RESEARCH ON CANDIDATE MATERIALS FOR FUEL CLADDING IN SUPERCRITICAL WATER COOLED REACTOR

Y.F. Yang[1], R. Ma[1], Y. Yang[1], Q.Z. Yan*[1], L.F. Zhang[2] and C.C. Ge[1]

[1] Institute of Nuclear Materials, University of Science and Technology Beijing, Beijing 100083, China
[2] School of Nuclear Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, China

Abstract

Modified AL-6XN austenitic steel and new types of 9%Cr and 12%Cr reduced activation ferritic-martensitic (RAFM) steels were developed as candidate materials for fuel cladding in supercritical water cooled reactor (SCWR) with focus on mechanical properties and corrosion behaviors in supercritical water (SCW) at 650 °C and 25 MPa up to 1000 h. The results indicated that modified AL-6XN exhibited superior mechanical properties over AL-6XN and good corrosion resistance with a very thin oxidation layer and no nodular corrosion morphologies was observed in SCW. However, the aging treatment degraded mechanical properties of modified AL-6XN greatly. The ultimate tensile strength of 9%Cr and 12%Cr RAFM steels reached 443 MPa and 365 MPa at 600 °C, respectively. The ductile brittle transition temperature of 9%Cr and 12%Cr RAFM steels were -25 °C and -90 °C, respectively. 9%Cr and 12%Cr RAFM steels exhibited enhanced mechanical properties, but presented poor corrosion resistance in SCW due to the absence of corrosion-resistant elements. In order to obtain better corrosion resistance and mechanical properties, the content of Ni and Mo should be increased up to 1% in modified 12%Cr ferritic-martensitic steel in further studies.

Keyword: Supercritical water cooled reactor, Reduced activation ferritic-martensitic steel, Austenite, Mechanical properties, Corrosion

1. Introduction

The Supercritical Water-cooled Reactor (SCWR) is considered as a candidate reactor in Generation IV nuclear energy systems due to its high thermal efficiency and simple reactor design without steam generators and steam separators. Compared with current Boiling Water Reactor (BWR) and light water reactor (LWR) designs, the design for the SCWR requires both a high system pressure (≥25 MPa) and a high operating temperature (500–650 °C) [1-2]. One of the key issues is the selection of an appropriate material to be used as the fuel cladding for an SCWR. Austenitic stainless steels, ferritic-martensitic (F/M) steels and nickel alloys have been considered as fuel cladding materials for the SCWR [3]. At the University of Science and Technology Beijing (USTB), three types of steels, including modified AL-6XN austenitic steel and new types of 9%Cr and 12%Cr reduced activation ferritic-martensitic (RAFM) steels (denominated as CNS-I and CNS-II, respectively), have been

*Corresponding author. Professor, PhD; Tel.: +86 13521602959.
E-mail address: qingzhiyan111@163.com (Q.Z. Yan)

developed with a focus on mechanical properties and corrosion behaviors to evaluate their feasibility for application in an SCWR,

2. Modified AL-6XN austenitic steel

2.1 Fabrication and alloy design

Austenitic steels have advantages in elevated temperature performance and corrosion resistance. AL-6XN alloy, a commercial superaustenitic stainless steel, exhibits far greater resistance to chloride pitting, crevice corrosion and stress corrosion cracking than the performance exhibited by the standard 300 series stainless steels, and is less costly than the traditional nickel-base corrosion resistant alloys. Modified AL-6XN (Mod AL-6XN) was patterned after AL-6XN [4] by introducing microalloy elements such as zirconium (Zr) and titanium (Ti) to increase the density of MX precipitates which are stable at high temperature and beneficial to intergranular corrosion resistance and void swelling resistance. The chemical composition of Mod AL-6XN is shown in Table 1.

Table 1 Chemical composition of Mod AL-6XN (wt. %)

C	N	Mn	Zr	Ti	Si	Ni	Cr	Mo	Cu	Co	Fe
0.039	0.17	0.26	0.06	0.05	0.60	24.31	20.53	6.72	0.57	0.25	Bal.

