A NOVEL PROCESS TO PRODUCE CHROMIUM FERROALLOYS BY USE OF SOLAR GRADE CRYSTALLINE SILICON CUTTING SLURRY WASTE

P. W. Han[1] P. X. Chen[1] S.J. Chu[1] L. B. Liu[2] R. Chen[2]

[1] School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, 100083, Beijing, China; e-mail: han-ferroalloy@foxmail.com;
[2] Jiangsu Jiayu Resource Utilization Co., Ltd., Lianyungang, 222115, Jiangsu, China;

ABSTRACT

A large amount of slurry waste was produced during the silicon wafer slicing process, which existed in the form of slurry mixed with silicon particles, abrasive silicon carbide (SiC) particles, cutting lubricant and metallic fragments. *The recycle and application of the slurry waste had drawn a lot of attention. The recycle of slicing liquid and SiC were mature enough, and investigations were mainly focused on the effective recycle of high-pure Si from the slurry at present. It is a big challenge to separate Si and SiC completely.* Although many methods had been proposed, most of the procedures were tedious, toxic or difficult to scale up. *A novel process was proposed to produce chromium ferroalloys by use of crystalline silicon cutting slurry waste in present paper. This novel process was based on the electro-silicothermic method, and the silicon and SiC in slurry acted as the reducing agent, which reduced the oxide of chromium and iron in chromium concentrate. Plant trails were carried out and chromium ferroalloys were produced successfully.*

KEYWORDS: *Crystalline silicon cutting slurry waste, recycle, electro-silicothermal method, chromium ferroalloys.*

1. INTRODUCTION

Photovoltaic cells become one of the important and promising sources of clean energy due to the environmental issues generated from the use of fossil fuels. Solar grade crystalline silicon, particularly polycrystalline silicon, is the most widely used material for making solar cells in which solar energy is converted into electrical energy in an environmental friendly way.

Solar grade polycrystalline silicon ingots are sawed into thin wafers with thickness of 180 μm which are used to fabricate solar cells. Wafers are sliced by a loose abrasive multi-wire saw with an abrasive slurry consisted of silicon carbide (SiC) particles in an ethylene glycol-based or glycerol-based solution. The wafer shares 68% of the manufacturing costs [1]. And about 25-50 mass% of silicon ingot is consumed as kerf loss slurry waste during the slicing process in the wafer manufacturing. The kerf loss increases as the wafer thickness decreases [2]. Cutting slurry waste is mainly comprised of silicon particles, abrasive SiC particles, cutting lubricant and metallic fragments worn down from the saw wire. A typical composition of cutting slurry waste is 31.4 mass% ethylene glycol, 28.4 mass% Si, 34.5 mass% SiC and 5.7 mass% metallic fragments [3].

Attention has been attracted to the recycle of cutting slurry waste and the separation of cutting lubricant and larger size SiC has been industrialized [4][5]. The metallic fragments can be removed by the acid treatment, electrokinetic method and superconducting magnetic separation [6][7][8]. However, it is still a great challenge about the recycle of high pure Si and the separation of Si particles and smaller size SiC particles. And various methods have been developed to achieve the aim such as: hydrobromination [9][10][11], supercritical water [12], sedimentation process [4][5], phase transfer separation [4][13][14], alloying process [15], electrical field [2][16][17], centrifugation or heavy-fluid high-gravity centrifugation [3][18][19], froth flotation separation [20][21], filtration [22], ultrasonic waves and centrifugation [23], high temperature treatment [5][18] and directional solidification [18][24], hydrocyclone [25]. Although many methods have been proposed, most of the procedures are tedious, toxic or difficult to scale up [14].

To the best of our knowledge, there is no research about the use of cutting slurry waste as metallurgical furnace charge. In present paper, a novel process is proposed to produce chromium ferroalloys by use of polycrystalline silicon cutting slurry waste. Plant trails were carried out and chromium ferroalloys were produced successfully. The process is based on the electro-silicothermic method, and the Si particles and SiC particles in cutting slurry waste act as the reducing agent, which reduce the oxide of chromium and iron in chromium concentrate.

2. THEORETICAL ANALYSIS

The present process is based on the electro-silicothermic method in which silicon acts as reducing agent and the heat source mainly consists of reaction heat and electric heat. In present process, the most important reactions taking place in electric arc furnace (EAF) are the reductions of the oxides of Cr and Fe.

