typically has a Si content of 5.8 %. There isn't much Cr and Sb but that could be a characteristic of the iron ore from Mădăraș. In the pig iron samples prepared for metallographic analysis, polished but not milled, the rosette-type distribution of graphite is clearly visible (see **Figure 2.** a-b).
- During the XRF analysis of the steel samples copper was recorded (290 ppm), while the proportion of nickel decreased (38 ppm). The presence of zinc, aluminium and tin is a sign of a complex ore, yet it is unusual that these metals survived the melting temperature of the iron. The phosphorus and sulphur content of the steel produced there is low according to the XRF analysis (the spectrometer didn't reveal any of these elements), but EDS analysis done on different points of the polishes showed clearly that the composition of the steel sample varies from point to point. There are significant quantities of pollutants and the material is roughly slagygy which is typical for the technologies of those times.

As a result of the repeated heating and beating which was typical for the iron production of the age, the initially very non-homogenous material was homogenized, graphite burned out and slags were beaten out of it and thus it became usable steel product. If we could find and analyse larger quantities of pig iron and steel, we could obtain more precise results. Maybe a more comprehensive archaeological excavation could unearth more iron residues but that is unlikely as we know that even the iron nails used for fixing the parts of the gate were contained in the inventories.

4. Microstructural analysis of the materials

4.1. Analysis of the slag

From the materials collected on location we analysed the chemical composition of the slag with EDS method focusing on the surface shown in **Figure 3.a** which is the inner fracture surface of the slag. The intensity diagram of the EDS analysis and the composition that can be defined based on the diagram is shown in **Figure 3.b**. Repeating the EDS analysis on different spots we came to the conclusion that the mass percentage of iron is consistently between 42–44%, Silicon is around 7%, manganese content is 2–3% and aluminium is also resent at more than 1%. Comparing this with

Table 1. *Results of the XRF analysis (%)*

	Fe	Mn	Si	S	P	Cr	Ni	Cu	Zn	Mo	Al	Sb	Sn	As
Slag residues	38.3	3.2					0.0345	0.0092	0.0712			0.0077		0.0061
Pig iron residues	62.1	0.75	5.8	0.11	0.76	0.0498						0.0109		
Steel residues	74						0.0038	0.0290	0.0100	0.0020	0.0100		0.0100	

