Article

Complex Precipitates of TiN-MCx in GCr15 Bearing Steel

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Abstract: Nitride and carbide are the second phases which play an important role in the performance of bearing steel, and their precipitation behavior is complicated. In this study, TiN-MCx precipitations in GCr15 bearing steels were obtained by non-aqueous electrolysis, and their precipitation mechanisms were studied. TiN is the effective heterogeneous nucleation site for Fe7C3 and Fe3C, therefore, MCx can precipitate on the surface of TiN easily, its chemistry component consists of M3C and M7C3 (M = Fe, Cr, Mn) and Cr3C2. TiN-MCx with high TiN volume fraction, TiN forms in early stage of solidification, and MCx precipitates on TiN surface after TiN engulfed by the solidification advancing front. TiN-MCx with low TiN volume fraction, TiN and MCx form in late stage of solidification, TiN can not grow sufficiently and is covered by a large number of precipitated MCx particles.

Keywords: Non-aqueous electrolysis; TiN-MCx; Precipitation; Bearings; High carbon chromium bearing steel

1. Introduction

Controlling microstructures and second phase in steel plays an vital role in the quality of steel. Carbide (M3C, M5C3, M7C3, M = Fe, Cr, Mn)1,2 and TiN inclusion3,4 are common second phase in high carbon chromium steel. Due to the good wear resistance and solid solubility with alloy elements (Cr, Mn)5,6, carbide can keep good mechanical properties of bearing steel during heat treatment7,8. In recent years, utilization of inclusions has become attractive to improve steel performance. TiN is more harmful to bearing steel than Al2O3 in the same size9. Many studies have investigated TiN and Al2O3, MgAl2O4 and MnS, and NbC complex precipitation with inclusion10-13. Our previous study14 found that TiN inclusion were covered by carbide in the etched GCr15 bearing steel metallographic specimens. Considering the two-dimensional (2-D) of particles cannot reflect their real morphologies, it is necessary to observe their three-dimensional (3-D) morphologies in steel.

The non-aqueous electrolysis extraction of second phase from steel is an effective method to study their 3-D morphologies and composite interfaces. Fang et al.15 studied the behaviors of rare earth dissolved in α-Fe, Fe-Ce intermetallic compounds and rare earth inclusions via non-aqueous
electrolysis. Bi et al. [16] analyzed 3-D morphology, quantity and chemistry of inclusion in ferroalloys by the electrolysis method. Wang et al. [17] observed Al₂O₃-MnO-SiO₂(-MnS) inclusion in steel by non-aqueous electrolysis. X. W. Zhang et al. [18,19] analyzed Ca-Mg spinel in cord steel and MnS in heavy rail steel by the electrolysis. D. Zhang et al. [20] studied the suitable electrolytic conditions for 16MnCr55 steel.

In this study, 3-D morphologies of the carbide (MCₓ, M = Fe, Cr, Mn) and TiN-MCₓ precipitates extracted from GCr15 bearing steel specimens by the non-aqueous electrolysis were observed by field emission scanning electron microscope - energy dispersive spectrometer (FESEM - EDS). The MCₓ chemistry component was confirmed by X-ray diffraction (XRD) and FactSage™ phase diagram calculation. The precipitation mechanism of TiN-MCₓ with different volume fraction in GCr15 bearing steels was elucidated.

2. Experimental

2.1. Chemical Components Analysis

The chemical compositions of GCr15 bearing steel produced by the basic oxygen furnace (BOF)-landle furnace (LF)-vacuum degas (VD)-continuous casting (CC) process in a foundry were determined by direct-reading spectrometer (Model: ARL-3460 Optical Emission Spectrometer, Thermo Fisher Corporation). The total oxygen and total nitrogen contents were analyzed using a nitrogen-oxygen analyzer (Model: TC-600, LECO Corporation). The chemical compositions of the GCr15 bearing steel are shown in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Cr</th>
<th>N</th>
<th>Alt</th>
<th>Ca</th>
<th>O(T)</th>
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<tr>
<td>Concentration</td>
<td>1.01</td>
<td>0.25</td>
<td>0.36</td>
<td>0.012</td>
<td>0.0014</td>
<td>0.0078</td>
<td>1.46</td>
<td>0.0099</td>
<td>0.0049</td>
<td>0.012</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

