Discontinuous Precipitation during Isothermal Transformation in a 9–12% Chromium Ferritic Steel

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A study of discontinuous reaction in a 9–12% chromium ferritic steel was performed by means of many characterization methods, such as physicochemical phase analysis, electron backscatter diffraction, electron probe microanalysis. Isothermal aging treatments at 700°C after solution annealing were carried out for the period over 216 h. Cr-rich $M_{23}N$ were formed as the main precipitates, together with a small amount of Cr-rich $M_{23}C_6$ and Nb-rich MN. With the increase of isothermal aging time, precipitates were observed to be preferentially nucleated at the prior austenite grain boundaries and grew toward the interior of grains with the morphology of pearlite, and eventually formed a lamellae structure. The characterization of carbide and nitride was presented in detail. Besides, the growth of the discontinuous reaction was also documented. It was found that the isothermal decomposition reaction of over-cooled austenite could be summarized as: $\gamma \rightarrow \alpha + \text{Cr-rich carbonitrides}$. The growth of discontinuous precipitation involved the diffusion of chromium (short range) and nitrogen (long range).

KEY WORDS: discontinuous precipitation; characterization; 9–12% chromium ferritic steel; isothermal aging.

1. Introduction

Increased efficiency and improved environmental protection have been and remain the innovative driving forces in the development of 9–12% chromium heat resistant steel used for power generating plants.¹⁾ Due to the operation under the serious circumstance (at temperature around 600°C and pressure around 30 Mpa), this kind of steel contains many alloying elements so that the excellent properties can be ensured by solution strengthening and precipitation strength.

Carbides and nitrides are important microstructural constituents in steels. In alloy steels, carbides and nitrides play a significant role in the microstructural evolution so that their precipitation processes have been the subject of intensive studies.²⁾ This precipitation process is essentially the precipitation in multicomponent systems, in which more than two solutes are involved. Furthermore, a remarkable feature of the precipitation of the alloy carbides and nitrides is that the diffusivities of the precipitating substitutional solutes are several orders of magnitude smaller than those of the interstitial solutes, such as carbon and nitrogen. Thus the precipitation study of the alloy carbides and nitrides gives us an opportunity to study a typical multicomponent effect in precipitation processes. The precipitation behavior has been regarded as one of the most important features of alloying

steels because their mechanical properties are profoundly dependent on the formation of the second phases.^{3,4)} Precipitation characteristics, however, have been considered to be very complicated in that (1) small changes in the chemical composition, thermomechanical processing and aging conditions can significantly influence the formation of second phases; (2) it is not easy to distinguish one type of precipitate from another only by their morphologies.

For years, discontinuous precipitation had extended wide investigations in all kinds of austenitic stainless steels. Hsiao and Dulis⁵⁾ studied such precipitation in 23Cr-14Mn-0.43C-0.46N austenitic stainless steels. They identified the precipitates as $M_{23}C_6$. They determined isothermal transformation curves, measuring the total volume fraction of cells as a function of aging time and constructed an isothermal precipitation diagram for the discontinuous precipitation. They realized that the precipitation did not complete its coverage of the entire specimens. Tanaka and coworkers^{6–8)} studied precipitation processes in a series of 21Cr-4Ni-9Mn-0.5C-0.4N steels. They reconfirmed from observation of a series of steels with several combinations of carbon and nitrogen keeping a total interstitial solute concentration constant that the discontinuous precipitation of $M_{23}C_6$ was greatly enhanced by the addition of carbon and that the precipitation of Cr_2N took place in the steels containing high nitrogen with low or no carbon. Their interest laid in a relationship between intragranular precipitation and discontinuous precipitation. They also realized that the cell growth stopped before the cell covered the entire volume of the specimen.

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They interpreted this incomplete reaction as due to a pinning effect of the intragranular precipitates on migrating cell boundaries. Okamoto *et al.*⁹⁾ found the discontinuous precipitation of Cr₂N in high nitrogen austenitic stainless steels such as type 304N and type 316N steels in their series of studies on high nitrogen steels. They studied the discontinuous precipitation of Cr₂N in 18Cr-4Ni-0.59N and 18Cr-7Ni-0.66N austenitic steels without carbon. Kikuchi *et al.*¹⁰⁾ offered a qualitative explanation for the observed non-steady state growth features of the discontinuous precipitation of Cr₂N in Cr–Ni austenitic steels containing high nitrogen. They found unambiguously that such precipitation is not a steady state process.

