Journal of Nuclear Materials 389 (2009) 359–364

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Effects of the fabrication process parameters on the precipitates and mechanical properties of a 9Cr–2W–V–Nb steel

Tae Kyu Kim *, Jong Hyuk Baek, Chang Hee Han, Sung Ho Kim, Chan Bock Lee

Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseong, Daejeon 305-353, Republic of Korea

A R T I C L E I N F O

Article history:
Received 30 June 2008
Accepted 23 January 2009

A B S T R A C T

The effects of the fabrication process parameters such as a tempering temperature, cold rolling and annealing condition on the precipitates and mechanical properties of a normalized 9Cr–2W–V–Nb steel were evaluated. Nb-rich MX precipitates were found in the specimen tempered at 550 °C while $M_{23}C_6$, Nb- and V-rich MX ones were observed in the specimen tempered at 750 °C. A cold rolling and an annealing at 750 °C of the specimen tempered at 550 °C induced the formation of large inhomogeneous $M_{23}C_6$ carbides, causing a reduced tensile strength. However, the cold rolling of the specimen tempered at 750 °C provided fine precipitates due to a fragmentation of some of the $M_{23}C_6$ carbides, and an annealing at 700 °C for 30 min was found to be suitable to recover the degraded mechanical properties from a cold working.

1. Introduction

Ferritic/martensitic (FM) steels are being considered as an attractive candidate material for a fuel cladding of a sodium-cooled fast reactor (SFR) due to their high thermal conductivities, low expansion coefficients and excellent irradiation resistances to a void swelling compared with austenitic stainless steels [1–5]. When these steels are applied to a fuel cladding in a SFR, their temperatures are expected to approach 650 °C. Here, the fission gas becomes the source of an internal stress on the cladding [6]. The cladding should thus have excellent mechanical properties such as a good tensile strength and creep resistance at high temperatures.

The mechanical properties of the FM steels are mainly determined by the relevant factors which include the alloying elements, prior-austenite grain size, subgrain size, lath width, dislocation density and precipitates. The precipitates imply their amount, type, size, morphology, stability and distribution [7,8]. Many studies have focused on the formation of fine and stable precipitates since a coarsening of precipitates causes a degradation of the mechanical properties [9–13]. These fine and stable precipitates could be obtained by means of a control of the fabrication process parameters.

The fabrication processes of the FM steel cladding tubes are mainly composed of a melting, hot forging, hot extrusion, normalizing-and-tempering (N&T), cold pilgering and an annealing. The hot-worked steels are usually subjected to a N&T treatment before a cold working. Most of the $M_{23}C_6$ carbide precipitates dissolve into the matrix during a normalizing [14], and the precipitation reactions of the $M_{23}C_6$ carbide and V-rich MX carbonitride take place during a tempering [15]. From this point of view, it is possible to consider two routes; one is composed of a tempering at low temperatures where little or no precipitation reaction can occur, a cold working and then an annealing for both a precipitation reaction from a super-saturated solid solution and a recovery from a cold working. Basically, the concept of this route implies that the precipitates formed during an annealing are expected to be fine because the high density of the dislocations formed through a cold working would offer favorable nucleation sites for the precipitates. The other consists of a tempering at temperatures where a precipitation reaction can be completed, a cold working and then an annealing for a recovery. The precipitates and mechanical properties are expected to be different between these two routes. However, there has been little evaluation in relation to these fabrication process parameters of the FM steel cladding tubes.

Hence, this study focuses on the effects of fabrication process parameters such as a tempering temperature, cold rolling and annealing condition on the precipitates and mechanical properties of a 9Cr–2W–V–Nb steel.

2. Experimental procedure

A 9Cr–2W–V–Nb steel was designed, and the steel ingot was prepared by a vacuum induction melting process. Its chemical composition is given in Table 1. The steel ingot was hot-rolled after a preheating at 1150 °C for 2 h. The hot-rolled specimen was normalized at 1050 °C for 1 h, and tempered at 550 and 750 °C for 2 h, respectively. The specimen tempered at 550 °C was cold-rolled from 4 to 1 mm thickness, and then subjected to a subsequent heat treatment at 750 °C for 30, 60 and 120 min, respectively. The

* Corresponding author. Tel.: +82 42 868 8384; fax: +82 42 868 8549.
E-mail address: tkkim2@kaeri.re.kr (T.K. Kim).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.01.302

Table 1
Chemical composition of the 9Cr–2W–V–Nb steel (wt%).

Fe	C	Si	Mn	Ni	Cr	Mo	V	Nb	W	N
Bal.	0.051	0.060	0.419	0.450	8.62	0.493	0.208	0.204	2.08	0.051

specimen tempered at 750 °C was also cold-rolled from 4 to 1 mm thickness, and then subjected to a subsequent heat treatment at 650, 700 and 750 °C for 30 min, respectively. Air cooling was applied in all the cases. An additional specimen annealed at 700 °C for 30 min was cooled down in water and in furnace with a cooling rate of 2.7 °C/min to observe the effects of the cooling rate on the mechanical properties.

