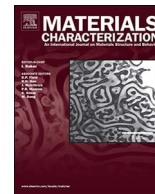




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# Mechanism for Z-phase formation in 11CrMoVNbN martensitic heat-resistant steel

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## ABSTRACT

The mechanism for the formation of Z-phase was investigated for samples of an 11CrMoVNbN steel aged at 593 °C for up to 50,000 h. X-ray diffraction indicates that Z-phase appears after 5000 h of aging, and its amount gradually increases up to 50,000 h aging at the expense of mainly Cr<sub>2</sub>N. Transmission electron microscopy shows that Z-phase nucleates in the V-enriched rim region of Cr<sub>2</sub>N precipitates, which forms due to the diffusion of V into the precipitates from the matrix. Nucleated Z-phase tends to grow relatively rapidly compared with the preexisting precipitates such as Nb(C,N) and M<sub>23</sub>C<sub>6</sub>. Z-phase seems to consume Cr<sub>2</sub>N by the nucleation and growth mechanism rather than the transformation mechanism. The main difference in the aged samples is that the Nb content of Z-phase is lower and that Z-phase does not replace Cr<sub>2</sub>N completely, compared to the results of the crept samples.

## 1. Introduction

The most effective way to enhance energy efficiency and reduce CO<sub>2</sub> emissions in coal-fired power plants is to increase the operating temperature and steam pressure. Therefore, it is important to develop advanced materials that exhibit superior mechanical properties at high temperatures. Various 9–12 wt% Cr martensitic heat-resistant steels have been developed and are commonly used for coal-fired power plants due to their high creep rupture strength and good oxidation resistance at high temperatures, as well as their low thermal expansion coefficient and relatively low cost [1–7].

However, the severe degradation in creep rupture strength of these steels has been reported after being exposed to high temperature for a long time. The formation of coarse Z-phase precipitates, which are Cr(V,Nb)N with a distorted body-centered tetragonal crystal structure with double layers of alternating atoms ( $a = 0.304$  nm and  $c = 0.739$  nm) [8], at the expense of fine precipitates, has been recognized to be responsible for the degradation. Fine MX-type precipitates with the NaCl (B1) structure, which contribute to precipitation strengthening, tend to gradually change into Z-phase after long-term service above 500 °C, resulting in the reduction of creep rupture strength [9–11]. Although Z-phase is thermodynamically stable, it is known to nucleate very slowly without being observed at

the early stage. However, once Z-phase precipitates nucleate, they tend to grow rapidly, consuming fine MX precipitates.

Danielsen and Hald [12] proposed two different mechanisms for the formation of the Z-phase. One is the formation of Z-phase by nucleation and growth, and the other is the direct transformation of MX precipitates. For both mechanisms, Cr diffuses into MX precipitates during aging at high temperatures. For the nucleation-and-growth mechanism, Z-phase precipitates nucleate at the surface of MX precipitates and grow at the expense of MX precipitates. In contrast, Cr-enriched MX precipitates directly transform into Z-phase precipitates for the transformation mechanism. Furthermore, Cipolla et al. [13] reported that the chemical transformation of MX precipitates into the metastable intermediate cubic Z-phase occurs after the uptake of Cr in MX precipitates, eventually followed by the crystallographic transformation of Z-phase into the tetragonal structure. Many studies have reported the relationship between MX and Z-phase precipitates in 9–12 wt% Cr martensitic heat-resistant steels [12–15].

Meanwhile, Sawada et al. [9] mentioned that M<sub>2</sub>X with a hexagonal structure, which usually appears as Cr<sub>2</sub>N in high nitrogen steels, can also change to Z-phase if the content of V and Nb becomes enriched in M<sub>2</sub>X. It is known that fine M<sub>2</sub>X precipitates, as well as MX precipitates, effectively inhibit dislocation movement in the matrix, thereby contributing to the strengthening effect [16]. Recently, our previous study

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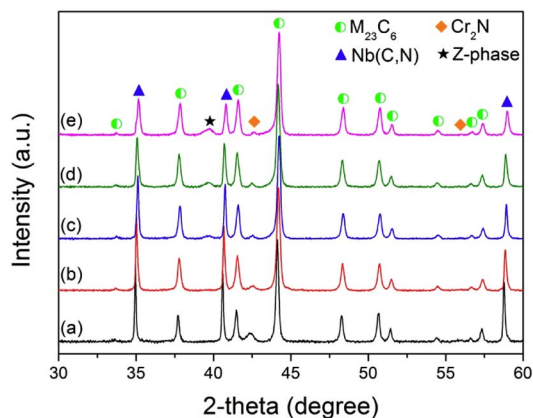
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**Table 1**  
Chemical composition of the 11CrMoVNbN steel (wt%).

Steel	Fe	C	Si	Mn	Cr	Ni	Mo	V	Nb	Cu	N
11CrMoVNbN	Bal.	0.16	0.25	0.56	10.4	0.35	0.86	0.17	0.38	0.13	0.06



**Fig. 1.** XRD patterns of the extracted precipitates from the (a) as-tempered and the samples aged at 593 °C for (b) 5000, (c) 10,000, (d) 15,000 and (e) 50,000 h.