A tendency for discontinuous precipitation has been observed mostly in alloyed austenitic steels, especially in high nitrogen (>0.4 wt.%) steels. However, little literature¹¹⁾ was reported on the discontinuous precipitation behavior of the 9–12 wt.% chromium ferritic steels with low nitrogen content (<0.2 wt.%) to the best of our knowledge. The objectives of the current study, therefore, are to investigate and characterize the discontinuous precipitation behavior and also discuss the growth of the cell.

2. Experimental

2.1. Material and Heat Treatment

The chemical composition of investigated steel is shown in **Table 1**. The as-received steel used in this investigation was in cast state. The samples machined from the cast ingot were solution treated at 1200°C for 6 h and then isothermally aged at 700°C for various periods. All steel samples were cooled in water to room temperature after isothermal transformation.

2.2. Metallography

The microstructural characteristics of the heat treated specimens were examined with an optical microscope (OM), scanning electron microscope (SEM) and transmission electron microscope (TEM). The samples were ground and polished in the standard manner. The polished samples were etched with a mixture of 10 g iron trichloride, 15 mL hydrochloric acid and 50 mL ethanol for 10 seconds. In order to identify the precipitates and determine the orientation relationship between precipitates and the matrix, grain boundary misorientations, the sample was observed and analyzed using SEM and electron backscatter diffraction (EBSD) respectively. The EBSD measurement was carried out at an accelerating voltage of 15 kV and step size of 0.02 μm . The used step size permits a resolution, which is high enough to resolve large precipitates, and low enough to ensure good statistic in one investigation field. To make sure no misinterpreted pixels were considered in the examinations, only subgrains and laths greater than the area of 5 pixels were counted. For the evaluation of the EBSD maps, misorientations were calculated for every pixel-neighbour

combination. If the misorientation showed a rotation angle less than 2°, the two points were interpreted to belong to the same lath or subgrain. For TEM study, thin foils for matrix microstructure observation were prepared in a twin-jet electropolisher, operated at 50 V, in a solution consisting of 95% acetic acid and 5% perchloric acid. The electrolyte temperature was maintained below –30°C. Conventional TEM observations and energy dispersive spectrometry (EDS) analyses were performed on a JEM-2100 instrument at operating voltage of 200 kV. The chromium and nitrogen distribution in the microstructure of aged sample were evaluated using an electron probe micro analyzer (EPMA). The EPMA measurement was carried out at an accelerating voltage of 15 kV and step size of 1 μm .

2.3. Physicochemical Phase Analysis

The phase identification of the residues 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 0.7 A 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 2 θ range from 20–120° was step-scanned with a scanning speed (2 θ) 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”.

Table 1. Chemical composition of the investigated steel in wt.%.

C	Si	Mn	P	S	Cr	Mo	Ni	W	V	Al	N	Nb
0.03	0.11	0.45	0.011	0.002	10.52	0.99	0.77	1.03	0.18	0.01	0.15	0.04

3. Results and Discussion

3.1. Microstructure Observations

Figure 1 shows the microstructure evolution of the steel isothermally aged at 700°C for different time. The grain boundaries were clean in the sample aged at 700°C for 2 h as shown in Fig. 1(a), indicating that the incubation time of precipitation was more than 2 h. In the sample aged at 700°C for 10 h, the precipitates were found along prior austenite grain boundaries and they had grown inward austenite grains (Fig. 1(b)). With the further increase of aging time, the precipitation region continued to grow. Meanwhile, the ferrite had already been transformed from austenite as shown by a box in Fig. 1(c) in the sample aged for 96 h. Aging at 700°C up to 168 h, martensite could be observed as shown with the red box in Fig. 1(d), which was transformed from austenite during the water cooling. This meant that there was still some untransformed austenite. Until the aging time reached 216 h, the overcooled austenite matrix was transformed completely. However, the precipitates did

not cover in a whole grain (Fig. 1(e)). Such precipitation clearly revealed the prior austenite grain size. As exemplified by the SEM micrograph in **Fig. 2**, the investigations

Fig. 2. SEM micrograph for cell precipitation obtained after isothermal aged at 700°C for 144 h.

