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The archaeometallurgical analysis of the slags from extincted blast furnace plants

Slovakia is mountainous country with harsh conditions of the nature but with rich sources of iron ore; wood and water energy. They had became a base of well-developed metallurgy and craftsman's processing of metals, dated from the Hallstatt period and culminated in the period between the 16th and 17th centuries and slowly extincted by the end of the 19th century. The tall shaft water blown bloom furnaces – "slovak furnaces" were main producers of iron by the half of the 19th century, although the first blast furnaces were blown - in this region in the end of the 17th century.

The pieces of cast iron – the typical product of the blast furnace could be product of the iron smelting in bloomeries at specific conditions (Pleiner, 1963, s.218). The cast iron was produced accidentaly in the Roman period, and experimental work has shown that it was possible to produce cast iron in a 2 m high bloomery furnace with a sufficiently large coal / ore ration (Tylecote, 1992, p.48, 76). The higher shaft furnaces (2 - 2,5m), transitional type destined to the blast furnace appeared in Russia (Rajkovecké hill-fort) in the 13th century (Колчин, 1953, c.29). The use of water power was other conditon of blast furnace development. It was used the first time in the iron smelting probably in Cardedeu (France, 1104). Water powered bellows were able to blow higher volume of air at higher pressure than the hand powered ones. The result was higher furnace with better conditions for production of high carburised iron – cast iron. The oldest blast furnaces were in Sweden (Lapphytan a Vinarhyttan, 1150 - 1350), Belgium (1345), England (1496 - 1520) and France (1517) (Tylecote, 1992, p.76).

Early blast furnaces had square stone structure with a sandstone lining. The furnace often used timber lacing and very soon iron rods were introduced as reinforcement. The blast was supplied by a waterwheel operating two bellows which were alternately compressed by cams (Tylecote, 1992, p.96, 97).

The charcoal blast furnace slags are usually acid with high content of SiO_2, low content of sulphur, P_2O_5 and Fe oxids. The CaO content grew since the half of the 18th century. The slags contain globular inclusions of the iron with low sulphur and high phosphorus contents. According to literary sources mineral fuel, the main source of the sulphur in the slags, was used in Slovakia since the end of the 19th century. The alternative source of the sulphur could be insufficient roasting of the ore with pyrite content. The slags from fineries and puddling furnaces contain 60 - 70 % of iron oxides, 10 – 25 % SiO_2 and 1 – 5 % P_2O_5. The slags – waste product of the first forging of bloom contains usually 50 – 60 % FeO, about 20 % SiO_2 and up to 0,8 % P_2O_5. The smithy slag is the result of the reaction of the scales with the silica sand, ash of the charcoal and the rests of the slag in the iron. The Fe_{tot} / FeO ratio is = 2, the P_2O_5 content is generally up to 1 %. The microstructure of the smithy slag is usually inhomogeneous with the "blocks" of wüstite (remnants of the scale). The pieces of the iron, generally in the form of the corrosion products, particles of the non-reacted silica sand and the "cell" structure (Stránsky – Rek, 1999, s.261; Stránsky - Mazač – Ustohal, 1992, s.40; Stránský - Rek - Štěpán - Merta, 1995, s.196; Stránský, 1997, s.205; Stránský - Rek - Winkler, 1990, s.303; Ustohal - Mazač - Stránský, 1989, s.520; Mihok - La Salvia – Roth, 1998, s.475).

The development of the blast furnace smelting in Slovakia was hindered the first of all by wars. The Turks occupied, except for Slovakia, in fact, all territory of the Hungarian kingdom between 1526 and 1685. Slovakia became the scene of defensive wars during the period, which, with repeated rebellions against the Habsburg dynasty resulted in devastation and in decline. The conservatism of the iron smelting plants owners, unstable flow in local water-courses and fact, that local iron ores were more appropriate for bloomeries, were other hindrances for the blast furnace smelting.

The first blast furnace in Slovakia was built in Ľubietová in 1692 (1595 in Bohemia and 1674 in Poland). The blast furnaces in Dobšiná, Revúca, Rejdová and Poniky were blowed-in in the first half of the 18th century. There were 5 blast furnaces and 124 bloomeries in 1776 in Slovakia. The cast iron smelted in blast furnaces exceeded the iron, smelted in bloomeries about 1830. The first coke fuelled blast furnace was blowed-in in Likier in 1885 (Šarudyová, 1989, s.130, 168; Pleiner, 1984, s.92, 104; Kadwan, 1963, s.104, 111).

