

# Wettability of TiN by Liquid Iron and Steel

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The wettability of liquid iron and steel in contact with TiN substrates was studied. Initially, Spark Plasma Sintering (SPS) was used to prepare the samples using different operational conditions. It was found that a relative density of 96% and surface roughness values smaller than 250 nm could be obtained by using the following settings: a 1873 K temperature, a 89.2 MPa pressure and a 5 min sintering time. Thereafter, the wettability of the liquid iron and steel in contact with the TiN substrates was measured based on video recordings, at the moment when the metals started to melt. The results show that the contact angle value for a TiN/pure Fe system (130 to 87.9 degrees for 900 s) is larger than the value for a TiN/steel system (110 to 50 degrees for 981 s). Therefore, it is concluded that TiN has good resistance to the corrosion of the liquid iron and steel. In the liquid iron case, its wetting behaviour occurs mainly due to the oxygen increase in liquid iron after a full melting. However, in the liquid steel case the contact angle decreases sharply due to both the effects of an oxygen increase in liquid steel and a precipitation of Ti(N,C,O) at the interface.

KEY WORDS: contact angle; TiN; iron; steel; solubility.

## 1. Introduction

Nitride ceramics have a good potential to become significant materials for some steel making applications. Currently, a lot of research work is concentrated on optimizing these ceramics in order to apply them into steel making processes.<sup>1–3)</sup> Generally, a ceramic material should fulfill many properties, such as a good resistance to corrosion by liquid steel, a good thermodynamic stability, a low solubility in liquid steel. Titanium nitride is one of these ceramics, which have the above mentioned important properties. However, Morohoshi *et al.*<sup>4)</sup> has pointed out that the solubility of titanium nitride may be affected by the silicon content in steel. This exemplifies that further research is necessary.

Although the wettability of liquid iron/steel with nitride ceramic is one of the most important properties, only Chuchmarev *et al.*<sup>5)</sup> and Amadeh *et al.*<sup>6)</sup> have presented contact angle data for these systems. This is due to the difficulty of preparation nitride substrates with high relative density and small surface roughness. The optimum condition ranges of key parameters such as temperature and pressure is essentially narrow. Therefore, it is generally difficult to find the best condition. Especially, the optimized temperature range will be sensitively shifted according to the powder size. Moreover, very few experiments have been conducted to analyze the continuous wetting process of the droplets. Therefore, the present work is focused on studying the making of TiN substrates with a high relative density and a low

surface roughness. Furthermore, the investigations were performed for the continuous wetting process of TiN substrates in contact with liquid iron and steel in an Ar atmosphere.

## 2. Experimental Work

### 2.1. TiN Substrate Preparation by SPS

One of the aims in this study was to prepare substrates with a high relative density and a low surface roughness, so as to insure that the reliability and reproducibility of the contact angle measurement is high. Here, the powder size, pressure, holding temperature, and its holding time are considered as important factors for obtaining a fully densified substrate sintered using the Spark Plasma Sintering (SPS) process.

#### 2.1.1. Sintering Procedure

The basic configuration of the SPS (Spark Plasma Sintering) apparatus (SPS-2050, Sumitomo Coal Mining Co. Ltd., Japan) used in the experiments is shown in **Fig. 1**. It consists of a uniaxial pressure device in which the water-cooled punches also work as electrodes. In addition, a water-cooled reaction chamber that can be evacuated, a pulsed DC generator, and a system controlling the pressure, temperature and punch position.

The prepared powders with prescribed powder sizes had weights ranging from 2 to 3 g, as shown in **Table 1**. These powders were packed into a cylindrical graphite die (outside diameter, 30.2 mm; inside diameter, 15 mm; height, 30.2 mm). Thereafter, they were sintered in a SPS apparatus at a vacuum pressure of about 5 Pa. The inner side of the

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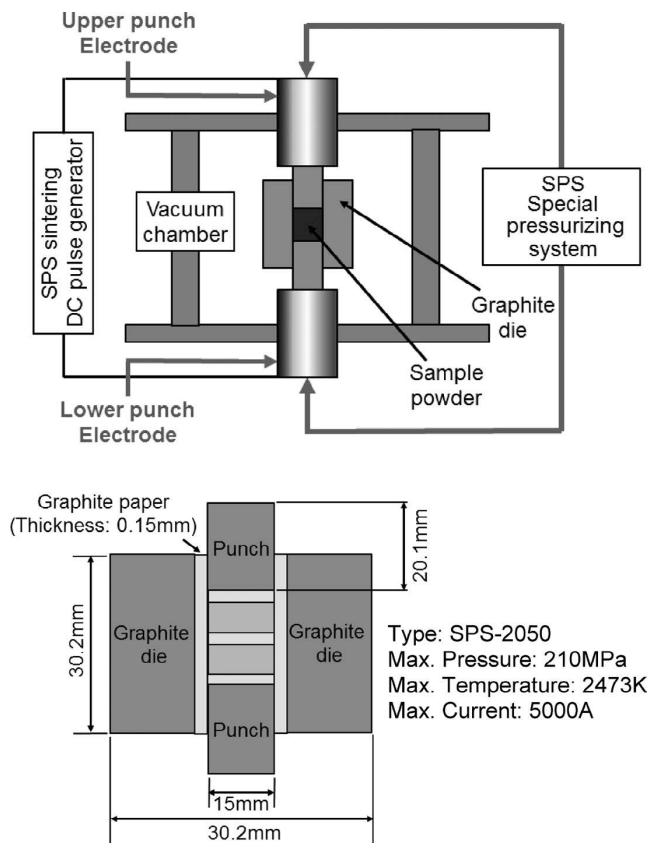


Fig. 1. Basic configuration of a SPS apparatus (SPS-2050, Sumitomo Coal Mining Co. Ltd, Japan).

Table 1. Characteristics of powders used in this work.

| Particle      | Purity [mass%]                        | Size [ $\mu\text{m}$ ]   | Specific surface [ $\text{m}^2/\text{g}$ ] | Supplier      |
|---------------|---------------------------------------|--------------------------|--------------------------------------------|---------------|
| Nano-size TiN | >98.5 (Fe < 0.1; Si < 0.05; Ni < 0.1) | 0.045–0.055              | 17–27                                      | Plasma Chem   |
| Coarse TiN    | >99 (74.7–80.1Ti)                     | Aver. 0.63 $\mu\text{m}$ | –                                          | Sigma Aldrich |

graphite die was always covered by graphite paper (thickness, 150  $\mu\text{m}$ ). When two substrates were simultaneously made in one trial using larger powders, they were separated by another graphite paper to avoid contact during the sintering process.

