THE ROLE OF PHOSPHORUS IN THE ARCHAEOMETALLURGY OF IRON

Summary of the PhD theses

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This dissertation, the comments of the reviewers and the log recorded on the defense are on show in the Dean's office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics

V. Kercsmár, Zs; **Thiele, Á**.: A belső-somogyi gyepvasércek genetikája és geokémiai jellemzői, földtani és archeometallurgiai megközelítés alapján / Genetic types and geochemistry of bog iron ore deposits from Inner Somogy, from a geological and archaeometallurgical perspective, Földtani Közlöny, (in press)

VI. **Thiele, Á**; Török, B.; Költő, L.: Energy dispersive X-ray analysis (SEM-EDS) on slag samples from medieval bloomery workshops – the role of phosphorus in the archaeometallurgy of iron in Somogy County, Hungary, Proceedings of the 39th International Symposium for Archaeometry, Leuven (2012), Eds: Rebecca B. Scott, Dennis Braekmans, Mike Carremans and Patrick Degryse, pp. 102-112

VII. **Thiele, Á**.; Hošek, J.;Kucypera, P.; Dévényi, L.: The role of pattern-welding in historical swords – mechanical testing of materials used in their manufacture, Archaeometry, (in press)

VIII. **Thiele, Á**.; Hošek, J.: Estimation of phosphorus content in archaeological iron objects by means of optical metallography and hardness measurements, Acta Politechnica Hungarica, (in press)

IX. **Thiele A**., Hošek J., Haramza M., Török B.: Revealing the surface pattern of medieval pattern welded iron objects – etching tests conducted on reconstructed composites, Archeologica Technica, (in press)

X. **Thiele, Á**.; Hošek, J.:Mechanical properties of medieval bloomery iron materials – comparative tensile and Charpy-tests on bloomery iron samples and S235JRG2, Periodica Politechnica – Mech, (in press)

Introduction

Archaeometallurgy is the interdisciplinary study of the historic production and processing of metals. During my previous research on the medieval iron smelting technology of the Carpathian basin it was evidenced that phosphorus had an important role both in the smelting and the processing of iron. I study the role of phosphorus in these two interpretations in my dissertation.

Phosphorus rich bog iron ores were often smelted in Europe in the Middle Ages, therefore there was a high risk of the production of phosphorus rich bloomery iron, whose hot- and cold-shortness restricted its use for the contemporary iron industry. Thus the question arises whether the medieval iron smelters in the Carpathian basin also encountered this technological problem, and if so, what solutions they found. In Chapter I of my dissertation I examine this issue in relation to Somogy county (Hungary), which was one of the bloomery centres in the Avar and Conquering Ages.

Phosphorus rich bloomery alloys were widely processed in the Middle Ages for a special purpose. This so-called phosphoric iron with weak mechanical properties was used in the production of pattern welded, ostentatious knife and sword blades, famous for their excellent mechanical properties. In Chapter II of my dissertation I try to establish the role of phosphoric iron in pattern welded blades.

The role of phosphorus in archaeometallurgy of iron in the Avar and conquering age in Somogy

Archaeological background

Several bloomery workshops have been excavated in Hungary in the recent decades. One of the most important iron smelting centres was in Somogy county (South-Western Hungary), where the remains of Avar and conquering age bloomery furnaces were found in 8 archaeological sites altogether.

There were two main bloomery furnace types used in the medieval Somogy; the free standing Avar- or nemeskéri-type was used by the Avars, while the embedded fajszi-type built into the side wall of a workshop pit was used by the conquering Hungarians.

Experimental background

I carried out several smelting experiments (see figure 1) using the embedded fajszi-type bloomery furnace, smelting phosphorus rich bog iron ores mined in the Nyírség (Eastern Hungary) and phosphoric iron (iron blooms of over 0.1wt% phosphorus content) were resulted. Hot shortness was a characteristic feature when phosphorus solved over ca. 2wt% due to the Fe-Fe3P eutectic appearing on the grain boundaries. This eutectic melted on the forging temperature of 1100-1300°C. Iron blooms could be processed when the phosphorus content was lower than 2wt% but cold shortness was observed.

