METALLOGRAPHIC ANALYSIS OF SELECTED HISTORICAL STEEL KNIVES BLADES

Matej Pašák[1,*], Martin Kusý[1], Matúš Sládok[2]

[1] Institute of Materials Science, Faculty of Materials Science and Technology, Slovak University of Technology, Paulinska 16, 917 24 Trnava, Slovak Republic
[2] Department of Archaeology, Faculty of Philosophy, Comenius University in Bratislava, Gondova 2, 814 99 Bratislava, Slovak Republic

[*]corresponding author: e-mail: matej.pasak@stuba.sk

Resume
Microstructural and metallurgic analysis of historical steel knives can reveal the technology which was used for their manufacturing and the used heat treatment. The subjects of research were two knife blades found near Čierna Lehota and Cígeľ, Slovak Republic, located in central Europe. The microstructure of the samples was observed in order to explain the technology of heat treatment of the blades. To gain more complex information about properties of the structure the hardness tests and tests of phosphorus segregation were performed along with the chemical analysis by GDOES and EDX. Observation of the polished samples revealed non-metallic impurities and texture after hand forging of the material.

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1. Introduction

A knife has always been an important tool suitable for universal purposes. At first the blades were made of stone, later of bronze, and finally of steel [1 - 3]. Knife is still important utensil, but nowadays can be made from progressive tool steels including sintered powder steels [4]. Historical knives were produced from raw iron. This raw iron was extracted from the raw ore. This material was then refined and homogenized by forging [5]. Hand hammering leaves characteristic signs on the thermomechanically treated steel of a knife blade.

General manner of knife investigation as well as approach to particular items are among archeometallurgists, archaeologists and multisciencists widely discussed on the present. The traditional morphological evaluation of knives undoubtedly yields only part of the information that can be deduced from these artefacts. Conservation survey is extremely useful because different kinds of decoration as well as further details can be quite reliably revealed. Furthermore, basic blade constructions can be clever determined in the course of conservation treatment by means of X-ray imaging or by a look of the original of the blade surface when revealed by sandblasting. But these methods depend on a surface condition and hence are not reliable for systematic analysis Therefore, metallography remains up to date the most powerful method for the blade construction investigation. If it is impossible to employ the surface examination and the blade construction and all the related information are demanded, then the cross sectional sampling is approached. Cutting, polishing and etching are traditional destruction techniques. However, it causes only minor damage and it is possible to glue the pieces back together. It can be then used for further analysis at a later date [1 - 3].

The subjects of research were two knife blades found near Čierna Lehota (district Bánovce nad Bebravou, GPS: N48.866 E18.333) and Cígeľ (district Prievidza, GPS: N48.713 E18.641), Slovak Republic. The first blade is dated to 13th or 14th century, while the age of the second blade is not accurately specified. Several analyses were performed on the samples to find out the production technology.

2. Experimental material and methods

Analysis of microstructure of the cross section is required for internal volume of analyzed item research [6]. The blade was divided into several parts: longitudinal and transversal cross-sections which were analyzed. Recommendations of an archeologist were taken into consideration concerning reparation after performing the analysis. In Fig. 1 there is knife no. 1 that was found in Čierna Lehota. The labels a-b marked the place of the material removal for longitudinal cut. The labels b-c marked the place of material removal for transversal cut while the cross section surface is on label b.

Fig. 2 shows the knife no 2. found in Cígeľ. The extracted material was embedded into dentacryl for better manipulation and sample edge retention. The same method of sample extraction as for the knife 1 was used. The samples were then metallographically prepared by using grinding paper and diamond polishing pastes. In the next step the microstructure was highlighted by etching in 2 % Nital reagent.

The microstructures on the transverse surface were recorded by using an optical microscopy. Scanning electron microscope (JEOL 7600F) was used for investigate of the presence of impurities and their chemical composition with use of EDX.

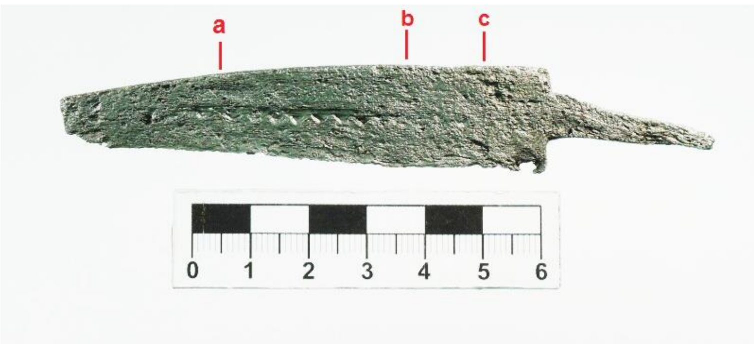

Fig. 1. Knife 1 with marked places for cutting.
(full colour version available online)

Fig. 2. Knife 2 with marked places for cutting.
(full colour version available online)

The longitudinal surfaces of the blades were used to observe segregation of the sulphur by Baumann print and segregation of the phosphorus by using the Heyne etching.

