Electrochemical Slag-Metal Reaction for Silicon Production

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Silicon is an important semiconducting and photovoltaic material. It is also widely used for chemical and metallurgical applications. The rapid growth in the demand of solar photovoltaic (PV) cell results in the shortage of solar-grade (SOG) silicon feedstock. Expensive scrap electronic grade (EG) silicon (99.9999999% Si) is commonly used as the raw material to produce SOG-Si (99.9999% Si). Many researchers have reported that relatively inexpensive metallurgical grade (MG) silicon (98-99% Si) can be used as an alternative raw material for refining of MG-silicon to produce SOG-Si.

The slag treatment on MG-Si for SOG-Si production is based on the principle of liquid-liquid extraction in steel industry. The slag used for the extraction of impurities must dissolve individual impurities better than molten silicon does, the solubility of silicon in the slag must be low, and the slag must be nonreactive with molten silicon and must differ markedly from it in density. The impurities with a higher oxygen affinity in comparison with silicon oxidize and pass into the slag. The process is particularly attractive for reducing the B and P content in the production of SOG-Si. In this method, liquid silicon is treated with CaO-SiO_2, CaO-SiO_2-CaF_2, CaO-SiO_2-Al_2O_3, CaO-SiO_2-Al_2O_3-MgO and other molten slags [1-2].

As known from literature [1-2], the partition ratio of boron between CaO-SiO_2 slags and liquid Si is between 2 and 5, what makes it possible to remove boron from silicon using chemical equilibration by slag. The idea is to enhance this process electrochemically, by using the Si-B liquid as an anode. Let us consider a liquid metal / molten slag two-phase system, with at least two components in both phases (they can contain more components): Si-B and SiO_2-B_2O_3. Let us suppose first chemical equilibrium in the system, with an equilibrium partition ratio of boron, L_B^o defined as the ratio of the mole fractions of boron oxide in slag to boron in metal. By applying an anodic potential to the Si-B alloy, ΔE, it can connected to the partition ratios as:

$$\Delta E \cong \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{L_B}{L_B^o}\right) \tag{1}$$

The sign of approximation means that we suppose diluted solutions of B in liquid metal and diluted solution of B_2O_3 in slag, i.e. we suppose the constancy of their activity coefficients, what is only an approximation. R = 8.3145 J/mol.K, F = 96485 C/mol, T in K. From Eq.(1) the requested value can be expressed as:

$$L_B \cong L_B^o \cdot \exp\left(\frac{3 \cdot F \cdot \Delta E}{R \cdot T}\right) \tag{2}$$

The calculated values are shown in figure 1. One can see that the partition ratio increases fast with applied potential.

The experiments were carried out in a vertical tube furnace with four Mo-Si resistance heating elements in this study to check the electrochemical behaviour of slag-metal reaction.

The schematic diagram is shown in figure 2. The top and bottom part of the furnace were designed so that they can suspend a crucible and also allow electrodes to be introduced from the top part of the furnace into the crucibles. Materials chosen for the anode and cathode electrodes required are Tungsten (W) (1.6 mm) and Molybdenum (Mo) (2 mm) respectively. High purity argon gas was used during the experiments. This is to ensure that the atmosphere condition in the furnace has very low moisture and oxygen content during experiment at 1550^0C. Slag of about 12 gm with 8 gm Silicon alloy (Si-B) was placed in an alumina crucible. The crucible was suspended in the furnace using an alumina pedestal from the bottom. The cathode wire was sheathed with alumina tube to avoid the contact with molten silicon. The anode was sheathed with alumina tube to avoid the contact with species (Si vapour or SiO vapour). A multimeter was used to measure the open circuit voltage (OCV) and it was connected with conduction wires. The experimental result is shown in figure 3. The experimental potential value is lower than the FactSage prediction but experimental result shows that slag-metal reaction involves electrochemical means.

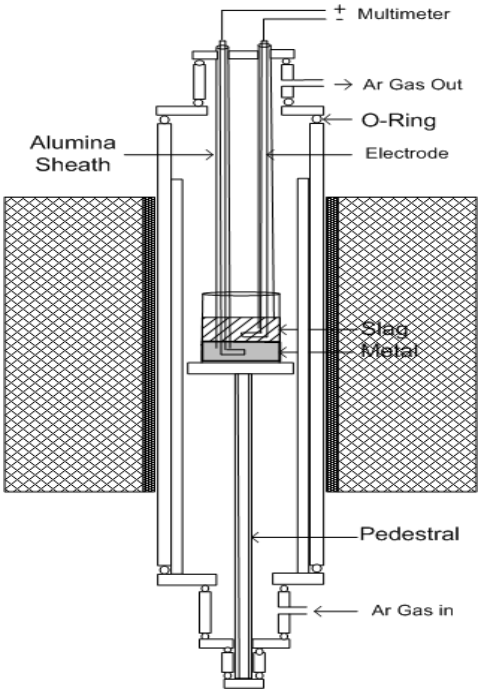

Figure 2: Schematic diagram of experimental setup

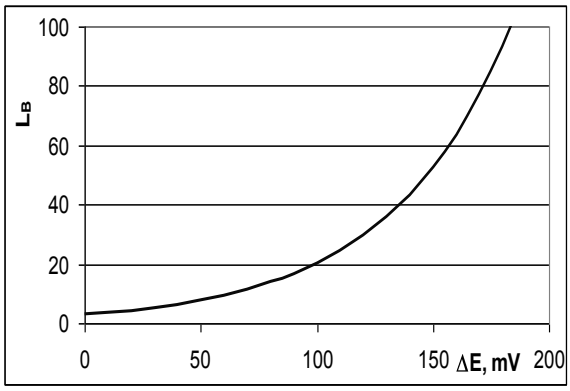

Figure 1: The dependence of the partition ratio of boron on the applied anodic potential calculated by Eq. (2) using $L_B^o = 3$, T = 1823 K.

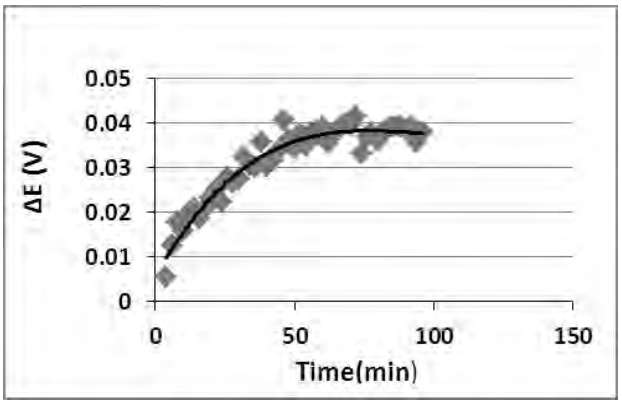

Figure 3: The potential difference (ΔE) between slag and metal with time.

References

1. Teixeira, L. and Y. Tokuda, *Behavior and State of Boron in CaO–SiO_2 Slags during Refining of Solar Grade Silicon.* ISIJ international, 2009. **49**(6): p. 777-782.
2. Johnston, M.D. and M. Barati, *Distribution of impurity elements in slag-silicon equilibria for oxidative refining of metallurgical silicon for solar cell applications.* Solar Energy Materials and Solar Cells, 2010. **94**(12): p. 2085-2090.