



Influence of tempering temperature upon precipitate phases in a 11%Cr ferritic/martensitic steel [☆]

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ABSTRACT

The effect of tempering temperature on the precipitate phases in a 11%Cr ferritic/martensitic steel normalized at 1050 °C for 1 h and tempered for 2 h at temperatures ranging from 600 to 780 °C has been investigated using transmission electron microscope and energy-dispersive X-ray spectroscopy. The results show that tempering temperature does not affect the existences of niobium-rich carbonitrides, $(\text{Nb}_{0.7}\text{V}_{0.2}\text{Cr}_{0.1})(\text{C,N})$ and $(\text{Nb}_{0.55}\text{V}_{0.35}\text{Cr}_{0.1})(\text{C,N})$, vanadium–niobium-rich carbonitride $(\text{V}_{0.45}\text{Nb}_{0.45}\text{Cr}_{0.1})(\text{C,N})$, chromium-rich carbonitride $(\text{Cr}_{0.83}\text{V}_{0.12}\text{W}_{0.05})_2(\text{C,N})$ and chromium-rich carbide $(\text{Cr}_{0.7}\text{Fe}_{0.25}\text{W}_{0.05})_{23}\text{-C}_6$, whilst the precipitations of vanadium-rich carbonitrides, $(\text{V}_{0.65}\text{Nb}_{0.2}\text{Cr}_{0.15})(\text{C,N})$ and $(\text{V}_{0.55}\text{Nb}_{0.25}\text{Cr}_{0.2})(\text{C,N})$ are dependent on tempering temperature, which were detected only at the higher tempering temperatures of 750 and 780 °C. No coarsening was occurred during the temperings for the niobium-rich and spherical vanadium-rich carbonitrides. There was a low coarsening rate for the chromium-rich carbonitrides and chromium-rich carbides with increasing the tempering temperature from 600 to 700 °C and 650 to 780 °C, respectively, and a high coarsening rate for the chromium-rich carbonitrides and chromium-rich carbides at the tempering temperatures 750 through 780 °C and 650 °C, respectively. The compositions show an increase in vanadium and a decrease in niobium and chromium contents for the niobium-rich carbonitrides, and a decrease in niobium and an increase in vanadium and chromium contents for the vanadium–niobium-rich carbonitrides, and an increase in vanadium and a decrease in tungsten contents for the chromium-rich carbonitrides. The chromium-rich carbides show an increase and a decrease in their iron and chromium contents, respectively, with increasing the tempering temperature from 650 to 780 °C.

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1. Introduction

Favorable mechanical properties, such as strength, ductility, creep rupture, fatigue, and creep–fatigue interactions, are some of desirable characteristics for the structural materials used for Generation-IV nuclear reactors [1]. Ferritic/martensitic (F/M) steels (9–12%Cr) have been suggested for structural applications in Generation-IV nuclear reactors [1,2]. The basic way in which creep-resistant steels (such as tempered martensitic 9–12%Cr steels) can be strengthened are by solute hardening, precipitation or dispersion hardening, dislocation hardening and boundary hardening [3–6]. To achieve enough strengthening using precipitation hardening effect, engineering creep-resistant steels usually contain several kinds of precipitate particles in the matrix and at grain boundaries: carbonitrides such as M_{23}C_6 , M_6C , M_7C_3 , MX and M_2X (where M denotes the metallic elements, C are the carbon

atoms and X are the carbon and nitrogen atoms), intermetallic compounds such as the $\text{Fe}_2(\text{Mo}, \text{W})$ Laves phase, Fe_7W_6 μ -phase, χ -phase and so on, and a metallic phase such as Cu [7].

The mechanical properties as well as creep rupture strengths of 9–12%Cr steels result from a balance of their chemical composition and their microstructure. It is evident that not only the chemical composition but also the heat treatment influences the creep properties very significantly [8]. The 9–12%Cr steels are normally delivered after a final heat treatment consisting of normalizing and tempering. Normalizing is done at a temperature, where the steels are austenitic (around 1050 °C), and tempering is carried out in the range 650–780 °C [9]. The normalizing and tempering heat treatments lead to a microstructure of tempered martensite with carbide and nitride precipitates, i.e., M_{23}C_6 (based on Cr_{23}C_6), MX (based on VN and Nb(C,N)/or NbC), M_2X (based on Cr_2N) and M_7C_3 (based on Cr_7C_3) which contributes to the creep strength of the 9–12%Cr steels at high temperature [8–13].

The aims of the present investigation are to judge the influences of tempering temperature on the types of precipitate phases and the changes in size and chemical composition for the precipitate phases in a 11%Cr F/M steel.

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

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2. Experimental procedures

The initial material used in this study was a hot-rolled 11Cr F/M steel plate with a thickness of 15 mm. The chemical composition 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 (in wt.%). The heat treatments of the steel plate included normalization at 1050 °C for 1 h, and then tempering for 2 h at 600, 650, 700, 750 and 780 °C, named after

FN43, FN44, FN45, FN46 and FN47, respectively. All steel samples were cooled in air to room temperature after the normalization and tempering.

Extracted carbon replicas were prepared by the method described in elsewhere [6]. The carbon replicas were examined by using a JEM-2000 FXII TEM equipped with a LINK EDX (energy-dispersive X-ray) system and operating at a 200 kV accelerating voltage. The compositions of the precipitate phases were detected by