The precipitates taken from the carbon extraction replicas were examined by using a transmission electron microscope (TEM) with an energy dispersive spectroscope (EDS). The carbon extraction replicas were prepared by means of a mechanical polishing, etching with a mixed solution (93 vol.% water, 5 vol.% nitric acid and 2 vol.% fluoric acid), carbon coating and removing the replicas by an electrochemical etching with a mixed solution (90 vol.% methanol and 10 vol.% hydrochloric acid). The size distribution of the precipitates was measured by using an image analyzer. A Vickers microhardness was measured by using a microhardness tester under a load of 0.5 kg_f. The tensile test samples were prepared according to ASTM E8-04 in the longitudinal direction of the hot- and cold-rolled specimens, and the tensile tests were carried out at a strain rate of 2×10^{-3}/s at room temperature and 650 °C. The phases in the specimen as a function of the temperature were calculated by using a computational thermodynamics program (ThermoCal).

3. Results

3.1. Microstructure

Fig. 1 shows the TEM images of the extraction replicas for the precipitates in the specimens tempered at 550 and 750 °C, and the representative compositions of the precipitates are given in Table 2. Nano-sized precipitates were observed in the specimen tempered at 550 °C. Their representative composition was determined to be (in at.%) 85Nb, 9 V, 4Cr and 2W, indicating a Nb-rich MX-type (M = Nb, V, Cr, W and X = C, N) carbonitride. No other type of precipitates was observed. On the other hand, $M_{23}C_6$, Nb- and V-rich MX-type precipitates were found in the specimen tempered at 750 °C. The representative composition of the $M_{23}C_6$ carbides was determined to be (in at.%) 63Cr, 30Fe, 4 W and 3Mo, indicating a complex compound of $(Cr, Fe, W, Mo)_{23}C_6$. The composition of the Nb-rich MX carbonitride was analyzed to be (in at.%) 87Nb, 10 V, 2Cr and 1 W. The V-rich MX carbonitride was normally composed of (in at.%) 63 V, 12Nb, 16Cr and 9 W, denoting a complex compound of (V, Nb, Cr, W)(C, N). The $M_{23}C_6$ carbides were mainly detected in the prior-austenite grain boundaries, but occasionally in the subgrains and lath boundaries. The MX precipitates were usually found in the lath and lath boundaries. The size distributions of these precipitates are plotted in Fig. 2. The precipitates in the specimen tempered at 550 °C tended to concentrate in the equivalent diameter range of 20–80 nm, and their mean equivalent diameter was measured to be 67 nm. The precipitates in the specimen tempered at 750 °C were mainly concentrated in the equivalent diameter ranges of 20–80 nm and 160–220 nm, and their mean equivalent diameter was analyzed to be 102 nm.

Fig. 3 shows the TEM images of the extraction replicas for the precipitates in the cold-rolled specimens. The cold rolling of the specimen tempered at 550 °C induced little change in the size and morphology of the Nb-rich MX precipitates. On the other hand, the cold rolling of the specimen tempered at 750 °C induced a movement of the prior-austenite grain boundaries, leaving the precipitates, which originally existed in the prior-austenite grain boundaries, in the grains. A fragmentation and separation of some of the $M_{23}C_6$ precipitates were also observed. As a result, the precipitates in the cold-rolled specimen became relatively fine in the prior-austenite grains.

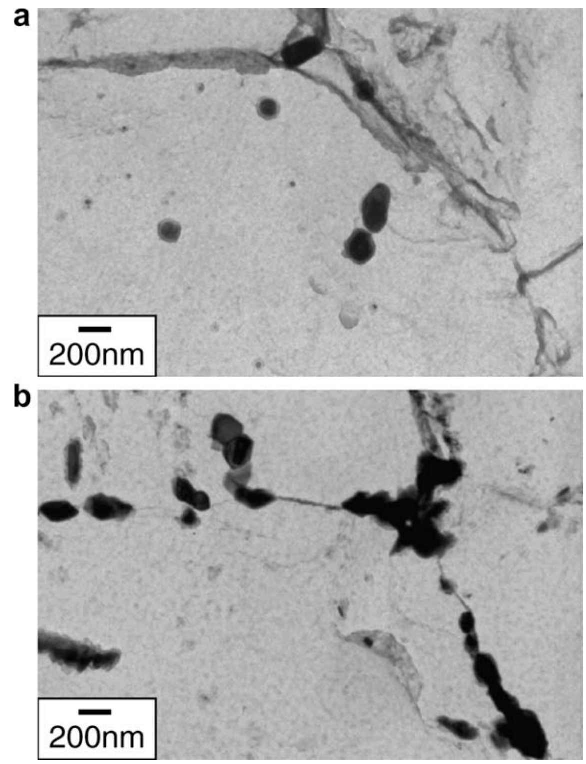

Fig. 1. TEM images of the extraction replicas for the precipitates in the 9Cr–2W–V–Nb steels after a normalizing at 1050 °C for 1 h and a tempering at (a) 550 and (b) 750 °C for 2 h, respectively.

