

CARBOTHERMAL REDUCTION OF COPPER SLAG FOR PROCESSING INTO PIG IRON

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Abstract

The article deals with the thermodynamics of the process in the ore-thermal processing of copper smelting slag, the experimental study of ore-smelting processing of copper smelting slag, and the development of a mathematical model for obtaining iron-containing alloys from copper slag, development of a technological scheme for obtaining iron-containing alloys from copper slag-information on the application and approbation of the technology in the production of the results.

The assessment of the possible direction of the carbothermic reactions that take place between the oxidised compounds in the slag and the carbon was carried out by changing the thermodynamic values of the system. Thermodynamic analyses were performed, taking into account the temperature dependence of the isobaric-isothermal potentials (Gibbs free energy).

Keywords: Carbothermal reduction, pig iron, copper slag, thermodynamic analyses

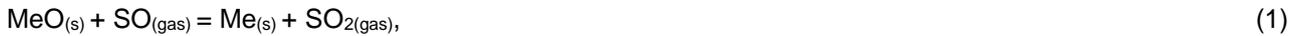
1. INTRODUCTION

Iron oxides are complex heterogeneous, physicochemical processes involving solids, liquids and gases. Changes in a system's thermodynamic and kinetic parameters are interrelated by the simultaneous passage of continuous chemical processes and physical events. The heat and mass transfer methods of reducing reagents and reaction products depend on the kinetics of oxidation dissociation processes, diffusion in gaseous forms, adsorption of gases in complete and incomplete media, external surfaces, etc. The kinetics of the process, temperature, pressure, regenerative composition, and the basic physical structure of the oxide significantly influence its change in the process. It also has a considerable effect on the kinetics of the process, temperature, pressure, chemical composition of the reducing agent, physicochemical state of the oxides, the degree of interaction of the phases, and so on. The structure of a solid surface is determined by the properties and laws of its internal structure, as well as complex and diverse chemical and physical processes and events (adsorption, desorption, formation of new designs, diffusion, etc.) that significantly affect the reaction ability of the oxide surface. More harmful substances are used about oxygen than iron as regenerators [1].

2. OBJECTS AND METHODS OF RESEARCH

As a result of many years of research, it has been determined to provide various mechanisms to explain the laws of solid oxide recovery: bonds, term dissociation, two-stage adsorption-autocatalytic (with SO regeneration), sublimation oxide, gas carbide, unstable gaseous substance recovery scheme, etc. suggested. The most widely used theory of G.I. Chufarova [1] is an oxide recovery scheme's two-stage adsorption-catalytic

method. According to this theory, the interactions between oxides and carbon are carried out by two-stage mechanisms involving the gas phase as follows, and the gasification is regenerated with carbon by reaction [1]:



First stage recovery with raw materials directly links way with a link on the local border oxide, and solid carbon reciprocal as a result of the effect increased a d i. Solid regenerator and oxide between direct link limited. If so, the mutual diffusion coefficient will be small. Reaction firm when, as usual, a thin layer on the surface of the oxide does not form a solid product, the reagents solid diffusion in phases.

Following places restored working gas phase through straightforward way goes with. The central part of the recovery will depend on the gasification kinetics of the carbon, the presence of oxidants, and the process temperature.

the lower When reduced by carbon-containing gases, the carbonisation of raw materials to carbon occurs. The carbon content depends on the temperature and the gas's $\text{CO}_2:\text{CO}$ ratio. When metals are restored, they can form bonds with carbon and form carbides [1].

Temperature, gas composition, pressure, the thickness of the recovered raw material layer, and other factors can alter the course of the diffusion or kinetic process. The change in order causes factors that affect the speed of the process. The development of adsorption-chemical methods of recovery of iron and its oxide compounds in a gaseous environment determines recovery kinetics. It plays a significant role in forming the porosity of the formed sand.

The role of indirect reduction reactions is determined by the temperature and strength of the oxide. More stable oxides, i.e., Cr_2O_3 , TiO_2 , ZrO_2 , etc., are thermodynamically weak monoxides, and in practice, it can be seen that the recovery of the solid phase in the gas phase is high [2].

Despite the analysis of theoretical teachings and practical research results, the thermodynamics and mechanism of the solid phase recovery process have not yet been sufficiently studied. Studies confirm that the tool of the process is that certain oxides travel between different temperatures. There is no single invariant law of the solid phase recovery process. For this reason, the methods of solid-phase recovery of any iron-containing compounds are based on the composition of the raw material being recovered.

