The manufacturing technology of a pattern-welded knife from Kobilić (Republic of Croatia)

Technologie výroby damaskovaného nože z Kobilić (Chorvatsko)

Ádám Thiele

A pattern-welded knife dated to the 13th century was found during an archaeological excavation conducted on the site of Kobilić 1 in 2010. Nowadays, pattern-welded knives are very popular due to their decorative appearance and supposedly excellent mechanical properties. This paper introduces some new experimental results gained during the manufacturing of a copy of the medieval pattern-welded knife using historical techniques. During this experimental work some new practical observations were taken in general about smelting and processing bloomery iron and concerning the decorative effect of phosphoric-iron used in pattern-welding.

experimental archaeology – pattern-welding – phosphoric-iron – knife – Middle Ages

Damaskovaný nůž ze 13. století byl nalezen při archeologickém výzkumu lokality Kobilić 1 roku 2010. V současné době jsou damaskované nože velmi oblíbené pro svůj dekorativní vzhled a údajně vynikající mechanické vlastnosti. Tento článek představuje některé nové experimentální výsledky získané při výrobě kopie daného středověkého nože s použitím autentických technologií. Během experimentálních prací byly vypozorovány nové praktické poznatky ohledně výroby a zpracovávání svářkového železa i ohledně zdobného účinku fosforového železa používaného v damaskových kompozitech.

experimentální archeologie – svářkový damask – fosforové železo – nůž – středověk

1. Introduction

Nowadays pattern-welded (referred to hereafter as PW) knives and also other PW objects (axes, swords, etc.) are very popular due to their decorative appearance and supposedly excellent mechanical properties; several companies are making and trading PW items to serve the needs of customers (although PW is a rather misunderstood term among enthusiasts, cf. the terminological mix-up of ‘pattern-welded’, ‘Damascus steel’ or ‘Wootz’). Although scientists are investigating PW artefacts and several well-trained craftsmen are forging reconstructions of medieval PW artefacts (usually even using bloomery iron as well), some details about the historical manufacturing technology and the archaeometallurgical background of PW objects remained unrevealed. This paper introduces some new experimental results gained during the manufacturing of a copy of a medieval PW knife applying historical techniques.

In PW a composite material was produced by the forge-welding of alternating layers of bloomery iron alloys. PW blades show decorative surface patterns after being correctly treated, i.e. fine ground and etched. The visibility and contrast of PW is significantly higher in an etched state, therefore it is generally accepted that PW iron objects were etched in the plast (*Pleiner 1993*; *Tylecote – Gilmour 1986*; *Buchwald 2005*; *Hošek – Bárta – Šmerda 2017*).

As for iron, three basic bloomery iron alloys were known and used by the medieval blacksmiths; 1) iron (sometimes also referred as 'plain iron'), non-quench-hardenable iron-carbon alloy containing less than 0.3 wt% of carbon, 2) steel, quench hardenable iron-carbon alloy containing more than 0.3 wt% of carbon and 3) phosphoric-iron (referred to hereafter as P-iron), non-quench-hardenable iron-phosphorous alloy containing more than 0.1 wt% of phosphorus (*Vega et al. 2003*). In the historical technique of PW, iron and P-iron or steel and P-iron were forge-welded together in 5–15 alternating layers and after forge-welding this layered bar was twisted in most cases. Thereafter, these bars were as rule forge-welded between the cutting edge and the back of the knife blades, and two or more bars as the core of sword blades or, in the form of surface panels, onto their core, etc. Ostentatious knife blades of simpler construction did not contain twisted composites, i.e. PW bars, but only strips of P-iron, which could be straight or serrated/wavy-shaped at the lower edge (*Boháčová – Hošek 2009*, 375).

