Evolution of a Needle Shaped Carbide in SA508 Gr3 Steel

Hyung-Ha JIN,1) Chansun SHIN,1) Do Hyun KIM,2) Kyu Hwan OH2) and Junhyun KWON1)

1) Nuclear Materials Research Division, Korea Atomic Energy Research Institute, Daejeon, 305-353, Korea. E-mail: hhajin2@kaeri.re.kr, hhajin2@snu.ac.kr
2) Department of Materials Science and Engineering, Seoul National University, Seoul, 151-742, Korea.

(Received on August 4, 2008; accepted on September 13, 2008)

Structural materials used for a nuclear reactor have various carbide precipitates in their matrix which contribute to a strengthening and toughening of these materials under service. Many investigations that focused on the role of a carbide for a fracture strength and toughness have been progressed extensively and they have established that large carbides on the grain/lath boundary are considered as major detrimental microstructural features.1–4) Nanometer sized carbides have attracted little attention in spite of their effect for an increase in the yield strength.2) However, an application of nanometer sized carbides in nuclear structural materials has emerged recently due to its significant capacity for a resistance to a material degradation as a consequence of an irradiation.5,6)

In SA 508 Gr3 steel used as a nuclear reactor pressure vessel (RPV) steel, it is well known that large carbides are formed on the grain/lath boundary whereas nanometer sized carbides with a needle shape are distributed densely in the ferrite matrix. Needle shaped carbides with a several nanometers width have been identified with β-Mo2C carbides.2) But according to studies on a carbide precipitation in a Fe–Mo–C ternary alloy, the formation of other carbides such as Ksi-carbide (Fe11Mo6C5 or Fe2MoC) and cementite (Fe3C) is also feasible at a low Mo content.7,8) Since an intensive characterization of nanometer sized carbides in SA508 Gr3 steel has been insufficient, its evolution in SA508 Gr3 steel still remains far from being fully answered.

The objective of the present work is to reveal the evolution of a needle shaped carbide in SA508 Gr3 steel used for a nuclear pressure vessel material in the hope of developing the design process for advanced structural steels.

The chemical composition of the SA508 steel for the present work was: Fe–0.19C–1.35Mn–0.82Ni–0.51Mo–0.17Cr–0.009Al–0.008Si (wt%). This SA508 steel ingot was fabricated through a vacuum induction melting and then it was forged. A subsequent heat treatment of this steel includes a homogenization at 910°C for 9 h, a tempering at 650°C for 9 h, an ausenitizing at 880°C for 8 h, a quenching and a tempering at 650°C during 1 h. The last tempering treatment is performed for a carbide formation and a stress relief.

To analyze the characteristics of the needle shaped carbide precipitates, we used a transmission electron microscope (TEM) with an Energy dispersive spectrum equipment (EDS). The foils used for the TEM examination were prepared by an electro chemical thinning and an ion milling. Thermodynamic calculation was carried out for an estimation of the phase fractions and the driving forces of the equilibrium carbides at a tempering temperature by the CALPHAD method.9) Thermo-Calc program was used for the calculation.10) The calculations allowed for the potential existence of cementite (Fe3C), β-Mo2C (HCP), Ksi-carbide, M6C and M23C6 in addition to ferrite.

Figure 1(a) shows the small needle shaped carbides observed in the experimental steel. A high resolution (HR) image taken by TEM was converted with a FFT image.
which helped us obtain the crystal structure information. Figure 1(b) presents an HR image obtained at a boxed region of a needle shaped carbide in Fig. 1(a). The FFT image in Fig. 1(c) is identical to a diffraction pattern with a [0001] zone axis of a $\beta$-Mo$_2$C carbide with a close-packed hexagonal crystal structure ($a=0.301$ and $c=0.473$ nm). Additionally, we observed another needle shaped carbide as shown in Fig. 1(d). The FFT image in Fig. 1(f) is very similar to a diffraction pattern with a [429] zone axis of a Ksi-carbide or that with a [512] zone axis of a cementite. The enrichment of molybdenum in the needle shaped carbides by the EDS analysis as shown in Fig. 1(g) indicates that a needle shaped carbide would be a Ksi-carbide rather than a cementite one.