The process of recovering iron from oxides proceeds step-by-step according to the Fe-O diagram, not only in oxides but also in the solid solutions. A.A.Baykov's transition from high oxides to low oxides on the principle of a sequence of cycles occurs in the following line: at temperatures above 560°C following $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ and below 560°C , hematite is reduced to ferrous metal $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$.

Based on this principle, several researchers have conducted their research, including [3], in which the properties of hematite recovery at low temperatures were considered. The removal of oxygen from the hematite surface causes an excess of iron ions, which causes the Fe^+ ions to cross the phase separation boundary. Enrichment of the Fe^+ phase section boundary with Fe^+ ions converts the hematite to a magnetite lattice. Simultaneously with the transfer of the border to the crystal, the free hematite surface is also advanced, resulting in the formation of channels. The growth process of the recovery product, which determines the process mechanism, is divided into diffusions within the boundaries of the phase section.

The research results also showed that it was found that the theoretical foundations and the practical foundations of the restoration of iron and its bases in the solid phases are sufficiently different from each other.

The known transition process of $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ in the temperature range of 600 - 620°C in the solid phase recovery of iron-containing sludge formed by the electric furnace process using carbon. Low temperature stability of FeO, the formation of cementite as a result of the reaction $3\text{FeO} + 3\text{C} = \text{Fe}_3\text{C} + 2\text{CO}_2$, and raising the temperature to 900 °C, resulting in the reaction of $\text{Fe}_3 + \text{CO}_2 = 3\text{Fe} + 2\text{CO}$ to obtain carbon monoxide and metallic iron. For this reason, it has been found that the recovery temperatures of different sludge vary.

The progress rate and completion rate of the solid phase recovery process depend on the heating rate of the sample discovered. [4] found that when the heating rate was increased from 2.9 to 9.8°C/min, the starting point of the hematite recovery temperature increased by 10-45 °C, and the recovery temperature of the wustite decreased by 20-60 °C. In this case, it can be determined that a sudden increase in the recovery temperature accelerates the recovery process of viscous iron.

The rate of dissociation of oxides is greatly affected by the reactivity of the regenerator. The recovery capacity of carbon-containing raw materials depends on the composition of the volatiles and ashes, the porous structure and the specific surface area. For this reason, the process of recovering iron-containing raw materials with coke, coal, lignite, graphite, and several other carbon-containing compounds has been studied by various researchers.

In particular, charcoal, with its high porosity and specific surface area, has several times higher recovery capacity than other carbon-containing compounds. It reacts at 650°C. With the onset of the recovery process, the volatile substances are bound, and the recovery phase of the iron-containing compounds begins in a short period. This means that its reactivity is high [5].

Furthermore, in [6], the researchers studied the kinetics of the recovery of iron oxides with Acheson graphite and charcoal as solid-phase regenerators. The experiments were performed in the temperature range of 950°C. Cementite is formed at significantly lower temperatures, and the amount of iron carbides decreases with increasing metal volume. The recovery process continues in the long run until the complete recovery of iron, the formation of which ends with the appearance of α -, γ -iron metal in solid solutions of carbon. $\gamma \rightarrow \alpha$ is formed to form α -iron, which contains up to 0.02 wt% carbon, and the residual carbon forms carbide in the process.

In another [7] study, a solid-phase recovery process using MPG6 carbon as a regenerator was performed, and it can be seen that the recovery of Fe_2O_3 was carried out in 3 stages:



The temperatures to achieve the maximum recovery rate are 780-980 and 1010°C. During the carbon-thermal recovery of magnetite enrichments [8], large amounts of metallized iron were formed only at temperatures above 900°C, with a metallization rate of 950°C reaching 33%. The degree of metallization at 1000°C is 27.4%. At temperatures below 900°C, the metallization rate is 5%. The highest degree of metallization is recorded at a temperature of 550°C. The conversion of iron oxide to magnetite is 11.1% in terms of oxygen.

In general, it was found that the kinetics, mechanism and reaction rate of the solid phase recovery process of iron-containing raw materials vary depending on the composition of the recovery and recovery products.

3. RESULTS AND DISCUSSION

For the study, the loading copper slag was 20 kg, the melting rate was 8 kg/h, and the size of the graph crucible was $\varnothing 60 \times \text{N}63$ in a gas furnace. The gas oven is equipped with a rotating mechanism, and loading and unloading are done manually.