The first objects displaying evidently deliberate PW are Roman swords dated to the second half of the 2nd century AD (e.g. *Gilmour 2007*; *Hošek – Beran – Komoróczy 2011*). PW swords reached the peak of their popularity around the 7th century (*Kucypera in press*), and then in the 8th–9th century, PW turned into the form of iron inlays forged into the surface of the blades (*Moilanen 2009*; *Williams 2012*, 62; *Hošek – Košta – Bárta 2012*). Finally PW disappeared from sword-making around the turn of the 11th century (*Kucypera in press*). As for knives, PW, striped and serrated or wavy-welded knife blades were manufactured between the 10th–14th centuries (*Boháčová – Hošek 2009*, 375; *Ottaway – Rogers 2002*; *Hošek – Zavyalov 2014*; *Pleiner 1982*, 275). PW and serrate-welded saxes were the predecessors of these knives (*Westphal 1984*), while in the 14th century PW knives were definitely substituted by blades decorated with non-ferrous inlays, as their fabrication was easier and faster. Besides swords and knives, a number of PW scramasaxes and spear-heads are known (*Hošek – Šilhová 2006*; *Pleiner 1993*, 214–222; *Anteins 1973*).

All PW blades achieve their pleasing appearance due to the use of P-iron containing as a rule 0.4 to 1.4 wt% of phosphorus (*Thiele – Hošek 2015a*). The crucial role of P-iron in PW blades was evidenced (*Tylecote – Gilmour 1986*; 251–252; *Buchwald 2005*, 283; *Hoyland – Gilmour 2006*, 77–79) but its reducing effect on their mechanical properties was also shown (*Thiele et al. 2015*). Although iron with increased amount of phosphorus has higher strength (phosphorus has the strongest solid solution hardening effect on ferrite among substitutional solid-solution strengtheners), phosphorus is an avoided element in modern steel industry for its detrimental effects (*Stead 1915*), which include various forms of embrittlement, decreasing ductility, dynamic and static toughness. It is for this reason that its content in modern steels is controlled to <0.04 wt% (*Boyer – Gall 1990*, 144). Characteristic values of toughness and ductility for typical P-iron used in historical PW are very low (e.g. impact energy, percentage elongation after fracture etc., cf. more details in *Thiele – Hošek 2015b*). Therefore, in historical blades, neither PW nor individual P-iron strips improved their mechanical properties, although the limited amount of P-iron in the blades did not cause the significant decline of mechanical properties. So P-iron and PW were used solely for aesthetic purposes. An advantageous property of P-iron is highlighted during etching applied for revealing the pattern of PW blades; P-iron is more resistant to solutions and vapours of various acids than non-P-iron and steel (*Thiele et al. 2014*), so it preserves its silver-like lustre and provides a contrastive pattern.