The longitudinal surfaces of the blades were used to observe segregation of the sulphur by Baumann print and segregation of the phosphorus by using the Heyne etching. The chemical analysis was performed on these surfaces to find out the amount of the residual chemical components. Hardness was measured on each area with its characteristic homogeneous microstructure. A Vickers hardness test with load of 9.81 N (HV1) and dwell time 10 s was used. Considering the standard procedure, hardness of the particular area was measured 3 times and the results were averaged. Thus we got an additional detail about mechanical properties of the analyzed microstructure.

3. Results

After etching, the cross-sections were observed under polarized light in order to increase contrast. In Fig. 3 there is a cross-section of knife 1. We can see that knife 1 consists of three main parts with different structure: A1 – edge, B1 – middle part, C1 – spine. Fig. 4 shows cross-section of knife 2 which consists only of: D1 – edge, E1 – spine.

3.1 Microstructural analysis of knife 1

Figs. 5 - 10 shows the microstructure of transverse surface of the knife 1 in details made with use of optical microscopy.

Fig. 5 shows the middle part. There is a clearly visible transition from fine-grained ferritic-perlitic structure to coarse-grained ferritic structure. This indicates that it is a diffusion hammer welding.

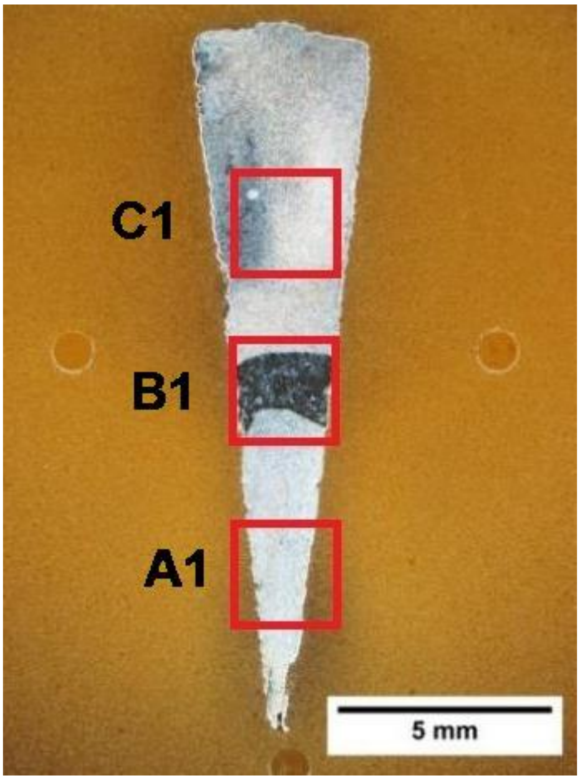

Fig. 3. Cross-section of knife 1.
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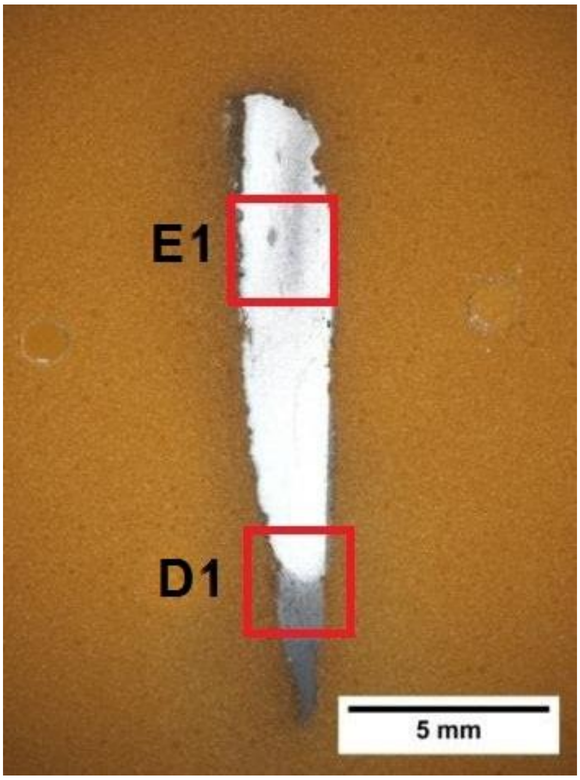

Fig. 4. Cross-section of knife 2.
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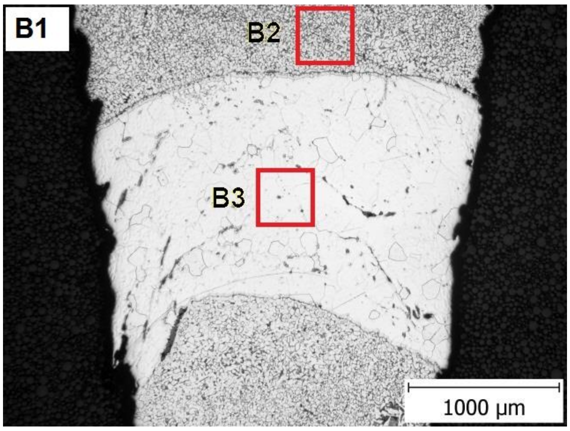

