

Conference Paper

Complex Processing of Copper Smelting Slags with Obtaining of Cast Iron Grinding Media and Proppants

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Abstract

The Ural region has a large number of metallurgical companies. The extraction of metals from ore is always accompanied by the accumulation of wastes. Currently, most of the wastes are stored in dumps and storage facilities forming technogenic deposits. One such that occupies huge areas is copper slag from the copper-smelting production. According to current estimations, about 2.2 tons of slag is formed for each ton of copper produced and about 24 million tons are produced annually [1]. In general, a copper slag contains about 35-45% iron and 0.4-0.5 copper, which indicates that this is a valuable secondary resource for recycling and utilization [33]. However, more than 80% of copper slag is not utilized, which makes it possible to consider this waste not only as a valuable material, but also as a potential hazard for the environment; it contaminates the soil and water with heavy elements [8]. Currently, only small amounts of the waste are recycled. In addition, technologies do not allow the complete extraction of valuable elements. This offers potential for the development of new highly efficient technologies for processing copper smelting wastes with extraction of valuable elements such as iron (Fe). Improvement of Fe quality requires a decrease in non-ferrous metal content, especially Cu. In recent years, extensive research was directed at the extraction of valuable materials from copper slags by high-temperature firing of copper conglomerates with subsequent magnetic separation or leaching of non-ferrous metals. However, these studies do not allow the complete processing of copper smelting slags. This work studies the production of iron-containing briquettes from copper-smelting slags, and their subsequent processing to obtain valuable products for metallurgical and oil companies.

Keywords: briquette, reduction, cast iron, proppants.

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1. Introduction

The world's high-grade iron ore reserves are depleting. It stimulates processing of iron-containing waste with extraction of iron from low-grade ores. In this regard, the construction of large plants with sinter and coke production facilities becomes less



profitable. Instead, the mini mills are more beneficial for processing of certain types of ore and waste [23].

One of these materials is copper slag forming by copper matte smelting and converting operations during pyrometallurgical production of copper. The high content of non-ferrous impurities, and especially copper, does not allow processing of this type of waste by the conventional method with production of sinter for the blast furnace process [35]. However, copper is not always a harmful impurity in limited steel grades. Copper increases the tendency of steel to atmospheric corrosion.

The reduction of iron from copper slag with subsequent pyrometallurgical separation was experimentally investigated in work [3]. It was observed that 95% iron could be reduced from briquettes. The resulting cast iron had high strength. Thereby, the mini mill for utilization of copper smelting slag and extraction of iron could be organized [25]. The production of metallized briquettes with further pyrometallurgical separation and production of demanded products might have positive effect on environment as well.

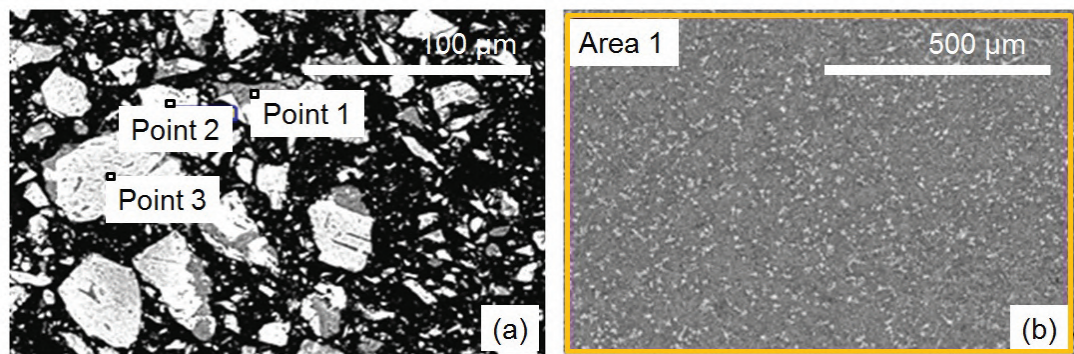
An objective of this work was to study the possibility of processing of metallized briquettes with subsequent pyrometallurgical separation of metal and slag for production of cast iron grinding media and proppants.

2. Materials and Methods

A slag was provided by the Karabash Copper Smelting Company. The reported chemical composition of the slag included about 40 % Fe, 11 % Si and 0.7 % Cu. The major phases of this slag are fayalite, magnetite and pyroxene, Figure 1.