2.2. Non-aqueous electrolysis and XRD detection

The non-aqueous electrolysis method was used to extract TiN-MCₓ particles from the GCr15 bearing steel. Samples with diameter of 10 mm and height of 100 mm were as anode and copper as cathode. The electrolyte consists of 1% tetramethylammonium chloride, 5% triethanolamine, 5% glycerol, and 89% anhydrous methanol (in volume percentage). The constant voltage DC power supply (model: DH1720A-1) was used to keep the current density between 40 - 60 mA/cm². The temperature of the electrolyte was kept at 268 - 278 K (-5 - 5 °C). Argon gas was used to stir organic electrolyte. After electrolysis, steel samples were placed to a beaker containing ethanol and vibrated with ultrasonic wave to separate all particles from the samples surface. MCₓ and inclusions in ethanol were further separated by the magnetism. The inclusion particles were transferred directly to the double-sided carbon bands attached to the conductive material, and then were observed by FESEM-EDS. After magnetic separation, MCₓ was analyzed by XRD (Model: XPert Powder, Malvern PANalytic Ltd. the detection parameters are that Cu Kαλ = 0.154178 nm, tube current 40 mA and tube voltage 40 kV, scanning scope 30 – 85°, step length 0.013 s, residence time 5 s).

3. Result

3.1. Observation for Particles

2-D morphologies of TiN-MCₓ in the metallographic specimens etched by 4% nitric acid alcohol are observed by FESEM-EDS and shown in Figure 1. The EDS points are the black crosses and the analysis for elements can be seen both in Figure 1. The dark grey particles are TiN inclusions, and the light grey particles are MCₓ. Figure 1(a) shows a long strip and large size TiN with a small amount
of MCx around it. Figures 1(b) to (d) show TiN with less pronounced aspect ratios and its covered by a larger number of MCx, which in some cases form a continuous layer rather than discrete particles.

<table>
<thead>
<tr>
<th>No.</th>
<th>EDS point analysis (element in atomic percentage)</th>
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<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>(a)</td>
<td>54.78</td>
</tr>
<tr>
<td>(b)</td>
<td>53.89</td>
</tr>
<tr>
<td>(c)</td>
<td>40.28</td>
</tr>
<tr>
<td>(d)</td>
<td>46.09</td>
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</table>

Figure 1. TiN-MCx particles and EDS point analysis for TiN part in etched metallographic specimens.

(a) long-strip and large size TiN with MCx; (b) - (d) small size TiN with MCx.

3-D morphologies, chemistries of TiN-MCx and EDS point analysis for TiN part were also observed by FESEM-EDS, the atomic percentage of element can be seen in each element mapping. Figure 2(a) shows TiN-MCx with large size TiN inclusion (in comparison to MCx) whose size is approximately 25 μm. This category of TiN-MCx is denoted as “TiN-MCx with high TiN volume fraction” in this paper. The elements mapping shows that Ti and V can form the solid solution, while the metallic elements in MCx are Fe and Cr, Mn can not be detected because of its low content. Figure 2(b) shows that TiN-MCx with small size TiN are approximately 5 μm, its shape is closer to a sphere. Compared with the TiN-MCx in Figures 2(a), TiN in the precipitates is clearly smaller. This category of TiN-MCx is denoted as “TiN-MCx with low TiN volume fraction”. The TiN-MCx with low TiN volume fraction is almost completely covered by MCx.
Figure 2. Morphologies and elements mapping of TiN-MC$_x$ and EDS point analysis for TiN part. (a) high TiN volume fraction; (b) low TiN volume fraction.