The main reactions and their standard free energy changes are shown in **Figure 1**. The standard free energy change of reaction is calculated from the standard free energy of formation of resultants and reactants. The data used are from **Reference** [26]. According to **Figure 1**, the reduction of iron oxides is prior to that of chromium oxides. The generated iron is beneficial to the reductions of chromium oxides, since iron can reduce the melting point of melts containing Cr and the activity of Cr.

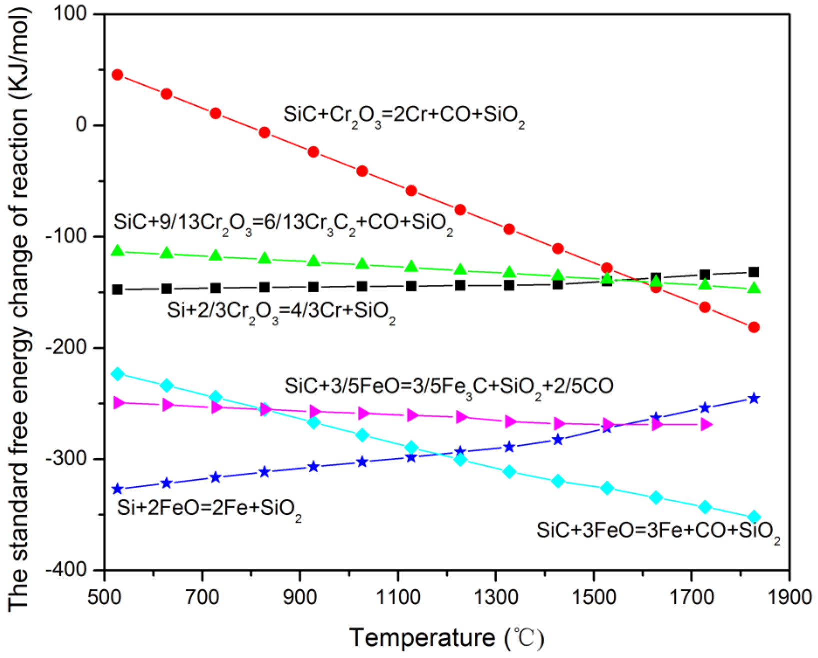

Figure 1: The standard free energy change of reactions between Si/SiC and the oxides of Cr and Fe in EAF

The standard free energy change of reaction between Si and chromic oxide is much less than zero and the reaction is exothermic. The reactions between SiC and the oxides of Cr are endothermic without forming Cr_3C_2, although the standard free energies of reactions are much less than zero. However, when it comes to forming Cr_3C_2, the reaction is exothermic. As shown in **Figure 1**, the reaction between Si and chromic oxide is prior to that between SiC and chromic oxide when the temperature is less than 1557℃. And Cr_3C_2 is preferentially generated rather than Cr by the reaction that SiC and chromic oxide take part in until the temperature reaches 1595℃. Thus, smelting temperature should be higher than 1595℃ to suppress the formation of Cr_3C_2. It should be noted that an increase in temperature is beneficial for the reactions that SiC and chromium oxides participate in with or without forming Cr_3C_2, while the standard free energy change of reactions between Si and chromium oxides increases as the temperature increases.

Considering that the occurrence of chromic oxide in chromium concentrates is chromite ($FeO•Cr_2O_3$) or chrome spinel ($MgO•Cr_2O_3$), both chromite and chrome spinel could be reduced by Si and SiC and their standard free energy changes are similar to that Cr_2O_3 is reduced by Si and SiC, but they are not shown in **Figure 1**.

3. EXPERIMENTAL

The cutting slurry waste was supplied by a company in Jiangsu Province, China. Pretreatments were carried out to recycle part of the larger size SiC particles and cutting lubricant firstly. After pretreatment, the slurry waste contains about 50 mass% Si particles, 20 mass% smaller size SiC particles and a certain amount of cutting lubricant and water. The cutting slurry waste after pretreatment was used as reducing agent in the production of chromium ferroalloys in present process.

Plant trails were carried out in Henan Province, China. The as-received cutting slurry waste was dried before being charged into EAF. The capacity and apparent power of EAF are 3 ton and 2250 KVA ,respectively. The furnace lining is built by carbon bricks. The arcing voltage is 230 V, and then furnace burden was charged mixed with the dried as-received cutting slurry waste, chromium concentrates and lime. Duration time was 45 min for charging. The voltage decreased to 160 V after the melting of burden. The total time for a heat is about 1 h. It needs about 0.8 ton as-received cutting slurry waste, 2.1 ton chromium concentrates and 1.8 ton lime to produce 1 ton of ferrochromium. And its electricity consumption is 2000 KWh per ton.