**Figure 2** (a) shows the TEM micrographs of a complex precipitate which has a long needle like shape with about a 5 nm width. HR images were taken with a beam direction along the [011]$_a$. Figures 2(b) and 2(e) show the HR images in the boxed regions at the left and right side of the carbide, respectively. The FFT image in Fig. 2(c) is identical to a diffraction pattern with a [356] zone axis of a Ksi-carbide. But an HR image in Fig. 2(e) at the right side of the needle shaped precipitate shows a hexagonal lattice image and the corresponding FFT image in Fig. 2(f) is identical to a diffraction pattern with a [0001] zone axis of a $\beta$-Mo$_2$C carbide. Consequently the needle shaped precipitate in Fig. 2 is comprised of a $\beta$-Mo$_2$C and a Ksi-carbide. In addition, it is thought that the complicated feature observed in the mid region might be due to the existence of two phases, a Ksi-carbide and a $\beta$-Mo$_2$C carbide or another phase formed during a transformation from a $\beta$-Mo$_2$C to a Ksi-carbide or the reverse. From the TEM examination results, we found that a Ksi-carbide and a complex carbide composed of a Ksi carbide and a $\beta$-Mo$_2$C are formed in SA508 Gr3 steel as well as a $\beta$-Mo$_2$C.

We looked into a crystal orientation relation between the carbides and the ferrite. Figure 2(g) shows a typical Pich-Schrader orientation relationship (PS-OR) between a $\beta$-Mo$_2$C and a ferrite (⟨200⟩$_a$/⟨1120⟩$_{Mo_2C}$, ⟨011⟩$_a$/⟨0001⟩$_{Mo_2C}$). In PS-OR, the $\beta$-Mo$_2$C grows along the ⟨002⟩$_a$/⟨1120⟩$_{Mo_2C}$ because of a small lattice spacing misfit. In the case of a Ksi-carbide, Figs. 2(d) and 1(f) indicate that the (331) plane and the (512) plane of the Ksi-carbide are parallel to the (011) plane of the ferrite ($\alpha$) and the lattice distance of the (331) plane and the (512) plane of the Ksi-carbide are similar to that of the (011) plane of the ferrite. Therefore, it is found that the Ksi-carbide does not have a specific crystal orientation relation with a ferrite unlike a $\beta$-Mo$_2$C.

We performed a thermodynamic calculation with the Thermo-Calc program to understand the development of the needle shaped carbide in SA508 Gr3 steel under a heat treatment. **Figure 3(a)** shows the equilibrium amount of carbides with the temperature. According to Fig. 3(a), a Ksi-carbide, a $\beta$-Mo$_2$C and a cementite are unstable above about 800°C. So it is expected that a Ksi-carbide and a $\beta$-Mo$_2$C are not formed in the matrix during a homogenization or an austenization. TEM examination was performed for an observation of the microstructure of the steel before tempering. **Figure 3(b, c)** shows schematic diagrams for superimposed diffraction patterns of the ferrite (black spot) and the Ksi-carbide and the $\beta$-Mo$_2$C (gray spot).
A tempering. A significant population of needle shaped carbides is not observed in a martensitic or bainitic ferrite lath/grain as shown in Figs. 3(b) and 3(c). It is thought that the pre-existing carbides dissolved in a matrix during an austenization at about 900°C and the formation of carbides was suppressed under a subsequent quenching. Therefore it is highly probable that needle shaped carbides are mainly formed under last tempering at 650°C rather than under any other heat treatment.

Table 1 summarizes the equilibrium amounts and driving forces for a nucleation of the carbides calculated at a tempering temperature of 650°C. For 650°C, a Ksi-carbide is a stable carbide whereas a $\beta$-Mo$_2$C, a M$_6$C and a M$_{23}$C$_6$ carbide are unstable in this steel. It is found that the driving force for a nucleation of a $\beta$-Mo$_2$C carbide is calculated as $-12.5$ kJ/mol and for a Ksi-carbide it is about $-8.4$ kJ/mol. For the calculation of the driving force for a nucleation, only ferrite except for carbides is considered in the calculation. Generally, the activation barrier to a nucleation is in proportion to the cube of an interfacial energy and is in inverse proportion to the square of the driving force for a nucleation. The higher driving force for a precipitation of a $\beta$-Mo$_2$C carbide and a lower interfacial energy due to its coherency with ferrite make its barrier to a nucleation lower. Therefore a $\beta$-Mo$_2$C carbide could be nucleated on the ferrite matrix due to its lower activation barrier and coherency with ferrite in spite of its instability. During a tempering heat treatment, the needle shaped carbides gradually transformed the $\beta$-Mo$_2$C to a stable Ksi-carbide.

Acknowledgement
This work was carried out as a part of the 'National mid- and long-term atomic energy R&D program' of the Korean Ministry of Education, Science and Technology. The authors are grateful to the National Nanofab Center in Korea for use of the TEM.

REFERENCES

Table 1. Equilibrium amounts and driving force for a nucleation of carbide.