Fig. 1. Optical micrographs for the microstructure formed during isothermal aging at 700°C for different time: (a) 2 h; (b) 10 h; (c) 96 h; (d) 168 h; (e) 216 h.

achieved at higher magnifications proved the two phase (precipitates+ferrite) in a cell. This was called as “discontinuous precipitation”.¹²⁾ The precipitate distribution almost presented alignment.

3.2. Characterization of Precipitates

XRD, EBSD and TEM allowed a through characterization of the domains of precipitation in every isothermal sample. The precipitates obtained by bulk electrolytic extraction were analyzed by XRD as shown in Fig. 3. In the XRD patterns, the peaks from Cr-rich M_2N were clearly visible. At early aging period, some peaks of inclusions were detected due to the lack of clearness in steel. Moreover, Nb-rich MN particles were also identified during the aging

Fig. 3. XRD patterns of electrolytically extracted residues in the samples isothermally aged at 700°C for different time.

process although their peaks were small, which was also demonstrated by TEM as shown in Fig. 4. As the aging going on, another Cr-rich particles $M_{23}C_6$ precipitated, also demonstrated by TEM observation in Fig. 5. The phase formed after the massive precipitation of Cr-rich M_2N . The weak intensity and little peaks of the precipitate reflections suggest a small volume fraction.

TEM observation (Fig. 6(a)) also showed that the cell comprised of precipitates and the matrix. These precipitates were predominantly of needle-like shape, which was consistent with the SEM morphology in Fig. 2. A selected area electron diffraction (SAED) pattern from the sample aged at 700°C for 96 h confirmed the presence of M_2X precipitates having the HCP structure with $a=0.4805$ nm, $c=0.4479$ nm. This kind of precipitate was recognized as Cr-rich M_2N based on its EDS spectrum (Fig. 6(c)). The high misfit strain of the Cr-rich M_2N tended to result in their various shape growth.¹³⁾ The Cr-rich M_2N particles exhibited a complex contrast behavior at their interface with the matrix. Such phenomenon was also observed by Ruedl *et al.*¹⁴⁾ The contrast corresponded to thickness fringe effect produced by the curvature of the particles' shape.¹⁵⁾

The cell microstructure was also investigated by EBSD method as shown in Fig. 7. The misorientation angle between two neighbouring points (point-to-point) was plotted along the line AB in Fig. 7(c). The cell precipitated from the high angle grain boundaries, *i.e.* the boundary having a misorientation angle (49.3°) greater than 15° , as shown in Figs. 7(b) and 7(c). Figure 7(d) showed the detection of Cr-rich M_2N precipitates and ferritic matrix by EBSD. It was obtained with fine scanning step size at higher magnification

Fig. 4. TEM analysis showing the presence of Nb-rich MN in the sample isothermal aged at 700°C for 96 h: (a) Bright field; (BF) micrograph; (b) Selected area electron diffraction (SAED) pattern; (c) EDS spectrum of a Nb-rich MN in (a).

Fig. 5. TEM analysis showing the presence of Cr-rich $M_{23}C_6$ in the sample isothermal aged at 700°C for 216 h: (a) Bright field; (BF) micrograph; (b) Selected area electron diffraction (SAED) pattern; (c) Dark field (DF) micrograph with $g=(200)_{Cr_{23}C_6}$ reflection; (d) EDS spectrum of a Cr-rich $M_{23}C_6$ in (a).

Fig. 6. TEM analysis showing the cell morphology obtained by isothermal aging at 700°C for 96 h: (a) needle-like Cr-rich M_2N precipitates; (b) SAED pattern of Cr-rich M_2N (c) EDS spectrum of a Cr-rich M_2N particle.

Fig. 7. (a) SEM micrograph showing cell microstructure obtained by isothermally aged at 700°C for 20 h; (b) Inverse pole figure (IPF) of Z direction; (c) corresponding misorientation line plot along line AB in (b); (d) Electron backscattering diffraction map for identifying the microstructure obtained by aging at 700°C for 20 h. The red regions are Cr-rich M_2N ; the blue regions are ferrite.

in Fig. 7(a). Therefore, the isothermal decomposition reaction of austenite could be summarized as: $\gamma \rightarrow \alpha + \text{Cr-rich } M_2N/\text{Cr-rich } M_{23}C_6$.

