

## **CORROSION TESTS OF CANDIDATE FUEL CLADDING AND REACTOR INTERNAL STRUCTURAL MATERIALS**

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### **Abstract**

Corrosion screening tests were conducted on candidate materials for nuclear fuel cladding and reactor internals of supercritical water reactor (SCWR) in static and flowing supercritical water (SCW) autoclave at the temperatures of 550, 600 and 650°C, pressure of about 25MPa, deaerated or saturated dissolved hydrogen (STP). Samples are nickel base alloy type Hastelloy C276, austenitic stainless steels type 304NG and AL-6XN, ferritic/martensitic (F/M) steel type P92, and oxide dispersion strengthened steel MA 956. This paper focuses on the formation and breakdown of corrosion oxide scales, and proposes the future trend for the development of SCWR fuel cladding materials.

### **1. Introduction**

Selection or development of materials for core structures, such as fuel cladding, grid, water rod and core shroud, remains one of the key issues facing the engineering practice of a demo supercritical water-cooled reactor (SCWR). The temperature of hot spot on the fuel cladding of both current pressure vessel and pressure tube conceptual designs exceeds 600°C at normal operations [1], and will be much higher during transients.

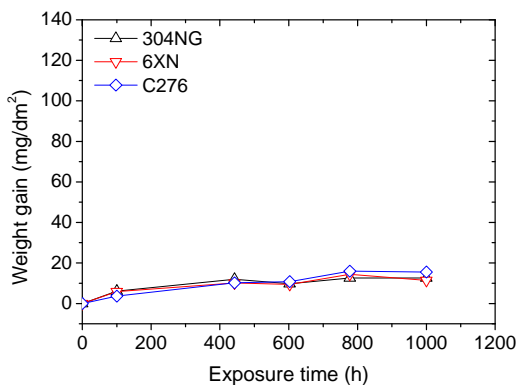
So far, the technical specifications of the cladding material for an SCWR have not been clearly given. Corrosion resistance is one of the most important issues for a number of reasons related to operation safety of the nuclear fuel. This paper focuses on the mechanism of general corrosion of some candidate materials for possible use in an SCWR as the nuclear fuel cladding or the internal structures.

### **2. Corrosion tests and results**

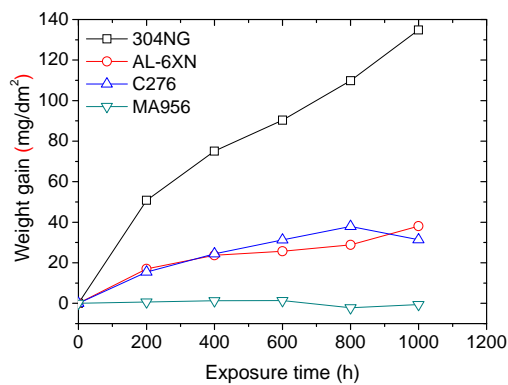
Austenitic stainless steel type 304NG and AL-6XN, ferritic/martensitic (F/M) steel P92, nickel based alloy C276 and oxide dispersion strengthened steel MA 956, were tested separately in SCW at temperatures of 550, 600 and 650°C, pressure at 25MPa for 1000 hours. The main chemical compositions of these materials are given in Table 1. The test results of these materials exposed in 550 and 600°C SCW have been reported in previous papers [2-3]. This paper mainly reports the results obtained on the samples after exposure in SCW at 650°C. Weight gains of the tested materials are shown in Figure 1. The morphologies of the surface oxide on each material are shown in Figure 2.

**Table 1 Chemical compositions of test materials (wt%)**

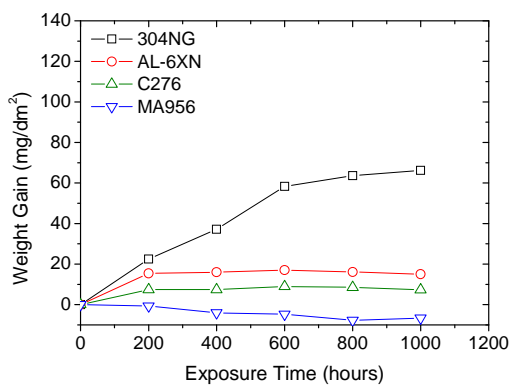
Material	C	Fe	Cr	Ni	Mo	Mn	Si	S	P	Co	W	V	Cu	Al	N	Nb	others
C276	0.001	5.35	15.88	Bal.	15.64	0.52	0.03	0.002	0.005	1.51	3.38	0.02	—	—	—		
P92	0.13	Bal.	9.0	≤0.40	0.30 ~0.60	0.30 ~0.60	≤0.50	≤0.010	≤0.020	—	1.50 ~2.00	0.20	≤0.25	≤0.040	0.050	0.07	
AL-6XN	0.020	Bal.	20.43	23.82	6.23	0.42	0.34	0.005	0.024	0.24			0.26		0.211		
304NG	0.018	Bal.	19.4	9.35	—		0.58	0.007	0.018	0.028			0.062		0.089		
MA956	<0.1	Bal.	20.0	—	—	≤0.30			≤0.02	≤0.3	Ti: 0.2/0.6		≤0.15	4.5			Y <sub>2</sub> O <sub>3</sub> : 0.34



