Non-equilibrium Precipitation Behavior of TiC during Rapid Solidification of TiC-reinforced Wear-resistant Steel

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(Received on August 22, 2019; accepted on September 13, 2019; J-STAGE Advance published date: January 17, 2020)

Precipitation behavior of TiC in TiC-reinforced wear-resistant steel was investigated using both thermodynamics and experiments. The carbide in TiC-reinforced wear-resistant steel is principally Ti-rich MC-type, which starts to precipitate at 1460°C in the solid-liquid zone. As the temperature decreased, there is no major change in the concentration of Ti and C in TiC. The results calculated by using equilibrium assumptions show that TiC can form when the solid fraction exceeds 0.24. However, the isolated primary TiC was observed in the sample cooled at rate of 162 K/s and 267 K/s, indicating that TiC can precipitate from the melts at the initial stage of solidification process. As an extension of Brody and Fleming’s model, the interface response functions relating the cooling rate with the interface composition and interface temperature, which consider interface non-equilibrium effect on the basis of incomplete mixing of solute in the liquid during solidification, were used to evaluate TiC precipitation behavior during rapid solidification for different cooling rates. In comparison with lower cooling rate, the effect of non-equilibrium behavior is strengthened under the condition of higher cooling rate, so that primary TiC can precipitate from the melts at the initial stage of solidification when a high cooling rate is imposed.

KEY WORDS: rapid solidification; TiC; non-equilibrium; TiC-reinforced wear-resistant steel; cooling rate.

1. Introduction

For TiC-reinforced wear-resistant steel, Ti is added to stabilize carbon and form titanium carbides due to the higher affinity of C with Ti than that of Fe, Cr and other metal elements.1–3) Titanium carbide (TiC) is with rock salt type structure (space group Fm̅3m) and its lattice parameter is a_{TiC} = 4.32 Å.3) As a typical transition metal carbide, TiC has been widely used in the fields of wear resistance tools due to its high melting temperature (3067°C), high Young’s modulus (410–450 GPa), and high Vickers hardness (28–35 GPa).3) Large TiC precipitates are considered detrimental for the process and properties of steels since TiC is hard to deform.

During solidification process, the solutes Ti and C will be rejected into the remaining liquid at/ahead of the solid/liquid interface since the equilibrium distribution coefficient of both Ti and C in steel melts are less than unity. As a result, the concentration of Ti and C in the remaining liquid would gradually increase with the proceeding of the solidification process, favoring TiC precipitation. Therefore, it is desirable to be able to model and predict the solute segregation behavior during the rapid solidification process of TiC-reinforced wear-resistant steel, which contributes to controlling the TiC precipitation during the preparation of TiC-reinforced wear-resistant steel. To examine the TiC precipitation behavior in the steel melts, Brody and Fleming’s model7) is usually adopted to calculate and predict the solute segregation during solidification. However, the analyses of the segregation behavior of solutes in the melts are under the assumption of equilibrium solidification.

As is known, the carbide precipitation during solidification of steels is controlled by solute diffusion. The diffusion of alloy elements is expected to be suppressed during solidification process, especially in the case of the solidification under the condition of greater cooling rate.8) In addition, the cooling rate (i.e., the rate of transport of latent heat away from the interface) will cause an interfacial undercooling which is the driving force for solidification. When cooling rate is sufficiently slow, the interfacial undercooling is negligible and the solidification process is heat flow limited. However, if the cooling rate becomes larger, the growth velocity increases to a point where the local equilibrium was ruled out and solute trapping must be taken into account. In this case, the solidification process occurs rapidly enough so that the composition of the solid and liquid on either side of the interface can not be given by the solidus and the liquidus on the phase diagram any more, which is one of the main features of non-equilibrium solidification. When the sample is placed under the condition of non-equilibrium solidification the microsegregation (i.e., solute boundary layers) develop at the interface for local equilibrium to be present, which in turn influence the concentration field when the liquid is rapidly solidified, and must be taken into account.
account in the investigation of the precipitation during the solidification process. Previous works\textsuperscript{9,10} concluded that the size of TiC is mainly dependent on the cooling rate and high cooling rate leads to smaller TiC size in samples. However, no evidence about the relationship between TiC precipitation and cooling rate during rapid solidification can be found until now, although refinement of TiC can be achieved with the increase of cooling rate in the steels. The nonequilibrium precipitation behavior of TiC at high cooling rate during solidification of TiC-reinforced wear-resistant steel remained unclear. Therefore, understanding of the precipitation behavior of TiC at high cooling rate under the condition of non-equilibrium solidification is important for the production and application of the TiC-reinforced wear-resistant steel. The aim of the current work is to investigate the nonequilibrium precipitation behavior of TiC in TiC-reinforced wear-resistant steel during solidification process.

