RETRACTION

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Retraction: Wetting Behavior of Single Crystal TiO₂ by Liquid Iron

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Wetting Behavior of Single Crystal TiO₂ by Liquid Iron

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The wetting behavior of TiO₂ by liquid iron was investigated by using the sessile drop method. A partial melting behavior was found to appear at the temperature below the melting point of the pure iron. Also a solid solution TiO_x-FeO phase was observed between the pure iron and TiO₂ substrate. The formation of this reaction layer is due to the reaction among the pure iron, TiO₂ substrate and the oxygen gas. The main source of the oxygen gas for reaction is from the TiO₂ substrate decomposition and a low partial pressure of oxygen near the sample.

KEY WORDS: wettability; partial pressure oxygen; TiO₂; decomposition.

1. Introduction

It has been known from previous research that a TiO₂ particle addition into the molten steel, can lead to the formation of an intragranular ferrite (IGF) nucleation.¹⁾ The agglomeration degree of the particles after TiO₂ addition has significant effect on both the particle number and size, which in turn, can affect the IGF nucleation efficiency. Wettability is one of the most important factors, since it has a big influence on the agglomeration behavior of the non-metallic inclusions in the melt. The free energy change of the system by collision, ΔG , can be calculated as follows:²⁾

$$\Delta G = 2\gamma_L \cdot \cos \theta$$

where γ_L is the surface tension of the liquid iron/steel, θ is the contact angle between the solid particle and melt. It can be seen that when the contact angle is smaller than 90 degrees, the free energy change becomes positive. In this case the agglomeration is unfavorable even though collisions among the inclusions are possible. On the other hand, when the contact angle is larger than 90 degrees, the free energy change becomes negative. This means that an agglomeration of particles is favorable. For an un-wetting case (contact angle > 90 degrees), the agglomeration behavior is promoted by the cavity bridge force.^{3,4)} Various previous studies^{5–12)} have been done to study the wettability of un-wetting oxides including Al₂O₃, MgO, Ti₂O₃, ZrO₂ and *etc.* However, very few experimental results for TiO₂ have been published before. Specifically Humenik *et al.*,⁵⁾ Amondarain *et al.*⁶⁾ and Muu *et al.*¹³⁾ made studies using sintered TiO₂ substrate. They reported a strong wetting behavior of TiO₂ in contact with the liquid iron. However, the wetting behavior of TiO₂ by liquid iron was not discussed in details and was not considered based on thermodynamics.

In the present work, the wetting behavior of TiO₂ in contact with liquid iron was performed by using the sessile drop method. Single crystal of TiO₂ with an orientation of (100) was selected for the measurement. After the experiment, the cross section of the sample was analyzed by using Scanning Electron Microscopy (SEM) in combination with Energy Dispersion Spectroscopy (EDS). The mechanism of the TiO₂ wettability behavior was discussed based on both the experimental results and thermodynamic considerations.

2. Experiment Method

Commercial single crystal TiO₂ (100) substrate (Ø10 mm, surface roughness ~5 nm) was used for the measurement of the wettability between TiO₂ and pure Fe at 1 813 K. The chemical composition of the pure iron specimen is given in **Table 1**. The weight of each iron specimen (Ø 3 mm, height of 4 mm) was about 0.22 g. The wettability measurements were performed by using the sessile drop method in a furnace under an Ar protective atmosphere. The sample was heated up to 1 813 K at a 100 K/min heating rate and kept at this temperature for 30 seconds. Images of the droplet profile on a substrate in the furnace were captured every few seconds by using a digital camera, through a visible light cut filter. In addition, the partial pressure of oxygen, P_{O₂}, for the inlet gas was monitored by using an oxygen sensor, and a stable value of about 9·10⁻²² atm was maintained during the experiments. The detailed description of the equipment setup has been reported in previous works.^{7,14)} The cross section of the sample after the wettability measurement was

Table 1. Chemical composition of pure iron specimen.

Content of elements [ppm]							
O	N	C	S	Cl	Cu	H	Si
17	4	8	2	40	14	5	5

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polished by using emery papers with the grit size grades ANSI 240, 320, 600 and 1 200. Also, ethanol was used as a lubricant during the polishing process. Afterwards, the 1 and 3 μm grade diamond paste was used for an additional polishing of the samples. Finally, the sample was cleaned by using acetone in an ultrasonic cleaning. After polishing, the cross section of the sample was analyzed by using Scanning Electron Microscopy (SEM) in combination with Energy Dispersion Spectroscopy (EDS). The working acceleration voltage of SEM-EDS is in the range between 15 and 20 kv.