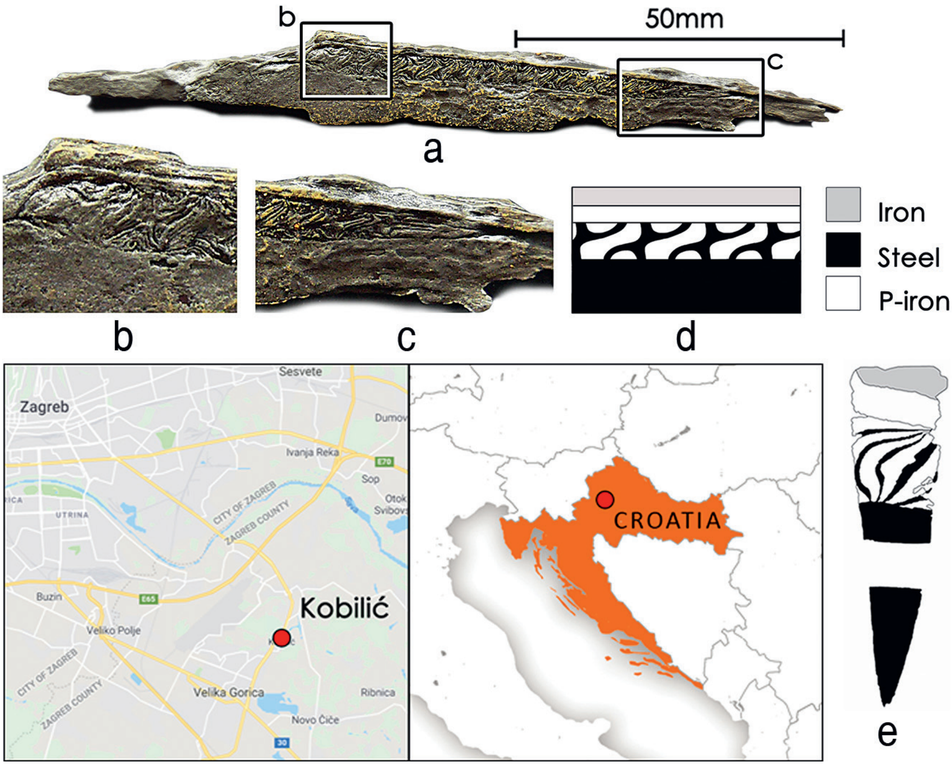

Fig. 1. The PN_52 PW knife and its construction: a) photo of the knife; b) and c) macro photos of the pattern-welded core; d) schematic drawing of the lateral construction of the knife showing the ferrous alloys used; e) schematic drawing of the cross section of the knife on the basis of the metallographic examination [23]. Photos and drawings in figs. 1–4 by Á. Thiele.
Obr. 1. Damaskovaný nůž PN_52 a jeho konstrukce: a) foto nože; b) a c) makrosnímky damaskového jádra; d) schematické znázornění boční konstrukce nože s vyznačením použitých slitin železa; e) schematický nákres průřezu nože na základě metalografické analýzy [23].

2. Materials and methods – the manufacturing of a copy of the PN_52 knife

2.1. Archaeological background and the construction of the PN_52 knife

The PN_52 whittle tang knife (*fig. 1: a*), which is the first PW knife known from Croatia, was found during an archaeological excavation conducted on the site of Kobilić 1 in 2010. This site is situated on the western edge of the present-day village of Kobilić. The knife is dated to the 13th century and was found in a presumable waste pit located farther from the majority of the settlement features (*Antonić – Rácz in press*). Taking into consideration that this knife is the only PW one known from the territory of Croatia to date, it is more likely that it was imported than locally produced (cf. details in *Thiele et al. 2017*).

The total length of the knife was 126 mm from which the blade was 85 mm with a max. width of 13 mm and max. thickness of 4 mm tapering to 2 mm. The overall construction

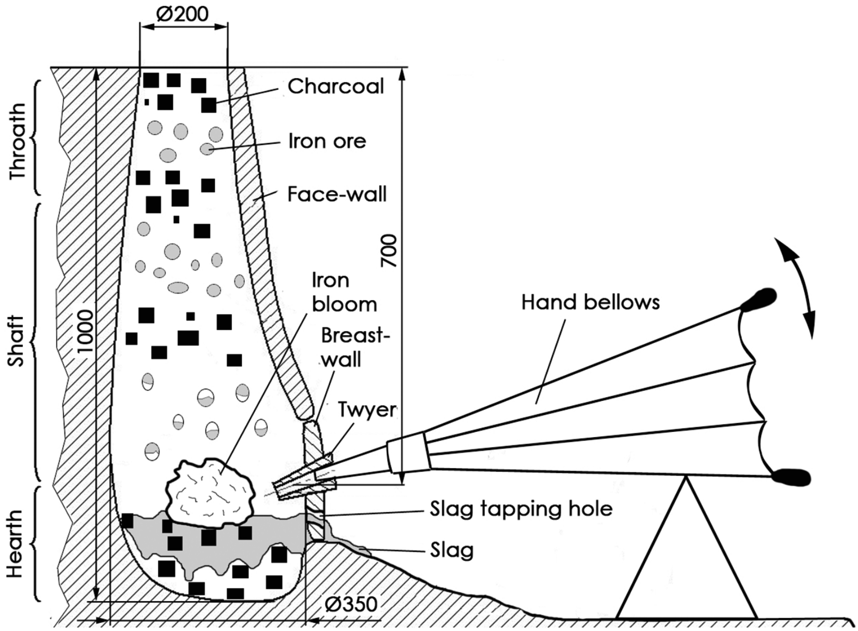

Fig. 2. The construction and the dimensions of the experimental furnace used for iron smelting.
Obr. 2. Konstrukce a rozměry experimentální pece použité pro tavby železa.