Particle size distribution of the as-received cutting slurry waste was carried out using static light scattering (LMS-30, Japan) with an aqueous solution containing 0.1 mass% alcohol as a dispersing agent. Phases were analyzed by X-ray diffraction (XRD; M21X, Japan). And particle morphology were observed by scanning electromicroscopy (SEM; CAMBRIDGE S-360, UK) equipped with energy disperse spectroscopy (EDS). The carbon content in the chromium ferroalloys products was determined by carbon/sulfur analyzer (EMIA-820V, Japan). And small pieces of the chromium ferroalloys products were crushed, ground and pressed into a disc suitable for X-ray fluorescence analysis (XRF; XRF-1800, Japan). Thus the compositions of the products were obtained.

4. RESULTS AND DISCUSSION

Particle size distribution of the as-received cutting slurry waste is shown in **Figure 2**. The major peak around 2 μm is ascribed to SiC particles, while the smaller peak is mainly contributed by Si particles. There also exist two peaks in **Reference** [2][4][5][16][17][18][27].

Figure 3 shows XRD patterns of the as-received cutting slurry waste. The sample shows high intensity of Si and weaker intensity of SiC. It should be noted that the metallic impurities are not obvious in the XRD patterns.

SEM image of the as-received cutting slurry waste is shown in **Figure 4**. The sizes of particles are larger than the results of particle size distribution showed in **Figure 2**. The discrepancy might be caused under such situation that the sample was dried at 373 K in air atmosphere in a drying oven for 1 hour before being observed by SEM. EDS analyses show that particles are comprised of Si, O, C and Fe elements. It implied that particles were partly contaminated during the drying process. It is suggested that the cutting slurry waste should be dried in inert atmosphere instead of in air atmosphere before being charged.