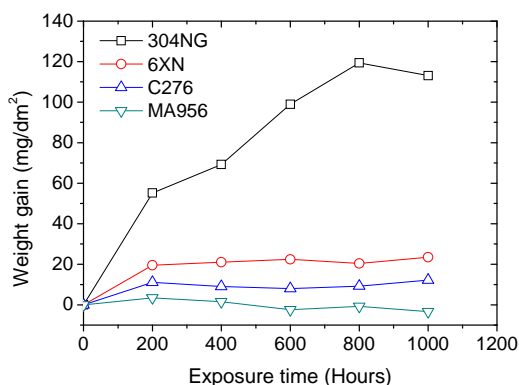
(a) 550°C, static



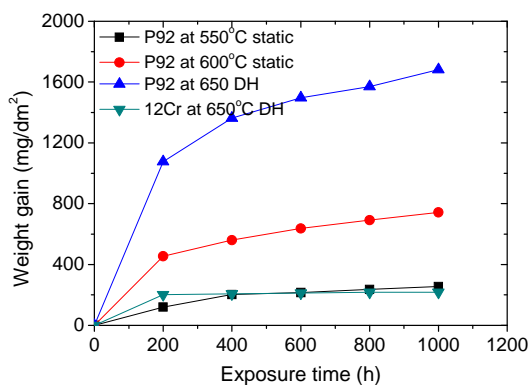
(b) 600°C, static



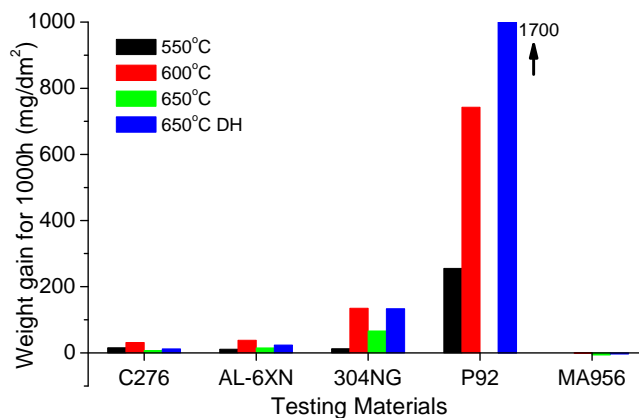
(c) 650°C, static



(d) 650°C, flowing

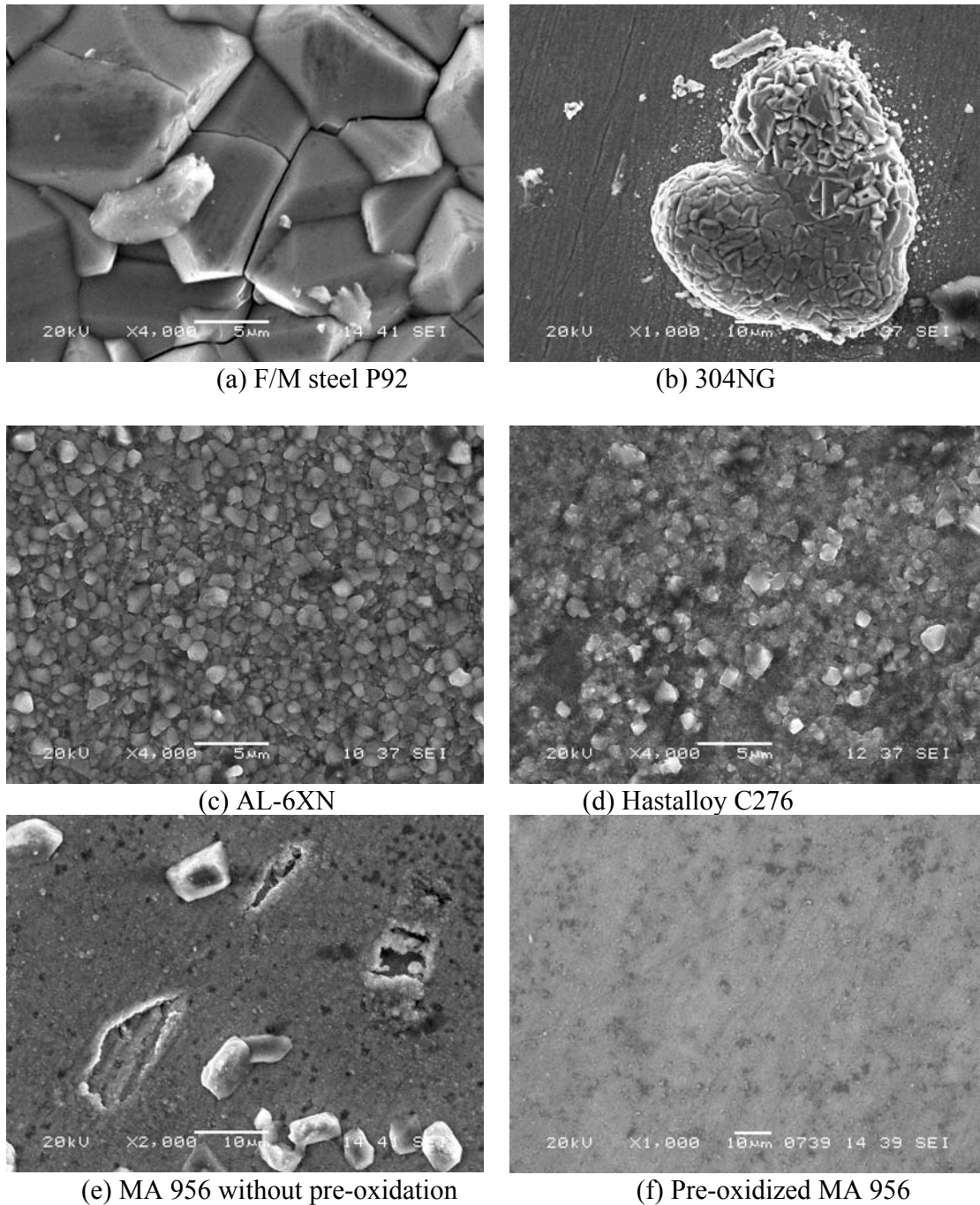


(e) Weight gain rate of F/M steels



(f) Compare of weight gain

**Figure 1 Weight gain of candidate materials in supercritical water**



**Figure 2 Morphologies of the surface oxide on specimens exposed in SCW at 650°C for 1000h**

### 3. Discussions

In high temperature water environment, oxidation and oxide deposition are the major contributors to weight gain during the corrosion of metallic materials, while dissolution and vaporization of alloying elements reduce the weight of the specimens. The balanced between these mechanisms can be revealed by the weight gain after exposure.

Formation of a dense, tenacious, stable and protective oxide film is the most important factor for engineering materials applied in high temperature water environment. On materials such as stainless steels, nickel based alloys and high chromium steels, it usually occurs in a short period of time. An increase of corrosion rate is caused by the breakdown of the protective oxide film, which may be caused by a variety of factors, such as by the increase of internal stress due to the growth of the oxide, or by the loss of oxide film stabilizing elements.

It is known that chromium is a necessary alloying element for making materials for high temperature service. A layer of corundum structure  $(Cr, M)_2O_3$  type or spinel structure  $(Cr, M)_3O_4$  type chromium rich oxide provide the protective barrier against corrosion in high temperature water or vapor. A High concentration of chromium in these two types of oxide scale stabilizes the film, and significantly reduces the penetration of oxygen and escape of base metal elements. Al is also an element that can form very stable corundum type oxide scale  $Al_2O_3$  under these conditions.

However, in high temperature water environments, Cr and Al in the oxide film react with water and produce volatile products, e.g.  $CrO_2(OH)_2$ ,  $Al(OH)_3$  [4,5]. Vaporization of Cr and/or Al deplete the concentration of these elements in the surface oxide, and reduces the protectiveness of the film. Diffusion of these stabilizing elements from the base metal to the oxide film makes up for their losses. If diffusion can not supply sufficient amount of these oxide film stabilizing elements, the surface oxide film loses its protectiveness to the base metal, and grows at a faster rate. Vaporization of the volatile products leaves pores or cracks in the oxide layer, and these defects become the route for penetration of water molecules, oxygen, OH from the environment and loss of metallic atoms from base metal.