of the knife is fairly typical of such 13th century PW ones. Only the cutting edge was hardened which had a tempered martensitic microstructure whose carbon content was estimated at 0.5–0.6 wt%. The hardness of the tip of the cutting edge was ca. 580 HV0.2. The PW core with an 'X' pattern appeared between the cutting edge and the back of the blade. The back was mostly corroded, but the lateral surface examination of the blade suggested that a simple decorative P-iron strip was forge-welded onto the patterned core (*fig. 1: b*), which ended before reaching the pointed part of the blade as well as the PW core (*fig. 1: c*). 12 alternating layers of steel and P-iron could be distinguished in the PW core in which the steel had a C-content of ca. 0.3 wt%, while the coarse-grained P-iron had a P-content of ca. 0.5 wt%. The pattern-welded core was bordered with a decorative strip of P-iron at the back of the knife to increase the overall decorative effect. The upper part of the back was iron with a pure ferritic microstructure. Detailed metallographic and SEM-EDS examination was published in *Thiele et al.* (*2017*).

2.2. Smelting iron

The reconstruction work was started from collecting suitable iron ores for smelting iron, steel and P-iron. P-iron could usually be extracted of phosphorus-rich bog iron ores.

Several bog iron ore deposits are known in Somogy County (South-West Hungary), where microbial bog iron ore lenses were formed in back marshes due to the precipitation of Fe(III) minerals (goethite) during the microbial and chemical oxidation of fluids containing solved Fe(II), streaming under the surface. Microbial bog iron ore lenses were redeposited by creeks in areas which uplifted from the Early Holocene on (*Kercsmár – Thiele 2015*). Bog iron ores from the microbial bog iron ore lenses and from the redeposited bog iron ore layers were smelted intensively during the Avar and conquering ages due to the abundance and high Fe-content of the ores.

But the smelting of these P-rich bog ores may result in non-forgeable P-iron as above a certain temperature and P-content (1048 °C and P=2.8 wt%, cf. the Fe-P dual phase diagram, *Okamoto 1990*) molten Fe-Fe_3P eutectic phase appears on the grain boundaries. P-content of the iron blooms could be decreased during the smelting by charging fluxes of high CaO content (such as limestone, bog iron ores with high CaO content or ash). The higher the CaO/SiO_2 ratio of the slag, the lower the activity factor of P_2O_5 due to the formation of a complex compound of $3CaO{\cdot}P_2O_5$ (tricalcium-phosphate), hence the lower amount of phosphorus dissolved in the iron (cf. the metallurgical and physico-chemical background more detailed in *Török – Thiele 2013* and *Thiele 2014*).

P-iron was smelted of bog iron ore collected from a redeposited bog iron ore layer that covers the bed of a fishpond near to the village of Lábod where furnaces from the Avar-Age (*Költő 1999*) and an iron bloom (*Török et al. 2017*) were also found. The chemical composition of this ore was measured by the means of ICP-OES method in the Mining and Geological Survey of Hungary (*tab. 1*).

#	Ore deposit site	Main oxides (wt%)							
		Al_2O_3	SiO_2	P_2O_5	CaO	MnO	Fe_2O_3	H_2O	Σ
1	Lábod	0,46	3,82	6,6	3,44	1,61	78,02	5,01	98,96
2	Barót	1	11,2	0,71	0,63	1,12	70,6	12,67	97,93

Tab. 1. ICP-OES analysis results for the main oxides of the iron ores used for iron smelting.
Tab. 1. Výsledky ICP-OES analýz hlavních oxidů železných rud použitých pro tavby železa.

For smelting iron and steel iron ore was collected in a sandstone mine near to the village of Barót (Transylvania, Central Romania). Iron ore appeared as ironstone concretions that grew in the spongy sandstone by precipitation from Fe(II)-rich post-volcanic thermal water and arranged themselves in near-concentric bands. This ore does not contain any phosphorus, its main mineral phase is also goethite but has an increased amount of SiO_2 originating from the surrounding sandstone (*tab. 1*).

