PRETREATMENT OF REDUCTIVE DEPHOSPHORIZATION SLAGS GENERATED IN HIGH SILICON FERRONICKEL PRODUCTION

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ABSTRACT

Nowadays, Nickel-containing stainless steel plays more important role due to its good mechanical properties including superior bending strength and hardness. Meanwhile, the phosphorus content of Ni-Fe alloys needs strict requirements when it is treated as the base material of stainless steel. Oxidizing dephosphorization and reductive dephosphorization (RDP) are two methods for dephosphorization of ferroalloys. However, the conventional oxidizing dephosphorization process is not a good choice for dephosphorization of High Silicon Ferronickel because silicon or other valuable metals will be oxidized in priority of phosphorous in the practical production. In this case, RDP has been noticed because of its protection of silicon and valuable metals as well as its excellent dephosphorization effect. Even though, there are still some problems which need to be solved. Like the reaction product of calcium phosphide (Ca_3P_2), is very active and produces the hazardous phosphine gas (PH_3) when it is exposed to the moist atmosphere which will pollute the environment and need to be treated to be environmental friendly. What is more serious, PH_3 is also very dangerous to human being. A small amount of inhalation can cause dizziness, headaches, sickness and vomiting. Severe PH_3 poisoning can cause damage to lungs, heart, liver and kidney, and even cause death. Therefore, it is very important to dispose the reaction product of Ca_3P_2, and suppress the evolution of PH_3. Then the RDP slag can be stacked safely or used as raw material for other products.

In the present study, the authors wish to exploit different kinds of oxidative metallurgical slags to oxidize the RDP slag, in order to make Ca_3P_2 transform into calcium phosphate ($Ca_3(PO_3)_2$) which is innocuous. This work aimed at reviewing studies on the treatment of reductive dephosphorization slags reported by several authors. The results showed that ferromanganese slag which contains MnO could be successfully used to treat Ca_3P_2 innocuously.

KEYWORDS: *Reductive dephosphorization (RDP), Calcium phosphide (Ca_3P_2), Phosphine gas (PH_3), Calcium phosphate($Ca_3(PO_3)_2$).*

1 INTRODUCTION

Phosphorus is a harmful element in stainless steel. It not only increases the segregation, but also has a bad effect on other mechanical properties such as corrosion resistance and welding performance. Therefore, attention has been attracted to the control of phosphorous content in stainless steels.

Nickel-containing stainless steel is of interest due to its good mechanical properties including superior bending strength and hardness [1-3]. Meanwhile, the phosphorus content of ferronickel needs strict requirements when it is used as the charging material of stainless steel. Oxidizing dephosphorization and reductive dephosphorization (RDP) are two methods for dephosphorization of ferroalloys. The concentrations of phosphate and phosphide in slag depend on the partial pressure of phosphorus, the partial pressure of oxygen and temperature [4]. Phosphorus is easy to be dissolved in the slag in the form of P^{3-} under a strongly reducing atmosphere, while the phosphorus is dissolved in the slag in the form of PO_4^{3+} under oxidizing conditions. The change of oxygen potential in the reactor can make the different products of dephosphorization. In general, oxidizing dephosphorization produces $Ca_3(PO_4)_2$ or $Ba_3(PO_4)_2$, while reductive dephosphorization produces Ca_3P_2 (as shown in Figure1).

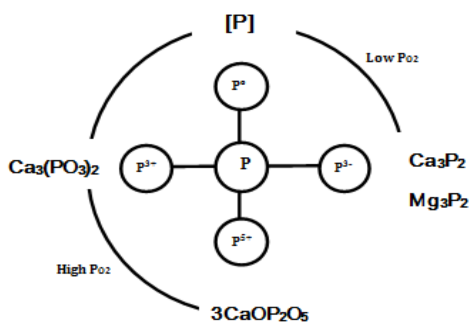

Figure1. Conversion of Phosphorus under different oxygen potential [5]

Under conventional oxidizing conditions, the dephosphorization reaction can be expressed by Eq (1)

$$\tfrac{1}{2}P_2+\tfrac{3}{2}O^{2-}+\tfrac{4}{5}O_2=PO_4^{3-} \quad (1)$$

On the other hand, under strongly reducing conditions phosphorus is expected to behave as phosphide as follows:

$$\tfrac{1}{2}P_2+\tfrac{3}{2}O^{2-}=P^{3-}+\tfrac{3}{4}O_2 \quad (2)$$

However, the conventional oxidizing dephosphorization process is not a good choice for dephosphorization of high silicon ferronickel because silicon or other valuable metals will be oxidized in priority of phosphorous in the practical production. Therefore, dephosphorization should be carried out under a strongly reducing atmosphere to reduce the phosphorus content of ferronickel.