Figure 3 shows the 3-D morphologies of MC$_x$ and elements mapping of Fe, Cr, and Mn. The morphologies of single MC$_x$ particles are not significantly different from that of MC$_x$ on the surface of TiN inclusion. Figure 3(a) shows a spherical MC$_x$ with a smaller size less 1 μm. Figure 3(b) shows a flat MC$_x$ with approximate 1 μm whereas a MC$_x$ with a shape of a long strip of length 6 μm in Figure 3(c), which is rarely found in steel. Figure 3(d) shows MC$_x$ transferred on the conductive carrier, and the MC$_x$ are predominantly spherical and flat. Figures 3(e) and (f) are cluster-like MC$_x$ with Fe, Cr and Mn elements mapping results. The size of cluster-like MC$_x$ are approximately 15 μm. However, the cluster-like MC$_x$ exhibits the morphology of banded or reticulated MC$_x$ in metallographic samples. In Figures 3(e) and (f), C is not shown since MC$_x$ and inclusions were transferred on the carbon bands.
Figure 3. Morphologies and elements mapping of MCx. (a) ball-like MCx; (b) flat-like MCx; (c) long stripe-like; (d) MCx transferred on the conductive carrier; (e) and (f) cluster-like MCx with elements mapping of Fe, Cr, and Mn.

3.2. XRD Result

Figure 4 shows the result of MCx XRD experiment, the structure of MCx are predominantly M3C and M7C3, with M3C being the dominant carbide. At $2\theta = 48.6^\circ$, there are a few Cr3C2. The results are similar to carbides in GCr15 bearing steel after electroslag remelting-continuous casting (ESR-CC) process by Du et al. [2]. The main MCx in that study were M3C, M3C2 and M7C3, and the content of Cr in their sample was 1.47\% and 0.31\% [2], respectively, which is similar to that in our steel.

Figure 4. XRD analysis result of the extracted MCx in the GCr15 bearing steel.
4. Discussion

4.1. Thermodynamic Analysis

The phase diagram of Fe-1.5%Cr-C system was calculated by using the FactSage™ 7.2 thermodynamic software and steel database[21]. The calculated phase diagram for the conditions, [pct Cr] = 1.5, [pct C] = 0.5 - 1.5 ([pct element] is mass percent of the element in steel), and the temperature range from 298 K (25 ℃) to 1873 K (1600 ℃), is shown in Figure 5 and the gray part presents the mushy zone of steel. When [pct C] = 1, equilibrium transformation of steel is that liquid → FCC + liquid → FCC → M3C + FCC → M3C + BCC + C → M3C + BCC + C + C + M3C + BCC + Cr3C2. The liquidus temperature and solidus temperature are close to the calculated values in our previous paper [liquidus and solidus temperature are 1723 K (1450 ℃) and 1601 K (1328 ℃), respectively][14]. When the temperature is slightly lower than 1173 K (900 ℃), M3C gradually precipitates from FCC phase; when the temperature is approximately 913 K (640 ℃), the carbide gradually transforms to M7C3; and when the temperature is slightly higher than 773 K (500 ℃), the carbide gradually transforms into Cr3C2. In the actual process, phase transformation will be difficult to be completed to the phase fraction dictated by the equilibrium phase diagram which leads to the transition layers. The main phases formed during temperature gradual decreasing are M3C, M7C3, Cr3C2, and their content decreases in turn. FactSage™ calculation results are consistent with XRD result, in which MCx are found to be M3C, M7C3 and Cr3C2.

Figure 5. Phase diagram for Fe-1.5%Cr-C system (the shadow part is the mushy zone of steel, C presents the pure substance C(s); M3C (Cementite) presents Fe3C with dissolved Cr, Mn; M3C presents carbide phase found in Cr, Mn-containing steels; FCC and BCC present the face-centered cubic iron (γ-Fe) and body-centered cubic iron (α-Fe), respectively).

According to the authors previous work[14,22], TiN precipitates in the mushy zone of GCr15 bearing steel, and their size is affected by the concentration of Ti and N around TiN crystal nucleus. Ti and N both are positive segregation elements (k > 0), their concentrations and consequently the supersaturation increases with solid fraction increasing, and TiN precipitation become easier during solidification process. Recently, Li et al.[23] studied the precipitation of TiN inclusions in GCr15 bearing steel during solidification by calculating the thermodynamics and growth kinetics considering solidification segregation of the solute elements, they believe that the effect of Ti content on the size of TiN inclusions is greater than that of N content.