There were 59 iron smelting plants producing iron by blast furnaces in Slovakia. The preliminary investigation with surface collection of the slag specimens was put into practice in Smižany, Zemplinske Hámre, Remetské Hámre, Osrblie, Červeňany, Javorina, Košice – Myslava, Gelnica and Jasov up to now (fig.1).

At first the pieces of slag were macroscopicaly described. The samples were taken from the slag pieces with the help of diamond saw cutting. The mineralogic surface was prepared by standard way by dry grinding and polishing by diamond, moisted with petroleum. The presence of sulphide inclusions was evaluated by Baumann test. The optic microscope NEOPHOT 32 was used for the microscopic analysis. The samples assigned for wet chemical analysis were pulverised in the vibrant mill. The presence of the secondary and the trace elements were evaluated by semiquantitative spectral analysis. Finally, the melting temperature, evaluated by high-temperature microscope Leitz-Wetzlar without protecting atmosphere and X-ray structural analysis were determined.

The chemical composition and melting temperature of analysed slags is in tabl. 1 and presence of secondary and trace elements in tabl. 2.

Smižany. In the period from 1803 to 1886 an iron smelting plant with blast furnaces, finery hearts and hammers, estabished by count Csáky, worked in the village Smižany (local part Maša) near Spišská Nová Ves. There were smelted iron ores, mined in Spiš, the first of all from Gretla. Only slag pieces can be found in the place of this extincted plant in present (Šarudyová, 1989, s.88).

P70A: The charcoal-grey piece of slag with blowholes, the dimensions 100 x 100 x 50 mm. The polished surface is porous, grey or green with sulfidic inclusions. The microstructure consists of glassy crystals of wollastonite, diopside and fassaite with blowholes and globular inclusions of iron (fig.2).

P70B: The grey piece of slag with blowholes, the dimensions 100 x 100 x 50 mm. The polished surface is rusty – brown. The slag is practicaly without sulfidic inclusions. The contents of sulphur is 0,07 %, it was 0,01 – 3 % in English slags, dated to the 17th – 19th centuries (Tylecote, 1992, p.126) and 0,12 – 3 % in present – day blast furnace slags (Лапин, 1956, c.144). The microstructure consists of grey glassy matrix with lighter strip – shaped particles of busmanite and $Mn_{0,8}Ca_{0,2}SiO_3$, globular particles of iron and blowholes can also be found (fig.3).

Conclusions: The chemical composition (the high contents of SiO_2, the contents of CaO and MgO, higher than natural, show their deliberate addition and contents of phosphorus) are charasteristic for blast furnace slags (Stránsky – Rek, 1999, s.261). A part of the analyzed slag containted sulphur as a result of mineral fuel used in the reduction process. Although according literary sources mineral fuel was used in Spiš since the end of the 19th century, this fact proves its occasional use in the course of the 19th century (Šarudyová, 1989, s.62).

Gelnica. The samples were found on the bank of the Hnilec river in the locality of extinced iron plant Matilda Huta (between 1810 - 1880) consisted of blast furnace, finery hearths, hammer and rolling mill (Šarudyová, 1989, s.88).

T91: The black – grey kidney – shaped piece of slag, the dimensions 50 x 50 x 50 mm. The polished surface is black. The microstucture consists of fayalite, iron calcium olivine and ferrous glass with globular particles of iron (fig.4).

Conclusions: The source of the sulphur could be pyrite in the ore part of the burden, because mineral fuel was not used in Spiš in the period of the existency of ironworks in Matilda Huta. The content of FeO and SiO_2 excludes blast furnace slag. The low phosphorus content excludes the refining slag. The low basicity excludes contemporary slag in the secondary position. The structure and chemical composition of the analysed slag are the same as the ones in the slags, produced by Slovak furnaces. Because this type of furnace was not used in Matilda Huta in the period of it's existence, the slag can be by-product of Slovak furnaces, which existency is mentioned in Gelnica between the 15th and the 19th centuries without the informations of their localisation.

Remetské Hámre. Iron smelting plant was established by count Sztáray at the end of the 18th century. The plant consists of blast furnace, finery hearths and hammers in 1828. The nails workshop was established in 1846. According the stock-in-trade dated to 1867 the plant consisted of the blast furnace, ore roast furnace, nails workshop, three hammers, rolling mill and puddling furnace. The blast furnace extincted at the end of the 19th century, rolling mill in 1922 (Šarudyová, 1989, s.75).

