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Titanium Removal from Metallurgical-Grade Silicon Melts Using High-Basicity Index Slag and Carbon Dioxide Injection

Xiao Long [1,*], Wenbo Luo [1,*], Jun Lv [2], Falou Chen [3], Xiang Li [1] and Shaolei Long [1]

[1] School of Materials and Energy Engineering, Guizhou Institute of Technology, Guiyang 550003, China; lixiang8656@163.com (X.L.); 20180875@git.edu.cn (S.L.)
[2] Mangshi Yonglong Ferroalloy Co., Ltd., Mangshi 678400, China; lvjun@wynca.com
[3] Yunnan Longling County Longshan Silicon Co., Ltd., Baoshan 678300, China; darlingylg@163.com
* Correspondence: xiaolong@git.edu.cn (X.L.); lwbcsu2021@163.com (W.L.)

Abstract: In this study, novel slags with a high basicity index were used to refine silicon melts with carbon dioxide injection to effectively remove Ti from metallurgical-grade silicon. Different compositions of the initial slag were used, and silicon samples were obtained during the refining. The results indicate that the Ti-removal rate initially increased with an increase in the basicity index, and it decreased after the basicity index exceeded 1.4. During the refining, silicon emulsification was observed at the slag–silicon interface, which was restricted by the increased basicity index of slags. Impurities that were concentrated in silicon droplets near the slag–silicon interfaces were oxidized, wetted by slags, and transferred to the slag phase. After 15 min of refining, up to 59 wt% of Ti in silicon could be removed and the Ti-concentrating phase in the slag contained 2.05 wt% of Ti. The results of this study provide a reference for low-cost Ti removal from metallurgical-grade silicon using a refining method.

Keywords: high-basicity index slag; metallurgical-grade silicon; refining; Ti removal; carbon dioxide

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1. Introduction

Metallurgical-grade silicon is a significant raw material for organosilicone and new energy industries [1–3]. It is usually produced by the reduction in silica ore using carbonaceous materials in submerged arc furnaces. During the manufacturing process, impurity oxides in the raw materials (such as Al, Ca, Ti, Fe, P, and B) can be reduced and transferred into silicon melts. As a result, ladle refining is usually required after tapping to remove parts of the impurity elements in silicon melts.

Currently, oxygen bottom-blowing is a widely applied method in silicon ladle refining, which has proven to remove Al and Ca impurity oxides effectively in industrial practices [4–6]. In fact, during the refining process, Si, Al, and Ca are oxidized in the silicon melts and transferred to form slag phases. Industrial experience in oxygen bottom-blowing shows that elements with a much higher affinity for oxygen, compared with silicon, can be removed effectively. Thus, Ti or Fe, which exhibit an approximately equal or weaker affinity for oxygen cannot be removed using this general ladle refining [7]. Therefore, high-purity raw materials, directional solidification, acid leaching, liquation refining (using alloys to absorb impurities), and external fields are usually adopted to control the content of Fe, Ti and other impurity elements in the final products [8–17].

Ti is a significant impurity in metallurgical-grade silicon which strongly affects organosilicone manufacturing and the economic value of products [18]. However, using low-Ti silica ore, directional solidification, acid leaching, and liquation refining can remove most of the Ti in metallurgical-grade silicon, which can decrease its efficiency and dramatically increase its cost. It follows that a novel, affordable, and highly efficient refining method is strongly required to remove Ti from metallurgical-grade silicon in the enormous reserve of high-Ti silica ore in Yunnan Province, China.

In this study, novel synthetic slags with high basicity indices (BIs) and low liquidus temperatures were used to refine metallurgical-grade silicon. As metallurgical-grade silicon manufacturing releases an enormous amount of carbon dioxide, it was adopted as the oxidizing agent to explore the possibility of its use in silicon refining, with the aim of decreasing carbon dioxide emissions. Related refining experiments were conducted in the laboratory and the Ti removal process is discussed in this paper.

