Influence of Boron on Precipitation Behavior and Mechanical Properties in modified 9Cr steel for SFR fuel cladding after aging

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1. Introduction

As a future nuclear energy system, sodium-cooled fast reactors (SFRs) are being developed with a view to greater economy, safety, reliability, and sustainability. SFRs use liquid sodium as a coolant and cause nuclear fission via fast neutrons. These reactors are currently being developed as next-generation models to follow the existing light-water reactors (LWRs). LWRs have been the dominant reactor type for electricity generation since nuclear power was introduced. However, the expected steady increase in demand for nuclear energy in the coming decades will require a faster reactor, considering the limited resources of natural uranium and buildup of LWR spent fuels. The breeding capability of fast reactors could increase the utilization of uranium by approximately 50 times compared with the once-through LWR fuel cycle. The burning or transmutation of harmful radioactive elements in fast reactors, and the compact treatment of fission products extracted from the spent fuels, could significantly reduce the volume of waste and degree of hazard. Because the nuclear fuel for SFRs has a higher operating temperature than that for LWRs, the nuclear fuel cladding tubes must have outstanding mechanical properties, such as high creep strength at operating temperatures.

Ferritic/martensitic steels are considered to be an attractive candidate material for fuel cladding in SFRs due to their low thermal expansion coefficients, high thermal conductivities, and excellent irradiation resistances to void swelling compared with austenitic stainless steels; however, they are known to have an abrupt loss of creep and tensile strength at temperatures above 600 ºC. Therefore, their high temperature mechanical properties should be improved significantly in order to apply these ferritic/martensitic steels as materials in SFR cladding tubes. The mechanical properties of ferritic/martensitic (FM) steels are primarily determined by their microstructural stability. This stability depends on the prior-austenite grain size, sub-grain size, lath width, dislocation density, and precipitates. The precipitate features include their size, type, amount, morphology, stability, and distribution [1]. Many studies have focused on the formation of fine and stable precipitates because a coarsening of precipitates causes a degradation of the mechanical properties [2]. Precipitates are when they exhibit thermal stability and slow growth even with the passage of time; such qualities can improve the high temperature mechanical properties and creep properties [3].

Among the FM steels already developed and commercialized, Gr.92 steel with its outstanding creep characteristics (e.g. the creep rupture strength at 650 ºC for 100,000 hours is 60 MPa) is the benchmark alloy. As a step toward developing high performance cladding tubes, the thermal properties, mechanical properties, and patents of conventional claddings were analyzed. After that, we made 36 model alloys of ingot through adjusting the B and N content in 9Cr-2W and two model alloys of ingot with the best creep characteristics were designed into cladding tube.

The alloys of cladding tube with optimized boron and nitrogen content exhibited better mechanical strength at 650 ºC than the reference alloy (Gr.92 steel). This study conducted transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), and nanoindentation analyses in order to investigate the microstructural changes that resulted from the aging time using long-term thermal treatments through adjusting the B and N content in the 9Cr-2W steels. Then, these alloys were compared in hardness and tensile strength according to the aging time. So we tried to find an improvement in creep properties of the new alloy cladding tubes in accordance with the addition of boron and nitrogen.

2. Experimental Procedure

9Cr steel for SFR fuel cladding was selected for this study. The chemical compositions of the steels are given in Table 1. The alloy 1 was arranged as high-boron content, and the alloy 2 was fabricated with high nitrogen content compared with Gr.92 steel. 2 alloys were austenitized at 1038℃ for 6 minutes followed by air cooling, and then tempered at 750℃ for 20 minutes. The material was sealed with quartz tubes in an atmosphere of argon gas, and it underwent long-term thermal treatment for a maximum of 20,000 hours at 650 ºC, which is a similar temperature to the core environment in sodium-cooled fast reactors.