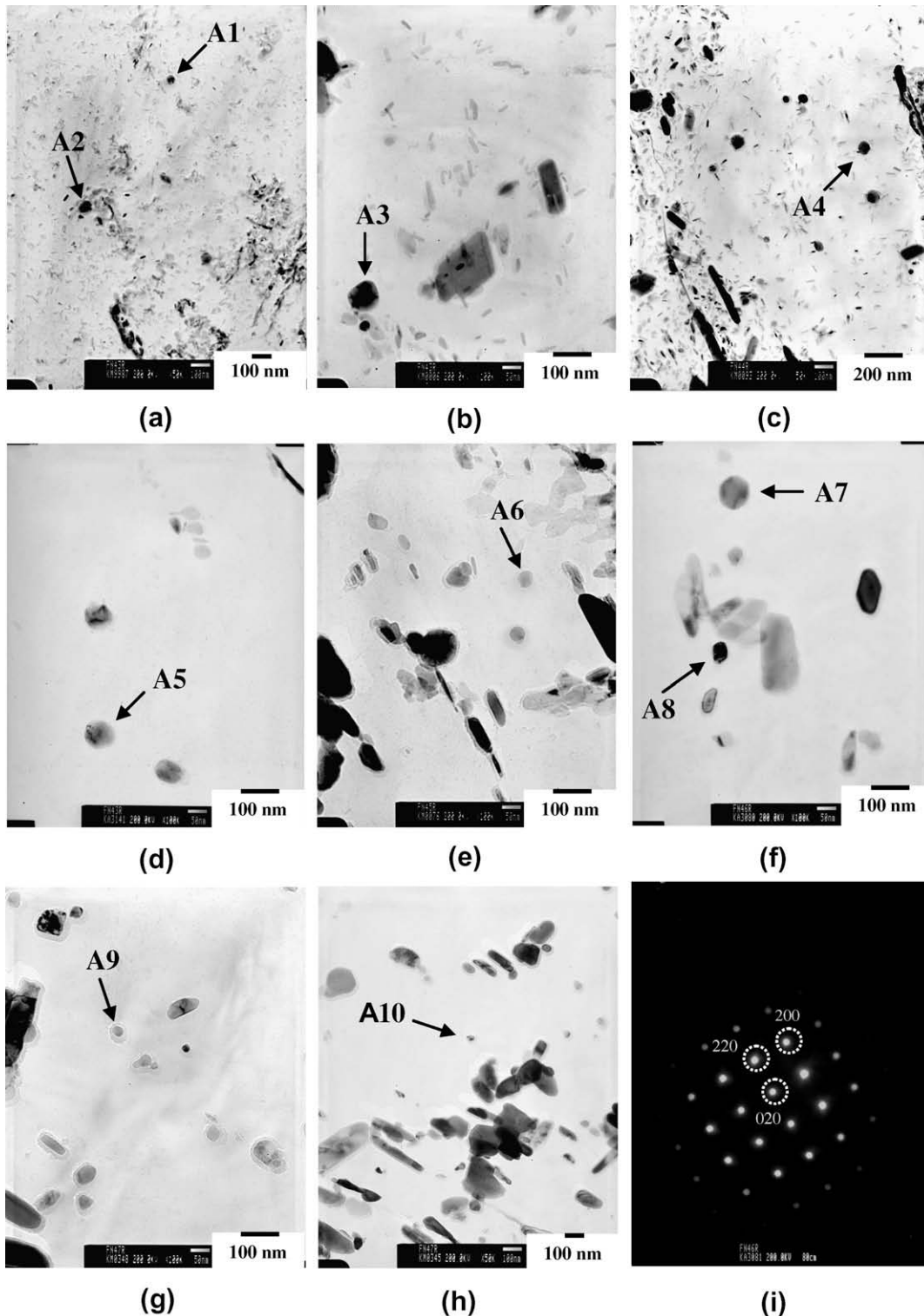


Fig. 1. TEM micrographs of extraction carbon replica samples from: (a) FN43, (b and c) FN44, (d and e) FN45, (f) FN46, (g and h) FN47 steel specimens showing niobium-rich M(C,N) precipitate phases marked with arrows, and micro-diffraction pattern, and (i) taken from precipitate A7 in the zone axis of [0 0 1].

EDX spectroscopy. Precipitate phases were identified by a combination of the micro-diffraction (MD) pattern and EDX analysis result.

3. Results and discussion

Fig. 1 shows the TEM micrographs of the carbon replicas of the 11%Cr steel specimens along with a MD pattern. The EDX results

revealed that the main constituents of these precipitate particles marked with arrows are niobium, vanadium, chromium and nitrogen. For instance, the chemical composition in atomic pct of the precipitates A7 and A8 was 39.35Nb, 6.64V, 4.24Cr, 0.35Fe, 1.6W, 47.8N and 26.85Nb, 19.66V, 8.91Cr, 1.88W, 42.7N, respectively. The MD pattern taken from the arrow-marked precipitate A7, as shown in Fig. 1i, was indexed in terms of a face centered cubic (f.c.c.) crystal structure, which completely coincides with the

