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Application of a Microprobe Analyser to the Examination of Ancient Iron Objects

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APPLICATION OF A MICROPROBE ANALYSER TO THE EXAMINATION OF ANCIENT IRON OBJECTS

A microprobe analyser is one of the most modern devices for examining various kinds of materials. The said apparatus enables one to determine the chemical composition of very small volumes of $1\mu m^3$, and to analyse by scanning the chemical composition of particular phases observed in a metallographic specimen. It is also possible to determine the changes in the concentration of particular elements along the determined lines, and to register them in some chosen elements (observations are usually made at a magnification of approx. $\times 400$ and more). These methods, known under the name of quantitative, semi-quantitative and qualitative analyses, have found wide application in various fields of investigations, and particularly in physical metallurgy and mineralogy. The only important drawback is a high price of the apparatus.

First attempts, aiming at an application of the microprobe analyser to the examination of early bloomery iron objects, were undertaken by O. Schaaber who made a qualitative analysis of the changes in the content of Ca, Fe and Mn in the slag inclusions[1]. H. E. Bühler and Chr. Strassburger[2] determined changes in the content of phosphorus in the place of welding steel and iron parts in a Frankish sword dating from the 9th century.

R. Pleiner used this apparatus to identify the process of welding in one of the examined iron objects from the Great Moravian State[3]. Nevertheless, he did not

[1] O. Schaaber, *Beiträge zur Frage des Norischen Eisens* (Contribution to the question of the Noric iron), Carinthia 1963, vol. 153, no. 1, p. 199; O. Schaaber, *Einige Folgerungen aus der metallurgischen Untersuchung von antiken Werkstoffen* (Some conclusions from the metallographic examinations of ancient materials), "Radex-Rundschau", 1967, no. 3/4, p. 551.

[2] H. E. Bühler, Chr. Strassburger, *Werkstoffkundliche Untersuchungen zu zwei fränkischen Schwertern aus dem 9. Jahrhundert* (Metallographic examinations of two Frankish swords from the 9th century), "Archiv für das Eisenhüttenwesen", 1966, vol. 37, no. 8, p. 613.

[3] R. Pleiner, *Zur Schmiedetechnologie des Grossmährischen Reiches und die Deutung der metallographischen Befunde von Eisenfundstücken* (On the technology of forging in the Great Moravian State and the importance of metallographic examinations of iron findings), "Acta Archaeologica Carpathica", 1971, vol. 12, p. 107. Cf. also: J. Piaskowski, *Über die Kennzeichen der Zementation und des Schweissens an den frühmittelalterlichen eisernen Gegenständen* (Diskussion mit R. Pleiner).

observe any differences in the distribution of phosphorus and did not publish more exact data on the examinations carried out.

When this paper was being prepared, another one, written by T. Hansson and S. Modin, was published. The two investigators determined the content of Ni, Co, As and Cu in some ancient iron objects[4].

And thus, the works on an application of the microprobe analyser have been so far rather scarce. In particular, it was not determined if and how (*i.e.* using what kind of analyses) this device can be used for determining the technology of manufacturing ancient objects made of bloomery iron.

The examinations described here were analyses of the changes in the content of particular elements along the lines marking a cross-section of the objects under examination. Their aim was to check if it is possible to use a microprobe analyser for determining the technology of manufacturing ancient iron objects and for identifying the type of the metal used.

1. DESCRIPTION OF THE EXAMINED IRON OBJECTS AND THEIR CHARACTERISTIC BASED ON THE EXAMINATIONS MADE SO FAR

For the examinations made with a microprobe analyser seven ancient objects were chosen. They were made of bloomery iron and either the technology of manufacturing them was very complicated, or some structural phenomena were revealed which have not been explained so far. The objects in question are following:

a) knife no. 3 from an early Mediaeval settlement at Piekary, Cracow district, (13th cent.),
b) knife no. 5 from an early Mediaeval settlement at Czeladź Wielka, Góra district (9th - 12th cent.),
c) axe from the settlement at Nowa Huta-Mogiła (Szpital-Wschód region), (Roman period),
d) Roman sword (?) from the cemetary at Sobótka, Łęczyca district (2nd-3rd cent. A.D.),
e) Malayan creese (Kriss) rendered accessible for the examinations by the Polish Army Museum in Warsaw,
f) socketed axe from Jezierzyce, Dzierżoniów district (Hallstatt period),
g) socketed axe from Wietrzno-Bóbrka, Krosno district (loose finding from the Hallstatt period).

2. RESULTS OF THE EXAMINATIONS

This paper relates the results of the examinations of some chosen iron objects using a microprobe analyser, but the authors considered it pertinent to omit a detailed description of the metal structure and of the slag inclusions, and the discussion on the possible origin of these objects. The information on this subject can be found in the respective footnotes' items. Table 1 relates only the results of the quantitative

(On the criteria of cementation and welding of the early Mediaeval iron objects, Discussion with R. Pleiner), "Acta Archaeologica Carpathica", 1971, vol. 12, no. 1-2, p. 130.

[4] T. Hansson, S. Modin, *A metallographic examination of some iron findings with a high nickel and cobalt content*, "Early Mediaeval Studies", 1973, no. 5, p. 5.

and qualitative (spectrographic) chemical analysis of the objects under examination; "+" marks obvious presence of residuals, whereas "o" marks only the presence of the last (most stable) lines of a given element.

Moreover, in Table 2 the results of the metallographic examinations (structural constituents and their grain-size) are stated, as well as the results of the measurements of microhardness of the structural constituents and metal hardness.

The data presented in Table 1 can be compared with the results obtained when using a microprobe analyser.

The paper will discuss in detail only those problems which directly refer to the results of the examinations carried out with a microprobe analyser.

a) KNIFE NO. 3 FROM THE EARLY MEDIAEVAL SETTLEMENT AT PIEKARY, CRACOW DISTRICT

Knife no. 3 from Piekary, Cracow district (13th cent.), represents a typical early Mediaeval technology of manufacturing knives. This technology consists in welding together an iron rod (back) and a steel rod (edge) with the successive hardening by heat treatment (quenching). This is illustrated in Fig. 1, showing the structure of the cross-section of the knife[5].

In knife no. 3 from Piekary we observe the presence of a typical seam and a stripe of slag inclusions in the part between the steel edge and the iron back (Fig. 2), *i.e.* the phenomena which confirm the process of welding[6]. Hence, the examinations made with a microprobe analyser aimed at a determination of the distribution of residuals in the steel and the iron part in knife no. 3 from Piekary, and also in the intermediate layer between those two parts.

The examinations did not reveal any visible difference in the Fe content in the steel and the iron part. The difference is very small and it results only from the variations in the content of carbon (about 0.6 - 0.8% C) and phosphorus (about 0.3% P) in the metal.

On the other hand, the process of welding is clearly marked on the curve of variations in the phosphorus content (Fig. A), the said content being considerably lower in the steel edge that in the iron back part. According to the volumetric analysis, the steel part contained 0.09% P, whereas the iron back part contained 0.39% P (*cf.* Table 1).

The examinations of the changes in the distribution of As (Fig. A) and also Si, Ni, Ti and Pb, both in the steel part (edge) and in the iron part (back), gave a result (number of impulses) at the level of the background, *i. e.* no marked presence of these residuals was noted. On the other hand, the presence of the traces of Mn, Cu and Zn was observed and the number of impulses for these elements was slightly higher than the level of the background.

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[5] J. Piaskowski, *Metaloznawcze badania zabytków archeologicznych z Wyciąży, Igołomii, Jadownik Mokrych i Piekar* (Metallographic examinations of the archaeological monuments from Wyciąże, Igołomia, Jadowniki Mokre and Piekary), "Studia z dziejów górnictwa i hutnictwa", 1958, vol. 2, p. 72.

[6] *Cf.:* J. Piaskowski, *Kryteria określania technologii wyrobów z żelaza dymarskiego* (Criteria for determining the technology of manufacturing bloomery iron objects), "Archeologia Polski", 1973, vol. 12, no. 1, p. 7.

TABLE 1 — Results of quantitative analysis and qualitative chemical analysis of ancient iron objects examined with a microprobe analyser

No.	Name of object	Origin	Content, %		Qualitative analysis*														
			P	Ni	Ag	As	Ba	Bi	Co	Cr	Cu	Mo	Ni	Pb	Sb	Sn	Ti	V	Zn
1	Knife no. 3	Piekary																	
	a) edge	Cracow district	0.09				o				+		+						+
	b) back	(I/36–38/52)	0.39				o				+		+						+
2	Knife no. 5	Czeladź Wielka Góra district (Are 2, quarter I, fire-place 5)	0.15	0.07		+	o				+		+	o(?)		o	o		+
3	Axe	Nowa Huta-Mogiła																	
	a) edge	(Are 56 C, 40)				+	+				+		+	o		o(?)	o(?)		+
	b) middle part		0.374	0.02		+	+				+		+	o		o	o		+
4	Sword	Sobótka																	
	a) edge	Łęczyca district	0.05	0.00	o(?)	+	+		o(?)		+		+	+		o	o(?)		+
	b) middle part	(Grave 2–3, cat. no. 1938/291)				o	+		o(?)		+		+	o		o	o(?)		+
5	Malayan creese	(?)	0.10	0.54	o(?)		o			+	+		+	o		o	o	o(?)	+
6	Socketed axe	Jezierzyce Dzierżoniów district	0.056			o	o	o			o		+	+			o		o
7	Socketed axe	Wietrzno-Bóbrka																	
	a) edge	Krosno district	0.087	4		+		+			+		+	+		+	o		+
	b) socket					+		o			+		+	+		+	o		+

* Moreover, C, Si Mn, P, S and Al, Ca, Mg which were present in all specimens.

TABLE 2 — Results of metallographic examinations, measurements of microhardness of structural constituents and hardness of iron objects examined with a microprobe analyser

No.	Name of object	Origin	Structural constituents	Grain-size number	Microhardness kg/mm²	Vickers' hardness kg/mm²
1	2	3	4	5	6	7
1	Knife no. 3	Piekary,				
	a) edge	Cracow	martensite		562	473
		district	troostite		412	407
	b) weld		?		429	
	c) back		pearlite			
			sorbite			
			ferrite			
2	Knife no. 5	Czeladź	martensite		474	297
		Wielka,	sorbite		267	199
		Góra district	ferrite	6	156	
3	Axe	Nowa Huta-Mogiła				
	a) edge		martensite		947	418
	b) middle part		ferrite	2	303	274

TABLE 2–cntd.