Three smelts were carried out in the same furnace which was the copy of the so-called Fajszi-type Conquering age Hungarian embedded furnace found first in Somogyfajsz (*Gömöri 2000*, 34). The construction and the dimensions of the experimental furnace can be seen in *fig. 2*. In each smelt, after 1 hour preheating with wood and then charcoal, the iron ore which was roasted and crashed to a grain size of 2–15 mm was charged (altogether 12.5 kg) mixed with charcoal into the charcoal filled warm furnace and after about 4 hours the iron bloom was removed from the furnace.

During the smelting of P-iron from the bog ore from Lábod, in order to keep the phosphorus content of the bloom in a range of 0.5–1.0 wt%, roasted 2–5 mm fine grained burned limestone (CaO) was charged in a ratio of 1 : 5 CaO : ore. The ratio of charcoal:ore was 0.5 : 1 while the air supply was 50 l/min in this experiment and the resulting P-iron bloom weighed 2.7 kg after the first compressing and 2.1 kg after forging to a billet (the bloom was forged with a power hammer and heated in charcoal fire). Iron and steel was smelted from the ironstone from Barót in the same way but without charging CaO and with a ratio of charcoal:ore of 0.5 : 1 and an air supply of 50 l/min respectively 1 : 1 and 100 l/min. The iron bloom was 2.3 kg from which a billet weighing 1.8 kg was forged. The increased amount of charcoal and air resulted in a steel bloom of 2.6 kg which was forged to a billet weighing 2.0 kg. All the three billets had a similar shape with a length of ca. 450 mm and a cross section (referred CS hereafter) of ca. 40 × 15 mm.

For purifying and homogenising, each billet was cut into 6–8 pieces then packed again and the packets were forge-welded and folded 3 times. Thereafter ca. 80 cm long bars with a cross section of ca. 15 × 15 mm were forged. The final phosphorus content of the P-iron bar was between 0.6–0.9 wt% measured using p-XRF on a ground side of the bar. The C-content was 0.2 wt% in the iron bar and 0.6–0.7 wt% in the iron and steel bar. The carbon content was calculated from the results of HRc hardness measurement done in water quenched state on a ground side of the bars. The iron and steel bars could also be distinguished by spark test.

2.3. Forging the knife blade

For the PW core, 6–6 flat layers forged from steel and P-iron (each was ca. 60 × 15 × 2 mm) were piled alternatingly and the stock was forge-welded then forged into a bar of 6 × 6 mm CS. The bar was twisted and hammered flat to a CS of 7 × 4 mm and was cut to 80 mm long pieces used later as the PW layer. Each piece was hammered to wedge-shape at the point to a CS of 7 × 2 mm. The iron back of the knife had a CS of 7 × 3 mm and was 95 mm long while the P-iron bar for the decoration strip was 80 × 7 × 1.5 mm. To keep the original triangle shape of PN_52 knife the steel cutting edge had to be wedge-shape with a length of 95 mm and a CS of 7 × 8 mm at the beginning and 7 × 3 mm at the point. These four layers prepared were kept together with a tong and then forge-welded, first at the point and then, after a second heat, the whole body of the blade. Forge-welding had to be done quite quickly because the temperature of the small workpiece decreased fast. The blade was then shaped. The final thickness of the blade was 6 mm. The main forging steps can be seen in *fig. 3: a–e*.

During the forging of the knife blade some practical observations were made. Due to the presence of slag inclusions in the metallic matrix, bloomery iron bears much less plastic deformation at room temperature before delaminating and cracking than the almost slag-free modern steels, i.e. the ductility of bloomery iron is much lower because of the notching and stress concentration effect of the slag inclusions (cf. *Thiele – Hošek 2015b*). The low ductility of bloomery iron was observed on the forging temperature as well, thus less plastic deformation is allowed in one forging step compared to modern steels. Also, in general, uniaxial stress state is preferred during the plastic deformation (preferably compressive stress and shear stress should be avoided) to prevent delaminating or cracking. It is also important to start forging from the forge-welding temperature (1300–1350 °C depending on the C-content) for re-welding the delaminated layers, as well as to avoid forging under the Ac3 temperature (the lower temperature of the austenite field).