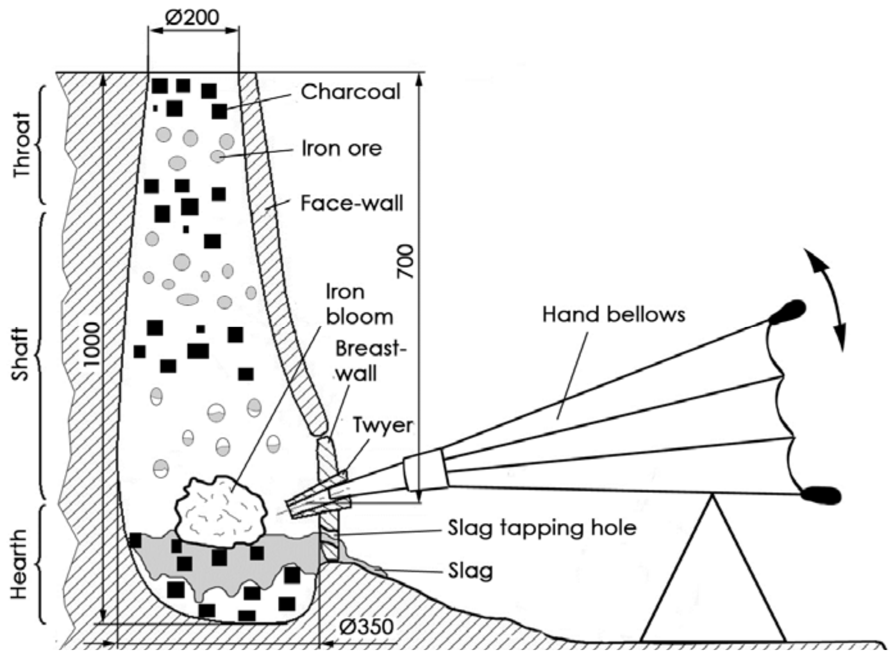

Figure 1: Fajszi-type furnace used in the smelting experiments and the terminology

Possible applications of the results

First of all, the importance of the results is represented in the field of the history of technology.

Furthermore, I see the applicability of the results in education, such as in the BSc course of "Archaeometallurgy" and the supplementary MSc specialisation of "Archaeometallurgy" at the Technological Materials Science faculty of the University of Miskolc, and in the PhD course unit of "Reconstructional Archaeometallurgy" at the Kerpely Antal Materials Science and Technology Doctorate Course.

Thirdly, the results may be applied in the field of tourism. Acknowledging the spectacular and humane nature of the medieval iron industry, numerous open-air museums display medieval iron culture as a permanent or temporary programme. The foundations of such a permanent display site have been laid in Ózd and in Somogyfajsz, promoting the tourism of both economically disadvantaged regions.

Publications

I. **Thiele, Á.**; Török, B. 2011: Vastermelés, vaskihozatal és a kohósított gyepvasércek minimálisan szükséges vastartalma az avar és Árpád-kori vasbucakohászatban / Iron production, iron yield and the minimal iron content of bog iron ores regarding Avar and Árpád-age bloomery iron smelting, Archeometriai Műhely, vol 8:(4), pp. 345-350

II. **Thiele, Á**. 2012: Smelting experiments in the early medieval fajszi-type bloomery furnace and the metallurgy of iron smelting, Periodica Politechnica – Mech. Eng. vol 54:(2), pp. 99-104

III. **Thiele Á**.; Dévényi, L. 2012: Modelling possibilities of the medieval bloomery process under laboratory conditions, Materials Science Forum, vol 729, pp. 290-295

IV. Török, B.; **Thiele, Á**. 2013: Smelting bog iron ores under laboratorial conditions – the role of phosphorus in the archaeometallurgy of iron in Somogy county, IOP Conference Series: Materials Science and Engineering, vol 47, 012034

on the mechanical properties. The reference material was the modern S235 steel. The most important characteristic values for strength, ductility and toughness were calculated from the results of Charpy- and tensile tests.
Methods of MCA (Multi Criteria Analysis) and AHP (Analysis Hierarchy Process) were employed to find the material preferences for medieval sword blades.

