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A possible medieval recycling technique – smelting iron using hammerscale

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A possible medieval recycling technique – smelting iron using hammerscale

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Abstract. Hammerscale is a common by-product of the forging process of iron and it may appear in a large amount in the ancient smithy workshops as well. Its recycling (i.e. re-smelting) in early bloomery furnaces might have been an economical and reasonable process, although it is not known whether it works or not, and also there is no archaeological evidence for this technique. In our recent investigation, flaky hammerscale was smelted using the copy of the 8-10th century embedded furnaces of the Avars and the conquering Hungarians. The resulting bloom was processed to a billet and its chemical composition was further examined. Hammerscale proved to be an excellent raw material for the early bloomery iron smelting technology: good iron yield could be achieved due to the high reaction surface and iron content. Moreover, the extracted bloomery iron had low carbon content and had a very low amount of undesirable impurities, e.g. P, As. Cu, S. etc.

1. Introduction

Hammerscale is a common by-product of the forging process of iron and its modern recycling by the steelmaking industry is well known: hammerscale or mill scale is reduced to sponge iron powder that can be used as raw material in the electric furnaces for steelmaking, eg. [1-3]. However, hammerscale may appear in a large amount also in ancient smithy workshops and its recycling (i.e. re-smelting) in early bloomery furnaces might have been an economical and reasonable process theoretically. It is not known whether it works or not, and there is no archaeological evidence for this technology. This paper shows the results of smelting experiments of hammerscale to describe its use in the archaeometallurgy of iron.

1.1. General characterization

Most studies basically distinguish between two forms of appearance, the flaky and the spheroid hammerscale. Flaky hammerscale forms in the forge fire during the heating of the workpiece in oxidizing atmosphere and at high temperature. The oxidation of the surface becomes faster after the hot workpiece is removed from the forge fire for further hot working, e.g. hammering, so flaky hammerscale forms mostly in this stage of the process. Most sources agree that spheroidal hammerscale is produced mainly during forge-welding [4,5]. Here it should be noted that the formation method of flaky and spheroid hammerscale depends on the temperature. Under its melting point (ca. 1300°C) a thin layer of solid hammerscale covers the surface of the workpiece due to the frontal oxidation (the oxidation of the workpiece can be frontal and inter granular). This brittle, solid hammerscale cracks and falls off the workpiece during its plastic deformation. Over the melting point of the hammerscale the steel workpiece starts to burn and in the beginning small sparks (which are burning steel particles or grains) are rejected. Later if the temperature is increased and/or the atmosphere turns more oxidizing, the sparking of the workpiece intensifies. When the hammerscale is molten, it can drip down into the forge fire during the heating process, or slip off from the surface of the workpiece during hammering, e.g. in case of forge welding. Molten, slipped off hammerscale takes the form of a sphere due to the surface tension (see figure 1. later). In a smithy workshop, flaky hammerscale appears in much larger quantities than spheroidal hammerscale.

Several studies deal with the typology of hammerscales mainly on the basis of their morphology and shape. McDonnel examined samples of hammerscale with SEM-EDS and identified two general shapes: flakes and spheroids. The microstructures of both types were similar, however the spheroids were often hollow and contained more phosphorus. It is suggested that the spheroid hammerscale formed during the forge welding process where flux (mainly sand) has an important role in their formation [6]. Hammerscales from smithy workshops of the Roman period in Britain were examined and classified by Allen (Awre, Gloucestershire) [7] and by Sim (Silchester, Hampshire) [8]. Allen identified twelve types of hammerscales on the basis of their shape and size. Although numerous examples of spheroid or droplet-shape hammerscales have been found as an evidence of the purification process of the bloom or semi-finished iron product, the most common shape was the flake. Dungworth and Wilkes discuss in detail in their summary study, illustrated by a large number of SEM images and results of EDS examinations, the characteristics of the hammerscales in terms of both the archaeological finds and the hammerscales produced by reconstruction experiments. In addition to the two general types of hammerscales mentioned above, a third type is also defined, the so-called miscellaneous hammerscale. It accounts to less than 10% of the total amount of hammerscale collected by them, has very variable shapes and sizes but many consist of half spheroids or sheets with a rather bubbly texture on one surface. It was found that hammerscale samples usually have relatively large equiaxed iron oxide grains with a small amount of silica along grain boundaries. The layers of flaky hammerscales indicated several periods of heating before the flake became detached. The spheroidal hammerscale has a more variable microstructure than the flakes but most commonly this consists of a hollow spheroid [4].

