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MELTING TEMPERATURE OF ARCHAEOMETALLURGICAL SLAG

Jozef Petrík*, Ľudmila Burdzová

Faculty of Metallurgy, Technical University of Košice,
Letná 9, 042 00 Košice, Slovak Republic

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Abstract

The aim of submitted work is to search the softening and melting temperature of archeometallurgy bloomery and blast furnace slag using high – temperature microscope. The high values of melting temperature of bloomery slag is a result of secondary oxidation of wüstite in the chamber of a microscope. The melting temperature increases with an increase in SiO_2 and decreases with increasing basicity of the slag.
Keywords: slag, melting temperature, archaeometallurgy

Introduction

The slag forms a multicomponent system, which has a direct contact with the melt in the smelting process. The composition of slag, its chemical properties, melting temperature, viscosity, surface tension and its other properties influence the quality of produced metal and the scale of production. The melting (liquidus) temperature T_L is the highest temperature of thermodynamic equilibrium between the solid and liquid phases, above which crystals of any kind are thermodynamically unstable. A low value of melting temperature generally results in a high value of liquidus viscosity η_{liq} of the system, and hence a large kinetic barrier to the atomic rearrangements necessary for crystallization [1]. At present, scientists lack comprehensive sets of information describing heterogeneous processes of slag at high temperatures, and obtainment of data is difficult [2]. Actually, the softening and melting of slag in the bloomery or blast furnace is quite a complex process. It involves the iron oxides reduction, liquid formation, carbonization and melting processes and various chemical reactions [3].

To determine the quality of the melting process and burden considerable effort has been invested in studies of softening and melting properties of slag. This paper reports the experimental results obtained by high temperature analysis of archaeometallurgical slag – a waste product of iron metallurgy found in Slovakia. Archaeological research of iron metallurgy in Slovakia is focused particularly on its

* Corresponding author: Jozef Petrík, jozef.petrik@tuke.sk

initial period with subsequent archaeometallurgical processing of excavated slag or iron artifacts, for example [4] [5] [6]. The industrial archeology relating to the blast furnace process is neglected. Therefore, the analyzed slag was dated primarily using archival data that illustrate the period of operation of the ironworks.

Table 1. The locality of the ironworks and the content of SiO_2, metallic iron Fe_{met}, FeO, CaO, MgO, MnO and Al_2O_3 (in %wt.) in analyzed slag.

No.	Locality	SiO_2	Fe_{met}	FeO	CaO	MgO	MnO	Al_2O_3
1	Spišská Belá	35.0	-	59.1	3.2	0.2	0.0	0.0
2	Spišská Belá	32.0	-	52.5	4.7	0.0	6.9	0.0
3	Veľký Folkmár	24.2	-	58.7	5.9	2.1	3.2	1.3
4	Remetské Hámre	70.9	5.6	-	20.4	0.0	0.2	4.3
5	Smižany	56.9	3.9	-	19.5	10.0	6.6	2.0
6	Smižany	62.3	1.2	-	18.4	12.9	2.1	0.1
7	Zemplínske Hámre	90.8	6.1	-	5.1	0.0	1.8	0.0
8	Osrblie – Tri vody	61.8	2.2	-	17.0	9.2	3.4	2.8
9	Červeňany – Sirk	58.8	1.7	-	31.4	0.0	3.7	2.2
10	Javorina	41.5	2.2	0.2	18.8	19.9	16.9	1.1
11	Betliar	35.4	4.7	-	23.7	32.2	3.4	1.1
12	Štítnik – Fesmuth	25.7	6.7	-	36.4	29.1	3.6	0.8
13	Revúca – Šramková	42.3	2.5	-	22.9	24.3	2.6	3.2

Slovakia is a mountainous country with rich deposits of iron ore exploited in the past. Unfortunately, these are practically exhausted at present. Archaeometallurgical slag, the product of iron smelting and smithing or rolling, is a valuable source of information for the analysis of extinct processes that produced them. The slag generally remained in the vicinity of the furnace. The transfer of slag in a dumping site, its secondary use as a source of iron (iron-rich bloomery or refining slag) appears only in the 19th and particularly in the 20th century. The "local stability" of the slag guarantees a high probability that the information obtained by the analysis can be related to given ironworks [7].

The analyzed samples of slag, listed in Table. 1, were obtained by surface collection in the places of past ironworks. The findings were not the result of archaeological research. The slag, found at the place of the ironworks was dated according to the period of the existence of the plant, generally using archival data.