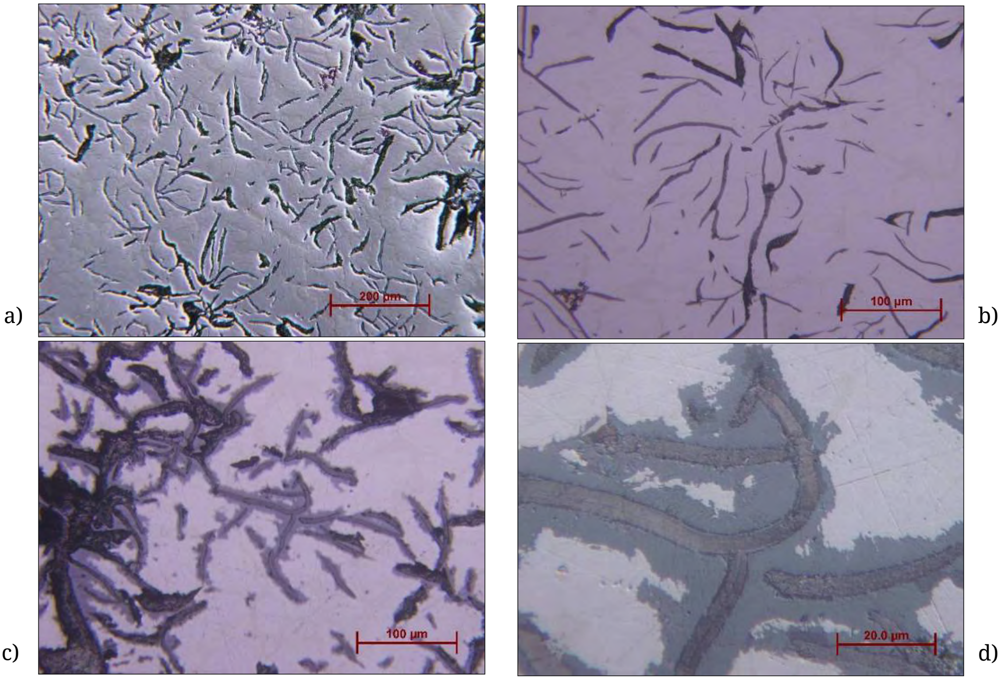


Figure 2. *Microstructure of the pig iron in polished state on the inside of the sample (a-b) and in the proximity of the corroded surface (c-d)*

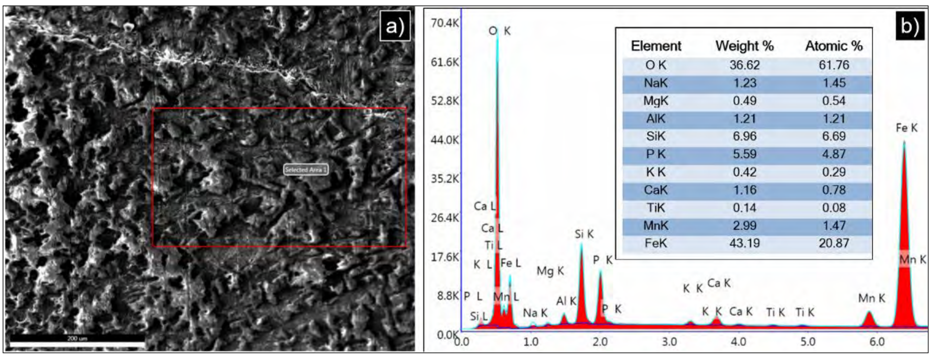


Figure 3. *Detail of the fracture surface of the slag (a) and the intensity diagram and the chemical composition that resulted from the EDS analysis made on the marked area (b)*

the results obtained by XRF it is striking that EDS gives a much higher phosphorus content (5–6%) which is evidence to the limitations of XRF analysis [7–10].

4.2. Analysis of pig iron

We took a sample from the found materials, we prepared a metallographic sample which was analysed by means of metallographic microscopy and scanning electron microscope in a polished state and after etching it with a 4% Nitaletchant. In Figure 2. we can identify, based on the ISO 945-1:2019 standard, the shape, dispersion and size of the laminar structured graphite. The shape falls between classes I. and II., the dispersion is class B type (rosette graphite) while the size is around 3rd and 4th on the 8 degree scale. Close to the surface of the sample, along the phase boundary between ferrite and graphite the material is strongly corroded as shown in Figure 2c–d.

Analysis in the polished state only allows us to determine the structure of the graphite, etching is necessary in order to identify the matrix [11]. But etching can destroy the corroded parts along the borders of the graphite plates in strata close to the surface therefore determination of the chemical

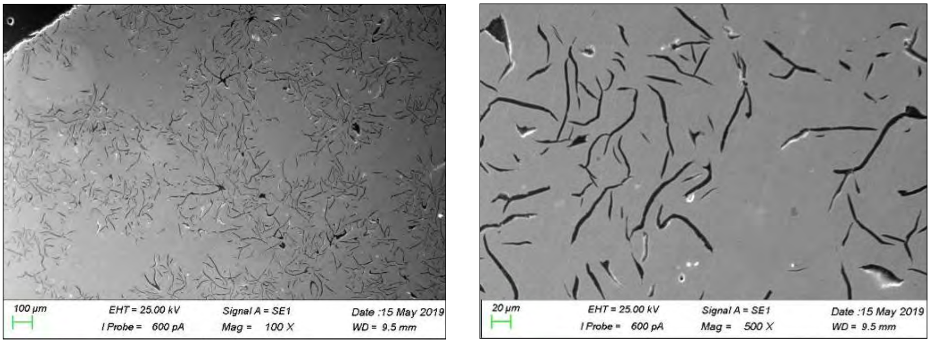
a)  b)