Fig. 4 shows the TEM/EDS results of the precipitates in the specimen after a tempering at 550 °C, and a cold rolling and an annealing at 750 °C for 30 min. Except for the Nb-rich MX precipitates which originally existed in the specimen tempered at 550 °C, finely distributed $M_{23}C_6$ and V-rich MX precipitates were observed in the entire matrix. Large inhomogeneous particles with a size range from 0.5 to 1.5 μm were additionally detected, and their chemical composition was analyzed to be (in at.%) 65Cr, 28Fe, 4Mo and 3 W, indicating that those were also $M_{23}C_6$ precipitates.

3.2. Mechanical properties

Fig. 5 shows the effects of the cold rolling and annealing on the Vickers microhardness of the specimens tempered at 550 and 750 °C. The hardness of the specimen tempered at 550 °C was measured to be about 354 Hv, and it increased up to 420 Hv after a cold rolling. However, the hardness was significantly reduced to a level of 175 Hv after an annealing at 750 °C for 30 min, and no more remarkable reduction of the hardness was observed until the annealing time was increased up to 120 min. The hardness of the

Table 2
Representative compositions of the precipitates in the 9Cr–2W–V–Nb steel after a tempering at 550 and 750 °C for 2 h, respectively.

Tempering temp. (°C)	Precipitates						
	Type	Representative composition (at.%)					
		Fe	Cr	Mo	W	Nb	V
550	Nb-rich MX	30	4		2	85	9
750	$M_{23}C_6$		63	3	4		
	Nb-rich MX		2		1	87	10
	V-rich MX		16		9	12	63

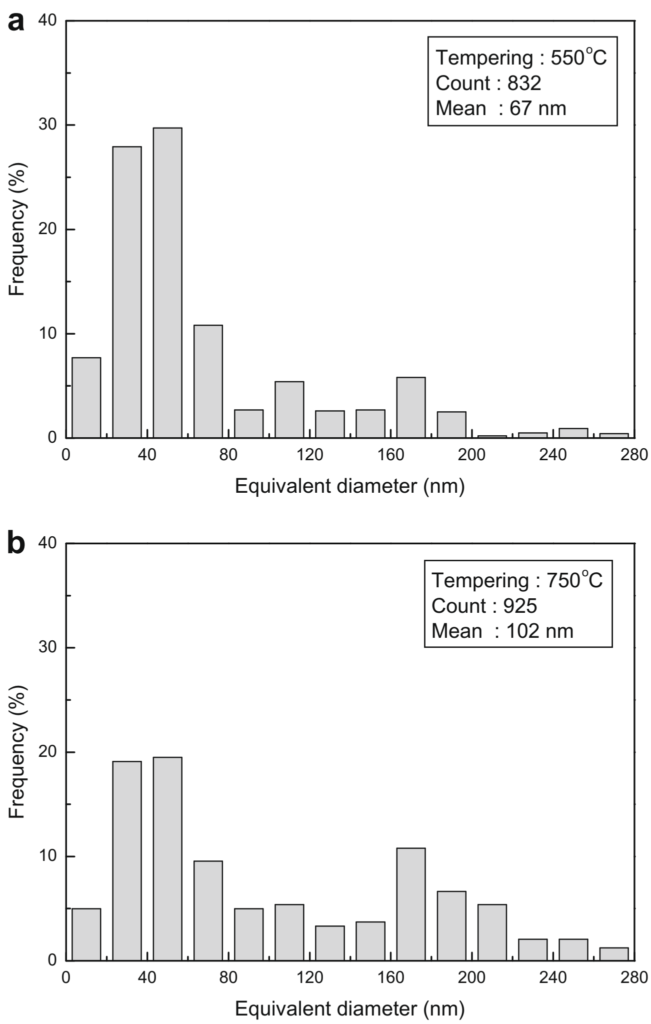

Fig. 2. Size distributions of precipitates in the 9Cr–2W–V–Nb steels after a normalizing at 1050 °C for 1 h and a tempering at (a) 550 and (b) 750 °C for 2 h, respectively.

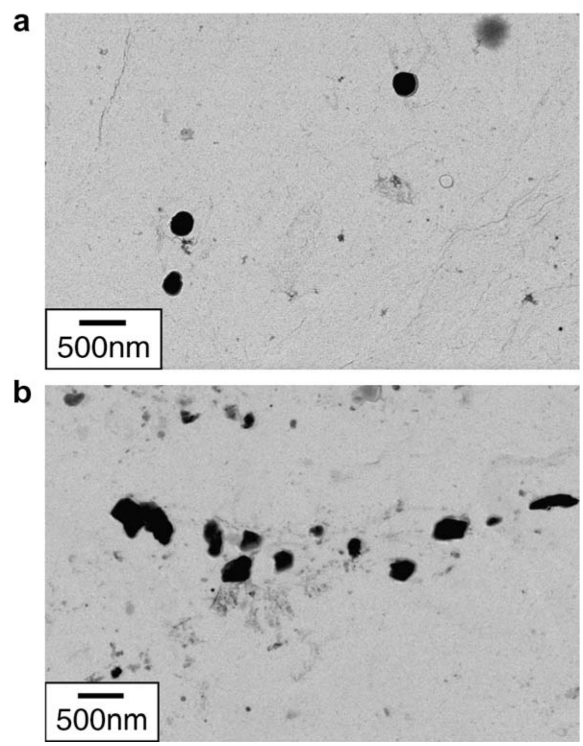

Fig. 3. TEM images of the extraction replicas for the precipitates in the cold-rolled 9Cr–2W–V–Nb steels: tempered at (a) 550 and (b) 750 °C before a cold rolling.