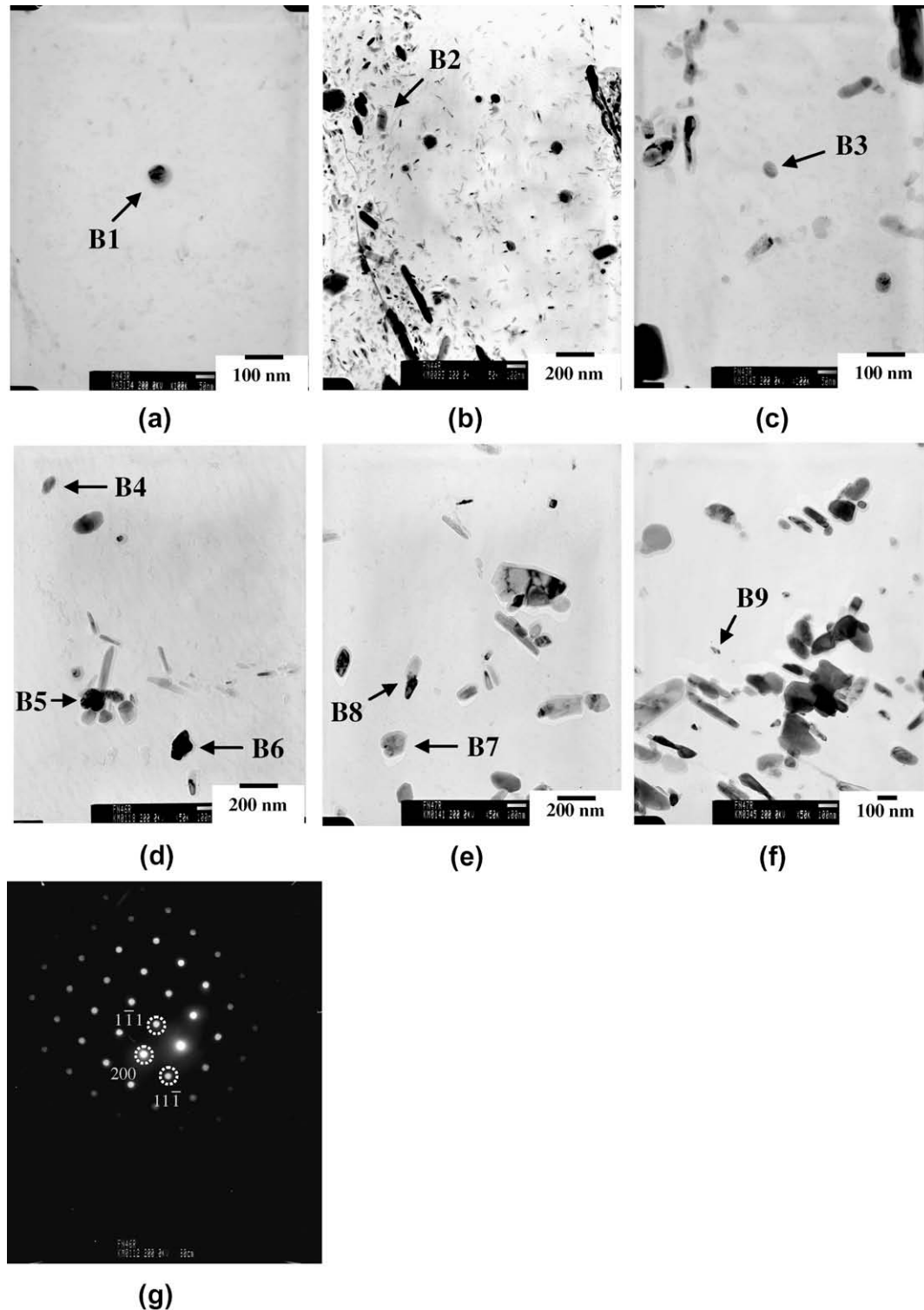


Fig. 2. TEM micrographs of extraction carbon replica samples from: (a) FN43, (b) FN44, (c) FN45, (d) FN46, (e and f) FN47 steel specimens showing vanadium–niobium-rich and vanadium-rich M(C,N) precipitate phases marked with arrows, and micro-diffraction pattern, and (g) taken from precipitate B4 in the zone axis of $[0\ 1\ 1]$.

diffraction pattern from niobium nitride (NbN, JCPDS file 38-1155, f.c.c., $a = 4.3927 \text{ \AA}$) in the zone axis of $[0\ 0\ 1]$. Also, the MD patterns from other arrow-marked precipitates in Fig. 1 matched with the diffraction pattern from the niobium nitride NbN, respectively. Since the EDX spectroscopy measurements do not take into account the carbon content of the steel, and the concentrations of nitrogen in the precipitates A7 and A8 were different from MN (M denotes metallic elements, hereinafter), which is simply 50% in atomic pct, carbon must be included in the precipitates. Therefore, these precipitate particles marked with arrows in Fig. 1 could be identified as niobium-rich carbonitride $M(\text{C,N})$ with a f.c.c. crystal structure and mainly containing vanadium and chromium.

The chemical composition in atomic pct of the metal fraction in the precipitates A1 and A2 examined from the replica sample of FN43 steel specimen was about 71.71Nb, 16.59V, 9.31Cr, 1.18Fe, 1.22W and 50.53Nb, 28.5V, 18.97Cr, 0.86Fe, 1.14W. The chemical formula of the precipitate particles A1 and A2, therefore, can be approximately expressed as $(\text{Nb}_{0.7}\text{V}_{0.2}\text{Cr}_{0.1})(\text{C,N})$ and $(\text{Nb}_{0.5}\text{V}_{0.3}\text{Cr}_{0.2})(\text{C,N})$, respectively. This result indicated that there are two kinds of niobium-rich carbonitrides containing vanadium and chromium at least in the FN43 steel specimen. The EDX analyses for more than ten precipitate particles regarding to the two kinds of niobium-rich carbonitrides indicated that the average chemical composition in atomic pct of the metal fraction in those precipitates was about 74.51Nb, 14.81V, 7.88Cr, 1.41Fe, 1.27W and 50.87Nb, 31.26V, 16.31Cr, 0.68Fe, 0.88W, their chemical formulae, therefore, can be approximately given by $(\text{Nb}_{0.75}\text{V}_{0.15}\text{Cr}_{0.1})(\text{C,N})$ and $(\text{Nb}_{0.5}\text{V}_{0.3}\text{Cr}_{0.2})(\text{C,N})$, respectively.

Similar niobium-rich carbonitride precipitates have been also observed in the carbon replicas of FN44, FN45, FN46 and FN47 steel specimens. The approximate chemical formulae of the precipitate particles can be expressed as $(\text{Nb}_{0.7}\text{V}_{0.2}\text{Cr}_{0.1})(\text{C,N})$ and $(\text{Nb}_{0.5}\text{V}_{0.4}\text{Cr}_{0.1})(\text{C,N})$ for FN44 (particles A3 and A4, respectively), $(\text{Nb}_{0.75}\text{V}_{0.15}\text{Cr}_{0.1})(\text{C,N})$ and $(\text{Nb}_{0.55}\text{V}_{0.35}\text{Cr}_{0.1})(\text{C,N})$ for FN45 (particles A5 and A6, respectively), $(\text{Nb}_{0.75}\text{V}_{0.15}\text{Cr}_{0.1})(\text{C,N})$ and $(\text{Nb}_{0.5}\text{V}_{0.4}\text{Cr}_{0.1})(\text{C,N})$ for FN46 (particles A7 and A8, respectively), $(\text{Nb}_{0.75}\text{V}_{0.2}\text{Cr}_{0.05})(\text{C,N})$ and $(\text{Nb}_{0.5}\text{V}_{0.35}\text{Cr}_{0.15})(\text{C,N})$ for FN47 (particles A9 and A10, respectively).

Fig. 2 also shows the TEM micrographs of the carbon replicas of the 11%Cr steel specimens, along with a MD pattern. The results of EDX analysis proved that the precipitates B1 through B9 indicated with arrows contain mainly vanadium, niobium, chromium and nitrogen, for example, the composition of precipitate was 57.41V, 10.41Nb, 15.87Cr, 0.27W, 16.04N for B4, 40.35V, 38.69Nb, 13.87Cr, 0.65W, 6.45N for B5 and 51.58V, 21.22Nb, 16.87Cr, 1.07Fe, 0.51W, 8.75N for B6. All the MD patterns from arrow-indicated precipitates in Fig. 2 matched well with the diffraction pattern from the vanadium nitride (VN, JCPDS file 35-0768, f.c.c., $a = 4.13916 \text{ \AA}$). Fig. 2g taken from precipitate B4 is an example, which matched with the diffraction pattern from the VN phase in the zone axis of $[0\ 1\ 1]$. Under the same consideration that carbon content cannot be detected by EDX spectroscopy and the concentrations of nitrogen in the precipitates were different from MN, precipitates B1 through B9 could be determined to be vanadium-rich carbonitride $M(\text{C,N})$ with a f.c.c. crystal structure and main constituents of niobium and chromium.

