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| Abstract | Carbothermic selective reduction of titanium concentrate ore for the preparation of titanium oxycarbide was presented and SiO_2 was found to be partly reduced during the process. The equilibrium relationship between Si dissolved in metallic Fe and SiO_2 existed in corresponding slag was analyzed thermodynamically, and then revealed by a series of designed equilibration experiments. The results are in accordance with the calculated values obtained from thermodynamic analysis and have well explained the phenomenon that part of SiO_2 is reduced during selective reduction processing of titanium concentrate ore. |

Equilibrium of [Si]/(SiO$_2$) in Carbothermic Selective Reduction of Titanium Concentrate Ore for the Preparation of Titanium Oxycarbide

JIUSAN XIAO, QI WANG, BO JIANG, and HONGMIN ZHU

Carbothermic selective reduction of titanium concentrate ore for the preparation of titanium oxycarbide was presented and SiO$_2$ was found to be partly reduced during the process. The equilibrium relationship between Si dissolved in metallic Fe and SiO$_2$ existed in corresponding slag was analyzed thermodynamically, and then revealed by a series of designed equilibration experiments. The results are in accordance with the calculated values obtained from thermodynamic analysis and have well explained the phenomenon that part of SiO$_2$ is reduced during selective reduction processing of titanium concentrate ore.
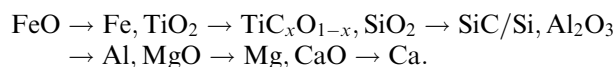
I. INTRODUCTION

TITANIUM and its alloys have received great attention from researchers worldwide due to its excellent properties such as high melting point and extraordinary corrosion resistance. However, its application has been limited by high cost arising from the Kroll Process.[1] In the past two decades, several new methods for producing titanium have been proposed, such as FFC Cambridge process,[2] Ono Suzuki (OS) process,[3,4] molten oxide electrolysis (MOE) process,[5] and the USTB electrolysis process.[6,7] In the USTB process, high-purity titanium can be collected at the cathode through the electrolysis of titanium oxycarbide (TiC$_{0.5}$O$_{0.5}$) as consuming anode in molten salt, while the carbon and oxygen component in the oxycarbide anode evolve into the carbon oxide (CO, CO$_2$) gases.

The anode material for the USTB process, namely titanium oxycarbide (TiC$_{0.5}$O$_{0.5}$), can be synthesized through not only carbothermic reduction of TiO$_2$, but also selective carbothermic reduction of titanium raw materials such as high-grade titanium slag and titanium-iron ores,[8] which mainly contains FeO/Fe$_2$O$_3$, TiO$_2$, CaO, MgO, SiO$_2$, and Al$_2$O$_3$. A lot of related researches focusing on the reduction of titanium raw materials have already been proposed since the 1950s.[9–15] Coley has studied the reduction mechanism of ilmenite into iron and titanium oxycarbide at temperatures ranging from 1587 K to 1790 K (1314 °C to 1517 °C).[16] Dewan has studied the carbothermic reduction of ilmenite concentrates in different gas atmospheres including hydrogen, argon, and helium, demonstrating the transformation from TiO$_2$ to Ti$_3$O$_5$ and then Ti$_2$O$_3$, which is converted to titanium oxycarbide.[17,18]

The equilibrium constants for relevant reactions during selective carbothermic reduction of titanium raw materials are plotted as a function of temperature in Figure 1. Since titanium sesquioxide (Ti$_2$O$_3$) will be reduced to titanium oxycarbide (TiC$_x$O$_{1-x}$) instead of titanium monoxide (TiO), the reaction sequence of carbothermic reduction of titanium raw materials is

$$FeO \rightarrow Fe, TiO_2 \rightarrow TiC_xO_{1-x}, SiO_2 \rightarrow SiC/Si, Al_2O_3 \rightarrow Al, MgO \rightarrow Mg, CaO \rightarrow Ca.$$

Therefore, in the presence of certain chemical potentials of carbon and oxygen at high temperature (*i.e.*, 1873 K [1600 °C]), the reactive elements, such as Si, Mg, Ca, and Al, are expected to form oxides, while titanium oxide is reduced to titanium oxycarbide (TiC$_{0.5}$O$_{0.5}$) and iron oxides are converted to liquid metallic Fe which is easily separated from the oxycarbide and slag phases, since Fe is supposed to dissolute in the molten salt before titanium oxycarbide during electrolysis, resulting in contamination. Similarly, oxides of Si, Mg, Ca, and Al should be removed due to their properties of insulation, which will bring a bad effect on the conductivity of anode. Thus, high-purity titanium oxycarbide can be synthesized from titanium raw materials and then

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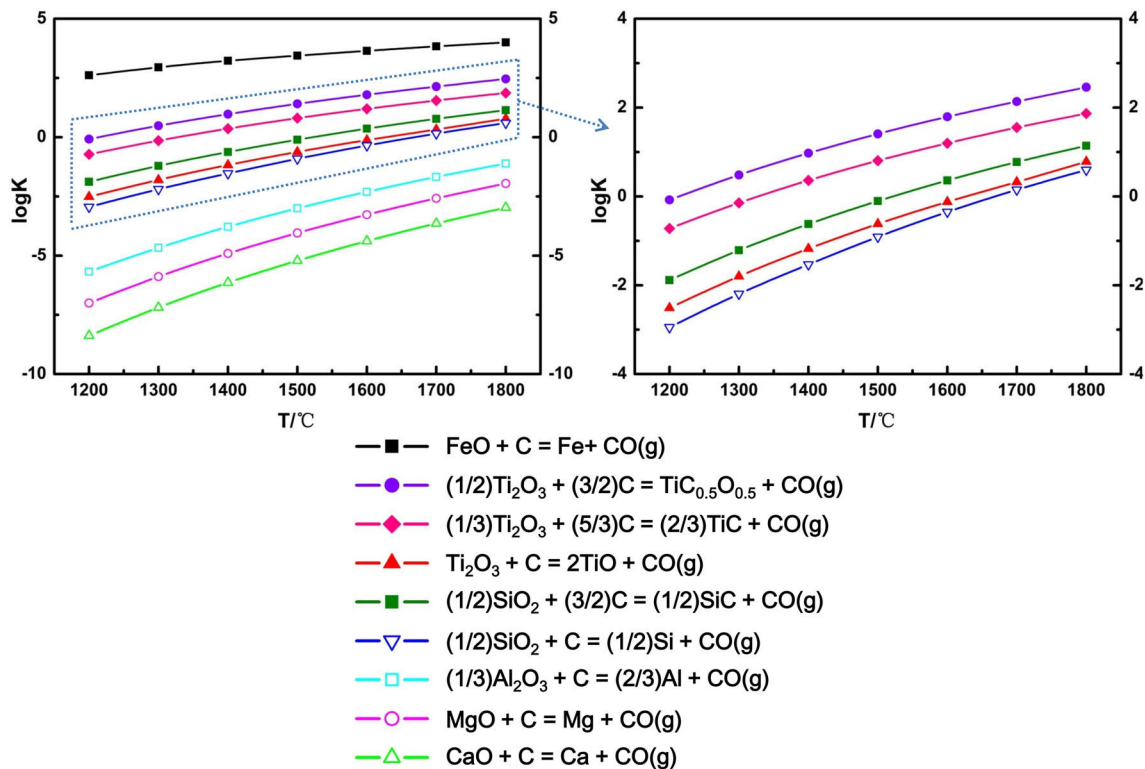Manuscript submitted April 3, 2018.