The uniaxial pressure program in the sintering process is shown in Fig. 2. A prescribed uniaxial pressure for pressing powder of 50, 89.2 or 100 MPa was applied during the sintering. However, these pressures were released at the end of sintering process. The shrinkage was also determined by a linear gauge, which could measure the vertical displacement. The temperature program in the sintering process is shown in Fig. 2. Prescribed holding temperatures of 1 473, 1 573, 1 673, 1 723, 1 773 or 1 873 K and holding times of 5, 10 or 20 min were applied in the experiments. Also, an optical pyrometer was focused on the surface of the graphite die, when the temperature had reached a value over 873 K. The temperature was monitored and regulated by this optical pyrometer. At the initial heating stage, the sharp temperature increase cannot be accurately controlled up to 873 K. Thus in order to obtain a stable temperature increase, an anneal-

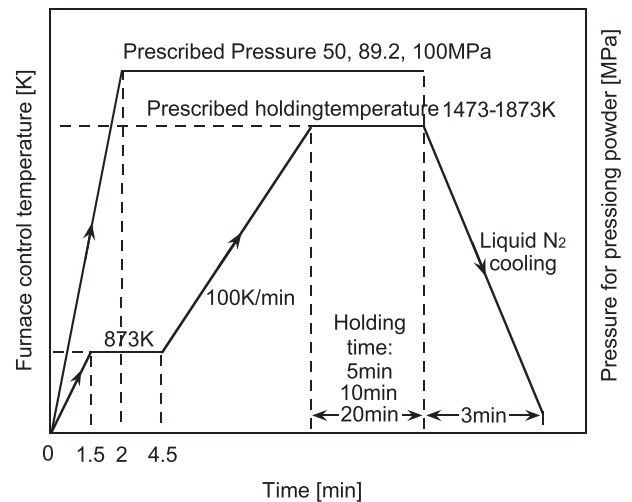


Fig. 2. Illustration of the SPS sintering conditions (an Uniaxial pressure program and a temperature program).

ing stage at 873 K for 3 min is necessary. A heating rate of 100 K/min was adopted for all trials up to the prescribed holding temperature. At the end of the sintering process, the pulse current was turned off and the substrate sample was cooled down to room temperature by using liquid  $\text{N}_2$ . Overall, the sintering steps, which include the heating and holding steps, were finished within 45 min for all trials.

Afterwards, the substrates were polished at room temperature. In order to remove surface contaminations from the graphite paper and graphite die, the following polishing procedure was used:

Step 1: Polishing by using emery papers with the following grit size grades: ANSI 240, 320, 600 and 1200.

Step 2: Electrolytic extraction (500 coulomb) with a 10%AA (10 v/v% acetylacetone-1 w/v% tetramethylammonium chloride-methanol) electrolyte and ultrasonic cleaning during 15 min with acetone. In order to make 10%AA, tetramethylammonium chloride (10 g) was dissolved in methanol (200–400 mL). Thereafter, acetylacetone (100 mL) was added, followed by an addition of methanol so that the volume became 1 000 mL.

Step 3: Polishing using a 3  $\mu\text{m}$  grade diamond paste and a 1 to 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  colloid as an abrasive (polishing using an abrasive with a different size for 10 min, respectively).

Step 4: Ultrasonic cleaning during 10 min with acetone.

## 2.1.2. Characterization of TiN Substrates

### 2.1.2.1. Relative Density

The densities of the sintered substrates were obtained by the Archimedes immersion method by using a 99.9% methanol solution as the immersion medium.

### 2.1.2.2. Surface Roughness

Surface roughness measurements were conducted by using a surface roughness equipment (Talysurf Ultra precision measurement system FTS PGI 800). The diamond tip diameter used during the measurements was 2  $\mu\text{m}$ . Furthermore, the measuring speed was 0.5 mm/s to obtain 4 mm data lengths. Each measurement was repeated for 3 times. In the evaluation of the results, the parameter arithmetic average of (Ra) was chosen as an average surface roughness value.

## 2.2. Wettability Measurements on TiN Substrate

The chemical compositions of the pure iron and steel materials are shown in **Table 2**. The iron or steel samples were machined into a cylindrical shape with a diameter of 3 mm and height of 4 mm. The weight of each cylinder was about 0.22 g.

The TiN substrates were made under the sintering condition of a 1 873 K as target temperature a 89.2 MPa as processing pressure and a 5 min as sintering time, as described more in detail in the results chapter 3.1. All the substrates were very smooth ( $< 200$  nm) and had a disk shape. The diameters were 10–15 mm and the thicknesses were 1–2 mm.

The iron or steel sample was placed on a substrate, which in turn, was placed on a platinum plate (diameter 13.0 mm; thickness 1.4 mm) on an  $\text{Al}_2\text{O}_3$  tube pedestal, as shown in **Fig. 3**. The temperature was measured using a thermocouple that was welded to the back of the platinum plate. Then, the sample was heated at 100 K/min through the quartz plates by two halogen lamps, under Ar gas atmosphere. The halogen lamps were separated from the sample chamber by quartz plates. The sample was maintained at 1 815 K for a prescribed time and then cooled at a 20 K/min rate. The oxygen partial pressure,  $\text{PO}_2$ , of the inlet Ar gas at the inlet was maintained at values between  $10^{-20}$  and  $10^{-22}$  atm at 923 K by using a gas purifying system.

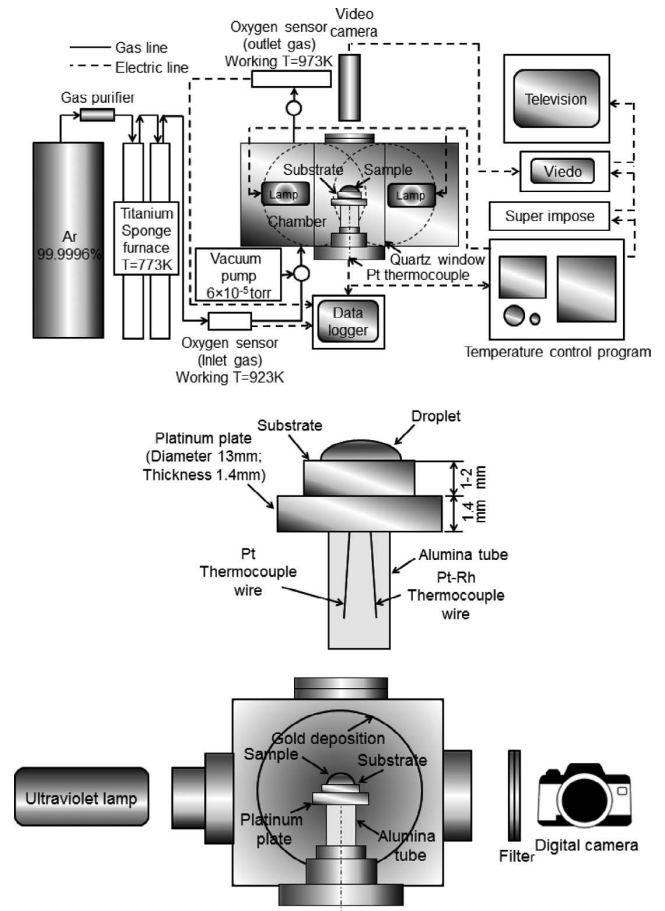
The contact angle of iron or steel melts on the substrate was continuously measured just after the metal sample was melted. The sample was monitored through a top window using a video camera, in order to check whether the sample is melt or not. The measured temperatures were superimposed on the video and recorded on a VHS tape during the course of the experimental work. The temperature and oxygen partial pressures,  $\text{PO}_2$ , were also recorded by a digital data logger. The sample was irradiated with ultraviolet light from the left side. Also the shape of the sample was observed through a visible light cut filter using a digital camera. After a temperature of 1 623 K was reached, the image of the sample was captured every few seconds. After the completion of the experiment, a cross section of the interface between the iron/steel melts and substrate was examined using a Scanning Electron Microscope (SEM) image in combination with Energy Dispersion Spectroscopy (EDS). The purpose of the SEM observation of the cross section is to mainly identify whether the reaction layer exist or not.

