Carbonitride Dissolution and Austenite Grain Growth in a High Cr Ferritic Heat-resistant Steel

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Dissolution of carbonitrides and growth of austenite grain in X12CrMoWVNbN10-1-1 steel under various austenitizing conditions were investigated. The experimental results showed that the carbonitrides existing in after-forging heat treated state were mainly Cr_{23}C_6 and small amounts of NbN and Cr_2N . However, Cr_{23}C_6 and Cr_2N precipitates were dissolved completely after austenitization at 1070°C for 60 min or at 1200°C for 15 min, only the NbN particles left. The state of dissolution of NbN particles was also studied in detail as a function of austenitization holding time (t_A) at different temperatures. Initially, the NbN particles dissolved with increasing t_A at 1070°C. When t_A reached over 360 min, the amount of NbN remained approximately constant. On the contrary, during the process of austenitization at 1010°C, no NbN particles dissolved into matrix. Starting from the fine and uniform grains, abnormal grain growth was observed after austenitizing at 1010°C for 960 min or at 1070°C for 180 min due to the heterogeneous distribution of NbN particles. The plot of grain size against t_A indicated that the NbN particle with mean diameter of 117 nm and volume fraction of 3.1×10^{-4} would be sufficient to inhibit the austenite grain size effectively. Finally, the EBSD measurements demonstrated that the high energy grain boundaries whose misorientation range is 20–45° might be responsible for abnormal grain growth.

KEY WORDS: austenite grain growth; carbide dissolution; solution product formula; pinning effect; X12CrMoWVNbN10-1-1 steel.

1. Introduction

The use of X12CrMoWVNbN10-1-1 steel for manufacturing the high and middle pressure rotors of Ultra Supercritical Power Unit has demonstrated its superiority in high corrosion resistance, high temperature creep strength, good weldability, superior swelling resistance and excellent thermal property.¹⁾ The rotors are commonly used in the extremely serious circumstances of high pressure and temperature requiring for the steel possessing comprehensive mechanical properties, which provides the impetus for its progressive development. The research on austenite grain growth is often of utmost significance, due to the tremendous effect of austenite grain size obtained from the subsequent cooling process on the microstructure and performance. The fine austenite grains contribute to the low stability of grain boundary which is a weakness for long-term creep strength of the steel. On the other hand, too large or heterogeneous austenite grains would cause the brittleness of steel. Besides, the ultrasonic inspection of the grain size is too difficult to carry out under such circumstance.²⁾ Therefore, it is necessary to study the austenite grain growth behavior so as to obtain desirable austenite grain size.

It is well known that small amounts of alloying elements

such as V, Nb and Ti can significantly improve the overall mechanical properties through the precipitation of second phases and subsequent retarding the grain growth of austenite. Several theoretical models^{3–8)} have been proposed to interpret the pinning effect of precipitates on austenite grain growth. Most of them were based on Zener's concept and therefore deduced to a similar formulation. These models were established from the equilibrium between the driving force for grain growth and the pinning force of the precipitates exerting on the grain boundaries.

There have been several studies about the effect of carbonitrides on austenite grain size in some steels. Estay *et al.*⁹⁾ followed the dissolution of carbide and the growth and shrinkage of austenite during the intercritical annealing of Fe–C–Mn dual phase steels. Considering the absence of detailed measurements of the relationship between particle size and density, Cuddy *et al.*¹⁰⁾ derived a phenomenological relation between steel composition and coarsening behavior of austenite grains, especially that between the grain coarsening temperature and the type and concentration of microalloying elements. They also proposed the factors that regulate particle dissolution. Gutiérrez *et al.*¹¹⁾ investigated the influence of the austenitizing holding time (t_A) and the heating rate to austenite on the development of a heterogeneous austenite grain size distribution in ASTM A213-T91 Steel at various austenitizing temperatures (T_A), taking into account the size distribution of pinning particles. Shome *et*