Fig. 1—Equilibrium constants for relevant reactions during selective carbothermic reduction of titanium raw materials.

utilized as the anode of USTB process for the preparation of metallic titanium. This process is found to be theoretically and experimentally feasible, which exhibits great potential for the utilization of low-grade titanium raw materials, a unique, cost-reducing feature to the USTB process.

The relationship between the reduction of TiO_2 and SiO_2 is further evaluated through thermodynamic calculation under temperature of 1873 K (1600 °C), as shown in Figure 2. The equilibrium constant of reaction from Ti_2O_3 to TiC_xO_{1-x} changes with the concentration of solid solution, since the mixing Gibbs free energy of TiC_xO_{1-x} exhibits quadratic relationship with the corresponding composition.[19] SiO_2 is supposed to maintain in oxide form during the selective reduction process when the stoichiometric amount of carbon is provided only for the sufficient reduction of FeO/Fe_2O_3 to Fe and TiO_2 to $TiC_{0.5}O_{0.5}$. However, based on our previous work, a slight amount of SiO_2 will be reduced into Fe-Si alloy in the selective reduction process due to the decrease of Si activity in liquid Fe,[20] leading to the fact that part of the carbon which is designed to reduce TiO_2 to $TiC_{0.5}O_{0.5}$ will react with SiO_2, causing the insufficient reduction of TiO_2. Thus in this paper, we presented carbothermic selective reduction of titanium concentrate ore, and then performed a series of equilibration experiments to investigate the equilibrium relationship between Si in metallic Fe and SiO_2 in slag with the presence of titanium oxycarbide. The results were interpreted with the aid of thermodynamic analysis.

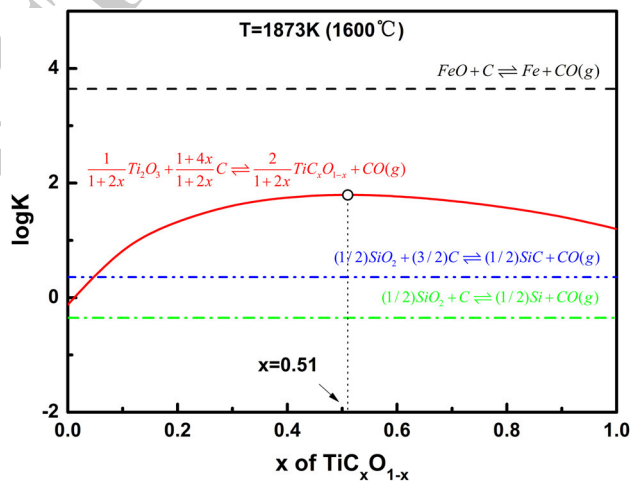Fig. 2—Equilibrium constants for the carbothermic reduction of FeO, Ti_2O_3, and SiO_2 related to x of TiC_xO_{1-x} at 1873 K (1600 °C).

II. EXPERIMENTAL DETAILS

A. Carbothermic Selective Reduction

High-purity graphite (99.9 pct, Aladdin Chemistry Co., Ltd) and titanium concentrate ore (Chongqing Iron and Steel Co., Ltd) were used as raw materials in selective reduction experiment. The chemical composition of titanium concentrate ore was tested by X-ray fluorescence (XRF, XRF-1800, Shimadzu Corporation), as listed in Table I. The stoichiometric amount of carbon is provided only for the sufficient reduction

Table I. Chemical Composition of Titanium Concentrate Ore

	TiO$_2$	FeO	Fe$_2$O$_3$	CaO	MgO	SiO$_2$	Al$_2$O$_3$
Weight Percent	44.9	41.4	2.4	0.3	4.2	4.3	2.5

119 of FeO/Fe$_2$O$_3$ to Fe and TiO$_2$ to TiC$_{0.5}$O$_{0.5}$ due to the
120 aim of selective reduction process. Ingredients were
121 mixed uniformly according to appropriate ratio by ball
122 milling over 4 hours and then pressed into pellets of
123 50 mm in diameter and 15 mm in height. The pellets
124 were placed in a graphite crucible lined with molybde-
125 num plate, sintering at 1873 K (1600 °C) over 4 hours
126 under flowing argon atmosphere. The reductive pro-
127 duct was analyzed by X-ray diffraction (XRD,
128 M21XVHF22, MAC in Japan), scanning electron
129 microscopy (SEM, ZEISS-EVO 18, Carl Zeiss AG),
130 and energy dispersive X-ray spectroscopy (EDX) after
131 cooling to room temperature. The concentration of Si
132 dissolved in metallic Fe collected from obtained pro-
133 duct was analyzed by Inductive Coupled Plasma
134 Emission Spectrometer (ICP, OPTIMA 7000DV, Perk-
135 inElmer Co., Ltd).