## 3. Results

### 3.1. TiN Substrate Preparation

3.1.1. Relative Density of TiN Substrate (Coarse Powder Size, Aver.  $0.63 \mu\text{m}$ ; Nano-powder Size, Aver. 50 nm)

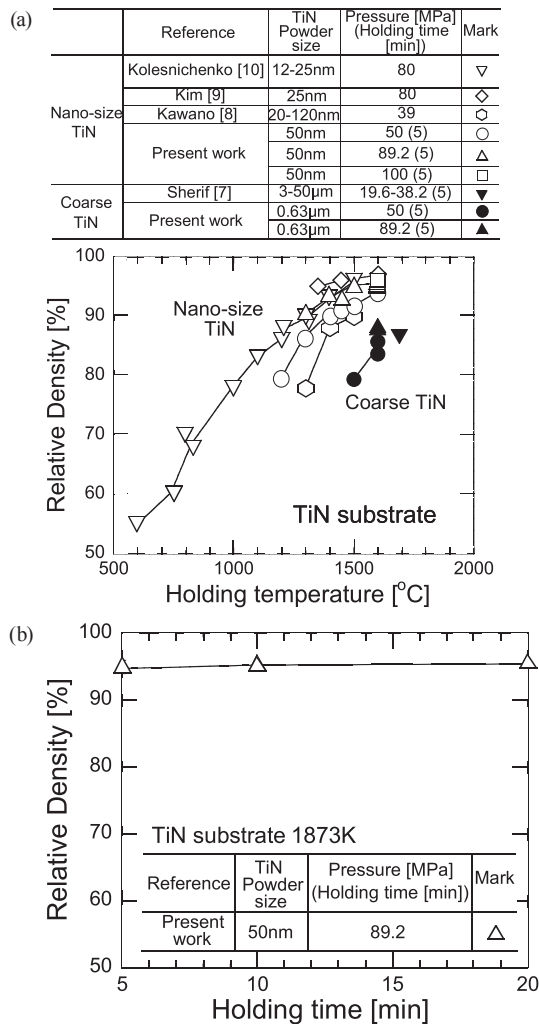
**Figure 4(a)** shows a comparison of the relative density,  $\rho_r$ , data for a TiN substrate obtained in the present work with data from previous research.<sup>7–10</sup> It can be seen that the relative density of the TiN substrate clearly increased with an increased holding temperature, regardless of the powder size. For nano-size powder sintered TiN substrates at temperatures over 1 473 K, all  $\rho_r$  values (from 79.5% to 96.3%) correspond quite well with those of previous



**Fig. 3.** Schematic diagram of contact angle measurement apparatus.

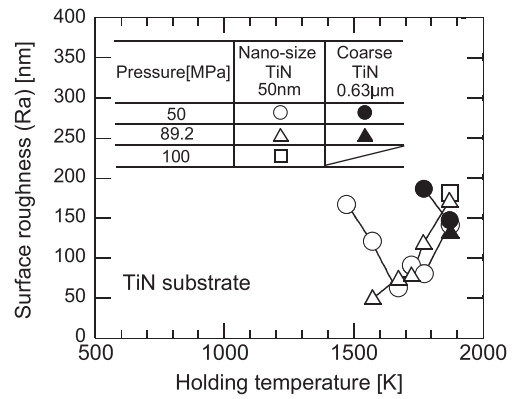
**Table 2.** Chemical composition of the pure Fe and carbon steel samples.

| Pure Iron/steel      | Composition |        |      |       |       |      |       |       |
|----------------------|-------------|--------|------|-------|-------|------|-------|-------|
|                      | O           | N      | H    | S     | P     | Mn   | C     | Al    |
| Pure Fe [mass ppm]   | 67          | 7      | 5    | 2     | —     | —    | 8     | —     |
|                      | Cr          | Cu     | Si   | Mo    | Cl    | Ni   | V     | Ti    |
|                      | —           | 14     | 5    | —     | 40    | —    | —     | —     |
| Carbon steel [mass%] | O           | N      | H    | S     | P     | Mn   | C     | Al    |
|                      | 0.0015      | 0.0126 | —    | 0.042 | 0.012 | 1.43 | 0.28  | 0.013 |
|                      | Cr          | Cu     | Si   | Mo    | Cl    | Ni   | V     | Ti    |
|                      | 0.18        | —      | 0.65 | 0.037 | —     | 0.13 | 0.084 | 0.022 |

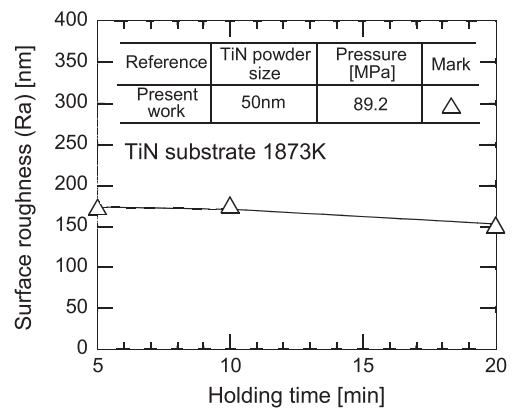


**Fig. 4.** Relative density of TiN substrate. (a) Relative density change with different powder sizes, pressures and holding times. (b) Effect of holding time during sintering on the relative density of TiN substrate.

studies<sup>7-10)</sup> (from 78% to 97%). In addition, it is seen that a higher pressure (89.2 MPa, 100 MPa) also promotes the densification of substrates, compared to a lower pressure (50 MPa). However, such a difference between the 50 MPa and 89.2 MPa pressures became smaller from 4.2% to 1.0% with an increased the temperature from 1 573 to 1 873 K. For a 89.2 MPa pressure, the maximum values of the relative density for the substrates made by coarse TiN (0.63 μm) and nano-size TiN (50 nm) powders were 88.4% (1 600°C × 5 min, 89.2 MPa) and 96% (1 600°C × 5 min, 89.2 MPa), respectively. Sherif *et al.*<sup>7)</sup> and Kawano *et al.*<sup>8)</sup> obtained same tendencies as was found in the present work by comparing the relative densities of the substrates sintered by using different powder sizes. Meanwhile, W. Kim *et al.*<sup>9)</sup> obtained a TiN substrate with a  $\rho_r$  value of 97%, for sintering at a temperature of 1 873 K. This was also mainly due to the use of a finer TiN powder size (25 nm) in comparison to the present size (50 nm). Among three factors (powder size, pressure, and holding temperature), it can be concluded that both the powder size and holding temperature are the key factors to obtain a fully dense substrate. As for the substrates sintered with nano-sized TiN particles (50 nm), the effect of the holding time during sintering was also examined under the condition of a 1 873 K temperature and a 89.2 MPa pres-



**Fig. 5.** Effect of the powder size, pressure and holding temperature on the average surface roughness (Ra) of TiN substrates.