It was also observed that the yield strength of the bloomery iron is lower than that of modern steels at forging temperature. This is caused by the melting of the slag in the metal matrix, which led to less force-need for the same plastic deformation. The other reason

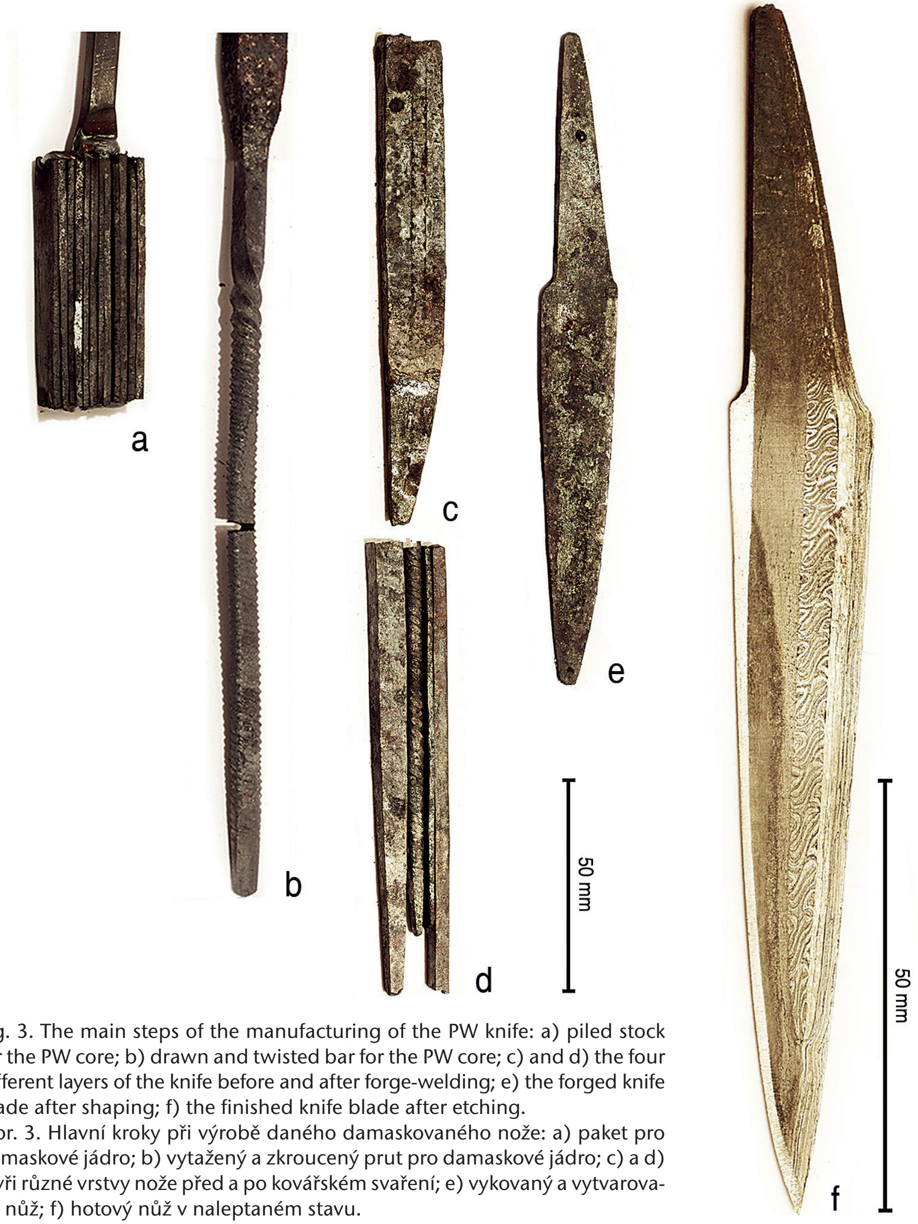

Fig. 3. The main steps of the manufacturing of the PW knife: a) piled stock for the PW core; b) drawn and twisted bar for the PW core; c) and d) the four different layers of the knife before and after forge-welding; e) the forged knife blade after shaping; f) the finished knife blade after etching.
Obr. 3. Hlavní kroky při výrobě daného damaskovaného nože: a) paket pro damaskové jádro; b) vytažený a zkroucený prut pro damaskové jádro; c) a d) čtyři různé vrstvy nože před a po kovářském svaření; e) vykovaný a vytvarovaný nůž; f) hotový nůž v naleptaném stavu.

could be the lack of alloying elements (such as Si and Mn), which are alloyed to almost all industrial steels for deoxidization and which provides a solid solution hardening effect in austenite.

