ANALYSIS AND USE OF Mn ORE FINES

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Abstract
This article deals with the analysis and use of Mn ore fines in the production of ferroalloys. The paper focuses on the evaluation of Mn ores in terms of their chemical and phase composition. Mn ore fines are formed in the process of mining, transport and processing of Mn ores in factories. These small particles cannot be directly put into the furnace; they should be edit before they are used. The most appropriate treatment method of Mn ore fines is sintering. Laboratory experiments were done with Mn ore from Turkey, Bosnia and Herzegovina and Bulgaria. Analyses of the Mn ores were performed in order to determine their various properties, according to which conditions were adapted for laboratory experiments to produce the best quality Mn sinter. Chemical and phase composition and thermal analysis have been performed on the ores. The phase analysis showed that the ore from Turkey and Bulgaria are in the carbonate form and the ore from Bosnia and Herzegovina is in the oxide form. DTG analysis showed that, by the thermally heating the biggest weight loss happened in the Mn ore from Bulgaria. For the best quality ore can be considered the Mn ore from Turkey because it contains the highest % of Mn, lowest content of SiO_2 and the ore has the lowest % of P. The sizing of Mn ore fines was carried out in laboratory conditions on a laboratory sintering pan. Produced Mn sinters were subjected to analysis of their chemical and phase composition. Produced Mn sinters have higher content of Mn_{tot} compared to Mn ores. As a result of Mn ore sintering the form of majority compounds changed - silicates, carbonates and hydrates of manganese in the starting Mn ores were in the produced Mn sinters analysed majority compounds based on the higher oxides of Mn and Fe, which is in the process for production of Mn ferroalloys positive.

Keywords: sintering, processing, grain size, analytical methods, x-ray diffraction (XRD)

1 Introduction

In connection with the increasing percentage of steel being made in electric furnaces and converters in foreign metallurgical practice, there is also a rising demand for ferrosilicomanganese and ferromanganese [1, 2]. Manganese is added into steel for its deoxidizing and desulfurizing and alloying effect [3, 4]. The main raw materials for the production of manganese ferroalloys are manganese ores and manganese sinters [5, 6]. In the production of manganese alloys one of the major costs is the price of manganese raw materials, especially the price of manganese ore. The contents of iron, silicon, and phosphorus impurities in manganese ores are limiting factors in the beneficiation process [7]. From the economical and environmental point of view optimization of raw materials is essential [8, 9]. Experience has

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shown that smooth and efficient operation of manganese ferroalloys smelting furnaces is achieved when close sizing control is practiced on the raw materials. The raw materials must secure good permeability for the gas to be distributed through the burden [10, 11]. The harmful effect of Mn ore fines depend on their chemical composition, particle size, and the process itself, whether it is a production of FeMn or FeSiMn, open or closed type of furnace and the size of the furnace [12, 13, 14]. Fines in the raw materials are particularly detrimental, causing poor charge porosity, which will result in high power consumption per ton of alloy, excessive fume and dust losses, and low productivity. Small particles must therefore be separated before the use of ore for metallurgical processing. It is estimated that 10 – 40 % undersize particles is produced from ores by the processing in steel plants. Manganese ore, which cannot be used directly in the process of production of ferroalloys can be adjusted by removing the volatile substances (moisture and CO_2), by reducing the amount of excess oxygen (pre-reduction), sizing (sintering). High quality fines are often agglomerated. Sintering, pelletizing, and briquetting are three principal technologies used for the agglomeration of ores and concentrates [10, 15, 16]. Sintering is a widely used method to agglomerate fine grained materials [10, 15]. The main raw materials for sintering are Mn ore fines, fluxes (limestone, dolomite) and fuel (coke, anthracite) [17]. Physical and chemical properties of sintered materials depend on the properties of individual components and on its microstructure, especially on the size distribution and the mutual interaction of the individual components [18]. A suitable device for processing of Mn ore fines in companies can be equipment which is use at the Chelyabinsk metallurgical combine [19]. An example of the production of Mn sinter abroad is the production of Mn sinter in the company Kalagadi, South Africa, where Mn sinter is used as part of the input materials [20].