The mechanical properties were evaluated using a Vickers microhardness test (HM-122) and a tensile test (INSTRON-3367). The Vickers microhardness test was performed with a load of 500 g. The tensile samples were prepared according to ASTM E8 in the longitudinal direction. The tensile tests were conducted at a strain rate of 0.005 mm/mm·min at 650 °C. The nanoindentation was undertaken using a nanoindenter XP system (MTS Nano Instruments) using a Berkovich indenter. The load–depth (L–h) curves were monitored in a displacement-controlled mode at a constant displacement rate of 2 nm/s. The nanoindenter test was conducted with a load of 1 mN. The indentation test measured the hardness of the grain boundary and the grain interior based on analyses of the load displacement curves and the variation of these properties according to the penetration depth using the continuous stiffness measurement (CSM) technique. The microstructures of the specimens that underwent thermal treatment were observed using an optical microscope after being etched with a mixture solution of distilled water (95 vol.%), nitric acid (3 vol.%), and hydrofluoric acid (2 vol.%). In order to observe the types and shapes of the precipitates, TEM was used with the carbon replica method, and the EDS attached to the TEM was used to measure the chemical composition within the precipitates. The specimens whose microstructures were observed using an optical microscope underwent carbon coating and these carbon replica specimens were placed under room temperature conditions in a mixture of hydrochloric acid and methanol with a volume ratio of 1:9 and a voltage of 1.8 V. The changes in the quantity and sizes of the precipitates from different aging times were comparatively analyzed using an image analyzer through observing each precipitate sampled onto the carbon replica film. In addition to the TEM analyses of the specimens. The Nano-SIMS method was also used to observe the boron behavior. The specimens were etched with a mixture solution of distilled water 95 vol. %, nitric acid 3 vol. %, and hydrofluoric acid 2 vol. %, and the CAMECA NANO-SIMS 50 equipment analyzed the boron. The primary ions used a CS+ gun under an ion-impact energy condition of 16 keV and a current of 0.4 pA, and it detected the11B16O- and 52Cr16O-ions and received images of the B and Cr. The CAMECA IMS 7f magnetic sector SIMS equipment used to observe the carbon behavior. The primary ions used a CS+ gun under an ion-impact energy condition of 10 keV and a current of 1nA, and received images of the C.

Table 1. Chemical compositions of steels. (wt%)

	C	Cr	Mo	B	N	Ta
Alloy 1	0.07	8.89	0.44	.013	.020	.040
Alloy 2	0.06	9.09	0.45	.004	.077	.040

3. Experimental Results and Discussion

The hardness of new cladding tube containing adjusting the B and N contents in the 9Cr-2W measured at 650 °C under the as-received and different aging conditions are depicted in Figure 1. For Alloy 2, an increase in the aging time resulted in the tendency that the hardness decreased. Containing higher B content than Alloy 2, Alloy 1 did not exhibit significant change in strength regardless of the aging time. In Alloy 1 after aging for 500 hours, hardness remained almost constant. We believe that this result is because boron (B) reduces the coarsening of M23C6 carbides. M23C6 is the majority of precipitate of 9-12% Cr steel and it is also known to be a primary cause of declining creep properties because long-term aging coarsens the precipitates. Suppressing coarsening of the precipitate is prevents the effective fixation of the mobile dislocation that is generated during creeps. Boron reduces the rate of Ostwald ripening of M23C6 carbides during creep. Abe et al. [4] have shown that martensitic 9Cr steels the migration of lath or block boundaries causing the coarsening of the lath or block is closely correlated with the oneset of tertiary creep and that the coarsening of lath or block by the migration of boundaries with absorbing excess dislocations is the major process in tertiary creep. The stabilization of fine M23C6 carbides by an enrichment of boron suggest that a large pinning force for boundary migration is maintained up to long times and the onset of tertiary creep is retarded to long times. This effectively decreases the minimum creep rate and increases the time to rupture.