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*al.*¹²⁾ explained successfully the grain growth kinetics in the heat affected zone of HSLA-100 steel by tracking the change in the size of the dissolving particles. FU Liming *et al.*¹³⁾ derived a kinetic equation for austenite grain growth concerning the mutual effect of NbC and Nb solute in low carbon Nb-microalloyed steels. However, all these previous works have been carried out over a rather short t_A range (shorter than 360 min) at different T_A . For the large forging (e.g. the maximum diameter is $\phi 1440$ mm), austenitization for a long time is necessary for the homogeneity in temperature. Moreover, most of the previous studies focused on the austenite grain size as a function of austenitizing temperature. Although Lizhan Han *et al.*¹⁴⁾ have already investigated the behavior of austenite grain growth of X12CrMoWVNbN10-1-1 steel, there have been no convincing evidences to explain the results. The relationship between carbonitride dissolution and isothermal austenite grain growth in this steel with longer holding time (up to 960 min) has yet to be further resolved. Thus, it would be investigated in detail in present paper.

2. Experimental

The chemical composition of X12CrMoWVNbN10-1-1 steel is given in **Table 1**. The steel was received in the after-forging heat treated state, *i.e.* it was forged at a temperature range from to 1250°C and cooled in furnace from the forging temperature down to 690°C, held at this temperature for 250 h and finally cooled in air down to room temperature.

In order to investigate the behavior of austenite grain growth, the heat treatments were performed in an electric resistance furnace. When the furnace reached a desired temperature, the samples with dimensions of 80 mm×40 mm×40 mm were put into it. They were soaked at a temperature in 1010°C–1200°C for different time ranging from 5 min to 960 min and then quenched in water. For a clear display of austenite grain size, additional heat treatment was done by holding at 700°C for about 40 h to facilitate the formation of carbonitrides decorating the grain boundaries. The microstructural characterization was performed on an optical microscope, Observer D1 m produced by Carl ZEISS. For eliminating the effect of decarburization and oxidation, the surface of samples was ground to remove 5 mm on the surface and then sectioned, mounted in resin, mechanically polished and etched using a mixture of 100 ml distilled water, 2 g picric acid, 50 ml sodium alkyl sulfonate, 6 drops of hydrochloric acid. The linear intercept method^{15,16)} in optical micrographs was employed to estimate the average austenite grain size.

In order to reveal the size of NbN particles and determine the grain boundary misorientations, the samples were observed and analyzed using scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) respectively. The EBSD measurement was carried out at an accelerating voltage of 20 kV and step size of 0.15 μm . If the

misorientation showed a rotation angle less than 1°, the two points were interpreted to belong to the same lath and sub-grain.

The phase identification of the carbonitrides was done on the extracted residues obtained by electrolytically dissolving the matrix in a solution consisting of 5% glycerol, 1% citric acid monohydrate, 5% hydrochloric acid and methanol in volume fraction. The electric current was 0.7A and the temperature was in the range of –5°C to 0°C. The residues extracted were identified by X-ray diffraction (XRD) performed on a D/max 2550X-ray diffractometer at 35 kV and 200 mA. Cu K α radiation was used and a 2θ range from 20–120° was step-scanned with a scanning speed (2θ) of 3°/min.

The quantitative analyses of constituent elements in the carbonitrides were carried out in the following procedures. The extracted residues were filtered by a microporous membrane, followed by washing sequentially with an ethanol solution of citric acid (10 g/L), an aqueous solution of citric acid (10 g/L), an aqueous NaOH (10 g/L) solution, and finally distilled water. The membrane and precipitates were placed into a 250 mL beaker, and then 10 mL H₂SO₄ and 20 mL HNO₃ were added into the beaker. This mixture was then heated with an electric cooker, until the membrane was completely dissolved, yielding a transparent homogeneous solution. After cooling the mixed solution, distilled water (20–30 mL) was added, followed by slow addition of a 4 mL citric acid solution (500 g/L). Finally this mixed solution was transferred into a 100 ml volumetric flask and distilled water was then used to dilute the solution until its volume reached 100 mL. Inductively coupled plasma emission spectrometer (ICP-AES), ICAP-6300, provided by Thermo Company, was then employed to measure and determine the content of each alloying elements in the solution. In addition, the content of nitrogen in the precipitates was measured according to the international standard UDC 669.14/.15:543.24:546.17, namely, “The volumetric method for the determination of nitrogen content after distillation separation”.

The size distribution of extracted particles was measured on a Small Angle X-ray Scattering (SAXS) instrument, X’Pert Pro MPD produced by PANalytical Company, at 40 kV and 40 mA. Cu K radiation and slits (1/32, 1/16, 1/4, 0.04 mm) were used. The shape of particles was assumed to

Fig. 1. XRD patterns of the extracted residues from the as-received steel.