2 Experimental materials and methods

Three samples of Mn ore fines were analysed: Mn ore from Turkey, Mn ore from Bosnia and Herzegovina (further B and H) and Bulgarian Mn ore.

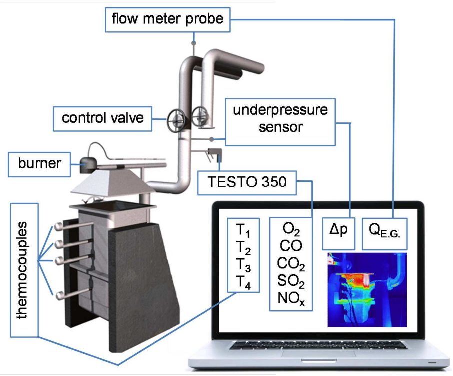

Fig. 1 Schematic diagram of the laboratory sintering pot (LSP)

The samples of Mn ores and sinters were analysed for chemical and phase composition. Thermal analysis was performed only on samples of Mn ores. The analysis of chemical composition of the input Mn ore and produced Mn sinters was realized by combining analytical methods AAS elemental analysis of the prepared solutions and optical quantification method.

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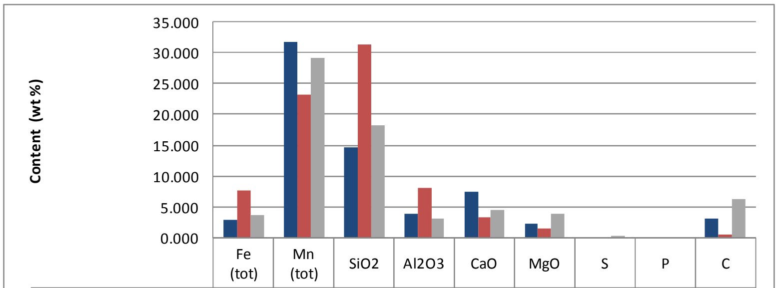
Phase composition was determined by X ray diffraction X-ray analysis on the diffraction spectrometer SEIFERT XRD 3003 / PTS. Thermal analysis of the samples of Mn ores was carried out on Derivatograph C-fy MOM Budapest. The sample was heated in a Pt crucible to 800 °C with a temperature gradient of 10 °C/min in air atmosphere. Al_2O_3 was used as reference material . The samples of Mn ores (considering the humidity), were not adjusted (not dried or crushed), but they were homogenized. During the laboratory sintering a laboratory sintering pan (LSP) (**Fig. 1**) was used.

3 Results and discussion

In ferroalloy factories, where manganese ferroalloys are produced a large quantity of Mn ore fines is formed. The aim of the study was to analyse the individual Mn ores, explore the possibility of sintering and evaluate the produced Mn sinters. The results of the analysis of the chemical composition of Mn ores are evident from **Fig. 2**. The comparison of the chemical composition of the different Mn ores shows that the highest levels Mn_{tot} are in the Mn ore Turkey (31.82 %) and Bulgaria (29.20 %). Whereas the lowest content of Mn_{tot} is in Mn ore from B and H (23.28 %). The highest content of SiO_2 is in the ore from B and H (31.33 %). Content of harmful impurities (S and P) in all analysed ores is higher than that in the quality Mn ores (e.g. The JAR and Australia). The highest content of sulphur is in the ore from Bulgaria (0.36 %). The highest basicity has the Mn ore from Turkey – 0.69, and the lowest basicity has the Mn ore from B and H – 0.16 due to the high content of SiO_2.



	Fe (tot)	Mn (tot)	SiO2	Al2O3	CaO	MgO	S	P	C
Turkey	3.090	31.820	14.660	4.120	7.690	2.400	0.052	0.153	3.130
Bosnia and Herzegovina	7.790	23.280	31.330	8.120	3.350	1.650	0.182	0.190	0.540
Bulgaria	3.650	29.200	18.250	3.110	4.540	3.860	0.360	0.160	6.270