2. Materials and Methods

2.1. Materials and Experimental Process

The contents of typical impurity elements in the silicon sample for the experiments are listed in Table 1. The impurity elements were measured using an ICP-MS, PerkinElmer NexION 2000. The compositions and basic physical properties of the refining slags with different BIs are listed in Table 2. The calculation method for the BI is given by Equation (1) [19]. The liquidus temperatures of the slags are approximately equal to the break temperature (T_{br}) (i.e., the temperature below which the viscosity increases sharply upon cooling (at 6 K/min)), indicating the precipitation of crystals in liquids. The viscosity upon cooling was measured using a high-temperature rotational viscosimeter (graphite bobs with a diameter of 15 mm and a graphite crucible with an inner diameter of 60 mm).

$$BI = \frac{1.53(CaO + BaO) + 1.51MgO + 1.94Na_2O + 3.55Li_2O + 1.53CaF_2}{1.48SiO_2 + 0.1Al_2O_3} \tag{1}$$

Table 1. Contents of impurity elements in metallurgical-grade silicon for experiments, wt%.

Fe	Al	Ca	Ti	P
0.531	0.462	0.073	0.058	0.006

Table 2. Composition and basic physical properties of initial slags, wt%.

No.	BI	Viscosity$_{1673k}$, Pa.s	T_{br}, K	CaO	SiO_2	CaF_2	Al_2O_3	MgO	$Na_2O + BaO + Li_2O$	C_{free}
1	1.2	0.428	1527	15	46	8	5	6.5	17.5	2
2	1.3	0.397	1512	15	44	8	5	6.5	19.5	2
3	1.4	0.314	1488	15	42	8	5	6.5	21.5	2
4	1.5	0.195	1481	15	40	8	5	6.5	23.5	2

The slag samples were prepared using analytical reagents ($CaCO_3$, SiO_2, Na_2CO_3, Li_2CO_3, $BaCO_3$, MgO, Al_2O_3, and CaF_2) and high-purity graphite powder (free C). The samples were pre-melted in graphite crucibles in a resistance furnace (except for graphite powder), cooled in air, and then ground with graphite powder. For each experiment, 200 g of metallurgical-grade silicon lump and 20 g of slag powder were loaded into a high-purity magnesia crucible with an inner diameter of 40 mm and melted in a vertical tube furnace using $MoSi_2$ heating elements at a holding temperature of 1773 K. A high-purity quartz tube (inner diameter of 3 mm and external diameter of 5 mm) was inserted into the liquid silicon for carbon dioxide injection (0.1 L/min). Slag and silicon samples were obtained during refining using another quartz tube at 5, 10, and 15 min of carbon dioxide injection (approximately 5 g for each silicon sample and 1 g for each slag sample). The quartz tube that was used for the carbon dioxide injection did not melt, and only devitrification and fragmentation were observed with an immersion time of less than 15 min. After 15 min of refining, the crucible was cooled, and its content was maintained in the furnace at 1773 K for 5 min.

2.2. Measurements

ICP-MS (PerkinElmer NexION 2000) was used to measure the impurity elements in the silicon samples. Scanning electron microscopy (SEM, FEI Nova Nanosem 450) and energy dispersive spectroscopy (EDS) were used to inspect the slag features, especially the structure and composition at the slag–silicon interfaces. Samples for SEM were prepared by mounting slag and silicon in resin, polishing with an alumina suspension, and sputter-coating with gold. X-ray diffraction was used to detect possible Ti-bearing crystals in the final slags. The yield of silicon was calculated using the weight loss of the silicon after refining the weight of the silicon samples that were obtained during refining was also counted).

3. Results and Discussion

3.1. Effect of Basicity Index of Slags on Ti-Removal Efficiency

The measured Ti content of the silicon samples that were obtained at different refining times is illustrated in Figure 1. The results indicate that after 15 min of refining, the highest Ti-removal rate was 59% when using slag with a BI of 1.4, and the Ti content decreased from 0.0580 wt% to 0.0238 wt%.

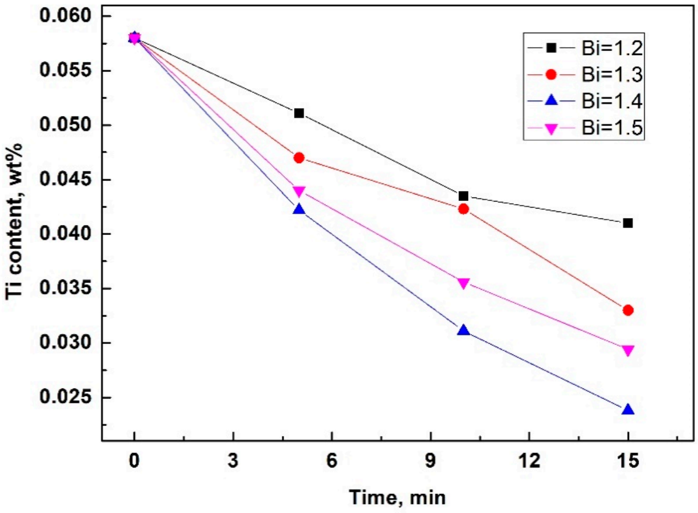

Figure 1. Ti contents of metallurgical-grade silicon during refining (using slags with different basicity indices).