**Fig. 6.** Effect of the holding time during sintering on the average surface roughness (Ra) of TiN substrates.

sure (Fig. 4(b)). It was found that an increase of the holding time from 5 to 20 min cannot affect the  $\rho_r$  value. This result is consistent with the findings of Torbov *et al.*<sup>11)</sup>

### 3.1.2. Surface Roughness

As mentioned earlier, each measurement was repeated for 3 times. In the evaluation of the results, the parameter arithmetic average of (Ra) was chosen as the average surface roughness value. As shown in **Figs. 5 to 6**, all the nitride substrates are regarded to be smooth ( $< 250$  nm), although this surface roughness measurements might be crude due to the use of a diamond tip diameter of 2 μm.

Figures 5 and 6 show the surface roughness (Ra) of TiN substrates as a function of the holding temperature and holding time, respectively. The value range of Ra for TiN substrates varies between 50 and 200 nm in the present work. It can be seen that in the range of values determined at temperatures lower than 1 673 K the surface roughness of the TiN substrate (powder size 50 nm, pressure 50 MPa) decreased with an increased holding temperature. This phenomenon indicates that the substrate was densified as the holding temperature was increased from 1 473 to 1 673 K. Thereby, the number of open pores near the surface decreased. However, after reaching a temperature of 1 673 K, the surface roughness of the substrate increased. This is probably because of an increased grain size of the substrates. According to Fig. 6, it is found that the surface roughness (Ra) decreased slightly with an increased holding time.

### 3.1.3. Grain Size

The grain size of TiN substrates increases with increasing holding temperatures, regardless of the powder size and pressure, as shown in Fig. 7. Thus, this phenomenon has led to an increase of the surface roughness with temperature. This is due to that there is a clear correlation between the surface roughness and grain size, as shown in Fig. 8. As seen in Fig. 7, the results in this work show a good agreement with those of Kolesnihenko *et al.*<sup>10)</sup> and Kawano *et al.*<sup>8)</sup> Moreover, the present values are a half of those of Kim *et al.*<sup>9)</sup> The grain size is  $0.87\ \mu\text{m}$  for  $1\ 573\ \text{K} \times 5\ \text{min}$  and  $89.2\ \text{MPa}$ ,  $1.02\ \mu\text{m}$  for  $1\ 673\ \text{K} \times 5\ \text{min}$  and  $89.2\ \text{MPa}$ ,  $2.09\ \mu\text{m}$  for  $1\ 773\ \text{K} \times 5\ \text{min}$  and  $89.2\ \text{MPa}$ ,  $2.90\ \mu\text{m}$  for  $1\ 873\ \text{K} \times 5\ \text{min}$  and  $89.2\ \text{MPa}$ ,  $2.18\ \mu\text{m}$  for  $1\ 873\ \text{K} \times 5\ \text{min}$  and  $50\ \text{MPa}$ , and  $4.55\ \mu\text{m}$  for  $1\ 873\ \text{K} \times 20\ \text{min}$  and  $89.2\ \text{MPa}$ , respectively. This is shown more clearly in

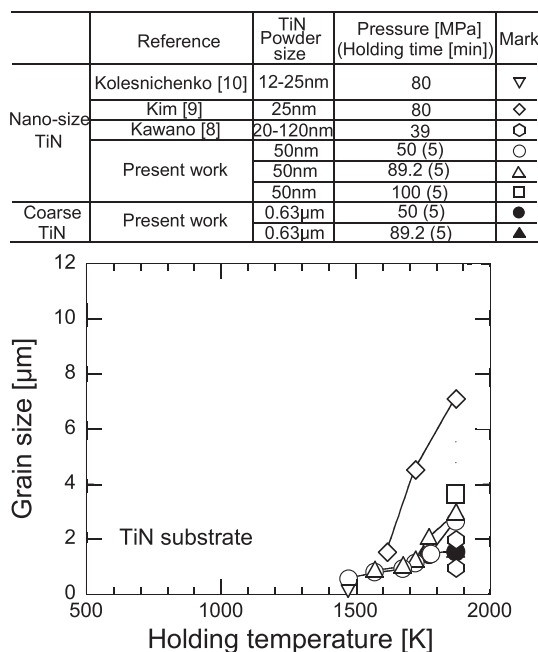


Fig. 7. Effect of the powder size, pressure and holding temperature on the average grain size of TiN substrates.

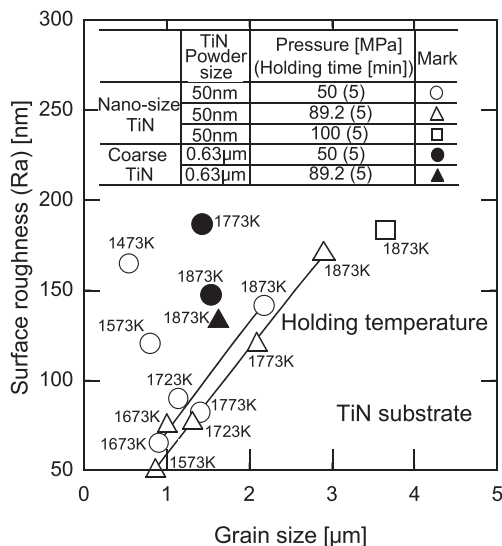


Fig. 8. Relationship between the surface roughness and grain size of TiN substrates.

Table 3.

In order to make TiN substrates with a high relative density and a low surface roughness, the sintering condition of  $1\ 873\ \text{K}$ ,  $89.2\ \text{MPa}$  and  $5\ \text{min}$  sintering time was adopted in the present work.

### 3.2. Contact Angle of Iron/Steel Melt on TiN Substrates

The aim of this study was to observe the continuous wetting process of the pure Fe and steel melt in contact with TiN substrates. This was done in an Ar atmosphere, where the oxygen partial pressure was controlled during the experiments.

The contact angle was measured at both the left and right sides of the sample at the triple point between the gas, substrate, and iron or steel melt. This was done by using the images obtained after the sample was melted. The average value of the measured contact angle is plotted as a function of the time in Figs. 9(a) and 10(a). In addition, the contact angle values from previous studies<sup>5,6)</sup> are also plotted in the figures. The temperature and oxygen partial pressures,  $\text{PO}_2$ , data are also plotted in Figs. 9(b) and 10(b). Also, the time at which iron was just fully melted, is defined as the initial point of the measurement, as seen in Figs. 9 to 10.

