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Exploration of boron removal from molten silicon by introducing oxygen resources into ammonia blowing treatment

Zhiyuan Chen *, Yuliu You* and Kazuki Morita

Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, Tokyo, Japan

ABSTRACT
Ammonia gas blowing has been successfully applied to the silicon refining process for boron removal. Molten iron catalyst could effectively promote the boron removal ratio in the progress. It inspired the attempt of combining ammonia blowing with other refining treatments. Oxygen resources were introduced into the process in order to further decrease the boron content in silicon. However, neither slagging + ammonia blowing nor humidification + ammonia blowing shows a significant positive improvement in the silicon refining process, respectively. The experimental results implied that the introduction of oxygen sources into the ammonia system would decrease boron nitride activity or produce Si_2N_2O which retard the efficient generation of boron-bearing volatiles.

RÉSUMÉ
On a appliqué avec succès le soufflage de gaz ammoniac au procédé d'affinement du silicium pour l'enlèvement du bore. Le catalyseur de fer fondu pouvait effectivement promouvoir le rapport d'enlèvement de bore au cours de ce procédé. Ceci a inspiré la tentative de combiner le soufflage d'ammoniac avec d'autres traitements d'affinage. On a introduit des sources d'oxygène dans le procédé afin de réduire davantage la teneur en bore du silicium. Cependant, ni la scorification + le soufflage d'ammoniac ni l'humidification + le soufflage d'ammoniac montrent une amélioration positive importante du procédé d'affinage du silicium, respectivement. Les résultats expérimentaux impliquaient que l'introduction de sources d'oxygène dans le système d'ammoniac diminuerait l'activité du nitrure de bore ou produirait du Si_2N_2O, lesquels retardent la production efficace de volatils porteurs de bore.

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Silicon refining; boron removal; solar-grade silicon; wet gas blowing; slag; catalytic molten metal; purification; moisture

1. Introduction

To produce solar-grade silicon (>6 N) using an efficient and low-cost process, many metallurgical methods have been developed and patented to remove the impurities in silicon [1–4]. B is one of the principal impurities that affect the properties of solar cells. Moreover, B is the most difficult impurity to be removed due to the high segregation coefficient ($k_0 = 0.8$) and low-saturated vapour pressure (6.78×10^{-7} Pa, 1823 K) [5–7]. The gas blowing treatment is a widely studied technology in silicon refining to remove B [8–12]. The moisture-containing gas blowing treatment is considered to be one of the most efficient and environmentally friendly methods till now. Moreover, combination of several technologies, such as slagging and gas blowing [13–16], or alloying and gas blowing [17], has been developed to handle the issue of boron removal. Most researchers introduced oxygen resources into the combined treatments. A synergistic effect of boron removal was achieved in these combined treatments.

Recently, NH_3 was used in the gas blowing treatment to remove the B in the metallurgical grade silicon [17,18]. The idea to combine other methods with the NH_3 blowing treatment to remove boron comes naturally. The NH_3 treatment of the Cu–Si alloy has already been reported to successfully enhance the boron removal process [17]. With proper reaction process design, 80% of the boron in the Si–Cu alloy could be removed (the initial content of B is 50 ppmw). Furthermore, with the help of catalytic molten metal, boron in silicon could be removed from 120 to lower than 1 ppmw at 1823 K in 6 h with boron removal ratio of 99.3% [18]. Usually, boron content in metallurgical silicon is around 10–50 ppmw [19]. Hereby, we further verify the method with silicon with an initial boron content of 20 ppmw with the same method as in Ref. [18]. Two grams of boron dropped

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CONTACT Zhiyuan Chen z.chen-5@tudelft.nl, aha_c@126.com
*Present address: Department of Materials Science and Engineering, Delft University of Technology, Delft, Netherlands.

silicon was melted in a crucible with an inner diameter of 12 mm at 1550°C. Pure NH_3 gas was blown from a gas outlet to the surface of the molten silicon with a distance of 370 mm. The NH_3 gas blowing treatment combined with the addition of 1000 ppmw iron as a catalyst could remove boron in silicon from 20 to 0.11 ppmw after 6 h treatment. Figure 1 shows that the boron removal ratio was 99.5% with the help of catalyser iron rather than only 59.2% without iron dopant. The results confirmed that the boron removal ratio can be higher than 99% with varying initial boron content in silicon.