Table 1. Chemical composition of X12CrMoWVNbN10-1-1 steel in wt.%.

C	Si	Mn	P	S	Cr	Mo	Ni	W	V	Al	N	Nb
0.11	0.08	0.41	0.008	0.004	10.35	1.00	0.80	1.03	0.18	0.02	0.051	0.040

be a sphere.

Transmission electron microscopy (TEM) observations and energy dispersive spectrometry (EDS) analyses were performed on a JEM-2100F instrument at operating voltage of 200 kV to identify the precipitates as well. Foils for TEM observation were prepared from the center of the austenitized samples, mechanically ground from 300 μm down to 40 μm , cutting into $\phi 3$ mm discs. These foils were subsequently electropolished at -25°C with an operating voltage of 75 V using a MTP-1A twinjet polisher in a solution containing 95% acetic acid and 5% perchloric acid.

3. Results

3.1. Characterization of the Precipitates in As-received Steel

The XRD pattern (Fig. 1) shows the presence of Cr_{23}C_6 , Cr_2N and NbN in as-received state. Figures 2–4 are the results of TEM micrographs showing the morphology of the precipitates and their constituent elements contained. From Fig. 2(a), it can be seen that the precipitated phase M_{23}C_6 is easily observed and identified by its selected electron diffraction pattern (Fig. 2(b)) and $\text{M} = \text{Cr}$ (the main constituent element), Fe, Mo, *etc.* as indicated by the EDS spectrum in

Fig. 2. (a) TEM bright field (BF) micrograph of as-received steel, showing the M_{23}C_6 precipitate particles, (b) and (c) are the SAED pattern and EDS spectrum respectively, taken from the circled particle in (a).

Fig. 3. (a) TEM BF micrograph showing a NbN particle in as-received steel with corresponding (b) SAED pattern and (c) EDS spectrum.

Fig. 4. (a) TEM BF micrograph showing Cr₂N particle existing at subgrain boundaries in as-received steel with corresponding (b) SAED pattern and (c) EDS spectrum.

Fig. 2(c).

The precipitate NbN was also confirmed with a size of about 300 nm in diameter (Fig. 3). However, most of them are smaller than this size as seen in **Fig. 5**. Besides, the presence of Cr₂N was also recognized in as-received steel, forming along the subgrain boundaries (Fig. 4). Therefore, the as-received steel contains the ferritic matrix with numerous Cr₂₃C₆ and small amounts of NbN and Cr₂N, as consistent with that report in Ref. 17).

3.2. Growth Behavior of Austenite Grains

The optical micrographs of grain size in different austenitized states are shown in **Fig. 6**. In Figs. 6(b) and 6(c), several grains are found to have grown abnormally compared to the others nearby. This stage can be considered as a ‘heterogeneous’, or sometimes called ‘abnormal’ grain growth (AGG). As t_A increased, normal grains were being continuously consumed by abnormal grains and even completely disappeared after 1 070°C/960 min, as seen in Fig. 6(d). In view of this, it is reasonable to expect that AGG is a transient phenomenon occurring in grain size controlled materials under specific heat treatment conditions. However, no AGG is observed for austenitizing at even higher T_A , e.g. 1 200°C (Figs. 6(e) and 6(f)). **Figure 7** shows the dependence of average austenite grain size on t_A at various temperatures. It is shown that the austenite grains grow slowly at 1 010°C. However, at 1 070°C, the austenite grain growth rate is very slow in the beginning period but an abrupt increase in austenite grain size was observed after 120 min. Instead, there is always a rapid growth rate of austenite grain size when austenitized at 1 200°C.