specimen tempered at 750 °C was revealed to be 244 Hv, and increased to 316 Hv after a cold rolling. It was gradually reduced as the increased temperature, and it was found that the hardness after an annealing at 700 °C for 30 min was similar with that of the specimen tempered at 750 °C for 2 h before a cold rolling.

The results of the tensile tests at room temperature and 650 °C of the specimen normalized at 1050 °C for 1 h and tempered at 750 °C for 2 h are given in Table 3. At room temperature, the yield and tensile strengths and the elongation were measured to be 556 MPa, 665 MPa and 20%, respectively. At 650 °C, they were evaluated to be 272 MPa, 294 MPa and 25%, respectively. The effects of an annealing time at 750 °C on the tensile properties of the tempered at 550 °C and cold-rolled specimen are shown in Fig. 6. The results of the tensile tests at room temperature and 650 °C indicated that as the annealing time at 750 °C was increased, the yield and tensile strengths were continuously decreased while the elongation was slightly increased. However, these yield and tensile strengths were estimated to be far inferior when compared with those of the specimen tempered at 750 °C (Table 3). The effects of an annealing temperature on the tensile properties of the tempered at 750 °C and cold-rolled specimen are shown in Fig. 7. The tensile properties at room temperature and 650 °C appeared to be dependant on the annealing temperature; as the annealing temperature increased, the yield and tensile strengths were decreased while the elongations were increased. The tensile properties after the annealing at 700 °C for 30 min were evaluated to be similar with those after a tempering at 750 °C for 2 h (Table 3).

The effect of the cooling rate after an annealing at 700 °C for 30 min on the hardness of the cold-rolled specimen is given in Table 4. The hardness was shown to be similar with a value of about 245 Hv when a water quenching and air cooling were applied. However, a furnace cooling with a cooling rate of 2.7 °C/min resulted in a significantly lower hardness with a value of about 190 Hv. The effects of the cooling rate after an annealing at 700 °C for 30 min on the tensile properties of the cold-rolled specimen are

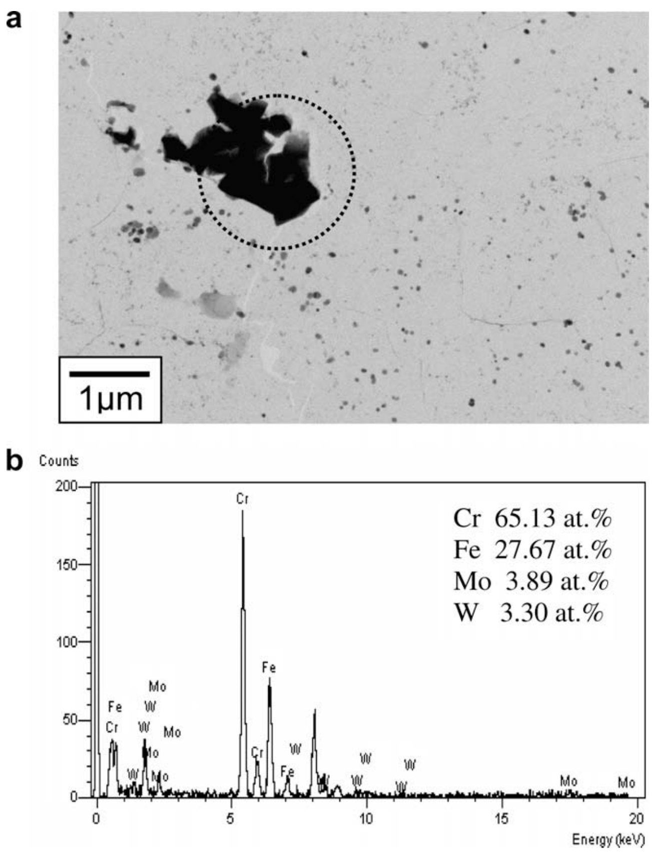

Fig. 4. TEM/EDS results of the precipitates in the 9Cr–2W–V–Nb steels after a tempering at 550 °C, and a cold rolling and an annealing at 750 °C for 30 min: (a) TEM image and (b) spectrum for the precipitation marked by a circle in (a).

