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Effect of the Boron and Nitrogen on precipitation behavior in modified 9Cr steel for SFR fuel cladding after aging

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1. Introduction

A Sodium-cooled Fast Reactor (SFR) is a reactor operated by high-energy neutrons that enables it to recycle the spent fuel from a conventional light water reactor. The fuel cladding tube is the most important safety barrier in fission nuclear reactors. It suffers thermal creep and void swelling by fission gas at high temperature for service time. Ferritic-martensitic steels are being considered as an attractive candidate material for a fuel cladding of a SFR due to their low expansion coefficients, high thermal conductivities and excellent irradiation resistances against void swelling [1,2]. Because of its superior dimensional stability against fast neutron irradiation, Ferritic-martensitic steel of 9Cr and 12Cr steels are preferable to utilize in the fuel cladding of an SFR in KAERI. The soluble boron reduces the coarsening rate of $M_{23}C_6$ carbides along boundaries near prior austenite grain boundaries during creep, enhancing the boundary and sub-boundary hardening for up to long times. The enhancement of boundary and sub-boundary hardening retards the onset of acceleration creep, which decreases the minimum creep rate and improves the creep life. It has been reported that the excess addition of boron and nitrogen promotes the formation of boron nitrides during normalizing heat treatment, which significantly reduces soluble B and N concentrations and offsets the benefit due to boron and nitrogen. In addition, they effectively decreases the creep rates in the transient region by precipitation strengthening due to fine MX and it also retards the onset of acceleration creep by microstructure stabilization due to boron [3]. KAERI also developed the 9Cr steels for SFR fuel cladding by changing B and N contents, but the precipitation behaviors of these alloys with log-term heat treatment has not been studied yet. The objective of this study is to compare the effect of the boron and nitrogen contents on the microstructure of modified fuel cladding materials for SFR with aging. Alloys were fabricated with different boron and nitrogen contents and they aged up to 7000 hours. The microstructures observations were conducted using OM, TEM and the segregation behavior of B were observed by Secondary Ion Mass Spectroscopy(SIMS). Based on the mechanical properties obtained from the experimental studies, as well as from correlations with detailed information on precipitation behaviors, the boron and nitrogen effects on modified 9Cr steels with aging time are discussed.

2. Experimental Procedure

12Cr 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 760℃ for 30 minutes. After the tempering process, the alloy 1 and 2 were treated at 650℃ for 500, 1000, 3000, and 7000 hours.

The observations of the microstructure were conducted using an optical microscope (OM). The observations of the precipitates were conducted using transmission electron microscope (TEM). To investigate overall distribution of carbides and to analyze individual carbide particles in detail, carbon extraction replica technique had been employed. Carbon extraction replicas were examined using JEM-2000FX2 transmission electron microscope.

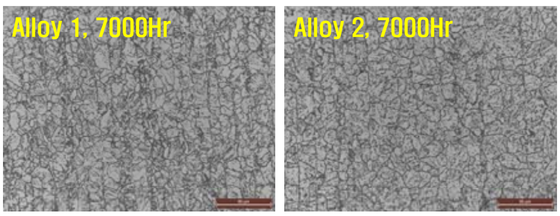
The size and distributions of precipitates were analyzed and compared using the Leica image analyzer software.

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

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

3. Experimental Results and Discussion

Fig. 1 shows the optical micrographs of the aged model alloys after 7000 hours. Two alloys were revealed as a typical tempered martensite



(a) (b)

Fig. 1 Optical micrographs of aged (a) alloy 1 and (b) alloy 2 microstructure, and the size of prior austenite grains were also similar. When compare the size of prior austenite grains of alloys with different aging time, there are no big differences. Hence, both the boron and nitrogen has no significant effects on prior austenite grain size with aging.

Fig. 2 shows the precipitation behaviors of the alloys before and after aging. Both alloy 1 and alloy 2 show similar tendencies in non-aged condition. However, the size of precipitates in alloy 2 was significantly increased after aging, compared with alloy 1. To compare the precipitation behaviors quantitatively, the images of each alloys were analyzed by the Leica image analyze software. The images of precipitates were obtained by TEM, and at least 50 images were analyzed for each condition.