3.3. Extracted Particles in Austenitized Steel

The extracted precipitates from the steel austenitized at 1 070°C are mainly NbN as identified by XRD (**Fig. 8**), although a trace amount of Cr-rich precipitates was detected at its very beginning (e.g. t_A = 15 min) and also confirmed

Fig. 5. The size distribution of NbN particles in after-forging heat treated steel.

by SEM (**Fig. 9**). The chemical analyses of extracted particles reveal that the main constituent element is Nb in such precipitates as shown in **Table 2**. No Cr was detected in the residues from the samples austenitized at 1 070°C for longer than 60 min or at 1 200°C for longer than 15 min, suggesting that the Cr₂₃C₆ has almost completely dissolved under these conditions, and only NbN left. This result falls in agreement with Gutiérrez *et al.*¹¹⁾ who reported that Cr-rich M₂₃C₆ carbide dissolved completely after 15 min at 1 060°C or 1 080°C with the heating rate of 1°C/s or 50°C/s.

Table 2 also shows that Nb-content of the extracted particles decreases slowly with the increasing t_A when austenitized at 1 070°C, indicating that the dissolution of NbN did occur. However, when t_A gets over 360 min, Nb content seems further unchanged up to 960 min, implying that NbN did not dissolve any longer. Comparing with the data of Nb after austenitization, partial NbN dissolves further with the increasing T_A from 1 070°C to 1 200°C as its mass fraction

Fig. 6. Optical micrographs of the steel austenitized at T_A/t_A : (a) 1010°C/360 min, (b) 1010°C/960 min, (c) 1070°C/180 min, (d) 1070°C/960 min, (e) 1200°C/5 min, (f) 1200°C/60 min, and then held at 700°C for about 40 h and finally quenched in water.

Fig. 7. Average austenite grain size as a function of holding time at different austenitization temperatures.

Fig. 8. XRD patterns of extracted residues from the samples austenitized at 1070°C for different t_A .

of Nb decreases correspondingly. While, NbN does not dissolve during austenitization at 1010°C for 960 min because of the same content of Nb (0.04 wt.%) in extracted particles detected in the after-forging heat treated state. The mean particle size (average of 150 particles for each) under dif-

ferent austenitization conditions was measured with SEM observations in **Table 3**, showing that the size of particles increases with t_A .

Fig. 9. Cr-rich precipitates in steel austenitized at 1070°C for 15 min (a) SEM micrograph (b) EDS spectrum of Cr-rich precipitates.

Table 2. The elements contained in extracted particles in steels under different conditions (in wt.%).

States	Cr	Nb	N
As-received	1.408	0.04	0.051
1010°C/960 min	0.093	0.04	0.0097
1070°C/15 min	0.056	0.032	0.0047
1070°C/60 min	—	0.031	0.0046
1070°C/120 min	—	0.029	0.0044
1070°C/180 min	—	0.028	0.0043
1070°C/360 min	—	0.027	0.0040
1070°C/960 min	—	0.027	0.0039
1200°C/5 min	0.011	0.0063	0.0013
1200°C/15 min	—	0.006	0.0012
1200°C/60 min	—	0.0058	0.0012

Note: “—” represents not detected.

Table 3. The volume fraction and mean radius of NbN in steel after various austenitization conditions.

States	Volume fraction, $\times 10^{-4}$	Mean Diameter, nm
1010°C/960 min	4.15	119
1070°C/15 min	3.21	89
1070°C/60 min	3.11	98
1070°C/120 min	3.10	117
1070°C/180 min	2.90	168
1070°C/360 min	2.80	221
1070°C/960 min	2.80	300

4. Discussion

4.1. Effect of Austenitizing Temperature on the Dissolution of NbN

For the dissolution of a carbonitride MX into its soluble components, $MX \rightleftharpoons [M] + [X]$, the solubility product can be expressed by

$$\log [M][X] = A - B/T \quad (1)$$

where A and B are constants known from published solubility data, T is the absolute temperature in K, $[M]$ and $[X]$ are the equilibrium concentration (wt.%) of M and X in matrix.

Table 4. Solubility products* for NbN in steel.

Compound	Metal	Non-metal	A	B	Reference
NbN(1)	Nb	N	2.8	8500	[18]
NbN(2)	Nb	N	4.04	10230	[19]
NbN(3)	Nb	N	3.7	10800	[20]
NbN _{0.87} (4)	Nb	N _{0.87}	2.86	7927	[21]
NbN(5)	Nb	N	4.2	10000	[22]

*The data refer to M_aX_b following the Eq. (2) with concentrations measured in mass fraction (wt.%) and T in K.

$$\log ([M]^a[X]^b) = A - B/T \quad (2)$$

Due to the crucial significance of the equilibrium solubility product formulae (SPF) in relevant theoretical work and practical application, the bulk of work has already been carried on to derive the formulae for common carbonitrides in steels by experiment or thermodynamics derivation. In the light of the difference in experiments and assumed derivation conditions, the calculated results from the different SPF for the same precipitated phase have an enormous range. There are several SPF proposed for NbN in austenite as listed in **Table 4**. It is essential to select the suitable SPF for practical application.