All these successes inspired researchers to combine other methods with the NH_3 gas blowing treatment to improve the current process. In this study, the attempt to combine slagging and humidification with the NH_3 blowing treatment will be introduced and analysed. Both slag and water vapour are oxygen resources in the process. This report aims to provide necessary practical and theoretical information of oxygen introduced NH_3 blowing treatment to the researchers working on the related processes.

2. Experiments

Boron-doped silicon was prepared with solar-grade silicon (purity: ~7 N), to which known concentration of boron (Soekawa Chemicals Co. in Japan, purity: ≥ 99.9 mass%) was added. For this study, 2 g of pure silicon and 163 or 146 ppmw of boron were placed in a high purity graphite crucible and pre-melted at 1450°C in pure argon atmosphere for 2 h. The reactant gas used to remove B was diluted ammonia, which is prepared by diluting the Ar + 3 vol.-% ammonia gas (Sumitomo Seika Chemicals Company Ltd. in Japan) with high purity argon gas (Jyotou Gas Co. in Japan). The reactant gas passed through soda lime, CaO and $Mg(ClO_4)_2$ to remove CO_2 and water, respectively, before introduced into the reaction furnace. The gas feeding rate was set at 300 mL min^{-1}. Before the reaction, the B-doped silicon was held in a pure argon atmosphere at the reaction temperature for 20 min. In the experiments of combined gas blowing and slagging, pre-melted slag with CaO: $SiO_2 = 0.75$ in mass ratio was added into the graphite crucible (inner diameter 13 mm) on the top of the silicon. The mass ratio of slag:Si was 1.25. Reaction continues for 6 h at 1500°C. In the experiments of the moist gas blowing treatment, no slag was added, and the reaction time was controlled as 2 h at 1500°C. The samples were quenched and picked out after the reaction. The boron content in the samples was detected using an inductively coupled plasma atomic-emission spectroscopy (ICP-AES, SII SPS7700 or SPS 3500, Hitachi High-Tech Science Corporation in Japan).

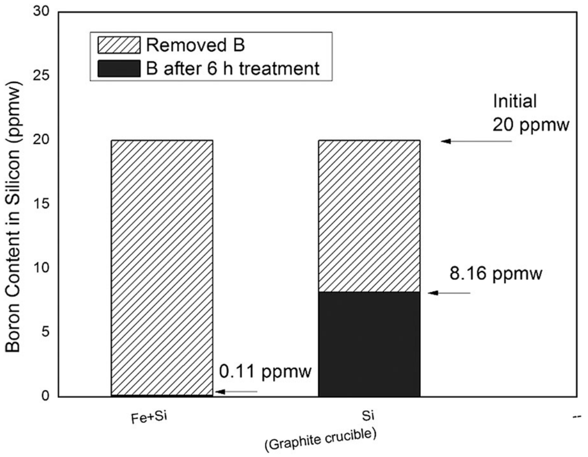

Figure 1. Boron removed from silicon after 6 h treatment in ammonia at 1450°C.

3. Results and discussion

3.1. Combining NH_3 blowing with slagging

The combination of NH_3 gas blowing and slagging for B removal relies on the nitridation of the B in Si and the high nitride capacity of slag. The higher the nitride capacity of the slag the more BN was transferred from Si to slag, i.e. the more B was removed from Si. Therefore, the investigation on the nitride capacity of slag, C_N, is in need. We investigate the nitride capacity of slag in the appendix. In the combined treatment, we could employ the basic slag of CaO–SiO_2 binary, with a reported $\log C_N$ around −11.8 [20]. It is an acceptable value within the reported values of molten slag in Table A2 in the appendix. Besides thermodynamics, the dissolution rate of nitride into slag should also be taken into consideration during the refining process. The reports on nitrogen dissolution in oxide melts [21,22] indicated that the equilibrium of gas and slag could be reached from 70 min to more than 4 h at 1600°C due to different slag compositions and gas flow rates. Comparing to the refining time of other gas treatment, it is not a rapid reaction [10,23,24].