1.2. Chemical and mineral composition

Hammerscale has a mineral composition of mainly iron oxides in the mineral form of magnetite (Fe_3O_4) which causes a notable magnetic character [1, 4]. The formation of hammerscale starts at temperatures between 500-600°C and becomes more rapid at around 800°C. Its structure is generally characterized by a layer of wüstite (FeO), sticking to the hot iron workpiece, a thicker central zone of Fe_3O_4 (magnetite) and sometimes an outer, very thin, easily flaked layer of Fe_2O_3 (hematite).

The chemical composition of hammerscale depends on the stage of the iron purification process and no sharp line can be drawn between slag and hammerscale. During the medieval bloomery iron smelting process high amount of slag forms from the unreduced iron oxides and gauge of the ores (mainly SiO_2, little CaO, Al_2O_3, etc), this slag may contain very little amount of magnetite, it consists mainly of fayalite ($2FeO•SiO_2$) and glassy phase. After the smelting process the spongy iron bloom is compressed and forged. During this compressing process slag (it is still rather slag than hammerscale) melts off from the bloom into the forge fire and also splashes off during compressing and later at the forging phase as well. The relative iron content of the slag increases during this process, i.e. its wüstite (FeO) and magnetite (Fe_3O_4) content increases, while the SiO_2-content and the amount of other alkaline compounds decreases. Finally, in case of the forging of a compact iron bar almost pure iron oxide, hammerscale forms. Hammerscale may contain residues of flux that may be applied for forge-welding (e.g. pure quartz, SiO_2) and elements that burned off from the surface of modern alloyed steel materials (e.g. Mn). In Sim's extensive survey (1998), 17 different samples of hammerscales from bloom purification, forging and welding were demonstrated. These were archaeological finds and results of reproduction experiments and modern processes. Chemical analyses of the experimentally produced hammerscales revealed that silica content decreased as iron was refined from the state of bloom towards a workable product and higher iron oxide content could be detected in the stage when well-refined billets were manufactured [8].

1.3. Archaeological background

Hammerscale is usually unearthed in iron-related archaeological excavations and may provide important information regarding the function of the excavated archaeological feature. According to Pleiner, iron losses of 3-4 % could be expected in a single heating, and even a higher percentage in longer and higher temperature heating [9]. The ferromagnetic property of hammerscale may help to identify forging operations during the archaeological excavation. In some sites of ancient and medieval forges, hundreds or even thousands of grams of hammerscale have been found. On the excavation site, the location of hammerscale can also help to locate the smithing activity precisely because it is often found in the immediate vicinity of the smithing hearth and anvil.

In the archaeological excavations, hammerscale is one of the most important evidence of iron smithing activity. However, it is often too small to be noticed during unearthing but can be detected using a magnet. The surface of the floor of a smithy workshop should be sampled throughout at 0.2–0.5m intervals in order to examine the distribution of hammerscale. 0.2 litres of sample is adequate for magnetic the susceptibility screening and quantification of hammerscale [10].

In the literature of archaeometallurgy there are numerous studies of hammerscale found mainly in Roman smithy workshops. One of the earliest (1941) identifications of hammerscale in the archaeological papers comes from the excavation report ("…the material is the magnetic oxide of iron, Fe_3O_4, containing ferrous oxide in considerable amount and some metallic iron. There can be no doubt that it is a mill-scale or smithy scale…") of the Roman fort of Benwell on Hadrian's Wall [11]. A good example is the Roman smithy workshop at Nailly in France, where the magnetite layer of the examined samples of hammerscale pieces was covered by a thin layer of hematite or fayalite [9].

An analysis of a sample of hammerscale from a Roman iron smelting workshop of Ashwicken (England) showed more than 85 % magnetite and the rest of the material was fayalite in the form of a thin cementing layer [12]. Tylecote identified hammerscale as a by-product of forging including different iron oxides (wüstite, magnetite and hematite) covered by a cementing film of silica originating from the slag inclusions of the bloom and from the sand used as flux [13].

2. Methods and results

2.1. Investigations of hammerscale

Hammerscale was collected in the smithy workshop of Ádám Thiele, where ca. 40 kg of hammerscale accumulates each year as a by-product of forging axes, knives, etc. This hammerscale was flaky for the most part and it contained spheroidal hammerscale only in traces. The chemical composition of the hammerscale was analysed by the means of wavelength-dispersive X-ray spectroscopy (type S8 TIGER) in the Dunaferr Labor Nonprofit Ltd. The result for the main oxides are summarized in table 1.