Fig. 2 Chemical composition of Mn ores

In the samples of Mn ores the phase composition was analysed (**Table 1**). The comparison of the phase composition of Mn ores have shown that there are different forms of Mn in the ores. In the Mn ore from Turkey Mn is mostly in the form of braunite. The Mn in Mn ore from B and H is located in a pyrolusite, braunite, and in the compound $Fe_3Mn_3O_8$ .In Mn ore from Bulgaria Mn is in the form of rhodochrosite and manganite. Amorphous content is highest in the Mn ore from B and H (81.2 %). Based on the phase analysis the behavior of the Mn ore samples during the thermal analysis can be assumed. **Fig. 3** shows a record from derivatograph of Mn ore sample from Turkey. The graph shows that the weight loss is about 16 wt. %.
Input moisture of the sample was 4 wt. % and a small amount of water was bound in hydrates. The release of the free water corresponding to the temperature interval 50 - 350 °C. The first substantial peak can be attributed to the decomposition of rhodochrosite which decomposes at the temperature range 200 - 550 °C.

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Table 1 Phase composition of Mn ores

Identified phase composition		**Content (wt %)**		
Chemical formula	**Mineralogical name**	**Turkey**	**B and H**	**Bulgaria**
$Ca_{0.01}Fe_{0.18}Mg_{0.13}Mn_{6.68}O_8(SiO_4)$	Braunite	37.7	1.8	-
$MnCO_3$	Rhodochrosite	14.3	-	53.4
SiO_2	Quartz	12.3	65.9	-
$MgCa(CO_3)_2$	Dolomite	11.3	-	28.3
$Ca(Mg_{0.3}Fe_{0.6}Mn_{0.1})(CO_3)_2$	Ankerite	7.9	-	-
MnO_2	Pyrolusite	-	5.7	-
$Fe_3Mn_3O_8$	-	-	4.4	-
Fe_2O_3	Hematite	-	5.2	2.5
FeO(OH)	Lepidocrocite	-	15.7	-
MnO(OH)	Manganite	-	-	5.8
Fe_3O_4	Magnetite	-	-	9.9
Amorphous content		-	81.2	13.9

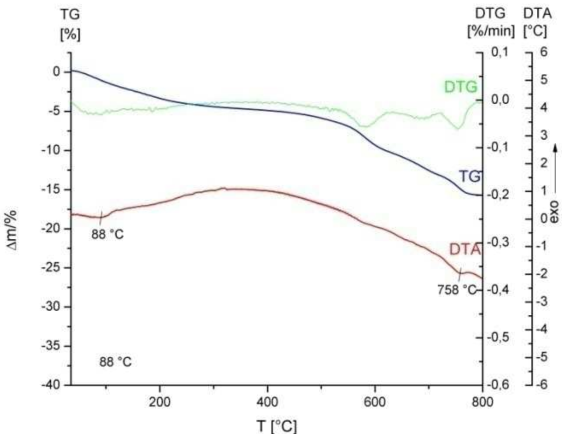

Fig. 3 Record from derivatograph of Mn ore sample from Turkey

The peak relates to strong decomposition that occurs at the temperature 550 °C. Another less continuous peak is associated with the decomposition of ankerite. In the temperature range 450 - 750 °C dolomite decomposes which is related to a significant decrease in TG curve. **Fig. 4** shows a record of derivatograph of Mn ore from B and H. The decrease of the total weight was approximately 10 wt. %. In analytical sample the input moisture was 5.5 %, and a small proportion of bound water. The input humidity of Mn ore from B and H 16 % was reduced to 5.5 % as a result of the ore storage in the hall for 6 weeks. The release of water occurs in the temperature range 50 - 350 °C. Further decrease in mass of the sample, which is evident from the TG curve and another less pronounced coherence peak of the DTG curve is attributed to the decomposition of manganese oxides. On the basis of the thermodynamic analysis, it is assumed that there occurs a decomposition of MnO_2 to Mn_2O_3, and Mn_2O_3 to Mn_3O_4. The decomposition of Mn_3O_4 to MnO is carried out at higher temperatures.