136 B. *Equilibrium Experiment*

137   The product obtained from selective carbothermic
138 reduction of titanium raw material is composed of
139 titanium oxycarbide, slag phase, and metallic Fe with a
140 slight amount of dissolved Si.[20] The equilibrium system
141 consists of three parts: titanium compound for the
142 fixation of chemical potential, Fe-Si alloy, and slag
143 phase including CaO, SiO$_2$, MgO, and Al$_2$O$_3$.
144   For the preparation of Fe-Si alloy, Fe powder
145 (99.9 pct, Aladdin Chemistry Co., Ltd) and Si powder
146 (99.9 pct, Sinopharm Chemical Reagent Co., Ltd) were
147 mixed uniformly by ball milling over 4 hours. The
148 ingredients were placed into a corundum (Al$_2$O$_3$)
149 crucible and melted at 1873 K (1600 °C) in a MoSi$_2$
150 resistance furnace under flowing argon atmosphere for
151 10 minutes. Samples were cooled to room temperature
152 after melting and crushed into powders for the following
153 equilibration experiments. Particularly, we have intro-
154 duced metallic Fe powder ($x_{[Si]}$ = 0 pct) and Fe-Si alloy
155 with a certain concentrations of Si ($x_{[Si]}$ = 10 pct) for
156 comparison.
157   The constitution of slag phase (slag 1) naturally comes
158 from the chemical composition of titanium concentrate
159 ore, as listed in Table I. Besides, we have introduced a
160 different kind of slag phase (slag 2) with a lower melting
161 point (1507 K [1234 °C][21]) in equilibration experiments
162 for comparison. The chemical compositions of these two
163 kinds of slags are listed in Table II. Powders of CaO,
164 MgO, SiO$_2$, and Al$_2$O$_3$ (99.9 pct, Sinopharm Chemical
165 Reagent Co., Ltd) were mixed uniformly by ball milling
166 over 4 hours, and then fused under flowing argon
167 atmosphere at 1573 K (1300 °C) for 10 minutes. The
168 melted and solidified sample was crushed into powders
169 after cooling to room temperature.

Table II. Chemical Composition of Simulative Slags Utilized in Equilibration Experiments

	CaO	MgO	SiO$_2$	Al$_2$O$_3$
Slag 1				
Weight Percent	2.7	37.2	38.0	22.1
Mol Pct	2.7	50.7	34.7	11.9
Slag 2				
Weight Percent	30.5	7.3	43.7	18.5
Mol Pct	33.3	11.1	44.5	11.1

170   Ingredients including titanium compound, Fe-Si
171 alloy, and pre-fused simulative slag were mixed uni-
172 formly according to appropriate ratios by ball milling
173 over 4 hours. Mixed powders were placed in a graphite
174 crucible lined with molybdenum plate, and then sintered
175 under flowing argon atmosphere at 1873 K (1600 °C)
176 over 4 hours for the achievement of equilibrium. The
177 concentration of Si in obtained Fe-Si alloy was analyzed
178 by Inductive Coupled Plasma Emission Spectrometer
179 (ICP).

III. RESULTS AND DISCUSSION 180

A. *Carbothermic Selective Reduction* 181

182   Firstly, we have performed carbothermic selective
183 reduction of titanium concentrate ore for the prepa-
184 ration of titanium oxycarbide. The amount of
185 graphite utilized as the reductant was carefully con-
186 trolled according to the chemical composition of
187 titanium concentrate ore, as listed in Table I, which
188 indicates that titanium concentrate ore primarily
189 consists of TiO$_2$ and FeO, together with a slight
190 amount of Fe$_2$O$_3$, CaO, MgO, SiO$_2$, and Al$_2$O$_3$. The
191 XRD patterns of raw material and reductive product
192 are shown in Figure 3, declaring that titanium con-
193 centrate ore with a main phase of FeTiO$_3$ is substan-
194 tially transformed into metallic Fe and titanium
195 oxycarbide after selective reduction process, together
196 with a slight amount of unreduced Mg$_2$TiO$_4$ and
197 Ti$_2$O$_3$. This phenomenon is consistent with Dewan's
198 research, which demonstrates that the completion of
199 carbothermic reduction to titanium oxycarbide under
200 argon atmosphere is achieved with a reaction time
201 longer than 5 hours.[17] The carbothermic reduction
202 process similarly proceeds in two stages: (1) the
203 transformation of FeTiO$_3$ into metallic iron and
204 titanium dioxide; (2) the reduction of titanium dioxide
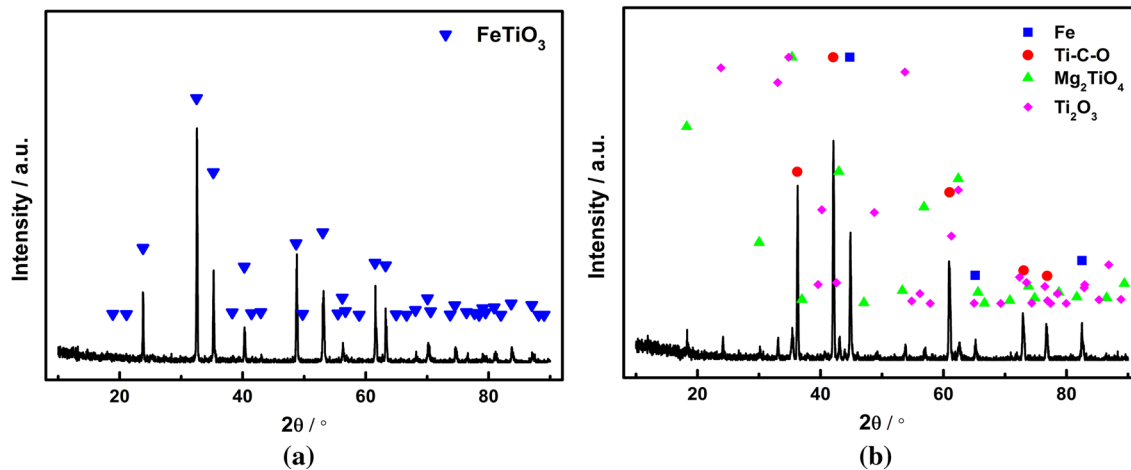205 to titanium oxycarbide.[15]

Fig. 3—XRD patterns of (*a*) titanium concentrate ore and (*b*) corresponding product of carbothermic reduction.

