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Identification of precipitate phases in a 11Cr ferritic/martensitic steel using electron micro-diffraction ☆

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ABSTRACT

The precipitate phases in a 11Cr ferritic/martensitic steel normalized at 1050 °C for 1 h followed by tempered at 750 °C for 2 h have been studied through electron micro-diffraction combined with EDX analysis. Two niobium-rich carbonitride phases, $(Nb_{0.75}V_{0.15}Cr_{0.1})(C,N)$ and $(Nb_{0.5}V_{0.4}Cr_{0.1})(C,N)$, with the same f.c.c. structure were identified. Three vanadium-rich carbonitride phases were identified to be $(V_{0.65}Nb_{0.15}Cr_{0.2})(C,N)$, $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$ with the same f.c.c. structure. Chromium-rich carbonitride $M_2(C,N)$ and chromium-rich carbide $M_{23}C_6$ phases with a hexagonal and a f.c.c. crystal structure as well as a typical chemical formula of $(Cr_{0.8}V_{0.2})_2(C,N)$ and $(Cr_{0.7}Fe_{0.25}W_{0.05})_{23}C_6$, respectively, were also identified in the steel sample. The size of each kind of precipitate phase was examined. The morphologies and precipitation sites along with the amount of observed precipitate phases were described and discussed.

1. Introduction

Owing to higher creep-rupture strengths combined with good oxidation and corrosion resistance at elevated temperature, ferritic/martensitic (F/M) steels (9–12%Cr) are promising candidate materials for a number of next-generation nuclear reactors, such as gas-cooled fast reactor, lead-cooled reactor, sodium-cooled fast reactor and super critical water-cooled reactor. They are also considered for core structure materials of fusion reactors [1–3]. The 9–12Cr F/M steels are commonly used in normalized-and-tempered condition. The high (9–12%Cr) chromium steels are either full austenitic or have a duplex (austenite plus δ-ferrite) structure at austenitizing temperatures in the range 850–1200 °C. The austenite phase transforms to martensite during air cooling or rapid quenching to ambient temperature, and steels are subsequently tempered at temperature below the A_1 (the temperature at which the $\alpha \rightarrow \gamma$ transformation commences on heating) to obtain a good combination of strength, ductility, and toughness [1]. The precipitate phases formed during tempering associated with the creep strength of 9–12Cr F/M steels at high temperature. It has been reported that for martensitic 12CrMoVNb steels the M_2X and secondary MX phases occur as fine particles, uniformly distributed throughout a matrix, and initially they contribute to the creep strength of the steels by acting as barriers to dislocation movement at high temperatures, i.e., classical precipitation strengthening [4].

The study on the precipitate phases in 9–12Cr F/M steels is important to understand the creep properties of the steels. We have reported on the precipitate phases in an extra-low carbon 9Cr steel after normalizing and tempering treatments [5]. In this paper, we reported the results for identifying the precipitate phases in a 11Cr F/M steel using transmission electron microscope (TEM) and energy-dispersive X-ray (EDX) analysis.

2. Experimental

The study material was a 11Cr ferritic/martensitic steel prepared by melting, casting to obtain an ingot. The ingot was heated to 1150 °C for 2 h and hot-rolled in a range of temperatures from 1150 to 970 °C into a plate with a thickness of 15 mm. The plate was normalized at 1050 °C for 1 h, cooled in air and then tempered at 750 °C for 2 h, followed by air cooling. The chemical composition in weight pct of the steel was 0.08C, 11Cr, 0.2Mo, 2.6W, 0.2V, 0.05Nb, 0.45Mn, 2.5Co, 0.2Si, 0.004B and 0.08N.

Extracted carbon replicas were prepared by the method described in reference [6]. The replicas were examined using a JEM-2000 FXII TEM equipped with a LINK EDX system and operating at an accelerating voltage of 200 kV. The compositions of the precipitate phases were detected by EDX spectroscopy. Precipitate phases were identified by a combination of the electron micro-diffraction (MD) pattern and EDX analysis results.