In order to examine the change of the interface during an experiment using the TiN/pure Fe system, different holding times ( $t=150\ \text{s}$  and  $900\ \text{s}$ , respectively) were selected in the present work. The results show that the contact angle has a constant value around  $130\ \text{degrees}$  during the first  $150\ \text{s}$ , as seen in Fig. 9(a). Thereafter, the contact angle decreases gradually. Finally, the contact angle reaches a value of  $87.9\ \text{degrees}$  at a holding time of  $900\ \text{s}$ . It was confirmed that the contact angle values at  $t=0\ \text{s}$  (the moment when the iron sample melted) were  $132.8\ \text{degrees}$  in Trial 504 and  $125.7\ \text{degrees}$  in Trial 507, respectively. Furthermore, these values corresponded well to the value of  $132\ \text{degrees}$  reported by Chuchmarev *et al.*,<sup>5)</sup> which was obtained for experiments using a  $\text{NH}_3$  atmosphere. In addition, the contact angle values by Amadeh *et al.*<sup>6)</sup> ( $125 \rightarrow 120\ \text{degrees}$  for  $1\ 000\ \text{s}$  at  $1\ 823\ \text{K}$ ;  $110 \rightarrow 85\ \text{degrees}$  for  $1\ 000\ \text{s}$  at  $1\ 843\ \text{K}$ ) partially corresponded to the present results ( $132.8 \rightarrow 87.9\ \text{degrees}$  for  $900\ \text{s}$  in Trial 504;  $125.7 \rightarrow 122.8\ \text{degrees}$  for  $150\ \text{s}$  in Trial 507). Possible reason for this discrepancy is mentioned in the discussion section.

For the TiN/steel system, different holding times ( $t=298\ \text{s}$  and  $981\ \text{s}$ , respectively) were selected. It was confirmed that the contact angle decreased drastically from a value of  $110$  to  $76\ \text{degrees}$  during the first  $50\ \text{s}$ , as seen in Fig. 10(a). Thereafter, the contact angle value decreases gradually with time. Finally, the contact angle reaches a value of  $50\ \text{degrees}$  at a holding time of  $981\ \text{s}$ . It was confirmed that the contact angle values at  $t=0\ \text{s}$  (the moment when the iron sample started to melt) were  $110.2\ \text{degrees}$  in Trial 511, and  $111.2\ \text{degrees}$  in Trial 513, respectively. Furthermore, these values were only a little bit lower than the value of  $122\ \text{degrees}$  reported by Chuchmarev *et al.*,<sup>5)</sup> which was measured using a  $\text{NH}_3$  atmosphere. In addition the contact angle values were reported by Amadeh *et al.*<sup>6)</sup> ( $80 \rightarrow 60\ \text{degrees}$  for  $1\ 823\ \text{K}$ ;  $60 \rightarrow 50\ \text{degrees}$  for  $1\ 843\ \text{K}$ ). Note, that those data do not fit to the present results during the first stage of the experiments. However, they fit during the final stage of the present results ( $110.2 \rightarrow 62.5\ \text{degrees}$

**Table 3.** SEM image of a TiN substrate (50 nm) using a  $\times 4\,000$  magnification.

| Temperature [K]<br>(Holding time<br>[min]) | SEM image |          |
|--------------------------------------------|-----------|----------|
|                                            | 50 MPa    | 89.2 MPa |
| 1 573 (5)                                  |           |          |
| 1 673 (5)                                  |           |          |
| 1 773 (5)                                  |           |          |
| 1 873 (5)                                  |           |          |
| 1 873 (20)                                 |           |          |

for Trial 511; 111.3 $\rightarrow$ 49.6 degrees for Trial 513).

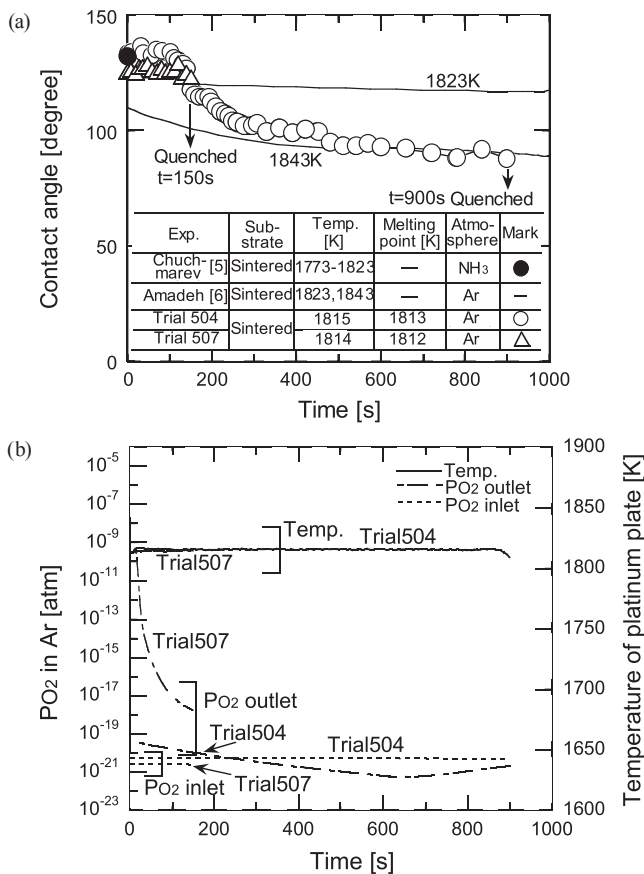
Figure 9(b) illustrates the dynamic change of the platinum plate temperature and oxygen partial pressure ( $\text{PO}_2$  inlet gas & outlet gas). At the beginning of the experiment, even if the vacuum treatment ( $\sim 10^{-5}$  torr) was performed, small amount of  $\text{O}_2$  still remained in the chamber. Thus,  $\text{PO}_2$  of outlet gas is slightly higher than that of inlet gas, as shown in Fig. 9(b). Moreover, the decrease of  $\text{PO}_2$  difference between inlet gas and outlet gas during holding time is due to the absorbing of  $\text{O}_2$  into the liquid droplet, as shown in Fig. 13(a). The recorded outlet  $\text{PO}_2$  value was controlled to be below  $10^{-16}$  atm after a holding time of 200 s, in order to avoid oxidation reactions.

In summary, it was found that the contact angle value for a TiN/pure Fe system (130 to 87.9 degrees for 900 s) is larger than the value for a TiN/steel system (110 to 50 degrees for 981 s).

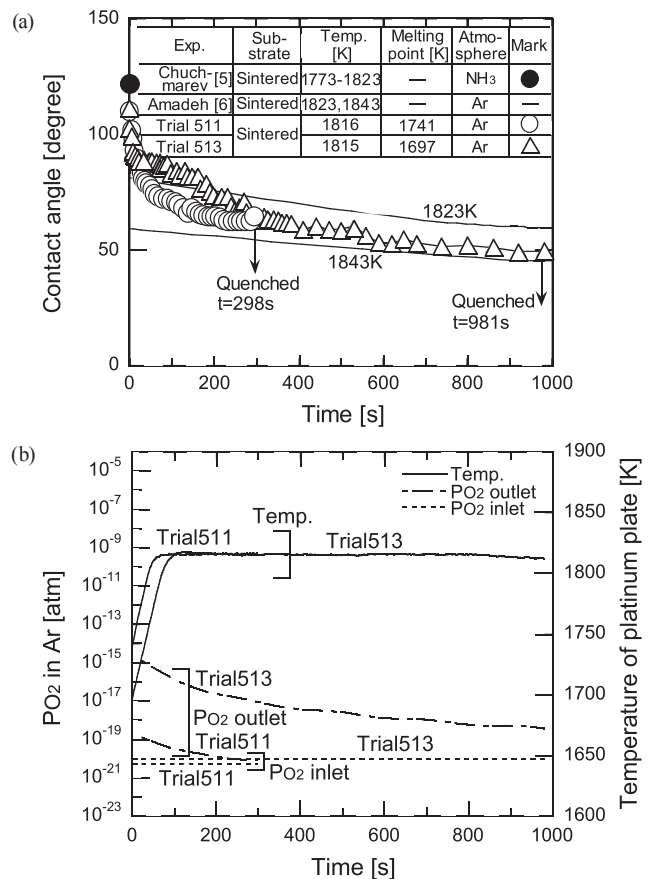
### 3.3. Observations of the Interface between an Iron or Steel Melt and a TiN Substrate