In order to avoid precipitates such as the sigma phase, appearing between 400 and 1080 °C and which would deteriorate the mechanical properties and corrosion resistant of Mod AL-6XN, hot working was performed in the temperature range of 1100 to 1250 °C. A full anneal was also introduced between 1100 and 1250 °C plus quenching heat treatment. The morphology of Mod AL-6XN after solution treatment is shown in Fig. 1, the average grain size is about 30 μm.

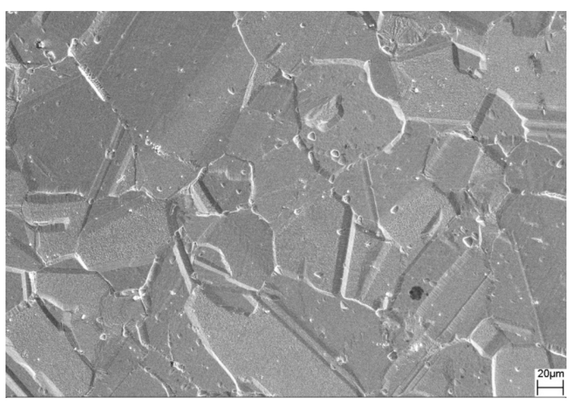

Fig. 1 Microstructure of Mod AL-6XN after solution treatment at 1100 °C

2.2 Mechanical properties

As shown in Fig. 2, the curves of the ultimate and yield strength vs. temperature for Mod AL-6XN and commercial AL-6XN steel match very well. The ultimate tensile strength is still above 550 MPa at 600

°C. Mod AL-6XN exhibits superior plasticity to the commercial steel. The total elongation of Mod AL-6XN is always above 53 % in the temperature range from room temperature (RT) to 600 °C.

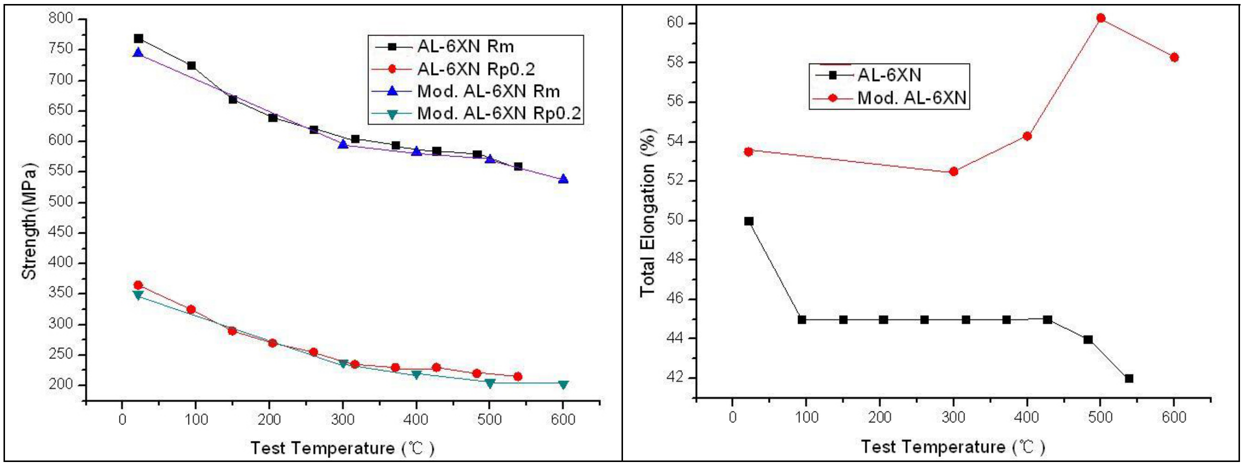

Fig. 2 Comparison of tensile properties between Mod AL-6XN and commercial AL-6XN steel

As illustrated in Fig. 3, Mod AL-6XN, annealed at 1150 °C for 60 min followed by water cooling (W.C.), exhibits excellent toughness at RT and sub-zero temperatures compared to the commercial material. The absorbed energy at RT can be beyond 300 J for Mod AL-6XN while it is 190 J for the commercial one. Even at -100 °C, the absorbed energy can be up to 230 J. However, the aging treatment decreased the impact toughness significantly. A 200 J decrease in absorbed energy can be observed in the temperature range from RT to -100 °C for samples aged for 50 hour.

