Experimental Study on Phosphorus Removal from Ferrosilicon Alloys under Electromagnetic Levitation

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Abstract. Along with the growing demand of green energy, the study of solar energy continues to deepen and the production of solar cells is increasing ceaselessly. However, the cost of solar power has become an economic constraint to the large-scale production of solar power equipment. In order to meet the demand of solar power generation, metallurgical grade silicon may be used to replace solar grade silicon to generate electricity. The challenge is that metallurgical grade silicon contains phosphorus impurities. In this paper, electromagnetic levitation is recommended to remove the phosphorus in metallurgical grade silicon. The results show that when the mass of levitated droplets is 0.59-0.64g, the input current is 300-400A, the frequency is 280kHz, and the input power range is 3000-4500W, the removal rate of phosphorus in the ferrosilicon sample is as high as 41%. Therefore, it is feasible to use metallurgical grade silicon to replace solar grade silicon.

1. Introduction
Silicon is the second largest element in the earth's crust. It is an ideal material for solar cells for its optimized properties. As technology requirements increasing, a larger amount of silicon feedstock will be needed to meet the demand. At present, polycrystalline Si with photovoltaic application manufacturing target is produced by improved SIEMENS method. The technology produces 90% of polysilicon production capacity [1], but it still faces some problems such as high energy demand and high cost caused by equipment and energy demand. In recent years, with the increasing demand for green energy and the reduction in the supply of fossil fuels, solar energy research and the production of solar cells are also increasing [2]. However, the cost of solar power is still much higher than that of fossil fuels. Solar grade silicon (SOG-Si), which is used to produce solar cells, accounts for 20% of the manufacturing cost. In order to meet the economic constraints of the large-scale production of solar power generation equipment, it is necessary to explore alternative energy sources which can produce SOG-Si. At present, the raw material for solar cell production comes from the super silicon of the semiconductor industry [2]. Because of the large demand for silicon raw materials to meet the future demand of solar power generation, we must design a cost-effective production line, to be used to produce SOG-Si. One possible way is to upgrade metallurgical grade silicon (MG-Si) by reducing the impurity to the level required by SOG-Si. Johnston et al. [3] described the latest developments in the production of Metallurgical Route SOG-Si in a comprehensive report.
2. Method and Principle

2.1 The principle of electromagnetic levitation
The principle of suspension refining technology is that when a metal sample is placed in an induction coil with high frequency current, the alternating electromagnetic field produces a high frequency eddy on the surface of the conductive metal specimen, and the high frequency eddy will interact with the external magnetic field, causing a Lorentz force in the metal sample. Under suitable space configuration, the direction of electromagnetic force generated will be opposite to gravity. By changing the power of high-frequency power, the electromagnetic force and gravity can be numerically equal, so as to achieve electromagnetic levitation. At the same time, the Joule heat generated by the eddy on the metal can melt the metal body and reach the purpose of melting the metal [4], and then the reaction gas is passed in to make the chemical reaction of the droplet sample and through the gas, to reduce the content of the excess impurities in the sample, and to control the composition of the sample, so as to achieve the purpose of refining. The electromagnetic force (Lorenz force) described by the formula (1) [5] can be suspended by balancing the gravitational force.

\[ J \times B = \rho g \]  

Where, \( J \)—Induced eddy current, \( N \cdot (Kg \cdot m \cdot T) \); \( B \)—Magnetic induction intensity, T; \( \rho \)—Density of suspended droplets, \( \text{kg} \cdot \text{m}^{-3} \); \( g \)—Universal gravitational constant, \( N \cdot \text{m}^2 \cdot \text{Kg}^{-2} \).

Because of resistivity, semiconductor materials at room temperature are much larger than ordinary metals. The resistivity of semiconductor materials will decrease sharply with the increase of temperature. Therefore, the semiconductor material has a preheating link, which needs to be preheated to a certain temperature to achieve suspension. For melting stability, materials with high surface tension and viscosity are easy to maintain stable suspension [6]. The results show that in all shapes, the torque of the spherical droplet specimen is the smallest in the magnetic field of the suspended coil, and the sample is best made in advance, and the spherical droplet has good suspension stability [7] in the approximate axisymmetric magnetic field which is produced by the suspension coil.