Combining EDX results and MD patterns, it can be concluded that the precipitates B1, B2 and B3 taken from the carbon replicas of FN43, FN44 and FN45 steel specimens, respectively, were vanadium–niobium-rich carbonitride phase containing chromium with an approximate chemical formula of $(\text{V}_{0.45}\text{Nb}_{0.45}\text{Cr}_{0.1})(\text{C,N})$. For precipitates B4, B5 and B6 observed on the carbon replica of FN46 steel specimen, the chemical composition of the precipitates in atomic pct of the metal fraction was about 68.38V, 12.4Nb, 18.9Cr, 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. This

indicated that three kinds of vanadium-rich/or vanadium–niobium-rich carbonitride phases, $(\text{V}_{0.65}\text{Nb}_{0.15}\text{Cr}_{0.2})(\text{C,N})$, $(\text{V}_{0.45}\text{Nb}_{0.4}\text{Cr}_{0.15})(\text{C,N})$ and $(\text{V}_{0.55}\text{Nb}_{0.25}\text{Cr}_{0.2})(\text{C,N})$, coexisted in the same FN46 steel specimen. Also in the carbon replica of FN47 steel specimen, three types of vanadium-rich/or vanadium–niobium-rich carbonitride phases were observed. The chemical composition in atomic pct of the metal fraction was 69.46V, 12.2Nb, 17.38Cr, 0.82Fe, 0.14W and 45.4V, 33.86Nb, 18.15Cr, 1.29Fe, 1.3W, as well as 54.61V, 28.37Nb, 9.7Cr, 2.72Mo, 2.38W for the precipitates B7 and B8 as well as B9, respectively.

Therefore, in the present 11%Cr F/M steel vanadium–niobium-rich carbonitride phase existed under the conditions of tempering at 600 through 700 °C, whereas both vanadium–niobium-rich and vanadium-rich carbonitride phases existed when tempering carried out at the higher temperatures of 750 and 780 °C. In view of the results on 9%Cr F/M steel [9,14,15], it can be expected that the vanadium–niobium-rich carbonitride phase in FN43 through FN47 steel specimens belong to be undisclosed vanadium carbonitrides during the normalization of the specimens, and other two vanadium-rich carbonitride phases in the FN46 and FN47 steel specimens should be the vanadium-rich carbonitrides precipitated during the temperings at the higher temperatures.

Fig. 3 shows the TEM micrographs of the carbon replicas of the 11%Cr steel specimens, showing the precipitates C1 through C5 indicated with arrows, and the MD pattern from precipitate C4. By EDX analysis, it has been found that precipitates C1 through C5 contain mainly chromium, vanadium, nitrogen, and a small quantity of tungsten, niobium, iron as well as molybdenum. For example, the composition of precipitate C4 was detected to be 63.54Cr, 9.67V, 0.41Nb, 0.60Fe, 1.4Mo, 0.75W, 23.63N. The MD patterns recorded from precipitates C1 through C5 matched well with the diffraction pattern from chromium nitride (Cr_2N , JCPDS file 01-1232) with a hexagonal crystal structure and the lattice parameters of $a = 4.78 \text{ \AA}$ and $c = 4.4 \text{ \AA}$. As an example, the MD pattern shown in Fig. 3f matched well with the diffraction pattern from the Cr_2N phase in the zone axis of $[0\ 2\ 3]$. Because the concentration of nitrogen in the precipitate C4 was different from M_2N , which is simply 33% in atomic pct, carbon must be included in the precipitate C4. Therefore, precipitates C1 through C5 were identified to be chromium-rich carbonitride $\text{M}_2(\text{C,N})$ with a hexagonal crystal structure and containing vanadium, tungsten, niobium, iron and molybdenum.

Fig. 4 shows a group of TEM micrographs taken from the carbon replicas of the 11%Cr steel specimens along with a MD pattern. The composition in atomic pct of the precipitate D4 was detected by EDX spectroscopy to be 65.44Cr, 27.29Fe, 0.82V, 0.5Nb, 1.41Mo, 4.54W without nitrogen. The compositions in atomic pct of other precipitates indicated with arrows in Fig. 4 were also analyzed to be similar with that of precipitate D4. The MD pattern from precipitate D4, as shown in Fig. 4f, matched well with the diffraction pattern from chromium carbide (Cr_{23}C_6 , JCPDS file 35-0783, f.c.c., lattice parameter $a = 10.6599 \text{ \AA}$), so did the MD patterns from the other arrow-indicated precipitates. Depending on the EDX analyses and MD patterns, precipitates D1 through D5 have been identified to be chromium-rich carbide (M_{23}C_6) containing mainly iron and tungsten.

Table 1 lists the results for mean sizes of the precipitate phases in the 11%Cr steel specimens tempered for 2 h at different temperatures. The sizes of the precipitates were measured in the TEM micrographs of the carbon replicas. About 20 measurements made on each precipitate type in a given carbon replica except for the vanadium-rich $M(\text{C,N})$ precipitates on the carbon replicas of steel specimens tempered for 2 h at 600 and 650 °C, which were rarely detected during the present observations. It has been found that no large difference in the sizes of niobium-rich carbonitride and spherical vanadium-rich carbonitride particles was measured