Theses

Thesis 3: Based on the results of SEM-EDS analysis of medieval pattern welded knife and sword blades, phosphoric iron of a phosphorus content of 0.4-1.4wt% was used in their manufacturing. This phosphoric iron was very brittle, characteristic values for ductility and toughness were very low; the average impact energy of KV=2J, the average absorbed specific fracture energy of W_c=20 J/cm^3, the average percentage elongation after fracture of A=5% and the average percentage reduction of area of Z=3% [VII, VIII, X].

Thesis 4: The technique of pattern welding employed in the manufacture of historical knife and sword blades – as opposed to the contrastive statements of several literatures and popular belief – does not have any important positive effects on mechanical properties. The function of pattern welding was rather decorative [VII-X].

> Based on the comparative mechanical testing of samples made on the basis of the archaeometrical investigation of medieval pattern welded knife and sword blades, the mechanical properties of pattern welded composites are much poorer than those of iron or steel. Characteristic values for ductility and toughness are the average of those of the base materials irrespective of the pattern.

Thesis 5: The best material combination for the pattern welded core of historical swords regarding the loads which they should resist was the phosphoric iron and the hardened and tempered steel [VII].

> This could be concluded by employing the methods of MCA and AHP on the results of comparative mechanical testing of pattern welded samples made of iron, steel (normalised and hardened and tempered state) and phosphoric iron on the basis of the archaeometrical investigation of medieval pattern welded knife and sword blades.

Aim of the research, questions

Questions arise based on the observations during the smelting experiments whether iron smelters met with the serious technological problem caused by phosphorus and if so, how they could solve it.

Investigated materials and applied methods

During field researches together with geologist Zsolt Kercsmár we mapped the bog iron ore deposits of Somogy and we found out that microbial bog iron ore lenses and their redeposited, enriched bog iron ore layers were the most important iron ore bases of the iron smelting of the contemporary iron industry. Samples were taken for further X-Ray fluorescence analysis.

Comparative archaeometrical investigations were carried out on tap slag samples from archaeological excavations and smelting experiments. I also investigated the effect of charging CaO during smelting experiments for decreasing the phosphorus content of the iron bloom.

Theses

Thesis 1: Bloomery iron of high phosphorus content could be extracted by the smelting of phosphorus rich bog iron ores in Somogy County (Hungary) in the Avar and conquering ages [I-IV].
This can be confirmed by the following conclusions:

- Microbial bog iron ore lenses and their redeposited, enriched bog iron ore layers, which were the iron ore bases of the iron smelting of the contemporary iron industry, had high phosphorus content of 3-7wt%, because bog iron ores of these with high surface area absorbed the phosphate ions solved in the water originating from the decomposition of the vegetation of the area;
- Smelting experiments carried out using these phosphorus rich bog iron ores resulted in phosphoric iron of P content of 0.9-4.5wt% with hot- and cold-shortness;
- Tap slag samples from the archaeological excavations of bloomery workshops from the Avar and conquering ages had a high average P_2O_5 content of 2-8wt%. The results of earlier archaeometrical investigations of iron blooms showed high P-content of 0.4-1.22wt% from the archaeological excavation of the bloomery workshop of Somogyfajsz.

Thesis 2: The phosphorus content of the iron blooms resulted by the smelting of phosphorus rich bog iron ores in Somogy County (Hungary) in the Avar and conquering ages was decreased by charging fluxes of high CaO content (such as limestone, bog iron ores with high CaO content or ash) in Somogy County (Hungary) in the Avar and conquering ages [IV-VI].