2. Experimental Procedure

The chemical compositions of the experimental steel is C 0.35, Al 0.23, Ti 3.0, Si 0.5, Mn 0.35, Cr 0.68, Mo 0.28, Ni 0.51 (wt%). To obtain various solidification conditions and investigate the non-equilibrium precipitation behavior of TiC during rapid solidification, remelting experiments were conducted under different cooling rates (0.2, 162 and 267 K/s) by a vacuum resistance tube furnace under high-purity argon atmosphere. The dimension of the cylindrical shaped ingot is o.d. 7 × 60 mm. The morphology and size of TiC were analyzed by electron probe micro-analyzer (EPMA) and scanning electron microscopy (SEM) equipped with EDS.

3. Theoretical Model

For a long time, attempts have been made to model the solute diffusion and solute redistribution during solidification processing.\textsuperscript{7,11} If the solute diffusion in the liquid (perhaps assisted by the effects of the convection) is assumed complete, while that in the solid is neglected (no back diffusion), solute redistribution can be described by the classical Scheil’s equation.\textsuperscript{11} The main difference between the classical lever rule and Scheil’s equation is whether considering the back diffusion or not. Obviously, these models represent two different extreme conditions which deviate significantly from real situations. As a result, by quantifies the effect of solid state diffusion in the intermediate regime, Brody and Flemings have presented a solute redistribution model.\textsuperscript{7}

\[
C_S = k_0 [1-(1-2\alpha k)f_b]^{1/(1-2\alpha k)} \quad \ldots \quad (1)
\]

where \(\alpha\) is the dimensionless back-diffusion coefficient, \(C_0\) the initial alloy composition and \(C_S\) the solute concentration in the solid.

However, it is clear that all of these models did not take nonequilibrium solidification into account. Thus, solidification parameters predicted by these models can not accurately reflect the changes in phase equilibrium due to the increase of solidification velocity under rapid solidification conditions. Therefore, the equilibrium interface conditions (i.e., solute composition in the liquid at the solid/liquid interface, interface temperature, partition coefficient, etc.) should be replaced by velocity-dependent ones when deriving the model for the rapid solidification process. Moreover, complete mixing in the liquid is assumed in Brody-Flemings models. However, due to the time limit caused by the rapidly moving solid/liquid (S/L) interface under high cooling rate during solidification, the assumption of complete diffusion in the liquid without strong convection will become invalid, especially for the substitutional element with small diffusion coefficient. Therefore, incomplete mixing of solute in the liquid during solidification should be assumed when deriving the model for the rapid solidification process.