Figure 4. *Microstructure of pig iron in polished state on secondary electron image*

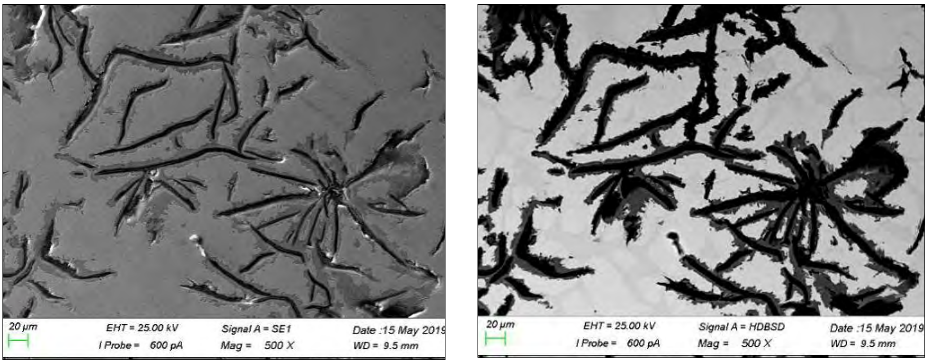
a)  b)

Figure 5. *Microstructure of pig iron close to the surface in polished state on secondary electron image*

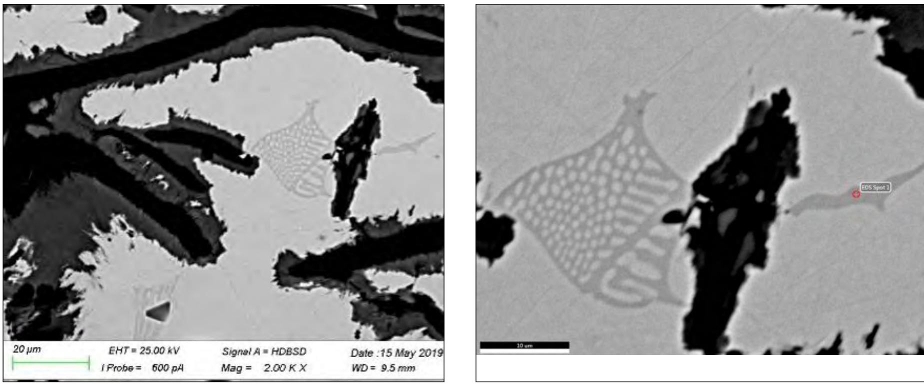
a)  b)

Figure 6. *The part of the microstructure that contains phosphide eutectic on secondary electron image*

composition of the materials in certain characteristic points by means of the scanning electron microscope EDS analyser had to be performed before etching. **Figure 4.** shows the secondary electron image of the polished sample. Analysing the entire surface shown in **Figure 4b.** the quantity of the main components – without iron and carbon – is as follows: Si = 0.77%, Mn = 1.17%, P = 1.72%.

The image of the part close to the surface is shown in **Figure 5.** On the phase borders of the graphite plates, corrosion products formed in which EDS analysis showed atomic proportions of 43% iron and 56 % oxygen which is close to the Fe/O atomic proportion of magnetite. **Figure 6** shows a magnified detail of **Figure 5b** on which a section containing phosphide-eutectic is clearly visible. The atomic proportion of phosphorus in this eutectic is 17%, in the phosphide plate it is 25%.

