Mill scale recycling by SHS metallurgy for production of cast ferrosilicon and ferrosilicoaluminium

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Abstract. The possibility of utilizing the industrial wastes of metallurgical production and secondary raw materials (aluminum) by organizing self-propagating high-temperature synthesis (SHS) and obtaining cast ferroalloys (Fe–Si; Fe–Si–Al, and Fe–Si–Al(Cr, Mn)) was investigated. The main production operations of the preliminary preparation of the starting raw materials were worked out and cast ferroalloys providing high concentration Si, Al and B were revealed. The possibility of processing the industrial wastes of metallurgical production and obtaining cast ferroalloys was shown.

1. Introduction.

The metallurgical industry is one of the most massive material forming industries. High amount of by-products in the form of mill scale sludge is generated every year in each section of steel making plants due to hot rolled metal processing at elevated temperatures. Mill scale, often called as scale, is the flaky surface consisting of the iron oxides iron (II) oxide (FeO), iron (III) oxide (Fe₂O₃), and iron (II,III) oxide (Fe₃O₄, magnetite). It can be considered as a valuable metallurgical raw material for iron and steel making industry [1, 2]. The strict environmental regulations as well as the valuable metallic content cause the ability to recycle mill scales become an important issue. Currently, many metallurgical plants have accumulated high amounts of mill scale in the dumps containing oils (4–12%) and moisture (4–18%). After the removal of oil and water, this material contains up to 70% iron with a minimum amount of sulfur compounds and can be effectively used in both blast and steel smelting operations. The solution of this task is becoming more effective due to the world deficit and the constant growth of the cost of iron ore, as it allows to reduce raw materials dependence and improve the ecology. So, there has been a big tendency to recover the valuable iron content in the production process.

Accordingly, to recycle the iron content wastes, briquettes are smelted using blast furnace or electric arc furnace (EAF) [3]. These processes allow better utilization of iron oxide, but are not cost-effective. For this reason, energy efficient technologies should be used. It is also required to expand the nomenclature of products obtained from the recycled scale.

In this regard, the present study was aimed at the evaluation of the possibility, efficiency, and consequences of the reduction of mill scale by combustion. A promissory route to production of cast ferroalloys is the SHS technology of high temperature melts or SHS metallurgy [4, 5]. This is an energy-saving technique due to the use of internal energy released in high-caloric combustion reactions. Previously, we first showed the possibility of obtaining cast ceramic coatings of the inside of metallic pipes by means of reprocessing the mill scale [6].
2. Experimental

2.1. Experimental Procedure of Investigations
This study involved three stages:
(i) the preliminary investigation of starting reagents (industrial mill scale) and the selection of optimal modes of their heat treatment for purification;
(ii) the study of correlation between the green mixture composition and final composition of ferroalloys (ferrosilicon, ferrosilicoaluminum and ferroboron);
(iii) the investigation of phase and chemical composition of synthesized ferroalloys and the study of the effect of experimental conditions on formation of the final composition.

In our experiments, iron oxide mill scale (Fe\textsubscript{x}O\textsubscript{y}) generated from steel making plants, recycled aluminum (Al), and alloying additives (AD) were used as starting reagents for preparation of cast ferroalloys. The average particle size of scale and aluminum (brand PA - 4) was 50–100 μm and less than 140 μm, respectively. The weight of the green mixture was constant (1200 g). Combustion was carried out in graphite crucible 80 mm in diameter. The internal surface of graphite crucibles was laminated with Al oxide (Al\textsubscript{2}O\textsubscript{3}) to avoid reactive interaction between the crucible and metal melt.

The overall scheme of reaction can be represented by the following scheme:

\[ v_1\text{Fe}_x\text{O}_y + v_2\text{Al} + v_3\text{AD} \rightarrow v_4\text{Fe}_x\text{Si(B)}_y + v_5\text{Al}_2\text{O}_3 \]

where AD is the alloying additive such as Si, SiO\textsubscript{2}, B, and B\textsubscript{2}O\textsubscript{3}.

The initial compositions of mill scales contained admixtures, such as iron, oil, paraffin, etc. In order to remove the organic additives, we calcined the scales in shallow trays. It was found that such heat treatment should be carried out for 2–3 h at the temperature of 300–350°C. After calcining, the scales were refined to a particle size below 400 μm.

Figure 1 schematically illustrates the SHS process for fabrication of cast materials. After initiation with an igniting coil, the reaction frontally propagates downward. Because the attained temperatures (up to 3000°C) exceed the melting points of reaction products, the melt represents a mixture of mutually insoluble metallic (alloy) and oxide (Al\textsubscript{2}O\textsubscript{3}) phases. Due to strongly different specific weights, these phases undergo gravity-assisted phase separation and subsequent crystallization. As the result, the lower layer is target material (ferroalloys); the upper one, Al\textsubscript{2}O\textsubscript{3}.

![Figure 1. Schematic of the SHS process for fabrication of cast materials: (a) charge preparation, (b) combustion, (c) phase separation, (d) pattern formation. Here, 1 igniting coil; 2 refractory crucible; 3 green mixture; 4 combustion front; 5 MMC globules in the metal melt; 6 oxide phase (Al\textsubscript{2}O\textsubscript{3}); and 7 cast alloy (ingot).](image)
number and concentration of components. Therefore, the synthesis of the as cast alloy under study was carried out using a centrifugal SHS setup (figure 2) with the possibility of forming the necessary synthesis conditions in a broad range of specified overloads. The main features of the SHS installation include systems for initiating the reaction mixture, controlling the rotation velocity of samples, and measuring the sample temperature after synthesis (at the cooling stage). The centrifugal installation has a working rotation range from 50 to 3000 rpm, which makes it possible to implement the overloads from 10 to 1200 g.