At the beginning of forging the spongy structured bloom there was no need to use any flux as it contained enough slag for forge-welding. Later, when the billet was dense and its slag-content decreased, borax was used as flux. However, bloomery iron is easier to forge-weld than modern steels probably also due to its slag inclusions and the lack of alloying elements which decelerate the recrystallization, which is important during forge-welding.

Finally an interesting observation was that P-iron had a special smell (probably caused by the vapour of phosphorus) at forging temperature, which may also help to distinguish P-iron from non-P-iron.

2.4. Finishing the PW knife blade

The forged knife blade was roughly ground and sharpened on a manual sandstone water-cooled grinding wheel. As the blade was narrow, the ground surface remained almost flat and the blade had a simple 'V'-shape CS with a 2–3 mm wide sharpened cutting edge. The roughly ground blade had a thickness of 4 mm, so ca. 1 mm of material was removed from each sides. The cutting edge of the blade was subsequently quenched in oil in a width of ca. 10 mm from a temperature of ca. 900 °C (water quenching was also tried but the edge was cracked). There was no annealing applied. After heat treating, the blade was ground again using fine grained flat grind whetstones with grit sizes of 80, 120 and 240. The cutting edge was sharpened again.

The next step is the finishing of the surface with a kind of etching. It is yet unknown how the historical PW objects were exactly etched, but without a special treatment the fine ground or polished surface does not show any clear pattern (there is no contrast between the layers of different chemical composition), although the slag inclusions that follow the forge-welding lines might be seen with the naked eye. There are three possible methods for making the pattern visible, the etching method (in which the surface of the blade is exposed to liquid organic or inorganic acids, *Thiele et al. 2014*), the method of abrasive grinding (*Mäder 2001*), and finally the so-called controlled corrosion process. Following this latter technique (described in details in *Hošek – Bárta – Šmerda 2017*) the knife blade was positioned on a holder on its flat back (*fig. 4: a*) approximately 10 mm above the level of 10% vinegar in room temperature and exposed to its vapours in a closed container for 24 hours. The forming corrosion products (*fig. 4: a*) were mechanically removed from the treated surface by a wet rag every 8 hours. Then the blade was washed and the final surface treatment consisted of slight hand polishing using a hand polishing pad of 1200 grit size. The nice, contrastive pattern of the finished PW knife can be seen in *fig. 3: f* and in *fig. 4*. As the PN_52 knife was originally probably also slightly bigger, the total length of the reconstructed knife was 135 mm from which the blade was 90 mm with a max. width of 15 mm and max. thickness of 4 mm tapering to 2 mm.

Some practical observations regarding the etched surface could also be made. The P-iron layers were not only shiny compared to the grey coloured iron or steel layers but individual crystals of the P-iron could also be recognized. This phenomenon was observed only after the controlled corrosion process using the vapour of vinegar and not in case of etching in liquid etchants (*Thiele et al. 2014*). This secondary decoration effect of P-iron is caused by its highly coarse-grained microstructure in which the ferrite grains have a size of 0.1–1 mm (*fig. 4: b*).

Areas with a different shade are also visible in the layers of iron and steel because of the difference in their carbon content and microstructure, i.e. the different cooling speed of the edge and the back of the blade. The historical use of P-iron for a decorative purpose