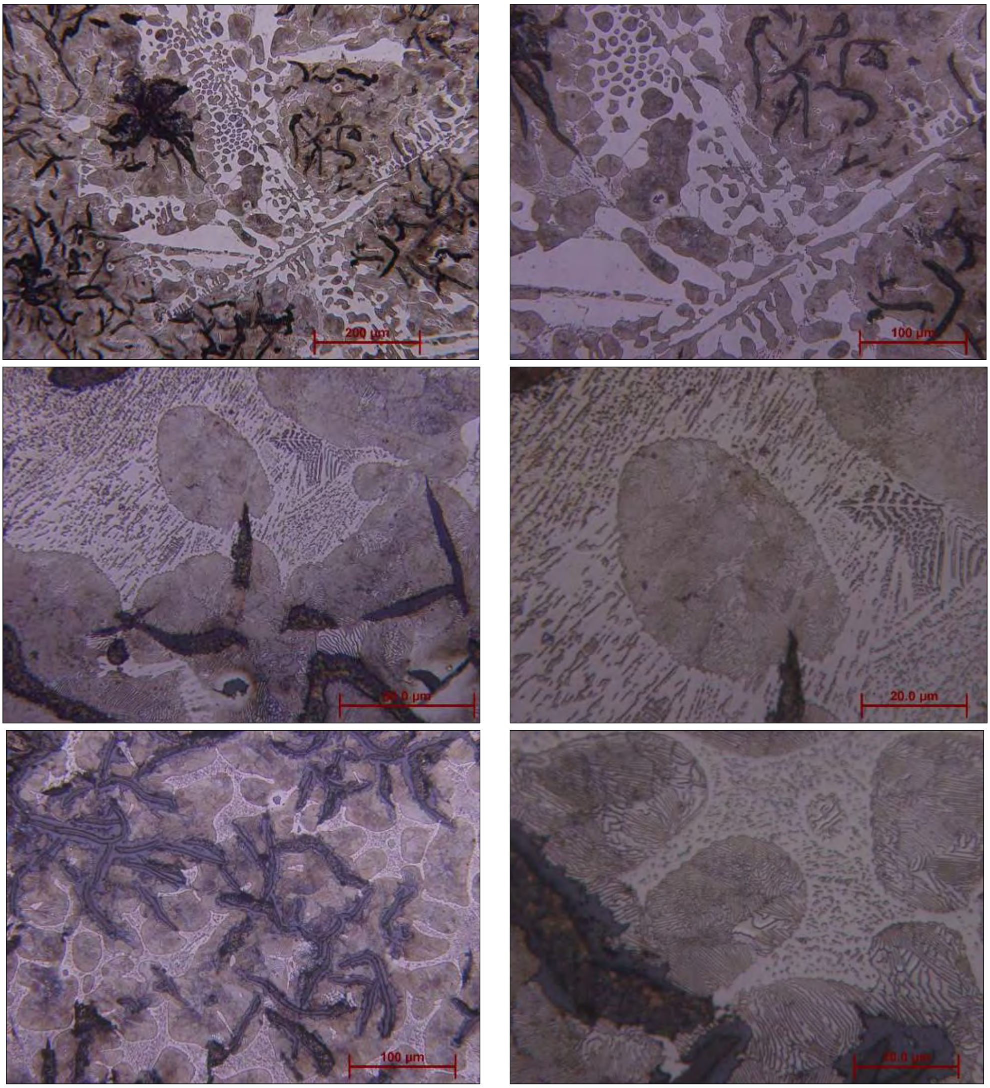
Etching with Nital elevated excellently the morphological characteristics of the iron-rich elements of the microstructure. From the images in **Figure 7.** of the molten material that is cooled down to eutectic temperature becomes austenite. The rest becomes ledeburite. Cooling must have been fairly rapid, which can be seen from the fact that the structure of the ledeburite, as well as that of the pearlite formed from austenite, is very fine.