In this study, with an increase in BI the removal rate of Ti first increased and then decreased after the BI exceeded 1.4. This phenomenon occurs because the increased BI lowers the viscosity and liquidus temperature of the slags to provide better dynamic conditions for impurity dissolution in the slags and in Ti removal. However, slags with an excessively low viscosity could affect the emulsification behavior of the slag–silicon system, which may restrict the interfacial reaction and lower the efficiency of the Ti-removal process. Figure 2 and Table 3 show the typical size distribution of silicon droplets in the slag at the slag–silicon interface (samples were obtained and quenched after 5 min of refining, SEM inspection area 1 mm × 1 mm). The results indicate that the BI of slags can affect the emulsification behavior of the slag–silicon system in this study, i.e., emulsification can be restricted by increasing the BI. Fine droplets of silicon at the slag–silicon interfaces decreased with an increased slag BI, which reduced the slag–silicon interfacial area and restricted the transfer of impurities to the slag. A further investigation of this process is still required.

Thus, as far as we know, the Ti-removal efficiency was controlled by at least two slag properties that can affect dynamic conditions: viscosity and emulsification feature. The opposite effect of the BI on those properties was the main reason why an increase in BI caused the removal rate of Ti to first increase before decreasing after the BI exceeded 1.4.

Although the emulsification of silicon was observed in the quenched samples that were obtained during refining, no obvious emulsification was detected in the final crucibles (holding temperature for 5 min after refining and then cooling in the furnace). Figure 3 shows a typical silicon lump and the slag layer in contact with the silicon that was cooled in the furnace, demonstrating good separation capability. The calculated yields are shown in Figure 4. With an increase in the BI, the yield of silicon gradually decreased, and no significant change in the yield was observed after the BI of the slag exceeded 1.4.

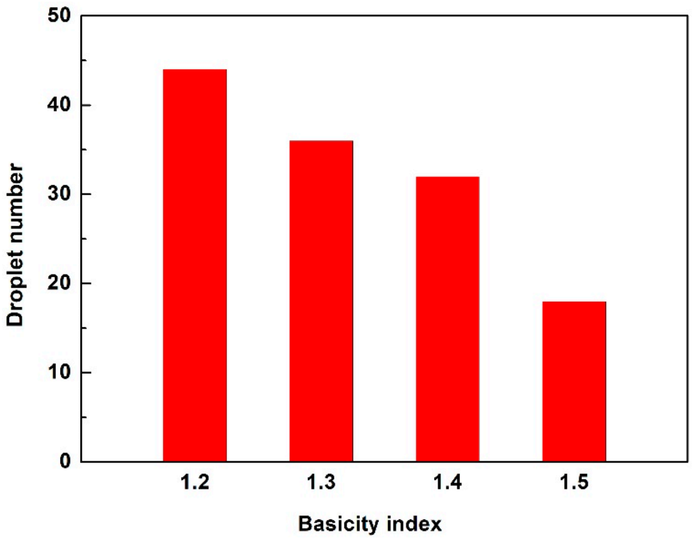

Figure 2. Effect of slag basicity index on the overall number of silicon droplets at the silicon–slag interface (inspection area: 1 mm × 1 mm).

Table 3. Statistics of silicon droplets with different sizes (in a 1 mm × 1 mm area).