Fig. 5. Middle part of knife 1.
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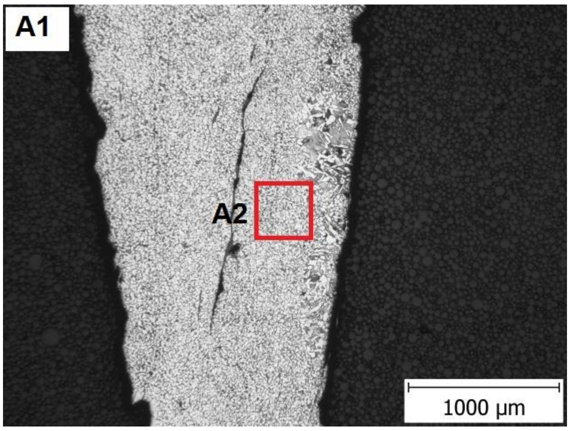

Fig. 6. Detail of split edge.
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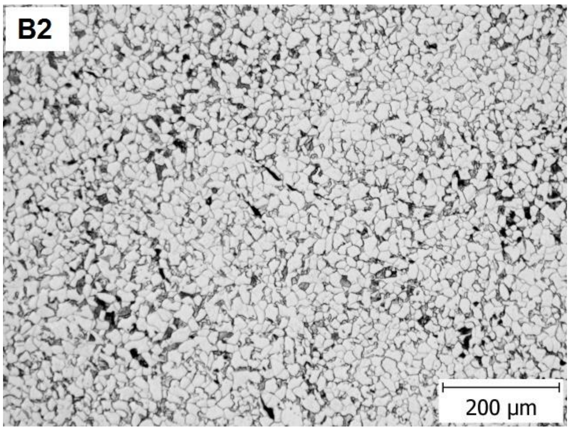

Fig. 7. Detail from spine, hardness 112HV1.

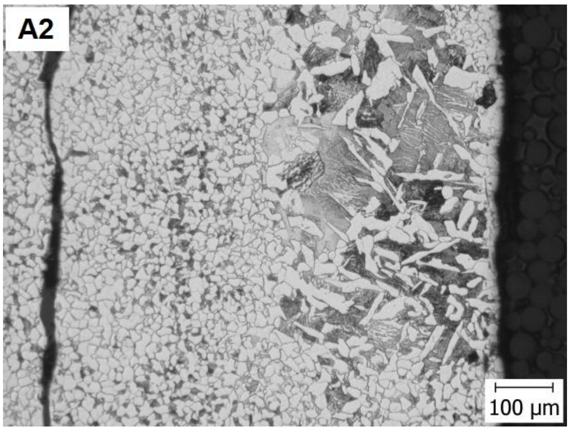

Fig. 8. Widmanstätten structure, hardness 119HV1.

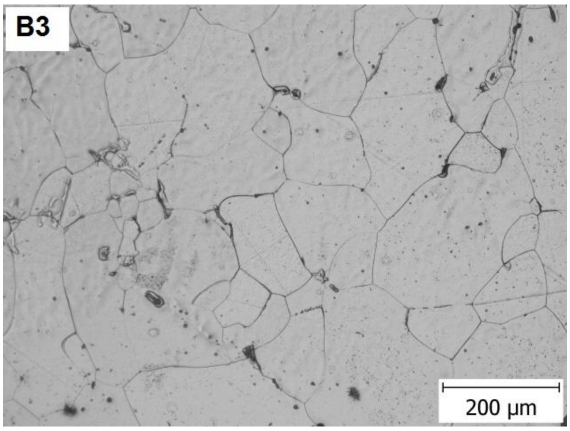

Fig. 9. Detail of middle part hardness 115HV1.

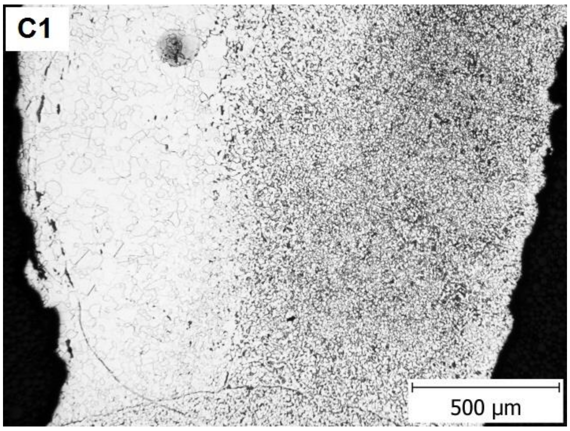

Fig. 10. Transition of various microstructures.

Fig. 6 represents the detail of the edge. In the middle of the edge there is a disruption which was probably formed due to insufficient diffusion by hammer welding. Fig. 7 describes the spine area close to the middle part. This area consists from ferritic-perlitic microstructure with hardness of 112 HV1. Fig. 8 describes the detail of the edge area. In the subsurface there can be seen the Widmanstätten structure. The measured hardness of the edge area was 119 HV1.