4.3. Analysis of steel

From this sample a metallographic polish also prepared and analyzed in a polished state and after etching it with Nital. Microstructural images in **Figure 8.** show that the material of the sample suffered significant transformation after it was made into pig iron. The main characteristics of the formed microstructure are the following:

a) Along its thickness the material is segmented into zones with very different carbon content. In the parts with low C content only the boundaries of the ferrite grains were etched while the darker segments contain more C since the composition of the material in these segments is almost entirely eutectic. In **Figure 8.e** for example, 95% of all the constitutions are pearlite, while proeutectoide ferrite is only 5%.

b) The material is very significantly slaggy, slag enclosures are dense especially in strata close to the surface. However, in this zone close to the



a) b) c) d) e) f)

Figure 7. *Microstructure of the pig iron in polished state in the inside of the sample (a-b) and in the proximity of the corroded surface (c-d).*

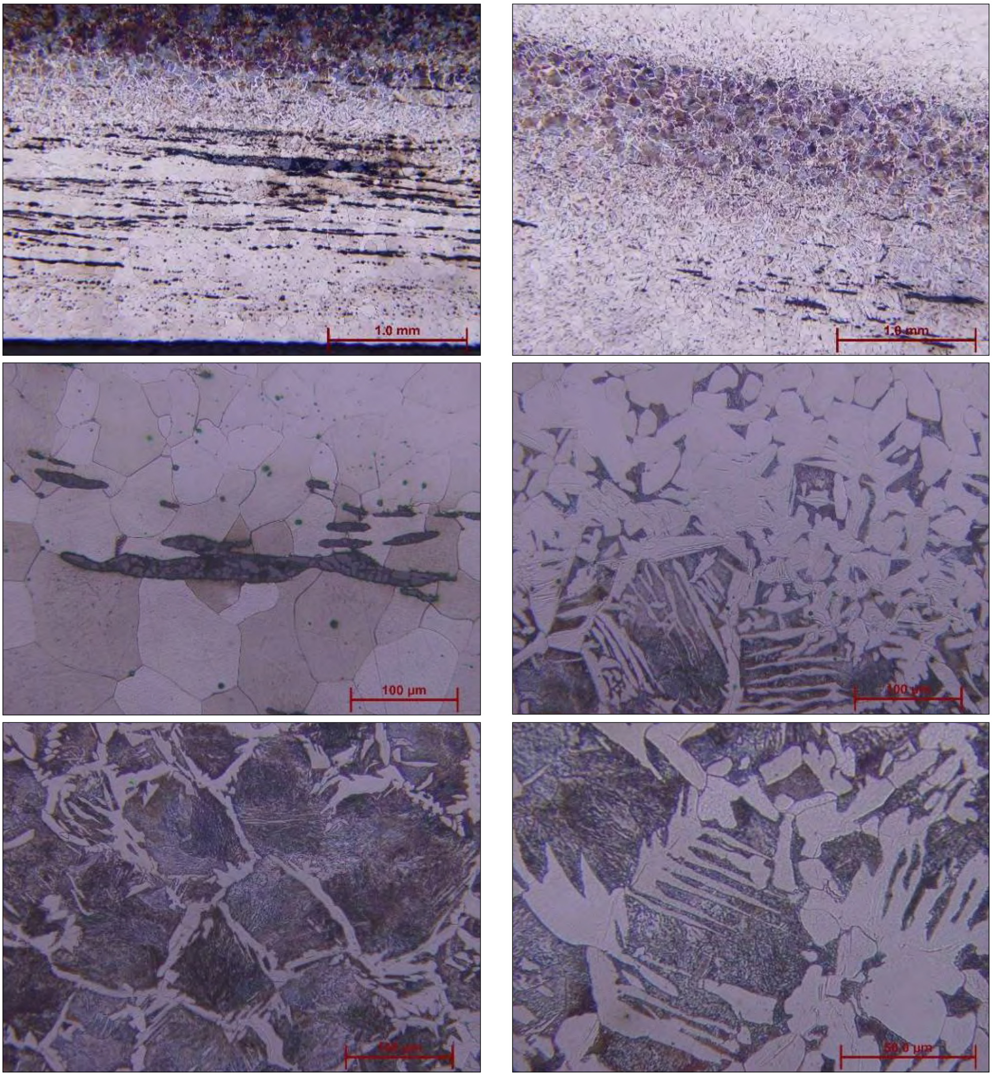
surface C-content is lower, 0.037% according to SPECTROTEST analysis. Besides carbon, Si, Mn and Sulphur was almost completely burned out, P content is also only 0.079%. The burning of the components and the high degree of slag inclusions shows that smithing was done at very high temperatures and with lengthy annealing, and that the surface could not be properly protected from oxidizing.