Boron in silicon could be reduced from 163 to 47 ppmw in 0.3 vol.-% NH_3 atmosphere with the slagging treatment. As a comparison, treatments under other atmosphere were also carried out. As Figure 2 shows the distribution coefficient of boron in slag and silicon, which is defined as L_B, was 2.3 in Ar atmosphere. As the experimental results of Teixeira et al. [25] showed, the value of L_B was also 2.3, and the final boron concentration in silicon phase was 24.7 mass ppm when it was refined using slag with CaO: $SiO_2 = 0.75$ (C/S = 0.75) at 1550°C for 18 h. The value of L_B in 0.3 vol.-% NH_3

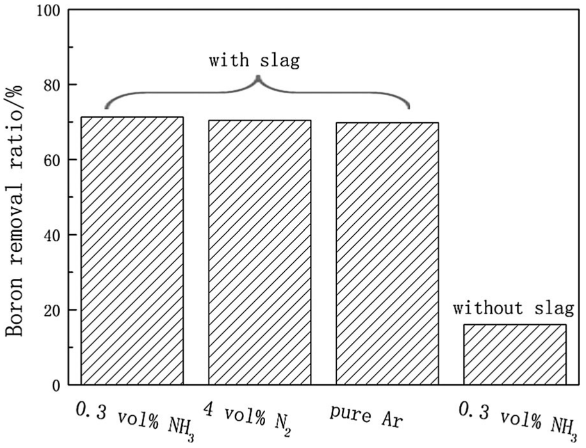

Figure 2. Boron removal ratio of silicon for 6 h at 1500°C in different atmosphere.

and 4 vol.-% N_2 was 2.5 and 2.3, respectively (where the rest of the gas mixture is argon in both). The experimental results suggest that the ammonia gas blowing treatment could remove around 16% boron from silicon, and the slag treatment could remove ∼70% boron from silicon. It is expected that introduction of nitrogen resource, including N_2 and NH_3 could remove ∼86% boron from silicon. However, there is no obvious promotion of boron removal ratio when combining the ammonia gas blowing and slagging treatment. Consequently, the effect of the two silicon refining methods could not be simply overlaid. In other words, gas blowing could not efficiently produce boron-bearing volatiles in the combined treatment.

It is easy to know that the overall reaction rate of the nitridation could be accelerated when increasing the partial pressure of ammonia. However, only 0.3 vol.-% NH_3 was employed here based on the consideration of thermodynamics. Thermodynamics can decide the principle products and the limit of boron removal ratio in the nitriding reaction. The illustration of equilibrium states of related reactions is listed in Figure 3. Partial pressures of vapours are assumed to be 10^{-4} atm in the reactions. Five reactions are investigated in this work. The relationship between the activity of boron in silicon and the partial pressure of NH_3 were estimated from the definition formulas of the chemical equilibrium constants. Correspondingly, five curves are plotted in Figure 3. As Figure 3 shows boron concentration in molten silicon could be decided by the equilibrium of B and Si_3N_4 rather than the equilibrium of B and NH_3. The calculation results indicate that $B_3H_6N_3$ rather than boron nitride will be mainly produced at low ammonia pressure (<0.022 atm). Moreover, when ammonia pressure is higher than 0.044 atm, SiH_4 is one of the principal products, resulting in potential significant silicon loss.

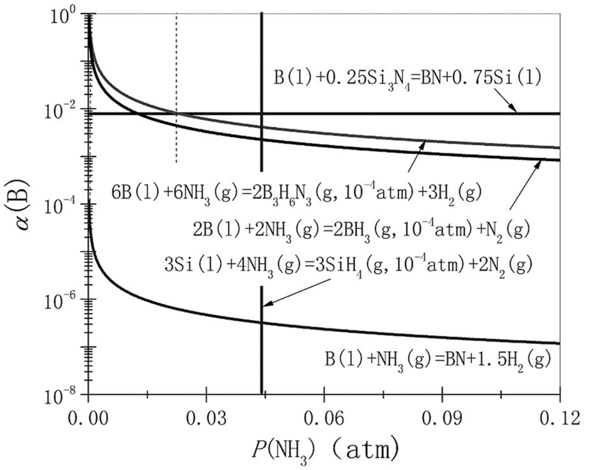

Figure 3. Illustration of the relationship between boron activity and ammonia partial pressure in the equilibrium.

Therefore, the partial pressure of NH_3 was kept at a low value (0.3 atm) to reduce silicon loss in the process.