In Fig. 9 there is a detail of the coarse-grained middle part. There is clearly ferritic microstructure visible. The hardness of this region is 115 HV1. The grain coarsening was caused by long and probably repeated heating of the material in process of iron recycling. The detail of upper part of the spine is shown in Fig. 10. There we can see that the spine has a heterogeneous microstructure.

3.2 Microstructural analysis of knife 2

The series of optical micrographs in Figs. 11 – 16 shows the transverse surface of the knife 2 in details made by optical microscopy.

Fig. 11 shows a transition between two microstructures indicating that the knife was made of at least two intermediate products. The edge was carburized firstly and then forged together with the spine of the blade. Darker microstructure in the edge (Fig. 15) proves higher amount of carbon in the edge compared with the microstructure of spine (Fig. 13). The gradual transition of the microstructure from the core to the blade surface is visible in Fig. 12. The microstructure changes from fine-grained high-carbon in the core to coarse-grained low-carbon right under the surface. While being forged, the core was less influenced by the temperature and air oxygen.

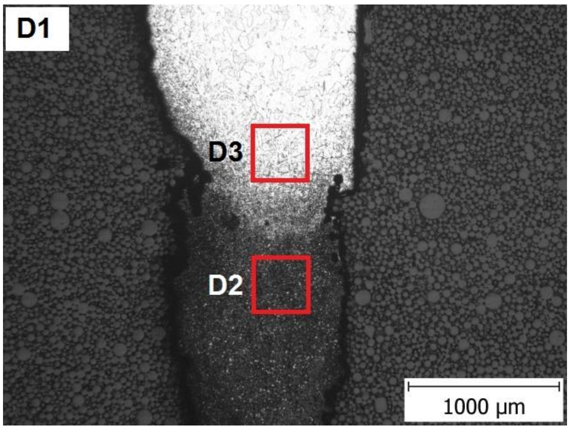

Fig. 11. Transition between spine to edge.
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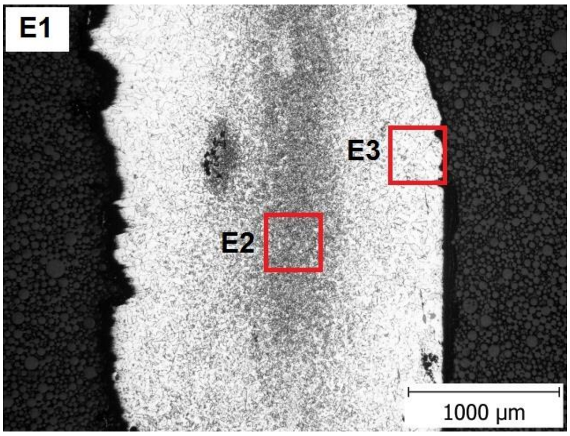

Fig. 12. Detail of knife 2 spine.
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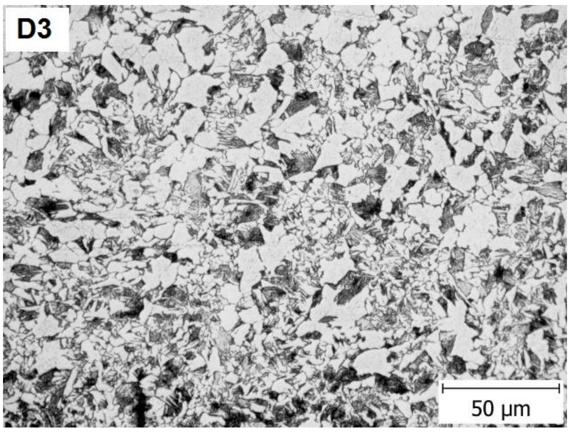


Fig. 13. Detail of spine, hardness 113 HV1.

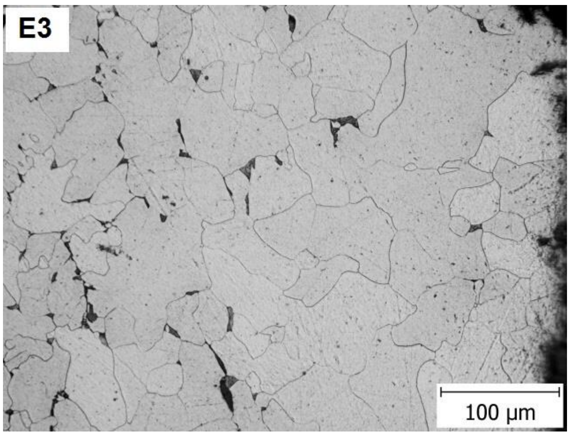


Fig. 14. Microstructure under surface of spine, hardness 130 HV1.