Fe, Cr, Mn, and C can precipitate on TiN, which is the heterogeneous nucleation site for MCx. It is seen in Figure 2(a) that the size of TiN is large and consequently, TiN would be formed at the early
stage of solidification, and has enough time to growth. TiN in Figure 2(b) precipitates at the late stage of solidification. The diffusion coefficients $D_i$, $i = \text{Cr, Ti, Mn, C, N}$ in $\gamma$-phase were calculated according to the phase diagrams, when $[\text{pct C}] = 1$ and FCC precipitates at 1673 K (1400 $^\circ$C). The relationship between diffusion coefficients and temperature from 1673 to 1173 K (1400 to 900 $^\circ$C) is shown in Figure 6(a), and the parameters are shown in Table 2. From Figure 6(a), in 1673 - 1642 K (1400 - 1369 $^\circ$C), $D_N > D_C > D_Ti > D_{Mn}$; in 1642 - 1173 K (1369 - 900 $^\circ$C), $D_C > D_N > D_{Ti} > D_{Mn}$.

The results indicate that the diffusion of C and N plays a dominant role, the diffusion of C is more efficient than N after the temperature decreased under 1642 K, while the diffusion of Cr, Ti, and Mn are extremely small in $\gamma$-phase, the content of Cr is much larger than that of Mn and Ti, this would not affect the precipitation of MCx. That means that TiN may precipitate more easily in the range of temperature of 1673 K - 1642 K, while MCx precipitates easily during the following decreasing temperature process.

<table>
<thead>
<tr>
<th>Element</th>
<th>Equilibrium Partition Coefficient, $k$</th>
<th>Diffusion Coefficient in $\gamma$-phase (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.34</td>
<td>0.0761·EXP(-134600/RT)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.85</td>
<td>0.0012·EXP(-219000/RT)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.78</td>
<td>0.486·EXP(-276100/RT)</td>
</tr>
<tr>
<td>Ti</td>
<td>0.33</td>
<td>0.15·EXP(-251000/RT)</td>
</tr>
<tr>
<td>N</td>
<td>0.48</td>
<td>0.91·EXP(-168500/RT)</td>
</tr>
</tbody>
</table>

The segregation degree of C, Cr, Ti, Mn, and N during solidification is calculated according to Equations (1) to (5)[28], in Figure 6(b), at cooling rate of 0.5 K/s, temperature of 1723 K to 1601 K (1450 $^\circ$C to 1328 $^\circ$C), corresponding solid fraction is 0–1. The order of segregation from high to low is Ti, C, N, Mn and Cr at the same solid fraction. The segregation degree of C at the late stage of solidification reaches tens of times of the initial content. Therefore, MCx precipitation on the TiN surface becomes easier at the late stages of solidification.

$$\frac{[\text{pct } X]_t}{[\text{pct } X]_0} = \left[ 1 - \left( 1 - \frac{\beta k_i}{1 + \beta} \right) \cdot \frac{f_s}{1 + \frac{\beta k_i}{1 + \beta}} \right]^{k_i - 1}$$  \hspace{1cm} (1)

$$\beta = \frac{4D_i^f}{L^2}$$ \hspace{1cm} (2)

$$\tau = \frac{T_i - T_s}{R_c}$$ \hspace{1cm} (3)

$$L = 143.9 \times R_c^{-0.386}, \left( [\text{pct C}] = 1 \right)$$ \hspace{1cm} (4)

$$T = T_{Fe} \cdot \frac{T_{Fe} - T_i}{1 - f_s \cdot \frac{R_c}{T_{Fe} - T_s}}$$ \hspace{1cm} (5)
Here, \([\text{pct } X]_t\) is the C concentration at solidification front, \([\text{pct } X]_0\) is the initial C concentration; \(f_s\) is solid fraction; \(k_i\) is equilibrium distribution coefficient of C, Cr, Mn, Ti, and N in \(\gamma\)-phase; \(D_i^{\gamma}\) is diffusion coefficient of C, Cr, Mn, Ti, and N in \(\gamma\)-phase, \(\text{cm}^2/\text{s}\); \(\tau\) is the local cooling time, \(\text{s}\); \(R_c\) is the local cooling rate, \(\text{K/s}\); \(L\) is secondary arm space, \(\mu\text{m}\); \(T_{\text{Fe}}, T_{\text{li}}, \text{and } T_s\) are the melting point of pure iron \((1809 \text{ K} (1536 \text{ °C}))\), the liquidus temperature \((1723 \text{ K} (1450 \text{ °C}))\) and the solidus temperature \((1601 \text{ K} (1328 \text{ °C}))\) of GCr15 steel[14], respectively.