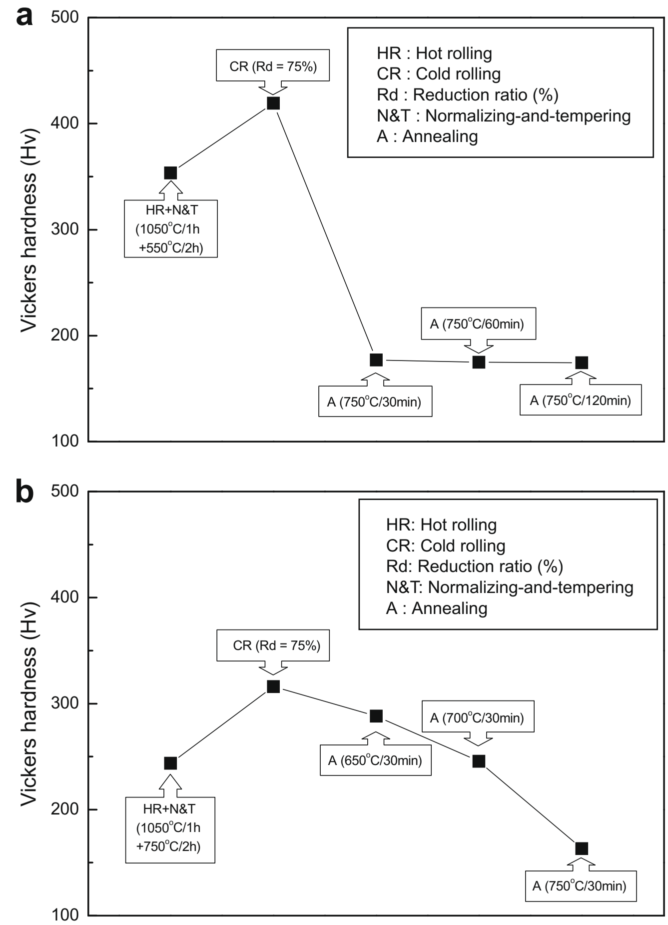

Fig. 5. Effects of the cold rolling and annealing on the Vickers microhardness of the 9Cr–2W–V–Nb steels tempered at (a) 550 and (b) 750 °C.

shown in Fig. 8. The results of the tensile tests at room temperature and 650 °C exhibited a similar trend in accordance with those of the hardness ones; the yield and tensile strengths and the elongation revealed to be similar when a water quenching and air cooling were applied, but a furnace cooling induced a reduced tensile strength and an increased elongation.

4. Discussion

The type and size distribution of the precipitates in the normalized specimen are significantly dependent on the tempering temperature (Figs. 1 and 2, Table 2). On the basis of the chemical composition (Table 1), the phases in the 9Cr–2W–V–Nb steel as a function of the temperature calculated by using a computational thermodynamics program are plotted in Fig. 9. This steel can contain 4 types of precipitates; $M_{23}C_6$, Laves, V- and Nb-rich MX. The $M_{23}C_6$ carbides are found to be stable at temperatures up to 820 °C. It is well known that the Laves phase is usually formed after an aging treatment for a long time at around 600 °C under a stress or not [15,16]. The V- and Nb-rich MX precipitates are stable at temperatures up to about 1070 and 1300 °C, respectively. It is thus possible to explain a behavior of the precipitates during the N&T treatment as follows; the $M_{23}C_6$ carbides dissolve fully into the austenitic matrix during a normalizing at 1050 °C, but the Nb-rich MX still remain in the normalized specimen. The V-rich MX particles are also assumed to dissolve into the matrix at 1050 °C even though they are stable at temperatures up to about 1070 °C. The driving force for a precipitation reaction is not sufficient with a tempering at 550 °C for 2 h, thus the remaining precipitates are Nb-rich MX carbonitrides (Fig. 1(a), Table 2). However, a tempering

Table 3
Results of the tensile tests at room temperature and 650 °C of the specimen normalized at 1050 °C for 1 h and tempered at 750 °C for 2 h.

Test temp. (°C)	YS (MPa)	UTS (MPa)	Elongation (%)
20	556	665	20
650	272	294	25

at 750 °C for 2 h appears to be sufficient to precipitate the other precipitates such as the $M_{23}C_6$ carbides and V-rich MX carbonitrides (Fig. 1(b), Table 2), thus causing a change in the size distribution of the precipitates (Fig. 2).

No intermediate heat treatment during a cold rolling from 4 to 1 mm thickness which is in accordance with a reduction ratio of 75% is necessary, indicating that the specimens tempered at 550 and 750 °C reveal an acceptable cold workability.

After a cold rolling, there is little change in the size and morphology of the Nb-rich MX precipitates (Fig. 3(a)), implying that these precipitates are harder than the matrix. However, some of the $M_{23}C_6$ carbides are observed to be fragmented (Fig. 3(b)). It is assumed that these results could be closely correlated with the size of the precipitates; during a cold rolling the large-sized $M_{23}C_6$ carbides would be more easily fragmented than the small-sized MX precipitates (Fig. 1). The detailed mechanism of a destruction of the carbides in a steel during a thermomechanical treatment has been reported [17]. These fragmentations are considered to be favorable to obtain fine $M_{23}C_6$ carbides. Large inhomogeneous