2.2 Electromagnetic levitation equipment
The electromagnetic suspension device used in this study is shown in Figure 1. The device is composed of a quartz tube room (15mm O.D., 13mm I.D., 304 mm length), a copper suspension coil, a rotary platform for holding copper mold and an alumina rod. A 1/8 inch diameter copper tube is used to wrap the water-cooled suspension coil. The quartz tube chamber is sealed at the upper end, and the O ring is connected to the optical level fused quartz observation window (2mm thickness) to allow the temperature measurement from the dual color infrared (IR) pyrometer. The lower part of the pipe chamber is inserted into the O ring which seals the rotatable platform. The platform cover is made of polycarbonate and PVC, and the bottom plate is made of aluminum. The platform, which is used for droplet quenching die, as well as for the solid sample into the suspension zone of alumina rod.

Figure 1. Electromagnetic levitation device
2.3 The principle of electromagnetic suspension dephosphorization

Adjusting the input current and frequency to make power in a suitable range, the size and distribution of the magnetic field within the suspended space can meet the suspension conditions of a certain quality of the ferrosilicon alloy. Phosphorus in ferrosilicon alloy will be effectively removed after successful suspension and refining of ferrosilicon alloy. The equation of phosphorus removal by Ar-H$_2$ mixed gas is formula (2) [8].

$$2[P]Fe(wt\%, \ H \text{ dissolve Fe}) = P_2(g) \quad (2)$$

The analysis shows that in the process of suspension refining, the hydrogen in the gas system will melt into the ferrosilicon alloy and react with it to help remove the phosphorus impurities in the sample of the droplet. The dissolved hydrogen is considered to be able to cause phosphorus resistance and evaporation effect in ferrosilicon alloy, so as to achieve the purpose of dephosphorization.

2.4 Experimental design of dephosphorization in suspension refining

The test design and parameters [9] are as follows:

1. The incoming gas is Ar-H$_2$ mixed gas, and the flow rate is controlled at a low speed of 500mL·min$^{-1}$.
2. The mass range of suspended droplet specimen is 0.59-0.64g.
3. According to the quality range of the sample, the input current is 300-400A and the frequency is 280kHz, and the input power range should be 3000-4500W.
4. The suspended droplet specimen is ferrosilicon, where silicon is semiconductor, and it needs to be heated to a certain temperature before it can be suspended. Therefore, a pre-heating is needed. The temperature range of the molten sample is 1355 -1720°C.
5. The selection standard of ferrosilicon alloy is mainly based on the activity coefficient of phosphorus in the alloy. Under controlled phosphorus partial pressure, the addition of iron can effectively improve the dephosphorization level. For achieve a specific component of ferrosilicon, the ferrosilicon’s interaction leads to a decrease in phosphorus content [10]. Therefore, the sample is 15%Fe-85%Si alloy.
6. The suspended time intervals of samples were determined as 6min, 10min, 20min and 40min, to study the relationship between suspension time and dephosphorization effect.

3. Results and Analysis

The dephosphorization effect of the same sample at different time intervals is shown in Figure 2. It can be seen from Fig. 2 that the trend of the three lines is similar, phosphorus content is decreasing along with the increase of time. The dephosphorization effect is very significant in the first 20 minutes, almost removed the phosphorus content by 41%, but after 20 minutes, the phosphorus content could hardly be reduced.

![Figure 2. Dephosphorization effect of sample](image-url)
After the droplet sample was suspended, the small equipment supply current made the sample drop, and the Joule heat decreased rapidly and was affected by Ar cooling during the falling process. When the specimen fell to the crucible at the lower part of the quartz tube, the sample had been solidified and the sample was removed by adjusting the rotating disc to analyze the composition. In order to directly reflect the dephosphorization effect of suspension refining ferrosilicon samples, the data in the map are made in Table 1, as follows:

| Number | Suspension time(min) | Phosphorus content 1(%) | Phosphorus content 2(%) | Phosphorus content 3(%) |
|--------|---------------------|-------------------------|-------------------------|-------------------------|
| 1      | 0                   | 0.0512                  | 0.0205                  | 0.0487                  |
| 2      | 6                   | 0.0426                  | 0.0202                  | 0.0448                  |
| 3      | 10                  | 0.0414                  | 0.0155                  | 0.0385                  |
| 4      | 20                  | 0.0297                  | 0.0148                  | 0.0317                  |
| 5      | 40                  | 0.0296                  | 0.0143                  | 0.0302                  |

4. Conclusion
According to the experimental results, it is feasible to reduce phosphorus in metallurgical grade silicon by electromagnetic levitation. When the mass of the suspended droplet sample is 0.59-0.64g, the input current is 300-400A, the frequency is 280kHz, and the input power range is 3000-4500W, the removal rate of phosphorus is up to 41% in the sample of ferrosilicon.

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