

Formation of Vanadium Nitride Phase in 9Cr-ODS Steel

Y.Z. Shen, J. Jang jjang@kaeri.re.kr

Nuclear Materials Research Center, Korea Atomic Energy Research Institute
1045 Daedeok-daero, Yuseong, Daejeon 305-353, KOREA (south)

1. Introduction

Oxide dispersion strengthened (ODS) steel is one of the candidate materials for the fuel cladding or in-reactor components of Generation IV nuclear reactors due to its improved high temperature mechanical properties and good radiation resistance relative [1-3]. Typical microstructure of 9Cr-ODS steel is composed of two matrix phases, oxide particles, dislocations and intra/inter-granular precipitates [4]. In this study, the microstructural evolution during an isothermal heating at 600°C of 9Cr-ODS steel with different cooling rates after a normalization have been investigated.

2. Experimental

The material used in this study was a ODS steel prepared by a mechanical alloying, a hot isostatic pressing, and a hot rolling. The chemical composition of the steel was 9Cr-0.5Y₂O₃-0.5V (in wt. %). The hot-rolled steel samples were normalized at 1150°C for 1 h and cooled with cooling rates of 800, 5, and 0.5°C/sec, corresponding to water quenching (WQ), air cooling (AC) and furnace cooling (FC) respectively, and then tempered at 750°C for 1 h followed by an air cooling. Three kinds of heat-treated samples were isothermally heated at 600°C for 1 h. Carbon replicas were prepared by the evaporation of carbon onto a polished and etched sample surface followed by a dissolution of the metallic matrix in a solution of 10%HCl-methanol at 2 V at 20°C. The carbon replicas were examined using a transmission electron microscope (TEM) equipped with an energy dispersive spectroscope (EDS).

3. Results and discussion

Figure 1 shows the TEM images of the carbon replica of WQ specimen after isothermal heating at 600°C and the microdiffraction pattern recorded from precipitate particle 1. The microdiffraction pattern well matched with the standard diffraction pattern from vanadium nitride (VN, JCPDS file 35-0768) in the beam direction of [011]. Combining the EDS analysis results, precipitate 1 was determined to be a vanadium-rich nitride phase. Many vanadium-rich precipitates with different morphologies, precipitates 2-7 in Figure 1, were also observed in the same replica sample. The chemical compositions of the observed vanadium-rich precipitates were averaged to be about 57V-12Cr-14O-14N (at.%). Vanadium-rich nitride precipitates were also observed in the AC and FC specimens after

isothermal heating at 600°C, as shown in Figure 2, and the amount of vanadium-rich nitride precipitates decreased with reducing the cooling rates after the normalization treatment.

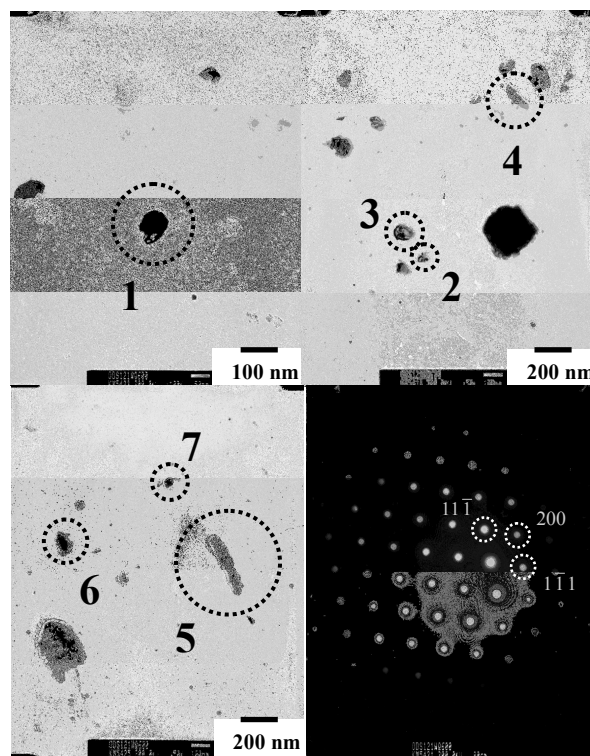


Figure 1. TEM images of the WQ specimen after isothermal heating at 600°C showing vanadium-rich nitride precipitates and microdiffraction pattern from the precipitate particle 1 in the beam direction of [011]

After the normalization at 1150°C for 1 h followed by a water quenching and then a tempering at 750°C, the concentration of the interstitially dissolved nitrogen in the ferrite phase of the steel specimen must be higher than that in other specimens.

The solubility of nitrogen in γ Fe at 600 and 750°C is about 8.5 and 9.5 at.%, respectively, and that of nitrogen in α Fe at 592°C is about 0.40 at.% [5]. Assuming that there is no change in the nitrogen concentration during the quenching, the nitrogen content in ferrite after a tempering at 750°C could be estimated to be about 3 to 9.5 at% from the phase diagram [5]. The average nitrogen concentration of the ferrite phase in the tempered WQ specimen in this study was measured to be about 5.07 at%. Therefore, super saturated nitrogen in ferrite would precipitate to form nitride during the isothermal heating at 600°C.

TEM observation indicated that present isothermal heating temperature (600°C) and holding time (1 h) are enough for the precipitation of vanadium nitride in the WQ, AC and FC specimens during the isothermal heating.