The metallographic, chemical, spectral and X-ray diffraction analysis of samples were carried out prior to determination of the softening and melting temperatures. The basicity of analyzed slag was calculated using formula (1). As can be seen in Fig. 1 most of the slag has acidic character. Practically only charcoal was used as a fuel in the blast furnace process in Slovakia by the end on the 19th century. It was not therefore necessary basic slag to solve problems with sulfur in the pig iron.

$$B = \frac{CaO + MgO}{SiO_2} \tag{1}$$

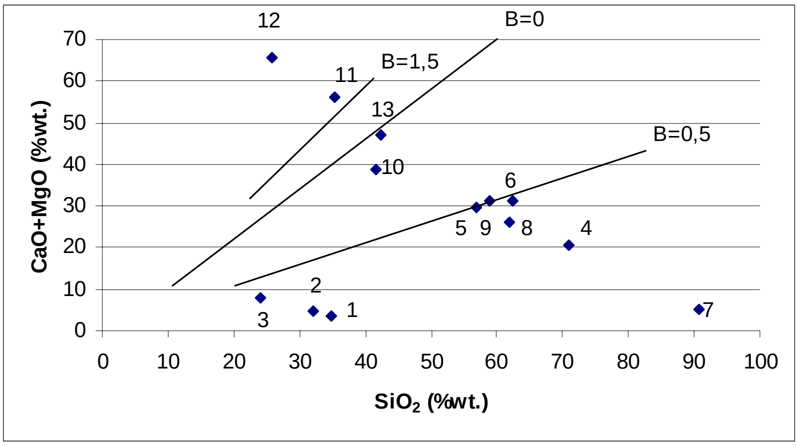

Fig. 1. The basicity of analyzed slag.

Equipment and method

The heating microscopy is commonly used method for determining the slag melting and softening temperature. It is quite a simple method which uses only a minor sample weight, although it is a time consuming. High temperature microscope LEITZ-Wetzlar was used as the main equipment. The web camera scans the contour of the test piece with an output to PC. The magnified contour is projected onto the monitor equipped with a grid that facilitates accurate reading of dimensional changes. Described arrangement allows contact-less measurement of both positive and negative dimensional changes during heating and to determine the melting point according to standard DIN 51730 [10]. Automatic scanning specifies the measurement of physical quantities of the sample and finally removes the subjective appraiser's error in measuring and evaluating. The temperature of the sample was measured with a digital thermometer THERM 3280-6 (accuracy of ± 2°C) [11]. The disadvantage of this equipment set up is the exclusion of possibility to apply the reducing atmosphere because it may damage the heating element.

The powdered slag (0.2 g in average, depending on the specific weight) was wetted with water and pressed into a cylindrical test piece with a diameter of 2 mm and high 6 mm. It was placed on a holder in the chamber of a microscope and heated. The temperature increased about $3°Cs^{-1}$. The softening temperature (T_S) is associated with the initial deformation of the test piece and the melting temperature (T_L) is determined when the test piece attained a half-sphere shape [12].

Measurement

Samples No. 1 and 2 found near by Spišská Belá (N49°12'39" E20°22'02") are broadly dated to the 17^{th} - 18^{th} century [13]. The slag is a likely product of a direct reduction of iron in 2 - 4 m high shaft water – blown bloomery furnace "Windischer Ofen" or so-called "Slovak furnace". It was the most widespread furnace type used in iron metallurgy between the 13^{th} and the first half of 19^{th} century in Slovakia [14]. The microstructure consists of fayalite 2 FeO SiO_2, iron calcium, olivine and ferrous glass, Fig. 2. The absence of wüstite shows the high quality of smelting process [15]. The softening temperature of the slag No. 1 is 1423°C and the melting temperature is 1448°C. The softening temperature of the slag No. 2 is 1322°C and the melting temperature is 1450°C.

Fig. 2. Sample No. 2, Spišská Belá, magnification $200\times$.

The sample No. 3 found in Veľký Folkmar (N48°50'58" E21°00'47") is dated to the 15th - 19th century and is also a product of "Windischer Ofen" [16]. The microstructure consists of fayalite, iron calcium, olivine and ferrous glass, Fig. 3. High content of iron oxides (wüstite, about 30 %) suggests low efficiency reduction process [17]. The softening temperature 1445°C and also the melting temperature 1460°C are high as a result of the secondary oxidation of wüstite.