☆ Experimental work in this study was done at Korea Atomic Energy Research Institute.

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3. Results and discussion

3.1. Niobium carbonitride phase

Fig. 1 shows the TEM micrographs of the carbon replica of the 11Cr steel and the MD patterns recorded from the arrow-marked precipitates A, B, and C. The EDX results revealed that the chemical composition in atomic pct of the precipitates A, B, and C was 39.35Nb, 6.64V, 4.24Cr, 0.35Fe, 1.6W, 47.8N and 26.85Nb, 19.66V, 8.91Cr, 1.88W, 42.7N, as well as 69.54Nb, 19.42V, 6.45Cr, 0.54Fe, 0.71W, 3.33N, respectively. The MD patterns in Fig. 1c–e have been indexed in terms of a face centered cubic (f.c.c.) crystal structure, which completely coincides with the diffraction patterns from niobium nitride (NbN, JCPDS file 38-1155, f.c.c., $a = 4.3927$ Å) in the zone axis of [0 0 1], [0 1 3] and [0 1 3], respectively. Therefore, spherical precipitates A, B and C were determined to be a Nb-rich carbonitride phase with a f.c.c. crystal structure and mainly containing V and Cr.

Since the composition in atomic pct of the metal fraction in the precipitates A, B and C was about 75.39Nb, 12.72V, 8.13Cr, 0.68Fe, 3.07W and 46.86Nb, 34.32V, 15.55Cr, 3.28W, as well as 71.94Nb, 20.09V, 6.68Cr, 0.56Fe, 0.73W, the chemical formula of the Nb-rich carbonitrides A, B and C can be approximately expressed as $(Nb_{0.75}V_{0.15}Cr_{0.1})(C,N)$, $(Nb_{0.5}V_{0.35}Cr_{0.15})(C,N)$ and $(Nb_{0.7}V_{0.2}Cr_{0.1})(C,N)$, respectively.

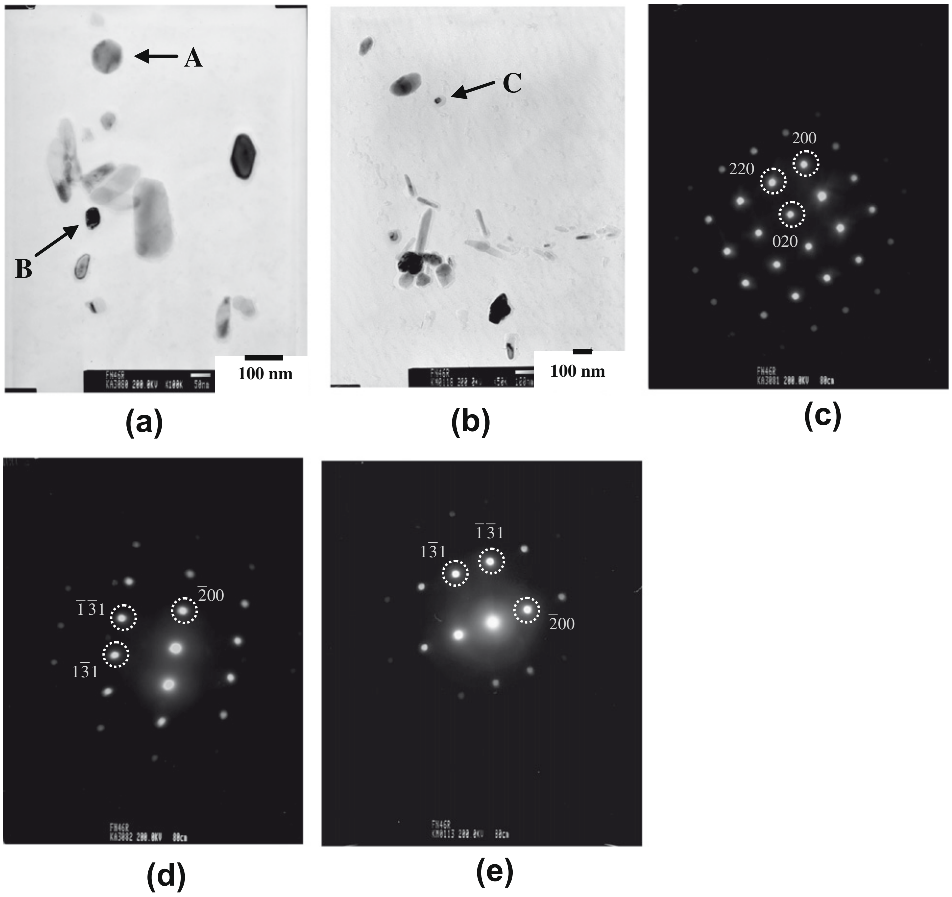
It seems that at least two kinds of Nb-rich carbonitrides with the same f.c.c. crystal structure and different chemical composition existed in the present steel sample. To confirm this suggestion, ten Nb-rich carbonitride precipitates have been examined by EDX, showing that their chemical compositions are similar with those of precipitates A/C or B, and nitrogen was detected in all the examined precipitates. The average chemical composition in atomic pct of the metal fraction in those precipitates was about 73.67Nb, 16.40V, 7.41Cr, 0.62Fe, 1.90W, and 51.40Nb, 38.01V, 7.75Cr, 1.25Fe, 1.59W, for the two kinds of Nb-rich carbonitride precipitates respectively. Therefore, typical chemical formula of Nb-rich carbonitride in the present steel can be expressed as $(Nb_{0.75}V_{0.15}Cr_{0.1})(C,N)$ and $(Nb_{0.5}V_{0.4}Cr_{0.1})(C,N)$ approximately.