3. Results and Discussion

3.1. Contact Angle between TiO_2 Substrate and Liquid Iron

Table 2 shows the dynamic change of the wetting process for the pure iron cylinder on the single crystal TiO_2 substrate. It can be seen that a small melting region started to appear at a temperature of 1 739 K. This moment was selected as an initial time ($t = 0$ s) for the future observations. When the temperature reached 1 813 K ($t = 45$ s), the iron specimen was fully melted and had strong wetting on the substrate. During the following 30 seconds of holding at the temperature 1 813 K, the droplet of the liquid iron was spread on the substrate surface. The method for measurement of contact angle, θ , between the iron specimen and TiO_2 substrate at different time of experiment is shown schematically in Fig. 1. In this study, the “melting region” corresponds to the separate liquid phase between the solid/liquid iron and the solid substrate. A detailed discussion of this melting region is presented in sections 3.2 and 3.3.

Fig. 1. Schematic illustration of the measurement of the contact angle, θ , between a solid TiO_2 substrate and (a) solid and (b) liquid iron. (Online version in color.)

The measured temperatures and wetting contact angles θ are shown in Fig. 2 as a function of the holding time. It can be seen that the measured wetting contact angle decreased from 45 to 37 degrees during 45 s with an increased temperature in the furnace. When the full melting stage is arrived at 1 813 K, the θ value continuously decreased from 37 to 30.5 degrees within 30 s at the given temperature before the quenching. This wetting behavior for TiO_2 substrate observed in present work is consistent with that of Humenik *et al.*⁵⁾ and Amondarain *et al.*⁶⁾ Amondarain *et al.*⁶⁾ reported that the value of contact angle between TiO_2 and liquid iron can significantly decrease with an increasing of holding time at constant temperature.

3.2. Investigation of Melting Region between Substrate and Pure Fe

As was shown in Table 2, a melting region appears at 1 739 K, which is much lower than the melting temperature of pure iron ($\sim 1\,813$ K). According to the FeO– TiO_2 phase diagram shown in Fig. 3,¹⁵⁾ a phase of the melting region near 1 739 K (1 466°C) is close to the solid solution of $\text{FeO} \cdot 2\text{TiO}_2$. In order to determine a composition of this melting region, a cross section of the iron specimen and substrate after the experiment was investigated by using an EDS analysis. The typical SEM image of investigated melting region is shown in Fig. 4. It was found from the elemental mapping (Fig. 5) that the melting region is a complex oxide

Fig. 2. Contact angle, θ , between a TiO_2 substrate, the melting region and the furnace temperature as a function of the holding time.

Table 2. Dynamic observation of a pure Fe sample on a TiO_2 substrate at different temperatures, T , and holding times, t .

phase containing mostly Ti and Fe oxides. The contents of the Fe and Ti elements in this melting region are on average 25.0 and 37.5 mass%, respectively. According to the ratio of Fe/Ti, this complex oxide phase can be roughly judged to consist of a mixture of $\text{FeO} \cdot 2\text{TiO}_2$ and $\text{FeO} \cdot \text{TiO}_2$.

The vertical cross section of the interphase layer between the Fe droplet and TiO_2 substrate at the central part was analyzed by using a SEM-EDS spot analysis, as is shown in

Fig. 3. FeO-TiO_2 phase diagram.¹⁵⁾

Fig. 4. Cross section of micrograph of a solidified pure Fe droplet on a TiO_2 substrate including the observed melting region.

Fig. 6. It can be seen that the complex oxide layer between the Fe droplet and TiO_2 substrate has on average a $7 \mu\text{m}$ thickness. It was found that the composition of the complex

Fig. 6. Cross sectional analysis of the complex oxide layer between a Fe droplet and a TiO_2 substrate at the central part of the sample.

Fig. 7. Ti/O ratio in a TiO_2 substrate including the $\text{TiO}_x\text{-FeO}$ reaction layer.

Fig. 5. Element mapping of melting region between pure Fe droplet and TiO_2 substrate. (Online version in color.)

oxide phase near the pure iron droplet is close to a $\text{FeO} \cdot \text{TiO}_x$ phase and the composition near the TiO_2 substrate is close to a $\text{FeO} \cdot 2\text{TiO}_x$ phase. The presence of such “reaction layer” between the sintered TiO_2 substrate and the Fe/steel droplet in similar experiments has also been observed by other researcher.^{5,6)} However, the mechanism of the reaction layer formation in those studies was not considered in details.

Moreover, even though the O content in material can only be determined roughly by the EDS analysis, it is clear that the ratio of Ti/O (in atomic percentages) on a substrate surface is close to TiO_2 , as is shown in Fig. 7. However, this ratio inside a substrate varied mostly between TiO_2 and Ti_2O_3 . It indicates that some decomposition of the TiO_2 substrate has taken place at the given experimental condition.