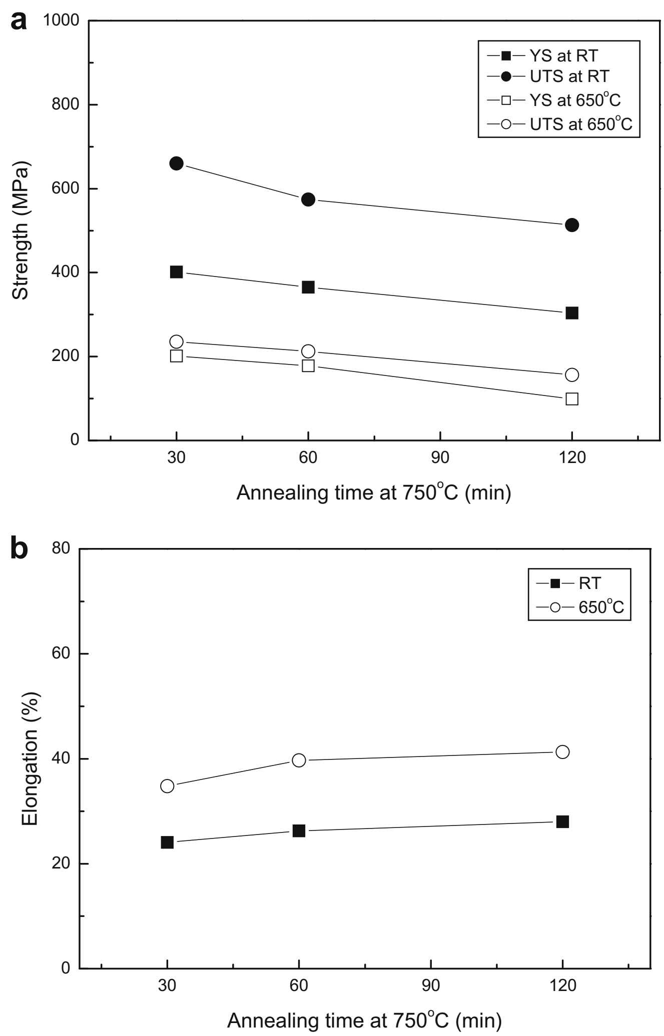

Fig. 6. Effects of an annealing time at 750 °C on the (a) strength and (b) elongation of the tempered at 550 °C and cold-rolled 9Cr–2W–V–Nb steel.

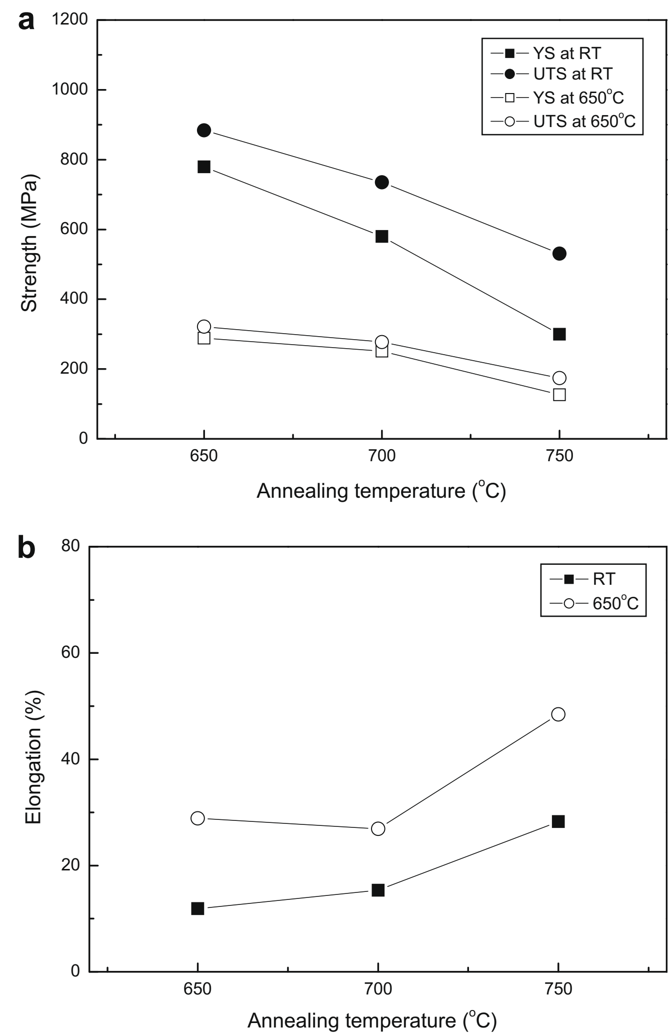

Fig. 7. Effects of an annealing temperature on the (a) strength and (b) elongation of the tempered at 750 °C and cold-rolled 9Cr–2W–V–Nb steel.

$M_{23}C_6$ carbides are detected in a specimen after a tempering at 550 °C, and a cold rolling and an annealing at 750 °C (Fig. 4). A recrystallization of the matrix is also observed. It has been reported that the interfaces of deformation bands caused by a severe cold rolling were exploited as inhomogeneous nucleation sites for precipitates [18], and an excess strain energy accumulated through an intensive cold rolling caused an inhomogeneous nucleation and a growth of recrystallized grains [19]. It is thus considered that the excess strain energy stored through a cold rolling causes the formation of large inhomogeneous carbides in the recrystallized grains during annealing at 750 °C.