Table 1. Main oxides of the hammerscale (wt%).

Fe_2O_3	SiO_2	Al_2O_3	CaO	MnO	MgO	K_2O	Na_2O	P_2O_5
87.9	6.11	2.16	0.54	0.7	0.21	0.15	1.08	0.28

The hammerscale collected from the floor of the smithy workshop was not pure iron oxide, its iron content calculated to hematite (Fe_2O_3) was 87.9 wt% (which means 56 % of elemental iron). High SiO_2 and Al_2O_3 content may be caused by the clay minerals coming from the mud brought on the shoes into the building of the workshop. High Na_2O content could be explained by the use of borax, sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) as flux for forge welding. The relatively high MnO content could come from the Mn alloyed structural and tool steels that are mainly forged in the workshop (S235 and 90MnCrV8**,** both have a Mn content of ca. 1.5-2 wt%). The weight percent of other oxides were under 0.5 wt%.

Macro photos and SEM micrographs were made of flaky and spheroid hammerscale. The spheroid hammerscale samples (cf. figure 1) were produced for this investigation only. The burning steel workpiece was removed from the fire, and the showering sparks were collected into a simple tin can. The hollow spheroid hammerscale grains had a diameter of ca. 20-80µm (see figure 1/B).

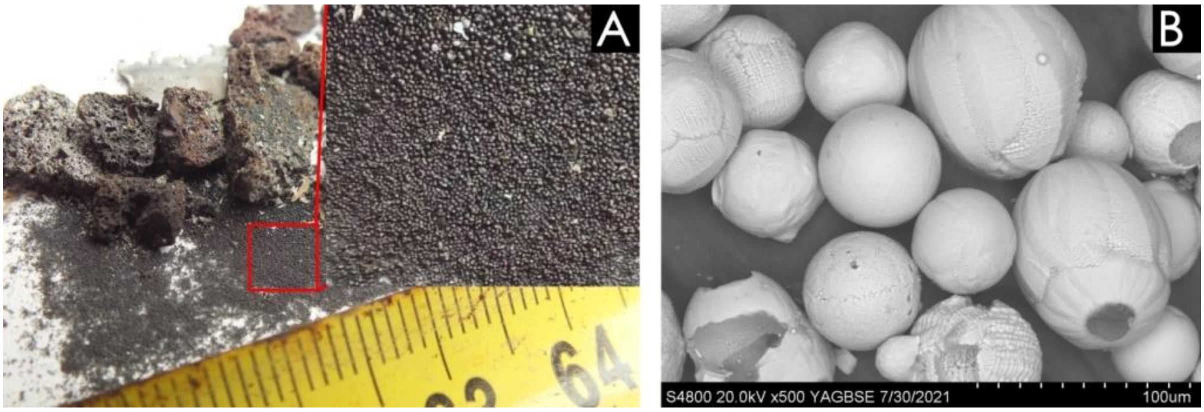

Figure 1. Marco photo (A) and SEM micrograph of hollow spheroid hammerscale (B).

A more detialed SEM-EDS examination has also been carried out on some samples of flaky hammerscale (figure 2/A) on which Zeiss EVOMA10 electron microscopy equipped with EDAX energy dispersive spectroscopy was used. The measured thickness values of 150-350 µm of the cross sections (figure 2/B and C) are in line with the thickness of the layers of hammerscales mentioned by Dungsworth and Wilkes [4]. In figure 2/D a layered structure of the cross section can be observed clearly. In most cases of the examined samples the two sides could be distinguished by their colour: on the grey side (figure 2/E and F) only iron oxide could be measured by EDS while on the black side hollow microstructures (figure 2/G) and special shaped formations (figure 2/H) could be observed at a higher magnification in some places. In the black side EDS examination resulted in 2.0-4.5 wt% Na. 1.5-2.5 wt% Si. 0.5-0.6 wt% Ca and 3.2-3.6 wt% Mn probably originated from the flux and/or slag.

2.2. Experimental smelting of hammerscale

The hammerscale was smelted using the copy of the 8-10th century embedded furnaces of the Avars and the conquering Hungarians. The experimental furnace was built in a steep hillside of a clay-sand mixture. Its height was 75 cm above the level of the twyer (shaft) and its depth was 25 cm under the twyer (hearth). The biggest inner diameter of the furnace at the level of the twyer was 35cm. The furnace was closed with a breast wall during smelting. For thermal insulation, earth dust was heaped into the lower part of the furnace to increase the temperature of its hearth. Air was supplied (ca. 150 litre/min) through the twyer using a centrifugal fan chocked with a piece of paper. A slag tapping hole was punched through the breast wall under the twyer for slag tapping if necessary. Fig 3 shows the structure and main parts of the experimental furnace.