![Figure 2. Experimental setup: 1 electric motor; 2 tachometer; 3 collector; 4 rotor; 5 photodiodes; 6 graphite or silica container; 7 green mixture; and 8 igniting coil.](image)

3. Results and Discussion

3.1. Analysis of Starting Components

To calculate the ratio of the starting components, we should know the mutual concentration relation of iron and oxygen in the scale ($x$ and $y$ values) exactly. The analysis of the chemical and phase composition of two studied scale (table 1), which were supplied from different plants, revealed the difference in the mutual relationship of iron oxides.

| Sample no. | FeO:Fe$_2$O$_3$, wt % | Particle size, mm | Impurities, wt % |
|------------|------------------------|-------------------|------------------|
| 1          | 46:48                  | 1–5               | 6                |
| 2          | 68:28                  | 0.5–10            | 4                |

The first party contained a larger amount of Fe$_2$O$_3$ (48 wt %), while the second one preferentially consisted of FeO. The size of scale particles varied from 0.5 to 10 mm. Both compositions had impurities including inclusions of iron, silicon oxide, alumina, and organic compounds (oil, paraffin, etc.). The presence of the latter can substantially affect the SHS process by intense gas liberation (gasifying the impurities) and can lead to the complete or partial emission of reaction products in the course of combustion. Therefore, it became necessary to carry out preliminary the calcination of scale. The use of various heat treatment modes and the subsequent analysis of the composition of the processed scale allowed us to reveal the optimal temperature and time range of calcination: $T = 300–350^\circ$C for 2–3 h (in the plane bottom plates). Calcination at $T < 300^\circ$C led to an essential increase in the calcination time (up to 10 h). At $T < 200^\circ$C, it led only to the partial gasifying of organic impurities. The annealing at $T > 400^\circ$C is undesirable because the selfignition of the evaporating gases occurs in some cases.

After calcination and cooling, the scale was subjected to mechanical milling. It was found experimentally that the optimal particle size should be smaller than 400 μm. It should be noted that the most expensive component of the starting mixture is the aluminum powder. According to our analysis, it was established that replacing chemically pure aluminum (brand PA-4) by secondary one (the worked scrap) made it possible to decrease the cost of the starting mixture by more than 25%. However, the
processed aluminum contains mainly impurities, the basic ones being iron (up to 5 wt %) and silicon (up to 1 wt %). It should be noted that these impurities cannot be attributed to “harmful” from the viewpoint of implementation of the SHS process. It even seems likely that their presence is desirable, since makes it possible to somewhat reduce the synthesis temperature, while the presence of silicon promotes the formation of target product (ferrosilicon and ferrosilicoaluminum).

3.2. The phase and chemical composition of synthesized ferroalloys

It is well known that complete melting of system components is a prerequisite for good sensitivity of the process to gravity forces [5, 6]. The investigation on III stage (the effect of experimental conditions on the formation of final compositions) revealed that the burning velocity ($U$) increases with increasing $a/g$ (overload). The effect is most pronounced within the range of $a = 10$–200 g.

Strong influence of mass forces on the burning velocity was associated with intensification of convection and deformation within the reaction zone, which improves the completeness of combustion reaction. An increase in $a/g$ (where $a$ is the artificial gravity, $g$ is the earth gravity) is also accompanied by a decrease in material loss ($\eta_{\text{spat}}$) and an increase in the yield of target product ($\eta_{\text{ingot}}$). More than 50(±5) g, the $\eta_{\text{ingot}}$ values get close to theoretical ones.

As is seen in figure 3, synthesized ferrosilicoaluminum alloys can be obtained within a wide range of parameters $\alpha_{\text{Si}}$ (the mass fraction of Si in final ingot). Thus, prepared ferrosilicon samples exhibited no residual porosity that is typical of cast materials and a small contraction cavity at the center. An increase in $\alpha_{\text{Si}}$ was found to slightly affect the $U$: it decreased from 4 to 3 cm/s.

![Figure 3. Overall view of combustion products derived from ferrosilicon with different Si content (Si varies in range from 10 to 45% mass).](image)

XRD data presented in figure 4 show that cast ferrosilicon contains three ($\text{Fe}_2\text{Si}$, $\text{FeSi}$, and $\text{FeSi}_2$) phases. The increase in $\alpha_{\text{Si}}$ in the initial mixture favors the formation of high concentrated ferrosilicon phase ($\text{FeSi}_2$).

![Figure 4. X-ray diffraction pattern of synthesized Fe–40Si cast ferrosilicon by SHS.](image)
Figures 5 and 6 show the microstructure and composition of SHS produced as-cast ferroalloys by reprocessing of mill scale wastes.

|          | Al | Si  | Mn | Fe  | Total |
|----------|----|-----|----|-----|-------|
| Sp.1     | 4.3| 23.2| 0.6| 71.9| 100   |

**Figure 5.** SEM image and EDS data of synthesized cast ferrosilicoaluminium Fe–Si–Al.

|          | Al | Si  | Cr | Mn | Fe  | Total |
|----------|----|-----|----|----|-----|-------|
| Sp.1     | 4.0| 20.0| 3.4| 4.8| 67.8| 100.0 |

**Figure 6.** SEM image and EDS data of synthesized additionally alloyed cast ferrosilicoaluminium Fe–Si–Al(Cr, Mn).

4. Conclusions

The analysis of the obtained data allows drawing a conclusion about the prospects of materials under investigation and the method of their production for the formation of bulk materials for steel making industry. The production of complex alloyed ferroalloys can be realized in combustion mode (SHS) for powder mixtures based on scale. The process of obtaining high-alloy ferroalloys is completely energy independent, which makes it attractive for practical realization.

Acknowledgments

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