3.3. Nitrogen and Chromium Distribution in Aged Sample

The nitrogen and chromium concentration profiles were determined by means of EPMA along the line across the cell between the untransformed matrix and the cell as shown in Fig. 8. The cell with lamellar precipitates of Cr-rich M_2N in a white contrast was easily identified. In contrast to the chromium and nitrogen concentration in the untransformed matrix, a higher degree of these two elements was observed in the cell (Figs. 8(b) and 8(c)). From the Fig. 1(e), it can be seen that after the completion of isothermal transformation, no one cell covered any prior austenite grain. They distributed along the prior austenite grain boundaries. This implied that N locating at the center of prior austenite grains would diffuse to the vicinity of prior austenite grain bound-

aries assuming that all the chemical elements distributed uniformly. Moreover, the average prior austenite grain size in this investigation was measured about 280 μm , indicating that N would diffuse the long distance of 140 μm . Therefore, it was demonstrated unambiguously the long range diffusion of nitrogen from the untransformed matrix to the cell, which agreed well with the conclusion drawn by Srinivas *et al.*²¹⁾ The precipitates in the cell were mainly Cr-rich M_2N , involving the diffuse of chromium. The diffusion rate of Cr and N at 700°C are about $2.81 \times 10^{-17} \text{ m}^2/\text{s}$ and $1.55 \times 10^{-13} \text{ m}^2/\text{s}$ respectively, showing that the diffusion rate of Cr is so slow that it unlikely diffuse with long range. When the isothermal transformation completed, N precipitated totally from the matrix, as shown in Table 2. Based on the stoichiometric ratio of Cr_2N , the ratio of relative atomic mass of Cr to N is 52:7. Only 1.114% Cr was required to form Cr_2N , which agreed well with the experimental data (1.1%) in Table 2. However, the given chemical content of Cr is about 10.35%. Therefore, Cr near the prior austenite grain

Fig. 8. (a) SEM micrograph of the cell precipitation with Cr-rich M_2N in the sample aged at 700°C for 100 h; (b) chromium concentration profile along the white line in (a) with EPMA; (c) nitrogen concentration profile along the white line in (a) with EPMA.

Table 2. The elements contained in extracted residues in samples under different conditions (in wt.%).

Time	Fe	Cr	Mo	W	V	Nb	N
Solution	—	—	—	—	0.0006	0.0006	0.0012
10 h	0.064	0.106	0.0010	0.070	0.0051	0.018	0.013
48 h	0.138	0.377	0.031	0.206	0.028	0.025	0.049
96 h	0.173	0.736	0.033	0.175	0.072	0.029	0.101
144 h	0.185	0.952	0.060	0.212	0.102	0.034	0.120
192 h	0.236	1.070	0.068	0.270	0.116	0.039	0.138
216 h	0.335	1.100	0.112	0.496	0.117	0.040	0.149

Note: “—” represents not detected. “Solution” represents austenitization at 1200°C for 6 h and cooled by water.

was sufficient to form Cr-rich M_2N . In other words, it was not necessary for Cr to diffuse with long range. On the basis of the results, it was deduced that such precipitation involved two diffusion mechanisms: the long range diffusion of an interstitial N and the short range diffusion of a substitutional Cr.

3.4. Microchemistry Analyses

It is acknowledged that the precipitation sequence depends primarily on the relative diffusivities of the alloy elements and the ease of nucleation, the chemistry of the steel is also an important consideration determining which precipitates are favored. The microchemistry analysis was well established to show the precipitation evolution during the aging based on the elements contained in precipitates as shown in Table 2.