An average sample of copper slag was prepared for the test, the composition of which is given in **Table 1**.

Table 1 Chemical composition of copper slag (wt%)

CuO	ZnO	PbO	Fe ₂ O ₃	S	SiO ₂	Al ₂ O ₃	CaO + MgO	Etx.
1.34	1.04	0.2	42.4	1.3	33.3	5.4	5.0	10.02

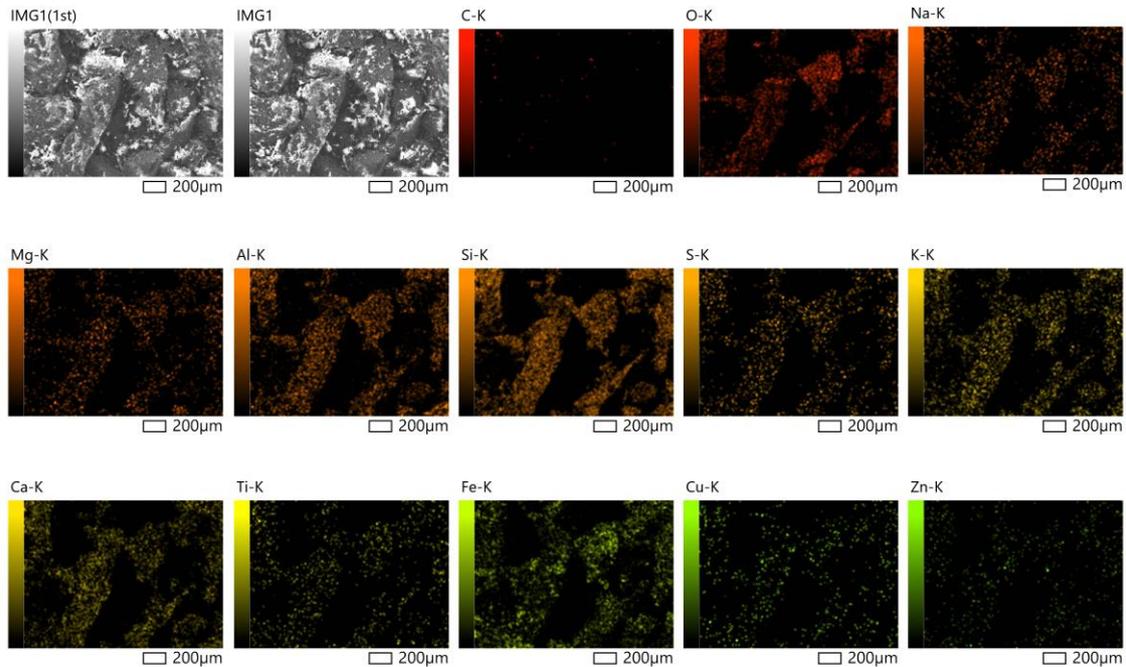


Figure 2 Map energy-dispersive spectroscopy (EDS) analysis of copper slag

The charge loaded on a graphite crucible was placed in a gas furnace. The oven temperature went from 1300-1400 °C.

An increase in the consumption of the regenerator does not lead to the formation of cast iron for the reasons given above but instead to a decrease in the silicon.

The effect of the degree of metallization of iron on the melting temperature was realised in several stages. Melting time was chosen to be 60 minutes. The results are shown in **Figure 2**.

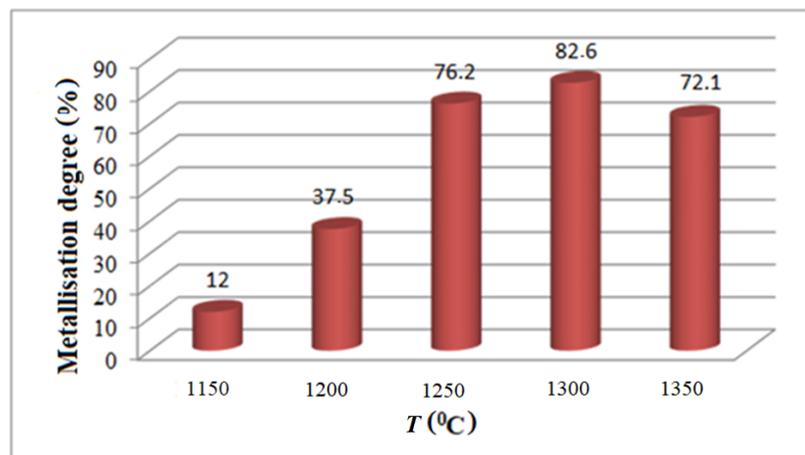


Figure 3 The effect of the degree of metallization of iron on the melting temperature. Melting time - 60 min