The mechanical properties of the FM steels could be closely correlated with the N&T conditions. The N&T temperatures for the ASTM grade 92 (9Cr–0.5Mo–1.8 W–V–Nb) steel are recommended to be in the ranges of 1040–1080 °C and 730–800 °C, respectively. In this study, the mechanical properties such as the hardness and tensile strength of the 9Cr–2W–V–Nb steel after a normalizing at 1050 °C and a tempering at 750 °C could be regarded as a reference (Fig. 5(b), Table 3).

In the case of the tempering at 550 °C, the annealing at 750 °C after the cold rolling of the specimen tempered at 550 °C resulted in a significant reduction in the hardness as well as the tensile strength (Figs. 5(a) and 6(a)) when compared with those of a reference (Fig. 5(b), Table 3). These results could mainly be attributed to

Table 4
Effect of the cooling rate after an annealing at 750 °C for 30 min on the hardness of the cold-rolled 9Cr–2W–V–Nb steel.

	Water quenching	Air cooling	Furnace cooling
Hardness (Hv)	243.5	245.5	189.5

the recovery as well as the large inhomogeneous $M_{23}C_6$ precipitates that form as a result of a heat treatment for forming the $M_{23}C_6$ and V-rich MX precipitates (Fig. 4). Almost constant microhardness in the annealing time range from 30 to 120 min at 750 °C is assumed to prove that the recovery and the precipitation reactions are complete within 30 min (Fig. 5(a)).

In the case of the tempering at 750 °C, the hardness and tensile strengths of the cold-rolled specimen are gradually decreased with an increasing annealing temperature (Figs. 5(b) and 7(a)). After an annealing at 700 °C for 30 min, the hardness and tensile properties reveal to be similar with those of the reference (Fig. 5(b), Table 3). These results indicate that the degraded mechanical properties from the cold working can be recovered by a suitable annealing heat treatment. It is thus concluded that the route composed of a tempering at 750 °C, and a cold rolling and an annealing at 700 °C for 30 min would be an effective way of avoiding the

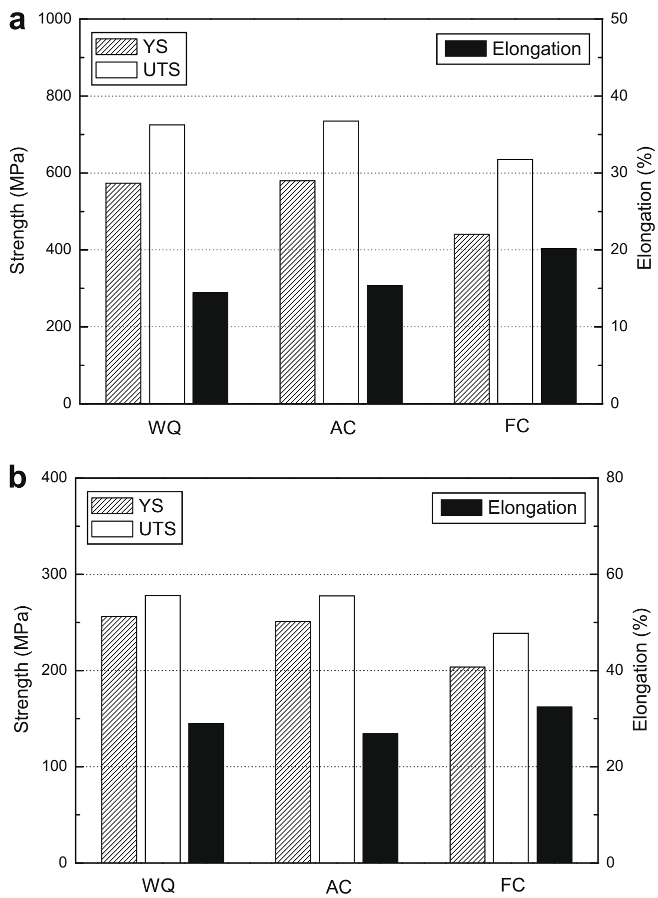

Fig. 8. Effects of the cooling rate after an annealing at 700 °C for 30 min on the tensile properties of the cold-rolled 9Cr–2W–V–Nb steel at (a) room temperature and (b) 650 °C.

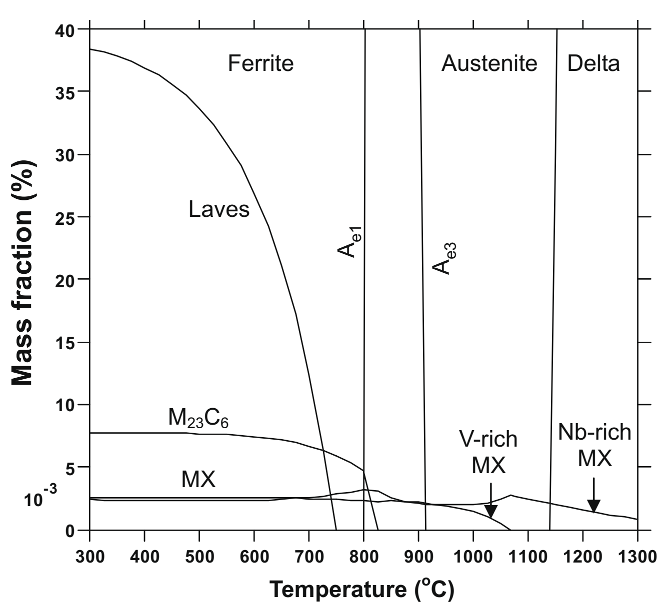

Fig. 9. The phases in the 9Cr–2W–V–Nb steel as a function of the temperature as calculated by the computational thermodynamics program.

