

# The Influence Of Boron And Phosphorus Content By Multi-Fluxes Addition In Metallurgical Grade Silicon

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## ABSTRACT

The focal points of this solar-grade poly-silicon refinement study are following the directions of reduction of cost, pollution, and energy consumption. Therefore, this research adopted the process of oxide fluxes with low cost and low pollution to eliminate the impurities from metallurgical grade silicon. In here, various types of multi-fluxes with different adding quantity were designed. Then, process with vacuum melting and directional solidification, after that silicon ingots were sliced to analyze the content of impurities. Therefore, we can figure out the relations between types, relative ingredient, and adding quantity of multi-fluxes with impurities removal in metallurgical grade silicon. Experimental results shown that the implementation of vacuum melting and directional solidification processes indeed improve the purity of silicon. Although the removal of Boron was not so outstanding, the effectiveness of element elimination, such as Iron and Phosphorus were superior. By cross-examining the results of 9 combinations of multi-fluxes found that silicon dioxide plays an important role in poly-silicon refinement, and adding small amount of calcium oxide and alumina can further facilitate the removal of impurities with their high oxygen affinity nature. We also find that, with little amount of sodium bicarbonate addition, the viscosity of liquefaction silicon can be reduced and improved the fluidity to assist impurities float. Therefore, researcher suggested that the best combination of multi-fluxes to purify the metallurgical grade silicon is  $8\text{SiO}_2\text{-1CaO-1Al}_2\text{O}_3$ , and with 10 wt.% addition. For Iron content can be reduced from 190 ppm. to 7 ppm. with almost 96% removal rate. As for the Phosphorous content, it can be reduced from 9 ppm. to zero, leading to 100% removal rate. Although this flux has shown limited effectiveness in Boron removal, it still reached a removal rate of around 10%.

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

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## REFERENCES

[1] 陳子素, “ 太陽能電池產業製程及污染防治簡介 ”, 財團法人台灣產業服務基金會。

- [2] 維基百科, <http://zh.wikipedia.org/zh-tw/>。
- [3] 香港矽片回收網, <http://www.gdfpw.com/show.asp?id=271>。
- [4] 單晶矽及多晶矽相關知識彙總, <http://www.energytrend.com.tw/bbs/viewthread.php?tid=44>。
- [5] 王旭昇, “太陽能光電產業(二)”, 台灣工業銀行, 2007年。
- [6] 吳雅萍, 張劍, 高學鵬, 李廷舉, “多晶矽的真空感應熔煉與定向凝固研究”, 特種鑄造及有色合金, 2006年第12期。
- [7] 蘇英源, 郭金國, “冶金學”, 全華科技圖書公司, 2001。
- [8] Da-wei LUO, Ning LIU, Yi-ping LU, Guo-liang ZHANG, Ting-ju LI, “Removal of boron from metallurgical grade silicon by electromagnetic induction slag melting”, *Trans. Nonferrous Met. Soc. China* 21, pp.1178-1184, 2011.
- [9] 梁達科, “工業矽精煉的試驗研究”, 輕金屬, 1988年第7期。
- [10] 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。
- [11] 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.