Assuming the reaction reached equilibrium after 6 h, the activity of boron and silicon-related species in both molten silicon and slag could be obtained from the following two equations:

$$[B] + 0.25(Si_3N_4) = 0.7[Si] + (BN);\ K_1 \tag{1}$$

$$[B] + 0.75(SiO_2) = 0.75[Si] + 0.5(B_2O_3);\ K_2 \tag{2}$$

Boron content in liquid silicon in the equilibrium with solid Si_3N_4–BN was reported by Noguchi et al. [26] and Yoshikawa and Morita [27]. Boron contents in refined silicon in the equilibrium with CaO–SiO_2 (C/S = 0.75) slag was also predicted based on Refs. [25,28]. As Figure 4 shows the experimental data of treatment with slag is close to Equation (2). Therefore, the residual B content in molten silicon is principal decided by Equation (2) in this condition. While, the residual B content in the silicon with only the gas blowing treatment follows Equation (1). Moreover, the residual B content of the sample after treatment without slag was higher than that treated with slagging in Figure 4, it could be proposed that α(B) follows the same sequence:

$$\alpha(B)_{\mathrm{inEquation(1)}} > \alpha(B)_{\mathrm{inEquation(2)}} \tag{3}$$

Correspondingly, based on the definition of the equilibrium constant, K, it is known that:

$$\frac{2\alpha(BN)}{K_1\alpha(Si_3N_4)} > \frac{\alpha(B_2O_3)}{3K_2\alpha(SiO_2)} \tag{4}$$

in their respective equilibrium states. A simple calculation result indicates that the value of $\alpha(BN)/\alpha(Si_3N_4)$ decreased by around 14 times in the experimental system. In other words, the activity of nitrides in CaO–SiO_2 slag was low, and the activity of BN in slag was even lower.

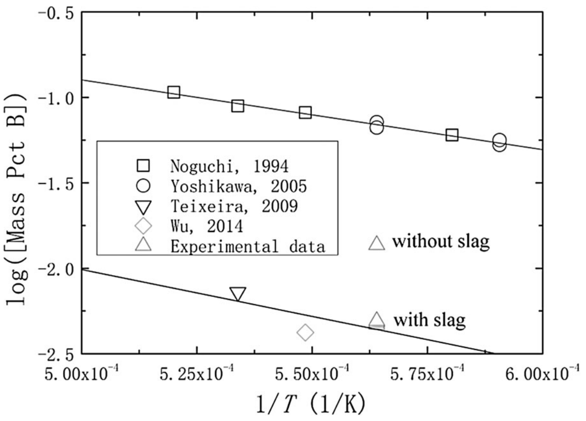

Figure 4. Boron content in refined silicon in comparison with reported data in the equilibrium with Si_3N_4–BN and CaO–SiO_2 (C/S = 0.75), respectively.

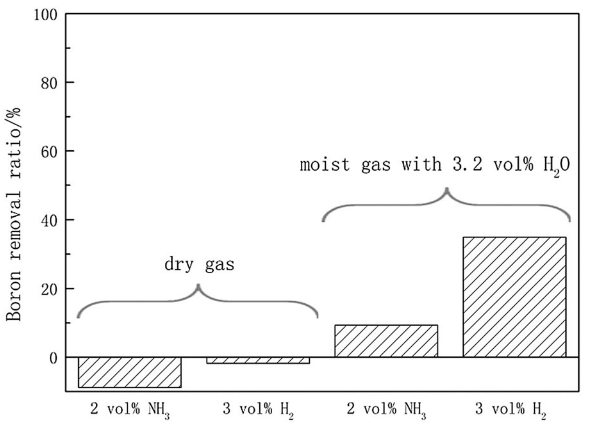

Figure 5. Boron removal ratio of silicon for 2 h at 1500°C in different atmosphere.

As a result, the reaction of BN in molten slag with NH_3 on the surface of slag was extremely difficult due to the unfavourable thermodynamic condition.

As another illustration of the failed NH_3 gas blowing treatment, Van Den Avyle et al. [29] used SiO_2 crucible in the experiment. SiO_2 introduced the same level of oxygen into the system and acts as slag in Equation (2). Therefore, the boron level could not be reduced to <1 ppmw as what they expected.