Figure 11 shows a SEM image and SEM-EDS analysis of a cross section of the interface between a solidified iron and TiN substrate. It can be seen that the iron is penetrated into the open pores near the interface and that some peelings have occurred. The penetration phenomena was recognized as TiN and Fe and the peeled-off particles were identified as  $\text{Ti}(\text{N},\text{O})$  inclusions. Furthermore, from the distribution of the [Ti] and [N] contents at the iron side of the interface obtained by SEM-EDS analysis, the [Ti] content at the interface was increased from 1.23 mass% to 2.38 mass% with an increased holding time from 150 s in Trial 507 to 900 s in Trial 504. It was also found that the TiN substrate has been slightly dissolved into the iron.

The penetration of the steel into the open pores near the interface was not detected, as shown in Fig. 12. From the distribution of the [Ti] and [N] contents in the steel side of the interface obtained by SEM-EDS analysis, as the



**Fig. 9.** Contact angle of TiN/pure-Fe as a function of time after melting of a sample. (a) Contact angle of TiN/pure-Fe as a function of time after melting of a sample. (b) Change of PO<sub>2</sub> (in the inlet & outlet gas) and experimental temperature of platinum plate as a function of the elapsed time after melting of a sample.



**Fig. 10.** Contact angle of TiN/steel as a function of time after melting of a sample. (a) Contact angle of TiN/steel as a function of time after melting of a sample. (b) Change of PO<sub>2</sub> (in the inlet & outlet gas) and experimental temperature of platinum plate as a function of the elapsed time after melting of a sample.

evidence of melting behaviour of TiN substrates, the slight high-Ti content regions (for example, Ti=3.61 mass%, and 2.69 mass%) was found in metal side near the interface, as shown in the right-hand figures of Fig. 12, although it cannot be confirmed from the left-hand figures of Fig. 12. Meanwhile, the [Ti] contents at the interface were 3.61 mass% for Trial 511 at a holding time of 298 s and 2.69 mass% for Trial 513 at a holding time of 981 s, respectively.

## 4. Discussion

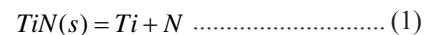
### 4.1. Verification of the SEM-EDS Spot Analysis at the Interface

The verification of the SEM-EDS spot analysis was done for light elements (N and O) at the interface between the solidified iron or steel and the TiN substrate. A carbon/sulfur combustion analyzer (EMIA-920V2, Horiba, Ltd., Japan) and an oxygen/nitrogen/hydrogen combustion analyzer (EMGA-920, Horiba, Ltd., Japan) were used to measure the chemical composition C, S, N, O of the TiN substrate. The analysis results of TiN substrate are C=0.138 mass%, (=0.355 at%), S=not detected, O=2.27 mass% (=4.38 at%), N=20.7 mass% (=45.65 at%). For the oxygen content, it is mainly due to the powder filling process into the graphite die treated in the open air. Furthermore, for the carbon content it is due to the use of a graphite die and a paper during sintering of the TiN substrate by SPS. These

chemical analysis results fit well to the SEM-EDS spot analysis data for the bulk of the TiN substrate, as is shown in Figs. 11 and 12. Consequently, it is confirmed that the TiN substrates in this work contained about O=2.27 mass% (=4.38 at%). In addition, it is found that their carbon contents could be neglected.

### 4.2. Time-dependent Change of the Contact Angle

Morohoshi *et al.*<sup>4)</sup> pointed out that the solubility product of TiN in a steel melt is changed by the [Si] content in iron or steel. Thus, the formation of TiN is thermodynamically estimated by considering the [Si] content, according to following equations:



$$\Delta G^\circ = -RT \ln K = -2.303RT \log K \quad \text{..... (2)}$$

$$\log K = -19800/T + 7.78 \quad \text{..... (3)}$$

$$K = a_{\text{Ti}} \cdot a_{\text{N}} \quad \text{..... (4)}$$

where  $\Delta G^\circ$  is Gibbs free energy of TiN formation, R is gas constant, K is equilibrium constant for reaction (1). Furthermore,  $a_{\text{Ti}}$  and  $a_{\text{N}}$  are the activity of Ti and N in iron or steel melt, respectively. These can be expressed by the following equations, respectively.

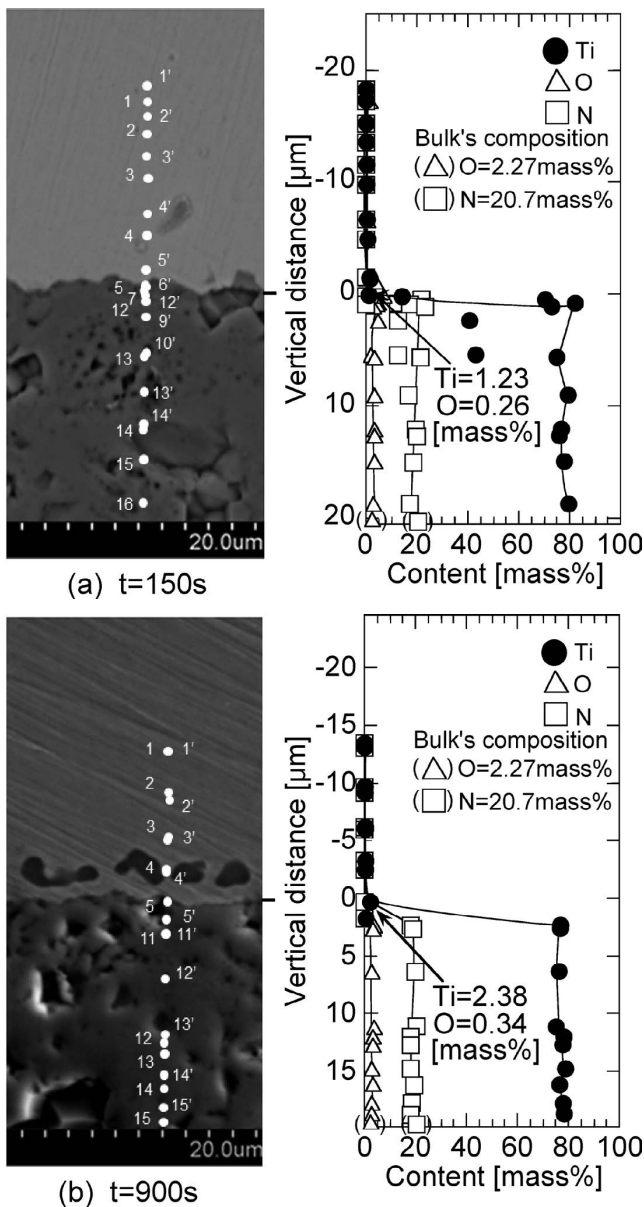


Fig. 11. Cross section analysis for (a) the TiN/Fe- trail 507 ( $t=150$  s) and (b) the TiN/Fe- trial 504 ( $t=900$  s) using a  $\times 2\,000$  magnification.