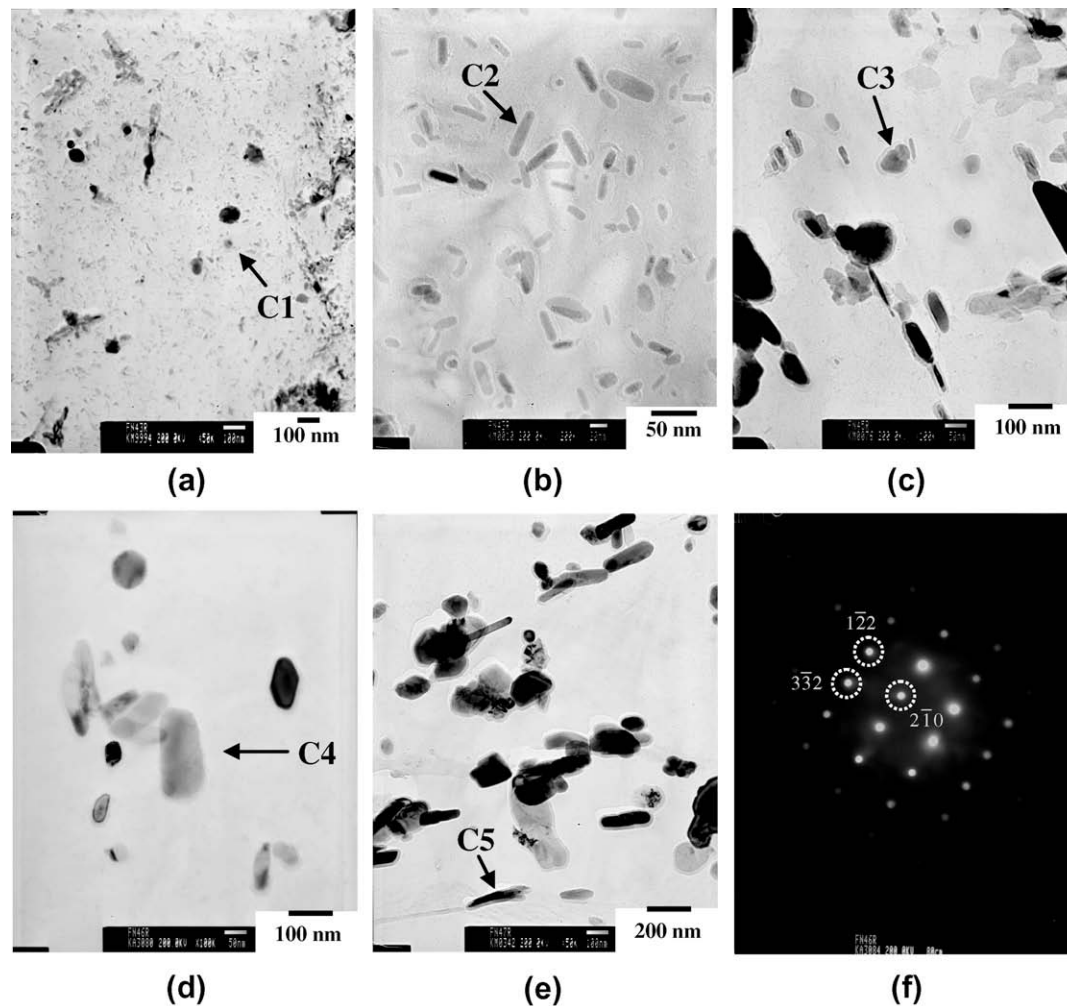


Fig. 3. TEM micrographs of extraction carbon replica samples from: (a) FN43, (b) FN44, (c) FN45, (d) FN46, (e) FN47 steel specimens showing chromium-rich $M_2(C,N)$ precipitate phases marked with arrows, and micro-diffraction pattern, and (f) taken from precipitate C4 in the zone axis of $[0\ 2\ 3]$.

among the carbon replicas of the steel specimens tempered for the same time of 2 h at different tempering temperatures, indicating that the two kinds of precipitate phases are resistant to coarsening and the tempering at a higher temperature of 750 or 780 °C caused no further coarsening. On the contrary, the vanadium-rich carbonitride precipitates in the shape of spindle were not stable, both short and long axes of the precipitates were increased significantly as the tempering temperature was increased from 700 to 750 °C. For chromium-rich carbonitride precipitates with two kinds of morphologies, their sizes were increased with increasing tempering temperature. Furthermore, it has been found that the precipitates have relative small size after the tempering in the temperature range from 600 to 700 °C, and the sizes of the precipitates strikingly were increased when tempering temperature was increased up to 750 and 780 °C. These results proved that the coarsening rate of chromium-rich carbonitride precipitate is lower during the tempering in the temperature from 600 to 700 °C and higher at the tempering temperatures of 750 and 780 °C. The size of the chromium-rich carbide has been found to be strikingly increased when tempering temperature was increased from 600 up to 650 °C for both block and rod-shaped precipitates, and have no large change for block-shaped precipitates as well as a slight increase in the long axis of the rod-shaped precipitates with increasing the tempering temperature from 650 to 780 °C, revealing a high

coarsening rate at 650 °C and a better resistance to coarsening in the tempering temperature range from 650 to 780 °C.

Fig. 5 shows the average chemical compositions in atomic pct of the metal fraction for the precipitate phases in the 11%Cr steel specimens tempered for 2 h at different temperatures. The compositions shown in Fig. 5 are the average values of about 10 through 15 measurements made on each precipitate phase in a given carbon replica except for the vanadium–niobium-rich carbonitride ($V_{0.45}Nb_{0.45}Cr_{0.1}(C,N)$) in the carbon replica of FN43 and FN44 specimens. Fig. 5a and b indicates that the contents of niobium and chromium in the two kinds of niobium-rich carbonitrides decreased slightly, while the content of vanadium increased when tempering temperature was increased from 600 to 780 °C. These changes may be related to a phenomenon of re-dissolving of niobium-rich carbonitride phase during a progress of tempering. Tamura et al. [16] studied the precipitation behavior of NbC in a 9%Cr1%Mo0.2%VNb steel, and found that a part of the stable particles of NbC, which were precipitated during a normalizing for 1 h at 950 °C, are re-dissolved by the re-heating for 2 h at a tempering temperature of 800 °C, resulting in a change in the chemical compositions of NbC particles, i.e., increase in niobium, vanadium and iron contents, decrease in chromium and molybdenum contents. It is noted that their results show a slight increase in niobium content in NbC particles after the tempering, on the contrary, our data