After solution treatment at 1200°C for 6 h, enormous quantities of constituent elements, such as Fe, Cr, W, were

dissolved into matrix. However, there were still a trace amount of Nb (0.0006%) existed, implying the existence of Nb-rich MN particles. After aging at 700°C for 10 h, these alloying elements, as well as nitrogen, were detected due to the precipitation of nitrides. As the aging continued, the increase in concentration of constituent elements was detected, indicating that the formation of precipitates occurred during aging. When the aging time reached 192 h, Nb-rich MN particles could be regarded to precipitate completely because the concentration of Nb contained in precipitates was 0.039%, almost the same as that in the given chemistry of investigated steel. It is also indicated that after aging beyond 192 h, the increase of the concentration of N can be attributed to the formation of Cr-rich M_2N . In the sample aged for 216 h, the nitrogen precipitated completely in the form of precipitates. The nitrogen contained in this steel precipitated totally in the form of chromium-rich and niobium-rich nitrides.

4. Discussion

4.1. The Precipitation of Carbides and Nitrides during Aging

In this kind of steel, the main precipitates were Cr-rich M_2N , with a small amount of Cr-rich $M_{23}C_6$ and Nb-rich MN due to the more nitrogen content than carbon. Pettersson²²⁾ carried out the comparison with the experimental results and thermodynamic calculation of element activities and the driving force for precipitation of different phases. It was found that the driving force of Cr-rich M_2N (Cr-rich $M_{23}C_6$) increased (decreased) with the increasing nitrogen content. Briant *et al.*²³⁾ found nitrogen to delay sensitization of 304 type steels at any given carbon concentration and attributed this to reduction of the nucleation and/or growth of carbides. These arguments were also invoked by Beneke and Sandenbergh²⁴⁾ to explain the retardation of carbide precipitation with nitrogen alloying in 304/316 steels. A further explanation, that nitrogen reduces the diffusivity of carbon, was put forward in the review by Lai.²⁵⁾ With increasing nitrogen content, the formation of Cr-rich $M_{23}C_6$ could be retarded because the substitution of small amount of nitrogen in Cr-rich $M_{23}C_6$ could result in its complete dissolution,²⁶⁾ causing the amount of Cr-rich M_2N to be significantly increased. Knutsen *et al.*²⁷⁾ found that vanadium promotes formation of M_2X -type precipitates by the discontinuous precipitation reaction in a 24Cr-18Mn-1N austenitic stainless steel. In the present work, the atomic ratio of nitrogen to carbon is 5.2, which should be enough for the promotion of the nitride precipitation relative to carbide.

Although the concentration of V in this steel was higher than that of Nb, V-rich MX precipitates were not found in the microstructure during heat treatment. Instead, the EDS analyses (including above mentioned in Figs. 4(c) and 6(c)) revealed that V distribution was confined to its presence as a component of Nb-rich MN and Cr-rich M_2N .²⁸⁾ This probably attributed to the addition of aluminum. Magnusson²⁹⁾ found that the aluminum addition can reduce the MX phase fraction of VN type. That was why V-rich MX precipitates were not found in this kind of steel. As the microchemistry analysis in Table 2, solution annealed sample contained substantial alloying elements as well as carbon and nitrogen far above the solubility limit. The amount of strong MX (X=C or N) forming elements such as niobium and vanadium was very small and there was no titanium. The supersaturated carbon is precipitated in the form of Cr-rich $M_{23}C_6$.

From the perspective of simulation, the isopleth for this investigated steel in equilibrium was calculated with different nitrogen content by Thermo-Calc software (Fig. 9). The vertical (dashed) line denoted the chemical composition of the alloy investigated, and the horizontal (solid) line indicated the isothermal aging temperature of the present study. The absence of the Laves phase did not mean that the experimental results was not consistent with the simulation results. The Laves phase is thermodynamically stable in this system, especially below 815°C,³⁰⁾ but their formation is sluggish and controlled by various elements. For a definite conclusion long duration tests would be required. Therefore, the discontinuous precipitation products consisted of ferrite, Cr-rich M_2N and Cr-rich $M_{23}C_6$. And the volume fraction of Cr-rich M_2N and Cr-rich $M_{23}C_6$ were 1.35×10^{-4} and

Fig. 9. The equilibrium phase diagram calculated by using the Thermo-Calc software.

7.24×10^{-8} , respectively, which was consistent with the experimental results.