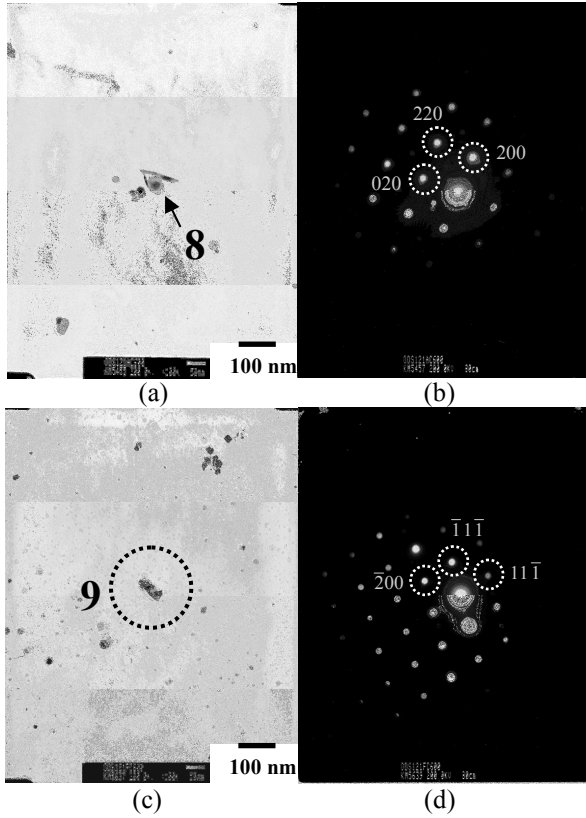
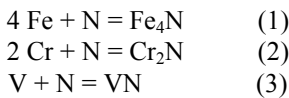


Figure 2. TEM images of the (a) AC and (c) FC specimens after isothermal heating at 600°C showing vanadium-rich nitride precipitates and microdiffraction patterns (b) and (d) from the particle 8 and 9 in the beam directions of [001] and [011] respectively.

According to the chemical composition of the 9Cr-ODS steel, the possible reactions to precipitate nitride from ferrite of the steel specimens are as follows:



By using the thermochemical data of Fe, N, Cr, V, Fe₄N, Cr₂N and VN [6], and an expression for Gibbs energy change with temperature during a reaction [7], i.e.,

$$\Delta G_T^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p^0 dT - T \Delta S_{298}^0 - T \int_{298}^T \frac{\Delta C_p^0}{T} dT$$

standard free energy changes for reactions (1) to (3) were calculated and plotted as a function of temperature in Figure 3, implying that all the three reactions are spontaneous and VN would have priority over Fe₄N or Cr₂N to precipitate from the ferrite with super saturated

nitrogen during the isothermal heating of the steel specimens.

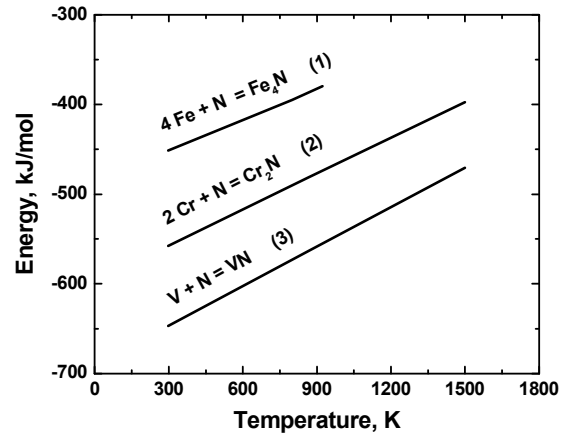


Figure 3. Free energy changes associated with reactions (1) to (3) as a function of temperature

4. Conclusions

The microstructural evolution of 9Cr-ODS steel with different cooling rates after the normalization has been investigated by isothermal heating the steel samples at 600°C and TEM observation along with EDS analysis. Vanadium-rich nitride precipitate phase with various morphologies was observed in the steel samples by water-quenching, air-cooling and furnace-cooling after normalization treatment, and the amount of vanadium-rich precipitates increased with the cooling rates after the normalization treatment. The precipitation of vanadium-rich nitrides was due to super saturated nitrogen in ferrite matrix of the steel probably originated from the mechanical alloying process.

REFERENCES

- [1] R. Schäublin, A. Ramar, N. Baluc, V. de Castro, M. A. Monge, T. Leguey, N. Schmid, C. Bonjour, J. Nucl. Mater., Vol. 351, p. 247, 2006.
- [2] S. Ukai, M. Fujiwara, J. Nucl. Mater., Vol. 307-311, p. 749, 2002.
- [3] S. S. Hwang, B. H. Lee, J. G. Kim, J. Jang, J. Nucl. Mater., 2007. (in press).
- [4] H. Sakasegawa, S. Ohtsuka, S. Ukai, H. Tanigawa, M. Fujiwara, H. Ogiwara, A. Kohyama, Fusion Eng. Des., Vol. 81, p. 1013, 2006.
- [5] C. Cayron, E. Rath, I. Chu, S. Launois, J. Nucl. Mater., Vol. 333, p. 83, 2004.
- [6] M. Binnewies, E. Milke, Thermochemical Data of Elements and Compounds, 2nd, Wiley-VCH Verlag GmbH, Weinheim, pp. 416-865, 2002.
- [7] O. Kubaschewski, C. B. Alcock, P. J. Spencer, Materials Thermochemistry, 6th, Pergamon Press, England, p. 21, 1993.