When the steel reaches an equilibrium state at 1070°C, the calculated solubility products of Nb and N in mass fraction with SPF (1)–(5) are 2.96×10^{-4} , 2.65×10^{-4} , 4.55×10^{-5} , 9.07×10^{-4} and 5.68×10^{-4} respectively. However, according to the measured data shown in Table 2 the maximum solubility product of Nb and N (1070°C/960 min) is 6.123×10^{-4} . The results calculated with SPF (1), (2), (3) and (5) are smaller than the experimental one, indicating that Nb and N can not be dissolved in matrix so much when the samples were austenitized at 1070°C, but actually they did. Therefore, SPF (1), (2), (3) and (5) can be excluded. On the other hand, the solubility product calculated with SPF (4) is larger than that measured in present experiment, which indicates that Nb and N are not saturated in matrix when the samples are austenitized at 1070°C. Based on the chemical composition of the as-received material (Table 1), the complete solution temperature of NbN calculated with the SPF (4) is about 1200°C, which is closed to that reported in Ref. 23). It is worth to note that it is a value in equilibrium state. Although NbN was still observed in the sample austenitized at 1200°C for 90 min as shown in **Fig. 10**, signifying that

Fig. 10. (a) TEM bright field (BF) micrograph of the sample after austenitization at 1200°C for 90 min, showing a NbN particle, (b) dark field (DF) micrograph of NbN particle, (c) the SAED pattern and (d) EDS spectrum taken from the particle.

the equilibrium state did not reach under such a condition. The complete solution temperature of NbN (1200°C) is higher than 1070°C and this is the reason why there is still room in matrix to allow Nb and N dissolution. However, after austenitization at 1070°C for 360 min the amount of NbN remains unchanged.

As discussed above, SPF (4) is suitable for the present work. Theoretically, the carbonitrides exhibiting the strongest effect on grain growth control should be the most stable, *i.e.* the one with the highest solution temperature.²⁴⁾ The absence of Cr₂₃C₆ at 1070°C implies that such an austenitizing temperature is higher than that required to completely dissolve it. Therefore, the presence of Cr₂₃C₆ must have little influence on grain growth.

4.2. Calculation of Volume Fraction of Precipitate

Supposing the concentration of the elements M and X in MX_x (wt.%) is *M* and *X* respectively, when the investigated temperature *T* is lower than the complete solution temperature, the two requirements should be considered, *i.e.* the SPF and the stoichiometric ratio of MX_x.

$$[M][X]^x = 10^{A-B/T} \quad \text{..... (3)}$$

$$\frac{M - [M]}{X - [X]} = \frac{A_M}{xA_X} \quad \text{..... (4)}$$

Where *A_M* and *A_X* are the relative atomic mass of M and X respectively. Combining the Eqs. (3) and (4), [M] and [X] at temperature *T* can be calculated. Then, the volume fraction of MX_x in this steel, *f*, at this temperature can be obtained:

$$f = (M - [M] + X - [X]) \times \frac{d_{Fe}}{100d_{MX}} \quad \text{..... (5)}$$

$$= (M - [M]) \times \frac{A_M + xA_X}{A_M} \times \frac{d_{Fe}}{100d_{MX}}$$

where *d_{Fe}* = 7.8 g/cm³, *d_{NbN}* = 8.371 g/cm³ are the density of Fe and NbN respectively.^{25,26)} From this equation, it is obvious that the volume fraction of NbN is dependent on the amount of Nb contained in NbN particles. Therefore, the volume fraction of NbN after austenitization at 1070°C can be calculated, based on the data in Table 2 and Eq. (5), as listed in Table 3. The magnitude order of volume fraction of NbN is 10⁻⁴, which is consistent with the result of Ref. 27).