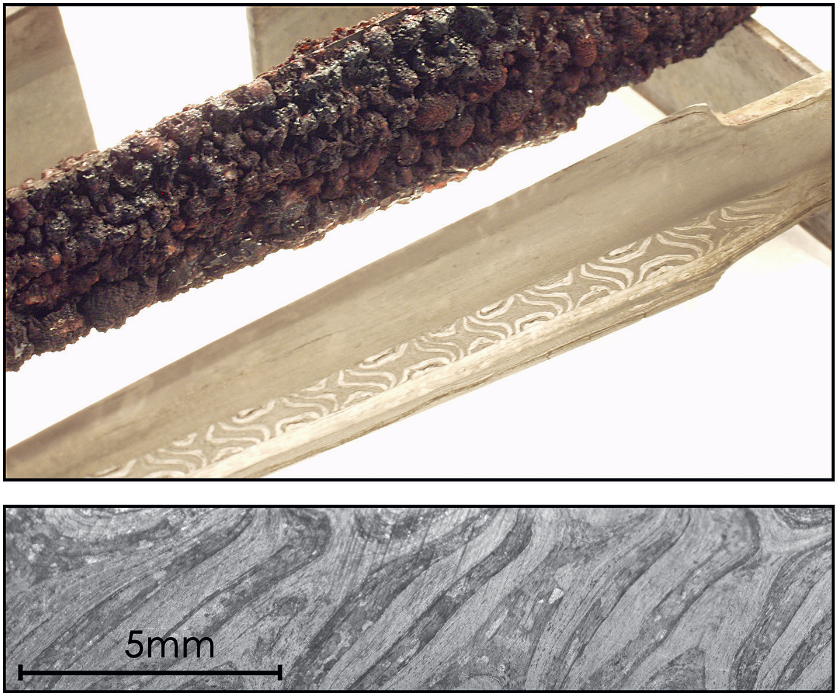

Fig. 4. Etching the PW knife with controlled corrosion in the vapour of 10% vinegar: a) above, corrosion products on the surface of the blade after 8 hours; below, the revealed pattern after washing and removing the corrosion products after the first 8 hours of etching; b) the secondary decorative effect of coarse grained structure of P-iron visible with the naked eye in the PW core under stereo-microscope after etching.
Obr. 4. Leptání damaskovaného nože pomocí řízené koroze ve výparech 10% octa: a) Nahoře, korozní produkty na povrchu čepele po osmi hodinové expozici; dole, vzorování viditelné po omytí a odstranění produktů koroze z čepele po prvních osmi hodinách leptání; b) sekundární dekorativní efekt hrubozrnné struktury leptaného fosforového železa, viditelný v damaskovém jádru čepele i pouhým okem, zdokumentovaný pomocí stereomikroskopu.

is also supported by the observation that the appearance of etched P-iron is rather homogeneous (apart from its visible grains) compared to iron or steel because carbon content remains low in P-iron according to the high P-content as phosphorus is a ferrite-stabilizing element in which phase the solubility of C is very low, i.e. over ca. 0.65 wt% of phosphorus the allotropic transformation of ferrite to austenite disappears (cf. Fe-P dual phase diagram: *Okamoto 1990*). And finally, slag inclusions in and between the layers also remained visible after etching (*fig. 4: b*).

3. Conclusions

During the experimental work of manufacturing a copy of the 13th century PN_52 PW knife from Kobilić, several new practical observations were made in general about smelting and processing bloomery iron and regarding the decorative effect of P-iron in PW.

1. P-iron was smelted of P-rich bog iron ore and it was possible to regulate the P-content of the iron bloom by charging burned limestone. Iron and steel was extracted by smelting P-free ironstone; increasing the air supply and the charcoal/ore ratio led to the carburizing of the iron bloom.
2. Compared to modern steels, bloomery iron:
   - has lower ductility at the forging temperature, so bears less plastic deformation in one forging step due to the presence of slag inclusions in the metallic matrix;
   - has lower yield strength at the forging temperature, caused by the melting of the slag inclusions and the lack of alloying elements;
   - easier to forge-weld;
   - P-iron has a special smell at the forging temperature.
3. After etching the fine ground PW knife blade in the vapour of vinegar, P-iron remained bright and shiny providing a contrastive surface pattern. A secondary decoration effect was also observed as the controlled corrosion process made the highly coarse-grained ferritic microstructure also visible.

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ÁDÁM THIELE, Budapest University of Technology and Economics, Department of Materials Science and Engineering, Bertalan Lajos str 7., bdg MT, H-1111 Budapest; thiele.adam@gmail.com