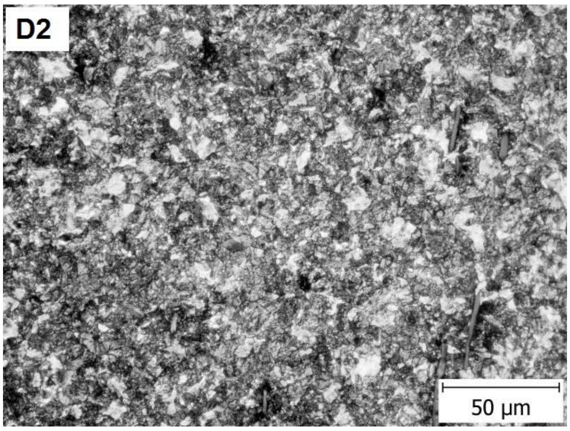


Fig. 15. Detail of edge, hardness 323 HV1.

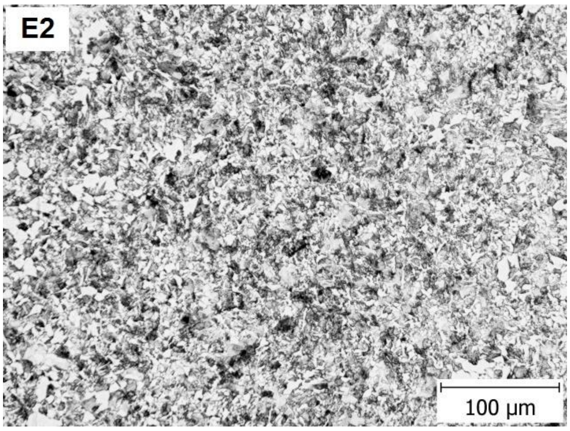


Fig. 16. Core of spine, hardness 197HV1.

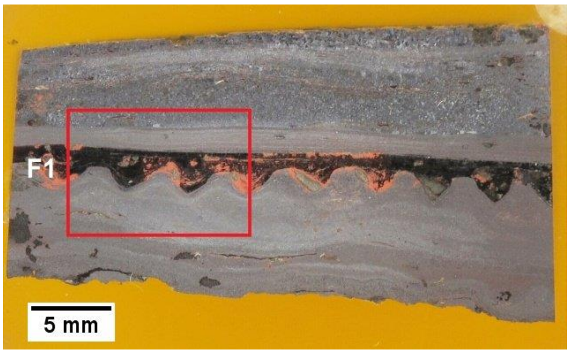


Fig. 17. Heyne etched longitudinal surface of knife 1 in polarized light.
(full colour version available online)

Fig. 18. Heyne etched longitudinal surface of knife 2 in polarized light.
(full colour version available online)

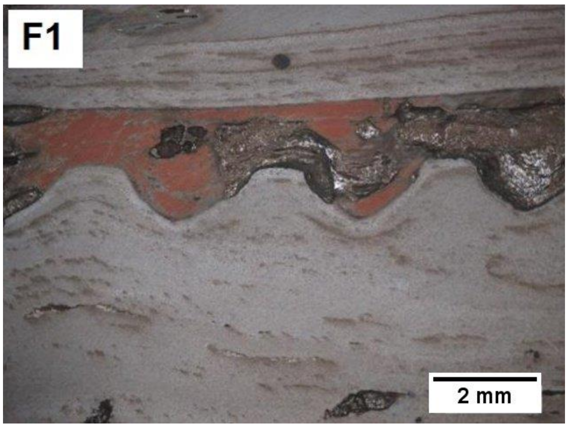


Fig. 19. Detail of teeth from knife 1.
(full colour version available online)

Table 1

Chemical composition (in wt %) of selected areas.

Specimen	Fe	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Mg
Knife 1 - spine	98.619	0.011	0.048	0.066	0.015	0.010	0	0	0	0.002	0
Knife 1 - edge	98.735	0.403	0.080	0.044	0.005	0.008	0	0	0	0	0
Knife 2 - spine	99.007	0.048	0.042	0.019	0.013	0.007	0	0.061	0	0.036	0

The Fig. 14 suggests that the amount of carbon decreases and the grain size increases up to the surface. In the core of the spine (Fig. 16) there is high-carbon fine-grained microstructure that was less influenced by the air oxygen and high temperature.

3.3 Segregation of phosphorus

The Heyne etching was used to highlight the segregation of phosphorus on the longitudinal surfaces. Fig. 17 represents the segregation on the knife 1 and Fig. 18 the segregation on the knife 2.

The most interesting formed structure of the knife 1 is showed in details in Fig. 19. There is clearly visible that the serrations were made by hand hammering forming.

3.4 Chemical analysis of material

The chemical analysis using GDOES was performed on the selected areas of longitudinal surfaces. The amounts of the measured chemical elements are specified in Table 1. However the middle part of knife 1 and the edge of knife 2 were too small to be analyzed.

The impurities were found on the edge of knife 1 (Fig. 20) as well as on the edge of knife 2 (Fig. 21), observed on polished cross-section surface by SEM. In COMPO mode the chemical elements of higher atomic weight can be seen as white areas, while the elements of lower atomic weight or non-metallic elements can be seen as dark areas. The dark impurities orientated in longitudinal stripes can be found in both knives.

The impurities were found on the edge of knife 1 (Fig. 20) as well as on the edge of knife 2 (Fig. 21), observed on polishedcross-section surface by SEM. In COMPO mode the chemical elements of higher atomic weight can be seen as white areas, while the elements of lower atomic weight or non-metallic elements can be seen as dark areas. The dark impurities orientated in longitudinal stripes can be found in both knives.