The product is characterized through SEM/EDX techniques, as described in Figure 4, indicating three phases of metallic Fe, titanium oxycarbide, and slag phase. According to a typical SEM/EDX image of the slag phase, as shown in Figure 5, it appears clumpy and the size is about 10 μm; particles of titanium oxycarbide distribute in the product, with a size of 2 μm, as shown in Figure 6, while Fe is found to be spherical in shape, with a diameter of 5 μm. Particularly, the EDX image of reductive product displayed in Figure 4 exhibits an overlap of the distribution of Si and Fe element, suggesting that there is a slight dissolution of Si in the metallic Fe, with a concentration of about 2.5 pct, according to the EDX result described in Figure 6.

For the preparation of titanium oxycarbide from titanium concentrate ore, the designed reactions are

$$FeO + C = Fe + CO(g), \quad [1]$$

$$TiO_2 + 2C = TiC_{0.5}O_{0.5} + 1.5CO(g). \quad [2]$$
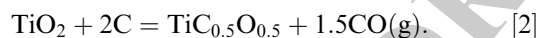
Based on the composition mentioned in Table I, there is a certain amount of mass change (33.9 pct) during the selective reduction process. The expected mass change is supposed to be lower than 33.9 pct due to unreduced Mg_2TiO_4 and Ti_2O_3 detected in XRD pattern. However, we have carefully estimated the weight of starting material and product, and the mass loss is higher than expected, as shown in Table III. This is attributed to the partly reduction of SiO_2 with the reaction of

$$SiO_2 + 2C = [Si] + 2CO(g). \quad [3]$$

This leads to the consumption of carbon that is originally designed to reduce TiO_2. Due to the deviation of mass change, the concentration of Si in Fe-Si alloy obtained from the reduction of SiO_2 is calculated to be 2.5 pct, which is in accordance with not only EDX results, but also the results of ICP analysis for the collected metallic Fe as listed in Table III. All the results suggest that the main part of SiO_2 (about 77 pct) in the titanium concentrate ore stays in slag in the form of composite oxide such as $MgO \cdot SiO_2$, as displayed in Figure 5, while the remaining SiO_2 is partly reduced to Si, as in Fe-Si alloy.

B. *Thermodynamic Analysis*

The reduction of pure SiO_2 thermodynamically occurs only after the transformation of Ti_2O_3 into $TiC_{0.5}O_{0.5}$ and even TiC, according to Figure 1, and thus SiO_2 is supposed to stay in the slag phase after selective reduction process, in condition of providing carbon only for the sufficient reduction of FeO/Fe_2O_3 to Fe and TiO_2 to $TiC_{0.5}O_{0.5}$. However, SiO_2 is found to be partly reduced into Si, as mentioned above, forming a separated phase of Fe-Si alloy at the chemical potential provided by titanium oxycarbide, due to the decreasing activity of Si,[20] indicating that there is equilibrium relationship between Si in Fe-Si alloy phase and SiO_2 remaining in the slag phase, and the concentration of Si in metallic Fe is determined by the chemical potential of titanium oxycarbide and the activity of SiO_2 in slag phase.

It is well known that titanium oxycarbide (TiC_xO_{1-x}, $0 \leq x \leq 1$) is a solid solution of TiC and β-TiO, and also a type of intermediate product between Ti_2O_3 and TiC during the carbothermic reduction of TiO_2.[22] Therefore, we intend to control the chemical potential of the system with two kinds of redox couples: Ti_2O_3/TiC_xO_{1-x} and TiC_xO_{1-x}/TiC. The corresponding chemical potential relationship for Ti_2O_3/TiC_xO_{1-x} and TiC_xO_{1-x}/TiC at 1873 K (1600 °C) is calculated in two different ways based on previous study on thermodynamic properties of TiC_xO_{1-x}.[23]

Ti_2O_3 can be easily reduced by carbon to TiC_xO_{1-x} in almost the whole composition range at 1873 K (1600 °C) and $TiC_{0.51}O_{0.49}$ exhibits the lowest chemical potential, as shown in Figure 2. However, $TiC_{0.51}O_{0.49}$ does not coexist with Ti_2O_3 at 1873 K (1600 °C) since they will react, forming titanium oxycarbide with lower concentration of TiC, according to Figure 7, which demonstrates the reacting capacity of Ti_2O_3 and
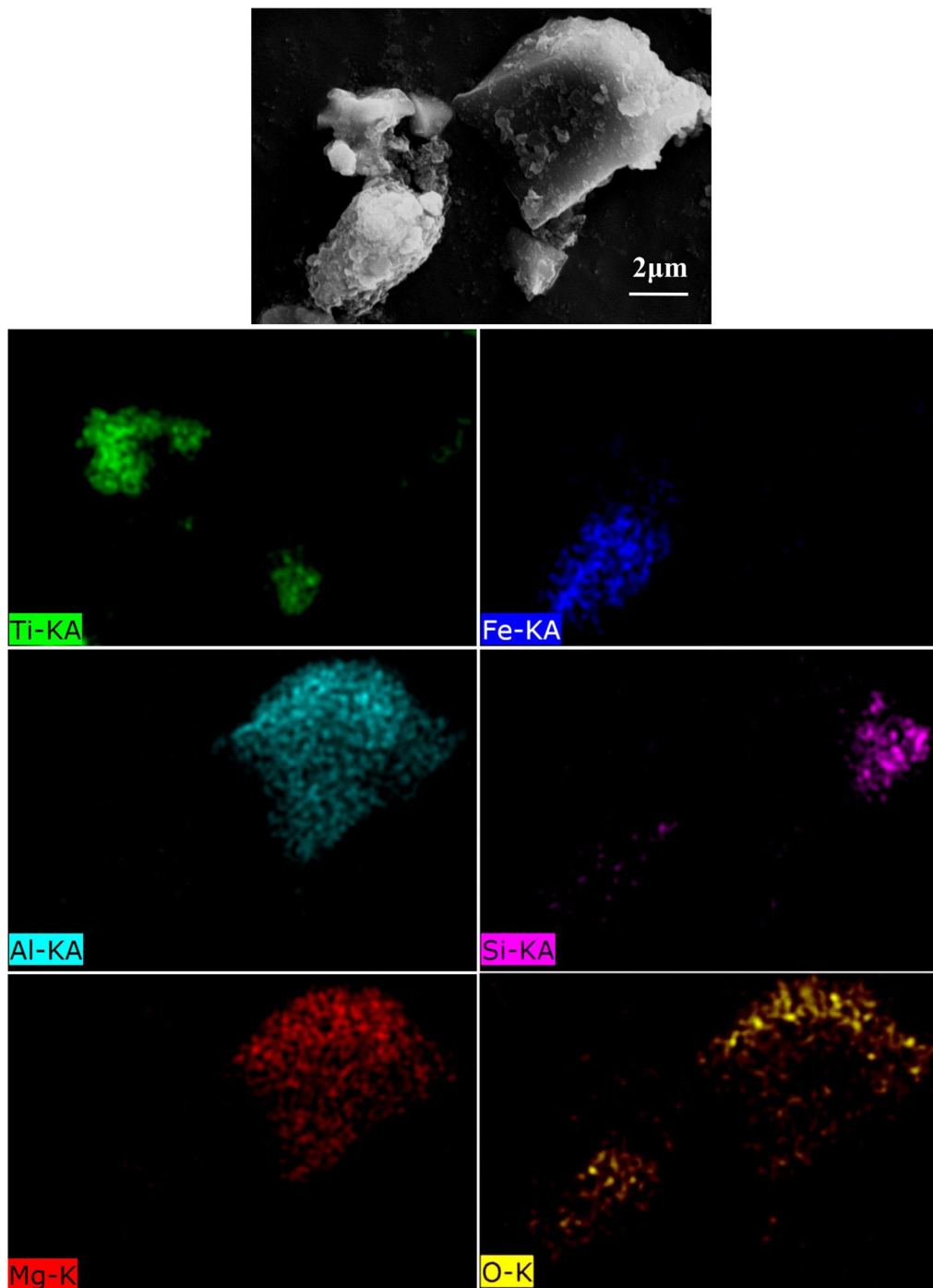
Fig. 4—SEM and EDX images of the product of carbothermic reduction from titanium concentrate ore.