1	2	3	4	5	6	7
4	Sword	Sobótka,				
	a) edge	Łęczyca	pearlite	5–7	243	131.9
		district	ferrite	7	131	
	b) ornamented part					
	1. iron I		ferrite	2	205	
	2. steel I		pearlite	8		
			ferrite	6	123	
	3. iron II		ferrite	2	216	206
	4. steel II		pearlite	8	243	141.7
			ferrite	6	123	
	5. iron III		ferrite	2	205	
	6. steel III		pearlite	8	205	
			ferrite	6	115	
	7. iron IV		ferrite	2	184	
	8. steel IV		pearlite	8	239	
			ferrite	6	126	
	9. iron V		ferrite	2	208	
	10. steel V		pearlite	8		
			ferrite	6		
	11. iron VI		ferrite	2		
	c) middle part		pearlite	4–6	255	193
			ferrite	7	124	

5	Malayan creese	?	bainite (?)		408	
			bainite (?)		387	
			bainite (?)		319	187
			ferrite	6	188	
			ferrite	6	194	
6	Socketed axe	Jezierzyce,				
	a) edge	Dzierżoniów	ferrite	6	154	
		district	acicular phase		435	165—134.7
			ferrite	6	156	
			acicular phase		447	
	b) socket		ferrite	3	162	121.9
			pearlite	4	288	
7	Socketed axe	Wietrzno-Bóbrka,				
	a) edge	Krosno				
	1. Layer I (steel)	district	ferrite	7	160	
			pearlite			113.1
	2. Layer II (nickel)		acicular phase		354	236
			unknown phase		179	
	3. Layer III (iron)		ferrite	6	158	95.8
	4. Layer IV (nickel)		acicular phase		323	221
			unknown phase		177	
	5. Layer V (steel)		ferrite	7	170	
			pearlite			121.9
	b) socket		pearlite	4	315	128.4
			ferrite		168	

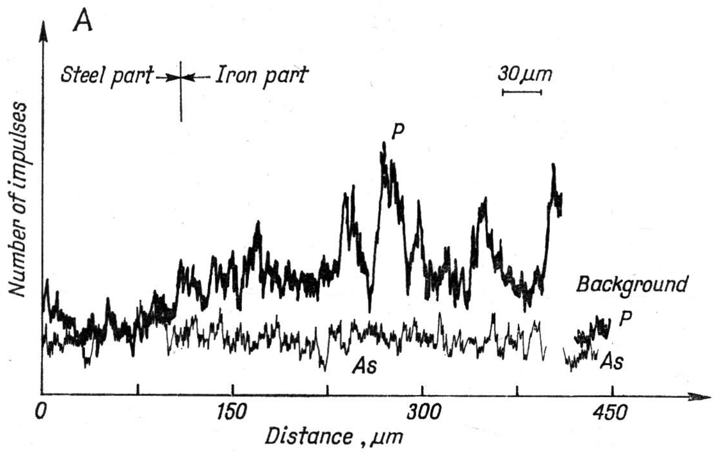

Fig. A. Diagram of changes in the content of P and As in knife no. 3 from Piekary, Cracow district (13th cent.)

b) KNIFE NO. 5 FROM THE EARLY MEDIAEVAL SETTLEMENT AT CZELADŹ WIELKA, GÓRA DISTRICT

Knife no. 5 from Czeladź Wielka, Góra district, was made of the bloomery iron of a ferritic structure with a relatively high content of phosphorus; the edge part included a region of higher carburization (Fig. 3). In this part martensite occurred, and farther from the cutting edge—sorbite. Carbon concentration varied to a high degree and the value of the gradient was also very high; (the structures are shown in the respective photograph, Fig. 4). Therefore, it was first decided that the knife was made by means of welding together an iron rod (back part) and a steel element (edge) with the successive quenching of the forged knife[7]. Nevertheless, the transition region between the carburized layer and the part of a ferritic structure was deprived of the characteristic seam with a stripe of rounded slag inclusions which were present, *e.g.* in knife no. 3 from Piekary, Cracow district (vid.: Fig. 2).

After a discussion with R. Pleiner, the presence of this stripe of inclusions was considered to be one of the main criteria of identification of the welding process in ancient bloomery iron objects[8].

The examinations carried out with a mircoprobe analyser did not reveal any difference in the Fe content in the transition region between the carburized layer and the metal of a ferritic structure. Visible minima of the Fe content were seen in the spots where the line of analysis came up against the slag inclusions (Fig. B).

The number of impulses, determined in the analysis of the content of Cu (Fig. B), As (Fig. C), Ni and probably also Ti, did not reveal any differences which points

[7] J. Piaskowski, *Metaloznawcze badania przedmiotów żelaznych z wczesnośredniowiecznej osady w Czeladzi Wielkiej, pow. Góra* (Metallographic examinations of iron objects from the early Mediaeval settlement at Czeladź Wielka, Góra district), "Silesia Antiqua", 1966, vol. 164.

[8] J. Piaskowski, *Technologie der Eisenherstellung im Grossmährischen Reiche* (Folgerungen aus den Forschungen von R. Pleiner) (Technology of manufacturing iron in the Great Moravian State, Conclusions from the investigations of R. Pleiner), "Acta Archaeologica Carpathica", 1969, vol. 11, no. 1, p. 111. *Cf.* also: J. Piaskowski, *Über die Kennzeichen der Zementation und des Schweissens an den frühmittelalterlichen eisernen Gegenständen* (On the criteria of cementation and welding of early Mediaeval iron objects), "Acta Archaeologica Carpathica", 1971, vol. 12, no. 1-2, p. 132.

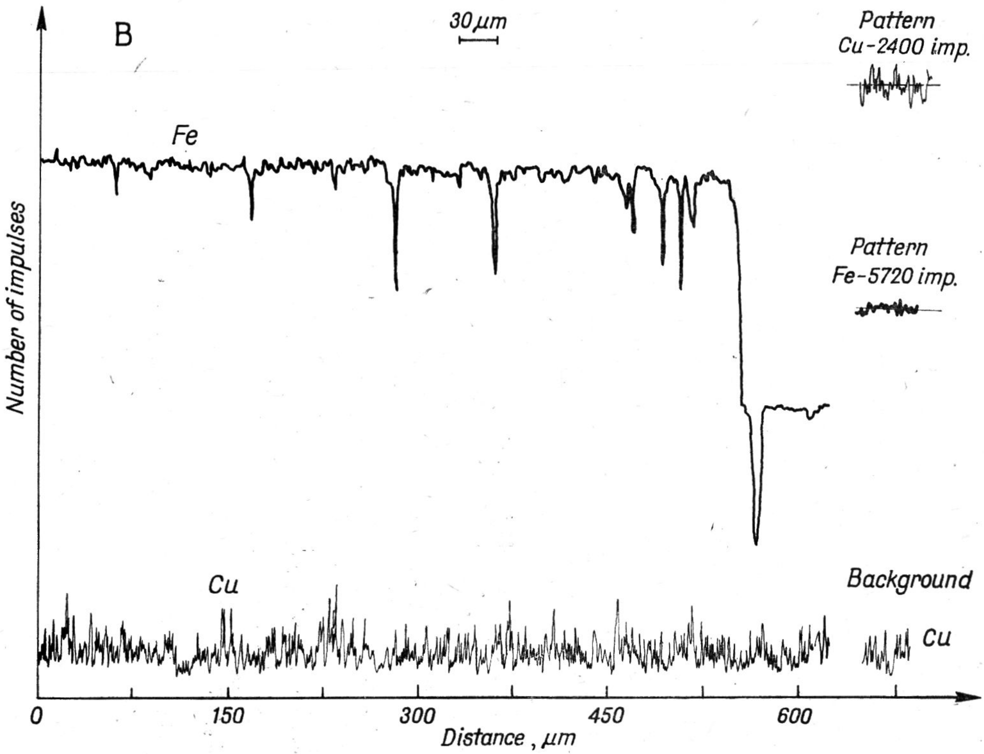

Fig. B. Diagram of changes in the content of Fe and Cu in knife no. 5 from Czeladź Wielka, Góra district (9th - 12th cent.)

out to the fact that these residuals were present only as trace elements. This was also confirmed by the spectrographic analysis (Table 1).

The examinations of the difference in the content of phosphorus in knife no. 5 from Czeladź Wielka, Góra district, revealed that there were some segregations of this residual. Nevertheless, between the carburized layer near the edge and the part of a ferritic structure in the regions distant from the edge (Fig. C) no distinct difference was observed, such as was visible in knife no. 3 from Piekary, Cracow district, which was composed of welded iron and steel parts (Fig. A). And therefore, it is possible that, in reality knife no. 5 from Czeladź Wielka, Góra district, was either not made by welding iron and steel as it was formely supposed, or that the steel and the iron parts did not contain varied content of phosphorus and of other analized residuals, such as As, Cu, Ni and Ti. The first possibility seems, however, to be more probable.

c) AXE FROM THE SETTLEMENT AT NOWA HUTA-MOGIŁA (ROMAN PERIOD)

The axe from the settlement at Nowa Huta-Mogiła (Roman period) was forged from high-phosphorus iron (containing, on the average, 0.374% P). There were welded sheets of steel at both sides of the edge; they were destroyed to a great extent

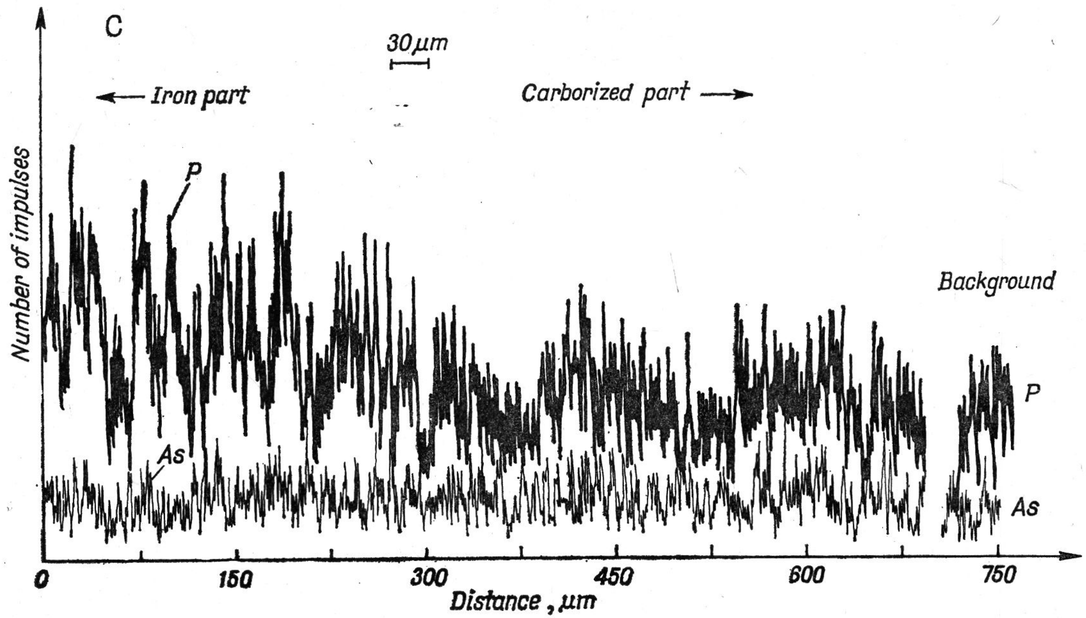

Fig. C. Diagram of changes in the content of P and As in knife no. 5 from Czeladź Wielka, Góra district
(9th - 12th cent.)

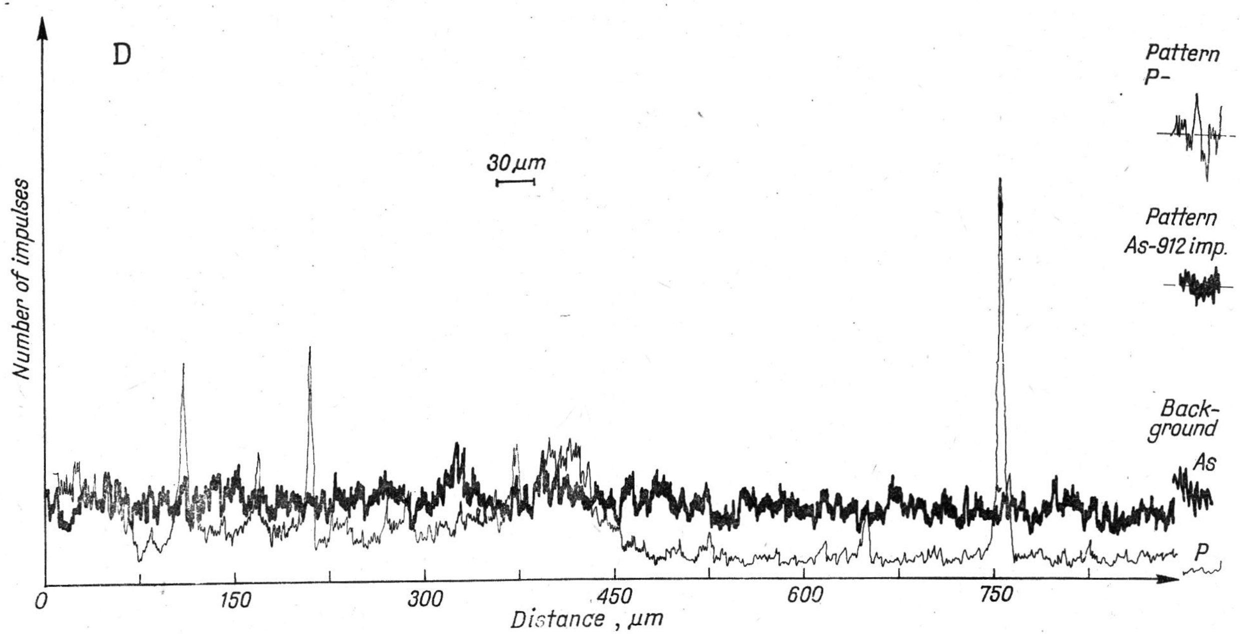

Fig. D. Diagram of changes in the content of P and As in the axe from Nowa Huta-Mogiła (Roman period) by corrosion (Fig. 5) .The structure of the steel layers was composed of martensite and troostite.