In Fig. 22 is a detail of impurities with marked areas for EDX analysis. Fig. 23a shows spectrum of the matrix where the main contents are Fe and C. Fig. 23b, c, d represent a spectrum of the impurities. Mostly the elements such as K, Ca, Cl, Na, Mn, O, Mg, Al and Si are present.

In Fig. 24 is a detail of impurities with marked areas for EDX analysis. Fig. 25a shows spectrum of the matrix where the main contents are Fe and C. Fig. 25b, c, d represent a spectrum of the impurities. Mostly the elements such as K, Ti, O, Al, Si, Mn, Na, Mg are present.

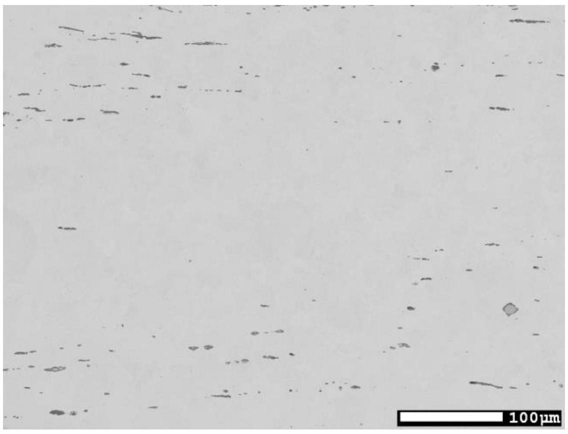


Fig. 20. Impurities from knife 2 edge.

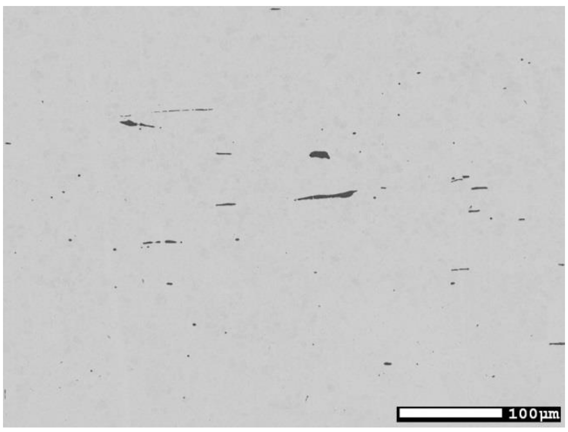


Fig. 21. Impurities from knife 2 edge.

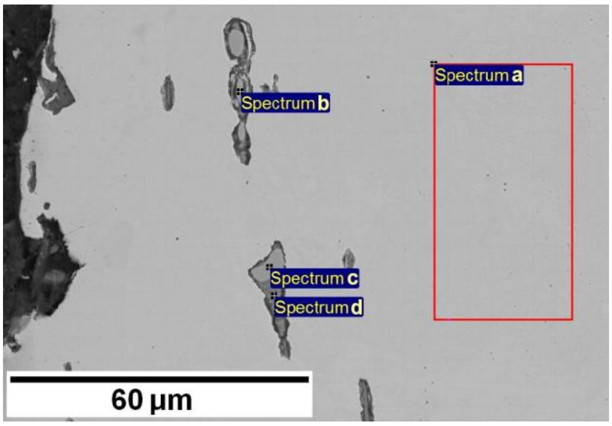
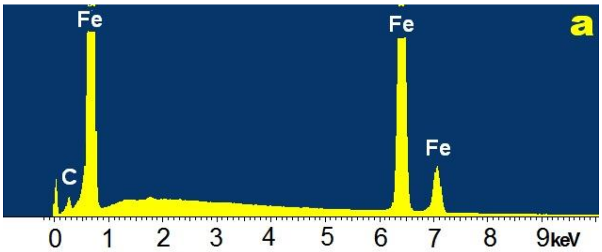
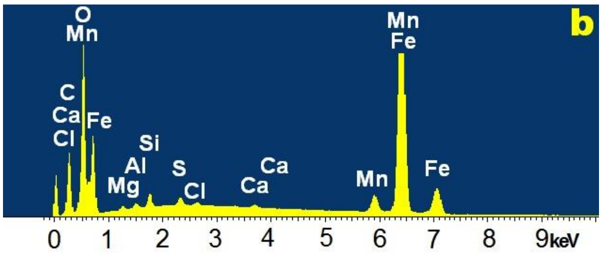


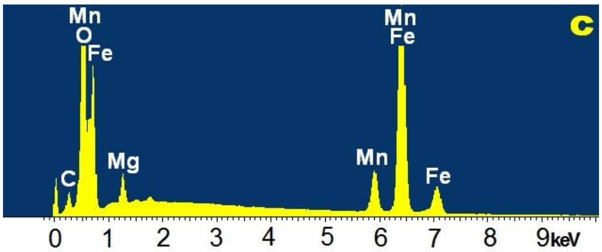
Fig. 22. Detail of impurities from knife 1.
(full colour version available online)