Basicity Index of Slag	1.2	1.3	1.4	1.5
Overall quantity	44	36	32	18
Diameter < 10 μm	30	23	20	4
10 μm < diameter < 100 μm	13	12	10	11
Diameter > 100 μm	1	1	2	3

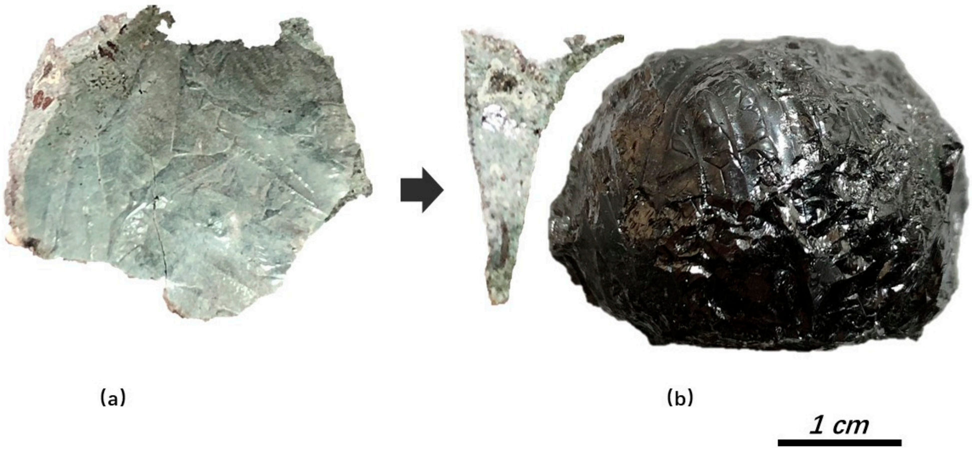

Figure 3. Solidified surface of slag that contacted with silicon (**a**) and cross-section of solidified slag and the contacted silicon lump (**b**).

3.2. Existence of Ti in Refining Slag

As the average content of Ti in the final slags was relatively low, which may not precipitate as individual crystals, no Ti-bearing crystals were found in the slags using X-ray diffraction measurements. EDS (area scan) was used to detect the Ti-bearing phase in the final slags, and the typical results are shown in Figure 5 and Table 4. The results showed that Ti had been transferred into the slags, and the Ti-bearing phase contained approximately 2.05 wt% Ti. Under the conditions in this study, the main Ti-bearing phase also contained CaO, SiO_2, MgO, Al_2O_3, Na_2O, and C. In this study, the point analysis of SEM-EDS indicated that the Ti-bearing phase was in an amorphous state that was dispersed in solidified slags; no obvious crystal particles were observed in this phase. Titanium dioxide is an amphoteric oxide that acts as a network former in basic slags, which can promote glass formation in slags.

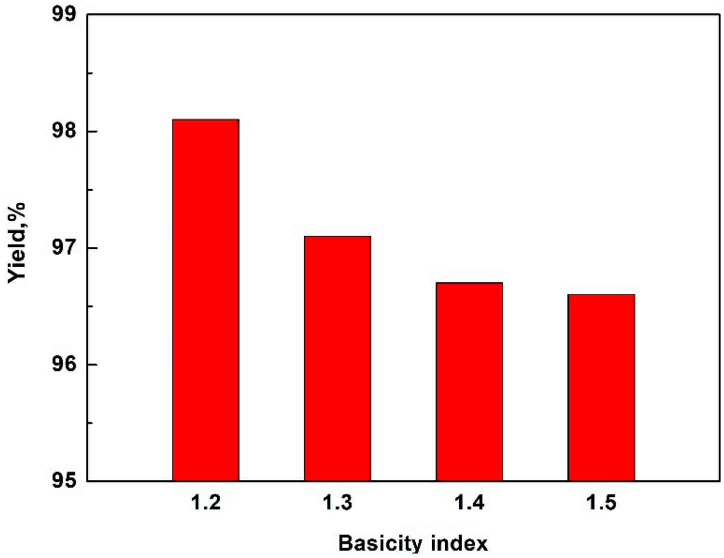

Figure 4. Effect of basicity index of slags on the yield of silicon after 15 min of refining.