In the middle iron part of a ferritic structure the presence of stripes was observed; the stripes were characterized by a varied content of phosphorus (Figs 6 and 7). The axe was quenched.

The measurements, carried out with a microprobe analyser near the edge of the axe, revealed a rapid change in the content of phosphorus in the steel socket and the iron part (Fig. D), the amount of this residual in the steel part was lower and approached 0.097 % P, whereas in the iron part stripes of different phosphorus content were present. Apart from the stripes containing about 0.29 % P, the presence of the stripes containing about 0.75 % P was also noted. This result is in agreement with the chemical analysis presented in Table 1[9].

The content of phosphorus in the slag inclusions was also determined, its amount being equal to 1.4 % P, that is, 3.22 % P_2O_5. Metal phosphorus-to-slag phosphorus content ratio was also calculated, the value of this ratio being equal to about 0.2 which confirmed the relationship derived by J. Piaskowski[10].

In the iron and the steel part no differences in the content of As (Fig. D), Cu, Ti and Ni were observed. The number of impulses in the analysis of the content of these residuals was almost the same as the background level.

d) SWORD FROM THE CEMETARY AT SOBÓTKA, ŁĘCZYCA DISTRICT (2ND - 3RD CENT. A.D.)

The sword from the crematory cemetary at Sobótka, Łęczyca district (2nd - 3rd cent.), represents the most complex technology of working iron and steel materials, both in the Antiquity and Early Middle Ages, namely the pattern welding[11].

The decorative (pattern) layer is obtained by welding, forging and twisting steel and iron rods[12].

Figure 8 shows a photograph of the structure on the transverse cross-section of the sword from Sobótka; the steel edge and a fragment of the decorative part can be seen. In Fig. 9 one can see the structure in the region of welding the steel part (edge) and the adjacent iron part which already belongs to the decorative stripe. The thin layer of steel (its thickness amounts to about 0.2 mm) between the layers of iron in the decorative stripe is shown in Fig. 10.

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[9] J. Piaskowski, *Metaloznawcze badania przedmiotów żelaznych z osady w Nowej Hucie-Mogile z okresu rzymskiego* (Metallographic examinations of the iron objects from the settlement in Nowa Huta-Mogiła from the Roman period), "Materiały Starożytne", 1964, vol. 10, p. 174.

[10] J. Piaskowski, *Correlation between the phosphorus content in iron ore or slag and that in bloomery iron*, "Archaeologia Polona", 1965, vol. 7, p. 91.

[11] J. Piaskowski, *Mataloznawcze badania starożytnych przedmiotów żelaznych z woj. łódzkiego (Zgłowiączka-Gledzianówek, Łódź-Marysin, Kurza, Sobótka, Ciosny)* (Metallographic examinations of the ancient iron objects from the district of Lodz—Zgłowiączka-Gledzianówek, Łódź-Marysin, Kurza, Sobótka, Ciosny), "Studia z dziejów górnictwa i hutnictwa", 1968, vol. 12, p. 15. *Cf.* also: J. Piaskowski, *Niektóre dziwerowane miecze rzymskie na ziemiach Polski* (Some pattern welded Roman swords on the territory of Poland), "Z otchłani wieków", 1965, vol. 31, p. 36.

[12] The technology of making pattern welded objects was described in the following works: J. Piaskowski, *Technika wczesnośredniowiecznych wyrobów dziwerowanych w świetle nowych badań* (Technology of manufacturing early Mediaeval pattern welded objects in the light of the modern investigations), "Przegląd Mechaniczny", 1959, vol. 18, no. 15, p. 495.

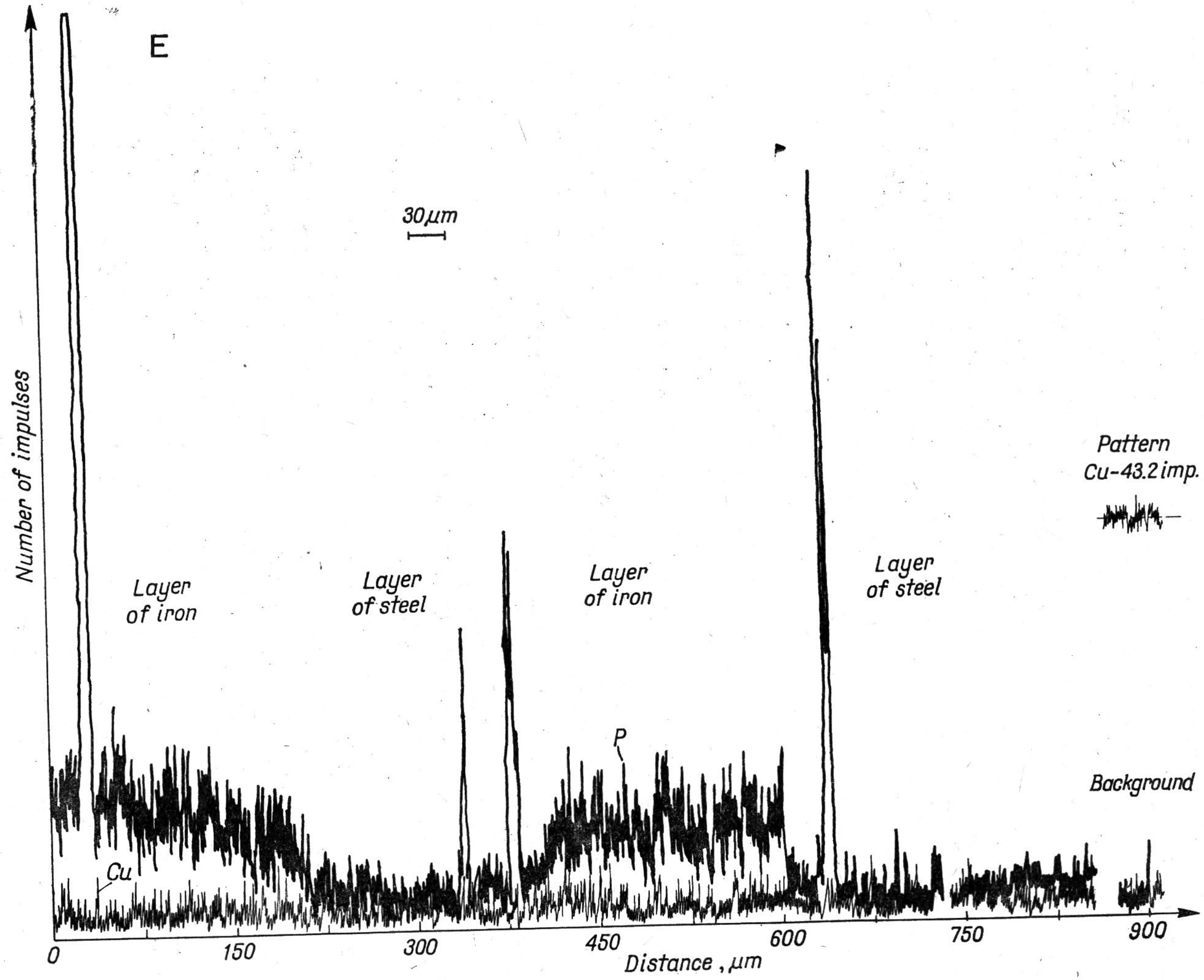

Fig. E. Diagram of changes in the content of P and Cu in the Roman sword from Sobótka, Łęczyca district (2nd - 3rd cent.)

In the case of pattern welded objects one does not observe such distinct traces of welding (seam, chain of slag inclusions) in the region of joining together the layers, as in other objects where this process was applied.

The linear analysis, carried out with a microprobe analyser, revealed that the content of phosphorus in the steel layers was lower than in the layers of iron. At the same time, rapid quantitative changes (Fig. E) were observed, similar to those encountered in knife no. 3 from Piekary, Cracow district, and in the axe from Nowa Huta-Mogiła. These changes are characteristic of the process of welding the parts of a different phosphorus content. On the other hand, the residuals of Cu (Fig. E), similarly as those of As, Ni, Pb, Si, Ti, Zn, and probably also of Mn, occurred only as trace elements (at the level of the background).

The Si distribution curve showed the maxima values in the places where the slag inclusions were present. For three slag inclusions the following percentages of the Si content were calculated: 5.03, 4.40 and 4.20%, *i.e.* approx. 10.8, 9.4 and 9.2% SiO_2, respectively. The values of the results are slightly lower than those obtained in the analysis of bloomery slag. This was caused, among others, by a strong absorption of the characteristic Si radiation by the radiation of Fe.

e) MALAYAN CREESE (FROM THE POLISH ARMY MUSEUM IN WARSAW)

Malayan creeses are very interesting objects, although up till now it has not been possible to determine exactly the technology which enabled to obtain a typical decorative surface pattern.

Examinations of the Malayan creese from the Polish Army Museum revealed[13] that it was forged from three sheets of metal (Fig. 11). The middle part was of iron with a low phosphorus content (Fig. 12) and its edges (the edges of the creese) were probably carburized. Both sides of the creese were of iron of a ferritic structure containing some layers of an acicular structure (bainitic structure?) (Fig. 13). These layers formed a pattern (dark lines) on the surface of the creese.

Inside the carbonized layers (?) there are present some slag inclusions. This confirms the process of welding (Fig. 14).

As it results from the linear analysis carried out with a microprobe analyser, the content of Fe, both in ferritic and bainitic (?) layers of iron, is almost the same (about 99%), the content of Fe in the latter one being, however, slightly lower (Fig. 14).

The minima on the curve of the Fe content values appear in the places where the slag inclusions occur; also, in these places the content of phosphorus was higher. Quantitative determination of the Fe content in the iron or the bainitic (?) layer was useless. On the other hand, an approximate content of iron in the slag inclusions was calculated and the result was 44.2% Fe. And indeed, this amount of Fe occurs most often in bloomery slag[14].

[13] J. Piaskowski, *Technologia wyrobu krysów malajskich* (Technology of manufacturing Malayan creeses), "Kwartalnik Historii Nauki i Techniki", 1975, vol. 20, no. 3-4, p. 515. Examinations of the Malayan creeses were described in the following works:
H. Jacobsen, *Dem javanesiske Kris* (The Javanese creeses) "Vaaben-historische Arbøger", 1937, vol. 2, p. 83; C. Panseri, *L'acciaio di Damasco nella leggenda e nella realtà* (The Damascus steel in legend and in reality), "Armi Antiche", 1962, p. 3. Malayan creeses were described by C. S. Smith, *A history of metallography*, Chicago 1960, p. 39.