According to the flux equilibrium equation (\(A1=A2+A3\)), the solute redistribution can be derived as Eq. (2) by using mass-balance equation within the volume element during a small increment of solidification, as schematically shown in Fig. 1.

\[
(C_L - C_S)\frac{dL}{d\tau} = \frac{1}{2} \frac{\delta_s dC_L + \frac{1}{2} \delta_d dC_S}{L} \quad \ldots \quad (2)
\]

where \(L\) is the length of the diffusion system, \(\delta_s\) and \(\delta_d\), the (back-diffusion) solute boundary layer and solute boundary layer in the liquid are given by

\[
\delta_s = \frac{2D_s}{V}, \quad \delta_d = \frac{2D_d}{V} \quad \ldots \quad (3)
\]

in which \(V\) is the local interface advance velocity and \(D_s\) and \(D_d\) are the solute diffusivity in the solid, respectively. It follows that

\[
(C_L - C_i)\frac{dL}{d\tau} = \frac{D_s}{VL} dC_L + \frac{D_d}{VL} dC_S \quad \ldots \quad (4)
\]

from which

\[
\int_0^L VL (C_L - C_i) d\tau = \int_{C_S}^{C_L} \frac{D_s}{C_s} dC_L + \int_{C_S}^{C_i} \frac{D_d}{C_d} dC_S \quad \ldots \quad (5)
\]

![Fig. 1. Schematic illustration of the solute redistribution during rapid solidification process.](image-url)
with $k_V$, the non-equilibrium partition coefficient. Integrating Eqs. (3) and (5) yields

$$C_L = C_0 \cdot \exp \left[ \frac{VL}{(D_e + k_V D_e)} (1 - k_V) f_s \right] \quad \text{(6)}$$

Equation (6) predicts the changing composition of the liquid at the solid/liquid interface during non-equilibrium solidification. In order to calculate the solute concentration of the liquid at the solid/liquid interface during non-equilibrium solidification, the non-equilibrium partition coefficient and interface advance velocity are not known a priori. According to the solute-trapping model of Sobolev, the non-equilibrium partition coefficient can be given as

$$k_V = \frac{V}{V_{Di}} + k_e \frac{V}{V_{Di} + 1} \quad \text{(7)}$$

where $k_e$ is the equilibrium partition coefficient and $V_{Di}$ is defined as the interface diffusive speed.

Assuming parabolic decrease in interface advance velocity with increasing time, $V$ can be expressed as

$$V = L / (2t_f f_s) \quad \text{(8)}$$

Here, the local solidification time can be expressed as

$$t_f = \Delta T / R \quad \text{(9)}$$

with $\Delta T$ as the temperature range of solidification which is assumed to be constant and $R$ the cooling rate.

Integration of the above equations leads to the modified solute redistribution equation and non-equilibrium partition coefficient for the rapid solidification process

$$C_L = C_0 \cdot \exp \left[ \frac{L^2 R}{2\Delta T(D_e + k_V D_e)} (1 - k_V) \right] \quad \text{(10)}$$

$$k_V = \frac{LR / 2\Delta T f_s V_{Di} + k_e}{LR / 2\Delta T f_s V_{Di} + 1} \quad \text{(11)}$$

After the velocity-dependent composition of the liquid at the interface is known, the interface temperature which is largely controlled by the cooling rate, determine the driving force for the transformation. According to previous work, the free energy change $\Delta G$ for solid–liquid interface migration can be expressed as:

$$\Delta G(V, T) = RT \frac{V}{V_0} \quad \text{(12)}$$

where $R$ is the gas constant and $V_0$ is the upper limit of the interface advance.

Integrating Eq. (12) and the expression of $\Delta G$ gives the LKT model. Furthermore, regarding the relaxation effect, it was obtained that

$$\Delta G(C, T) = (1 - C_s) \Delta \mu_s (C, T) + C_s \Delta \mu_B (C, T) + (C_L - C_s) \left[ \Delta \mu_B (C, T) + (1 - k_V) RT \frac{V}{V_D} \right] \quad \text{(13)}$$

where $V_D$ is the velocity of bulk liquid diffusion and $\Delta \mu_s (C, T)$ is the chemical potential difference between solid and liquid. Then combining Eqs. (12) and (13) yields