MX (M: metallic element, X: C, N) phase in a 12Cr steel containing 0.17C, 10.81Cr, 0.90Mo, 0.19V, 0.05Nb, etc. with a normalization (900–1100 °C/1 h) followed by a tempering (750 °C/1 h) condition has been reported to be Nb(C,N) having a chemical formula of $(Nb_{0.96}V_{0.03}Mo_{0.01})(C,N)$ [7]. The chemical formula of the niobium-rich nitride in a normalized (1050 °C/1 h)-and-tempered (600–780 °C/2 h) 9Cr F/M steel could be approximately expressed as $(Nb_{0.6}V_{0.3}Cr_{0.1})N$ [5]. These results are different from present result due to different chemical compositions of the steels probably.

The most observed Nb-rich carbonitride precipitates were spherical particles, which seem to precipitate in the matrix, and some of the precipitates have a block shape and a precipitation site of prior austenite grain boundary. The diameter/size of the observed Nb-rich carbonitride precipitates ranged from about 30 to 100 nm, and average diameter/size for the precipitate particles was about 60 nm.

3.2. Vanadium carbonitride phase

Fig. 2 shows the TEM micrograph of the 11Cr steel taken from the carbon replica and the MD patterns from arrow-marked precipitates A, B and C. By EDX analyzing, the composition of



(a) (b) (c) (d) (e)

Fig. 1. TEM micrographs (a) and (b) of 11Cr steel replica sample showing niobium-rich carbonitride precipitates A, B and C indicated with arrows, and micro-diffraction patterns (c), (d) and (e) recorded from precipitates A, B and C in the zone axis of [0 0 1], [0 1 3], and [0 1 3], respectively.