T86: The grey - pastel green or blue piece of slag, the dimensions 50 x 50 x 50 mm. The polished surface is porous, pastel green without sulfidic inclusions. The microstructure is glassy with the skeleton – shaped particles of diopside and globular inclusions of iron up to 1 mm with graphite (fig.5).

Conclusions: Analysed slag is typical waste product of charcoal blast furnace.

Snina. Jozef Rholl established iron smelting plant with the blast furnace about 3 km from Snina (in the centre of present - day village Zemplínske Hámre) in 1815. The smelted ore was mined in the east slope of Slanské vrchy (Zamutov, Banské, Hermanovce) or in local source. The statue of Hercules (today situated in courtyard of manor-house in Snina) was cast here in 1841. The blast furnace was blown – out in 1873 (Šarudyová, 1989, s.75; Hoffman – Stankovský, 1976, s.51).

P151: The glassy grey – green piece of slag, the dimensions 50 x 50 x 50 mm. The polished surface is porous, light green or brown without sulfidic inclusions. The microstucture is glassy with globular inclusions of the iron, the rest of the charcoal was found in the specimen. The presence of quartz, wollastonite, fayalite, magnetite and hematite by X-ray structural analysis was determined.

Conclusions: Analysed slag is typical waste product of charcoal blast furnace. The slag with low melting point has extremly low basicity, probably the result of the fact, that used iron ores were without sulfur.

Osrblie – Tri Vody. The company of bourgeois from Banská Bystrica established blast furnace plant in Osrblie, local part Tri Vody in 1795. The iron was refined in Bujakovo. Prihradny family had been the owner of the plant since 1850s. The iron ores, mined in Dobšiná, Bacúch and Ľubietová were smelted there. The blast furnace extincted in 1873 (Šarudyová, 1989, s.168).

T 88: The roundish pastel blue pebbles of the slag were found in the creek near the blast furnace. The polished surface is mildly porous, turquoise-colured or pastel grey-blue without sulfidic inclusions. The microstucture is homogeneous, glassy with globular inclusion of the iron (up to 10 μm).

Conclusions: Analysed slag is typical waste product of charcoal blast furnace.

Jasov. The abbey in Jasov established iron smelting plant "Ján Baptista" with blast furnace, finery hearths and rolling mill in 1790. The plant extincted about 1910 (Šarudyová, 1989, s.123).

T 92: The rusty – black piece of porous slag (dimensions 50 x 50 x 100 mm) was found on the bank of the Bodva river in the locality of extinced iron plant. The polished surface is black, porous with presence of sulfidic inclusions. Microstructure consists of inhomogeneous globular wüstite, the rest is silicate matrix composed of fayalite and iron calcium olivine and ferrous glass (fig.6).

Conclusions: The analysed slag is probably the wast material of rolling or smithy slag, because the microstructure, contents of phosporus and iron exclude blast furnace or refining slags.

Košice – Myslava. The iron smelting plant in Košice, local part Myslava established by company of bourgeois from Košice (1852 - 1867) consisted of the blast furnace, cupola furnace and machinery workshop (Šarudyová, 1989, s.109).

P 157: The light brown piece of porous slag (dimensions 100 x 80 x 100 mm) with pieces of charcoal was found in the locality of extinced iron plant. The polished surface is brown without of sulfidic inclusions. Microstructure consists of inhomogeneous globular wüstite, the rest is silicate matrix composed of fayalite and iron calcium olivine and ferrous glass.

Conclusions: The composition and microstructure of slag is typical for the waste product of iron smelting proces in the small shaft furnace, blown by hand - powered bellows, which could be situated (without literary sources) in this locality before the iron smelting plant was estabilished. The slag from spoiled smelting in the blast furnace or cupola furnace is improbable.

Sirk – Červeňany. The blast furnace of Hrlicko – tapolcsánska company was blown – in in Sirk, local part Červeňany in 1871. It smelted iron

ores mined in Železník, Sirk, Rákoš and Nandraž. The blast furnace extincted in 1903 (Šarudyová, 1989, s.134; Fräk, 1970, s.94).

T 85: The glassy black slag can be found arround reconstructed (in 1970) blast furnace. The polished surface is darkbrown, compact, without sulfidic inclusions. The microstucture is homogeneous, glassy with globular inclusion of the iron (fig.7).