[14] J. Piaskowski, *Klasyfikacja dawnego żużla dymarskiego występującego na ziemiach Polski*


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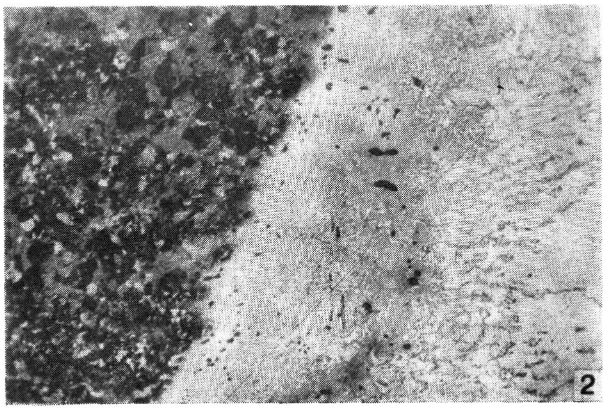
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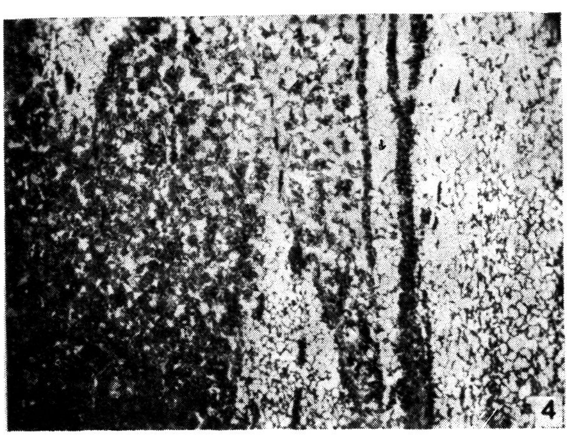
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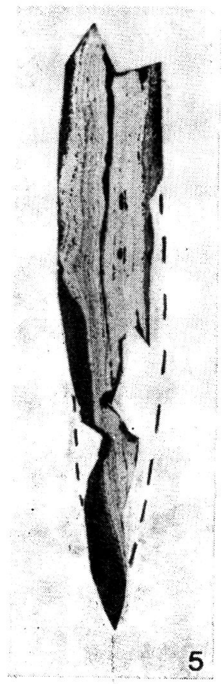
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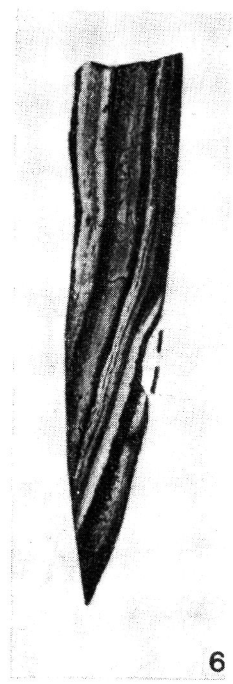
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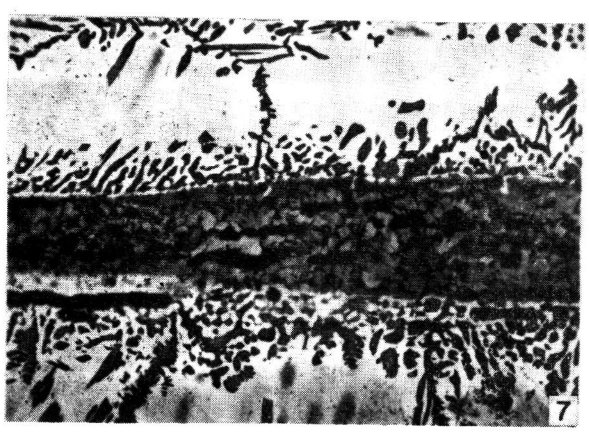
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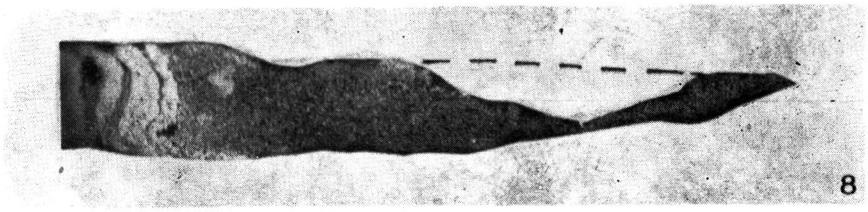

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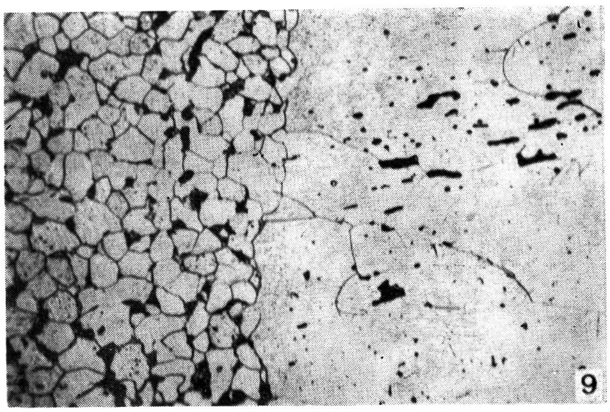

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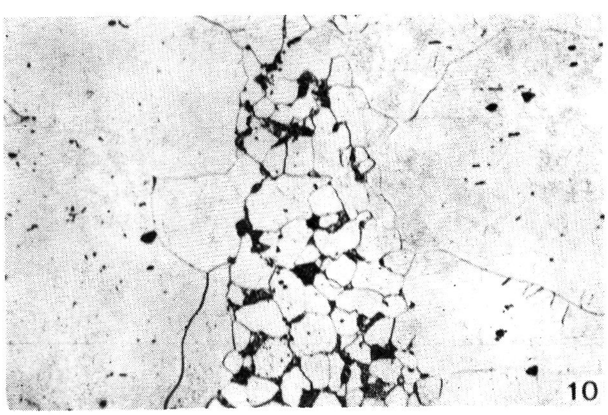

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Fig. 1. Macrostructure of the cross-section of knife no. 3 from Piekary, Cracow district (13th cent.). Nital etching. ×8

Fig. 2. Structure of welded parts—steel (left) and iron (right)—in knife no. 3 from Piekary, Cracow district (13th cent.). Nital etching. ×100

Fig. 3. Macrostructure of the cross-section of knife no. 5 from Czeladź Wielka, Góra district (9th - 12th cent.). Nital etching. ×8

Fig. 4. Structure of knife no. 5 from Czeladź Wielka, Góra district (9th - 12th cent.) near the cutting edge. The part was carburized from the right side. Nital etching. ×100

Fig. 5. Macrostructure of the cross-section of the axe from Nowa Huta-Mogiła (Roman period). Nital etching. ×5

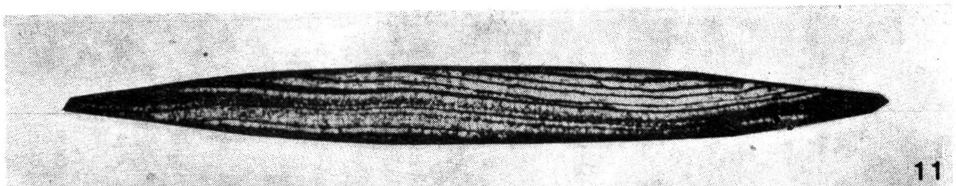
Fig. 6. Distribution of phosphorus on the cross-section of the axe from Nowa Huta-Mogiła (Roman period). Etching with Oberhoffer's reagent. ×5

Fig. 7. The stripe of a reduced phosphorus content in the axe from Nowa Huta-Mogiła (Roman period). Etching with Oberhoffer's reagent. ×50

Fig. 8. Macrostructure near the edge of the Roman sword from Sobótka, Łęczyca district (2nd - 3rd cent.). Nital etching. ×4

Fig. 9. Structure of the joint between the steel (right) and the iron part (left) in the Roman sword from Sobótka, Łęczyca district (2nd - 3rd cent.). Nital etching. ×100

Fig. 10. Structure of the decorative part in the Roman sword from Sobótka, Łęczyca district (2nd - 3rd cent.); the layer of steel between two iron layers is visible. Nital etching. × 100



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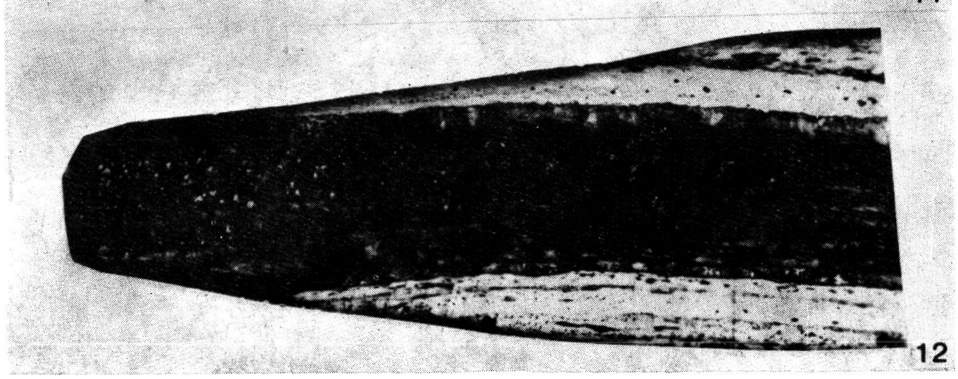

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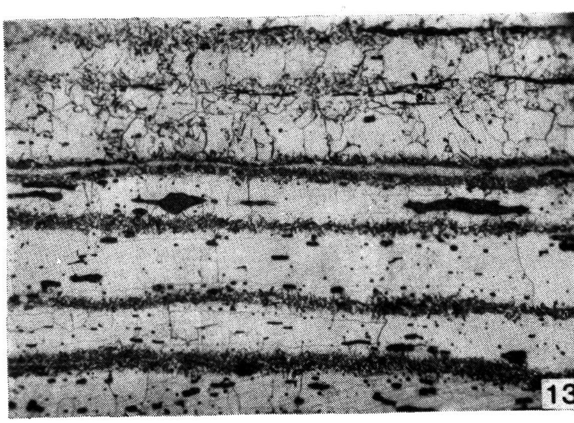

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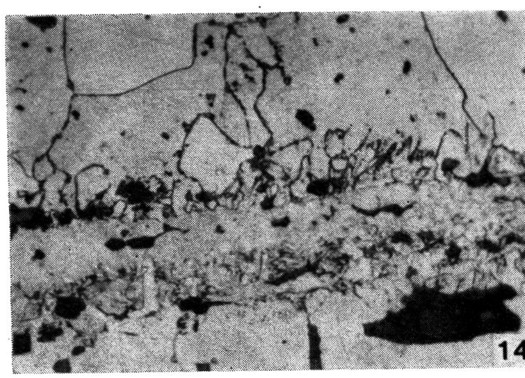