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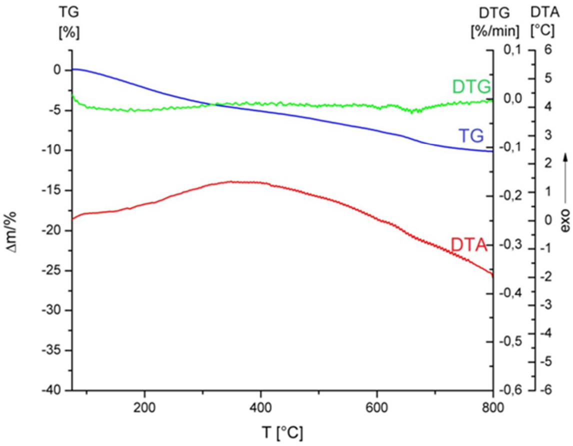

Fig. 4 Record from derivatograph of Mn ore sample Bosnia and Herzegovina

The total weight loss of the sample of Mn ore from Bulgaria amounted to about 38 wt. % (**Fig. 5**). The sample had a high content of bound water, which amounted to 28 wt. %.

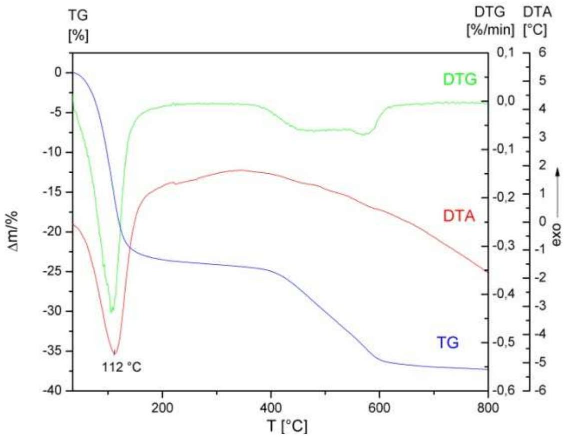

Fig. 5 Record from derivatograph of Mn ore sample Bulgaria

The release of free, bound water and water in the form of hydrates, is attributed to a drastic drop in the TG curve and a large peak of the DTG curve occurs at temperatures in the range 50 – 250 ° C.The first reduction of the weight is attributed to thermal decomposition of rhodochrosite that takes place in the temperature range 250 - 550 °C. The decomposition of $MnCO_3$ is recorded at temperatures 350 - 550 °C. Another significant decrease of the TG curve is related to the decomposition of dolomite, which covers the temperature range 450 - 750 ° C. The decomposition of dolomite is recorded at temperatures 450 - 650 ° C. After analysing of the Mn ore a series of laboratory sintering followed. Individual sintering mixtures consisted of the portion of individual Mn ore, to which the required amount of coke dust was added. For the production of Mn sinters from Bulgaria 3 sinterings were carried out.
During the sintering Mn sinters produced were: Turkey, Bosnia and Herzegovina (further B and H), Bulgaria A, B and C. The comparison of the chemical composition of Mn ores and sinters

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indicate that the Mn content in the sinter increased compared to the starting ore (**Fig. 6**). For the production of FeSiMn, suitable Mn sinters are from Turkey, Bulgaria C and B and H because they have low P content (**Table 2**).

Table 2 Chemical composition of Mn sinters

Name of element/compound	Mn sinter – content (wt. %)				
	Turkey	**B and H**	**Bulgaria A**	**Bulgaria B**	**Bulgaria C**
Fe_{tot}	4.99	8.45	6.11	6.47	11.14
Mn_{tot}	37.08	27.5	34.45	36.65	34.5
SiO_2	19.02	35.86	21.62	23.22	22.34
Al_2O_3	5.02	8.32	3.17	4.44	4.61
CaO	8.09	3.54	4.82	5.37	6.59
MgO	2.93	2.23	3.99	6.21	5.53
S	0.04	0.09	0.24	0.18	0.14
P	0.16	0.17	0.22	0.2	0.15
C	0.36	0.47	0.55	0.71	0.95