Conclusions: Analysed slag is typical waste product of charcoal blast furnace.

Ždiar – Javorina. The noble family Horváth-Palocsay established iron smelting plant in Ždiar, local part Javorina (1759 - 1875). It consised from the blast furnace, smelted iron ores mined in Smižany, Kišovce and local sources. The finery hearths, puddling furnaces and rolling mill were built during the 19th century. The part of iron, refined here came from blast furnace in Kučin (near Stropkov) (Šarudyová, 1989, s.79).

P 155: Compact, partly porous grey – black slag, pieces up to 70 mm. The core of the polished surface is yellow - green - grey, surface layer is glassy, grey – yellow – rusty. Sulfidic inclusion were detected by Baumann test. The microstructure is glassy with dull needles and iron globules.

Conclusions: Analysed slag is typical waste product of charcoal blast furnace. The source of the sulphur could be pyrite in the ore part of the burden, because mineral fuel was not used in Spiš in the period of the existency of ironworks in Javorina. The high content of MnO was probably the result of its deliberate addition as a flux (Tylecote, 1992, p. 96, 165).

Tabl. 1: Composition of analysed iron slags.

	Locality	SiO_2 (%)	Fe_{tot} (%)	FeO (%)	SiO_2/Fe_{tot}	CaO (%)	MgO (%)	Al_2O_3 (%)	MnO (%)	S (%)	P_2O_5 (%)	B	T_1 (°C)	T_2 (°C)
P131	Zemplínske Hámre	60.5	6.1	2.3	9.8	3.4	-	-	1.2	0.0	0.11	0.06	1181	1200
T86	Remetské Hámre	61.5	5.6	-	12.1	19.0	5.5	4.1	0.17	0.16	0.07	0.28	1236	1260
P70A	Smižany	45.3	3.9	-	11.7	15.4	9.0	1.6	5.3	0.84	0.13	0.32	1201	1240
P70B	Smižany	24.2	1.2	-	45.2	16.2	3.0	1.8	11.2	0.07	0.30	0.35	1184	1209
T88	Osrblie	38.9	2.2	-	26.8	16.2	5.8	2.7	3.2	0.003	-	0.42	1263	1274
T85	Červeňany	32.5	1.7	-	38.9	28.0	0.0	2.0	3.3	0.017	0.01	0.53	1265	1289
T94	Gelnica	28.2	48.6	54.9	0.58	3.4	0.0	1.0	0.05	0.09	0.182	0.12	-	-
P157	Košice-Myslava	18.2	39.2	60.9	0.31	3.4	0.0	3.0	0.03	0.029	0.080	0.18	-	-
T92	Jasov	14.0	33.6	42.7	0.26	6.3	0.0	0.8	0.53	0.114	0.128	0.44	-	-
P155	Javorina	46.1	2.2	0.3	20.9	22.1	0.8	1.2	18.8	0.24	0.098	0.49	1136	1182
Φ(1)		30.1	3.3			17.2	2.7	2.2	6.2	0.22				

(1) without iron smelting plants in Košice-Myslava, Gelnica and Jasov

B – basicity of slag $B = CaO+MgO/SiO_2 + P_2O_5$

T_1 - the softening point of slag

T_2 - the temperature of slag's melting

Tabl. 2: Presence of secondary and trace elements in the analysed slags.

	Locality	1-100%	0.01-1%	0.0001-0.01%
P151	Zemplínske Hámre	Fe Mg Si Ti	Mn Zn Al Cr V	Cu
T86	Remetské Hámre	Fe Ca Si	Mn Mg Al Sb Cr Pb Ti Zn V	Co Cu Ag
P70A	Smižany	Fe Mn Ca Si	Mg Al Sb Zn Co V	Ti Ag Cu
P70B	Smižany	Fe Mn Ca Si	Mg Al Sb Cr V Zn Co Ti	Sn Ag Cu
T94	Gelnica	Fe Ca	Al Cu Si Mn Sb Pb Mg Zn Ag	Ti
T88	Osrblie	Fe Mn Al Ca	Si Ti Mg V	Co Ni Cu Ag
P155	Javorina	Fe Mn Mg Si Ti	Al Cr Cu V	Zn
P157	Košice-Myslava	Fe Al Cr Si	Cu Mg Mn Ti V	In Zn
T92	Jasov	Fe Mn Ca	Al Si Cu V Mg Pb Ti	Zn Ag Co Ni
T85	Červeňany	Fe Mn Al Ca	Si Ti Mg V	Co Ni Cu Ag