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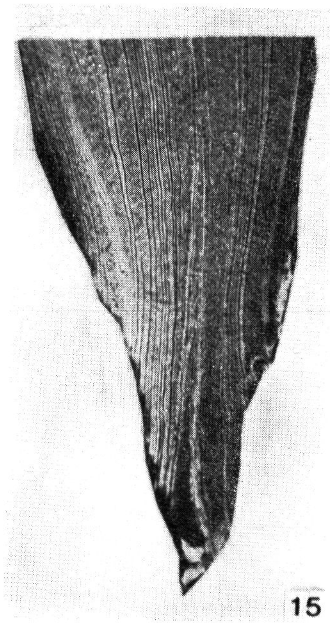
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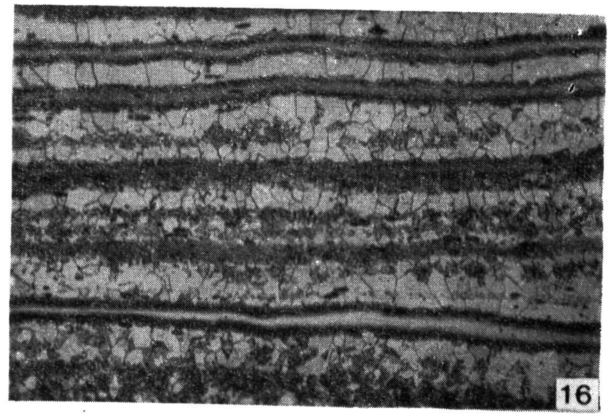
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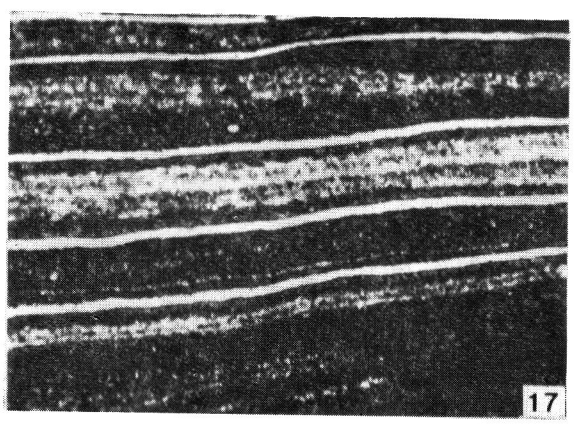
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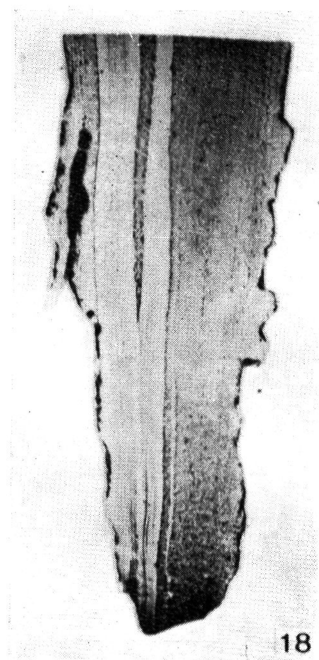
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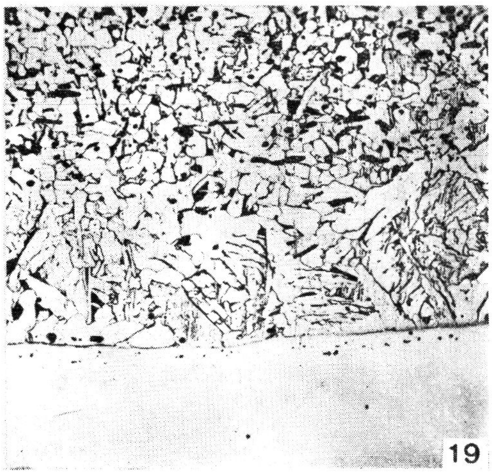
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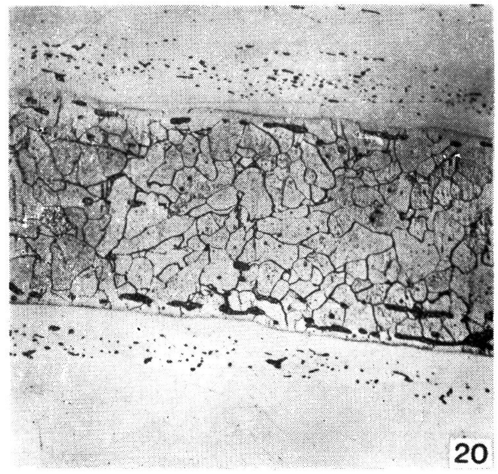
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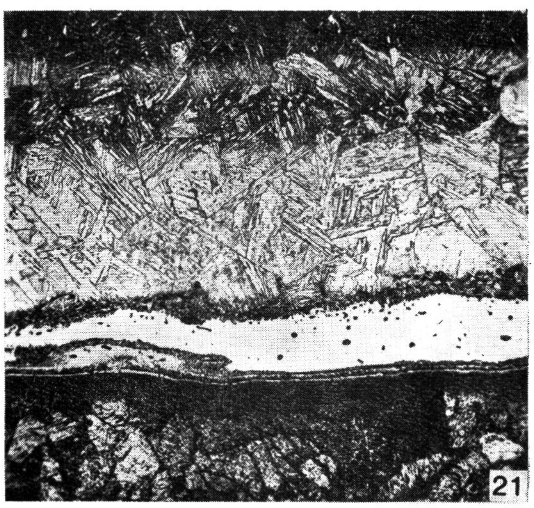
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Fig. 11. Macrostructure of the cross-section of the Malayan creese. Nital etching. ×11

Fig. 12. Distribution of phosphorus on the cross-section of the Malayan creese. Etching with Oberhoffer's reagent. ×50

Fig. 13. Structure of the outer (decorative) layer of the Malayan creese. Layers of acicular structure are visible (dark colour). Nital etching. ×100

Fig. 14. Structure of the layer of acicular structure in the Malayan cresse as seen under large magnification. Nital etching. ×500

Fig. 15. Macrostructure of the cross-section of the edge of the axe from Jezierzyce, Dzierżoniów district. Nital etching. ×10

Fig. 16. Structure of the edge of the axe from Jezierzyce, Dzierżoniów district. Nital etching. ×100

Fig. 17. Distribution of phosphorus on the edge of the axe from Jezierzyce, Dzierżoniów district. Etching with Oberhoffer's reagent. ×50

Fig. 18. Macrostructure of the edge of the axe from Wietrzno-Bóbrka, Krosno district. Nital etchingi ×6.5

Fig. 19. Structure of the joint between the steel (top) and the high-nickel content part (bottom). Nital etching. ×100

Fig. 20. Structure of the iron layer (in the middle) placed between two layers of high-nickel content in the edge of the axe from Wietrzno-Bóbrka, Krosno district. Nital etching. ×100.

Fig. 21. Structure occurring between the high-nickel layer (top) of acicular structure with the stripe of very high-nickel content (unetched) and the layer of low-carbon steel (bottom). Etching with a mixture of diluted picric acid and hydrochloric acid. ×100

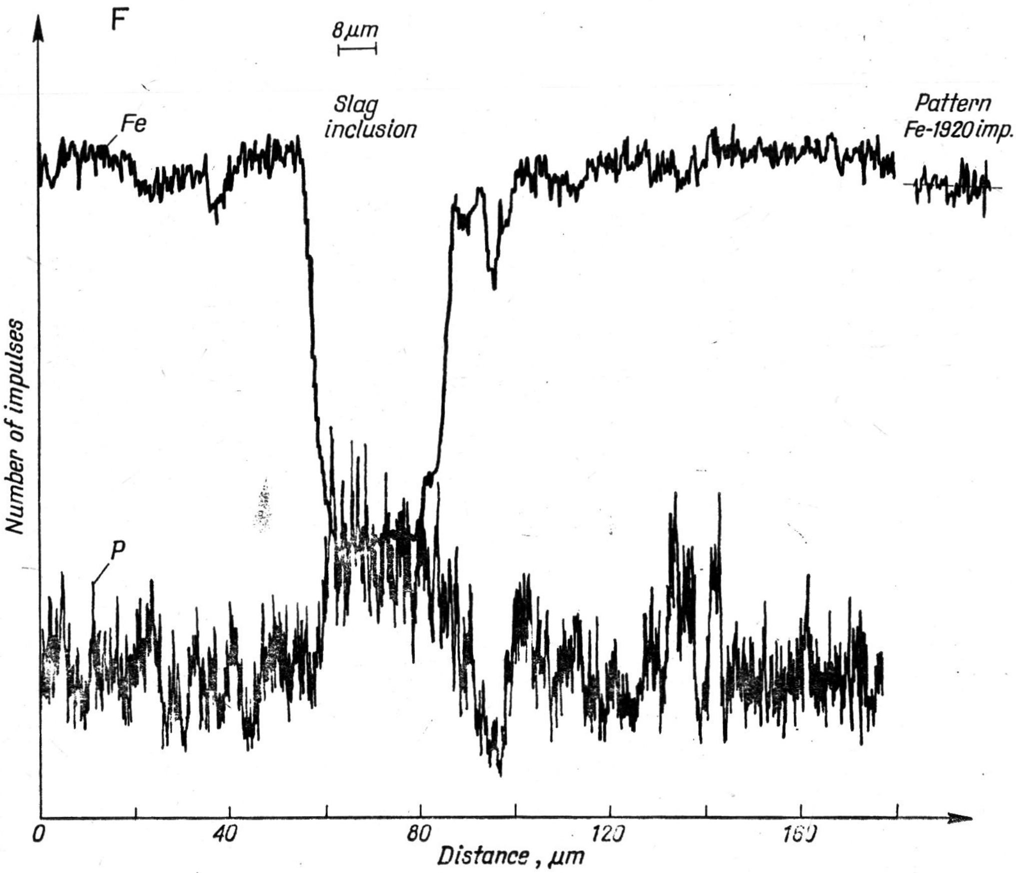

Fig. F. Diagram of changes in the content of Fe and P in the Malayan creese

Similarly, slag inclusions contain more phosphorus than the metal (Fig. F). On the other hand, no marked differences in the content of phosphorus in the layers of a bainitic (?) structure were observed.

In the bainitic layers of the outer part of the creese a high content of nickel was noted; it amounted to 1.8 - 2.0 % Ni, and in some places reached even the values of 3.3 - 3.9 % Ni. On the other hand, in the iron of a ferritic structure and also in the slag inclusions the content of nickel was almost none, *i.e.* at the level of the background (Fig. G).

The content of nickel in the Malayan creese, determined by means of the chemical analysis, was 0.54 % Ni (Table 1). This was an average obtained on all the layers of the metal.

Titanium was present as a trace element and its distribution was relatively even, *i.e.* the content of this residual, both in the ferritic and bainitic (?) layers, was identical and could hardly be distinguished from the level of the background. Higher

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w świetle statystycznej analizy składu chemicznego (Classification of ancient bloomery slag present on the territory of Poland in the light of the statistical analysis of the chemical composition),"Kwartalnik Historii Kultury Materialnej", 1966, vol. 14, no. 3, p. 343.