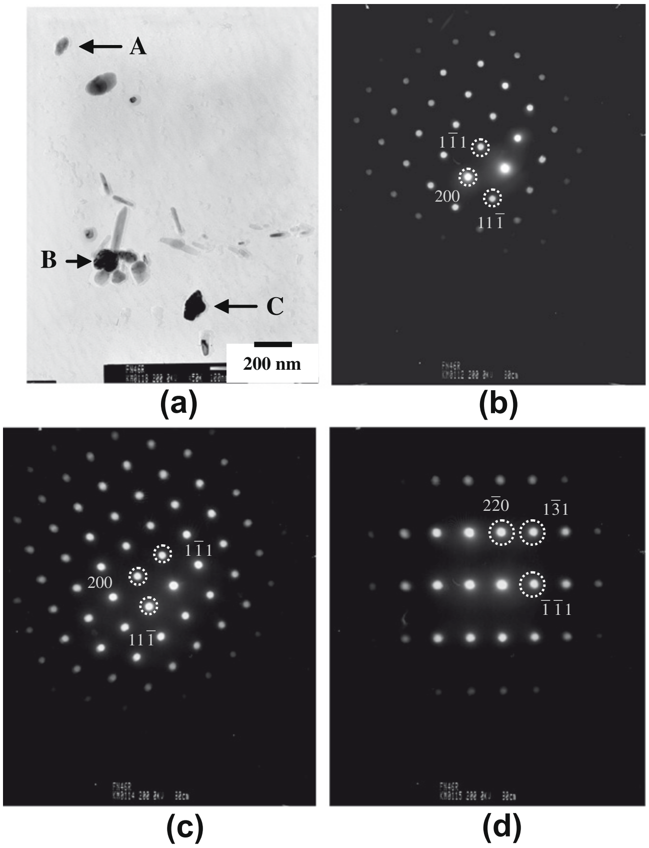


Fig. 2. TEM micrograph (a) of 11Cr steel replica sample showing vanadium-rich carbonitride precipitates A, B and C indicated with arrows, and micro-diffraction patterns (b), (c) and (d) recorded from precipitates A, B and C in the zone axis of [0 1 1], [0 1 1] and [1 1 2], respectively.

precipitates A, B and C was detected to be 57.41V, 10.41Nb, 15.87Cr, 0.27W, 16.04N and 40.35V, 38.69Nb, 13.87Cr, 0.65W, 6.45N as well as 51.58V, 21.22 Nb, 16.87Cr, 1.07Fe, 0.51W, 8.75N, respectively. MD patterns taken from precipitates A, B and C, as presented in Fig. 2b–d, matched with the electron diffraction patterns from the vanadium nitride (VN, JCPDS file 35-0768, f.c.c., a = 4.13916 Å) in the three beam directions of [0 1 1], [0 1 1] and [1 1 2], respectively. The composition in atomic pct of the metal fraction in the precipitates A, B and C was detected to be 68.38V, 12.40Nb, 18.90Cr, 0.32W and 43.13V, 41.35Nb, 14.82Cr, 0.69W as well as 56.53V, 23.25Nb, 18.49Cr, 1.17Fe, 0.55W, respectively. Therefore, precipitates A/C and B were determined to be a V-rich and a V–Nb-rich carbonitride phase mainly containing Nb/Cr and Cr with a f.c.c. crystal structure respectively, their chemical formulae can be approximately expressed as $(V_{0.65}Nb_{0.15}Cr_{0.2})N$, $(V_{0.45}Nb_{0.4}Cr_{0.15})N$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})N$ respectively.

The chemical composition of sixteen V-rich and V–Nb-rich carbonitride precipitate particles have been examined by EDX, showing that nitrogen was detected in all the examined precipitates. The average chemical composition in atomic pct of the metal fraction in examined particles was about 68.38V, 12.40Nb, 18.90Cr, 0.32W and 44.65V, 42.21Nb, 11.29Cr, 0.27Fe, 1.58W, as well as 55.07V, 23.94Nb, 18.90Cr, 0.98Fe, 0.54W for the three kinds of V-rich and V–Nb-rich carbonitride precipitates respectively. Therefore, typical chemical formula of V-rich and V–Nb-rich carbonitrides in the present steel can be expressed as $(V_{0.65}Nb_{0.15}Cr_{0.2})(C,N)$, $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$, approximately.