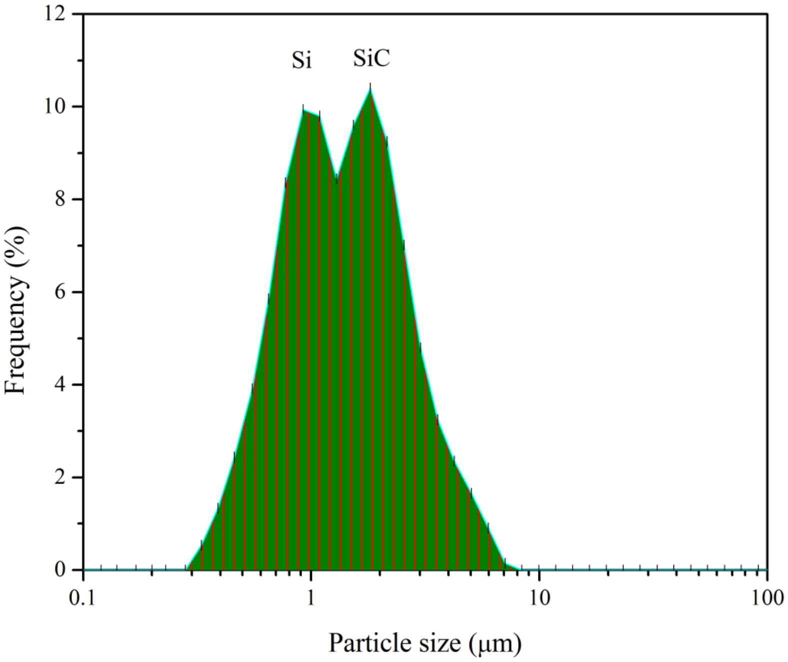

Figure 2: Particle size distribution of the as-received cutting slurry waste

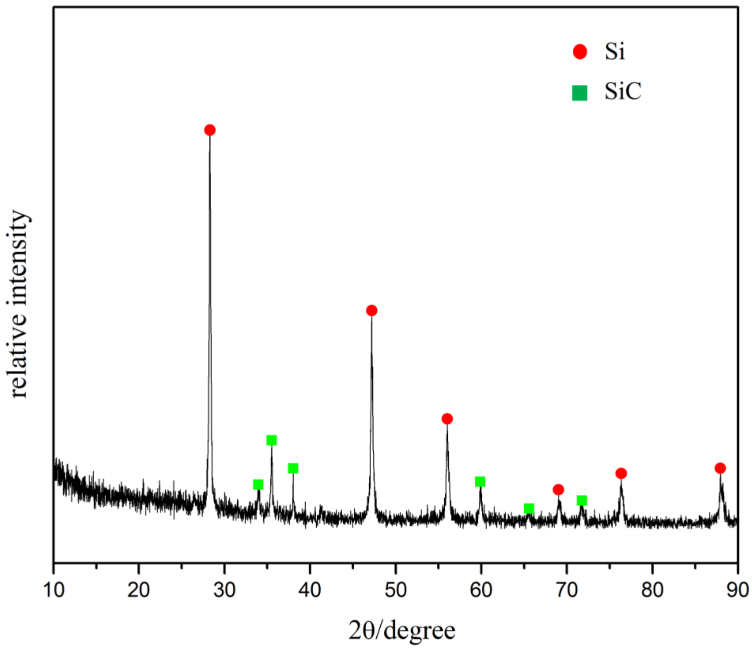

Figure 3: XRD pattern of the as-received cutting slurry waste

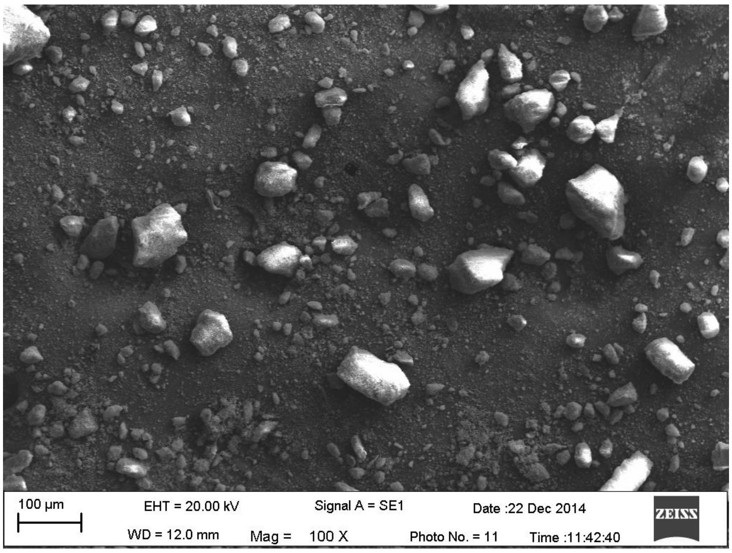

Figure 4: SEM image of the as-received cutting slurry waste

The products of chromium ferroalloys are shown in **Figure 5(b)** and **Figure 5(c)**. The as-received cutting slurry waste is also shown in **Figure 5(a)**. The compositions of chromium ferroalloys products by present process are shown in **Table 1**. Products of Heat 1114-01 and 1114-02 are high carbon ferrochromium (HCFeCr) and it is Silicochromium ferroalloy (FeCrSi) for Heat 1115. Comparison with standards is shown in **Table 2**, the carbon and silicon contents of product of Heat 1114-01 are within the range of the standard grade FeCr-C50Si7LP, while the chromium content is slightly less than the lower limit of FeCr-C50Si7LP. Similar situation occurs between the product of Heat 1114-02 and the standard grade FeCr-C70Si6LP. Although the compositions of products are close to some standard chromium ferroalloy grade, there are problems that the carbon and silicon contents of HCFeCr products are somewhat high.

Considering an extreme case that the carbon in the as-received cutting slurry waste remained completely in the product, it would be 4.8 mass% for the carbon content in products. The value was less than the actual carbon contents in HCFeCr products. It meant that carbon lining was eroded. It was suggested that the carbon content could be reduced by replacing the carbon lining with basic lining. Keeping smelting temperature higher than 1595℃ could suppress the formation of Cr_3C_2 and be helpful to reduce the carbon content. The silicon content in HCFeCr products could also be reduced by increasing the amounts of chromium concentrates and lime. However, it leaded to an increase in slag bulk and Cr_2O_3 content in slag and a decrease in the yield of Cr element by increasing the amount of chromium concentrates. And it resulted in an increase in slag basicity and slag bulk by increasing the amount of lime.