One could propose another possibility that the reaction between B_2O_3 and NH_3 could potentially reduce the boron content in slag. Nordstrand and Tangstad's experimental work [8] indicated pure H_2 without oxygen source cannot remove boron from silicon. At the equilibrium state of slag and silicon, oxygen partial pressure is very low in the system. For instance, the equilibrium between Si and SiO_2 is as follows [30]:

$$(SiO_2) = Si + O_2;\ \Delta G = 605.709\ \text{kJ mol}^{-1} \text{at } 1450^\circ\text{C} \tag{5}$$

It can be calculated that the partial pressure of O_2 is 4.45×10^{-18} atm at 1450°C [31]. Comparably, oxygen partial pressure in H_2 gas with 3.2 vol.-% moisture is 1.8×10^{-10} atm (HSC Chemistry 7, which is authorised to University of Science and Technology Beijing). The oxygen pressure in the slag-silicon system is too low to provide enough oxygen sources for B–H–O volatiles production.

3.2. Moist ammonia blowing

Hydrogen could provide oxygen for potential B–H–O volatiles production, so the moist and dry gas blowing methods were compared experimentally. Dry 2 vol.-% NH_3 gas was injected into the system but could not move boron from silicon efficiently, principally because of serious silicon loss in the process. As Figure 3 shows SiH_4(g) with partial pressure 10^{-4} atm could be produced in 0.046 vol.-% NH_3 containing atmosphere. Since 3 vol.-% H_2 owns the same hydrogen amount as 2 vol.-% NH_3, 3 vol.-% H_2 was employed for boron removal. However, there is no positive result of dry H_2 gas blowing (Figure 5). Same as the experimental results in reference [8], one can observe a significant boron removal effect of 3 vol.-% H_2–3.2 vol.-% H_2O gas mixtures. Although moisture could both improve boron removal efficiency of H_2 and NH_3 gas blowing treatments, only 9% of boron removal ratio could be achieved in NH_3 containing atmosphere.

The reason of low boron removal ratio in the moist NH_3 gas blowing treatment is supposed to be the introduction of nitrogen into the reaction system. Safarian et al. [9] reported the negative effect of nitrogen in the boron removal process with moist gases. Their results suggested that N_2–3 vol.-% H_2O gas mixtures could remove less boron from molten silicon than Ar–3 vol.-% H_2O gas mixtures at the same time.

HSC Chemistry 7 was employed for thermodynamic calculation to estimate the products in different atmospheres. A calculation result of the equilibrium state of 1 mol silicon doped with 150 ppmw B and 1 mol N_2–3 vol.-% H_2O gas mixtures show that 5.5×10^{-3} mol Si_2N_2O(s) is produced as the largest amount of solid chemicals at 1500°C. Comparatively, SiO_2(s) is the largest amount of solid products (9.0×10^{-3} mol) in the equilibrium state of 1 mol silicon doped with 150 ppmw B and 1 mol Ar–3 vol.-% H_2O gas mixtures. Based on the thermodynamic calculation results, it is possible that Si_2N_2O covered on the surface of molten silicon, retarding the boron removal process.

4. Conclusions

The combined ammonia blowing and slagging treatment shows no positive effect on the boron removal process.

The reason is that the low activity of boron nitride in slag. To understand the possibility of reaction between boron and ammonia with oxygen supplier, the moist ammonia blowing treatment was studied. However, it shows the slightly positive effect on the boron removal process. The formation of Si_2N_2O could be the reason for the lower boron removal efficiency in N–O–H gas than O–H gas system. Therefore, oxygen resources are not recommended to be introduced into the ammonia blowing treatment process.

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Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Zhiyuan Chen http://orcid.org/0000-0002-7993-7386

Notes on contributors

Dr. Zhiyuan Chen received his BS and PhD degree from the University of Science and Technology Beijing. He is post-doc researcher in TU Delft and was project researcher in the University of Tokyo. Dr. Chen is interested in the kinetics of sustainable metallurgical process and properties of melts at high temperature.

Dr. Yuliu You received her BS (2011) and MS (2013) degree in Materials Science and Engineering from Tsinghua University and PhD (2017) degree in Materials Engineering from The University of Tokyo. From Nov 2017, Dr. You worked in TU Delft as a post-doc researcher up to present.

Professor Kazuki Morita took BS degree in 1983, MS degree in 1985, and Doctor of Engineering in 1988 from the University of Tokyo at the Department of Metallurgy. He works at the Department of Materials Engineering in the University of Tokyo. Professor Morita has his expertise in physical chemistry on high-temperature materials processing mostly related to iron- and steelmaking, silicon refining, and materials recycling.