On the line of the above background, RDP has been noticed because of its protection of silicon and valuable metals as well as its excellent dephosphorization effect. However, the reductive dephosphorization slag has a certain content of calcium phosphide (Ca_3P_2), which is the reaction product of reducing dephosphorization. And the calcium phosphide (Ca_3P_2), which is a reaction product of the reducing dephosphorization mechanism, is very active when it is exposed to the moist atmosphere, the hazardous phosphine gas (PH_3) evolves [6],[7]. The reaction of the emission of phosphine gas can be written as follows:

$$Ca_3P_2(s)+3H_2O(g)=3CaO(s)+2PH_3(g) \quad (3)$$

$$Ca_3P_2(s)+3H_2O(g)=3Ca(OH)_2(s)+2PH_3(g) \quad (4)$$

Phosphine is a highly toxic gas which ignites spontaneously in air. It's hazardous to environment as well as to human being [8]. A small amount of inhalation can cause dizziness, headaches, sickness, and vomiting. Severe PH_3 poisoning can cause damage to lungs, heart, liver and kidney, and even cause death. Therefore, it is very important to dispose the reaction product of Ca_3P_2, and suppress the evolution of PH_3. In the meanwhile, the RDP slag can be stacked safely or used as raw material for other products.

This work aimed to review studies on the treatment of reductive dephosphorization slags reported by several authors. The treatment could be classified into two methods: treatment before the separation of slag and melt and treatment after the separation of slag and melt.

2 Overview of treatment of reductive dephosphorization slags

2.1 Conversion of Ca_3P_2 to calcium phosphate by oxygen injection before the separation of slag and melt [9]

Oxygen is blown to the slag before the separation between the slag and the steel. This method is easy and effective. Part of calcium phosphide is translated into phosphorus which can evaporate into the air, and the other is translated into calcium phosphate ($Ca_3(PO_3)_2$). The reaction is given as follows:

$$(Ca_3P_2)+\tfrac{3}{2}O_2(g)=3(CaO)+P_2(g) \quad (5)$$

$$2(P)+\tfrac{5}{2}O_2(g)=P_2O_5 \quad (6)$$

$$3(CaO)+P_2O_5=Ca_3(PO_5)_2 \quad (7)$$

However, the results showed that hot metal rephosphorization occurred with the advance of processing time. To solve this problem, it was suggested that churn of the liquid steel should be reduced to avoid the contact between generated from steel slag and the steel. Furthermore, film formation of CO gas on the steel-slag interface can prevent the contact between reductive dephosphorization of slag and steel. What's more, the partial pressure of phosphorus decreased by reducing the system pressure, phosphorus could easily volatilize.

2.2 Experiments after the separation of slag from hot metal.

2.2.1 Slag was separated from steel after reductive dephosphorization. Then the slag with less phosphorus can be blended with the carbon steel to oxidize calcium phosphide (Ca_3P_2) [9]. And the amount of Ca_3P_2 in the slag decreases rapidly during the oxidation process, while a small quantity of phosphorus gets into steel. Then, the issue of phosphorus of carbon steel can be solved easily by adding oxidizing agents. Therefore, the carbon steel has played an important role to deal with phosphorus-containing slag.

2.2.2 SHIN and PARK [10] tried to confirm the conversion of Ca_3P_2 to calcium phosphate by oxygen injection into the molten RDP slag. RDP slag was melted in the graphite crucible at 1773 K using a high frequency induction furnace with a graphite heater under a purified Ar-3%H_2 atmosphere. After the slag was melted, the power of the furnace was switched off, and then the slag was slowly cooled down. At this time, the gas was switched from Ar–H_2 gas mixture to purify O_2 gas, and then O_2 gas was injected while oxygen lance was kept 5 mm above the bottom of the crucible. The schematic diagram of the experimental apparatus is shown in Figure 2.The experimental results show that oxygen blowing is effective for reducing PH_3 emission from RDP slag.