titanium oxycarbide. The antioxidant capacity of titanium oxycarbide is gradually enhanced with the decrease of the concentration of TiC, reaching an equilibrium composition of $TiC_{0.417}O_{0.583}$, according to Figure 7, which suggests that TiC_xO_{1-x} with a concentration of TiC ranging from 0 to 0.417 could coexist with Ti_2O_3, while TiC_xO_{1-x} with a concentration of TiC above 0.417 will be oxidized by Ti_2O_3. Thus, the appropriate composition for redox couple Ti_2O_3/TiC_xO_{1-x} is $Ti_2O_3/TiC_{0.417}O_{0.583}$.

For redox couple TiC_xO_{1-x}/TiC, since the mixing Gibbs energy of TiC_xO_{1-x} at 1873 K (1600 °C) is negative in the whole concentration range,[24] TiC will spontaneously dissolve in TiC_xO_{1-x}, forming a different type of TiC_xO_{1-x} with a higher concentration of TiC. Besides, titanium oxycarbide (TiC_xO_{1-x}) itself is a special kind of redox couple: TiO(in TiC_xO_{1-x})/TiC(in TiC_xO_{1-x}), while the chemical potential changes with the composition. Therefore, the appropriate
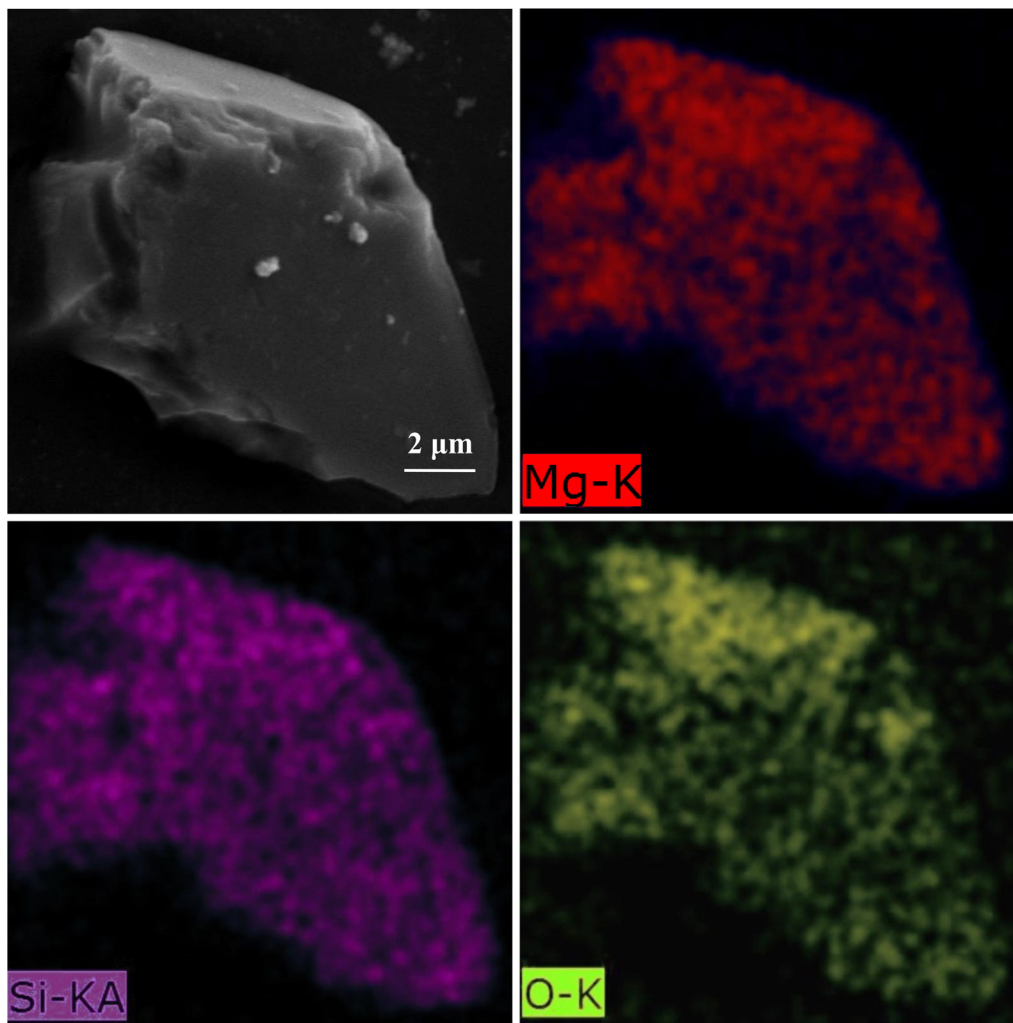
Fig. 5—SEM and EDX images of typical slag phase in product of carbothermic reduction from titanium concentrate ore.