$$T = T_0 + m(V) \cdot C_L + \frac{m_k V}{(1 - k_e) V_0} \quad \text{(14)}$$

where $m(V)$ is the slope of the nonequilibrium liquidus line in the phase diagram, which can be given as

$$m(V) = \frac{m_k}{1 - k_e} \left[ 1 - k_e + \ln \frac{k_e}{k_{e0}} + (1 - k_e)^2 \right] \frac{V}{V_D} \quad \text{(15)}$$

with $k_e = m_i / m_0$ as the equilibrium partition coefficient and $k_{e0} = C_0 / C_L$ the non-equilibrium partition coefficient. It should be mentioned here that the curvature undercooling by dendritic growth is not considered in Eq. (14), because the solidification model in this study treats a plane front. A detailed derivation for Eqs. (14) and (15) is available in the work.

4. Results and Discussion

4.1. Precipitates Formation in TiC-reinforced Wear-resistant Steel Calculated through Thermo-Calc

Phase transformation and precipitation behaviour of TiC in TiC-reinforced wear-resistant steel were calculated by using Thermo-Calc software with the TCFE8 database. Figure 2 shows the mole fraction of precipitated phases and transitions between phases during liquid steel solidification process. There were two types of phases precipitating from TiC-reinforced wear-resistant steel, i.e. Ferrite, and TiC when the liquid was slow cooling to room temperature under the condition of thermodynamic equilibrium. Although the quantity of TiC was very small, its formation happened shortly after Ferrite precipitation during the solidification process.

The series in Fig. 3 represent the change in the elements contents of TiC and liquid as a function of temperature. From Fig. 3(a), TiC started to precipitate at 1460°C (1733 K) in the solid–liquid zone. The main components of TiC were Ti and C, but the fraction of Ti is higher than that of C. As the temperature decreased, there is no major change in the concentration of Ti and C. With the precipitation of TiC, the concentration of Ti at the solidifying front increased and that of C decreased during the solidification process of TiC-reinforced wear-resistant steel.
liquid steel, as shown in Fig. 3(b).

4.2. Thermodynamics of TiC Formation in Fe–Ti–C Melts

The reaction equilibrium for the formation of pure solid TiC in liquid Fe–Ti–C melts can be written as follows: 21)

\[
[Ti] + [C] = [TiC] \quad \text{(16)}
\]

\[
\lg K_{\text{TiC}} = \frac{9459}{T} - 5.36 \quad \text{(17)}
\]

\[
K_{\text{TiC}} = \frac{\alpha_{\text{TiC}}}{h_T h_C} = \frac{1}{f_T f_C[g(\%\text{Ti})/g(\%\text{C})]} \quad \text{(18)}
\]

where \(K_{\text{TiC}}\) is the equilibrium constant and, \(h_T\) and \(h_C\) are the Henrian activities of titanium and carbon relative to 1 mass\% standard state in liquid iron, and \(f_T\) and \(f_C\) are the activity coefficients of titanium and carbon, respectively. Under the current experimental conditions, the activity of TiC can be regarded as unity.

Based on Eqs. (17) and (18), the following equation can be obtained

\[-\frac{9459}{T} + 5.36 = \lg f_T + \lg [\%\text{Ti}] + \lg f_C + \lg [\%\text{C}] \quad \text{(19)}\]

Table 1 lists the first-order interaction coefficients used in the current work. 22–25) Using the thermodynamics parameters, Eq. (19) and Wagner’s formalism, 25) the equilibrium relationships between carbon concentration and titanium concentration in Fe–Ti–C melts at different temperatures can be determined. Figure 1 compares the predictions of equilibrium solubility product of carbon and titanium for TiC formation in Fe–Ti–C melts at 1873 K, liquidus temperature \((T_L = 1767 \text{ K})\), and solidus temperature \((T_S = 1752 \text{ K})\), respectively. The point P in Fig. 4 represents the concentration of carbon and titanium in the experimental steel. As is known, TiC will precipitate from the melts when the solubility product of carbon concentration and titanium concentration in the melts exceeds the equilibrium solubility product at a given temperature according to thermodynamics. It is apparent from the data point P in Fig. 4 that the solubility product of carbon concentration and titanium concentration in the current work is lower than the equilibrium solubility product at the liquidus temperature. Thus, it can be inferred that TiC would not precipitate from the melts under equilibrium condition.