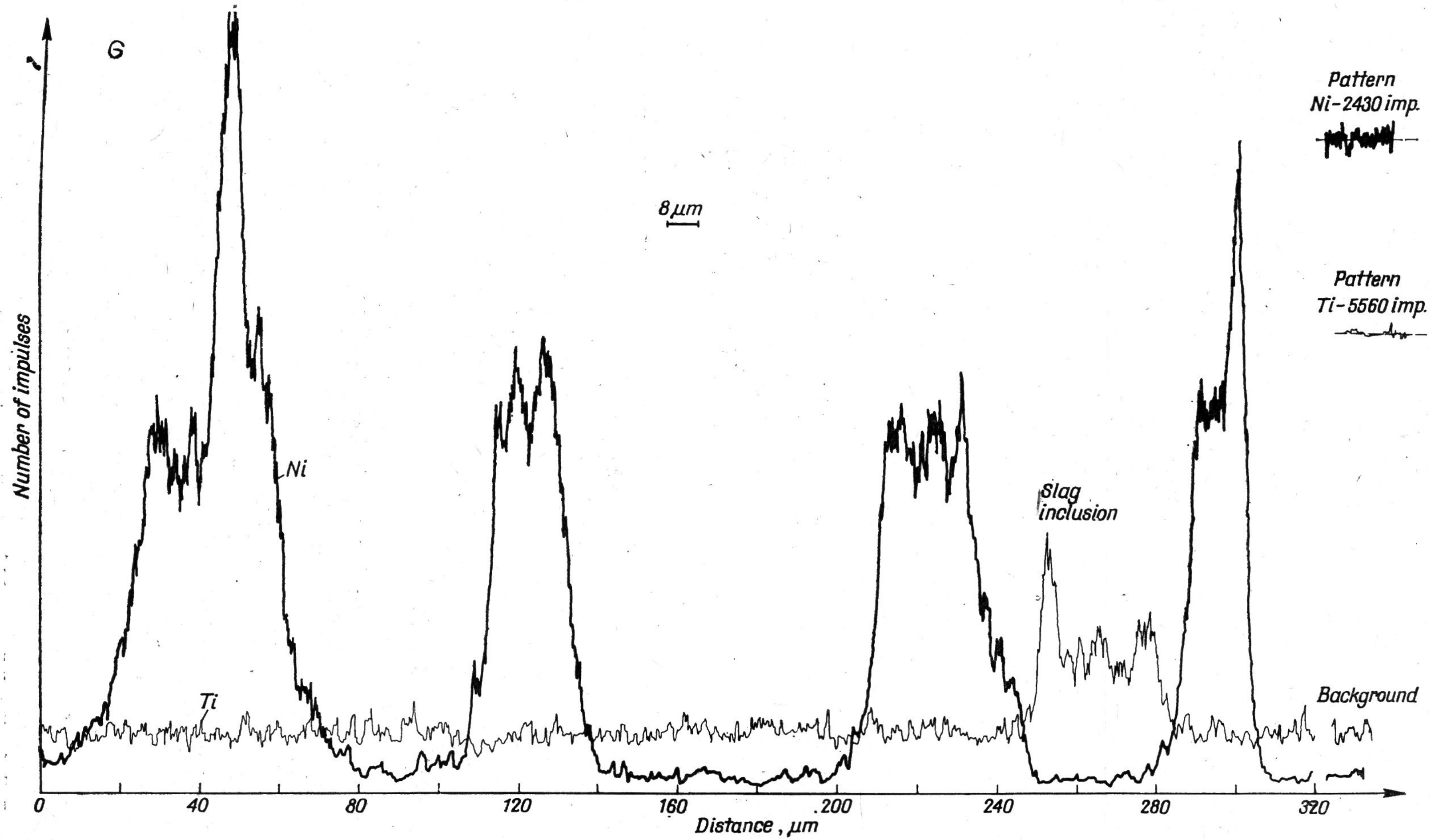

Fig. G. Diagram of changes in the content of Ni and Ti in the Malayan creese

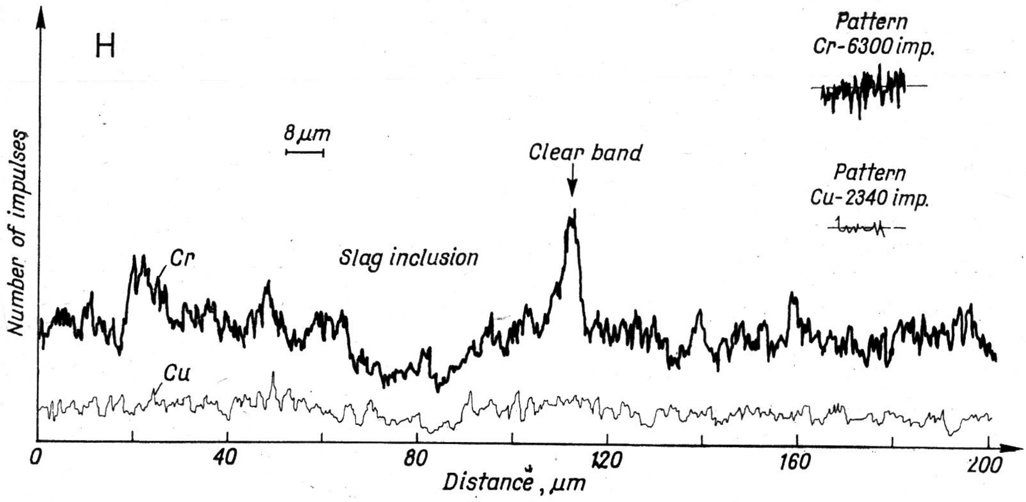

Fig. H. Diagram of changes in the content of Cu and Cr in the Malayan creese

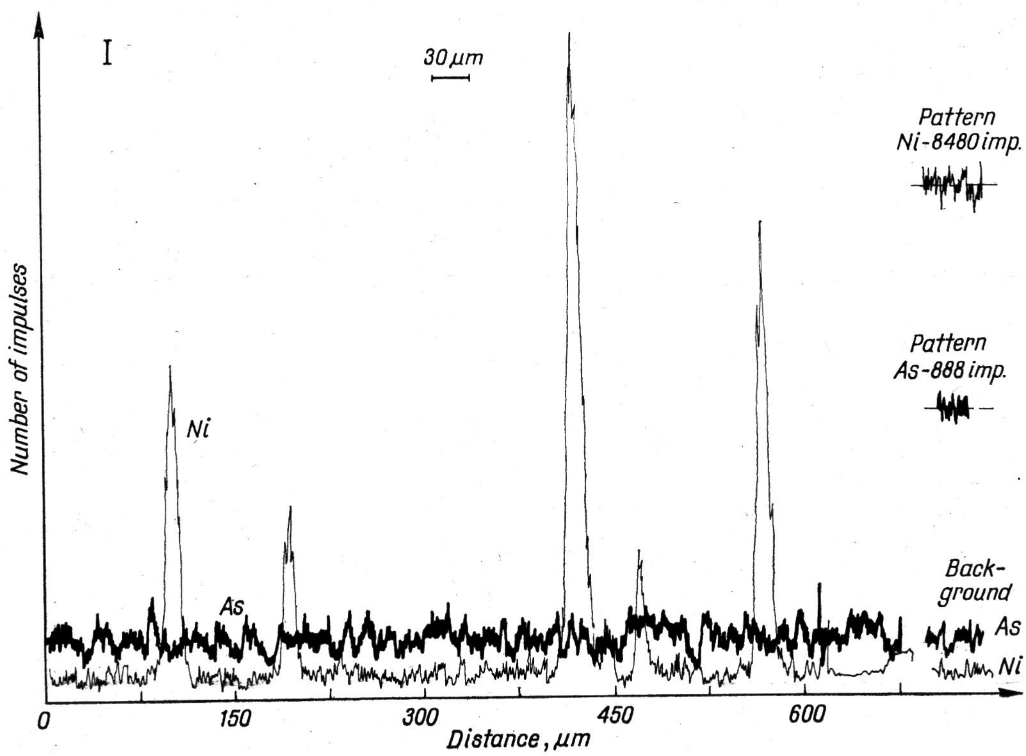

Fig. I. Diagram of changes in the content of Ni and As in the socketed axe from Jezierzyce, Dzierżoniów district amounts of titanium were present in the slag inclusions. Their content was about 0.17 % Ti, and sometimes reached even 0.39 % Ti (Fig. G). Chromium, on the other hand, was not present at all in the slag inclusions and occurred mainly in the metal (Fig. H).

Copper was also present as a trace element, both in the iron and in the bainitic layers (Fig. H).

The examinations of the Malayan creese made with a microprobe analyser create a new problem which requires solution, namely, an explanation of the method in which the bainitic layer was enriched in nickel. It is probable that the process of cementation of iron with nickel was carried out, however, up till now it has not been established what substance was used by the manufacturers of creeses.

f) SOCKETED AXE FROM JEZIERZYCE, DZIERŻONIÓW DISTRICT (HALLSTATT PERIOD)

The socketed axe from Jezierzyce, Dzierżoniów district (from the Hallstatt period) was forged from the metal in which the presence of numerous stripes was observed (Fig. 15). After Nital etching two types of the stripes were distinguished. The stripes of the first type had an acicular (martensitic) structure, whereas those of the second type contained inside an additional layer which resisted Nital etching and preserved its light colour (Figs. 16 and 17). These layers resisted the action of the Oberhoffer's reagent as well (Fig. 17) which enables a suggestion that they include high content of phosphorus.

A similar structure occured in the socket of the axe which means that the axe was forged from one piece of metal[15].

It should also be mentioned here that the identical stripe structure was observed in the axe from Eskilstun; that axe was examined by T. Hansson and S. Modin[16]. In the layer of a structure determined by them as martensitic, nickel and cobalt were supposed to be present in the amounts of 5 % and 0.7 %, respectively. Between the layers the content of these elements was different and amounted to 0.6 % Ni and 0.3 % Co, respectively.

On the surface of the axe from Eskilstun the pattern was revealed which resembled that encountered in Malayan creeses.

The examinations carried out with a microprobe analyser showed great differences in the nickel content in the socketed axe from Jezierzyce, Dzierżoniów dis-

[15] J. Piaskowski, *Metaloznawcze badania wyrobów żelaznych z okresu halsztackiego i lateńskiego, znalezionych na Śląsku* (Metallographic examinations of iron objects from the Hallstatt and La Tène periods found in Silesia), "Przegląd Archeologiczny", 1960, vol. 12, p. 134.
J. Piaskowski, *Études des plus interessantes techniques de fabrication des objets en fer employés en Pologne du VIIIe au IIe siècle av. J. C.* (Studies on the most interesting technologies of manufacturing iron objects used in Poland in the period between the 8th and 2nd cent. B.C), "Métaux-Corrosion-Industries", 1965, no. 455-456, p. 292.
J. Piaskowski, *Metallographische Untersuchungen der Eisenerzeugnisse in der Hallstattzeit im Gebiet zwischen Oder und Weichsel. Beiträge zur Lausitzer Kultur, Referate der Internationalen Arbeitstagung zu Problemen der Lausitzer Kultur vom 24 bis 26 November 1967 in Dresden.* (Metallographic examinations of iron objects from the Hallstatt period on the territory between Oder and Vistula. Contribution to the Lusatian Culture. Papers presented at the International Conference on the Problems of the Lusatian Culture from 24th to 26th November 1967 in Dresden), VEB Deutscher Verlag der Wissenschaften, Berlin 1969, p. 190.

[16] T. Hansson, S. Modin, *op. cit.*, p. 14.

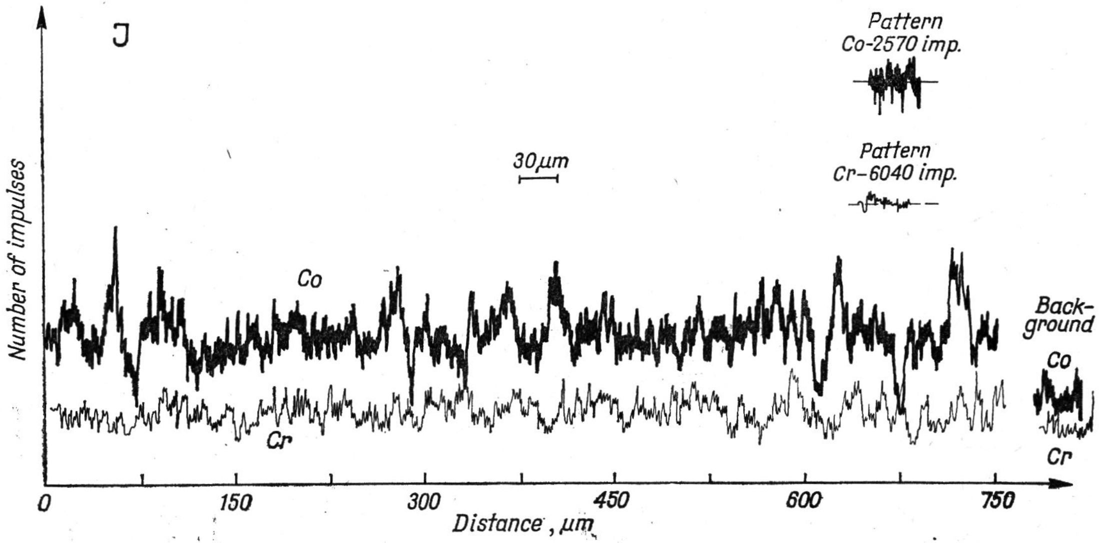

Fig. J. Diagram of changes in the content of Co and Cr in the socketed axe from Jezierzyce, Dzierżoniów district

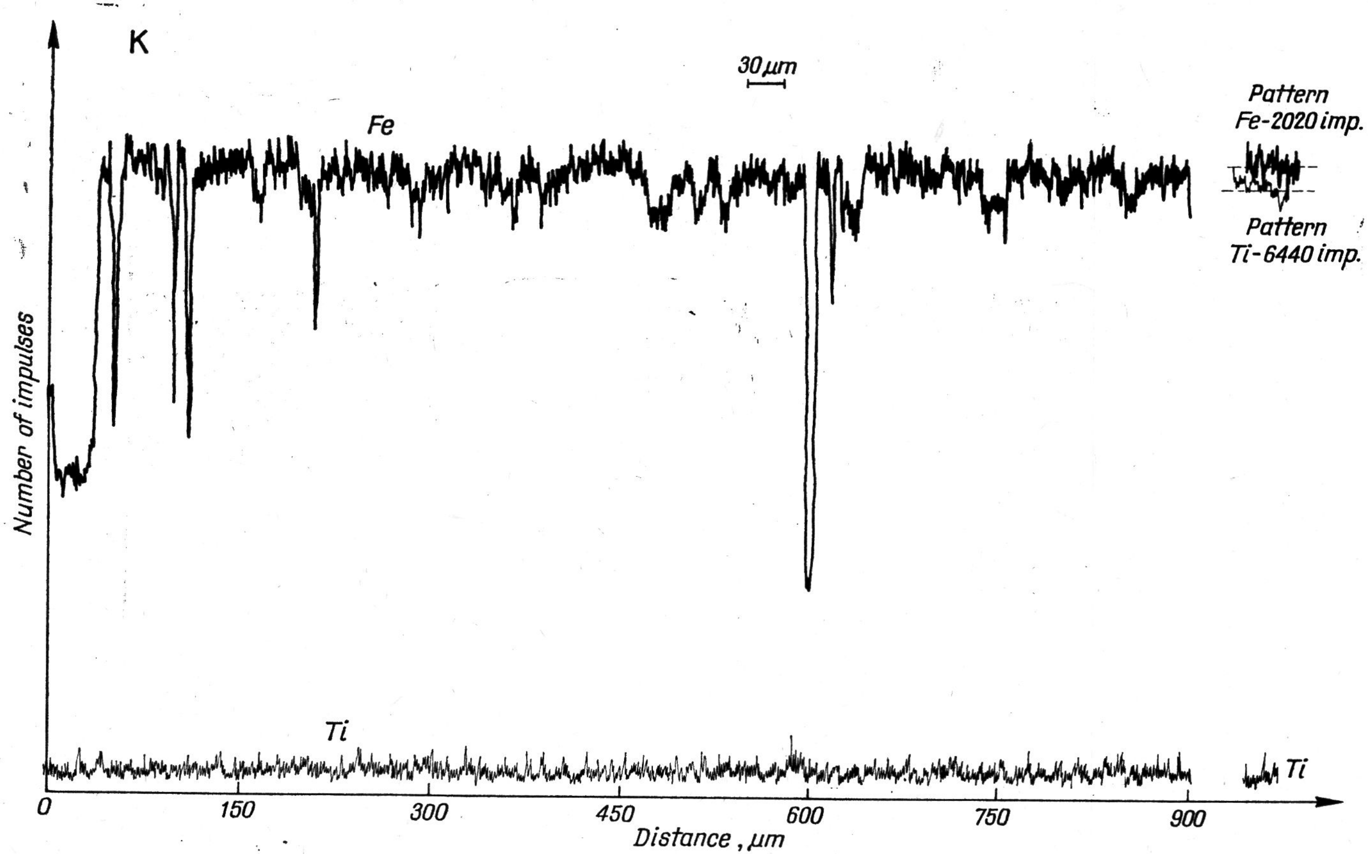

Fig. K. Diagram of changes in the content of Fe and Ti in the socketed axe from Jezierzyce, Dzierżoniów district