4.2. The Growth of Discontinuous Precipitation

After certain incubation time of precipitation, the prior austenite grain boundaries were occupied by precipitates. The grain boundaries have been believed to be the preferential nucleation sites for heterogeneous precipitation. The discontinuous precipitation started at grain boundaries and propagated into the grains. Discontinuous precipitation of Cr-rich M_2N was proved to be a complex precipitation phenomenon. Here, the growth of this precipitation was analyzed from the aspect of concentration of chromium and nitrogen. As the morphology of the discontinuous precipitation was similar to that of pearlite in carbon steel, this kind of precipitate was often termed as “false pearlite”.^{31,32)} The occurrence of discontinuous precipitation in 9–12% chromium ferritic steel was observed for the first time. It was worthy to note that no cell colonies was found to be precipitate directly inside the grains, which is different from the results obtained by Fernanda.³²⁾ The precipitation of chromium nitrides and the corresponding depletion of chromium and nitrogen in the matrix lead to instability of the austenite and promoted the appearance of ferrite. The islands of ferrite were very often surrounded by lamellar colonies. With increasing isothermal aging time, the precipitates grew toward the austenite phase, resulting in local Cr depletion around these precipitates. With the growth of ferrite in cell during isothermal aging, more Cr atoms could be eject to its adjacent region. The Cr-rich M_2N therefore, could be formed in this region with the aid of the high diffusivity of nitrogen in matrix. A systematic study of discontinuous precipitation was made on Cr–Ni alloys with nitrogen levels ranging from ~0.4 to ~0.6 wt%.³³⁾ The authors pointed out that the features of cellular growth in alloys containing both substitutional and interstitial solutes were different from the cellular precipitation pattern in binary solute alloy systems and concluded that long range nitrogen diffusion was important. Direct evidence for diffusion of nitrogen over long distances in grains exhibiting cellular Cr-rich M_2N formation was recently obtained for Cr–Ni–N steel by X-ray microanalysis.³⁴⁾

The growth of the cell, that was the migration of the cell boundary, corresponded to the longitudinal growth of all the

Cr-rich M_2N precipitates in the cell, which was governed by the long-range volume diffusion of N atoms from the untransformed austenitic matrix to ferrite of the lacking N. Knutsen *et al.*²⁷⁾ considered the principal driving force of boundary migration is the difference in chemical potential associated with the transformed and untransformed austenite. The cell continuously grew with the increase in aging time, accompanying decrease of nitrogen content in the untransformed matrix. Finally, as the interstitial N atoms precipitated completely, the growth of the cell stopped. The above considerations were supported by the experimental result that the volume fraction of the cell increased during aging until the whole nitrogen precipitated in the form of precipitates, which was reflected by the data in Table 2.

5. Conclusions

(1) Aging of solution annealed samples of the 9–12% chromium ferritic steel with more nitrogen (0.15%) than carbon (0.03%) at 700°C lead to the precipitation of Cr-rich M_2N , Cr-rich $M_{23}C_6$ and Nb-rich MN. The main precipitates found in this steel were Cr-rich M_2N , and the discontinuous precipitation sequence was intergranular precipitation (along the grain boundaries) and then intragranular precipitation with “false pearlite” morphology. After aging for 192 h, Nb-rich MN particles could be regarded to precipitate completely. During the period between 192 h and 216 h, Cr-rich M_2N precipitation continued until the nitrogen was completely precipitated.

(2) The cell growth started from the prior austenite grain boundaries, towards the interior of the grains. The high angle grain boundaries were favored by the precipitates. The discontinuous precipitation did not occur directly within the grains. And it was the first time to observe such cellular precipitation behavior in 9–12% chromium ferritic steel. Moreover, some ferrite had been transformed from overcooled austenite after ageing for 96 h. Therefore, the isothermal decomposition reaction of austenite could be summarized as: $\gamma \rightarrow \alpha + \text{Cr-rich carbonitrides}$.

(3) The growth of discontinuous precipitation involved the diffusion of chromium (short range) and nitrogen (long range).