From the data in **Figure 3**, it can be seen that the degree of metallization increases with increasing temperature. However, the rate of occurrence of reduction reactions is not high. This fact can be explained by the fact that the newly formed metal can be re-oxidized by iron. It should also be noted that the degree of metallization decreases at temperatures above 1250 - 1300 °C.

At these temperatures, the slag raw materials soften completely, partially melt, and the flow of reduction reactions becomes difficult. These circumstances had to be taken into account in continuing the process.

In the study's second phase, the optimal melting time was determined. The experiments were performed with slag of the same composition, and the retention time at constant temperature (1400 °C) ranged from 5 to 30 min. The results of the study are shown in **Figure 4**.

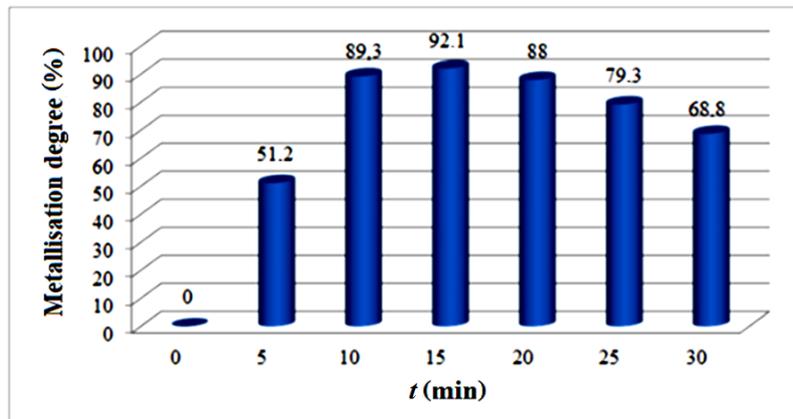


Figure 4 Time dependence of the degree of metallization of iron

As shown in **Figure 4**, an increase in temperature accelerates the melting time. However, performance on the alloy is associated with high-temperature consumption. It is thermodynamically impossible to obtain cast iron by reducing it by 10-15% of iron, so it is necessary to arrange a coke filter when receiving cast iron. Extracting copper from a poor iron alloy is tricky, and its solution is not yet available.