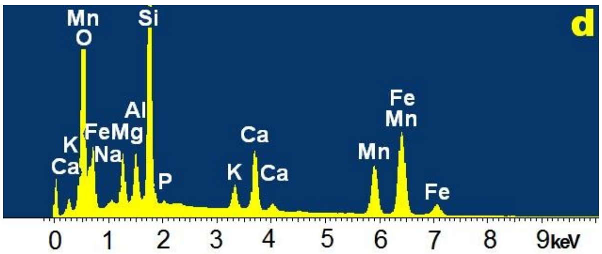
a)



b)



c)



d)

Fig. 23. Knife 1 EDX spectrums: a) Spectrum of matrix, b) Spectrum of bright impurity, c) Spectrum of grey impurity, d) Spectrum of dark impurity.
(full colour version available online)

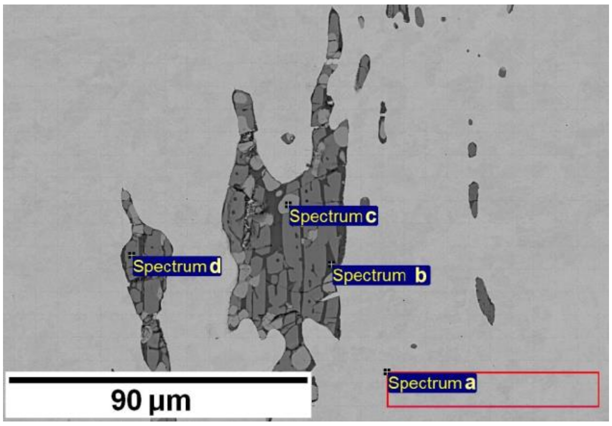
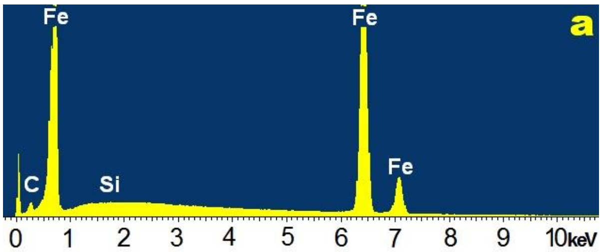
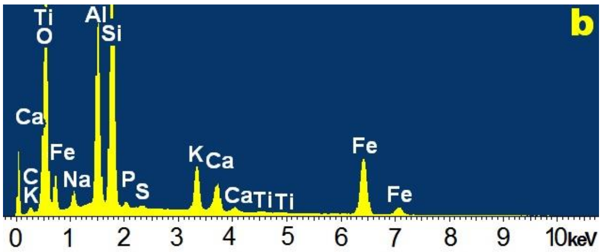


Fig. 24. Detail of impurities from knife 2.
(full colour version available online)



a)



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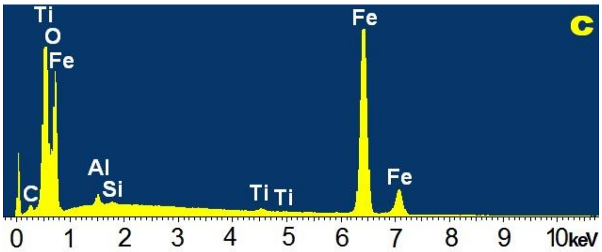

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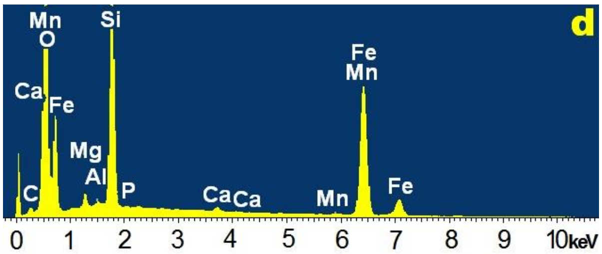

d)

Fig. 25. Knife 2 EDX spectrums: a) Spectrum of matrix, b) Spectrum of dark impurity, c) Spectrum of bright impurity, d) Spectrum of grey impurity.
(full colour version available online)

4. Discussion

4.1 Knife 1

Knife 1 had a tang for a wooden handle. The grind is full, flat and V-shaped. In the macrograph of the cross-sectioned blade of knife 1, there is clearly visible that the blade consists of several areas with different microstructures. The detail view in the micrograph (Fig. 5) shows the sharp transition from fine-grained to coarse-grained microstructure. This proves that the blade was made by hammer welding of several pieces of material with different chemical composition. Different scenario could be seen from the Fig. 10. The area with ferrite microstructure is connected with ferrite-perlite microstructure via rather broad gradual transition. This bond could be explained by forging of two pieces with different chemical composition which were exposed for a longer time to higher temperatures and possibly also deformation during processing.

The middle part (Fig. 9) also consists of a very coarse-grained ferritic microstructure. Significant growth of the grain was probably caused by repeated hand forging and long time heating during the manufacturing process.