Figure 5: Photograph of (a) the as-received cutting slurry waste, (b) product of Heat 1114-01, (c) product of Heat 1114-02

Table 1: Sample compositions of the chromium ferroalloy products

Heat No.	Grade	Chemical composition / mass% Cr	C	Si	P	Ti
1114-01	HCFeCr	43.43	5.68	6.35	0.020	0.37
1114-02	HCFeCr	42.97	7.62	7.68	0.020	0.41
1115	FeCrSi	28.29	0.80	28.61	0.019	0.20

Table 2: Standards for chromium ferroalloys [28]

Grade	Standard	Chemical composition / mass% Cr	C	Si	P
FeCr-C50Si7LP	ISO 5448-81	45.0-75.5	4.0-6.0	5.0-10.0	≤0.03
FeCr-C70Si6LP	ISO 5448-81	45.0-75.5	6.0-8.0	5.0-8.0	≤0.03
FeCrSi33	ISO 5449-80	≥43.0	≤1.0	28.0-38.0	≤0.05

HCFeCr is usually produced by carbothermic process in submerged arc furnace (SAF). About 0.5 ton of coke, 2.4 ton of chromium concentrates and 0.1 ton of silica is needed to produce 1 ton of HCFeCr, with energy consumption of 3000-3400 KWh [28]. The price of chromium concentrates, coke, silica, as-received cutting slurry waste, lime and electricity are 200 $/t, 160 $/t, 29 $/t, 128 $/t, 48 $/t and 0.08 $/KWh, respectively. Thus, unit costs of HCFeCr produced by different processes are obtained and shown in **Table 3.** Taking no account of the agglomeration cost, the unit cost of HCFeCr produced by present process is about 768.8 $, which represents the reduction by about 34.1-66.1 $ in comparison with that in carbothermic process. There might be more profits for the HCFeCr produced by present process considering the low phosphorous content.

Table 3: Unit cost comparison between carbothermic process and present process

Item	Carbonthermic process Consumption	Cost / $	Present process Consumption	Cost / $
Reductant	Coke: 0.5 ton	80	Cutting slurry waste: 0.8 ton	102.4
Chromium concentrates	2.4 ton	480.0	2.1 ton	420.0
Fluxes	Silica: 0.1 ton	2.9	Lime: 1.8 ton	86.4
Energy consumption	3000-3400 KWh	240-272	2000 KWh	160.0
Total cost	--	802.9-834.9	--	768.8

5. CONCLUSIONS

Plant trails were carried out to produce chromium ferroalloys by use of polycrystalline silicon cutting slurry waste. The present process was based on the electro-silicothermic method. Chromium ferroalloys were successfully produced in EAF. It needed about 0.8 ton of as-received cutting slurry waste, 2.1 ton of chromium concentrates and 1.8 ton of lime to produce 1 ton of ferrochromium with electricity consumption of 2000 KWh. The total time for heating was about 1 h. The specific conclusions from the present study were:

(1) The as-received cutting slurry waste should be dried in inert atmosphere instead of in the air atmosphere to avoid being oxidized before being charged.

(2) The HCFeCr products had low phosphorous content and could be classified into the low phosphorous grade. However, the carbon and silicon contents of HCFeCr products were somewhat high, which could be reduced by replacing the carbon lining with basic lining and increasing the amounts of chromium concentrates and lime, respectively.

(3) Without regard to the agglomeration cost, the unit cost of HCFeCr produced by present process reduced by about 34.1-66.1 $ in comparison with that in carbothermic process. There might be more profits for the HCFeCr produced by present process considering the low phosphorous content.

6. REFERENCES

[1] Na, W., Lee, J., A development of recycling technology of solar cell wafering slurry. The Journal of Korea Navigation Institute, 14(2010)3, pp.426-431.

[2] Tsai, T., Modified sedimentation system for improving separation of silicon and silicon carbide in recycling of sawing waste. Separation and Purification Technology, 78(2011)1, pp.16-20.

[3] Lin, Y., Wang, T., Lan, C., et al., Recovery of silicon powder from kerf loss slurry by centrifugation. Powder Technology, 200(2010)3, pp.216-223.

[4] Xing, P., Guo, J., Zhuang, Y., et al., Rapid recovery of polycrystalline silicon from kerf loss slurry using double-layer organic solvent sedimentation method. International Journal of Minerals, Metallurgy and Materials, 20(2013)10, pp.947-952.

[5] Li, D., Xing, P., Zhuang, Y., et al. Recovery of high purity silicon from SoG crystalline silicon cutting slurry waste. Transactions of Nonferrous Metals Society of China, 24(2014) 4, pp.1237-1241.

[6] Tsai, T., Huang J., Metal removal from silicon sawing waste using the electrokinetic method. Journal of the Taiwan Institute of Chemical Engineers, 40(2009)1, pp.1-5.