The briquettes were prepared from the following mixture: 72% copper slag, 18 % coal and 10 % binder. The 4 different types of binders were selected:

1. liquid glass represented by an aqueous alkaline solution of sodium silicates $\text{Na}_2\text{O}(\text{SiO}_2)_n$,
2. an alumino-borophosphate concentrate (ABFC) which is a viscous liquid without mechanical impurities with a density of $1.5\text{-}1.7 \text{ g / cm}^3$ and $\text{pH} \geq 0.1$ (mass fraction of contained 8 – 9 % Al_2O_3 , 36 – 39 % P_2O_5 , and 1.3 – 2.0 % B_2O_3 ,
3. Aluminum-chromophosphate ($\text{Cr}_n\text{Al}_{(4-n)}(\text{H}_2\text{PO}_4)_2$) with a density of $1.55\text{-}1.65 \text{ g / cm}^3$ (mass fraction contained 3.7 – 4.5 % Cr_2O_3 , 8 – 10 % Al_2O_3 , 36 – 39 % P_2O_5 ,
4. silica-salt which is a colloidal solution consisting of a dispersed material representing amorphous silica micelles.



	O	Mg	Al	Si	S	Ca	Fe	Cu	Zn	Phase
1 (a)	52.7	0.1	0.0	0.9	6.7	0.1	35.9	1.5	2.1	Magnetite Fe ₃ O ₄
2 (a)	59.0	6.1	0.0	13.7	0.0	0.3	20.2	0.1	0.8	Fayalite 2FeO·SiO ₂
3 (a)	62.0	0.3	3.5	19.6	0.3	5.4	7.9	0.1	0.8	Pyroxene CaFeSi ₂ O ₆
1 (b)	61.0	1,1	1,6	11,6	0,9	1,4	21,8	0,3	1,1	Average, at %
1 (b)	36.0	0,9	1,6	11,6	1,1	1,9	43,6	0,7	2,5	Average, wt %

Figure 1: The chemical and phase composition for (a) initial slag and (b) slag subjected to quenching

One group of the briquettes was dried at 200 ° C in a muffle furnace. The obtained briquettes were subjected to strength measurements.

The experiments were conducted in three stages:

1. The first stage of the experiments was carried out in a muffle furnace. A tightly closed graphite crucible was installed inside the furnace. The briquettes were placed in the crucible, and the remaining space was filled with a reducing agent in the form of coal particles. The furnace was heated to 1020 ° C and held for an hour. After reduction, the furnace was switched off and the samples were cooled down with the furnace to room temperature. After the experiment, the samples were epoxy resin mounted, polished and examined using optical and electron microscopes. The chemical composition of the phases was determined by the micro X-ray spectral method using a JEM microscope JSM-6460LV.
2. The second stage of the experiments was carried out in an induction furnace. A graphite crucible with metallized briquettes was inserted in the furnace. The furnace was heated to complete smelting. After smelting the briquettes, the melt was kept for 10 minutes and cast into the chute. After experiment, the slag and iron samples were separated. Cast iron was melted and cast into a chill mold to obtain grinding balls.
3. The third stage of the experiments was also carried out in an induction furnace. A graphite crucible was inserted in the furnace. The resulting slag was placed in the

crucible with addition of MgO and fluorspar. The furnace was heated to complete melting. When the material was smelted, the melt was kept for 20-30 minutes and cast onto a specially prepared mechanism for producing proppants. The resulting proppants were heat treated and tested.