In Fig. 8 there is a ferritic-perlitic microstructure with the highest amount of carbon of all microstructures observed on the blade. The highest amount of carbon on the edge was also proved by chemical analysis (Table 1). Higher amounts of carbon in iron results in creating an intermetallic phase cementite, which increases the mechanical properties of material. This was the reason why the high quality material with the best mechanical properties was used to make the edge which was then forged together with the spine made of lower quality material. Those days such a technological process was used very often [7, 8].

Size of the grains increases from the inside up to the surface of the material. This was caused by the forging process using charcoal, when the blade was exposed to the heat in order to be heated up to the forging temperature. The area came into contact with embers and this lead to local overheating of the material and rapid increase of the grain size. The irregular heating followed by cooling inflicted the creation of Widmanstätten structure.

Any of the microstructures of the knife 1 (Fig. 5 – Fig. 10) does not show the signs of quenching. It is assumed that blades of knifes were cooled down slowly on open air. Also, the measurements of hardness have not proved any possible signs of quenching. More non-quenched blades were found in other localities too [8] which may represent rather common practice in knife production. Despite the quenching as a process of thermal treatment leading to improved properties of the blade was known, the knife was not quenched for a reason of easier maintenance of the sharp edge.

4.2 Knife 2

Knife 2 had a tang for wooden handle too. The micrograph Fig. 4 shows that it only consists of two main parts, the edge and the spine. Fig. 11 proves that the material with higher amount of carbon (Fig. 15) was hand forged together with the spine made of the material with lower amount of carbon (Fig. 13). This caused higher strength and durability of the knife’s edge.

In Fig. 12 the slow transition of the microstructure from the core up to the surface is visible. The microstructure changes from fine-grained with higher amount of carbon in the core (Fig. 16) to a coarse-grained with lower amount of carbon right under the surface (Fig. 14). During forging process the core was less exposed to the impact of high temperature and air oxygen. The fine-grained microstructure was created by repeated recrystallization during thermo-mechanical treatment.

In Fig. 14 we can observe that the amount of carbon in the material decreases and the size of the grains increases up to the outer surface. This signifies that the knife was exposed to the high temperature and the influence of air within longer time, probably during process of heating up the material in fire while being forged. Hence, the material was decarburized and size of the grains under the surface increased.

4.3 Heyne etchant and impurities

In longitudinal surface, through the segregation of phosphorus we can observe a texture after forging (Fig. 17, 18). The segregation stripes of phosphorus are not perfectly parallel. However, the stripes are predominantly orientated in longitudinal direction, what proves that the blade was forged manually and was made of an intermediate product or another recycled material. Forging was also proved by the texture of impurities (Fig. 20, 21).

The serrations of knife 1 (Fig. 19) might have some purpose. The texture suggests that the knife was constructed by following these steps: the area of serrations with good mechanical properties was forged together with the spine made of lower quality material. The stripes of phosphorus copy the shape of serrations. Thus we can state that the serrations were probably formed by using a spike. If the stripes were interrupted, the serrations could be created by using grinding file.

By comparing with similar findings [9, 10] the serrations were made for decorative purpose. These decorated knives used to have fancy blades with decorative wavy weld. Steel with lower amount of carbon was used to fill the missing space (Fig. 9). The coarse-grained structure was probably caused by repeated forging using high temperature in order to decrease the amount of carbon in the steel.

Steel with high amount of carbon and steel with low amount of carbon have different properties. Steel with higher amount of carbon is appearing darker than steel with lower amount of carbon. The darker appearance of surface is caused by casting of a shadow from cementite particle on ferrite. After a long period of time a natural patina begins to occur. Different corrosion resistance of the steels causes the contrast of ornaments which is still observable even after long time.

To observe the process of forming and segregation of sulphur the method of Baumann print was used. Yet the prints did not indicate the presence of sulphur. This was probably caused by using the charcoal which contains only a small amount of sulphur. The residual sulphur could create oxides in the form of a gas in the process of hand forging at high temperature and with the presence of oxygen.

4.4 EDX analysis of chemical composition

The EDX analysis proved that both knives consist of relative pure Fe matrix. Pure Fe matrix was confirmed by EDX spectrum that you can observe in Fig. 23a and Fig. 25a. In this matrix we can observe the impurities in particular areas. The impurities are the mechanic mixture of various elements with low atomic weight as shown in spectrums in Fig. 23b, c, d and Fig. 25b, c, d. Probably these elements were brought to the matrix in the process of forging and part of them might also be present in the raw ore.

5. Conclusions

Microstructural analysis by optical microscopy together with measurements of hardness proved that the knives were not quenched. Higher strength was reached by using the material with higher amount of carbon and by forging the material with the spine that was made of lower quality material. Technology of production by forging was proved by the presence of phosphorus stripes and also by stripes of impurities observed by SEM.

On the knives there was not found any deficiency in the process of production. Knife 1 with its decorative serrations was made for rather esthetical purpose than practical. If the knife was made to cut food, its utility properties were convenient. Moreover, it was easier to restore the sharpness of the edge on the non-quenched blade. The procedure of production of knife 2 was simpler. It was important to make the edge wear resistant.

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