[7] Tsai, T., Pretreatment of recycling wiresaw slurries-iron removal using acid treatment and electrokinetic separation. Separation and Purification Technology, 68(2009)1, pp.24-29.

[8] Nishijima, S., Izumi, Y., Takeda, S., et al., Recycling of abrasives from wasted slurry by superconducting magnetic separation. IEEE Transactions on Applied Superconductivity, 13(2003)2, pp.1596-1599.

[9] Tomono, K., Okamura, Y., Furuya, H., et al. Selective hydrobromination of metallurgical-grade silicon in a flow reactor system. Journal of Materials Science, 47(2012) 7, pp.3227-3232.

[10] Tomono, K., Miyamoto, S., Ogawa, T., et al., Recycling of kerf loss silicon derived from diamond-wire saw cutting process by chemical approach. Separation and Purification Technology, 120 (2013), pp.304-309.

[11] Tomono, K., Furuya, H., Miyamoto, S., et al., Investigations on hydrobromination of silicon in the presence of silicon carbide abrasives as a purification route of kerf loss waste. Separation and Purification Technology, 103(2013), pp.109-113.

[12] Yoko, A., Oshima, Y., Recovery of silicon from silicon sludge using supercritical water. The Journal of Supercritical Fluids, 75 (2013), pp.1-5.

[13] Lin, Y., Tai, C, Recovery of silicon powder from kerfs loss slurry using phase-transfer separation method. Separation and Purification Technology, 74(2010)2, pp.170-177.

[14] Hsu, H., Huang, W., Yang, C., et al., Silicon recovery from cutting slurry by phase transfer separation. Separation and Purification Technology, 133(2014), pp.1-7.

[15] Wang, H., Tan, Y., Li, J., et al., Removal of silicon carbide from kerf loss slurry by Al-Si alloying process. Separation and Purification Technology, 89(2012), pp.91-93.

[16] Wu, Y., Chen, Y., Separation of silicon and silicon carbide using an electrical field. Separation and Purification Technology, 68(2009)1, pp.70-74.

[17] Tsai, T., Silicon sawing waste treatment by electrophoresis and gravitational settling. Journal of Hazardous Materials, 189(2011)1-2, pp.526-530.

[18] Wang, T., Lin, Y., Tai, C., et al., A novel approach for recycling of kerf loss silicon from slurry waste for solar cell application. Journal of Crystal Growth, 310(2008)15, pp.3403-3406.

[19] Wang, T., Lin, Y., Tai, C., et al., Recovery of silicon from kerf slurry waste for photovoltaic applications. Progress in Photovoltaics: Research and Applications, 17(2009)3, pp.155-163.

[20] Shibata, J., Murayama, N., Nagae, K., Flotation separation of SiC from wastes in the silicon wafer slicing process. Kagaku Kogaku Ronbunshu, 32(2006)1, pp.93-98.

[21] Wang, Y., Jiang, C., Liang, H., Recovery and separation of Si and SiC in wire cutting waste slurry from photovoltaic silicon. Key Engineering Materials, 512-515(2012), pp.1541-1544.

[22] Zhang, L., Ciftja, A., Recycling of solar cell silicon scraps through filtration, part I; experimental investigation. Solar Energy Materials and Solar Cells, 92(2008) 11, pp.1450-1461.

[23] Jang, H., Kim, H., Kil, D., et al. A novel recovery of silicon nanoparticles from a waste silicon sludge. Journal of Nanoscience and Nanotechnology, 13(2013)3, pp.2334-2338.

[24] Mühlbauer, A., Diers, V., Walther, A., et al., Removal of C/SiC from liquid silicon by directional solidification. Journal of Crystal Growth, 08(1991)1-2, pp.41-52.

[25] Sergiienko, S., Pogorelov, B., Daniliuk, V., Silicon and silicon carbide powders recycling technology from wire-saw cutting waste in slicing process of silicon ingots. Separation and Purification Technology, 133(2014), pp.16-

21.
[26] Barin, I., Thermochemical data of pure substances, 3rd Edition. Wiley-VCH Verlag Gmbh, Weinheim, Germany, 1995.
[27] Tsai, T., Shih, Y., Recovering low-turbidity cutting liquid from silicon slurry waste. Journal of Hazardous Materials, 271(2014), pp.252-257.
[28] Zhao, N., Zhang, Q., Practical technology manual of ferroalloys production. Metallurgical Industry Press, Beijing, China, 1998.