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Appendix

Saturated concentration of BN in slag

Nitrogen can dissolve in slag via mechanisms of chemical bonding and physical dissolving [1]. Nitride capacity is defined as follows:

$$C_N = (\text{mass\%N})\frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \quad (1)$$

where C_N is the nitride capacity, P is the partial pressure of gas. This equation is corresponding to the following ionic gas-slag reaction:

$$\frac{1}{2}N_2 + \frac{3}{2}(O^{2-}) = (N^{3-}) + \frac{3}{4}O_2 \quad (2)$$

Therefore, high nitrogen pressure and depressed oxygen pressure are beneficial for high nitrogen content in slag. Nitrogen solved in slag is indicated to be as both free and incorporated N^{3+} [2,3]. Nitride capacity is determined by temperature and slag compositions. The nitride capacities of slag systems obtained by the gas-slag equilibrium were summarised in references [4,5]. The collected data in the two reports show that temperature has a great effect on nitride capacity. The report of Sasabe et al. [6] indicated that the nitride capacity increases with increasing temperature, which shows the relationship as follows:

$$\log C_N = -\frac{a}{T} + b \quad (3)$$

Adding nitride formers, of which the corresponding nitrides are relatively stable, could increase the nitride capacity [7]. The order of the positive effect on the nitride capacity by adding nitride formers is summarised in Table A1. It could be noticed that TiO_x containing slag has high nitride capacity.

Martinez et al. [8] also reported that adding titania at high CaO/$AlO_{1.5}$ has a strong effect on the solubility of incorporated nitride. In CaO–SiO_2–CaF_2 ternary, the maximal values of nitrogen content were at 48 mass% CaO and in high-SiO_2 region [2]. However, some compounds have complex effects on nitride capacity. Shin et al. [9] reported that CaF_2 promotes nitride capacity when the molar ratio of CaO/Al_2O_3 is lower than 2, otherwise it is ineffective. Compounds in different system also show different effects. Increasing the Al_2O_3 content in CaO–Al_2O_3–CaF_2 ternary at a certain CaO/CaF_2 ratio decreases nitride capacity of slag [9], while in CaO–$AlO_{1.5}$ binary promotes it instead [7]. Furthermore, Table A1 suggests that not only TiO_x, but also ZrO_2 and $AlO_{1.5}$ have a positive effect on nitride capacity. However, the silicon refining temperature is 1500°C, which is 50–100°C lower than the typical temperature of the system containing TiO_x, ZrO_2 and $AlO_{1.5}$. Therefore, the three oxides cannot be effectively used in silicon refining. Another promising candidate, B_2O_3, could not be introduced, for the reason that high boron content could dissolved into silicon from it. Therefore, in the combined treatment, we could employ the basic slag of CaO–SiO_2 binary, with a reported $\log C_N$ around – 11.8 [18]. It is an acceptable value within the reported values of molten slag in Table A2.

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Table A1. Order of the positive effect on nitride capacity of oxides.

Priority	Slag system	Temp. (°C)	Remark	Ref.
(M)TiO_x>ZrO_2>SiO_2>MgO	CaO–$AlO_{1.5}$–MO_x	1600	$X_{CaO}/X_{AlO1.5} = 0.4–0.7$	[7]
(M)TiO_x>$AlO_{1.5}$>MgO	CaO–SiO_2–MO_x	1600	$X_{CaO}/X_{SiO2} = 1.0–1.5$	[7]
ZrO_2>TiO_x>SiO_2	CaO–SiO_2–$AlO_{1.5}$–MO_x	1473–1632		[6]
$BaCl_2$>SiO_2 and TiO_2	CaO–CaF_2–$AlO_{1.5}$	1500		[8]
TiO_x>CeO_2>ZrO_2>SiO_2> $AlO_{1.5}$>B_2O_3>	MgO>CaO>BaO		review paper	[10]
TiO slag>Ti_2O_3 slag>TiO_x	slag> TiO_2 slag> CaO–$AlO_{1.5}$ slag		CaO–$AlO_{1.5}$(–TiO_x)	[10]

Table A2. Nitride capacity in slag.