formation of large undesirable $M_{23}C_6$ precipitates and of recovering the degraded mechanical properties from a cold working.

There is little difference in the mechanical properties when a water quenching and air cooling after an annealing at 700 °C for 30 min are applied, but a furnace cooling gives a softening of the hardness and the tensile strength (Table 4, Fig. 8). It is considered that the furnace cooling could provide longer duration at high temperatures for recovery than water quenching or air cooling.

5. Conclusions

In order to evaluate the effects of the fabrication process parameters on the precipitates and mechanical properties of the 9Cr–2W–V–Nb steel, the normalized specimens were tempered at two temperatures, cold-rolled with a reduction ratio of 75%, and then annealed at several conditions. Only Nb-rich MX precipitates were found in the specimen tempered at 550 °C while $M_{23}C_6$ carbides, Nb- and V-rich MX carbonitrides were observed in the specimen tempered at 750 °C. The cold rolling and annealing at 750 °C of the specimen tempered at 550 °C resulted in the formation of large inhomogeneous $M_{23}C_6$ precipitates, causing a reduced tensile strength. The cold rolling of the specimen tempered at 750 °C provided fine precipitates mainly due to the fragmentation and the separation of some of the $M_{23}C_6$ precipitates during a cold working. An annealing at 700 °C for 30 min was found to be suitable to recover the degraded mechanical properties from a cold working. It is thus concluded that the route composed of a tempering at 750 °C, and a cold rolling with a reduction ratio of 75% and an annealing at 700 °C for 30 min would be an effective way of avoiding the formation of large undesirable $M_{23}C_6$ carbides and of recovering the degraded mechanical properties from a cold working. In addition, little difference in the mechanical properties was observed when a water quenching and air cooling from 700 °C for an annealing were applied.

Acknowledgements

This study was supported by the Korea Science and Engineering Foundation and the Korean Ministry of Education, Science and Technology, through the National Nuclear Technology Program.

References

[1] F.A. Garner, M.B. Tgoloczko, B.H. Sencer, J. Nucl. Mater. 276 (2000) 123.
[2] D.S. Gelles, J. Nucl. Mater. 108&109 (1982) 515.
[3] Y. Dai, B. Long, Z.F. Tong, J. Nucl. Mater. 377 (2008) 115.
[4] S.H. Kim, W.S. Ryu, I.H. Kuk, Nucl. Eng. Tech. 31 (1999) 561.
[5] S.H. Kim, B.J. Song, W.S. Ryu, J.H. Hong, J. Nucl. Mater. 329–333 (2004) 299.
[6] R.L. Klueh, A.T. Lelson, J. Nucl. Mater. 371 (2007) 37.
[7] C.S. Jeong, S.Y. Bae, D.H. Ki, K. Watanabe, B.S. Lim, Mater. Sci. Eng. A 449–451 (2007) 155.
[8] H. Tanigawa, H. Sakasegawa, N. Hashimoto, R.L. Klueh, M. Ando, M.A. Sokolov, J. Nucl. Mater. 367–370 (2007) 42.
[9] F. Abe, T. Horiuchi, M. Taneike, K. Sawada, Mater. Sci. Eng. A 378 (2004) 299.
[10] J.S. Lee, H.G. Armaki, K. Maruyama, T. Muraki, H. Asahi, Mater. Sci. Eng. A 428 (2006) 270.
[11] M. Taneike, F. Abe, K. Sawada, Nature 424 (2003) 294.
[12] R.L. Klueh, N. Hashimoto, P.J. Maziasz, J. Nucl. Mater. 367–370 (2007) 48.
[13] F. Abe, Mater. Sci. Eng. A 387–389 (2004) 565.
[14] J.M. Vitek, R.L. Klueh, Metall. Trans. A 14A (1983) 1047.
[15] M. Hattestrand, H.O. Andren, Acta Mater. 49 (2001) 2123.
[16] L. Korcakove, J. Hald, M.A.J. Somers, Mater. Charact. 47 (2001) 111.
[17] V.I. Movchan, A.S. Kovzel, Met. Sci. Heat Treat. 31 (1989) 464.
[18] L.P. Troeger, E.A. Starke Jr., Mater. Sci. Eng. A 293 (2000) 19.
[19] T. Narita, S. Ukai, T. Kaito, S. Ohtsuka, T. Kobayashi, J. Nucl. Sci. Technol. 41 (2004) 1008.