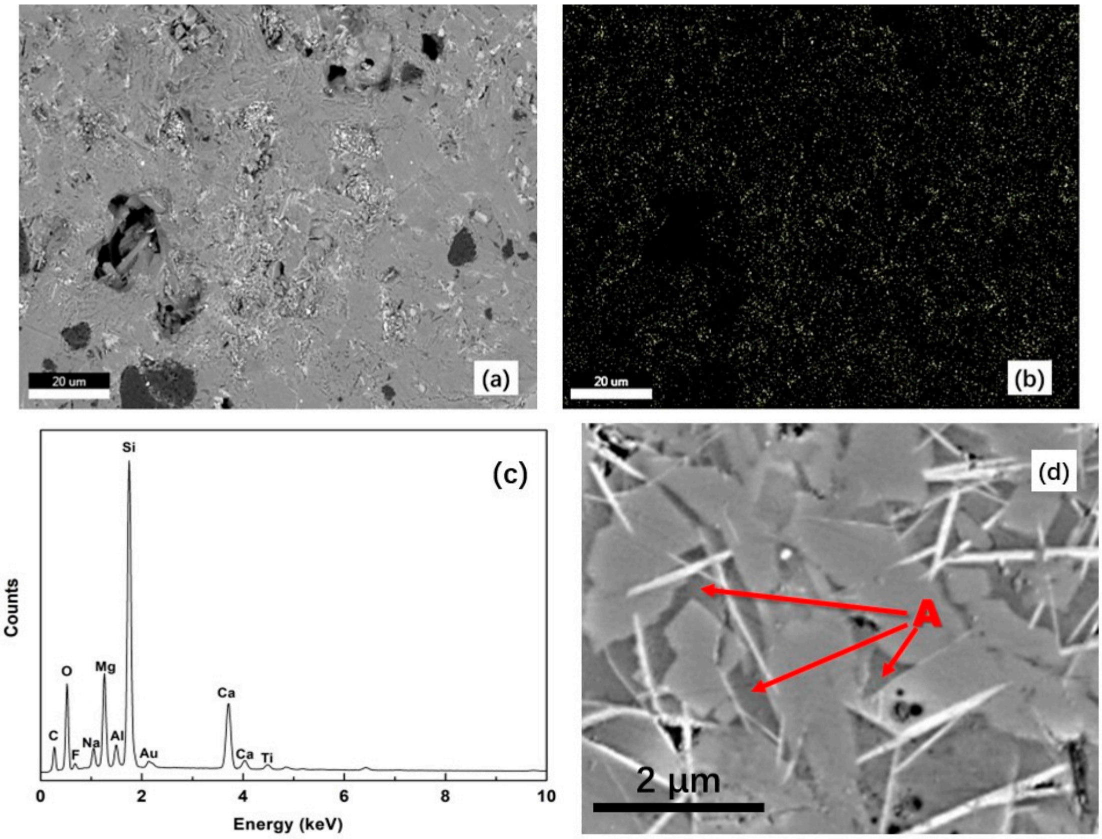

Figure 5. Typical backscattered electron image of final slag (**a**), distribution of Ti-bearing phase (**b**), and EDS analyses of the Ti-bearing phase (**c**). Ti-bearing phase (A) is in an amorphous state that is dispersed in solidified slags (**d**). Sample obtained in slag with basicity index of 1.4.

Table 4. Typical composition of Ti-bearing phase in solidified slag, wt%.

C	Si	Ti	Mg	Na	O	Al	Ca
9.84	22.11	2.05	10.07	4.95	38.33	2.65	6.32

3.3. Discussion on Ti-Removal Procedure

The Ellingham diagram of oxides indicates that, under the same conditions, Ti is more easily oxidized than silicon. The oxidation illustration of silicon and Ti are shown in Equations (2) and (3), respectively. However, the average Ti content in metallurgical-grade silicon is usually lower than 1 wt%, which can lower the activity and restrict the oxidation of Ti in silicon melts based on Equation (4). This equation calculates the actual Gibbs free energy change (ΔG) of the oxidation based on the standard Gibbs free energy change (ΔG^{θ}) and the activities of related substances ($a_{(TiO2)}$, $a_{[Ti]}$, and $a_{[O]}$).

$$[\mathrm{Si}] + 2[\mathrm{O}] \Leftrightarrow (\mathrm{SiO_2}) \tag{2}$$

$$[\mathrm{Ti}] + 2[\mathrm{O}] \Leftrightarrow (\mathrm{TiO_2}) \tag{3}$$

$$\Delta G = \Delta G^{\theta} + \mathrm{RTln}\left[{}^{a_{(\mathrm{TiO2})}}\Big/{}_{a_{[\mathrm{Ti}]}\cdot a^2_{[\mathrm{O}]}}\right] \tag{4}$$