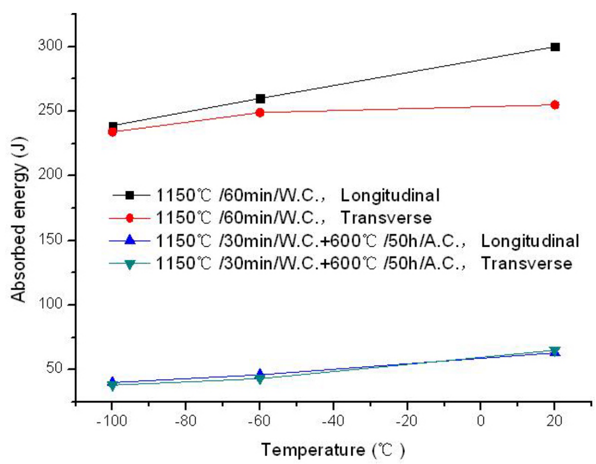

Fig. 3 Absorbed energy as a function of temperature under various conditions

2.3 Corrosion behaviour

The corrosion behaviour of Mod AL-6XN was evaluated by weight gain measurements and surface and cross-sectional analyses. The materials were cut into 40mm×20mm×1.5mm sample plates and mechanically finished to a 1um diamond finish. Then the samples were cleaned with acetone and ultra-pure water. Exposure tests were performed in a 1.5 liter autoclave with operating temperature of

650°C, pressure of 25Mpa for 1000h. For the inlet water, the dissolved oxygen concentration was controlled under 5 ppb by bubbling pure nitrogen. The resistivity of the inlet ultra-pure water was about 18.2 MΩ·cm, 2 MΩ·cm for the outlet water. After exposure to supercritical water (SCW) at 650 °C and 25 MPa up to 1000 h, Mod AL-6XN exhibits good corrosion resistance. As shown in Fig. 4, after 1000 h exposure the weight gain of Mod AL-6XN (solution treatment) and Mod AL-6XN (aging treatment at 600 °C for 50 h) reach 33.66 mg·dm^{-2} and 29.39 mg·dm^{-2}, respectively. However the weight gains do not reach a plateau after 1000 h exposure. The surfaces of Mod AL-6XN are covered with polyhedron-shaped oxide crystals, as illustrated in Fig. 5. Isolated crystals are scattered across a smooth oxide film and no nodular corrosion morphologies are observed in SCW. The corrosion layer on Mod AL-6XN is very thin consisting of two layers: a loose Fe-rich outer layer about 3 μm, and a relatively compact Cr-rich inner layer about 2 μm thick. A layer of chromium rich oxide can be protective to some extent due to its relatively compact dimensions, which can prevent the outward diffusion of cations and inward diffusion of oxygen [5].