It has been noted that three kinds of V-rich and V–Nb-rich carbonitride precipitates with the same crystal structure and different chemical composition coexisted in the present 11Cr F/M steel. The present V-rich carbonitride phase with an approximate chemical formula of $(V_{0.65}Nb_{0.15}Cr_{0.2})(C,N)$ is similar to the V-rich nitride in a 9Cr F/M steel reported by Shen et al. [6], i.e., $(V_{0.6}Nb_{0.2}Cr_{0.2})N$, and the V-rich nitride in a ferritic 11Cr steel, 57V–15Cr–10Nb–15N (approximately given by $(V_{0.7}Nb_{0.1}Cr_{0.2})N$), reported by Pickering et al. [8], but different from VN phase in a 9Cr steel, 55V–26Cr–3Nb–9Fe (wt.%) (approximately expressed as $(V_{0.6}Cr_{0.3}Fe_{0.1})N$) [9].

As reported by Shen et al. [6], V–Nb-rich nitride phase, $(V_{0.45}Nb_{0.45}Cr_{0.1})N$, existed in a 9Cr F/M steel, similar V–Nb-rich carbonitride precipitate phase, $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$, was also observed in the present 11Cr F/M steel. No report regarding to V-rich carbonitride precipitate phase, $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$, observed in the present steel has been found.

According to the result that vanadium nitride precipitates with the chemical formulae of $(V_{0.45}Nb_{0.45}Cr_{0.1})N$ and $(V_{0.4}Nb_{0.4}Cr_{0.2})N$ were frequently observed in the 9Cr F/M steel normalized at 1050 and 1150 °C for the time from 1 to 2 h, whereas they were dissolved out during a normalization at 1200 °C for 1 h [6,10], so that it could be expected that in the present steel $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ precipitates were undissolved V–Nb-rich carbonitride precipitates after the normalization, while $(V_{0.65}Nb_{0.15}Cr_{0.2})(C,N)$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$ precipitates were V-rich carbonitride precipitates formed during the tempering.

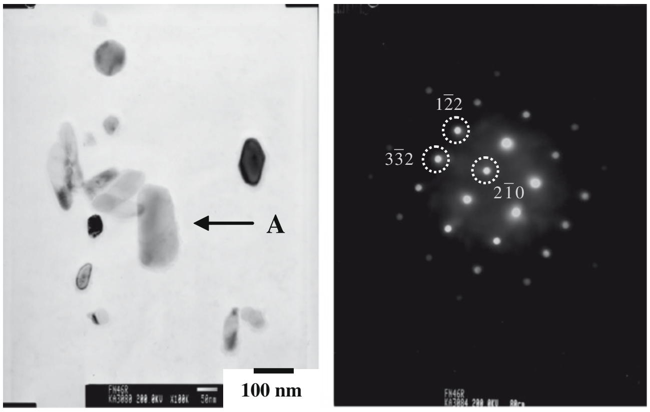
Based upon the present TEM observation, we knew that the V-rich and V–Nb-rich carbonitride precipitates have two kinds of morphologies: one was spherical particle with a diameter range of about 30–130 nm and an average diameter of 60 nm, another was spindle particle (or short rod) with a average size of about 40 and 110 nm in length of the short and the long axes of the precipitates, respectively. The size ranged in short and long axes of the precipitates were about 20–100 nm, and 30–160 nm. A small number of V-rich and V–Nb-rich carbonitride particles seem to precipitate at martensite lath boundaries and in the matrix as well as the matrix within martensite laths. The precipitation site of most observed particles from carbon replica sample cannot be known clearly due to the limitation of carbon replica sample.

3.3. Chromium carbonitride phase

Fig. 3 is the TEM micrograph of the carbon replica sample from the 11Cr steel and MD pattern from the block precipitate A. The composition of precipitate A was 63.54Cr, 9.67V, 0.41Nb, 0.60Fe, 1.4Mo, 0.75W, 23.63N detected using EDX spectroscopy. The MD pattern taken from precipitate A, as shown in Fig. 3b, matched well with the electron diffraction pattern from chromium nitride (Cr_2N, JCPDS file 01-1232) with a hexagonal crystal structure and lattice parameters of a = 4.78 Å and c = 4.4 Å in the zone axis of [0 2 3]. Thereby, precipitate A can be determined to be Cr-rich carbonitride phase, $M_2(C,N)$, having a hexagonal crystal structure and mainly containing V.