**Table 2**  
Relative precipitate amount analyzed by the Rietveld refinement of the XRD patterns in Fig. 1a (wt%).

Aging time	M <sub>23</sub> C <sub>6</sub>	Nb(C,N)	Cr <sub>2</sub> N	Z-phase
As-tempered	65.6	18.0	16.4	0
5000 h	76.8	15.3	7.5	0.4
10,000 h	75.4	14.8	5.3	4.5
15,000 h	74.7	14.2	5.0	6.1
50,000 h	74.4	11.9	3.8	9.9

[17] confirmed, using X-ray diffraction (XRD) and transmission electron microscopy (TEM), that Z-phase precipitates evolve by replacing Cr<sub>2</sub>N precipitates during long-term creep tests in an 11 wt% Cr martensitic heat-resistant steel with high nitrogen content (11CrMoVNbN). However, we failed to propose the detailed mechanism for the formation of Z-phase replacing Cr<sub>2</sub>N. The purpose of this study is to clarify the role of M<sub>2</sub>X in the formation of Z-phase and to propose the detailed mechanism for the formation of Z-phase in samples of 11CrMoVNbN steel aged for up to 50,000 h at 593 °C. Additionally, long-term precipitation behavior will be compared between the aged and crept samples, which were obtained in the previous study [17].

## 2. Experimental and Computational Procedure

The 11CrMoVNbN steel was provided by Doosan Heavy Industries & Construction. The chemical composition of the steel is given in Table 1. The solution treatment was carried out at 1100 °C for 1 h, followed by water quenching and subsequent tempering at 677 °C for 8 h. Finally, the tempered samples were aged at 593 °C for up to 50,000 h. Precipitates in the aged samples were identified using a Bruker D8 Advance XRD with Cu K $\alpha$  radiation. The precipitates for the XRD measurement were extracted from the as-tempered and aged

samples by an anode decomposition method using electrolyte solution (95% methanol + 5% HCl). The step size and counting time were 0.02° in 2-theta and 10 s per step, respectively. The morphology, crystal structure and composition of the precipitates in the aged samples were observed by an FEI Tecnai F20 TEM with energy dispersive X-ray spectroscopy (EDS). Additionally, Super-X EDS compositional mapping and line profile analyses were conducted using an FEI Talos F200X TEM to obtain in-depth compositional information on the precipitates in the aged samples. For the TEM observation, extracted carbon replicas were prepared by the evaporation of carbon onto polished and etched sample surfaces. The phase equilibria were calculated using the thermo-kinetic software, MatCalc (version 5.61) [18,19] together with the mc\_fe thermodynamic database (version 2.57).

## 3. Results and Discussion

Fig. 1 shows the XRD patterns of extracted residues from the as-tempered sample M<sub>23</sub>C<sub>6</sub>, which is mainly chrome carbide, MX-type Nb(C,N) and M<sub>2</sub>X-type Cr<sub>2</sub>N are identified as major precipitates. The intensities of the Nb(C,N) and Cr<sub>2</sub>N peaks tend to decrease with aging time. On the other hand, Z-phase starts to distinctly appear after 10,000 h of aging, and the peak intensity gradually increases with aging time. The quantitative analysis of the XRD patterns was performed using Rietveld refinement, and the result is summarized in Table 2. It is clearly confirmed that the amount of Z-phase increases as that of Cr<sub>2</sub>N and Nb(C,N) decreases with aging time, implying that Z-phase replaces both Nb(C,N) and Cr<sub>2</sub>N during long-term aging. However, it should be noted that the amount of Cr<sub>2</sub>N is relatively much smaller compared to that of Nb(C,N). The overall precipitation trend for the aged samples is similar to that of the crept samples in our previous study [17], although Z-phase was not clearly observed until 14,679 h in the crept samples and Cr<sub>2</sub>N almost completely disappeared during long-term creep tests.

The distribution of the metallic composition of the precipitates investigated by TEM-EDS is presented in a ternary diagram to understand the composition evolution during aging (Fig. 2). The composition points in the diagrams are classified into M<sub>23</sub>C<sub>6</sub>, Nb(C,N), Cr<sub>2</sub>N and Z-phase. It is noted that the V content in Cr<sub>2</sub>N gradually increases with aging time, whereas the composition of Nb(C,N) remains relatively intact. After long-term aging (> 5000 h), the composition of Cr<sub>2</sub>N tends to shift toward Z-phase with an increase in V content, and then Z-phase starts to form with higher V contents. This implies that the route to the formation of Z-phase via Cr<sub>2</sub>N is predominant over that via Nb(C,N), which is consistent with the result of the Rietveld refinement (Table 2). The results after 10,000 h of aging are similar to those after 5000 h of aging, although they are not presented here. It is also noteworthy that scattering of the Nb composition in Z-phase is quite large, especially after 50,000 h of aging, which implies that some of Z-phase originates from Nb(C,N) (open star symbols in the figure). It is also noted that the Nb content is lower in the aged samples compared to the composition of Z-phase in the crept samples investigated in our previous study [17]. Table 3 summarizes the size range of each precipitate in the as-tempered and aged samples observed by TEM. Overall, the precipitate size gradually increases with aging time. The size of M<sub>23</sub>C<sub>6</sub> is similar to that of Nb(C,N), although Nb(C,N) is slightly larger than M<sub>23</sub>C<sub>6</sub>. The size of Cr<sub>2</sub>N is quite fine, below 110 nm, compared with M<sub>23</sub>C<sub>6</sub> and Nb

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