3.3. Mechanism of Melting Region Formation

The liquid melting region in the temperature range from 1 739 to 1 813 K can appear by oxidation of a Fe on surface of iron specimens with following formation of a TiO_x -FeO solid solution. The latter has a significantly lower melting temperature than pure Fe (1 813 K). Suzuki *et al.*²⁰⁾ has reported a high solubility of FeO in the TiO_2 . Iron can be oxidized by the oxygen: a) that has remained in a furnace chamber after a vacuum pre-treatment before a wetting experiment, b) from Ar gas used in the chamber for protection during the experiments and c) obtained as a result of a decomposition of TiO_2 substrate at a high temperature and a low partial pressure of oxygen near the sample, P_{O_2} .

In order to explain the strong wetting behavior of a TiO_2 substrate in contact with pure iron, the formation mechanism of the melting region needs to be considered thermodynamically. The main possible reactions and standard Gibbs free energies in the respective temperature intervals are listed in Table 3. Unfortunately, reliable thermodynamic data of a $\text{FeO} \cdot 2\text{TiO}_2$ formation are missing in publications up to now.

The calculated relationships between the equilibrium P_{O_2} values and the temperatures for the main possible reactions from Table 3 are shown in Fig. 8. These calculations were done under the assumption that the activities of other components in these reactions (such as a_{Fe} , a_{FeO} , a_{TiO_x} , $a_{\text{FeO} \cdot \text{TiO}_2}$ and $a_{2\text{FeO} \cdot \text{TiO}_2}$) were equal to unity. In this figure, Reactions

(1) and (2) between the O_2 gas and solid/liquid Fe are presented by the solid lines. Reactions (7) and (8) representing a formation of $\text{FeO} \cdot \text{TiO}_2$ and $2\text{FeO} \cdot \text{TiO}_2$ correspond to the dash lines. It should be pointed out that the ΔG° values for these reactions were obtained for the temperature interval from 1 173 to 1 373 K. In this study, the obtained thermodynamic relationships for these reactions were extrapolated to the temperatures of the wetting experiment. Reactions (9)–(11) represent the possible decomposition of TiO_2 substrate and are presented by the dotted lines. In addition, the gray zone corresponds to the temperature interval during the wetting experiment at which the melting region was observed visually. It is apparent that Reactions (1), (2), (7) and (8) will take place, when the P_{O_2} near the sample is larger than the equilibrium P_{O_2} value of the respective reactions. However, the Reactions (9)–(11) representing a decomposition of TiO_2 substrate will take place, if the P_{O_2} value near the sample is smaller than the equilibrium P_{O_2} for these reactions.

Depending on the different P_{O_2} levels near the sample, the following three possible mechanisms for a formation of a melting region during experiments can be considered:

Mechanism I. If the P_{O_2} value near the sample is >

Fig. 8. Relation between the equilibrium P_{O_2} and temperature for different reactions.

Table 3. Standard Gibbs free energy change for different reactions.

No.	Chemical reaction	ΔG° [J/mole]	T [K]	Ref.
1	$\text{Fe(s)} + 1/2 \text{O}_2(\text{g}) = \text{FeO(s)}$	$-264\,002 + 64.591 \cdot T$	298–1 650	[18]
2	$\text{Fe(l)} + 1/2 \text{O}_2(\text{g}) = \text{FeO(l)}$	$-256\,061 + 53.681 \cdot T$	1 644–2 273	[16]
3	$\text{Ti(s)} + \text{O}_2(\text{g}) = \text{TiO}_2(\text{s})$	$-940\,982 + 177.569 \cdot T$	298–1 943	[16]
4	$3\text{Ti(s)} + 5/2 \text{O}_2(\text{g}) = \text{Ti}_3\text{O}_5(\text{s})$	$-2\,435\,080 + 420.492 \cdot T$	298–1 943	[16]
5	$2\text{Ti(s)} + 3/2 \text{O}_2(\text{g}) = \text{Ti}_2\text{O}_3(\text{s})$	$-150\,256 + 258.069 \cdot T$	298–1 943	[16]
6	$7 \text{Ti}_3\text{O}_5(\text{s}) = 5 \text{Ti}_4\text{O}_7(\text{s}) + \text{Ti(s)}$	$127\,680 + 59.9 \cdot T$	1 750–1 950	[17]
7	$\text{Fe(s)} + 1/2 \text{O}_2(\text{g}) + \text{TiO}_2(\text{s}) = \text{FeTiO}_3(\text{s})$	$-271\,600 + 63.35 \cdot T$	1 173–1 373	[19]
8	$\text{Fe(s)} + 1/2 \text{O}_2(\text{g}) + \text{FeTiO}_3(\text{s}) = \text{Fe}_2\text{TiO}_4(\text{s})$	$-282\,400 + 62.93 \cdot T$	1 173–1 373	[19]
9	$4 \text{TiO}_2(\text{s}) = \text{Ti}_4\text{O}_7(\text{s}) + 1/2 \text{O}_2(\text{g})$	$380\,352 - 109.607 \cdot T$	1 750–1 950	*
10	$3 \text{TiO}_2(\text{s}) = \text{Ti}_3\text{O}_5(\text{s}) + 1/2 \text{O}_2(\text{g})$	$387\,866 - 112.215 \cdot T$	298–1 943	*
11	$2 \text{TiO}_2(\text{s}) = \text{Ti}_2\text{O}_3(\text{s}) + 1/2 \text{O}_2(\text{g})$	$379\,908 - 97.069 \cdot T$	298–1 943	*