3. Results and Discussion

3.1. Strength of the briquettes

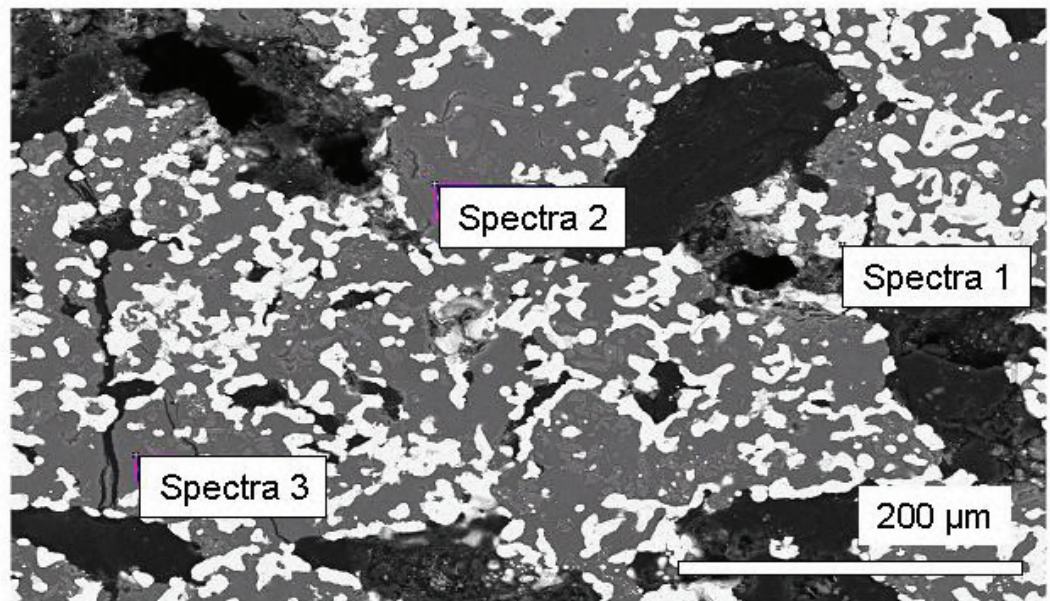
The strength of the briquettes was tested according to the standards for such a type of a product. The study revealed that in samples without firing the highest strength was in the sample with an ABFC binder. Contrary, in the fired briquettes with ABPC binder the strength decreased; it was explained by the low thermal resistance of this sample. The strength of the other samples increased as a result of the positive effect of firing. The samples were also tested for heat resistance; the samples were heated to 1000 °C, and it was found that the samples with ABFC and AHFS binders melted.

3.2. Reduction of Iron

In samples with liquid glass and silica sol, the reduction degree was 96.5%. In samples with other binders, the degree of reduction was 72.5%. Thereby, about 12% of iron in the form of pyroxene was not reduced. An increase in temperature led to melting of Fe. Thus, during solid-state reduction by carbon from briquettes with ABFC and AHFS binders, iron was reduced from magnetite and fayalite, and reduction of iron from pyroxene was almost negligible. Contrary, the reduction of iron from pyroxene under the same conditions occurred when the liquid glass and silica sol were used as a binder. And Fe was almost completely reduced. It is also worth noting that the metal was not saturated by sulfur during reduction, Figure 2.

3.3. Production of grinding media

During separation of metal and slag by smelting, the metal was saturated by sulfur and carbon and cast iron was formed which was used for production of grinding balls, Figure 3 (a). The grinding balls were tested according to the standards for such a type of a product. The hardness of the balls was 52 units on the Rockwell scale, which corresponds to the grade II hardness according to the GOST 7524 "Steel grinding balls for ball mills" and the technical conditions of ST RK 2310-2013 "Cast-iron grinding balls".



	O	Si	Ca	Fe
Spectra 1	0	0.3	0	98.1
Spectra 2	58.4	34.5	6	1.1
Spectra 3	58.3	34	6.7	0.9

Figure 2: The SEM analysis of a briquette with a liquid glass binder after reduction

During repeated drop tests from a height of 4 m onto a cast iron slab, no chipping or dents were observed on the surface of the balls. The microstructure of cast iron throughout the cross section of the balls corresponded to white cast iron, but two phases of cementite and perlite were observed. The placeFeS inclusions were also found in the samples, Figure 3 (b).