composition for redox couple TiC_xO_{1-x}/TiC is $TiC_{0.5}O_{0.5}$, namely TiO(in $TiC_{0.5}O_{0.5}$)/TiC(in $TiC_{0.5}O_{0.5}$), considering the aim of the selective reduction process.

C. Thermodynamic Equilibrium

1. Equilibrium experiment

Based on the thermodynamic analysis above, we have designed a series of equilibrium experiments focused on the reaction between a redox couple consisting of a titanium compound and that of silicon (SiO_2/Si), as listed in Table IV. To fix the chemical potential of the equilibrium system, we designed two equilibrium compositions of titanium compounds, including $Ti_2O_3/TiC_{0.417}O_{0.583}$ (experiments 1 to 4) and TiO(in $TiC_{0.5}O_{0.5}$)/TiC(in $TiC_{0.5}O_{0.5}$) (experiments 5 to 6). Metallic Fe powder ($x_{[Si]}$ = 0 pct) and Fe-Si alloy ($x_{[Si]}$ = 10 pct) were used, which is below and above the equilibrium concentration ($x_{[Si]}$ = 2.7 pct) obtained in selective reduction process, for the distinct presentation of equilibrium process from two different sides. Besides, the total amount of Fe-Si alloy was carefully

controlled to be smaller enough in all the equilibrium experiments than that of not only titanium compound but also SiO_2 existed in slag; thus, there is rarely any composition change of titanium compound and SiO_2 during the equilibration.

Samples including titanium compounds ($Ti_2O_3/TiC_{0.417}O_{0.583}$ and $TiC_{0.5}O_{0.5}$), crushed powders of Fe-Si alloy, and pre-fused slag were treated at 1873 K (1600 °C) for 4 hours to equilibrate, and the obtained Fe-Si alloys were carefully gathered and processed after cooling to room temperature for the determination of concentration of Si. The results together with corresponding experimental details are described in Table IV.

For experiments 1 and 2, the chemical potential of reacting system is controlled by $Ti_2O_3/TiC_{0.417}O_{0.583}$. The concentration of Si in Fe-Si alloy decreases from 10 to 4.0 pct and 6.8 pct, after equilibrating with slag 1 and slag 2, respectively, indicating that during the equilibration a certain amount of Si in Fe-Si alloy has been oxidized into SiO_2, dissolving in slag phase, while a part of Ti_2O_3 has been transformed into TiO, dissolving into TiC_xO_{1-x} solid solution.
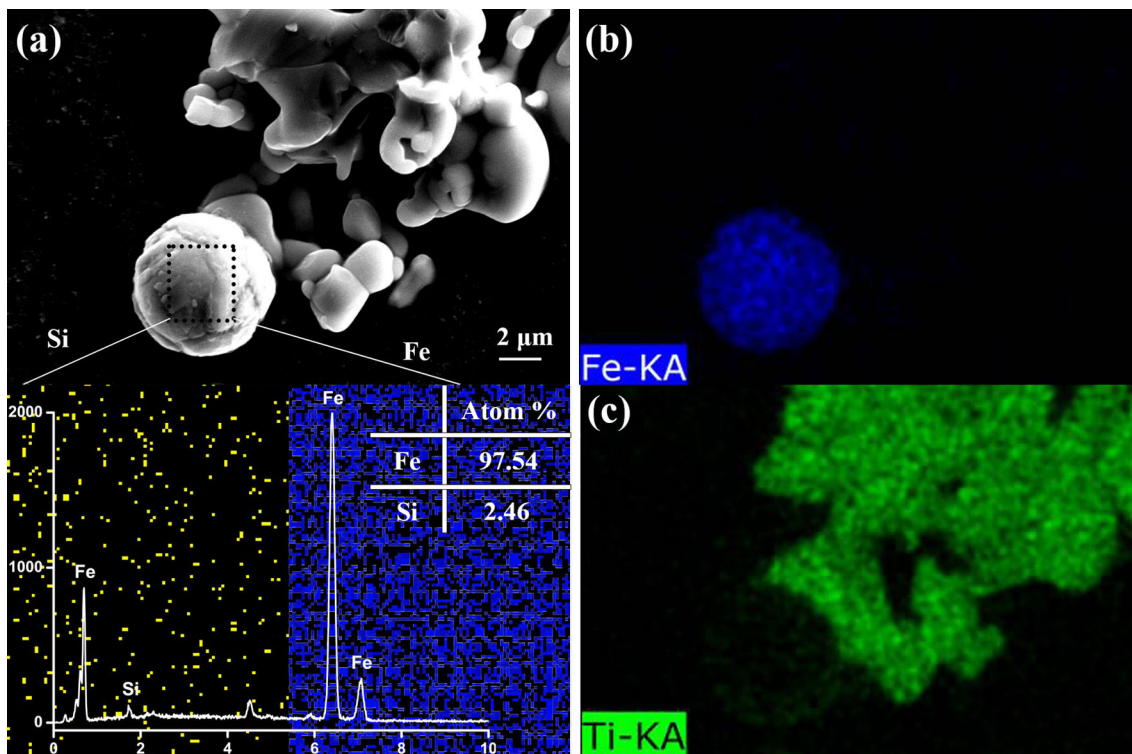
Fig. 6—SEM image of (*a*) product of carbothermic reduction from titanium concentrate ore and corresponding EDX images of element (*b*) Fe and (*c*) Ti, together with compositional analysis of Fe concentrate.