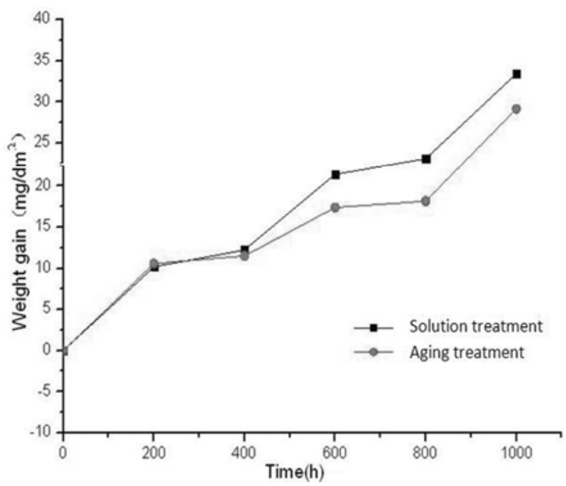

Fig.4 The weight gain of Mod AL-6XN exposed to SCW at 650 °C and 25 MPa

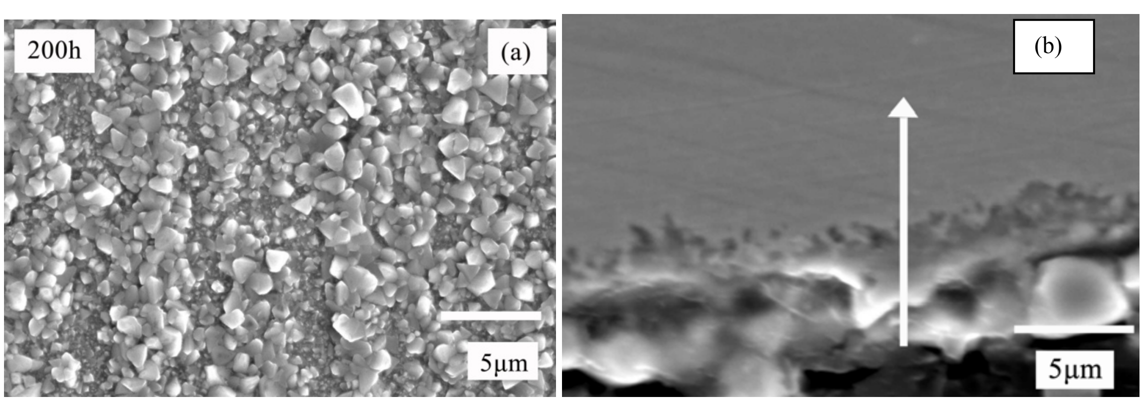

Fig.5. SEM images of the surface morphology (a) and cross-section (b) of Mod AL-6XN exposed to SCW at 650 °C and 25 MPa for 200 h and 1000 h, respectively.

3. 9%Cr and 12%Cr reduced activation ferritic-martensitic steel

3.1 Alloy design and fabrication

Due to the high thermal conductivity, low thermal expansion coefficient and inherently good dimensional stability under intense irradiation conditions in comparison to austenitic steel, ferritic-martensitic (F/M) steels have been considered as one of candidate materials for SCWR fuel cladding and in-core components, and the primary emphasis has been put upon high-chromium (9-12 wt% Cr) steels [6-7]. Typical alloy elements such as Mo, Nb and Ni that activate to produce radioactivity with long half-lives are substituted by W, V, Ti and Ta in order to obtain reduced activation. The addition of 2-3wt% W is made for further solid-solution strengthening, while the addition of the carbide and nitride formers V, Ta, Ti and N is made for precipitate strengthening. These MX precipitates, which are stable at elevated temperature, can retard growth of austenite grains to obtain good impact toughness. As shown in Table 2, 11-12wt% Cr are contained in CNS-II steel for improved elevated temperature strength and corrosion and oxidation resistance under SCWR operating condition.

Table 2 Chemical composition of CNS-I and CNS-II (wt. %)

	C	Cr	W	Mn	Si	V	Ta	N	Ti	B	Fe	S P
CNS-I	0.096	9.04	2.41	0.45	0.043	0.21	<0.05	0.077	0.026	0.0069	Bal.	≤0.005
CNS-II	0.14	11.06	2.30	0.89	0.30	0.010	0.08	0.036			Bal.	≤0.005

Hot-working between 850-1150 °C can introduce a high density of dislocations that act as nucleation sites for a fine distribution of MX precipitates. In general, 9-12% Cr steels often contain a few δ-ferrite and α-ferrite phases which lower the impact toughness and also cause anisotropy in it. Therefore, both CNS-I and CNS-II steels are designed by balancing austenite and ferrite stabilizers to obtain 100% austenite during austenitization and subsequently a full martensite structure during a normalizing or quenching treatment. In order to obtain small prior austenite grain size to improve mechanical properties, for CNS-I, the normalization is performed at 950 °C for 30 min followed by water quenching and tempering is performed at 780 °C for 90 min followed by air cooling. For CNS-II, the normalization is performed at 1000 °C. Measurements show that a full martensitic microstructure is obtained both in CNS-I and CNS-II, as shown in Fig. 6 and Fig. 7. The average grain size of CNS-I and CNS-II are about 4 μm and 25 μm, respectively.