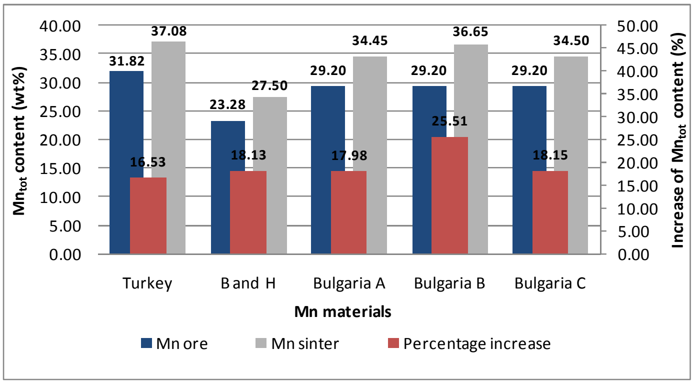

Fig. 6 Content of Mn_{tot} in Mn materials

Mn sinter Turkey has the highest % of Mn – 37.08 % of all sinters (percentage increase of 16.5 %), and the lowest content of Fe and SiO_2. P content is 0.16 %. Mn sinter B and H has the highest proportion of SiO_2 – 35.86 % and high % of Fe – 8.45, because the input ore had already a high proportion of gangue constituents. Mn content in the sinter B and H is 27.5 % (percentage increase of 18.1 %). Mn sinter Bulgaria A has Mn content of 34.4 % (increase of 17.9 %), and Fe content of 6.11 %. P content is high 0.22 %, which is disadvantageous for the production of Mn ferroalloys. Mn sinter Bulgaria B has a Mn content of 36.65 % (percentage increase of 25.51 %). The sinter is high in P – 0.2 %. Mn sinter Bulgaria C has a Mn content of 34.5 % (percentage increase 18.15 %). The sinter has the highest % of Fe among all of produced sinters – 11.14 %. This is because of the addition of the return sinter Bulgaria B to the charge. The sinter has the highest % of C – 0.95, because the charge contained a higher percentage of coke and coke was brought by the undersize sinter Bulgaria B too. P content is 0.15 %. From the analysis of the phase composition of the Mn sinters (**Table 3**) it is obvious that manganese is in sinters mainly in the form of various oxides.

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Table 3 Phase composition of Mn sinters

Identified phase composition		**Mn sinter -content (%)**				
Chemical formula	**Mineralogical name**	**Turkey**	**B and H**	**Bul. A**	**Bul. B**	**Bul. C**
$Fe_{1.5}Mn_{1.5}O_4$	-	-	-	31.7	31.7	35.9
Mn_3O_4	Hausmannite	30.3	8.7	14.6	10.7	6.5
MnO	Manganosite	-	-	13.3	11,8	11.1
SiO_2	Quartz	6.5	12.9	1.6	2.7	2.9
Mn_4SiO_7	Welinite	-	-	20.2	25.4	27.1
Fe_2O_3	Hematite	-	-	5.0	2.2	0.7
$Na_{6.04}Mn_{9.74}Al_{3.4}P_{12}O_{48}$	-	26.5	-	-	-	-
$Mn_7O_8(SiO_4)$	Braunite	12.1	-	-	-	-
$FeMnSiO_4$	-	9.9	-	-	-	-
$Fe_{26.4}Al_{13.6}Si_{24}O_{96}$	Almandine	7.0	-	-	-	-
Fe_2MnO_4	Jacobsite	6.0	-	-	-	-
$FeMn_2O_4$	-	-	44.3	-	-	-
$CaMn(SiO_3)_2$	Johannsenite	-	16.2	-	-	-
Amorphous content	-	-	56.3	39.5	38.0	35.4

Mn sinter Turkey contains the highest % of Hausmannite - 30.3 %. Mn sinter B and H has the highest content of $FeMn_2O_4$ – 44.3 %. The sinter has high content of SiO_2 – 12.9 % and high content $CaMn(SiO_3)_2$, which are less desirable in terms of quality of sinters than ferromanganese oxides and Mn oxides. The Mn sinters from Bulgaria Mn ore are high in $Fe_{1.5}Mn_{1.5}O_4$, and high in Mn_4SiO_7, which is less desirable in Mn sinters.

4 Conclusions

Analysis of Mn fines is necessary before the further processing. The processing of Mn fines from Mn ores has importance because it succeeded to produce Mn sinters. Quality assessments of the Mn sinters in terms of use in the manufacture of FeSiMn show that best suited are Mn sinters Turkey, Bulgaria C and B and H, because they have the lowest content of P. As a result of the sintering of Mn ores, the majority of the compounds modified their form - from silicates, carbonates and hydrates of manganese in starting Mn ores, in the produced sinters were analyzed compounds mainly based on higher oxides of Mn and Fe.

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