c) The extent of plastic deformation caused by the smithing process was significant.

d) The final heat treatment state in the decarbonized parts corresponds to complete annealing (**Figure 8.**c), while in the high C content strata of the 12 mm thick sample it corresponds to the acicular ferrite and fine plate pearlite structures that form as a result of a not too rapid cooling. In **Figure 9.**b the inner structure of a thick layer of slag is shown in polished (not etched) state.

5. Conclusions

This work is the first attempt at the reconstruction of the 16th century Mădăraș ironworks and the description of its products through methods of Material Science. Analysis shows that the used iron ore, the siderite wasn't the only mineral in a



a) b) c) d) e) f)

Figure 8. *Microstructure of the steel sample in the individual layers formed along its thickness (etchant: Nital-4)*

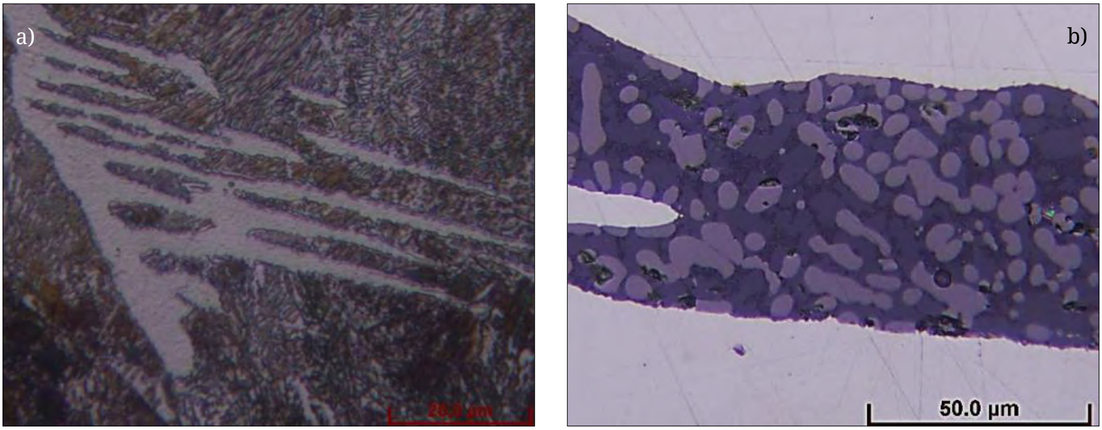


Figure 9. *a) Microstructure of the steel sample in high C content layers (etchant: Nital-4), b) Microstructure of the slag enclosure in polished state*

complex ore but it appeared alongside andesite tuffs, limestone, dolomite, crystallized slates etc. These are the sources of the chemical elements that make the composition of the Mădăraș iron unique.

Analysing the composition and structure of the residues shows that by modern standards, the steel products of the ironworks were characterised by significant inhomogeneity. This obviously had an influence on the mechanical properties of the products but it's very likely that the technologies of that age didn't allow for a better quality material in mass production.

During the ironworks' 170 year lifespan a significant amount of slag was accumulated containing precious elements (Zn, Ni, Sb etc.). Extracting those could be a timely task.

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