General conclusion

1. The higher effectivity of smelting process (lower content of iron in the slag) was observed at blast furnaces, situated in typical iron-smelting regions (Smižany, Osrblie, Červeňany).
2. The basic fluxes (CaO or MgO) were, besides Zemplínske Hámre, deliberately added into burden.
3. The higher content of MnO in the slags from Javorina and Smižany was probably the result of its deliberate addition for elimination of ineligible effect of sulphur.
4. Some slags, found in the plants with various technologies, originally considered to be blast furnace slags, were bloomery slags (Gelnica, Košice-Myslava) or smithy (rolling) slag (Jasov).

The archaeometallurgical analysis of the slags from extincted blast furnace plants

Petrík J., Mihok Ľ.

(Summary)

The object of study were slags, found in Smižany, Zemplinske Hámre, Remetské Hámre, Osrblie, Červeňany, Javorina, Košice – Myslava, Gelnica and Jasov at the locality of extincted iron smelting plants, dated to the 19th century. The majority of them were charcoal blast furnace slags, the bloomery slags were found in Gelnica and Košice – Myslava and smithy or rolling one in Jasov. The higher effectivity of smelting process (lower content of iron in the slag) was observed at blast furnaces, situated into typical iron-smelting regions (Smižany, Osrblie and Červeňany).

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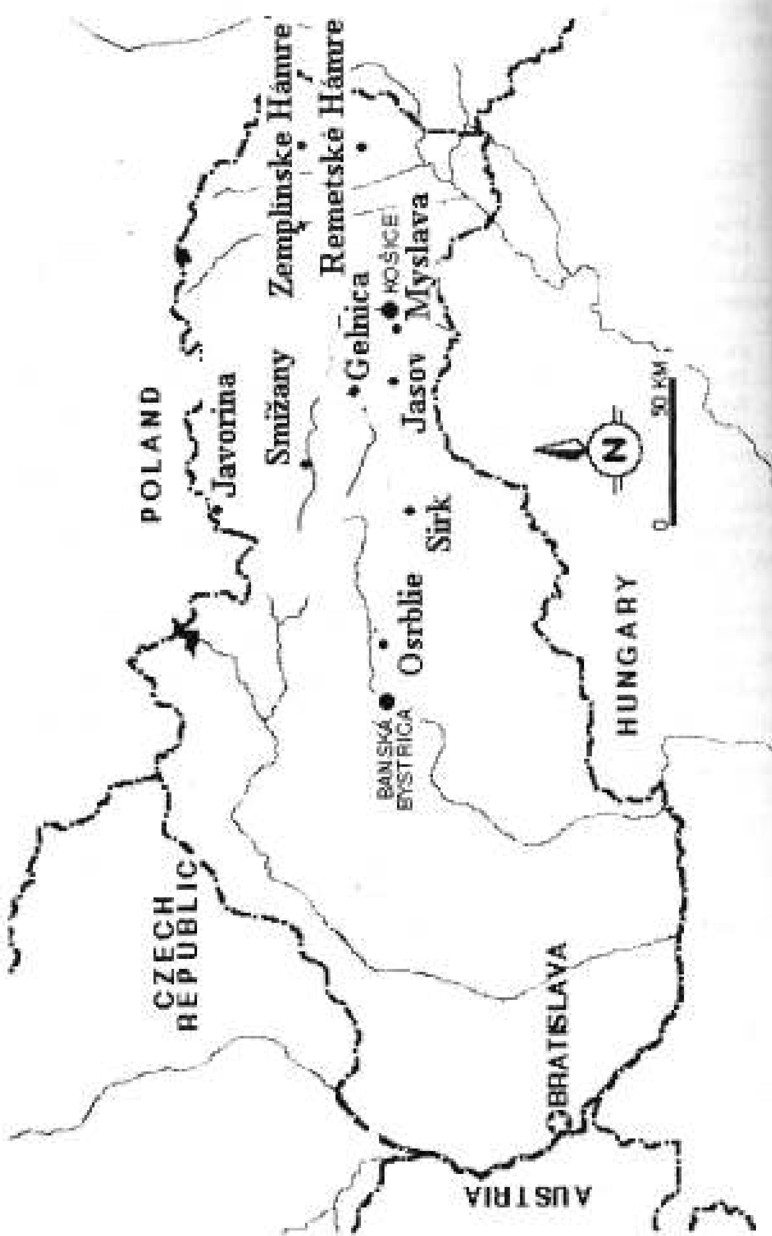