This can be confirmed by the following conclusions:

- High CaO content of 3-14wt% is a characteristic feature of bog iron ores of the uplifted area of Somogy County. Moreover, carbonate precipitations in the form of limestone lumps and layers can be observed in the area.
- Charging CaO in 1/10 and 2/10 weight ratio of CaO/roasted bog iron ore during the experimental smelting of phosphorus rich (P_2O_5 = 7wt%) bog iron ore from a bog iron ore deposit of high archaeometallurgical importance decreased the P content of the iron bloom from 4.5wt% to 0.9wt% and under the detection limit of 0.1wt%. This means that bloomery iron with low P content and acceptable mechanical properties could be produced by the smelting of P rich bog iron ores.
- Tap slag samples from the archaeological excavations of bloomery workshops of the Avar and conquering ages had a high average CaO content of 6-25wt% bounded in the form of calcium-phosphate, which can be observed as nails in their microstructure.

The role of phosphoric iron in historical pattern welded blades

Archaeometrical background

Myths and legends related to the excellent mechanical properties of pattern welded historical sword blades are widespread among enthusiasts and researchers as well. During archaeometrical investigations carried out on medieval knives and swords the use of phosphoric iron for pattern welding was evidenced. Pattern welding was employed in the middle part of the sword blades and on the top of the knife blades (see figure 2).

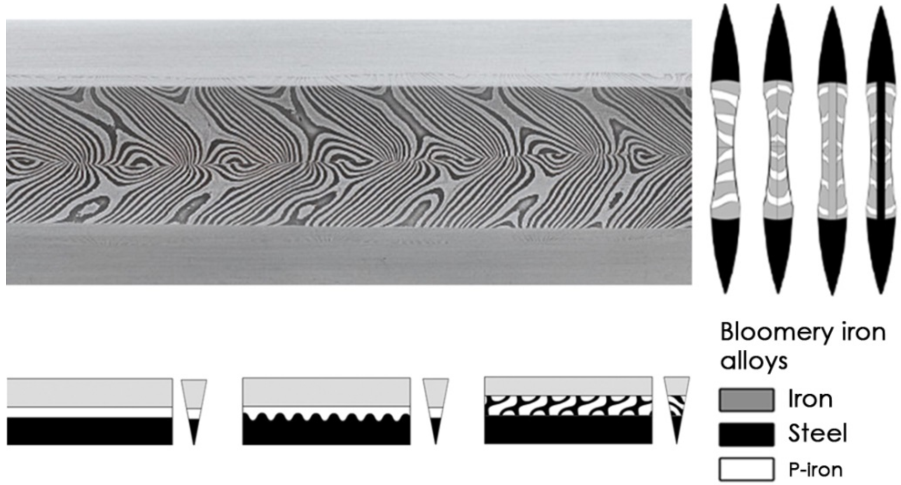

Figure 2: Pattern welded sword blades (6-10th century) and knife blades (9-15th century) decorated with phosphoric iron layers.

Aim of the research, questions

Questions arise based on the first part of the dissertation: what mechanical properties the phosphoric iron employed in historical pattern welded blades had, and whether the technique of pattern welding had a positive effect on mechanical properties or whether it was applied distinctly for aesthetic purposes.

Investigated materials and applied methods

Archaeometrical investigations on medieval pattern welded knife and sword blades were carried out and P-content was measured with SEM-EDS method in different phosphoric iron layers in cooperation with mechanical engineer Jiří Hošek from the Czech Republic. A combination of phosphoric iron + iron and phosphoric iron + steel was recognised in all samples which had undergone a heat treatment of normalising or hardening and tempering.

Mechanical testing of base bloomery iron alloys (iron, phosphoric iron and steel in normalised and hardened and tempered state) and pattern welded samples was carried out in order to examine the effect of pattern welding