Mismatch of the thermal expansion rate of the surface oxide produces internal stress which may leave cracks in the oxide film, or peel off the film, and hence cause the breakdown of the protective film. Selective oxidation in matrix inclusions, precipitates or other minor phases (with low concentration of corrosion resistant elements, such as Cr) may produce a rapid localized growth of oxide underneath the protective film, and the expansion of this localized oxide can easily break the surface film and form a corroded crater.

### 3.1 Corrosion of austenitic stainless steels

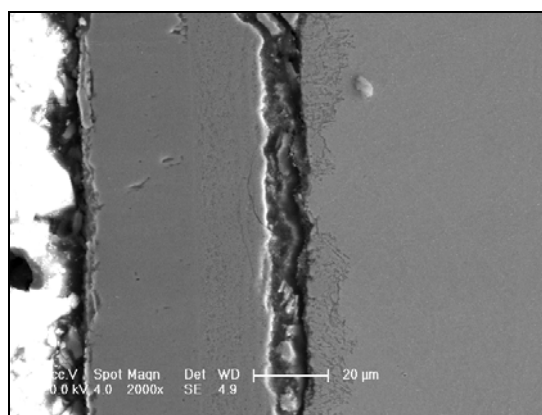
Austenitic stainless steel 304NG has been successfully applied in PWR internals, and it is considered to be a high priority candidate material for the SCWR also. Test results of general corrosion in SCW at 550°C showed acceptable performance. Their weight gain is comparable to nickel base alloys. But at temperatures above 600°C, the corrosion weight gain rate increases remarkably. A kind of nodular corrosion morphology was observed on the surface of 304NG exposed to every condition, see Figure 2b. The mechanism is explained clearly in reference [2, 3]. The diffusion rate of Cr atoms along grain boundaries is more than 2 orders faster than that through the grain interior. The oxide film above a grain boundary can receive enough Cr atoms by diffusion from base metal to make up the deficit due to vaporization, while the supply is less than the loss of Cr from oxide film above the grain interior. In this way, the oxide film above the grain interior is depleted of Cr, and loses protectiveness. As a result, an oxide island and a corrosion pit grow from the grain interior.

Austenitic stainless steel AL-6XN showed much lower weight gain than 304NG (Figure 1), and the oxide scale is denser and more compact, as shown in Figure 2c. The increased Ni concentration and

addition of Mo obviously play an important role. However we can not draw conclusions on which element plays more important role. Cr, Ni and Mo can not be observed in high concentrations in the oxide film, and this suggests the vaporization of these elements. AL-6XN has never been used in nuclear systems, and further investigation is required to clarify its feasibility for SCWR.

### 3.2 Porous oxide layer on F/M steel P92

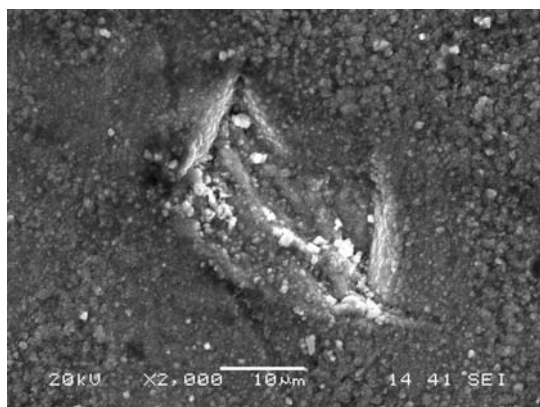
The weight gain of F/M steel P92 in SCW under every test condition showed a very high value which can not be compared with other tested materials. Exposure in SCW at 550°C, the surface oxide film is dense and tenacious with a double layered structure. Above 600°C, cracks are observed on the oxide films, and the layer of oxide just above the surface of base metal becomes porous, as shown in Figure 3. The general corrosion results show that P92 is neither suitable as a material for fuel or core internal.