To remove Ti from silicon melts, the activity of oxygen ($a_{[O]}$) should be increased and the activity of titanium dioxide in slag ($a_{(TiO2)}$) should be decreased. Because an oxygen-rich layer is formed near the injected oxygen bubbles during conventional refining, titanium dioxide can be formed in this zone. However, the top slag in ladles mainly results from the oxidation of Al, Ca, and Si in metallurgical-grade silicon (although CaO or other fusion agents could be added under some circumstances). The formation rate and basicity of these slags are relatively low, which can result in high viscosities of slags and poor dynamic conditions for impurity absorption at high temperatures. Slags with these characteristics are not suitable for the rapid absorption of impurities. If titanium dioxide cannot be rapidly absorbed by slag at slag–silicon interfaces, it can be easily reduced by the remaining Al and Ca in silicon melts (usually up to an order of magnitude that is higher than the content of Ti), or the yield of silicon can be quite low.

During the refining in this study, the injected carbon dioxide was decomposed at the refining temperature and an oxygen-rich boundary layer could be formed near the surface of the injected carbon dioxide bubbles. In fact, instead of forming pure titanium dioxide, it is more likely to form complex impurities with other oxides, such as Al_2O_3 and FeO, as shown in Figure 6 and Table 5.

Under the current conditions, samples from the slag–silicon interface were obtained and rapidly quenched after 5 min of refining. A typical SEM image of the quenched sample is shown in Figure 6, where a silicon droplet exists in the refining slag (approximately 40 μm in diameter). The features of impurities were preserved and no crystals were detected in the slag because of rapid cooling. The composition of the typical impurities in this droplet was measured using EDS (electron energy of 10 keV to avoid interference from the matrix or surrounding areas). Corresponding results are shown in Table 5. The Ti content at spot 1 is 2.48 wt%, 1.75 wt% at spot 2, and 0.49 wt% at spot 3. It should be noted that a certain amount of oxygen was detected at spot 3. In fact, further EDS analyses indicated that all impurities at the slag–silicon interfaces contained different contents of oxygen. In addition, wetting of the impurity phases with slag at the slag–silicon interface was observed (especially at spot 3). These results indicate that before solidification the impurities in the silicon melts were already concentrated, wetted by slag, and oxidized at the slag–silicon interfaces.