$$a_{Ti} = f_{Ti} [\text{mass\%Ti}] \quad (5)$$

$$a_N = f_N [\text{mass\%N}] \quad (6)$$

where  $f_{Ti}$  and  $f_N$  are the activity coefficients of Ti and N in iron or steel melt, respectively. The standard state of the above activity coefficients is based on Henry's law. These are expressed by the following equations, respectively.

$$\log f_{Ti} = \sum_i e_{Ti}^i [\text{mass\%}i] \quad (7)$$

$$\log f_N = \sum_i e_N^i [\text{mass\%}i] \quad (8)$$

The values of the interaction parameters,  $e_{Ti}^i$  and  $e_N^i$  used in Eq. (6) are shown in Table 4. Also, the solubility product line of TiN for pure Fe and steel with a 0.65 mass% Si content is presented in Fig. 13. The oxygen/nitrogen/hydrogen combustion analyzer (EMGA-920, Horiba, Ltd.,

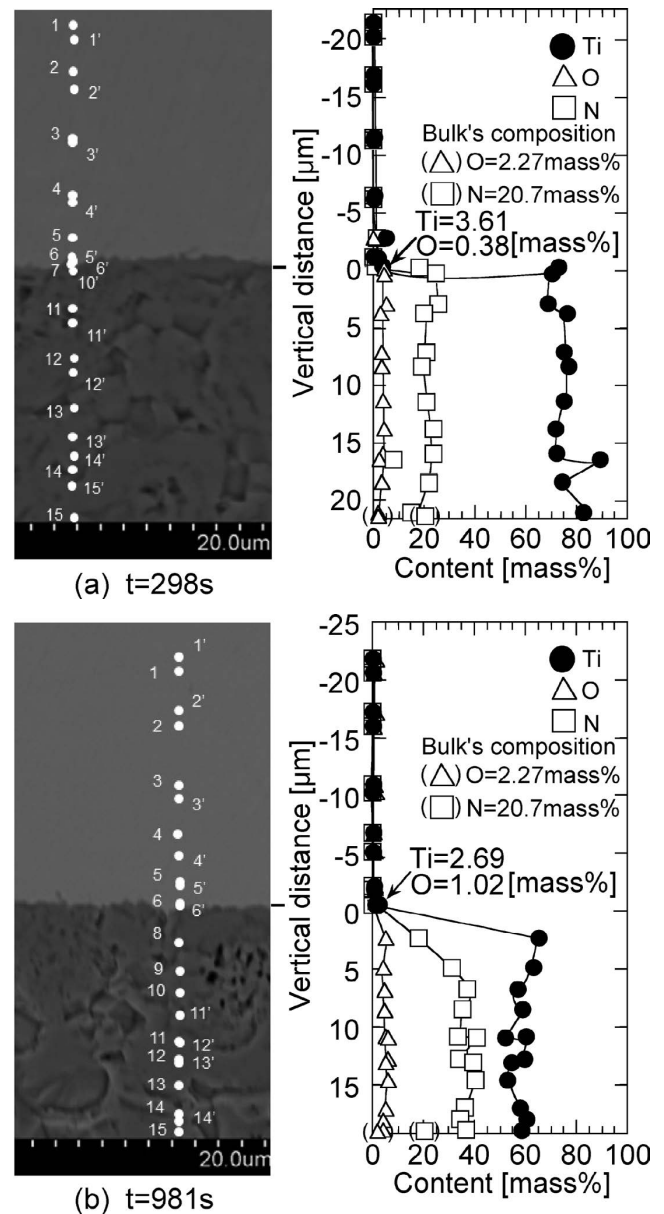


Fig. 12. Cross section analysis for (a) the TiN/Steel- trial 511 ( $t=298$  s) and (b) the TiN/Steel- trial 513 ( $t=981$  s) using a  $\times 2\,000$  magnification.

Japan) results and SEM-EDS analysis values of O, N and Ti for several positions of iron or steel side of the interface are plotted in Fig. 13.

It is considered that the solubility product line at 1 815 K is the border line between the dissolution and precipitation reaction, as shown in Fig. 13(b). Therefore, it can be seen that TiN is dissolved in the range of the lower side ( $t=0$  s, 80 s and 150 s for pure Fe case). Furthermore, that the TiN dissolution into iron or steel has a positive free energy of TiN formation. In addition, TiN is precipitated in the upper side of the figure ( $t=900$  s for pure Fe case and  $t=298$  s,  $t=981$  s for steel case), which corresponds to a negative free energy of TiN formation.

TiN/pure iron system:

In the first stage, the substrate will be slightly dissolved into the liquid iron until the melt composition approaches the solubility product line (up to a holding time of 150 s), as shown in Fig. 13(b). According to Fig. 13(a), this dissolution

process during 150 s after a full melting has occurred, can be proved by the remarkable increase of the Ti and N contents from 0.0001 to 0.057 mass% and 0.0008 to 0.0103 mass%, respectively. Therefore, the substrate surface became rough and it contained protuberances and peeled-off particles, as shown in Fig. 11. Based on Thermo-Calc calculation at the interface for 150 s, since it is close to the solubility line, a slight precipitation of  $\text{Ti}(\text{N}_{0.988}, \text{O}_{0.012})=0.036$  mass% and  $\text{Ti}_2\text{O}_3=0.778$  mass% is formed. Despite that such a small amount of  $\text{Ti}(\text{N}, \text{O})$  is precipitated, the initial composition of the TiN substrate is maintained. Also, it seems that the slight formation of  $\text{Ti}_2\text{O}_3$  does not have a strong effect on the contact angle results. Moreover, the increased oxygen content in the liquid iron can decrease the contact angle, as presented in previous studies.<sup>15–18)</sup> From Fig. 13(a) it can be seen that the oxygen content in iron is stable at a value of 0.0067 mass% for 0 s and 0.0066 mass% for 150 s. As a

result, the contact angle is constant during this time period.

In the middle and final stage, when the melt composition exceeds the solubility product line (after a holding time of 900 s), TiN is thermodynamically stable in liquid iron. In Fig. 13(a), the small increase of Ti (from 0.057 to 0.240 mass%) and N (from 0.0103 to 0.0164 mass%) also support this statement. At the interface, a  $\text{Ti}(\text{N}, \text{O})$  particle combined with a  $\text{TiO}_x$  particle is slightly precipitated. This precipitation reaction was predicted by using Thermo-Calc. Specifically, the reaction layer after 900 s of the experiment (Trial 504) is predicted as  $\text{Ti}(\text{N}_{0.980}, \text{O}_{0.020})=0.068$  mass% and  $\text{Ti}_2\text{O}_3=1.017$  mass%. However, such a precipitation amount is too small to have an influence on the contact angle value results. As for the oxygen effect, in Fig. 13(a) O content was found to be slightly increased from 0.0066 mass% at 150 s to 0.0129 mass% at 900 s. This increase should be mainly due to the oxygen absorbing from both the TiN substrate ( $\text{O}=2.27$  mass%) and the  $\text{O}_2$  in the argon atmosphere into the liquid iron. Hence, it is possible that the contact angle decreases gradually is due to this oxygen increase.