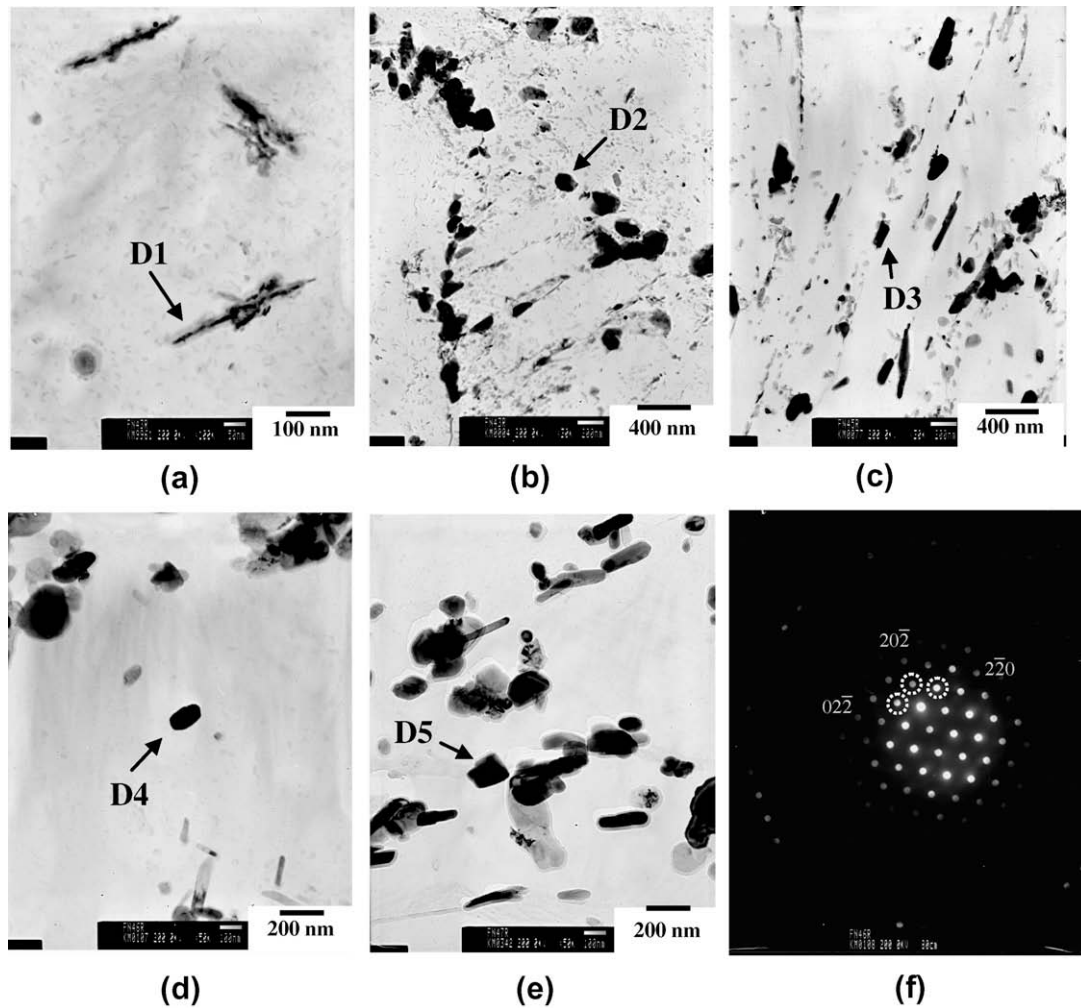


Fig. 4. TEM micrographs of extraction carbon replica samples from: (a) FN43, (b) FN44, (c) FN45, (d) FN46, (e) FN47 steel specimens showing chromium-rich $M_{23}C_6$ precipitate phases marked with arrows, and micro-diffraction pattern, and (f) taken from precipitate D4 in the zone axis of $[1\ 1\ 1]$.

Table 1

Mean size (nm) of precipitate phases in the 11%Cr steel specimens tempered for 2 h at different temperatures.

Temp. (°C)	Nb-rich carbonitride $M(C,N)$		V-rich carbonitride $M(C,N)$		Cr-rich carbonitride $M_2(C,N)$		Cr-rich carbide $M_{23}C_6$	
	Sphere/block		Sphere	Spindle	Block	Plate	Block	Rod
600	50		50	ND ^a	21	6/27	62	15/165
650	58		63	ND	41	15/65	148	50/239
700	45		43	11/41 ^b	44	11/67	172	47/254
750	58		58	40/114	130	30/178	182	83/275
780	57		53	34/118	162	34/197	163	65/287

^a Not detected.

^b 11 and 41 nm in length of short and long axes of the V-rich $M(C,N)$, respectively.

reveal a slight decrease in niobium content in the niobium-rich $M(C,N)$ with increasing tempering temperature. During the tempering the niobium-rich $M(C,N)$ phases released niobium and chromium into solution and absorbed vanadium from solution. The rise in vanadium content also provided a possible nucleation site for the spindle-like vanadium-rich carbonitride phase, like the suggestion that the larger spherical particles of $Nb(C,N)$ appear to act as nucleation sites for the plate-like V-rich nitrides during tempering [17]. Present result confirms that the phenomenon that the MX precipitate phase remained after a normalizing is re-dissolved into the matrix during a subsequent tempering could be occurred in the 11%Cr steel normalized at a higher temperature of 1050 °C during the tempering at the lower temperatures of 600 through 780 °C,

and the amount of the re-dissolved metallic elements are detectable.

Fig. 5c is the measurement results for the amount of vanadium, niobium and chromium containing in vanadium–niobium-rich carbonitride $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ in the steel specimens tempered at different temperatures. With increasing tempering temperature, the contents of vanadium and chromium were increased, whereas, the content of niobium was decreased. Because the coarsening of spindle-like vanadium-rich $M(C,N)$ precipitates in present steel specimens occurred during the temperings, especially at the higher temperatures 750 and 780 °C, as shown in Table 1, and a part of vanadium-rich $M(C,N)$ precipitates with a chemical formula of $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ were in the shape of spindle, meanwhile