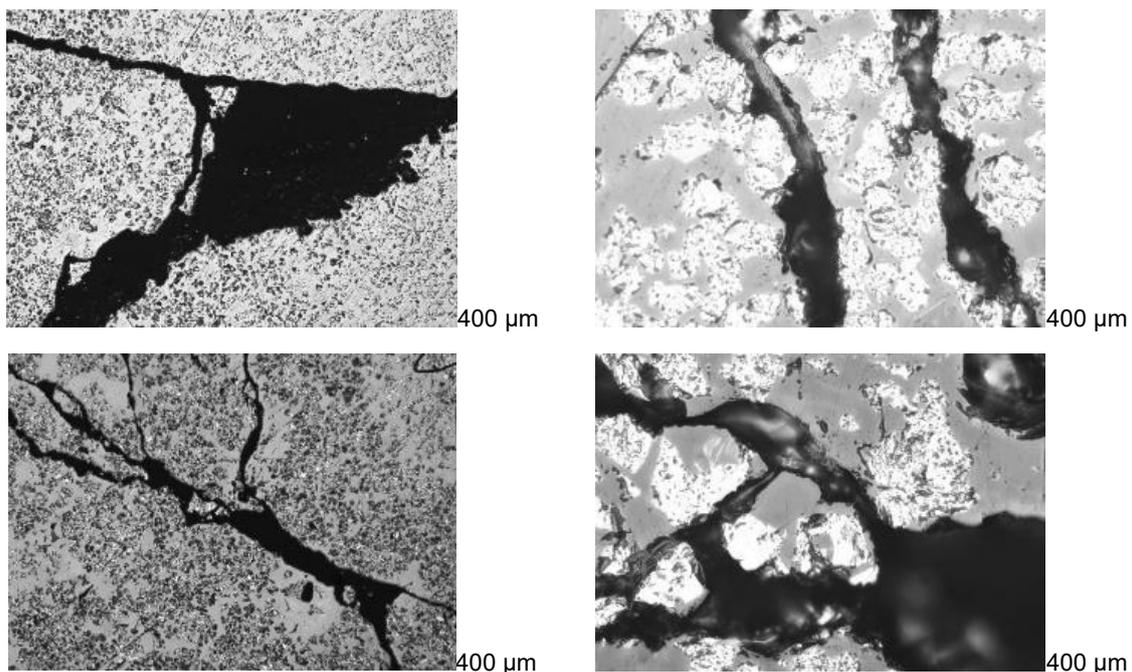


Figure 5 A microscopic view of the alloy formed

Figure 5 shows the appearance of molten slag under a microscope for 1 hour at a temperature of 1300-1400 °C, and the resulting iron-containing alloy and slag can be seen.

The ore-thermal processing of slag was a copper-iron alloy, which depends on the amount of recoverable iron; the copper content varies between 1.4-2.24 wt%. The transition of copper to the alloy was 55.7-75.6 wt%.

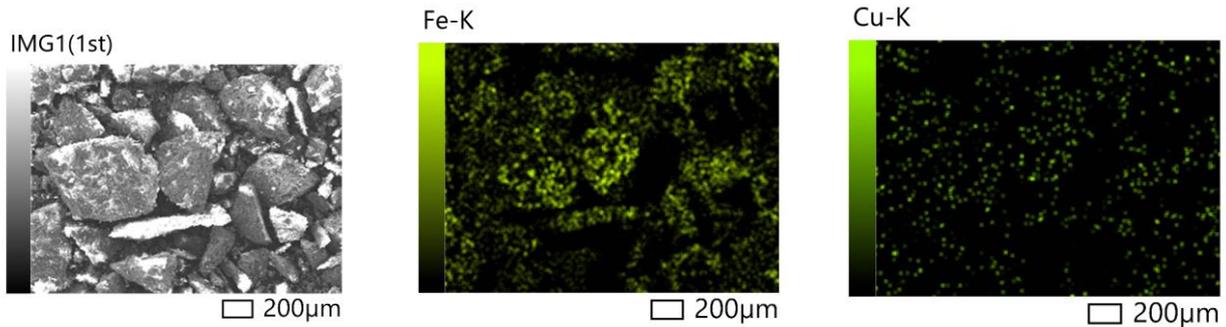


Figure 6 Map EDS analysis of the resulting alloy

The best performance was obtained through a two-step process. In the first stage, the amount of copper in the alloy was increased to 4-10 wt% by reducing the amount of iron by 10-15 wt%. In the second stage, an alloy containing <1 copper was obtained.

When the slag consumption was more than 20% of the initial slag mass, the total recovery of iron was up to 83 wt%, the iron content of the alloy was 84-93 wt%, and the copper alloy was 0.9-1.4 wt%.

4. CONCLUSION

From a thermodynamic point of view, the theoretical basis for the process of obtaining metallised products by reducing metal oxides in copper slag with carbon-containing reducing agents has been developed.

Chemical reactions of metal oxides in copper slags with the participation of carbon and carbon monoxide and the mechanism of these reactions were developed.

The effect of temperature increase on the change in Gibbs energy and equilibrium constant in the chemical reactions of this carbothermic recovery has been studied. Accordingly, all reduction reactions with solid carbon have positive results at 1573 K (or at 1300 °C), i.e. all chemical reactions occur in practice. However, it has been proved that in the process of recovery with is gas, only recovery reactions can take place in the presence of copper lower oxide and fayalite lime.

The values of the results obtained from the thermodynamic analysis of the process of reduction of metal oxides in copper production slags with solid carbon and carbon dioxide and the conclusions drawn from these values were found to be entirely consistent with the experimental results obtained from production practice.

It was concluded that it is possible to obtain metallised raw materials by processing silicate slags of copper production in furnaces smelting with solid carbon at 1573 K (or 1300 °C).

The best performance was obtained by a two-stage process, in which the first stage reduced the iron by 10-15%, and the alloy contained 4-10 wt% copper. Then, in the second stage, the alloy could be obtained with a copper content of <1. The slag consumption in the smelter was more than 20% of the initial slag mass, the total recovery of iron was up to 83 wt%, the iron content of the alloy was 84-93 wt%, and the copper alloy was 0.9-1.4 wt%.

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