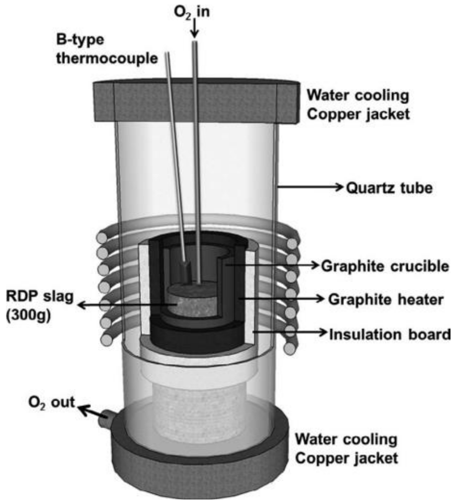

Figure2. Schematic diagram of the experimental apparatus [10]

2.2.3 Takahashi et al. [11] treat RDP slag with the waste nitric acid. For comparison, the experiments were tested with 10% HNO_3 and 10% HNO_3-2% HF. When the acid was added into the RDP slag, there would be a violent exothermic reaction. The amount of PH_3 changed with different solid-liquid ratio after the chemical reactions. The results showed that there was no PH_3 generated when the solid-liquid ratio was 0.2g /cc or less and PH was between 1 to11. But H_2S would be generated in the acidic side (PH<7), while NH_3 was formed in the alkaline side (PH>7). H_2S and NH_3 can be recycled through the purification apparatus. Therefore, the aim of treating RDP slag with industrial waste (hydrofluoric acid, nitric acid, etc.) is achieved.

2.2.4 Oxygen was blown to the surface of the RDP slag to produce protective film with CaO in the slag [12]. So the protective film can separate Ca_3P_2 from water vapour in the air. And RDP slag could also be transformed into raw materials of phosphorus chemical industry. For instance, combustion fabric is made of phosphine, formalin and hydrochloric acid as raw materials in the reaction.

Methods mentioned above provided very useful technological information for making RDP slag harmless. However, most of these studies only are "conceptual" work in literature and few reports can be achieved in practice. Therefore, cost-effective method is to deal with the reductive dephosphorization slag.

Zeng et al. [13] proposed a feasible method in practice to treat the RDP slag. It was proved that Liquid ferromanganese slag which contains MnO could be successfully used to treat Ca_3P_2 innocuously. A typical composition of slag was shown in Table 1.

Table 4: Chemical percentage of a ferromanganese slag

Ingredient	MnO	SiO_2	CaO	MgO	FeO	Al_2O_3	∑
%	10.72	35.61	16.14	2.53	0.82	20.53	86.35

MnO with oxidizing plays an important role. The method helps to recover part of the valuable metal and remove the phosphorus of reductive dephosphorization slag. The final form of phosphate is non-toxic phosphate. The reaction is as follows:

$$\mathrm{Ca_3P_2(s)} + 8\mathrm{MnO(s)} = \mathrm{Ca_3(PO_4)_2(s)} + 8\mathrm{Mn(s)} \quad \Delta G^{\theta} = -958800 + 520.45T \qquad (8)$$

The standard Gibbs free energy of reaction is about -260000 J / mol at 1600K, so it was possible that Ca_3P_2 could react with MnO. The work by Zeng showed that RDP slag without such treatment pulverized easily when it was cooled at ambient temperature, accompanied by the producing stinking smell of PH_3. The P content decreases in the slag decreases from 0.265%to 0.163% in 20 days. After the treatment, the chemical component and physical property of the dephosphorization slag remained the same which met the requirements of the industrial environmental protection and waste disposal.

Waste slag produced during the ferroalloy production is converted into things of value in this method. It's economical since it does not need any external energy and other raw materials. And also, the process does not produce toxic gases such as PH_3. Therefore, this technology is conducive to industrialization.

At the same time, some other waste slags such as ferronickel slag which contains FeO produced in metallurgical processes could also be reused in the treatment of RDP slag innocuously. This is worthy of further study.

3 Summary

1 The conventional oxidizing dephosphorization process is not a good choice for dephosphorization of high silicon ferronickel because silicon or other valuable metals will be oxidized in priority of phosphorous in the practical production. Therefore, reductive dephosphorization has been noticed because of its protection of silicon and valuable metals as well as its excellent dephosphorization effect.

2 The reductive dephosphorization slag contains a lot of calcification such as Ca_3P_2. And Ca_3P_2 is very active when it is exposed to the moist atmosphere, the hazardous phosphine gas (PH_3) evolves. Ferromanganese slag which contains MnO can be successfully used to treat Ca_3P_2 innocuously. Some other oxidative metallurgical slags could also be reused in the treatment of RDP slag innocuously that is very good for the environment.

4 Acknowledgement

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