4.3. Austenite Grain Growth Behavior

When the initial austenite grains are fine and uniform, the grain boundary area would be large and leads to a high total interfacial energy. From the thermodynamics point of view, the higher interfacial energy leads to the more unstable interface and tends to be lowered through the coalescence of fine grains. The theory of grain growth is based on the grain boundary interfacial free energy as the driving force. The driving force leading to grain boundary migration resulting in the grain growth is determined not only by the physical constants characteristic of the substances in bulk, but also by the shape and dimensions of the individual grains.²⁸⁾ In the present case, the presence of NbN, acting as barriers, impedes the grain boundary migration. In other words, the grain growth would not occur under the condition where the matrix grain boundaries are strongly pinned by NbN particles. This is the reason why the austenite grains grow so

slowly at 1010°C for 15–960 min or at 1070°C for 15–120 min. Meanwhile, it also suggests that it is the NbN that controls the austenite grain size effectively as expected and these particles with 117 nm in diameter and 3.1×10^{-4} in volume fraction are sufficient to restrict the growth of the matrix grains in this steel. As the Fig. 11 shows, the growing trend of NbN particles is almost the same as that of austenite grains and the NbN particles coarsen rapidly when AGG occurs. This means that the relatively larger NbN particles may also grow at the expense of the smaller ones. This is called Ostwald ripening.²⁹⁾ Gladman⁴⁾ pointed out the coalescence of the precipitate to a size in excess of the critical value permits the grain growth. Alternatively, the prolongation of holding time at 1070°C and the increase in temperature (from 1070°C to 1200°C) would cause more

Fig. 11. The size of austenite grain and NbN particle size vs. austenitizing time at 1070°C.

dissolution of NbN particles. The maximum volume fraction of undissolved NbN calculated at 1200°C is 6.64×10^{-5} , which is much less than that at 1070°C. According to the pinning theory,⁵⁾ the pinning force is proportional to the volume fraction of particles, and varies inversely as their mean size, *i.e.* the larger particles with little volume fraction will somehow result in the weakening of pinning effect. The grain boundaries whose driving force is larger than the pinning force migrate faster than any other grain boundaries, *i.e.* when the driving force reaches a critical value, the grain boundaries break away from the pinning atmosphere and undergo a discontinuous jump from dragged migration in the low-velocity to free migration in the high velocity.³⁰⁾ Therefore, the abrupt increase of austenite grain size at 1070°C after 120 min or at 1200°C can be attributed to the weak pinning force caused by coarsening of NbN and its decrease of volume fraction. In other words, the instability of the precipitates and their dissolution with increasing T_A are accompanied by rapid grain growth.

The occurrence of AGG (Figs. 6(b) and 6(c)) can be explained by the NbN heterogeneity, *e.g.* non-uniform distribution, different size and interparticle distance. AGG was commonly observed occurring in microalloyed steels.^{31–34)} At a higher temperature (1200°C), the dissolution of NbN precipitates allows more grains to grow and results in a form of grain growth that can be regarded as normal. This situation is also descriptive of the conditions existing in steel welding, since the heat affected zone (HAZ) austenite grains can grow fairly unhindered by second phase particles due to the high peak temperatures involved.^{35–37)} However, many researchers did not give any clear-cut answer to the question that which type of grain boundary is responsible for the

Fig. 12. EBSD analyses of grain boundaries in the steel austenitized at 1070°C for (a) 15 min (b) 120 min (c) 180 min (d) 360 min and (e) 960 min. The red curves represent the grain boundaries having different misorientations in the range of 20–45°.

Fig. 13. SEM micrograph of NbN particles in the steel austenitized at 1070°C for 3 h.

AGG. Although a lot of work has been published on the possible role of $\Sigma 9$ and other coincidence site lattice (CSL) boundaries on AGG,^{38–41)} this role has not been confirmed satisfactorily. Rajmohan *et al.*⁴²⁾ drew the conclusion that CSL boundaries are not responsible for the AGG in Fe-3%Si steel through computer experiment results. Rollett and Grest^{43,44)} demonstrated that variable grain boundary mobility and energy can lead to AGG. Monte Carlo's simulations have confirmed that two different conditions may initiate AGG. Firstly, anisotropy in the grain boundary energy can lead to rapid growth of grains having boundary energies much higher than the average. Secondly, AGG may arise from anisotropy in the grain boundary mobility.^{44–47)} Based on electron back scattered pattern (EBSP) measurements and Monte Carlo simulations,^{48–50)} Hayakawa *et al.* stressed the importance of systematic unpinning of precipitates on the high energy grain boundaries that are responsible for AGG. Meanwhile, they also argued that high energy grain boundaries whose misorientation range is in 20–45° play a role in AGG. A similar conclusion was also derived by Titorov^{51,52)} from experiment and grain misorientation analyses of pole figures.