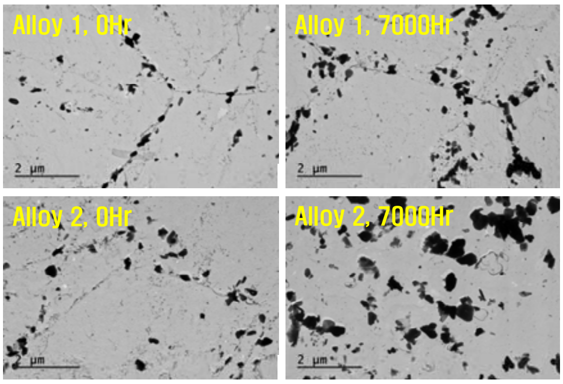


Fig. 2 Precipitation behaviors of the alloys before & after aging

Fig. 3 shows the mean size of $M_{23}C_6$ carbides in alloy 1 and alloy 2 after aging. From the EDS analysis, the smallest size of $M_{23}C_6$ was measured to be about 0.1μm. Therefore, to compare the tendency of $M_{23}C_6$ more specifically, the mean size of alloy 1 and alloy 2 were compared at the size over 0.1μm. In the case of alloy 1, the mean size of $M_{23}C_6$ was increased about 0.2μm after 7000 hours aging. In contrast to this, alloy 2, show significant increase of $M_{23}C_6$ after 7000hours aging.

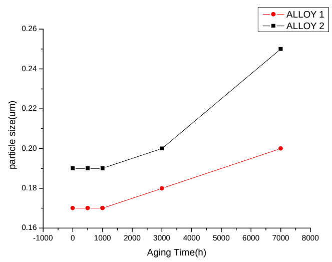


Fig. 3 Mean size of $M_{23}C_6$ of alloy 1 and 2 with different aging conditions

It has been reported that an addition of B in steel suppress the growth of $M_{23}C_6$ carbides by stabilization effect. B improves stability of $M_{23}C_6$ carbides by enriching into them, resulting in the stabilization of microstructure, especially in the vicinity of prior austenite grain boundaries, through the suppression of coarsening of them [4]. Accordingly, $M_{23}C_6$ carbides in the alloy 1 are expected to be more stabilized than those in the alloy 2.

Contrary to the Boron effect in an alloy 1, the nitrogen (alloy 2) mainly affects the small precipitates such as MX and M_2X. To compare the aging effects of those precipitates, the size distributions were obtained by image analyzer. Fig. 4 shows the size distribution of MX and M_2X in alloy 1 and alloy 2. It was confirmed by EDS analysis that almost small size (less than 0.1 μm) of spherical precipitates were MX that consisting of V, Nb, C and N. The needle type precipitates were confirmed as Cr_2N.

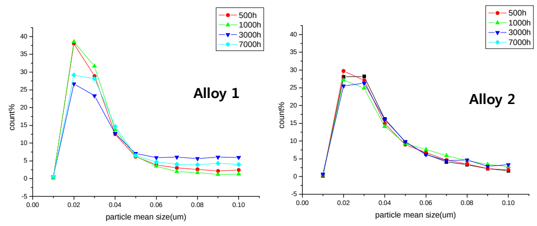


Fig. 4 Precipitation behaviors of MX and M_2X in the alloys before & after aging

In the case of alloy 1, the size distribution curve of MX and M_2X becomes broader than alloy 2 with increasing aging time. In contrast to this, alloy 2 show very similar tendency of precipitation growth in spite of 7000 hours of aging time. The addition of nitrogen may stabilize the nitride precipitates such as MX and M_2X, and further discussion will be required to investigate this phenomena. The differences between the Boron and Nitrogen effect in the viewpoint of precipitation behavior in 12Cr fuel cladding steels will be discussed with SIMS results in detail.

4. Summary

In this study, comparison of the microstructure and mechanical properties on SFR fuel cladding steel with different B and N contents after aging were carried out. The addition of B stabilizes the $M_{23}C_6$, hence the coarsening of $M_{23}C_6$ was not observed in alloy 1 after 7000hours aging. The size distribution of an alloy 2 was not largely changed with aging time, and this phenomena would be caused by an addition of nitrogen, by stabilize the nitride precipitates such as MX and M_2X.

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REFERENCES

[1] T. Fujita : Materials engineering in turbins and compressors, R.D. Conrey et al.(Ed), The Inst. Of Mate., London(1995), pp. 493
[2] V.K. Sikka : Pro. Inter. Conf. Production, Fabricaion, "Properies and Application of Ferritic Steels for High-Temperature Applicaions",A.K. Khare(Ed.), ASM(1983), pp. 65.
[3] Taneike M, Abe F, Sawada K. Creep-strengthening of steel at high temperatures using nano-sized carbonitride dispersions. Nature 2003;424;294-6