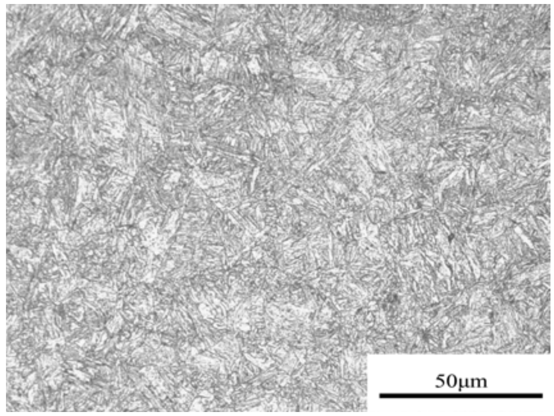

Fig. 6 Microstructure of CNS-I steel with 950 °C/30 min/W.C. plus 780°C/90 min/A.C. heat treatment

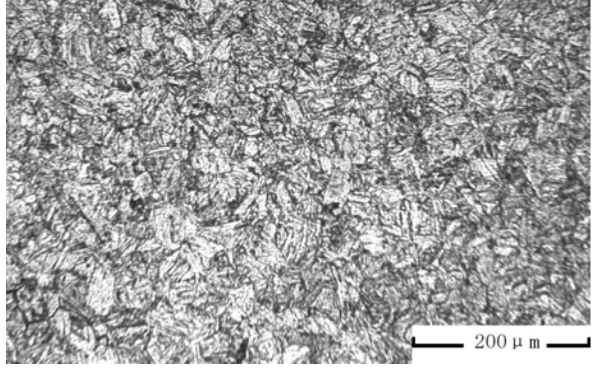

Fig. 7 Microstructure of CNS-II steel with 1000 °C/30 min/W.C. plus 780 °C/90 min/A.C. heat treatment

3.2 Mechanical properties

Tensile and impact properties were tested and the results are listed in Table 3. Investigation of CNS-I shows that the ultimate strength for CNS-I is 680 MPa at RT and 365 MPa at 600 °C, respectively. As for CNS-II the ultimate strength is 840 MPa at RT and 443 MPa at 600 °C, which are the highest among four kinds of steels but the total elongation is a little lower. CNS-I steel has identical high temperature instantaneous tensile properties and impact toughness compared with Eurofer97 [8] , while the ductile brittle transition temperature (DBTT) of CNS-I and CNS-II steels were -90°C and -25°C. Grain refining can improve toughness and strength simultaneously, the grain size of CNS-I is only about 4 μm. The higher DBTT of T91 [9] and CNS-II is attribute to the larger grain size, which is dependant on the austenitisation temperature and stability of precipitates that hinder grain growth at elevated temperature.

Table 3 Mechanical properties of CNS-I, Eurofer97, CNS-II and T91

	Temperature(°C)	Rm (MPa)	Rp0.2 (MPa)	A(%)	Z(%)	DBTT(°C)
CNS-I	RT	680	510	24.5	73.5	-90
	600	365	345	30.5	82.5	
Eurofer97	RT	652	537	20.8	79.9	-90
	600	292	277	29.3	94.1	
CNS-II	RT	840	663	22.5	64.5	-25
	600	443	410	27.0	86.0	
T91	RT	741		21.0		-30
	600	358		29.0		

3.3 Corrosion behaviour

The corrosion behavior of 9-12%Cr RAFM steels were also evaluated by weight gain measurements and oxide analyses, the corrosion test condition was the same as that of Mod AL-6XN. 9-12%Cr RAFM steels have poor corrosion resistance properties in SCW due to the absence of corrosion-resistant elements, such as Ni and Mo, and especially a low content of Cr as compared with austenitic steel. The results as shown in Fig. 8 indicate that the weight gain of CNS-II steel reach 632.8 mg·dm^{-2} after exposed to supercritical water at 650 °C/25 MPa for 1000 h. As shown in Fig. 9, the polyhedron-shaped surface oxide crystals grew with the exposure time and pores and crevices appeared in the surface oxides. The thickness of oxide film is about 50 µm. The drastic increase in weight gain places limits on the application of these low-Cr RAFM steels.