TiN/steel system:

For the initial stage, the solubility product line is shifted downwards due to a [Si] content of 0.65 mass% for the TiN/steel system as is shown in Fig. 13(b). It is found that at the initial point ( $t=0$  s), the melt composition ( $\text{O}=0.0015$  mass%,  $\text{N}=0.0126$  mass% and  $\text{Ti}=0.024$  mass%) is above the solubility product line. This means that the dissolution of TiN substrate is thermodynamically impossible. Therefore, the substrate surface is relatively smooth, as is shown in Fig. 12.

For the middle and final stage, a reaction layer at the interface can precipitate in form of  $\text{Ti}(\text{N}_{0.456}, \text{C}_{0.537}, \text{O}_{0.006})=0.154$  mass%,  $\text{Ti}_2\text{O}_3=0.477$  mass% and  $\text{TiO}=0.740$  mass% at 298 s (Trial 511) and  $\text{Ti}(\text{N}_{0.849}, \text{C}_{0.143}, \text{O}_{0.008})=0.351$  mass% and  $\text{Ti}_2\text{O}_3=3.005$  mass% at 981 s (Trial 513), respectively. These calculations were done using Thermo-Calc. The predictions fit with a gradual increase of the Ti (from 0.205 to 0.725 mass%) N (from 0.0153 to 0.0707 mass%) contents, as shown Fig. 13(a). It is known that the liquid iron has a quite strong wetting behavior in contact with TiC. More specifically, from the literature review<sup>19)</sup> the contact angle values are 49 degrees (1 773 K,  $\text{H}_2$ ), 36 degrees (1 773 K, He) and 41 degrees (1 773 K, Vacuum), respectively. In this case, since the carbon content in steel ( $\text{C}=0.28$  mass%) is much higher than that of pure Fe ( $\text{C}=8$  ppm), Ti (N,C,O) precipitates in steel. From the strong wetting behavior of TiC, the wettability of  $\text{Ti}(\text{N}, \text{C}, \text{O})$  also can be stronger than that of  $\text{Ti}(\text{N}, \text{O})$ . Thus a  $\text{Ti}(\text{N}, \text{C}, \text{O})$  precipitation at the interface is bound to lead to a sharp decrease of the contact angle, even though this precipitation layer is invisible. In addition, the oxygen increase in the steel from 0.0015 mass% at 0 s to 0.0106 mass% at 981 s can also lead to a decreased contact angle value.

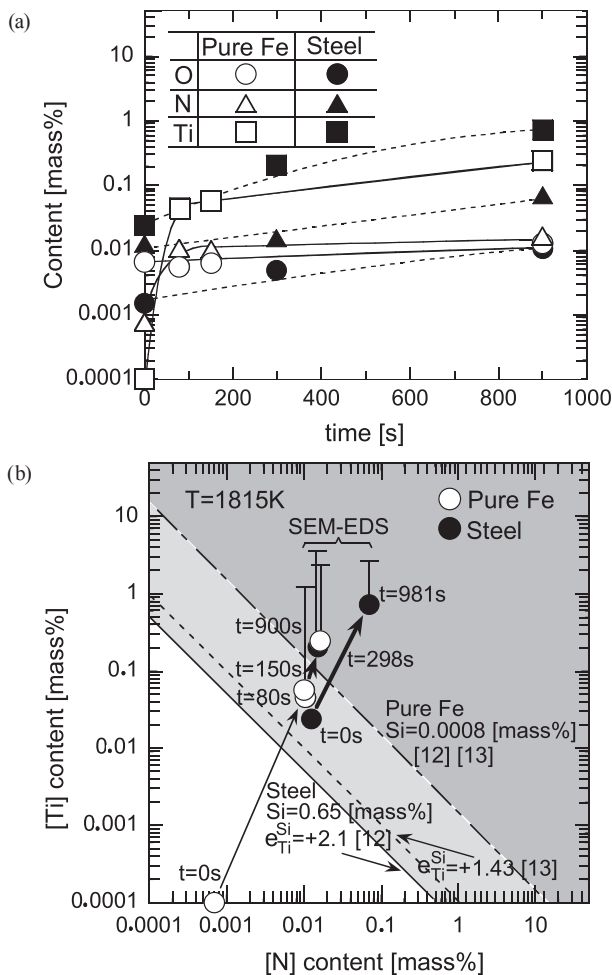


Fig. 13. O, Ti, N content change with the holding time and the solubility of TiN in pure Fe and steel. (a) Relation between the content of O, N, Ti and the holding time. (b) Solubility diagram for TiN in pure Fe and steel.

Table 4. Interaction parameters used in the thermodynamic calculations.<sup>4)</sup>

| Element i                  | C     | Si                                         | Mn     | P      | S      | Cr                    | Ti     | N     |
|----------------------------|-------|--------------------------------------------|--------|--------|--------|-----------------------|--------|-------|
| $e_{\text{Ti}}^{\text{C}}$ | —     | +2.1 <sup>12)</sup><br>+4.3 <sup>13)</sup> | −0.043 | −0.06  | −0.27  | +0.022 <sup>14)</sup> | +0.042 | −2.06 |
| $e_{\text{N}}^{\text{C}}$  | +0.13 | +0.048                                     | −0.02  | +0.059 | +0.007 | −0.046                | −0.6   | 0     |

## 5. Conclusion

The focus of the present study was the wettability of TiN samples in contact with pure Fe and steel liquids. Initially, TiN substrates were prepared by using the Spark Plasma Sintering (SPS) technique. Thereafter, the wettability between TiN and the metals were determined based on video recordings. The wettability was determined at the moment when the metals started to melt. The following most important results were obtained from this study:

- The particle size and holding temperature are key factors of determining the relative density during SPS sintering. Moreover, a higher pressure could promote the densification of substrates as well. However, the effect of pressure is decreased with an increased holding temperature. Also, an increase of the holding time from 5 min to 20 min cannot enhance the relative density.
- The relative density of 96% and the surface roughness of 250 nm were obtained with a 1 873 K temperature, a 89.2 MPa pressure and a 5 min sintering time.
- As for the wettability of TiN substrate, the contact angle for a TiN/pure Fe system (130 to 87.9 degrees in 900 s) is larger than the value for a TiN/steel system (110 to 50 degrees in 981 s).
- It is found that TiN has good resistance towards corrosion of liquid iron and steel. In the pure Fe case, the oxygen increase after a full melting should be the main factor for the contact angle decrease. As for the steel case, the steep decrease of the contact angle can mainly be attributed to the effects of both an increased oxygen content in the liquid steel and a formation of a Ti(N,C,O) particle at the interface.

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