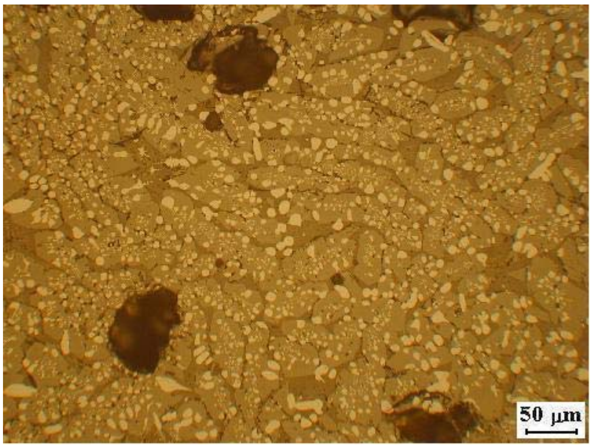

Fig. 3. Sample No. 3, Veľký Folkmár, magnification $200\times$.

The Turks occupied almost the entire of Hungarian kingdom with the exception of today's Slovakia between 1541 and 1690. The territory of Slovakia became the scene of defensive wars. These, together with repeated rebellions against the Hapsburg dynasty, epidemics (plague), famine and emigration resulted in a total devastation of the country. The slowdown in blast furnace technology reflected this decline. The first blast furnace was built in 1595 in Bohemia and in 1679 in Poland, for example, but only in 1697 in Slovakia in the town of Ľubietová. The first atmospheric steam engine in Central Europe was installed by Isaac Potter in the nearby town Nová Baňa in 1722. The parts of it were cast in Ľubietová. The blossom of the blast metallurgy in the second half of the 19th century (59 ironworks) terminated in 1920s. Only three blast furnaces are in operation in present time [14].

The sample No. 4 found in Remetské Hámre (N48°50'51" E22°11'02") can be dated between 1780 and 1920 [8][9]. It is a typical charcoal blast furnace slag. Microstructure consists of ferrous glass with skeleton shaped or dendritic particles of pyroxene mineral diopside $CaMgSi_2O_6$ and also inclusions of cast iron, Fig. 4. The volume of the sample significantly decreased without changing its contour at 1175°C probably due to polymorphic transformation. The softening temperature of the slag is 1236°C and the melting temperature is 1260°C.

Comparing it with bloomery slag it can be seen as a significant drop in temperatures. It is a result of absence of iron oxides in blast furnace slag [18].

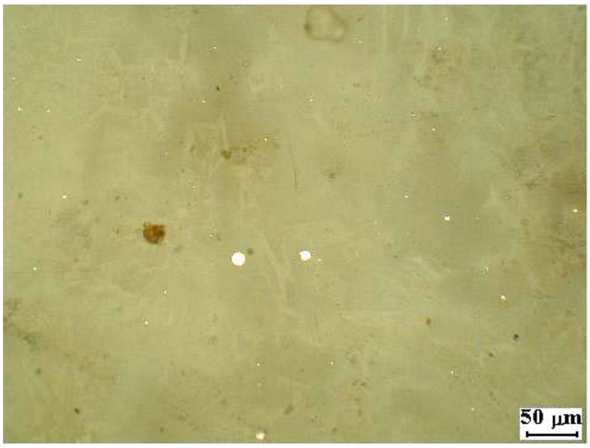

Fig. 4. Sample No. 4, Remetské Hámre, magnification $200\times$.

The samples of slag No. 5 and 6 found in Smižany (N48°56'57" E20°30'28") can be dated between 1803 and 1886 [8][9]. X-ray analysis identified the crystals of wollastonite $CaSiO_3$, diopside and fassaite $Ca(Mg,Fe,Al)(Si,Al)_2O_6$ in sample No. 5. Spherical iron inclusions were also obtained.

The microstructure of sample No. 6 consists of a basic ferrous glass with lighter strip-shaped particles. X-ray analysis detected busmanit and $Mn_{0,8}Ca_{0,2}SiO_3$, there are also spherical iron inclusions and pores, Fig. 5. Relatively low content of CaO and MgO, but higher than the natural, was detected in both slag samples. It indicates deliberate addition of the flux. The determination of the boundaries of the deliberate addition of the flux depending on the alkali content in used iron ore presented in [4] may not be universal. High content of sulfur in the sample No. 5 may be the result of experiments with a coke or a mixture of the coke and the charcoal as a fuel. The using of coke was rare in this region before the end of the 19th century [19]. The softening temperature of the slag No. 5 is 1201°C and the melting temperature is 1279°C. The softening temperature of the slag No. 6 is 1184°C and the melting temperature is 1209°C.