**Figure 6.** Diffusion coefficient change in \(\gamma\)-phase and segregation degree of C, Mn, Ti, C, N during solidification process (a) diffusion coefficient change; (b) segregation degree.

### 4.2. Crystallographic Analysis

Based on the disregistry theory[29,30], the inconsistency of lattice parameters between matrix and nucleating phase can indicate the effectiveness of nucleating catalysts. Choosing three crystal planes and three crystal orientations of the matrix and new phase crystal, the corresponding crystal parameters can calculate the disregistries between two phases by Equation (6). Since M₃C and M₇C₃ are substitutional solid solutions (Cr and Mn take the position of Fe in carbides)[31], the minimum disregistries of TiN-M₇C₃, TiN-M₃C, and Fe₃C-Fe₇C₃ were verified by the parameters of TiN[14], Fe₃C[32] and Fe₇C[33]. The parameters and calculated results are shown in Table 3, and the disregistries diagram is shown in Figure 7. The disregistry between \([\overline{1}1\overline{1}][110]\)TiN∥\([\overline{1}1\overline{1}][110]\)Fe₃C, \([\overline{1}1\overline{1}][110]\)TiN∥\([\overline{1}1\overline{1}][110]\)Fe₇C and \([011][100]\)Fe₃C∥\([011][100]\)Fe₇C are 1.49%, 5.16% and 7.40%, respectively.
respectively. The results show that the disregistries between TiN and Fe₇C₃ and Fe₃C are both small, and consequently TiN would provide suitable heterogeneous nucleation sites for Fe₇C₃ and Fe₃C.

\[
\delta^{(hkl)}_{(hkl)} = \frac{1}{3} \sum_{i=1}^{3} \left( \frac{d_{[uvw]^s} \cdot \cos \theta - d_{[uvw]^n}}{d_{[uvw]^n}} \right) \times 100\% 
\]

(6)

where \( \delta^{(hkl)}_{(hkl)} \) is disregistry between a solid plane \((hkl)^s\) and a nucleate plane \((hkl)^n\); \(d_{[uvw]^s}\) and \(d_{[uvw]^n}\) are the interatomic spacing along a low-index direction \([uvw]^s\) and the interatomic spacing along a low-index direction \([uvw]^n\); \(\theta\) is the angle between \([uvw]^s\) and \([uvw]^n\).

<table>
<thead>
<tr>
<th>Substance (space group)</th>
<th>Lattice parameters (length unit: Å)</th>
<th>(\alpha=\beta=\gamma(°))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₇C₃ (Pnma)[32]</td>
<td>a = 4.537, b = 6.892, c = 11.913</td>
<td>90</td>
</tr>
<tr>
<td>TiN-Fe₇C₃ ([hkl]^s)</td>
<td>([hkl]^n)</td>
<td>(d_{[hkl]^s}), (d_{[hkl]^n}), (\theta(°))</td>
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<tr>
<td>(100)TiN (|) (100)Fe₇C₃</td>
<td>(001) (|) (001)</td>
<td>2.118, 11.913, 0(°)</td>
</tr>
<tr>
<td></td>
<td>(011) (|) (011)</td>
<td>2.995, 13.763, 14.949, 6.52%</td>
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<td></td>
<td>(010) (|) (010)</td>
<td>2.118, 6.892, -</td>
</tr>
<tr>
<td></td>
<td>(1\bar{1}0) (|) (001)</td>
<td>2.995, 11.913, -</td>
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<tr>
<td>(110)TiN (|) (110)Fe₇C₃</td>
<td>(\bar{1}11) (|) (\bar{1}11)</td>
<td>3.668, 14.492, 0.556, 1.49%</td>
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<td></td>
<td>(001) (|) (\bar{1}10)</td>
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<td>(0\bar{1}1) (|) (0\bar{1}1)</td>
<td>2.995, 13.763, 5.275</td>
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<td>(\bar{1}10) (|) (\bar{1}10)</td>
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<td>([hkl]^n)</td>
<td>(d_{[hkl]^s}), (d_{[hkl]^n}), (\theta(°))</td>
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<tr>
<td>(100)TiN (|) (100)Fe₃C</td>
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<td>(011) (|) (011)</td>
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<td>[hkl]₀</td>
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Notes: Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 28 May 2019
Peer-reviewed version available at *Metals* 2019, 9, 641; doi:10.3390/met9060641
4.3. Pushing and Engulfment Behavior of Particles