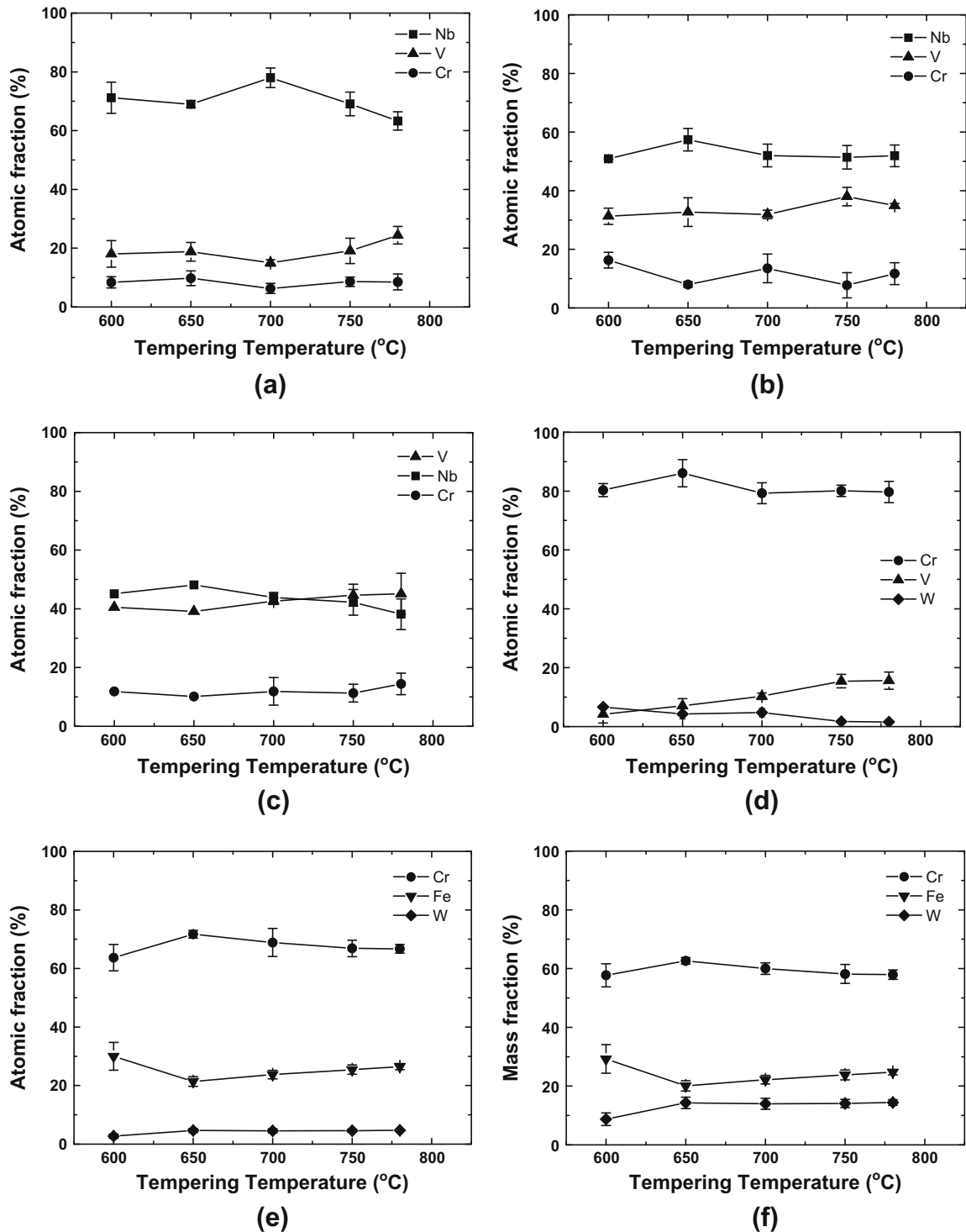


Fig. 5. The fraction of metallic elements in the precipitate phases: (a) $(\text{Nb}_{0.7}\text{V}_{0.2}\text{Cr}_{0.1})(\text{C,N})$, (b) $(\text{Nb}_{0.55}\text{V}_{0.35}\text{Cr}_{0.1})(\text{C,N})$, (c) $(\text{V}_{0.45}\text{Nb}_{0.45}\text{Cr}_{0.1})(\text{C,N})$, (d) $(\text{Cr}_{0.83}\text{V}_{0.12}\text{W}_{0.05})_2(\text{C,N})$ and (e and f) $(\text{Cr}_{0.7}\text{Fe}_{0.25}\text{W}_{0.05})_{23}\text{C}_6$, in the 11%Cr steel specimens tempered for 2 h at different temperatures.

their chemical compositions were analyzed using EDX spectroscopy, the average compositions of $(\text{V}_{0.45}\text{Nb}_{0.45}\text{Cr}_{0.1})(\text{C,N})$ precipitates were changed with the tempering temperatures. During the temperings spindle-like vanadium-rich $\text{M}(\text{C,N})$ precipitates released vanadium and chromium into solution to be absorbed by those precipitates of spindle-like vanadium-rich $\text{M}(\text{C,N})$ which were coarsening. The rise in vanadium and chromium contents was at the expense of niobium.

There was no obvious change in the compositions of vanadium-rich $\text{M}(\text{C,N})$ precipitates containing about 55% vanadium, just

showing a slight increase in vanadium and a slight decrease in niobium and chromium contents when tempering temperature was increased from 750 up to 780 °C. For the average compositions in atomic pct of the metal fraction of vanadium-rich $\text{M}(\text{C,N})$ precipitates containing about 65% vanadium, there was a slight increase in vanadium, an obvious increase and decrease in niobium and chromium contents, respectively, as tempering temperature was increased from 750 up to 780 °C. The increase in niobium and decrease in chromium contents probably due to the re-dissolving of niobium-rich $\text{M}(\text{C,N})$ phases during the temperings, which led to

an increase in niobium content in solution, and the precipitations of many chromium-rich $M_2(C,N)$ and $M_{23}C_6$ phases during the temperings at higher temperatures resulting in a decrease in chromium content in solution, respectively, thereby the vanadium-rich $M(C,N)$ precipitates containing a higher niobium and a lower chromium contents in the specimen tempered at 780 °C than that in the specimen tempered at 750 °C.

The average metallic fraction in atomic pct of the chromium-rich $M_2(C,N)$ precipitate phase in the steel specimens tempered at different temperatures is shown in Fig. 5d. It can be seen clearly that the content of vanadium and tungsten in the precipitate was increased and decreased with tempering temperature, respectively, meanwhile the general trend of chromium content in the precipitate maintained without significant changes with increasing tempering temperature. The present results show some differences compared with the results that with increasing the tempering temperature from 600 to 780 °C, chromium content was decreased, whereas vanadium content was increased, and there was no obvious change in the content of tungsten in the M_2N precipitate phase in a 9%Cr F/M steel [18], as well as that the content of chromium was increased in chromium-rich M_2X phase in a 5%Cr heat resistant steel as the tempering temperature was increased from 600 to 700/or 750 °C [19]. Since chromium-rich $M_2(C,N)$ precipitate phase in the steel specimens underwent a coarsening progress during the tempering with the increasing in temperature, which can be seen clearly from Table 1, the composition of the precipitate phase changed with increasing tempering temperature. During the temperings the $M_2(C,N)$ decreased in volume fraction, thereby releasing vanadium into solution to be absorbed by those precipitates of $M_2(C,N)$ which were coarsening. It also provided a source of vanadium for the vanadium-rich $M(C,N)$ phase which was being nucleated, and for that which pre-existed. The rise in vanadium content was at the expense of tungsten. As described earlier, the coarsening rate of the $M(C,N)$ phase was low under the tempering conditions with the temperature range from 600 to 700 °C, which would result in a low level of vanadium content in the solution and so that the $M_2(C,N)$ precipitates would be of the low vanadium type, and the coarsening rate was high at the tempering temperatures of 750 and 780 °C, leading to a high level of vanadium content in the solution and a formation of the $M_2(C,N)$ precipitates with a high content of vanadium.