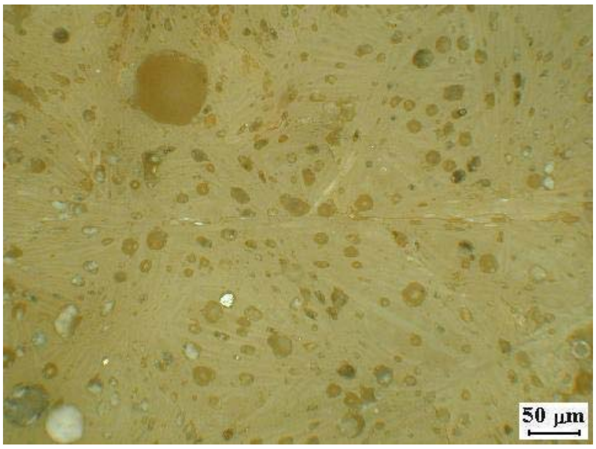

Fig. 5. Sample No. 6, Smižany, magnification $200\times$.

The sample No. 7 found in Zemplínske Hámre (N48°56'58" E22°09'19") can be dated between 1815 and 1873 [8][9]. The microstructure consists of homogeneous glassy material with particles of white cast iron. The X-ray diffraction shows that the base of sample is an amorphous substance of silica glass with quartz, wollastonite $CaO.SiO_2$, fayalite, magnetite and hematite. It is acidic fayalitic slag, rather typical for the early stages of blast technology [8][20]. A significant volume reduction without changing the contour was observed at 1176°C. The softening temperature of the slag is 1181°C and the melting temperature is 1200°C.

The sample No. 8 found in Osrblie – Tri vody (N48°43'34" E19°30'13") can be dated between 1795 and 1873 [8][9]. The microstructure consists of a homogeneous glassy phase with pores and inclusions of iron. This is a typical charcoal blast furnace slag with deliberate addition of basic flux in order to improve characteristics of the slag (fluidity, melting temperature) [19]. The softening temperature is 1263°C and the melting temperature is 1274°C.

The sample of slag No. 9 found in Červeňany - Sirk (N48°36'15" E20°06'32") can be dated between 1871 and 1903 [8][9]. Homogeneous microstructure forms glassy phase and inclusions of iron [19]. As in the previous case, this is a typical charcoal blast furnace slag with deliberate addition of basic slag additives. The volume of the sample reduced between the temperatures 858°C and 912°C by about 20 % and expanded at a temperature of about 1050ºC almost back to its original state. The softening temperature is 1203°C and the melting temperature is 1219°C.

The slag No. 10 of Javorina in the High Tatras (N49°16'07" E20°08'32") can be dated between 1759 and 1875 [8][9]. It has an increased content of sulfur and manganese. The microstructure consists of a homogeneous glassy phase with inclusions of iron. Someone could say that this is an atypical blast furnace slag. The increased content of sulfur (but less than in furnaces heated with coke or other mineral fuel - about 2.8 % [19]) may indicate pyritic component in the batch or experiments with the addition of mineral fuel. Local smelters strived to eliminate the content of sulfur with its side effects (red brittleness) by addition of MnO and CaO. High variability of the contour (tilting, creation and termination of projections) of heated sample was observed between 749°C and 953°C. The softening temperature of the slag is 1176°C and the melting temperature is 1183°C.

Sample No. 11 is a blast-furnace slag found in Betliar (N48°41'49" E20°29'54") with high content of sulfur and basic flux. It is assumed the using of coke as fuel. The slag can be dated between 1885 and 1905 [8][9]. The metallographic surface has glassy microstructure [21]. The expansion in the top of the sample has been observed at temperatures above 900°C. The softening temperature is 1246°C and the melting temperature is 1250°C.

The blast furnace "Fesmuth" in Štítnik (N48°40'13" E20°21'41") was in operation between 1833 and 1910 [8][9]. The slag No. 12 is the waste product of this furnace. The microstructure of the slag consists of a glassy matrix with particles of unburnt charcoal. The slag has a higher sulfur content, which can be a result of the coke and charcoal mixture in the burden or insufficient roasting of the ore containing sulphides. It is possible that this is the primary blast furnace slag, which remained affixed to the shaft wall and has been removed at shutdown of the blast furnace [21]. The contour of the sample changed irrelevant during the heating. The softening temperature is 1157°C and the melting temperature is 1160°C.

The blast furnace in Šramková - local part of town Revúca (N48°41'01" E20°05'27") was in operation between 1805 and 1884 [9][22]. Sample No. 13 has a glassy matrix of microstructure with iron particles [15]. The softening temperature of the slag is 1172°C and the melting temperature is 1175°C.