Ten Cr-rich $M_2(C,N)$ precipitates were examined by EDX. The average composition in atomic pct of the metal fraction in the examined Cr-rich $M_2(C,N)$ precipitates was about 80.07Cr, 15.44V, 0.42Nb, 1.18Fe, 1.16Mo, 1.71W, which was similar with 79.2Cr, 17.3V, 1.9Fe, 0.9Mo, 0.7W and 82.8Cr, 14.2V, 1.0Nb, 0.4Fe, 1.6Mo for Cr-rich M_2N nitride phase in tempered (750 °C/2 h) 9% chromium steels with extra-low carbon (<0.003C, in wt.%) [11]. Thus, the typical chemical formula of Cr-rich $M_2(C,N)$ phase in the present steel can be expressed as $(Cr_{0.8}V_{0.2})_2(C,N)$ approximately.

The average size of observed Cr-rich $M_2(C,N)$ precipitates was estimated to be about 130 nm for block particles, as well as 30 and 180 nm in thickness and length for the plate-like precipitates.



(a) (b)

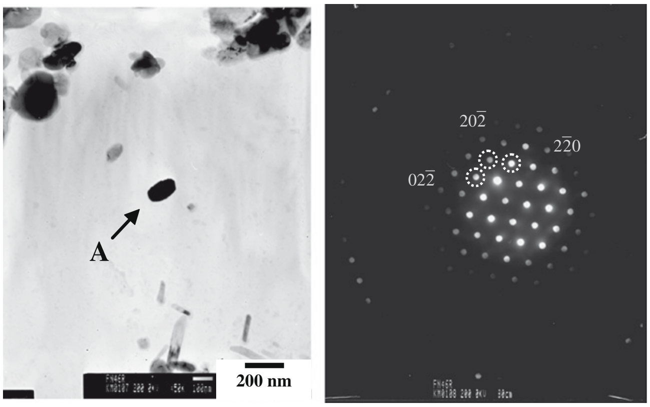
Fig. 3. TEM micrograph (a) of 11Cr steel replica sample showing chromium-rich carbonitride precipitate A indicated with arrow, and micro-diffraction pattern (b) recorded from precipitate A in the zone axis of [0 2 3].

It has been found that these Cr-rich $M_2(C,N)$ precipitates seem to precipitate in the matrix.

3.4. Chromium carbide phase

The TEM image of the carbon replica of the 11Cr steel and the MD pattern taken from the precipitate A marked with an arrow are shown in Fig. 4. The composition in atomic pct of the precipitate A was detected by EDX spectroscopy to be 65.44Cr, 27.29Fe, 0.82V, 0.5Nb, 1.41Mo, 4.54W without nitrogen. The MD pattern in Fig. 4b matched well with the electron diffraction pattern from chromium carbide ($Cr_{23}C_6$, f.c.c., lattice parameter $a = 10.6599$ Å, JCPDS file 35-0783) in the zone axis of [1 1 1]. Thus, precipitate A was identified to be Cr-rich $M_{23}C_6$ phase containing Fe and W and having a f.c.c. crystal structure and an approximate chemical formula of $(Cr_{0.65}Fe_{0.3}W_{0.05})_{23}C_6$.

From the EDX examination of ten precipitate particles, the chemical composition of Cr-rich $M_{23}C_6$ precipitate phase could be averaged to be about 66.87Cr, 25.46Fe, 1.21V, 0.62Nb, 1.26Mo, 4.58W so that typical chemical formula can be approximately written by $(Cr_{0.7}Fe_{0.25}W_{0.05})_{23}C_6$. This typical chemical formula is similar with that of $Cr_{23}C_6$ phase observed in a 9Cr steel containing 0.11C, 9.0Cr, 1.0Mo, 0.20V, 1.0W, etc. with a tempering treatment at 750 °C [9], but does not agree with the $Cr_{23}C_6$ phases, $(Cr_{0.59}Fe_{0.29}Mo_{0.11})_{23}C_6$ and $(Cr_{0.54}Fe_{0.26}Mo_{0.09}V_{0.11})_{23}C_6$, observed in a 12Cr steel [7].