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REFERENCES

- 1) R. Viswanathan and W. Bakker: *J. Mater. Eng. Perform.*, **10** (2001), 96.
- 2) D. Edmonds and R. Honeycombe: Precipitation processes in solids, Metallurgical Society of AIME, Warrendale, PA, (1978).
- 3) D. Peckner and I. M. Bernstein: Handbook of Stainless Steels, McGraw-Hill, New York, (1977).
- 4) A. Toro, W. Z. Misiolek and A. P. Tschiptschin: *Acta Mater.*, **51** (2003), 3363.
- 5) C. M. Hsiao and E. J. Dulis: *Trans. Am. Soc. Met.*, **49** (1957), 655.
- 6) M. Tanaka, O. Miyagawa and D. Fujishiro: *J. Jpn. Inst. Met.*, **38** (1974), 899.
- 7) M. Tanaka, O. Miyagawa and D. Fujishiro: *J. Jpn. Inst. Met.*, **41** (1977), 11.
- 8) M. Tanaka, O. Miyagawa, T. Sakaki and D. Fujishiro: *J. Jpn. Inst. Met.*, **40** (1976), 543.
- 9) M. Okamoto, R. Tanaka, T. Naito and R. Fujimoto: *Tetsu-to-Hagane Overseas*, **2** (1962), 25.
- 10) M. Kikuchi, M. Kajihara and S.-K. Choi: *Mater. Sci. Eng. A*, **146** (1991), 131.
- 11) X. G. Tao, L. Z. Han and J. F. Gu: *Met. Mater. Int.*, **3** (2015), 440.
- 12) F. Vanderschaeve, R. Taillard and J. Foc: *J. Mater. Sci.*, **30** (1995), 6035.
- 13) D. Sundaraman, P. Shankar and V. Raghunathan: *Metall. Mater. Trans. A*, **27** (1996), 1175.
- 14) E. Ruedl and G. Valdre: *J. Mater. Sci.*, **23** (1988), 3698.
- 15) H. Hashimoto, A. Howie and M. Whelan: *Proc. Royal Soc. Lond. Ser. A. Math. Phys. Sci.*, **269** (1962), 80.
- 16) K. Bywater and D. Dyson: *Met. Sci.*, **9** (1975), 155.
- 17) M. Kikuchi, R. Tanaka and M. Takada: Proc. Int. Conf. Sci. Technol. Iron Steel, Vol. 2, Suppl. Trans. Iron Steel Inst. Jpn., Tokyo, (1971), 1216.
- 18) R. Lagneborg: *ASM Trans. Q.*, **60** (1967), 67.
- 19) A. Ramirez, J. Lippold and S. Brandi: *Metall. Mater. Trans. A*, **34** (2003), 1575.
- 20) H. Kokawa, E. Story and T. North: *ISIJ Int.*, **35** (1995), 1277.
- 21) N. Srinivas and V. Kutumbarao: *Scr. Mater.*, **37** (1997), 285.
- 22) R. Jargelius-Pettersson: *Z. Metallkd.*, **89** (1998), 177.
- 23) C. Briant, R. Mulford and E. Hall: *Corrosion*, **38** (1982), 468.
- 24) R. Beneke and R. Sandenbergh: *Corros. Sci.*, **29** (1989), 543.
- 25) J. Lai: *Mater. Sci. Eng.*, **58** (1983), 195.
- 26) V. G. Gavriljuk and H. Berns: High Nitrogen Steels: Structure, Properties, Manufacture, Applications, Springer-Verlag, Berlin, (1999).
- 27) R. D. Knutsen, C. Lang and J. Basson: *Acta Mater.*, **52** (2004), 2407.
- 28) X. Tao, J. Gu and L. Han: *J. Nucl. Mater.*, **452** (2014), 557.
- 29) H. Magnusson and R. Sandström: *Mater. Sci. Eng. A*, **527** (2009), 118.
- 30) B. Weiss and R. Stickler: *Metall. Trans.*, **3** (1972), 851.
- 31) P. A. Carvalho, I. F. Machado, G. Solórzano and F. Padilha: *Philos. Mag.*, **88** (2008), 229.
- 32) I. F. Machado and F. Padilha: *ISIJ Int.*, **40** (2000), 719.
- 33) M. Kikuchi, S. Choi, Y. Ogura and R. Tanaka: *J. Jpn. Inst. Met.*, **45** (1981), 683.
- 34) M. Kajihara, S. Choi, M. Kikuchi, R. Tanaka, Y. O. T. Seo and Y. Kondoh: *Z. Metallkd.*, **77** (1986), 515.