In the beginning of the smelting experiment the furnace was preheated for 30mins by burning smaller wood branches. Then the furnace was filled up with charcoal and preheating was going on for an additional 15 mins. The charcoal used for the experiment was made from oak and beech wood and its grain size was between 5-40 mm (charcoal was broken into smaller pieces and then the powder was shifted). In the next 2 hours and 45 mins hammerscale and charcoal was charged into the preheated furnace in 300g portions, so their ratio was 1:1 during the smelting process. 12.5 kg hammerscale was smelted in total. Before the first charge of the hammerscale, 14 kg of charcoal was used (ca. 11kg to fill up the furnace and 3kg for preheating). After the opening of the furnace, 6 kg glowing charcoal was collected and cooled down, thus saved for a next smelting. 20.5 kg charcoal was used altogether. During the smelting process the twyer was clean, and no solid slag block choked the air supply in front of the twyer.

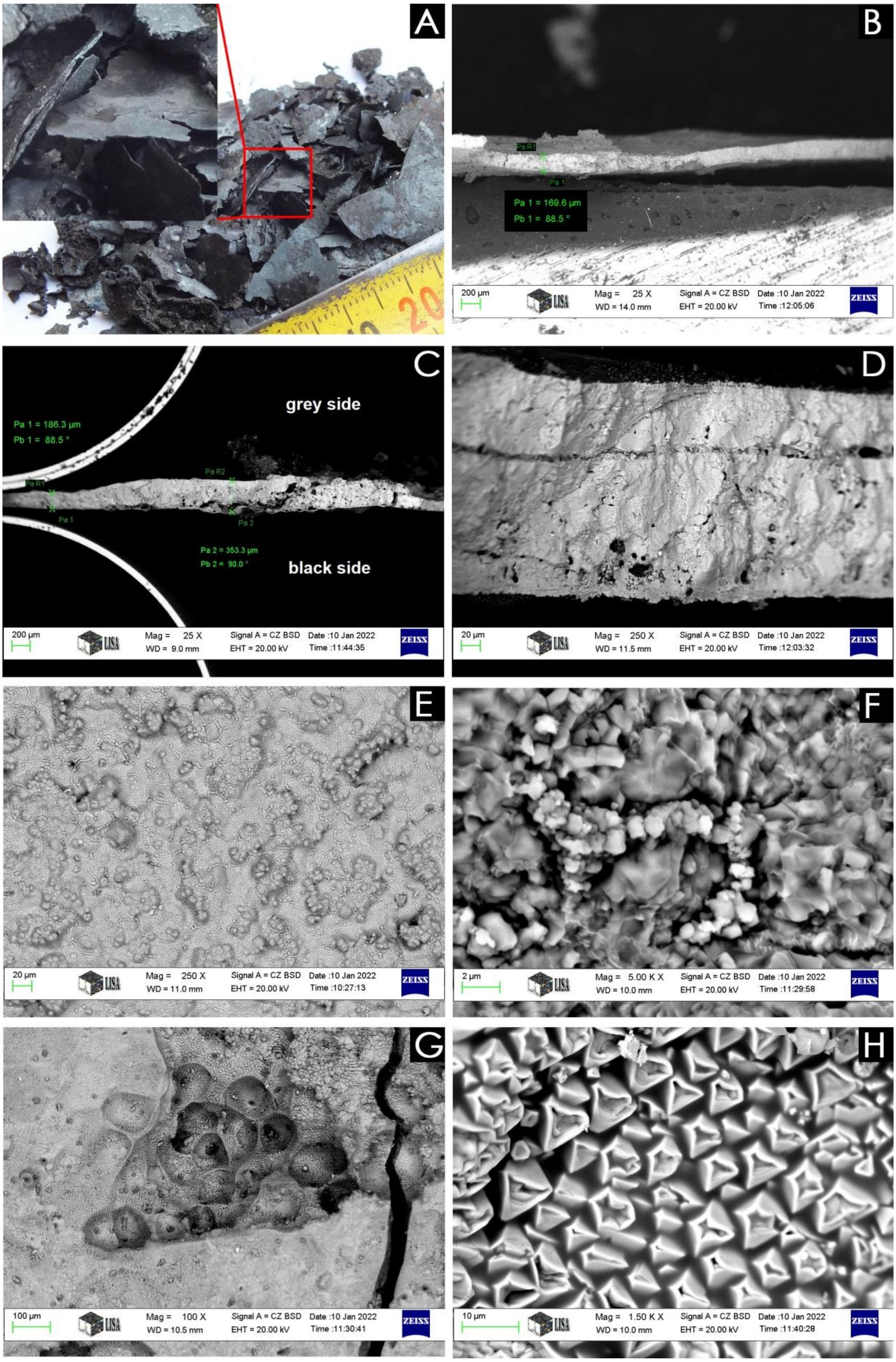

Figure 2. Marco photo (A) and SEM micrographs of flaky hammerscale (B – H).

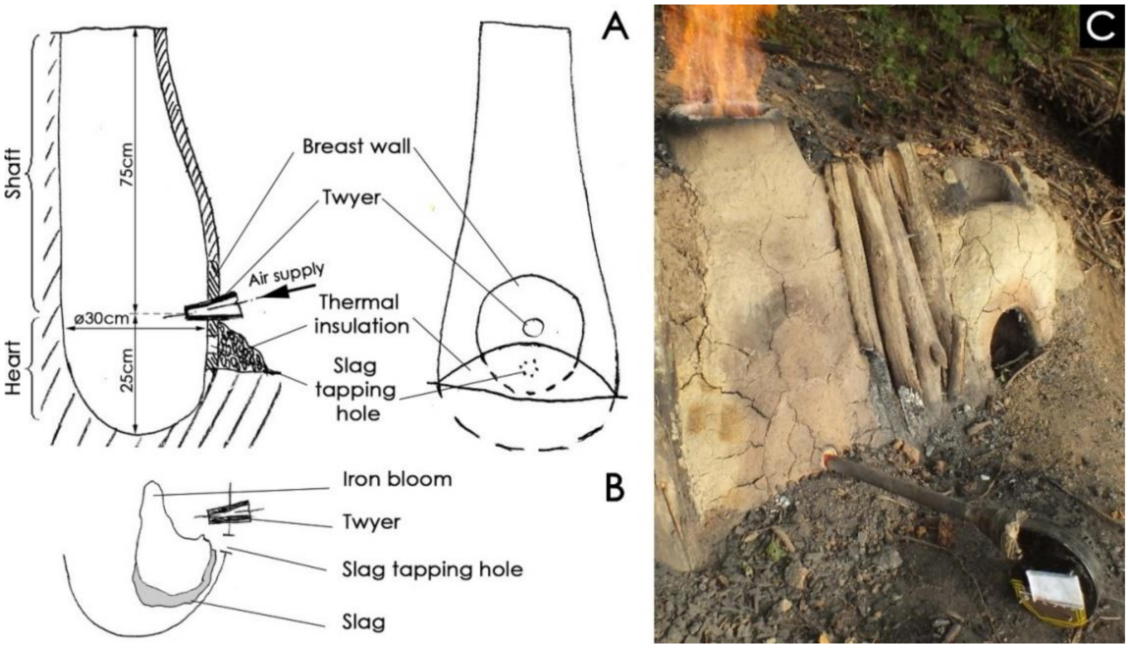

Figure 3. The structure and main parts of the experimental furnace. Schematic sketch of the furnace (A). Shape and position of the bloom at the end of the smelting process (B). Photo of the furnace (C).

The first slag tapping was needed 15 mins after the last hammerscale portion was charged and the slag was tapped three times ca. every 10 mins. The tapped slag weighed 2.3 kg in total. The tap slag had low viscosity at lower temperature (on red glow) as well, it had a narrow solidification range, so it was not glassy and sticky, its fracture surface was greyish black with a few bubbles. So, it was very easy to tap the slag of the hammerscale. For comparison, the tap slag of iron ores with low iron and high silica content is usually glassy, has high viscosity, a wide solidification range, its fracture is greenish black, contains much more bubbles and sometimes also pure quartz particles (white, marked with a red arrow, cf. Fig 4/B) visible with the naked eye. This kind of slag is hard to tap and usually marks a poor-quality bloom. Figure 4 shows the fracture surface of a tap slag sample of the hammerscale and a slag sample of a kind of bog iron ore (from Bátorliget, Hungary, Fe_2O_3=57%, SiO_2=28.4%, Al_2O_3=2.72%, CaO=2.81%, MnO=3.29% and P_2O_5=3.67%) smelted under the same conditions.