4.3. Precipitation of TiC during Solidification under Equilibrium Conditions

Figure 5 shows the variation of the temperature and solute concentration in the liquid at the solid/liquid interface with the solid fraction calculated by using the classical lever rule 26) under equilibrium solidification. It can be seen from Figs. 5(a) and 5(b) that the solute concentration at the solid/liquid interface increases gradually with increasing the solid fraction during equilibrium solidification. The concentration of titanium at the interface increases slower than that of carbon due to its higher equilibrium partitioning coefficient. It can be seen from Fig. 5(c) that the temperature at the solid/liquid interface decreases gradually with increasing the solid fraction during equilibrium solidification. This
suggests that TiC can form during solidification when the solute concentration reach the critical value required at a certain temperature.

Generally, the precipitation behavior of TiC during solidification can be evaluated by comparing the concentration product of carbon and titanium in the melts and the equilibrium solubility product under a certain temperature during equilibrium solidification. Using Eq. (19), the Wagner’s formalism and classical lever rule, the equilibrium solubility product of Ti and C (i.e., $K_{\text{TiC}}$) for TiC formation in the melts during equilibrium solidification can be obtained. The concentration product of Ti and C (i.e., $Q_{\text{TiC}}$) during equilibrium solidification can be calculated using lever rule.

Figure 6 compares the predictions of the log($K_{\text{TiC}}$) and log($Q_{\text{TiC}}$) during equilibrium solidification. It is apparent that the concentration product of Ti and C during solidification is higher than the equilibrium solubility product of Ti and C for TiC formation in the melts when the solid fraction exceeds 0.24. This indicates that TiC is expected to be formed in the steel melts when the solid fraction reaches about 0.24 during equilibrium solidification.

4.4. Comparison between Lower Cooling and Rapid Solidification

Figure 7 presents scanning electron microscope-backscattered electron (SEM-BSE) images of the samples under lower cooling rate (i.e., 0.2 K/s). Figure 8 presents SEM-BSE images of the samples under high cooling rate. The distinct difference between the $\gamma$ phase and microsegregation indicates the occurrence of the inevitable interdendritic segregation during non-equilibrium solidification. The $\gamma$ dendrites formed at rapid solidification are finer than those formed at lower cooling.

Figures 9(a) and 9(b) are SEM-BSE images showing the typical microstructures of the specimens under high cooling rate. Figure 9 shows a relationship between the existence positions of TiC particles and microsegregation. Along the interdendritic regions where microsegregation prevails, there are isolated cubic-shaped TiC particles existed, basically independent of the microsegregation.

Figure 10 shows the morphology and size of TiC observed in the microstructure under high cooling rate. EDS mapping analyses show that the square substance is enriched in Ti and C, as shown in Figs. 11 and 12. Accord-
Fig. 7. SEM-BSE images of samples under lower cooling rate (i.e., 0.2 K/s): (a) 500 times; (b) 1 000 times.

Fig. 8. SEM-BSE images of samples under high cooling rate: (a) 162 K/s; (b) 267 K/s.

Fig. 9. (a) SEM-BSE image showing the typical microstructures under high cooling rate in low magnification; (b) is an enlarged SEM-BSE images of typical TiC particles and microsegregation acquired from Fig. 9(a).

Fig. 10. The morphology and size of TiC observed in the microstructure under high cooling rate (a) 162 K/s; (b) 267 K/s.
Fig. 11. EDS mapping analysis of TiC precipitates observed in the current study. (a) SEM image; (b) Ti; (c) C; (d) Fe. (Online version in color.)