*: Reactions (9)–(11) representing a TiO_x decomposition were obtained by using a combination of the respective chemical Reactions (3)–(6).

$3 \cdot 10^{-11}$ atm, the Reactions (1), (2), (7) and (8) will take place and Fe on surface of iron specimen is oxidized only by the oxygen remaining in a chamber after a vacuum pre-treatment and oxygen from the Ar gas. As a result, a “melting region” containing the liquid FeO–TiO_x phases can be formed. However, at the given values of P_{O2}, a decomposition of the TiO₂ substrate is unlikely. These results contradict the obtained results for the Ti/O ratio in this substrate after an experiment (Fig. 7).

Mechanism II. If the P_{O2} value near the sample is varied from $2 \cdot 10^{-12}$ to $3 \cdot 10^{-11}$ atm, the Fe can be oxidized by the chamber oxygen (Reactions (1), (2), (7) and (8)) only at a low temperatures (< 1 700 K), at which the formed FeO–TiO_x phases are solid. However, partial decomposition of TiO₂ substrate (Reactions (9) and (10)) is thermodynamically possible if the temperatures are larger than 1 720 K. This is due to that the P_{O2} of oxygen near the sample is lower than the equilibrium P_{O2} value for these reactions. As a result, the produced O₂ and a high temperature can contribute to the formation of a liquid FeO–TiO_x phase between the TiO₂ substrate and iron specimen. Moreover, the O₂ gas, which is produced during decomposition of a TiO₂ substrate, can increase partial pressure of oxygen near the sample. Consequently, the oxidation reactions can take place at temperatures larger than 1 720 K.

Mechanism III. If the P_{O2} value near the sample is lower than $2 \cdot 10^{-12}$ atm, the Reactions (1), (2), (7) and (8) are thermodynamically unlikely. However, the decomposition of a TiO₂ substrate (Reactions (9)–(11)) will take place at temperatures < 1 700 K. As a result, the produced O₂ can oxidize the Fe only in a local zone at the contact surface between the TiO₂ substrate and iron specimen. An increase of the P_{O2} value near the sample and a possibility for oxidation reactions will depend on the extent of the decomposition reaction and the mass of the TiO₂ substrate used in the experiments.

According to the thermodynamic consideration and the obtained experimental results, it can be concluded that the *Mechanisms II* or *III* for a formation of a liquid melting region in the given wetting experiment are more likely in comparison to *Mechanism I*. In this case, the measurement of the wettability contact angle between the TiO₂ substrate and liquid iron is impossible due to the TiO₂ decomposition and the formation of the FeO–TiO_x melting region.

4. Conclusion

The present work is focused on a wetting of behavior of the TiO₂ substrate and liquid iron system. The sessile drop method was used to measure the contact angle under a controlled oxygen partial pressure. The following most

important conclusions have been found in the present work:

(1) A melting region appears between the TiO₂ substrate and iron specimen at a temperature below the melting point of the pure iron. This is due to the formation of a solid solution of TiO_x–FeO which has a lower melting temperature than iron.

(2) The TiO_x–FeO melting region formed due to the reactions among the pure iron, TiO₂(s) and the oxygen gas, which significantly dependent on the partial pressure of oxygen, P_{O2}, and temperature in the furnace chamber.

(3) The main source of the oxygen for these reactions is from the decomposition of the TiO₂ substrate at a high temperature and a low partial pressure of oxygen near the sample during the wetting experiment.

(4) The wetting contact angle, θ , of liquid TiO_x–FeO phase and TiO₂ substrate decreased continuously from 37 to 30.5 degrees within 30 s of holding at a 1 813 K temperature.

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