trict. In the metal this residual is present as a trace element (at the level of the background), whereas in the layers of an acicular (martensitic) structure the content of nickel amounts to 0.23 - 0.37% Ni; in the layer of an unknown phase the content of nickel is still higher and reaches 1.6 - 3.0% Ni (Fig. I).

In the second series of measurements, the linear analysis of the nickel content was repeated and the results obtained were from 0.5 to 2.3% Ni. The content of cobalt was also determined and it amounted to about 0.2% Co in the metal and increased up to about 0.5% Co in the acicular stripes containing also nickel (Fig. J). The results of these analyses were identical with those obtained in case of the axe from Eskilstun analysed by T. Hansson and S. Modin. These investigators probably determined too low a level of the background and therefore they obtained in their calculations some amounts of nickel (0.6% Ni) and cobalt (0.3% Co) between the layers of a martensitic structure.

Other residuals, such as As (Fig. I), Ti (Fig. K) and Cu occurred in the axe from Jezierzyce as trace elements (at the level of the background), no differences in the distribution in particular layers being revealed. On the other hand, it was not determined if the metal contained some small amounts of chromium (0.04% Cr). It is possible, however, that this result was caused by an inaccurate determination of the background level (Fig. J).

The X-ray microanalysis did not reveal any differences in the distribution of phosphorus; its content in the metal was very small (chemical analysis gave a value of 0.056% P—Table 1). Only in the slag inclusions the content of phosphorus was considerably higher than in the metal.

The distribution of Fe (Fig. K) showed minima in the place where the slag inclusions occurred; the calculated amounts of Fe in seven inclusions were: 54.7, 58.3, 69.8, 29.2, 49.4 and 44.6% P, respectively. These amounts of Fe do exist in bloomery iron[17].

On the basis of the examinations carried out so far, it can be supposed that the axe from Jezierzyce, Dzierżoniów district, was made by a cementation with a nickel-cobalt iron, and—possibly also—by carburizing with the successive faggoting.

If the amount of the substance used for the cementation with nickel was low, only a carburized stripe was obtained with a small content of nickel (0.23 - 0.37% Ni). If, on the other hand, the amount of this substance was high, then the layer of an unknown phase appeared, the said layer containing 1.6 - 3.0% Ni and about 0.5% Co.

g) SOCKETED AXE FROM WIETRZNO-BÓBRKA, KROSNO DISTRICT (HALLSTATT PERIOD)

The edge of the socketed axe from Wietrzno-Bóbrka, Krosno district (from the Hallstatt period), was composed of five layers, and namely: two outer layers of low carbon steel containing 0.1 - 0.3 % C, middle layer composed of iron of a ferritic structure, and two layers of the metal which, as it was supposed, contained considerable amounts of nickel (Fig. 18). The said layers occurred between the iron part and the outer steel layers. Basing on the average analysis value of all the layers,

[17] *Cf. supra,* Note 14.

this value being equal to about 4%, it was calculated that the layers of nickel iron contained about 8 - 10% Ni[18].

The socket was made of low-carbon steel; the same steel was used for the outer parts of the edge.

Figure 19 shows the structure of the edge in the axe from Wietrzno-Bóbrka, Krosno district, in the place where the outer part made of low-carbon steel and the layer made of nickel iron were joined together. In Fig. 20 one can see the middle part made of iron of a ferritic structure and placed between the two layers of nickel iron.

The use of a special etching reagent (a mixture of picric acid and hydrochloric acid) revealed that the layer of high-nickel iron is not uniform but contains the stripe of an acicular structure and the stripe of an unknown structure which resisted the action of the mixture of picric acid and hydrochloric acid (Fig. 21).

On the basis of these examinations it was concluded that the axe from Wietrzno--Bóbrka was made by means of welding low-carbon steel and high-nickel iron. This was one of the arguments confirming the statement that high-nickel iron was smelted by ancient metallurgists[19].

Using a microprobe analyser, linear analysis was made of all the five layers of which the edge of the axe was composed. The examinations proved that in the outer layers I and V of low-carbon steel of a ferritic-pearlitic structure, and in the middle layer III of iron of a ferritic structure, nickel appears as a trace element (at the level of the background), whereas in the intermediate layers (II and IV) the content of nickel is from 8.9 to 17.8% Ni, and in one layer it reaches even a value of 39.1% Ni. This elevated content of nickel is accompanied by an elevated content of cobalt equal to 0.95 - 1.07% Co. In the layers of iron and steel (I, III and V) the content of cobalt was slightly higher (?) than the level of the background (Fig. L).

The repeated linear analysis also revealed some traces of nickel in the steel and the iron parts (layers I, III and V) (at the level of background), whereas in the intermediate layers (II and IV) the content of this element was 8.6 - 13.6% Ni (maximum reached even 33.6% Ni) and 7.1 - 17.4% Ni in the first and the second layer, respectively.

In both layers of the elevated nickel and cobalt content (II and IV), the presence of As was also noted (Fig. M). The content of this element was 0.24 - 0.42% As (max. 1.15% As) in the first layer, and 0.14 - 0.94% As in the second layer, whereas in the layers of iron and steel the number of impulses remained at the level of the background.

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[18] J. Piaskowski, *Metaloznawcze badania wyrobów żelaznych z okresu halsztackiego i lateńskiego, pochodzących z Małopolski* (Metallographic examinations of iron objects from the Hallstatt and La Tène periods found in Little Poland), "Materiały Archeologiczne", 1960, vol. 2, p. 204. J. Piaskowski, *An interesting example of early technology: a socketed axe from Wietrzno-Bóbrka in the Carpathians*, "Journal of the Iron and Steel Institute", 1960, vol. 194, no. 3, p. 336. *Cf.* also Note 15, 2nd item, p. 283 and Note 15, 3rd item, p. 186.

[19] J. Piaskowski, *O produkcji żelaza wysokoniklowego w starożytności* (On the process of manufacturing high-nickel iron in the Antiquity), "Acta Archaeologica Carpathica", 1969-1970, vol. 11, no. 2, p. 319. *Cf.* also: J. Piaskowski, *Badania nad występowaniem stali o wysokiej zawartości niklu w starożytności* (Investigations on the application of high-nickel steel in the Antiquity), "Hutnik", 1970, vol. 37, no. 2, p. 117.

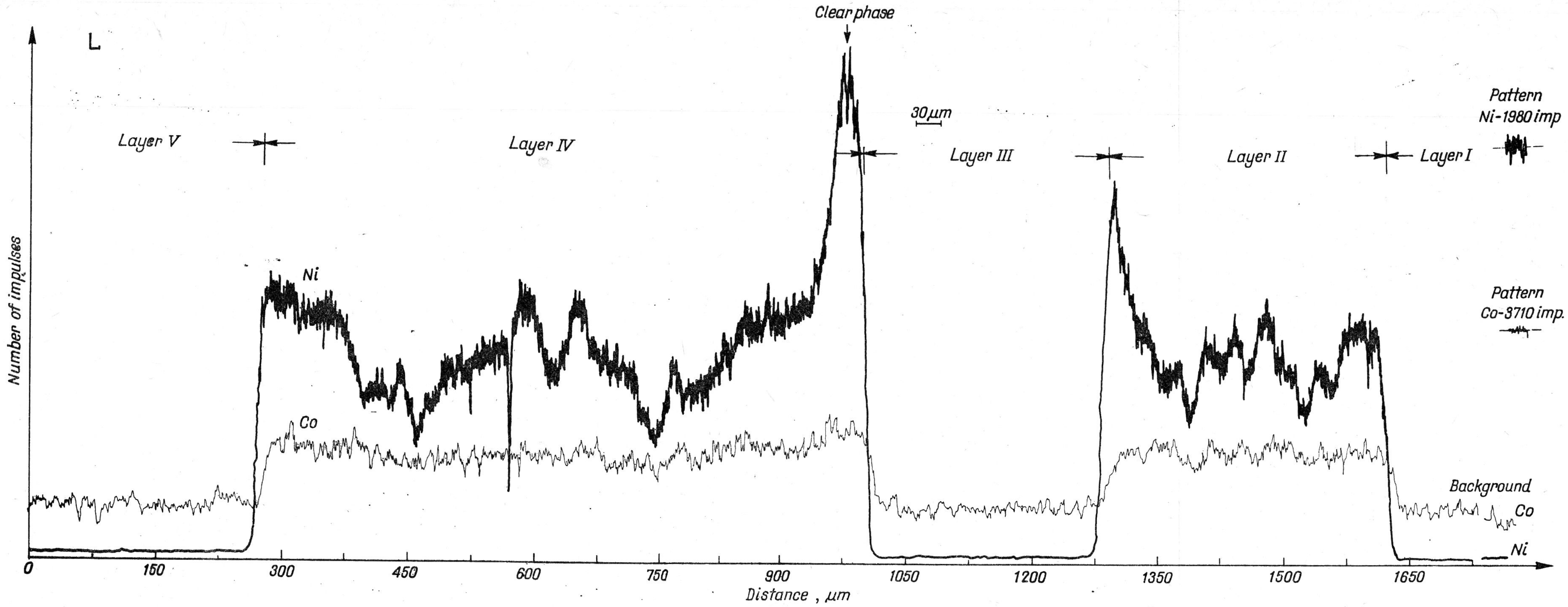

Fig. L. Diagram of changes in the content of Ni and Co in the socketed axe from Wietrzno-Bóbrka, Krosno district

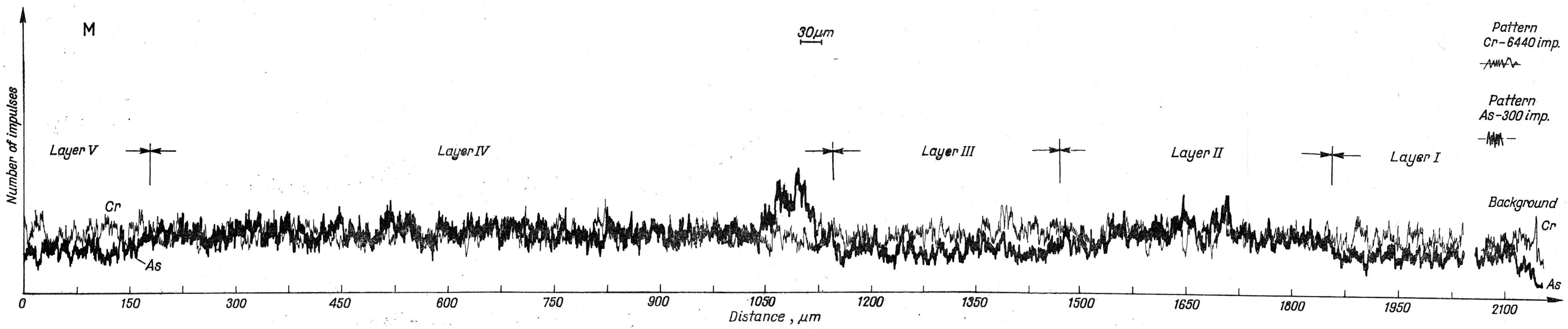

Fig. M. Diagram of changes in the content of As and Cr in the socketed axe from Wietrzno-Bóbrka, Krosno district