Fig. 12. EDS mapping analysis of a typical TiC precipitate observed in the current study. (a) SEM image; (b) Ti; (c) C; (d) Fe. (Online version in color.)
ing to previous work, \(^2\) Ti-carbide that precipitated earlier will form faceted particles. Concerning the Ti-carbide structures formed during the current experiment, it is probable that the observed cubic-shaped carbides are the primary solid particles that precipitated before and during solidification (as shown in Figs. 10, 11 and 12). It can be found that the isolated primary TiC was observed in the sample cooled at rate of 162 K/s and 267 K/s, indicating that TiC can precipitate from the melts at the initial stage of solidification process under the condition of high cooling rate. Thus, cooling rate plays an important role in the TiC precipitation behavior of TiC-reinforced wear-resistant steels. Therefore, it is not accurate to predict the precipitation behavior of TiC during actual solidification only using equilibrium approaches.

4.5. Non-equilibrium Precipitation Behavior of TiC during Rapid Solidification

Figure 13 compares the predictions of the \( \log(K_{\text{TiC}}) \) and \( \log(Q_{\text{TiC}}) \) under different cooling rate during non-equilibrium solidification. It is apparent that the concentration product of Ti and C during solidification is higher than the equilibrium solubility product of Ti and C for TiC formation in the melts when the solid fraction exceeds 0.0087 and 0.9 \( \times 10^{-6} \) under the condition of lower cooling rate (i.e., 0.2 K/s) and higher cooling rate (i.e., 162 K/s and 267 K/s), respectively. This indicates that TiC is expected to be formed in the steel melts at the earlier stage of solidification process under the condition of higher cooling rate, compared with lower cooling rate.

Equation (10) reveals the relationship between solute composition in the liquid at the solid/liquid interface and the cooling rate. Table 2 lists the values of the solidification parameters used in the current work. According to Eqs. (10), (11) and Table 2, the variation of the solute concentration in the liquid at the solid/liquid interface with the solidification length under different cooling rates can be obtained, as shown in Figs. 14(a) and 14(b). With the increase of the solidification length, solute concentrations in the liquid at the solid/liquid interface increase significantly. In contrast, the concentration plot predicted by lever rule shows a flat curve (the full curve). Comparison of the two results shows that the enrichment of solute concentration at the interface is much higher with the current model. It can be seen that the models that include the effect of the interface non-equilibrium and the solute balance at the solid/liquid interface.

Table 2. Values of the solidification parameters used in the current work.\(^2\)–\(^3\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ti</th>
<th>C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial solute concentration, ( C_0 ) (wt%)</td>
<td>3.0</td>
<td>0.35</td>
<td>[28]</td>
</tr>
<tr>
<td>Equilibrium distribution coefficient, ( k_0 )</td>
<td>0.38</td>
<td>0.19</td>
<td>[28]</td>
</tr>
<tr>
<td>Liquidus slope, ( m_L ) (K/\text{wt.%})</td>
<td>(-10.24)</td>
<td>(-78)</td>
<td>[28]</td>
</tr>
<tr>
<td>Solute diffusion coefficient, ( D_L ) (cm(^2)/s)</td>
<td>(7.3 \times 10^{-5})</td>
<td>(2.1 \times 10^{-4})</td>
<td>[29,30]</td>
</tr>
<tr>
<td>Solute diffusion coefficient, ( D_S ) (cm(^2)/s)</td>
<td>(1.2 \times 10^{-7})</td>
<td>(4.8 \times 10^{-5})</td>
<td>[28]</td>
</tr>
<tr>
<td>Velocity of sound for pure metals, ( V_0 ) (cm/s)</td>
<td>(4.0 \times 10^{-5})</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Melting point of pure solvent, ( T_s ) (K)</td>
<td>1 811</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquidus, ( T_L ) (K)</td>
<td>1 787</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solidus, ( T_S ) (K)</td>
<td>1 752</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
predicted the solute concentration a significant enrichment. On the contrary, the lever rule that used overall mass conservation coupling to predict the solute enrichment presented a very small solute enrichment.