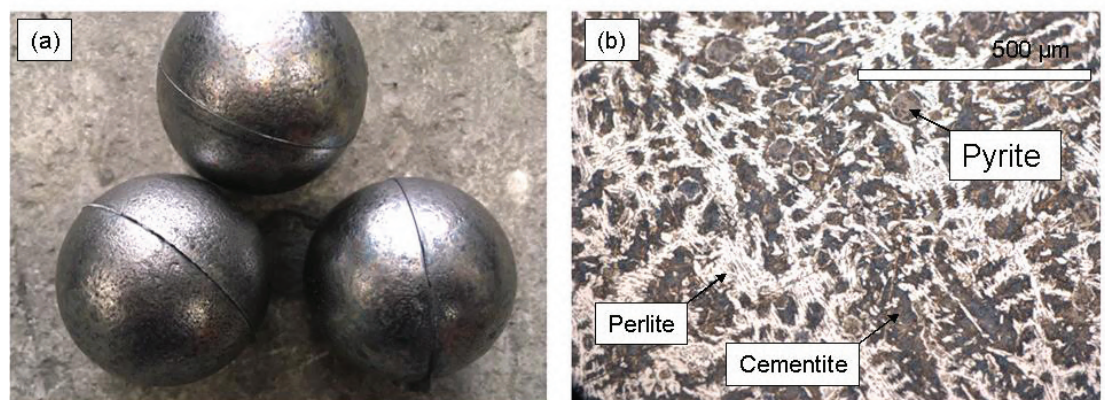


Figure 3: Cast iron grinding media (a) photograph of \varnothing 30 mm balls and (b) micrograph of cast iron structure

3.4. Slag utilization

After centrifugation the slag balls were obtained in a glassy state and with low strength properties; the photograph of the \varnothing 0.6 – 1 mm proppants is shown in Figure 4 (a). Heat treatment of proppants played an important role for obtaining of high strength properties. The transition to the crystalline state occurred at temperatures of 800-1000 °C.

The proper heat treatment plays a crucial role in obtaining of good mechanical properties. The structure of the proppants after improper and proper heat treatment is shown in Figure 4 (b) and (c), respectively. In a first case, the large ($> 5 \mu\text{m}$) crystals were formed and the mechanical properties were poor. The structure of the proppants with proper heat treatment was small ($<0.5 \mu\text{m}$) and the mechanical properties were improved.

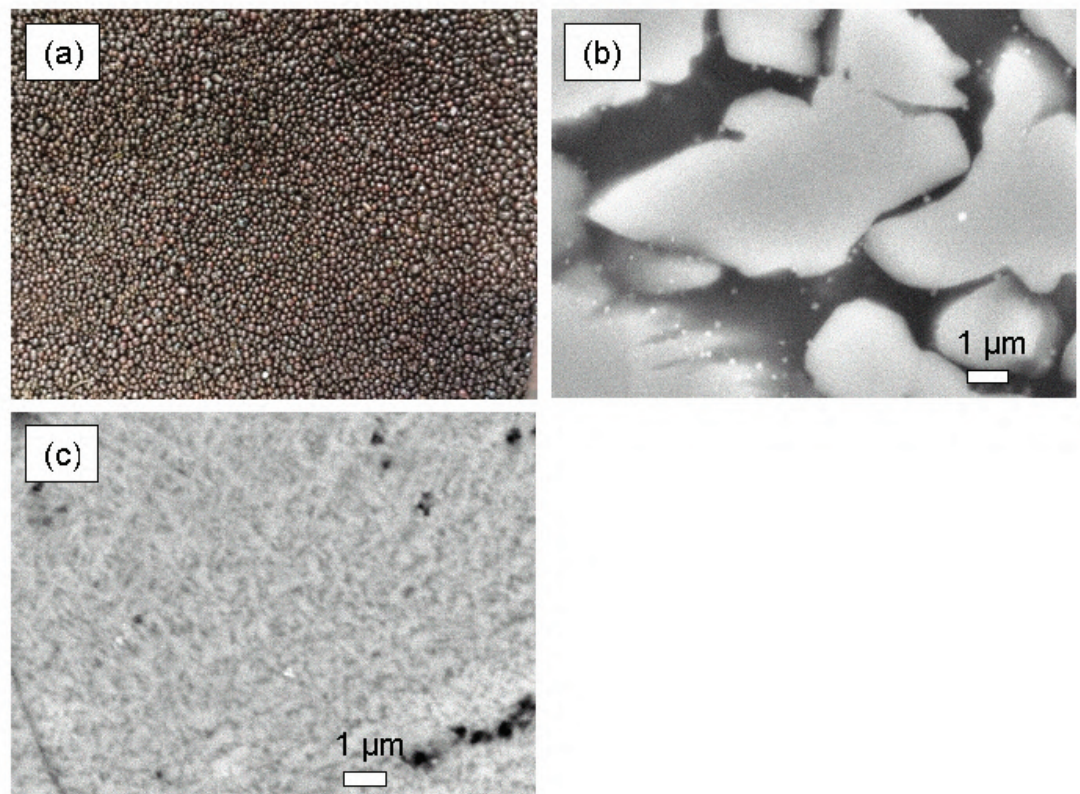


Figure 4: The proppants (a) photograph of \varnothing 0.6 – 1 mm balls, and SEM images for (b) large crystalline structure of proppants with improper heat treatment and (c) smaller crystalline structure with proper heat treatment.