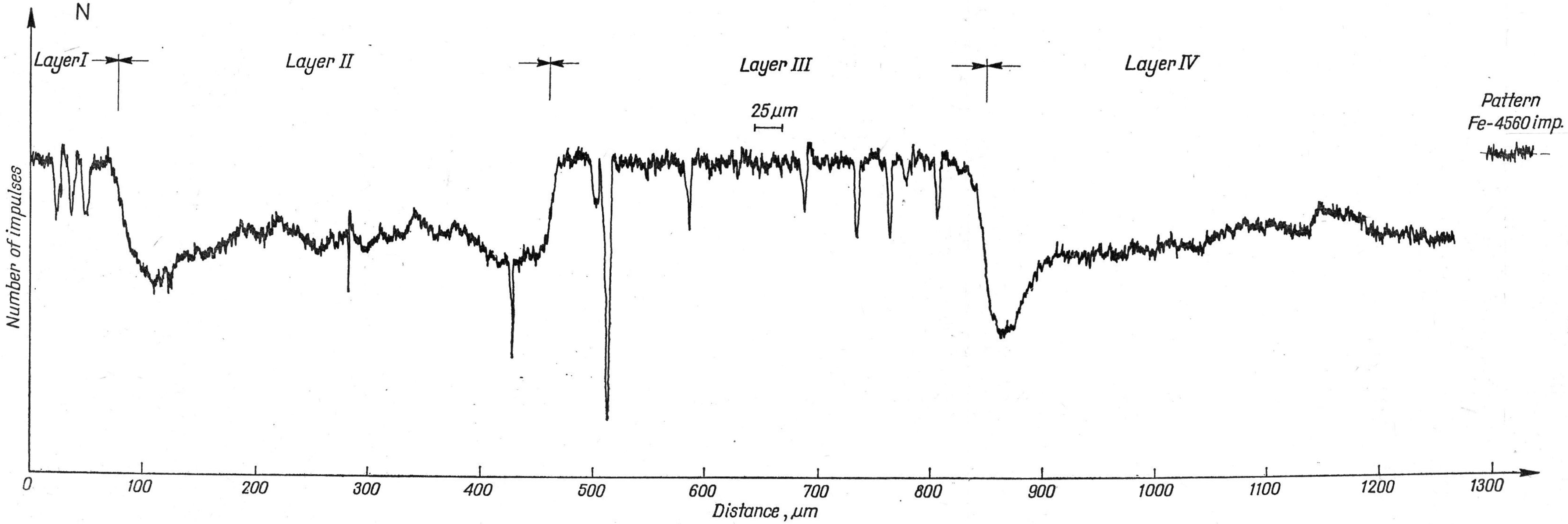

Fig. N. Diagram of changes in the content of Fe in the socketed axe from Wietrzno-Bóbrka, Krosno district

Chromium was not found in any one of the layers; the results of the linear analysis were at the level of the background (Fig. M).

The results of the examinations carried out so far point out also to the fact that the socketed axe from Wietrzno-Bóbrka, Krosno district, was welded from low-carbon steel (traces of carbon up to 0.3% C) and nickel iron (7.0 - 40% Ni) containing small amounts of cobalt (about 1% Co) and arsenic (about 0.15 - 1.2% As).

The content of Fe in the layers of iron and steel (I, III and V) was almost equal to 100% at the standard level, whereas in the nickel layer (II) it assumed a value of 82.6 - 69.6% Fe, and in the stripe of the highest nickel content its value reached even 46.2% Ni; in the second nickel layer (IV) the content of Fe was in the range of 78.2 - 60.8% Fe (Fig. N).

On the basis of the results it can be supposed that this type of an alloy was not obtained from the meteorite, as in such case it would contain, apart from nickel and cobalt, also chromium. An analysis of the *El Inco* meteorite revealed the following composition: 8.2% Ni, 0.22% Co, 0.345% Cr[20]. In the meteorite from Damerlande[21] small amounts of chromium (0.03% Cr) were encountered, apart from 7.8% Ni and 0.40% Co.

The nickel-cobalt-arsenic-iron alloy used for the socketed axes from Wietrzno-Bóbrka, Krosno district, and from Jezierzyce, Dzierżoniów district (and perhaps also for the cementation of iron in manufacture of Malayan creeses) could be smelted of a ferruginous chloanthite (Weissnickelerz—$(FeNiCoAs)S_2$)[22].

It might be supposed that this was the mineral "pyrimachos" which—according to Aristotle[23]—was used by the Chalybs in the production of the special grade of steel. This would be, then, the famous Chalybean steel mentioned so many times in the history of metallurgy[24].

The mineral "pyrimachos" has not been identified so far. Quite often, the explanations of this part of Aristotle's text where the mineral is mentioned were simply omitted[25]. Sometimes, it was thought that it was a pyrite or a silicate or even quarz[26], limestone[27] or a concentrate of iron ore obtained by washing the ore[28]. The critical

[20] F. Rinne, H. E. Boeke, *El Inco, ein neues Meteoreisen* (*El Inco*, the new meteoric iron), "Neues Jahrbuch für Mineralogie, Geologie und Paläontologie", 1907, vol. 1, p. 237.

[21] W. Fraenkel, G. Tammann, *Über meteorisches Eisen* (On the meteoric iron), "Zeitschrift für anorganische Chemie", 1908, vol. 60, p. 416.

[22] The analysis of the chloanthite containing 11.85% Fe, 2.44% Ni, 3.82% Co, 70.11% As and 4.78% S was published by J. D. Dana and E. S. Dana: *System of Mineralogy*, Yale University, 1837-1892 (7th edition, fully revised 1946), vol. 1, p. 344. In the 6th edition of this work a different analysis of the chloanthite from Andreasberg in Saxony was given, and viz.: 17.39% Fe, 7.00% Ni, 1.94% Co (p. 88).

[23] Pseudo-Aristotle, *De mirabilibus auscultationibus*, 25-26.

[24] L. Beck, *Geschichte des Eisens* (On the history of iron), Braunschweig 1891 (2nd edition), vol. 1, p. 263; R. J. Forbes, *Studies in ancient technology*, Leiden 1972 (2nd, revised edition), vol. 9, p. 231.

[25] L. Beck, *Geschichte des Eisens in technischer und kulturgeschichtlicher Beziehung* (History of iron from the technical and cultural point of view), Braunschweig 1891 (2nd edition), vol. 1, p. 263. R. F. Forbes, *Studies in ancient technology*, Leiden 1964, vol. 9, p. 202.

[26] H. Blümner, *Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römer* (Technology and terminology in craftsmanship and art of Greeks and Romans), Leipzig 1887, vol. 4, p. 213.

[27] R. J. Forbes, *Metallurgy in antiquity*, Leiden 1950, p. 383.

[28] H. C. Richardson, *Iron prehistoric and ancient*, "American Journal of Archaeology", 1934, vol. 38, no. 6, p. 556.

evaluation of these suppositions was published in a separate paper which deals with the problem of the ancient methods for smelting high-nickel iron[29].

Probably, the same alloy was used for the socketed axe from Jezierzyce, Dzierżoniów district, and also for the axe from Eskilstun. It is also possible that it was applied in the powdered form to the cementation of iron rods in the process of manufacture of Malayan creeses.

CONCLUSIONS

The examinations carried out so far confirm a possibility of using a microprobe analyser for the local analysis of small areas in early iron objects. As a matter of fact, this type of examinations had been made earlier by other investigators. The results of the analysis of the content of P and Ni in the examined iron objects were in agreement with the chemical analysis made previously.

Particularly important results were obtained during the analysis of the changes in the distribution of Ni, Co and As in the socketed axes from Jezierzyce, Dzierżoniów district, and Wietrzno-Bóbrka, Krosno district (from the Hallstatt period), and also in the Malayan creese.

The examinations enabled the authors to put forward a supposition that both axes were made of an iron-nickel alloy containing additions of cobalt and arsenic and smelted from the ferruginous nickel arsenide, known under the name of chloanthite. Most probably, this was the very mineral "pyrimachos" mentioned by Aristotle and used by the Chalybs for manufacturing the special grade of steel. It is also possible that an alloy of this type was used in the cementation when making Malayan creeses.

Moreover, it was stated that the examinations made with a microprobe analyser can also be useful when identifying the technology of manufacturing ancient iron objects, particularly the process of welding and possibly also carburizing (cementation). The rapid change in the content of the residuals, such as, *e.g.* P, Ni, Co or As, proves that the object was welded. An evaluation of this kind must be made, however, simultaneously with the metallographic examination of the structure of a given part and, if the structure does not contain any distinct indications confirming, *e.g.* the process of welding (the typical seam and the stripe of slag inclusions), then the examinations with a microprobe analyser may prove to be of great help.

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[29] *Cf. supra,* Note 19, 1st item, p. 235.

SUMMARY

Using a microprobe analyser seven iron objects of highly complex technology of manufacturing were examined. Knife no. 3 from Piekary, Cracow district (13th cent.), was welded of iron and steel rods, similarly as the Roman sword from Sobótka, Łęczyca district (2nd - 3rd cent.), which is a typical example of the technology of pattern welding which was used to obtain a decorative pattern on the surface of a given object. The axe from Nowa Huta-Mogiła (Roman period) was forged from steel and its surface was covered on both sides with a thin layer of steel. The examinations revealed a rapid change in the content of some of the constituents, *e.g.* phosphorus, in the place of welding.

On the other hand, the edge of knife no. 5 from Czeladź Wielka, Góra district (9th - 12th cent.), revealed a stronger carburization but, apart from the difference in carburization, no other marks of welding appeared (a stripe of slag inclusions). The examinations did not reveal any differences in the distribution of the constituents which are usually observed in welded objects, and hence it should be stated that the method of manufacturing this knife did not include the process of welding (joining) iron and steel.

The socketed axe from Jezierzyce, Dzierżoniów district (from the Hallstatt period), was forged from the iron rod which was cemented with an iron-containing alloy of nickel and cobalt, and then was faggoted. Carburized layers contained from 1.6 - 3.0% Ni and 0.2 - 0.5% Co.

A similar process was applied in manufacture of the Malayan creese which was composed of three layers: the middle one made of iron and with carburized edges (the edge of the creese), and two outer layers forming a typical pattern on the surface of the creese. Most probably, the two outer layers were made using a process of cementation with a nickel alloy with the successive faggoting. The content of nickel in the carburized layers was 1.8 - 3.9% Ni.

The edge of the socketed axe from Wietrzno-Bóbrka, Krosno district, was composed of five layers. The middle layer was made of iron, whereas two outer layers were made of low-carbon steel (0.1 - 0.3%C). Between the iron layer and the steel layers two additional layers were present, and namely the layer of nickel iron with an addition of cobalt and arsenic of acicular structure containing 8.1 - 17.4% Ni, about 1% Co and 0.24 - 0.94% As, and the layer of a still higher content of nickel and arsenic (32.6% Ni and 1.16% As). No presence of chromium in the metal was noted. The socket of the axe was an extension of the steel layers.

It seems that the nickel-cobalt iron was smelted of a ferruginous chloanthite, rich in the arsenides of nickel and cobalt, and that this metal was the famous ancient Chalybean steel.

The use of a microprobe analyser enabled the authors to establish, for the first time, the fact that the cementation with a nickel alloy containing cobalt and arsenic was applied as early as in the Hallstatt period.

Moreover, the examinations carried out so far proved that a microprobe analyser can be very useful in identifying the process of welding and carburizing in the ancient objects made of bloomery iron.