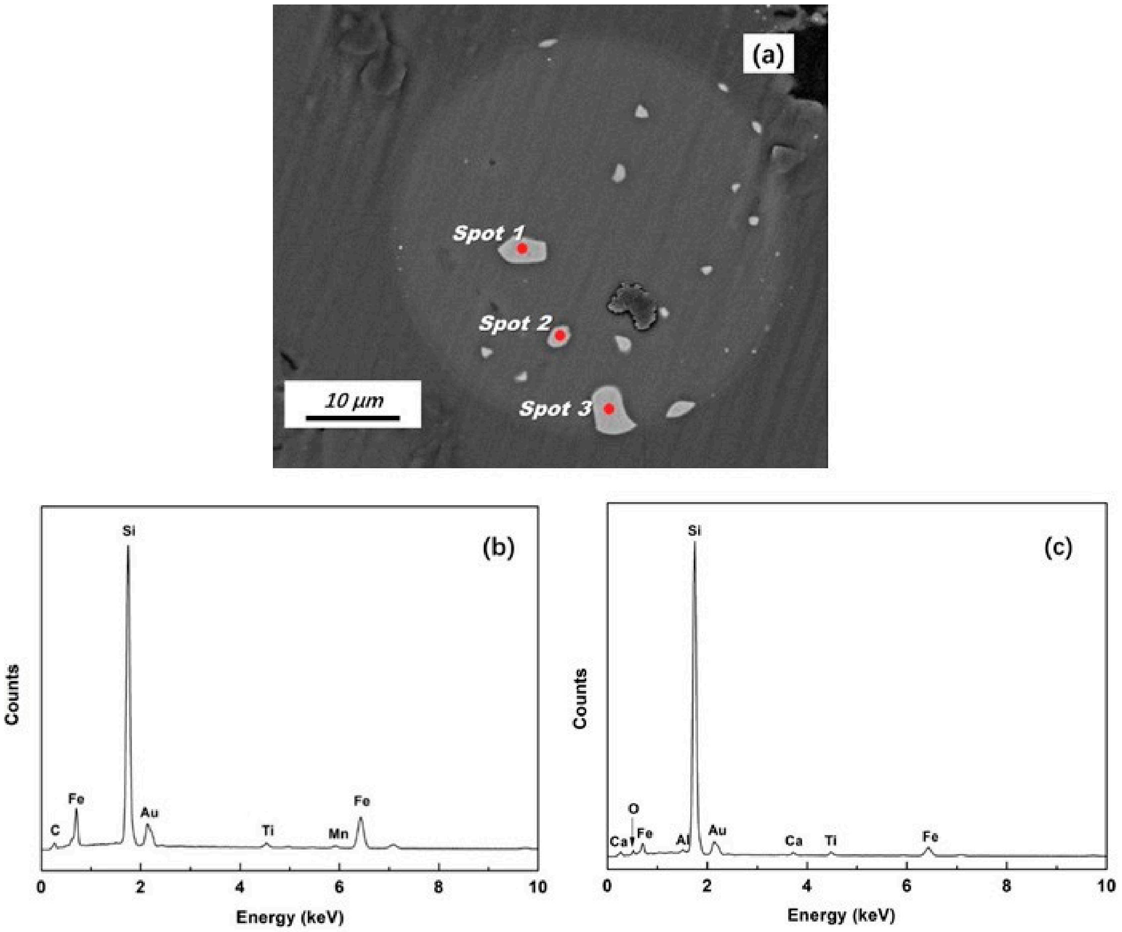

Figure 6. A typical backscattered electron image of silicon droplet in slag (BI = 1.4) near silicon–slag interface (**a**); EDS analyses at spot 1 (**b**) and spot 3 (**c**).

Table 5. Composition of impurities in silicon droplet, wt%.

Spot	C	Si	Ti	Mn	Fe	O	Al	Ca
1	10.51	44.78	2.48	1.63	40.60	-	-	-
2	10.93	55.27	1.75	1.36	30.69	-	-	-
3	-	76.99	0.51	-	19.32	2.60	0.25	0.33
Silicon matrix	-	99.31	-	-	0.31	-	0.38	-

The results indicate that Ti is concentrated in this silicon droplet, and its content in the impurity phases near the silicon–slag interface is obviously lower than the content in the impurity phases at the central area of the droplet. This suggests the following Ti-transferring mechanism: the impurity elements near the slag–silicon interfaces were concentrated, wetted by slag, oxidized, and then transferred to the slag phase. In addition, Fe displayed features that were similar to those of Ti. Further investigations are required on the Ti concentration mechanism at high temperatures and the potential Fe removal method.

Titanium dioxide is an amphoteric oxide that acts as a network former in slags with high BIs. In addition, titanium carbide can be formed in slag systems in the presence of carbon [20] (although no titanium carbide was observed in this case). All of these factors can decrease the activity of titanium dioxide in the slag and promote the oxidation of Ti in silicon melts. Moreover, a high basicity and relatively low liquidus temperature improved the stability and dynamic conditions of slags after the absorption of impurities (especially SiO_2). We demonstrated that Ti in the silicon melts was effectively concentrated and transferred to the slags.

The refining oxidation reactions are exothermic; thus, they could cause temperature differences when using different slags and after different refining times. Hence, the temperature measurements during the refinement were based on a B-type thermocouple that was placed at the bottom of the crucibles. The temperature of the silicon melts was also directly measured by immersing a B-type thermocouple into the silicon melts for a short time during the sample acquisition (the thermocouple was protected by a high-purity magnesia tube and preheated in the furnace). The results showed that the temperature differences at various refining times and slags were less than 15 K.

4. Conclusions

In this study, slag with a high BI and carbon dioxide injection was adopted to refine metallurgical-grade silicon melts in the laboratory. The following conclusions were drawn:

1. Ti in metallurgical-grade silicon can be removed using slags with high BIs and carbon dioxide injection. The removal rate of Ti first increases with the increasing BI of slags and then decreases for a BI of > 1.4. When using a slag with a BI of 1.4, 59% of Ti can be removed after 15 min of refining (Ti in silicon decreased from 0.0580 wt% to 0.0238 wt%). The Ti-bearing phase in the final slag contains 2.05 wt% of Ti;
2. Under the conditions of this study, emulsification of the slag–silicon system during refining was observed, which can be restricted with an increased BI of the slag. In this case, the yield of silicon first decreased and then became steady for a BI exceeding 1.4;
3. During refining, Ti was concentrated in silicon droplets as complex impurities with varied compositions, which were oxidized and wetted by slag at the slag–silicon interface, suggesting a Ti-removal procedure.

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