Fig. 5e shows the average compositions in atomic pct of the metal fraction in the chromium-rich $M_{23}C_6$ precipitates in the steel specimens tempered at various temperatures. With increasing the temperature from 650 to 780 °C, the content of chromium and iron was decreased and increased, respectively, while the content of tungsten was changed little. The compositional changes in mass fraction of the metallic elements in the $M_{23}C_6$ precipitates with the tempering temperatures show the same trend like the changes in atomic fraction, as given in Fig. 5f. Present results are similar with the change trends of metallic elements in mass pct for the $M_{23}C_6$ phase in a X20CrMoV121 steel containing 11.59%Cr and a 12Cr1MoV steel under the condition of tempering for 2 h in the temperatures increased from about 400 to 780 °C [9,20]. One can note that the content of chromium, iron and tungsten in the specimen tempered at 600 °C was lower, higher and lower than that of the specimens tempered at 650 °C or 650 through 780 °C, respectively, which was probably caused by the effect of precipitate size on its chemical composition. It has been suggested that the measurements of carbide compositions should be presented alongside the corresponding particle sizes, and proved that the concentration of substitutional solute element chromium in chromium-rich $M_{23}C_6$ carbide in a 12Cr1MoV steel tempered at 700 °C for 2 h was increased with increasing the size of $M_{23}C_6$ particle [20]. In the present case, the sizes of $M_{23}C_6$ precipitates observed in the specimen tempered at 600 °C, i.e., FN43 specimen,

was obviously smaller than that of the $M_{23}C_6$ precipitates observed in the specimen tempered at 650 °C and even other temperatures, as shown in Table 1, probably resulting in a low level of chromium content in the $M_{23}C_6$ precipitates in the specimen tempered at 600 °C. The fall in chromium and tungsten contents was at the supplement of iron.

From the results for average compositions of precipitate phases, the typical chemical formulae of the precipitate phases existed in the present steel specimens tempered at five temperatures are as the followings: $(Nb_{0.7}V_{0.2}Cr_{0.1})(C,N)$, $(Nb_{0.55}V_{0.35}Cr_{0.1})(C,N)$, $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$, $(Cr_{0.83}V_{0.12}W_{0.05})_2(C,N)$, and $(Cr_{0.7}Fe_{0.25}W_{0.05})_{23}C_6$ existed in all the specimens, as well as $(V_{0.65}Nb_{0.2}Cr_{0.15})(C,N)$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$ existed in the FN46 and FN47 specimens.

According to the present TEM observations for the carbon replicas, the most observed niobium-rich carbonitride precipitates with a spherical shape seem to precipitate in the matrix, and a few of the precipitates having a block shape have a precipitation site of prior austenite grain boundary. Vanadium–niobium-rich and vanadium-rich carbonitrides seem to mainly precipitate in the matrix and the matrix within martensite laths. For the chromium-rich carbonitrides, they precipitated in the matrix and the matrix within martensite laths, and at the martensite lath boundaries. Chromium-rich carbides have been found to precipitate at the prior austenite boundaries, martensite lath boundaries, as well as in the matrix and the matrix within martensite laths.

In addition, present TEM observations indicate that in the present steel specimens tempered at five temperatures the amount of chromium-rich $M_{23}C_6$ and $M_2(C,N)$ precipitate phases was more than that of other precipitate phases, whilst the amount of vanadium–niobium-rich $M(C,N)$ precipitate phase was least among the precipitate phases in the steel and vanadium-rich $M(C,N)$ precipitate phases were only detected in the FN46 and FN47 specimens. However, the amount and density of the precipitate phases in the present steel with the states of the tempering at different temperatures are difficult to be determined quantitatively only by the present TEM observations because the distributions of these precipitates on the present carbon replicas were not uniform and some of them were sometimes observed in a few cases, for example, the vanadium–niobium-rich $M(C,N)$ precipitates in the FN43 and FN44 specimens. It is necessary to quantitatively analyze these precipitate phases in the present steel in our next experimental work.

4. Conclusions

The results of the study on the precipitate phases in a 11%Cr F/M steel with the states of normalization and followed by tempering for 2 h at 600 through 780 °C can be summarized as follows:

- (1) Niobium-rich carbonitride $M(C,N)$, chromium-rich carbonitride $M_2(C,N)$ and chromium-rich carbide $M_{23}C_6$, are independent of tempering temperature. The precipitate phases with the chemical formulae of $(Nb_{0.7}V_{0.2}Cr_{0.1})(C,N)$, $(Nb_{0.55}V_{0.35}Cr_{0.1})(C,N)$, $(Cr_{0.83}V_{0.12}W_{0.05})_2(C,N)$, and $(Cr_{0.7}Fe_{0.25}W_{0.05})_{23}C_6$ were identified in all the steel specimens.
- (2) Vanadium–niobium-rich carbonitride $M(C,N)$ is independent of tempering temperature, whereas vanadium-rich carbonitride $M(C,N)$ is dependent on tempering temperature. The $(V_{0.45}Nb_{0.45}Cr_{0.1})(C,N)$ phase was identified in all the steel specimens. The $(V_{0.65}Nb_{0.2}Cr_{0.15})(C,N)$ and $(V_{0.55}Nb_{0.25}Cr_{0.2})(C,N)$ phases were identified only in the steel specimens tempered at the higher temperatures of 750 and 780 °C.
- (3) Niobium-rich and spherical vanadium-rich carbonitrides are resistant to coarsening during the temperings. The mean size

of the spindle-like vanadium-rich carbonitrides was increased with the tempering temperature from 700 to 750 °C. The coarsening rate of chromium-rich carbonitride during tempering is lower at 600 through 700 °C than that at 750 and 780 °C. Chromium-rich carbide has a high coarsening rate at 650 °C and a better resistance to coarsening at 650 through 780 °C.

- (4) With the increase of tempering temperature, the niobium-rich, vanadium–niobium-rich, and chromium-rich carbonitrides show changes in composition, with increases in vanadium and decreases in niobium as well as chromium contents, with decreases in niobium and increases in vanadium as well as chromium contents and with increases in vanadium and decreases in tungsten contents, respectively. The chromium-rich carbide shows a decrease in chromium and an increase in iron as well as tungsten contents with increasing the tempering temperature from 650 to 780 °C.

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