Table III.   Theoretical and Experimental Mass Change of Carbothermic Selective Reduction, Together with Concentration of Si ($x_{[Si]}$) in Reduced Fe-Si Alloy Obtained from Calculation, EDX, and ICP Results

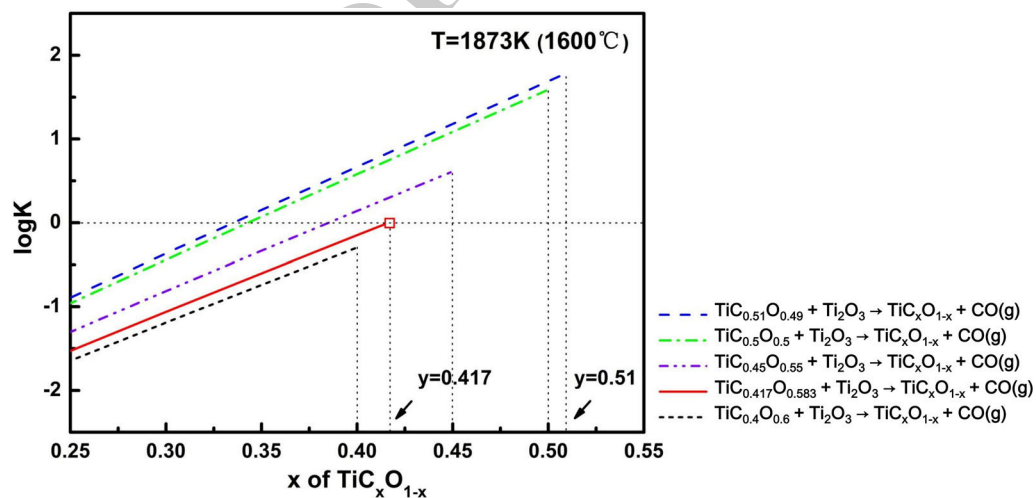| Mass Change (Theo.)	Mass Change (Exp.)	Reaction Ratio	$x_{[Si]}$ (Cal.)	$x_{[Si]}$ (EDX)	$x_{[Si]}$ (ICP)
33.9 pct	34.3 pct	101.2 pct	2.5 pct	2.46 pct	2.7 pct

Fig. 7—Equilibrium constants of the reaction between TiC_yO_{1-y} (y = 0.51, 0.50, 0.45, 0.417, and 0.40) and Ti_2O_3 turning into TiC_xO_{1-x} with a lower concentration of TiC at 1873 K (1600 °C).

For experiments 3 and 4, the reaction system is similar to experiments 1 and 2 except that the resource of Fe is pure iron instead of Fe-Si alloy. After equilibrating with $Ti_2O_3/TiC_{0.417}O_{0.583}$ and slag phase, Fe is transformed into Fe-Si alloy since the concentration of Si in obtained Fe-Si alloy is found to be 3.4 and 5.6 pct, declaring that some of SiO_2 in the slag phase has been reduced into Si, forming the Fe-Si alloy during the equilibration.

For experiments 5 and 6, the chemical potential of reacting system is controlled by TiO(in $TiC_{0.5}O_{0.5}$)/ TiC(in $TiC_{0.5}O_{0.5}$). During the equilibration, the concentration of Si in Fe increases to 2.3 and 4.5 pct, indicating that some of SiO_2 in the slag phase has been reduced into Si, dissolving in metallic Fe, while TiC in $TiC_{0.5}O_{0.5}$ was transformed into TiO.

2. Discussions

For experiments 1 to 4, the equilibrium equation of "$Ti_2O_3/TiC_{0.417}O_{0.583}$—Fe-Si alloy-slag-graphite crucible" system is

$$2.4TiC_{0.417}O_{0.583} + 1.6(SiO_2) = 1.2(Ti_2O_3) + 1.6[Si] + CO(g). \qquad [4]$$
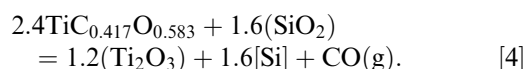
Substance existed in slag phase is surrounded with brackets, while substance in metallic Fe is decorated by square brackets. Since the activity of $TiC_{0.417}O_{0.583}$ (solid state) is reasonable to consider as 1 in the equilibrium system, the corresponding equilibrium constant is as described below:

$$K = \left(\frac{a_{[Si]}}{a_{(SiO_2)}}\right)^{1.6} \times a_{(Ti_2O_3)}^{1.2} \times P_{CO}, \qquad [5]$$

where $a_{[Si]}$, $a_{(SiO_2)}$, $a_{(Ti_2O_3)}$, and P_{CO} stand for the activity of Si in Fe-Si alloy, the activity of SiO_2 in slag phase, the activity of Ti_2O_3 in slag phase, and the partial pressure of CO, respectively. The equilibrium constant can be evaluated based on previous research of Jiang et al.[23] The relationship between the activity coefficient and the concentration of Si in Fe-Si alloy at 1873 K (1600 °C) is described below[25]:

$$\log \gamma_{Si} = -2.12 \times (1 - N_{[Si]})^2 - 0.22. \qquad [6]$$

Since the activity of Ti_2O_3 can be calculated through Factsage 6.0 based on the composition of slag phase,[26] the theoretical concentration of Si in Fe-Si alloy equilibrated with $Ti_2O_3/TiC_{0.417}O_{0.583}$ is plotted as a function of the activity of SiO_2 in Figure 8. It is clear that the concentration of Si in equilibrium Fe-Si alloy rises with the increase of the activity of SiO_2. The activity of SiO_2 can also be calculated through Factsage 6.0 based on the composition of slag phase (0.063 for slag 1 and 0.135 for slag 2), and thus the experimental equilibrium concentration of Si in Fe-Si alloy equilibrated with $Ti_2O_3/TiC_{0.417}O_{0.583}$ is plotted against the activity of SiO_2 in Figure 8. During the equilibration, the concentration of Si in Fe-Si alloy changes from two different sides (0 and 10 pct), approaching the values of equilibrium shown as the solid line in Figure 8.