Descotes et al. [34] found that TiN particles could be engulfed by the solid side at the solid-liquid interface in the solidification process. However, Pervushuin et al. [35] reported that TiN was pushed into the liquid side in molten steel during solidification. In our previous study [22], the local cooling rate and movement velocity of solidification front are confirmed as 0.7 K/s and 3 μm/s by the observation of confocal laser scanning microscope (CLSM), respectively. The changes of temperature, time, and distance are approximately 7 K, 10.6 seconds, and 32 μm, as shown in Figure 8. The critical velocity of pushing or engulfment $V_{cr}=23/R$ (R is the radius for globular particles) [36], when R comes to be 12.5 μm and 2.5 μm (the particles in Figure 2), $V_{cr}$ are equal to 1.84 μm/s and 9.2 μm/s, respectively. That means the large size TiN inclusion is easier to be engulfed than small size TiN. In the actual process, the local cooling rate is 0.5 to 10 K/s. The higher the local cooling rate is, the faster the solidification front moves, and the more easily the inclusions are engulfed.
Figure 8. Parameters and distance changes of solidification front in GCr15 bearing steel.

The size of TiN-MCx is larger than TiN, TiN-MCx moves more slowly than TiN and is easier to be swallowed by the solidification front. After the engulfment, particles will continue to grow through solid state diffusion, the rate of which will decrease with decreasing temperature. For TiN-MCx pushed to the liquid phase, elements segregation provides possibility for the growth of MCx on TiN, TiN-MCx keeps growing until its size is large enough to be engulfed by the solid phase. The precipitation mechanism of TiN-MCx in different solidification periods can be confirmed.

- TiN-MCx with high TiN volume fraction precipitates at the early stage of solidification and has better growth kinetics in the melt. After being engulfed by the solidification front, MCx grows at a lower rate on the surface of TiN.

- TiN-MCx with low TiN volume fraction precipitates in the late stage of solidification, and does not have enough time to grow to large size. Due to high C concentration and segregation, a large amount of MCx precipitates on TiN surface. When TiN-MCx is large enough and engulfed by the solidification front, the volume fraction of MCx is large to cover TiN particle.

5. Conclusion

In this study, TiN-MCx precipitation mechanism in GCr15 bearing steels were analyzed by combining the experiments of non-aqueous electrolysis, FESEM observation with EDS, and XRD analysis, and the theoretical analysis of thermodynamic and crystallographic analysis, and CLSM observation for pushing and engulfment behavior of particles. The main conclusions can be drawn:

1. TiN-MCx composed of TiN and MCx, TiN is the effective heterogeneous nucleation site for Fe7C3 and Fe3C, in which the MCx precipitates on the surface of TiN was observed in GCr15 bearing steel.

2. MCx (M = Fe, Cr, Mn) in GCr15 bearing steel smelted by converter is mainly composed of M3C, M7C3, and Cr3C2.

3. TiN-MCx with high TiN volume fraction precipitates at the early solidification stage. After being engulfed by the solidification front, MCx grows at a lower rate on the surface of TiN.

4. TiN-MCx with low TiN volume fraction precipitates in the late solidification stage, and does not have enough time to grow to large size. When the size of TiN-MCx is large enough and engulfed by the solidification front, the volume fraction of MCx is large to cover TiN particle because of high C concentration and segregation.
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