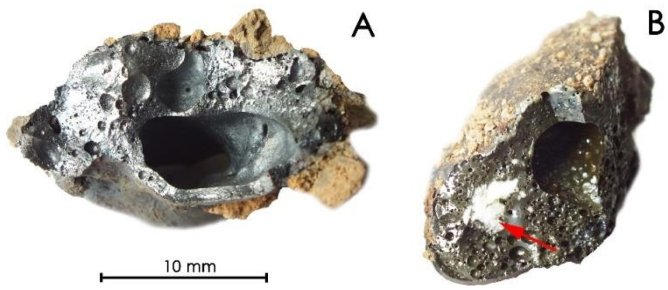

Figure 4. Fracture surface of a tap slag sample of hammerscale (A) and of bog iron ore with high silica content (B).

The smelting was ended, and the breast wall of the furnace was opened 45 mins after the last hammerscale portion was charged (so the smelting took 4 hours and 15 mins altogether). The iron bloom was unusually high, it towered ca. 10-15cm above the level of the twyer and it had an "L" shape with a spongy top and denser bottom. There was a little slag block glued to the bottom of the bloom (the slag block is usually bigger if the smelted iron ore has a lower iron content or is under-reduced in the furnace). Then the iron bloom was removed and compressed on a wood log with a wooden hammer. The bloom weighed 3.9 kg after this first compression. The slag block that broke to pieces weighed ca. 1.4kg.

A short video about this smelting experiment: https://youtu.be/UP8Dwi8JD30

2.3. Processing the iron bloom

After the first compression, the bloom was reheated in a charcoal fuelled smithy hearth (similar to the 8-10th century ones unearthed in excavations), and compressed further with wooden tools five more times. The compressed bloom weighed 2.8 kg. Using a power hammer and a modern coke-fuelled smithy forge fire, this bloom was forged into a 210 mm long and 60x20mm cross sectioned billet, which finally weighed 1.85 kg. There was no metallic iron loss during this forging step and the iron bloom was easy to forge, brittleness was not observed (bloomery iron smelted from bog iron ores rich in phosphorus or arsenic or copper-rich mineral ores usually shows hot-shortness and also cold-shortness).

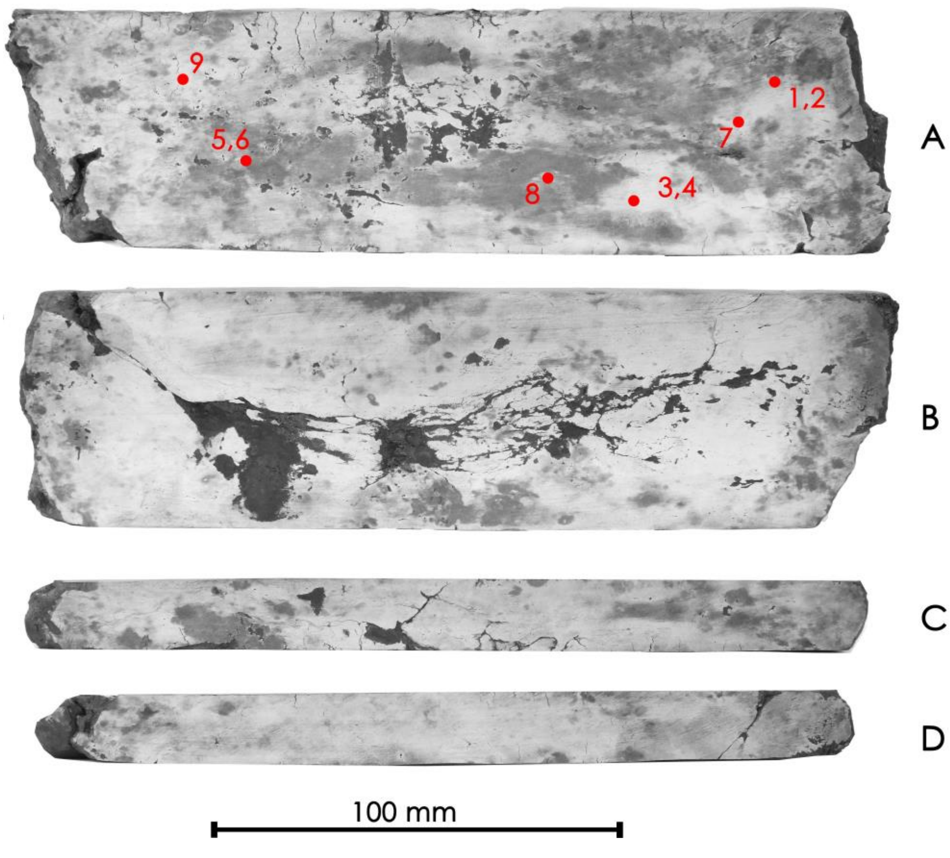

Figure 5. Four sides of the 10% nital etched billet.