In order to reduce the solubility of proppants in acid (mixture of acids), a bakelite coating was applied to their surface. The proppants were moistened with a solution of Bakelite, thoroughly mixed and dried. The dried proppants were heated in a muffle furnace (at 180 °C for 1 hour) for the polymerization of bakelite. As a result, the solubility

in a mixture of hydrochloric and hydrofluoric acids did not exceed 7% with a single coating and 3% with double; the GOST standard GOST R 54571-2011 requirement is 10 % and no more than 8% for aluminosilicate proppants.

4. Conclusions

1. The possibility of solid-phase carbothermal reduction of Fe from relatively low-melting point slags from copper-smelting production using low-grade steam coal as a reducing agent was investigated.

2. During reduction stage Fe was not saturated by sulfur. The sulfur saturation occurred during separation which was performed by smelting. The high content of sulfur and copper did not reduce the properties of cast iron.

3. The heat treatment of proppants should provide a crystal size less than 1 μm to obtain good mechanical properties. In order to reduce the solubility in acid the proppants should be coated with a protective coating.

4. The suggested technological scheme of mini mill is shown in Figure 5.

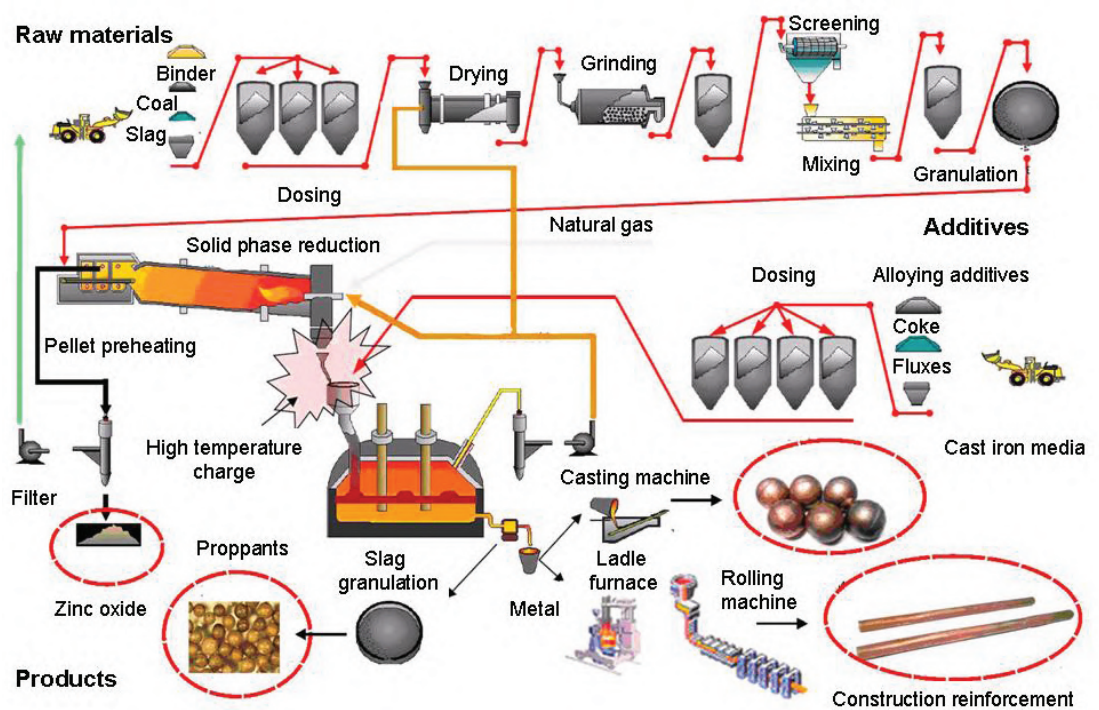


Figure 5: The suggested technological scheme of mini mill for copper smelting slag utilization

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