Figures 14(a) and 14(b) also shows a plot with lower cooling rate and the results show that the lower the cooling rate, the smaller the extent of solute enrichment. Similar trends that the hydrogen enrichment increases with increasing cooling rate were predicted by the numerical model developed by Han et al.\textsuperscript{32} It also can be seen from Figs. 14(a) and 14(b) that the content of Ti and C in the liquid at the solid/liquid interface in the sample cooled at rate of 162 K/s and 267 K/s can reach a high value immediately at the initial stage of solidification process. Therefore, TiC can precipitate from the melts at a very short solidification length of 0.35 cm when a high cooling rate is imposed. This can account for the observed primary TiC in the sample cooled at rate of 162 K/s and 267 K/s, as shown in Figs. 9 and 10.

In contrast with the corresponding relation assuming equilibrium solidification conditions (i.e., Brody and Fleming’s model), Eq. (14) implies that the interface temperature $T$ is dependent on the interface velocity $V$ and the liquid concentration at the interface $C_L$. The moving of interface temperature fields due to high cooling rate during solidification is another main feature of non-equilibrium solidification. Thus, the change of interface temperature exhibits a dominant effect on the precipitation behavior of TiC during solidification process of steel melts.

According to Eqs. (8)–(11), (14), (15) and Table 2, the change of the temperature in the liquid at the solid/liquid interface with the solidification length under different cooling rates can be obtained, as shown in Fig. 14(c). With the increase of the solidification length, the temperature in the liquid at the solid/liquid interface decrease gradually. Meanwhile, it can be inferred that this phenomenon will be more pronounced with the increase of cooling rate. It also can be seen from Fig. 14(c) that the temperature in the liquid at the solid/liquid interface in the sample cooled at rate of 162 K/s and 267 K/s can reach a low value immediately at the initial stage of solidification process. As is known, the product of the contents of titanium and carbon in the melts is lowered when the interface temperature is decreased. Therefore, TiC can precipitate from the melts at the initial stage at a very short solidification length of 0.35 cm when a high cooling rate is imposed. This can account for the observed primary TiC in the sample cooled at rate of 162 K/s and 267 K/s, as shown in Figs. 9 and 10.

5. Conclusions

In summary, a study of non-equilibrium precipitation behavior of TiC was carried out during solidification for different cooling rates using interface response functions proposed assuming interface non-equilibrium on the basis of incomplete mixing of solute in the liquid during solidification. The main results are summarized as follows:

(1) The carbide in TiC-reinforced wear-resistant steel is principally Ti-rich MC-type, which starts to precipitate at 1 460°C in the solid–liquid zone. As the temperature decreased, there is no major change in the concentration of Ti and C in TiC. With the precipitation of TiC, the concentration of Ti at the solidifying front increased and that of C decreased during the solidification process of liquid steel.

(2) According to the calculations based on equilibrium...
assumptions, TiC cannot precipitate directly in the melts and can form only when the solid fraction exceeds 0.24 during solidification. The observed cubic-shaped carbides are the primary solid particles that precipitated before and during solidification. It is not accurate to predict the precipitation behavior of TiC during actual solidification only using equilibrium approaches.

(3) It is found that the interface non-equilibrium exhibits a dominant effect on TiC precipitation behavior and determines the effective model adopted. Due to the strengthened non-equilibrium effect under the condition of higher cooling rate, primary TiC can precipitate from the melts at the initial stage of solidification when a high cooling rate is imposed.

Acknowledgements
This work is funded by the National Key R&D Program of China (2017YFB0305101).

REFERENCES