In the present study, the occurrence of AGG can also be explained with such conclusion by EBSD measurement (**Fig. 12**). The process of grain boundary migration does not take place through a jump of an atom from one grain to another grain, but through the exchange of vacancies.^{53–55)} The high-energy boundary is more capable to absorbing and emitting vacancies⁵⁶⁾ and the number of vacancies is related to the disorder in the grain boundary structure. A high-energy boundary has a more disordered structure, and therefore a higher number of vacancies and dislocations should contribute to a high mobility. On the other hand, an easier grain boundary diffusion along the high-energy boundary facilitates the diffusion-controlled coarsening of precipitates and therefore contributes to the weakening of the pinning effect. The coarse precipitates are frequently found inside large grains (**Fig. 13**). This fact supports the assumption that precipitates coarsen at the high-energy boundary. Following this argument, it is reasonable to assume that the high-energy boundaries have higher mobility than the low-energy boundary and thus move earlier. The experimental findings⁵⁷⁾ also demonstrated that the growing large grain has a high number of general high-energy grain boundaries. Additionally,

Table 5. EBSD-measured fraction of boundaries with different misorientation angles in the samples after austenitization at 1070°C for different t_A .

t_A (min)	Fraction of the high-energy boundary with misorientation ranging from 20° to 45° (%)	Fraction of the boundaries with misorientation lower than 20° (%)	Fraction of the boundaries with misorientation higher than 45° (%)
15	5.68	77.82	15.53
120	3.84	79.19	15.46
180	2.93	81.46	14.65
360	2.11	82.22	14.65
960	0.68	81.66	16.66

from the viewpoint of thermodynamics, the high energy of grain boundary is more unstable and tends to be lowered during the process of austenitization. Thus, the high-energy boundary is consumed for AGG. This is the reason why the fraction of grain boundaries having different misorientations in the range of 20–45°, as indicated by the red curves in **Fig. 12**, gets smaller with increasing time during austenitization at 1070°C, as shown in **Table 5**.

5. Conclusions

(1) For the X12CrMoWVNbN10-1-1 steel investigated, in its after-forging heat treated state the carbonitrides existed are mainly Cr_{23}C_6 and trace amounts of NbN and Cr_2N detected by XRD and TEM. The complete dissolution of Cr_{23}C_6 and Cr_2N finishes after austenitization at 1070°C for 60 min or at 1200°C for 15 min, and only NbN left. Moreover, the dissolution of NbN occurs with the extending of austenitizing holding time at 1070°C. However, when the time is over 360 min, the amount of NbN remains unchanged. However, during the process of austenitization at 1010°C, no NbN particles dissolved into matrix.

(2) The solubility product formula (SPF) of NbN suitable for the present study is $\lg\{[\text{Nb}][\text{N}]^{0.87}\}_\gamma = 2.86 - 7927/T$. The magnitude order of volume fraction of NbN is 10^{-4} .

(3) The austenite grains grow slowly at 1010°C and at 1070°C when t_A is shorter than 120 min, which is related to the effective pinning force of NbN particles. The NbN particles with 117 nm in mean diameter and 3.1×10^{-4} in volume fraction are sufficient to inhibit the austenite grain size effectively. However, at 1070°C with $t_A > 120$ min or at 1200°C, they grow quickly because of the weakened pinning effect of NbN caused by its coarsening and decreased volume fraction. The growing trend of NbN particles at 1070°C is almost the same as that of austenite grain and the NbN particles coarsened rapidly. The occurrence of abnormal grain growth (AGG) at 1010°C for 960 min or at 1070°C for 180 min can be attributed to the heterogeneity of NbN particles, *e.g.* non-uniform distribution, different size and interparticle distance. It is also demonstrated that the high energy grain boundaries whose misorientation range is 20–45° may also be responsible for AGG.

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