The bloomery slag when measuring temperatures behave differently from the blast furnace slag. Therefore, the following relationships were designed only for blast furnace slag. As shown in Fig. 6, with an increase in SiO_2 content there was a gradual increase of melting temperature. On the contrary, the basicity of the slag decreases the melting temperature (Fig. 7), Pearson's coefficient for softening temperature (T_S) r = 0.3251 and it for melting temperature (T_L) r = 0.4913 (medium correlation). The difference between the melting and softening temperature decreases with increasing basicity.

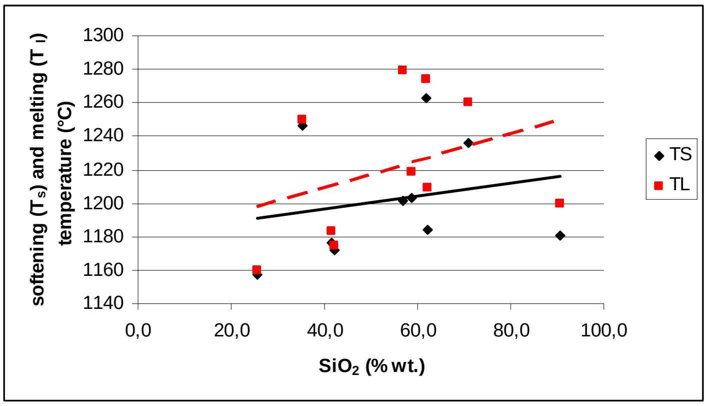

Fig. 6. The effect of SiO_2 on the softening and melting temperature of the blast furnace slag.

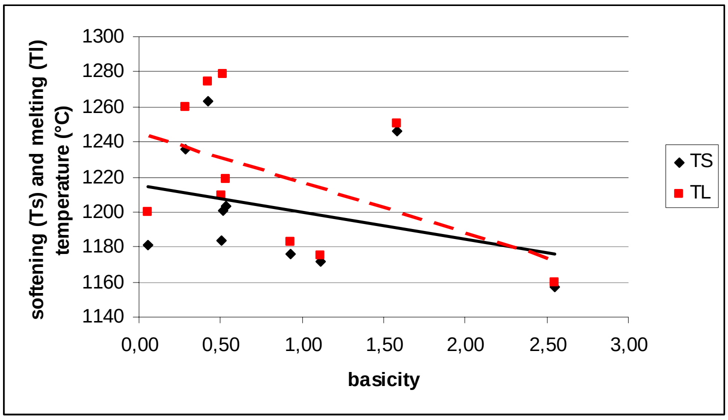

Fig. 7. The effect of basicity on the softening and melting temperature of the blast furnace slag.

The results, obtained by evaluation of archaeometallurgical and prepared slag were compared. B. M. Abel et al. [1] had investigated the phase relationships in the single alkaline earth and mixed $CaO/MgO–Al_2O_3–SiO_2$ systems. Powders of pure MgO, CaO, Al_2O_3 and SiO_2 were prepared for 120 different compositions. The content of Al_2O_3 was between 8 and 24 % wt. and thus it was higher than in analyzed archaeometallurgical slag. The compositions with high silica and low alumina content (up to about 18 %) are found to be dominated by cristobalite. The mixing of MgO and CaO is found to shift the liquidus temperature to lower values by suppressing the formation of anorthite and cordierite. The minimal melting temperature (1305°C) had slag containing 60.5% SiO_2, 16.6 % Al_2O_3, 19.0 % CaO and 3.8 % MgO (%wt.), the presence of anorthite ($CaAl_2Si_2O_8$), and cristobalite was confirmed by x-ray diffraction [1]. Liang et al. [23] evaluated the effect of a refining slag composition on the melting temperature. The composition of the slag 29.5 % CaO, 14.6 % SiO_2, 10.2 % MgO, 18.1 % Al_2O_3, 18.0 % FeO (% wt.) with melting temperature point of 1390°C was gradually changed. It was found that, with slag basicity increasing, melting temperature and viscosity would decrease deeply. Under the present condition the slag with basicity about 2.7 has melting temperature about 1400°C.

Conclusion

The slag, found in the places of past ironworks was analyzed using archaeometallurgical methods. Used methodology of the heating microscopy is not appropriate for the slag – product of bloomery process, as iron oxide in slag secondarily oxidize with negative effect on the melting temperature and interpretation of results. The melting and softening temperature decrease with increasing basicity and decreasing content of SiO_2. The lower melting temperature of archaeometallurgical slag is a result of low content of Al_2O_3 as compared with synthetic and industrial slag. Presence of other compounds such as MnO (and possible alkali as K_2O) decreases melting temperature of analyzed slag as well.

Acknowledgements

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