The four sides of the billet were then grinded and etched using 10 % nital macro etchant to make the carbon distribution visible. The etched billet can be seen in figure 5. Based on the etched surface, it can be stated that the carbon distribution is very heterogeneous and carburized parts appear mainly on the first side (figure 5/A). So, the bloomery iron material extracted from hammerscale had low carbon content, it can be qualified rather iron than steel (several similarly etched bloomery iron billets were examined earlier by the means of Glow Discharge Optical Emission Spectrometry (GDOES) method, and the carbon content corresponds to the darkness level of the etched surface [14]).

An Oxford Instrument portable X-ray fluorescence spectrometer (50 kV, Rh anode, Silicon Drift Detector, Measurement time: 30 sec.) has been used for the ED-XRF examination (the analyzed points are marked in red in figure 5/A). Fundamental parameter (Alloy FP) methods use a complex mathematical analysis to calculate the concentrations of elements (from 0 wt% to 100 wt%) in the sample. For metals with inherently unknown composition, such as excavation finds and products of reproduction experiments, it is recommended to use this method. Low alloy method includes the light elements as well. ED-XRF analysis results (summarized in table 2) suggest that the bloomery iron material contains a very small amount of alloys, it is unalloyed iron with a definitely low carbon content.

Table 2. P-XRF analysis results (wt%).

Nr.	Class	Al	Si	P	S	Ti	Cr	Mn	Fe	Ni	Cu	Mo
1	Low alloy	0.13	0.21	0.05	0.08	0.04	0.01	0.02	98.85	0.11	0.33	0.04
2	Alloy_FP					0.00	0.05	0.03	99.36	0.13	0.29	0.03
3	Low alloy	0.18	0.18	0.05	0.09	0.04	0.01	0.02	98.85	0.16	0.49	0.06
4	Alloy_FP					0.00	0.06	0.02	99.16	0.18	0.43	0.06
5	Low alloy	0.39	0.50	0.06	0.10	0.03	0.06	0.03	98.81	0.17	0.49	0.05
6	Alloy_FP					0.00	0.10	0.04	99.04	0.20	0.47	0.05
7	Low alloy	0.18	0.32	0.09	0.10	0.00	0.01	0.02	98.93	0.23	0.40	0.04
8	Low alloy	0.19	0.27	0.04	0.11	0.01	0.02	0.02	98.75	0.35	0.59	0.05
9	Low alloy	0.41	0.60	0.06	0.10	0.02	0.02	0.02	98.96	0.12	0.41	0.05

3. Discussion

Experimental smelting results suggest that hammerscale is not only a suitable but an excellent raw material for the early bloomery iron smelting technology. Firstly, flaky hammerscale has a high reaction surface due to its low thickness. However, the several mm width of the flakes prevents its fast sinking in the furnace and provides a longer time for reduction and does not choke the air flow in the furnace (dusty iron ores are not suitable for iron smelting). Secondly, hammerscale has a high iron content so a good iron yield could be achieved. This statement is supported by the small amount of slag (small slag block, little tapped slag) and the heavy bloom. The iron yield calculated from the weight of the compressed bloom is 22.4%, while from the iron billet it is 14.8%. And thirdly, hammerscale has low P, As, Cu, S, and other undesirable impurities that would have a detrimental effect on the mechanical properties of the bloomery iron.

Ancient smiths sometimes worked with bloomery iron that had high P and As content, also Cu might appear in much higher weight percent than in case of modern steels. All these elements caused cold and/or hot shortness, so their presence reduced the workability of the bloomery iron. However, we did not examine the hammerscale of these kind of bloomery iron materials with impurities (the enrichment of these elements in hammerscale could be a good question), but we can state that bloomery iron smelted from hammerscale with low P, As and Cu content could have been a very good raw material for the ancient smiths. This kind of bloomery iron could have had more or less carbon content depending on the smelting technology and could possibly have been a suitable raw material for a wide range of tools and weapons.

