

# The Effect of Fluxes to Metallurgical Grade Silicon Impurities Removal

謝昇財、廖芳俊、何文福

E-mail: 364850@mail.dyu.edu.tw

## ABSTRACT

According to the rapid growth of photovoltaic industry, the demand for 6N poly-silicon feedstock has been greatly increased. Even though the chemical refining approach of Siemens process is capable of producing silicon material with 9N purity, this process consumes a huge amount of energy with low production volume and high manufacturing cost. Also, the hazardous wastes generated during the production process will cause severe damage to the environment, thus its future use will be affected. The purpose of this study is to investigate and analyze how the variety and addition quantity of fluxes are going to affect the removal of all kinds of impurities within the metallurgical grade silicon. The fluxes we selected include CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> with high oxygen affinity, Ba(OH)<sub>2</sub> with high capability of removing metal element, and NaHCO<sub>3</sub> which is effectively reducing the viscosity of silicon melt. In this research we plan to use fluxes with single-constitute or multi-fluxes with certain content ratio, such that we can investigate the distribution and variation situations of impurities within solidified silicon ingots by changing the variety and addition quantity of fluxes. The experimental results show that the use of single-constitute fluxes can be effective in the removal of Iron (Fe) and Phosphorous (P) impurities in metallurgical grade silicon powder, expect for Al<sub>2</sub>O<sub>3</sub>, which has a rather insignificant effect in removing P. The addition quantity should not be too much, where the 2 wt.% is optimal. There is no significant effect in removal of Boron (B). As for multi-fluxes, if we take the CaO and SiO<sub>2</sub> with proper ratio and mix with a small dose of NaHCO<sub>3</sub>, it will have significant effectiveness in removal of Fe and P impurities. After the analysis on overall refining results, the suggested choice of multi-fluxes is the mixture of NaHCO<sub>3</sub>, CaO, and SiO<sub>2</sub> with a ratio of 1 : 3 : 6, and an addition quantity of 2~5 wt.% for the best impurity removal results.

Keywords : Metallurgical Grade Silicon、Fluxes、Directional Solidification、Refining

## Table of Contents

第一章 緒論...	1
第二章 文獻回顧...	3
2.1 矽純化簡介...	3
2.1.1 矽資源及提煉...	3
2.2 多晶矽應用領域...	4
2.3 矽純化製程...	4
2.3.1 西門子法...	5
2.3.2 ASiMi法...	6
2.3.3 流體床反應法...	6
2.3.4 管狀沉積法...	6
2.3.5 物理冶金法...	7
2.4 定向凝固...	9
2.5 造渣原理...	10
2.5.1 矽造渣純化...	10
第三章 實驗方法...	18
3.1 實驗材料...	18
3.2 實驗規劃...	18
3.3 實驗步驟與分析流程...	19
3.4 造渣劑的選擇...	20
3.4.1 造渣劑的添加量...	20
3.5 實驗器具與設備...	21
3.5.1 熔煉坩堝...	21
3.5.2 熔煉狀態...	22
3.6 試件取樣分析...	23
3.6.1 取樣消化與分析...	25
3.7 感應耦合電漿放射光譜儀(ICP-OES)...	26
第四章 實驗結果分析與討論...	29
4.1 實驗用粉狀矽料ICP-OES成份分析...	29
4.2 使用氧化鋁坩堝、添加單一造渣劑效果分析...	29
4.2.1 添加氧化鈣(CaO)造渣劑...	30
4.2.2 添加氧化鋁(Al <sub>2</sub> O <sub>3</sub> )造渣劑...	31
4.2.3 添加氫氧化鋇(Ba(OH) <sub>2</sub> )造渣劑...	33
4.2.4 添加二氧化矽(SiO <sub>2</sub> )造渣劑...	35
4.2.5 添加碳酸氫鈉(NaHCO <sub>3</sub> )造渣劑...	36
4.3 進行複合造渣劑添加效果之分析...	38
4.3.1 添加6CaO-4SiO <sub>2</sub> 複合造渣劑...	39
4.3.2 添加3Al <sub>2</sub> O <sub>3</sub> -5SiO <sub>2</sub> 複合造渣劑...	41
4.3.3 添加3CaO-1.5Al <sub>2</sub> O <sub>3</sub> -5SiO <sub>2</sub> 複合造渣劑...	42
4.3.4 添加1NaHCO <sub>3</sub> -3CaO-6SiO <sub>2</sub> 複合造渣劑...	44
4.3.5 添加2Ba(OH) <sub>2</sub> -1Al <sub>2</sub> O <sub>3</sub> -7SiO <sub>2</sub> 複合造渣劑...	46
4.4 單一造渣劑與複合造渣劑之比較...	48
4.4.1 SiO <sub>2</sub> 與6CaO-4SiO <sub>2</sub> 之比較...	48
4.4.2 CaO與6CaO-4SiO <sub>2</sub> 之比較...	50
4.4.3 SiO <sub>2</sub> 與3Al <sub>2</sub> O <sub>3</sub> -5SiO <sub>2</sub> 之比較...	51
4.4.4 Al <sub>2</sub> O <sub>3</sub> 與3Al <sub>2</sub> O <sub>3</sub> -5SiO <sub>2</sub> 之比較...	54
4.4.5 NaHCO <sub>3</sub> 與1NaHCO <sub>3</sub> -3CaO-6SiO <sub>2</sub> 之比較...	55
4.4.6 Ba(OH) <sub>2</sub> 與2Ba(OH) <sub>2</sub> -1Al <sub>2</sub> O <sub>3</sub> -7SiO <sub>2</sub> 之比較...	57
第五章 結論...	60
參考文獻...	62

## REFERENCES

- [1]維基百科, <http://zh.wikipedia.org/zh-tw/>。
- [2]矽石的純化, <http://tw.myblog.yahoo.com/tc-0952562689/article?mid=139>。
- [3]冶金矽與西門子法的製程比較, <http://www.docin.com/p-53088729.html>。
- [4]太陽能級多晶矽製造技術, <http://www.energytrend.com.tw/bbs/thread-1183-1-1.html>。
- [5]黃瑩瑩, 郭輝, 黃建明, 沈樹群, “精煉法提純冶金矽至太陽能級矽的研究發展”, 動能材料, 2007年第9期。
- [6]蘇英源, 郭金國, “冶金學”, 全華科技圖書公司, 2001。
- [7]Ji-Jun Mu etc., “Boron removal from metallurgical grade silicon by oxidizing refining”, Science Direct, 2009.
- [8]王新國, 丁偉中, 沈虹, 張靜江, “金屬矽的氧化精煉”, 中國有色金屬, 2002年第4期。

[9]梁達科, “工業矽精煉的試驗研究”, 輕金屬, 1988年07期。

[10]M.D. Johnston and M. Barati, “Distribution of impurity elements in Slag-silicon equilibria for oxidative refining of metallurgical silicon for solar cell applications”, Solar Energy Materials & Solar Cells 94, pp.2085~2090,2010.