(a) (b)

Fig. 4. TEM micrograph (a) of 11Cr steel replica sample showing chromium-rich carbide precipitate A indicated with arrow, and micro-diffraction pattern (b) recorded from precipitate A in the zone axis of [1 1 1].

TEM observation revealed that the morphologies of Cr-rich $M_{23}C_6$ precipitates in the present steel sample were block and short rod-like. Further, Cr-rich $M_{23}C_6$ phase precipitated at the prior austenite and martensite lath boundaries as well as in the matrix. Observed block Cr-rich $M_{23}C_6$ precipitate has a size ranged from about 70 to 330 nm and an average size of about 180 nm, whilst short rod-like particle has an average size of about 80 and 270 nm in the length of short and long axis of the precipitates, respectively. The length of short and long axis ranged from about 40 to 110 and from about 170 to 380 nm, respectively.

On the one hand, because the distribution of Nb-, V-, V–Nb- and Cr-rich carbonitride precipitates as well as Cr-rich carbide precipitates in the present replica sample was not uniform, on the other hand, the amount of some precipitates such as V-rich and V–Nb-rich carbonitride precipitates was small and they were also sometimes observed in a few cases, the quantitative analysis of these second precipitate phases is difficult only by present TEM observation. However, according to present TEM observation along with EDX analyses it seems that the amount of Cr-rich $M_{23}C_6$ precipitates was largest compared to other kinds of second precipitates, whilst the amount of V-rich and V–Nb-rich carbonitride precipitates was smallest among the second precipitates in the present replica sample of the steel. The amount of these second precipitate phases and the precipitation sites or distribution of the precipitate phases in detail in the present steel should be further studied in our next experimental work combined with the use of thin foil specimen for TEM/or HRTEM (High Resolution Transmission Electron Microscopy) observation and chemical composition examination.

4. Conclusions

(1) Two kinds of Nb-rich carbonitride phases with the same f.c.c. structure, different chemical formulae of $(Nb_{0.75}V_{0.15}Cr_{0.1})(C,N)$ and $(Nb_{0.5}V_{0.4}Cr_{0.1})(C,N)$, and a average size of 60 nm were identified in the steel. Observed spherical and block precipitate phases precipitated in the matrix and at the prior austenite grain boundaries.

(2) Three kinds of V-rich carbonitride phases, $(V_{0.65}Nb_{0.15}Cr_{0.2})(C,N)$, $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$, with the same f.c.c. structure were identified in the steel sample. The average diameter of spherical particle was about 60 nm, while the average size of spindle precipitate was about 40 and 110 nm in length of the short and the long axis respectively. Observed phases precipitated at lath boundaries and in the matrix as well as the matrix within laths.

(3) Cr-rich $M_2(C,N)$ phase with a hexagonal structure and a typical chemical formula of $(Cr_{0.8}V_{0.2})_2(C,N)$ was determined in the steel sample. The average size of the phase was about 130 nm, and 30 and 180 nm in thickness and length for block and plate-like precipitates, respectively. They precipitated in the matrix.

(4) Cr-rich carbide phase $M_{23}C_6$ with a f.c.c. crystal structure was identified in the steel sample. The observed $M_{23}C_6$ phase with a typical chemical formula of $(Cr_{0.7}Fe_{0.25}W_{0.05})_{23}C_6$ precipitated at the prior austenite and lath boundaries as well as in the matrix, and has an average size of about 180 nm for block particles, and about 80 and 270 nm in the length of short and long axis for short rod-like particles respectively.

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