The equilibrium equation of "$TiC_{0.5}O_{0.5}$—Fe-Si alloy-slag-graphite crucible" system is

$$TiC(in\ TiC_{0.5}O_{0.5}) + (SiO_2) = TiO(in\ TiC_{0.5}O_{0.5}) + [Si] + CO(g). \qquad [7]$$
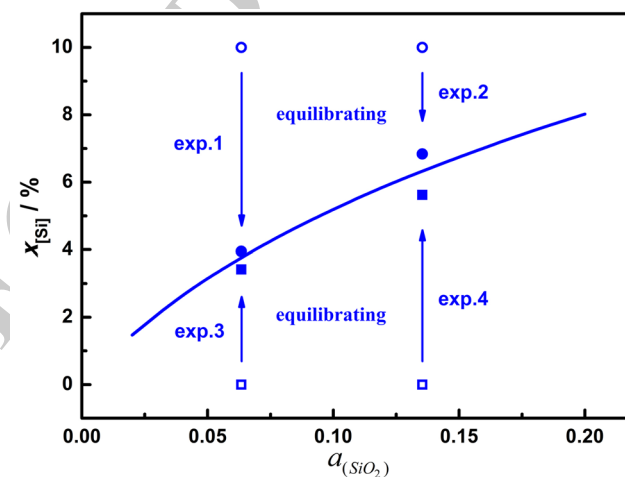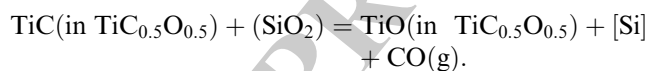

Fig. 8—Theoretical equilibrium concentration (line) and experimental concentration of Si in Fe-Si alloy before (hollow symbols) and after (solid symbols) equilibrated with $Ti_2O_3/TiC_{0.417}O_{0.583}$ and SiO_2 in slag related to the activity of SiO_2.

Table IV. Details of Equilibrium Experiments, Including Titanium Compound Utilized, Slag Type, and Concentration of Si in Fe-Si Alloy Before and After Equilibration

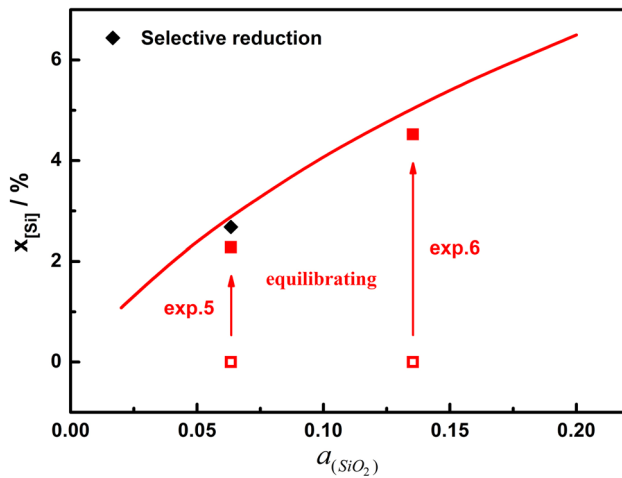|	Titanium Compound	Slag (SiO_2)	$x_{[Si]}$ in Fe-Si Alloy (Pct)	
			Before	After
1	$Ti_2O_3/TiC_{0.417}O_{0.583}$	slag 1	10	4.0
2	$Ti_2O_3/TiC_{0.417}O_{0.583}$	slag 2	10	6.8
3	$Ti_2O_3/TiC_{0.417}O_{0.583}$	slag 1	0	3.4
4	$Ti_2O_3/TiC_{0.417}O_{0.583}$	slag 2	0	5.6
5	$TiC_{0.5}O_{0.5}$	slag 1	0	2.3
6	$TiC_{0.5}O_{0.5}$	slag 2	0	4.5

Fig. 9—Theoretical equilibrium concentration (line) and concentration of Si in Fe-Si alloy before (hollow squares) and after (solid squares) equilibrated with $TiC_{0.5}O_{0.5}$ and SiO_2 in slag related to the activity of SiO_2, together with experimental concentration (solid diamond) of Si in reduced Fe-Si alloy obtained from selective reduction.

Since the activities of TiC and TiO are reasonable to consider as equal in the $TiC_{0.5}O_{0.5}$, on the basis of regular solution model introduced in previous research,[23] the corresponding equilibrium constant is as described below:

$$K = \frac{a_{[Si]}}{a_{(SiO_2)}} \times P_{CO}. \qquad [8]$$

Similarly, the theoretical concentration of Si in Fe-Si alloy equilibrated with $TiC_{0.5}O_{0.5}$ is plotted as a function of the activity of SiO_2 in Figure 9, together with experimental equilibrium concentration of Si in Fe-Si alloy obtained through not only equilibrium experiment but also selective carbothermic reduction of titanium concentrate ore. The concentration of Si in Fe-Si alloy increased from 0 pct, as displayed in Figure 9, approaching the values of equilibrium shown as the solid line. It is worth mentioning that the concentration of Si in Fe-Si alloy ($x_{[Si]} = 2.7$ pct) obtained through selective reduction of titanium concentrate ore is also very close to the theoretical value of equilibrium in the presence of $TiC_{0.5}O_{0.5}$. Therefore, the results of equilibrium experiments are in good agreement with the theoretical value obtained from thermodynamic analysis and properly explain the phenomenon that part of SiO_2 is reduced into Fe-Si alloy during selective reduction process of titanium concentrate ore.

IV. CONCLUSIONS

Carbothermic selective reduction of titanium concentrate ore for the preparation of titanium oxycarbide was demonstrated, and SiO_2 was found to be partially reduced into Fe-Si alloy during the process. The equilibrium relationship between Si dissolved in metallic Fe and SiO_2 in corresponding slag in the presence of titanium oxycarbide was analyzed thermodynamically, and then confirmed by a series of designed equilibration experiments. By controlling the chemical potential of the titanium compound, the concentration of Si in the Fe-Si alloy changes toward the value of equilibrium during the equilibration with slag phase containing SiO_2. The results of equilibration experiments agree with the thermodynamic analysis and have well explained the phenomenon of partial reduction of SiO_2 during the selective carbothermic reduction of titanium concentrate ore.

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