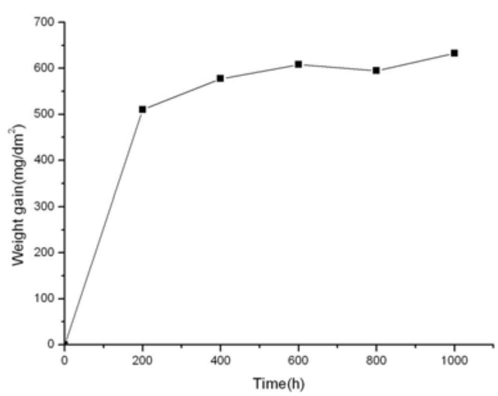

Fig. 8 The weight gain of CNS-II exposed to SCW at 650 °C and 25 MPa

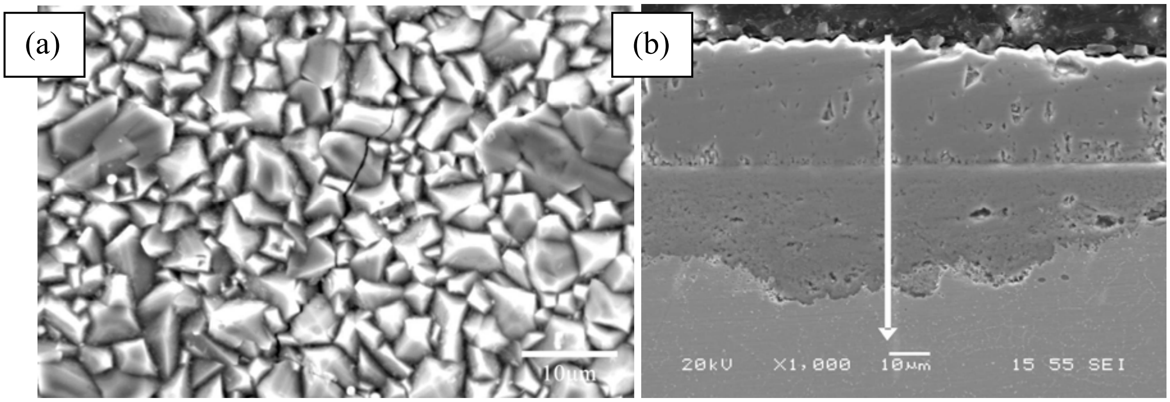

Fig. 9 SEM images of the surface morphology (a) and cross-section (b) of CNS-II exposed to SCW at 650 °C and 25 MPa for 1000 h

4. Conclusion

(1) Mod AL-6XN steel was patterned after AL-6XN steel by adding titanium and zirconium. By optimizing the thermo-mechanical treatment, Mod AL-6XN steel exhibits enhanced strength and superior plasticity and impact toughness compared to the commercial AL-6XN steel. In addition, Mod AL-6XN exhibits good corrosion resistance with a very thin oxidation layer and no nodular corrosion morphologies. However aging treatment at 600 °C degrades the impact toughness, plasticity and corrosion resistance of Mod AL-6XN steel significantly, which is unfavorable for the application of the steels as fuel cladding tube in SCWR.

(2) CNS-I steel has identical high temperature instantaneous tensile properties and impact toughness compared with the Eurofer 97, while CNS-II steel has good performance at elevated temperature, and there is still great space for the improvement of impact toughness. 9-12 wt% Cr RAFM steels have poor corrosion properties in SCW due to the absence of corrosion resistant elements such as Ni and Mo, and especially a low content of Cr as compared with austenitic steels. In order to obtain superior corrosion resistance and good performance on mechanical properties, the content of Ni and Mo should be increased.

5. Acknowledgements

This work is supported by National Basic Research Program of China (No. 2007CB209800)

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