The hammerscale we used in our experiment provided just enough slag for a compact bloom to form. The suitable amount of the slag is important during iron smelting because in the hearth of the furnace, it helps the diffusion welding of the iron particles reduced from the iron oxides in the shaft. Smelting experiments with pure industrial 0.3-5 mm grain sized hematite (Brazilian hematite from the ISD Dunaferr company, Fe_2O_3 = 97.9 wt%, SiO_2 = 1.3 wt%, Al_2O_3 = 0.62 wt% and CaO = 1.01 wt%) resulted in huge but very spongy iron blooms without slag. It was not possible to compress and forge these blooms because it broke into pieces due to the poorly diffusion welded iron particles. But charging sand (consisting mainly of quartz) to the pure hematite in a ratio of 1:6 provided enough slag, i.e. sand acted as flux for the diffusion welding of the iron particles. The flaky hammerscale collected from the floor of the smithy workshop had just enough flux (mainly simple mud powder) to get the suitable amount of slag and a dense bloom without decreasing the iron yield too much. But in case of smelting pure hammerscale that contains only iron oxides, charging some kind of flux (e.g. sand. dusty clay. wood ash. broken tap slag. etc.) might be necessary.

As hammerscale may have appeared as a large amount of by-product in a smithy workshop where bigger iron workpieces were processed for a longer period of time, the recycling (i.e. re-smelting) of the hammerscale in bloomery furnaces might have been an economical and reasonable process. There is no archaeological evidence of the extent to which this raw material was used in any of the historical iron smelting workshops, but the re-smelting of the hammerscale was theoretically and practically feasible. On the other hand, this recycling process suggests that the site of forging was close to, or at least in contact with, the smelting sites.

4. Conclusions

The results of reconstruction experiments and material examinations reveal that flaky hammerscale is an appropriate and self-fluxing raw material for the iron smelting process of the ancient bloomery. Good iron yield could be achieved due to the high reaction surface and iron content. The extracted bloomery iron had low carbon content and had a very low amount of undesirable impurities, e.g. P, As, Cu, S, etc.

References

[1] Martin M I, Lopez F A and Torralba J M 2012 Production of sponge iron powder by reduction of rolling mill scale *Ironmak. Steelmak.* **39(3)** 155–162
[2] Camci L, Aydin S and Arslan C 2002 Reduction of ion oxides in solid wastes generated by steelworks *Turk. J. Eng. Environ. Sci*. **26** 37–44
[3] Park J-W, Ahn J-C, Song H, Park K, Shin H and Ahn J-S 2002 Reduction characteristics of oily hot rolling mill sludge by direct reduced iron method *Resour. Conserv. Recycl.* **34(2)** 129–140
[4] Dungworth D and Wilkes R 2009 Understanding hammerscale: the use of high-speed film and electronmicroscopy *Hist. Metall*. **43** 33–46
[5] Veldhuijzen H A 2009 Of Slag and Scales; Micro-Straigraphy and Micro-Magnetic Material at Metallurgical Excavations UCL Institute of Archeology
[6] McDonnell G 1984 The study of early iron smithing residues *Crafts of the Blacksmith* ed Scott B G and Cleere H (Belfast: UISPP) pp 47–52
[7] Allen J R L 1986 Interpretation of some Romano-British smithing slag from Awre in Gloucestershire *Hist. Metall*. **20** 97–104
[8] Sim D 1998 *Beyond the Bloom. Bloom refining and iron artefact production in the Roman world* BAR International Series 725 (Oxford: Archaeopress)
[9] Pleiner R 2006 Iron in Archaeology. Early European Blacksmiths. *Archeologicky Ústav* AV ČR. Praha pp 110–1
[10] Bayley J, Dungworth D and Paynter S 2001 *Archaeometallurgy* (London: English Heritage Publications) p 6
[11] Simpson F G and Richmond I A 1942 The Roman Fort on Hadrian's Wall At Benwell *Archaeologia Aeliana* **19** 1–43
[12] Tylecote R F and Owles E 1960 A second-century iron smelting site at Ashwicken. Norfolk. *Norfolk Archaeology* **32** 142–162
[13] Tylecote R F 1962 *Metallurgy in Archaeology* (London: Edward Arnold) p 45
[14] Thiele Á, Török B Controlling possibilities of the carbon content in the iron bloom during the iron smelting. 5th International Conference on Archaeometallurgy. Hungary. Miskolc. 19-21th June. 2019 (poster)

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