Slag system	Temp. (°C)	(mass% N)	logC_N	Remark	Ref.
$CaO–AlO_{1.5}$	1600	$26.1–143 \times 10^{-4}$	−12.03∼−12.78		[7]
$CaO–AlO_{1.5}–MgO$	1600	$6.3–58.2 \times 10^{-4}$	13.33∼−13.97		[7]
$CaO–AlO_{1.5}–ZrO_2$	1600	$69.9–340 \times 10^{-4}$	−13.13∼−13.47		[7]
$CaO–SiO_2–MgO$	1600	$27.6–64.5 \times 10^{-4}$	−10.71∼−11.50		[7]
$CaO–SiO_2–TiO_x$	1600	$25.7–284 \times 10^{-4}$	−11.06∼−12.48		[7]
$CaO–SiO_2–AlO_{1.5}$	1473∼1568	0.66–4.27	−12.532∼−14.179	Si melt equilib	[6]
$CaO–SiO_2–AlO_{1.5}–TiO_2$	1500∼1520	0.056–0.474	−13.388∼−13.837	Si melt equilib	[6]
$CaO–SiO_2–AlO_{1.5}–ZrO_2$	1505∼1632	0.49–1.78	−11.432∼−13.153	Si melt equilib	[6]
$CaO–Al_2O_3–CaF_2$	1500	0.0091∼0.587	−12.49∼−15.30		[9]
$CaO–Al_2O_3–TiO_x$	1600	0.028∼0.66		Fe melt equilib.	[10]
$CaO–SiO_2$	1600	0.129∼0.261	About −11.8		[11]
$CaO–AlO_{1.5}–MgO$	1600	$4.7\sim1650 \times 10^{-4}$	−12.01∼13.40	Fe melt equilib.	[12]
$CaO–Al_2O_3–TiO_x$	1600	$1.2\sim36.5 \times 10^{-4}$		Ni melt equilib.	[13]
$CaO–Al_2O_3–TiO_x$	1600	$3.2\sim19.5 \times 10^{-4}$		Ni melt equilib.	[13]
$BaO–TiO_x$	1550	0.0093∼0.375		Cu melt equilib.	[4]
$BaO–TiO_x$	1600	0.0089∼1.14		Cu melt equilib.	[4]
$BaO–TiO_x$	1650	0.0243∼0.751		Cu melt equilib.	[4]
$CaO–SiO_2–AlO_{1.5}$	1550	$2.7\sim934 \times 10^{-4}$		Fe melt equilib.	[14]
$CaO–SiO_2–AlO_{1.5}$	1600	$1.4\sim1190 \times 10^{-4}$		Fe melt equilib.	[14]
B_2O_3		$10^{-1.4}\sim10^{-0.2}$	−9.7 at 1550°C	$\triangle H = 133$kJ mol^{-1}	[1]
$B_2O_3–CaO$	1550	Max. 0.24	About −14∼−10		[1]
$B_2O_3–SiO_2$	1550	Max. 0.65	About −12∼−10		[1]
$CaO–AlO_{1.5}$	1450	$3.3\sim24.0 \times 10^{-4}$	−14.16∼−14.36		[15]
$CaO–AlO_{1.5}$	1500	$13.6\sim13.9 \times 10^{-4}$	−13.44∼−13.47		[15]
$CaO–AlO_{1.5}$	1550	$39.2\sim189.5 \times 10^{-4}$	−12.78∼−13.00		[15]
$CaO–AlO_{1.5}$	1600	$59.8\sim73.0 \times 10^{-4}$	−12.12∼−12.21		[15]
$CaO–AlO_{1.5}$	1650	$23.9\sim248.3 \times 10^{-4}$	−11.67∼−11.74		[15]
$CaO–AlO_{1.5}$	1550	$3.1\sim6220 \times 10^{-4}$		Fe melt equilib.	[16]
$CaO–AlO_{1.5}$	1650	$3.2\sim2230 \times 10^{-4}$		Fe melt equilib.	[16]
$CaO–B_2O_3$	1350∼1503	0.016∼0.55	−12.31∼−14.20		[17]
$BaO–B_2O_3$	1425	0.063∼0.68	−11.99∼−13.05		[17]
$CaO–SiO_2–AlO_{1.5}$	1550	0.38∼0.75	−11.98∼−12.35		[18]
$CaO–AlO_{1.5}$	1600	0.028∼0.35			[19]
$CaO–SiO_2–AlO_{1.5}$	1550	0.01∼3.30		Kjeldahl	[20]

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