Fig 1 - The map of [illegible]

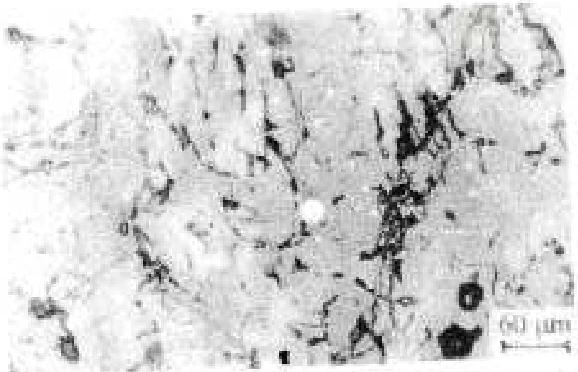

Fig.2 - The mineralogic surface of slag from Smižany, specimen A

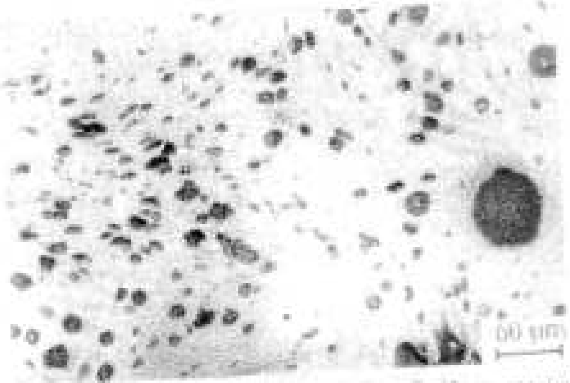

Fig.3 - The mineralogic surface of slag from Smižany, specimen B.

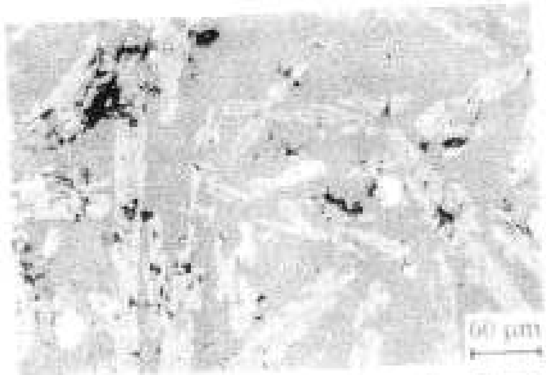

Fig.4 - The mineralogic surface of slag from Gelnica.

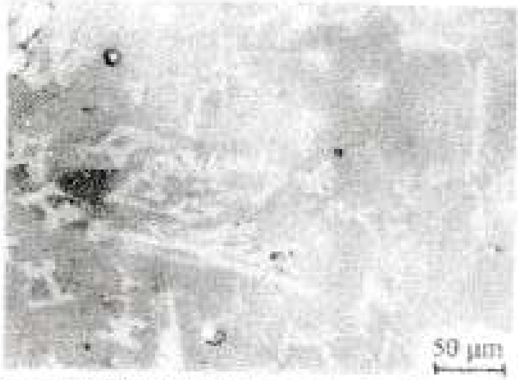

Fig.5 - The mineralogic surface of slag from Remetské Hámre

Fig.6 - The mineralogic surface of slag from Jasov

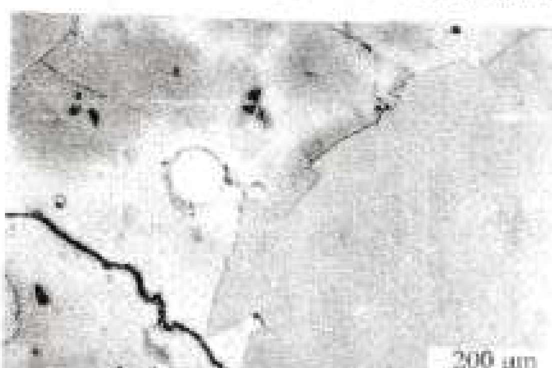

Fig.7 - The mineralogic surface of slag from Sirk - Červeňany