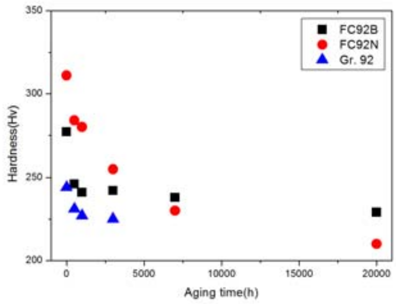


Fig. 2. Hardness of Alloy 1 and Alloy 2 with aging time

An enrichment of boron in M23C6 Carbides has already been reported for 9-12Cr steels [2]. Such B distribution is shown to move to grain-boundary Cr precipitates when the aging time reaches 7000 hours and contribute to suppressing the growth of M23C6 [2]. In order to examine the effect of B on hardness in the matrix by diffusing B to the C position in the M23C6, Nanoindentation test was carried out. The Nanoindentation test can compare the hardness of grain interior and grain boundary (Figure 2, 3). For the as-received state, the little difference in Nanohardness has been found between grain interior and grain boundary in Alloy 1 and Alloy 2. However, at the point where the aging time reaches 7,000 hours, the hardness of grain interior in Alloy 2 dropped compare to grain boundary in Alloy 2 after aging treatment. Containing higher B content than Alloy 2, Alloy 1 did not much drop solid solution strengthening during precipitate growth according to the aging time, remaining solid solution strengthening element in the matrix.

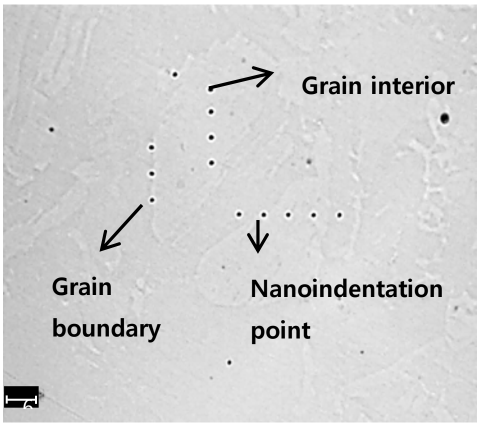


Fig. 2. Metallograph of the Alloy 1

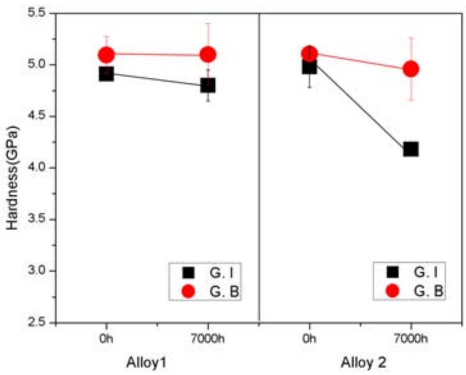
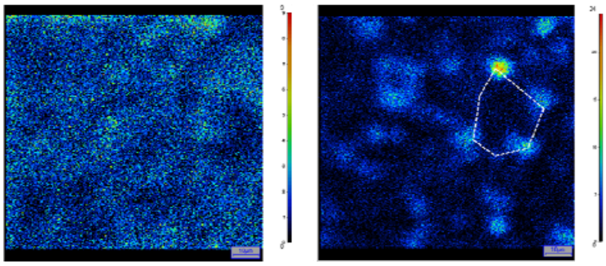


Fig. 3. Variation of nanoindentation hardness of grain boundary and grain interior with aging time

We believe that this result is because boron prevents the depletion of the carbon in the matrix by diffusing B to the C position in the M23C6, thereby stabilizing microstructures. The distribution of C was analyzed with SIMS to find out the solid-solution strengthening effect with the variation of B content (Figure 4). The Alloy 1 can be seen that the carbon is evenly distributed in the matrix. However, in the case of Alloy 2 was seen that the carbon concentrated at around the grain boundary. The addition of boron of 9Cr-2W steel is shown to keep the strength for long time while maintaining a solid solution strengthening element in the matrix. The addition of very small amount boron of 9Cr-2W steel has improved mechanical properties to suppress coarsening of precipitates and not much drop solid-solution strengthening effect according to aging treatment.



(a) (b)

Fig. 4. The distribution of C mapping with SIMS after 7000h of aging: (a) Alloy 1 (b) Alloy 2

4. Summary

1) The strength and hardness of Alloy 1 containing higher B contents keep almost stable with increasing aging time, whereas in the case of alloy 2, an increase in aging time showed a tendency that the strength and hardness is decreased.
2) Results of the hardness using the Nanoindentation of Alloy 1 and Alloy 2 of the as-received state are no difference between grain interior and grain boundary. However, at the point where the aging time reaches 7,000 hours, the difference of hardness values between grain boundary and grain interior of the Alloy 2 are larger than those of Alloy 1. This is because boron (B) prevents the depletion of the carbon in the matrix. Therefore, Alloy 1 is shown to keep the strength after aging treatment while maintaining a solid solution strengthening element in the matrix.

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