**Figure 3 Porous layer in oxide scale of P92 after exposed in SCW at 650°C for 1000h.**

### 3.3 Pitting on nickel base alloys

Nickel base alloys C276, 625 and X750 were exposed in supercritical water at temperature of 550°C and pressure of 25MPa for 1000h, C276 was also exposed at 600 and 650°C, showing low weight gain under every testing conditions, as shown in Figure 1. Nickel alloys are strengthened by precipitation of  $\gamma'$ ,  $\gamma''$  phase and carbides such as MC,  $M_6C$  (rich in Ni, Nb, and Mo), and  $M_{23}C_6$  (rich in Cr), and maintain high creep strength at elevated temperatures. Formation of a Cr-rich protective oxide film is also very important for nickel base alloys to be applied in high temperature aqueous environments. Micro-cracks were observed on C276 exposed in SCW at 550°C [2] which maybe the major cause of it higher weight gain rate compared with AL-6XN. At temperatures above 600°C, a dense and tenacious oxide film formed on the sample surface. However, spalling of surface material can be observed, as shown in Figure 4.

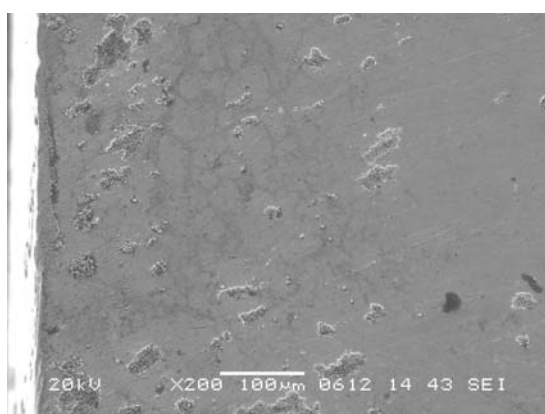


**Figure 4 Spalling of surface material on C276 after exposed in SCW at 650°C for 1000h.**

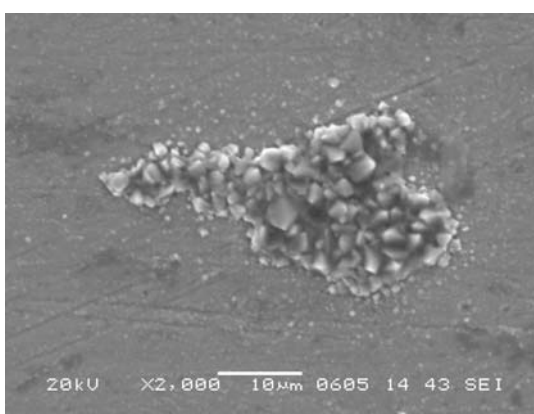
### 3.4 High Cr ODS steel MA956

MA 956 shows the lowest general corrosion rate of the materials tested. The nominal chemical composition of MA 965 is Fe-20Cr-4.5Al-0.5Ti-0.5Y<sub>2</sub>O<sub>3</sub>-0.02C. The presence of Al element in the metal forms and maintains a corundum Al<sub>2</sub>O<sub>3</sub> scale which is very compact and stable, protecting the matrix from oxidation. Therefore, MA 956 can serve in oxidizing environment at temperatures up to 1100°C. Pre-oxidation is generally required to form the protective surface scale before service. Samples with and without pre-oxidation were exposed in SCW at 650°C under flowing conditions. The surface morphologies shown in Figure 2e and f reveals that the pre-oxidized sample maintains protective film, while the sample without pre-oxidation develop craters on the surface, showing that MA 956 is susceptible to corrosion if the protective film breaks down.

MA 956 shows a weight loss in contrast to the other tested materials. Vaporization of the element Cr and Al is probably the major reason. Nodular oxide islands are also observed on samples exposed in flowing SCW at 550°C, as shown in Figure 5. The nodular oxide island is Fe<sub>3</sub>O<sub>4</sub> (magnetite), and its formation is attributed to the breakdown of the protective alumina in flowing SCW.



(a) Nodular corrosion morphology



(b) close view of oxide island

**Figure 5 Nodular corrosion on MA 956 after exposed in flowing SCW at 550°C for 800h.**

#### 4. Conclusion

The following conclusions can be drawn from these experiments:

- (1) F/M steel P92 is not suitable for use as either cladding or reactor internal material due to its high general corrosion rate, and the cracking of the oxide scale in SCW.
- (2) The results of 304NG reveal that it can probably still be used for reactor internals, but the application environment should be below 550°C.
- (3) The oxide scale on AL-6XN is stable in SCW up to 650°C. However, precipitation on grain boundaries may occur after long time of exposure at this temperature range, causing embrittlement of the material.
- (4) Spalling or surface oxide scale cracking can be observed on C276, and it is not likely usable in an SCWR.
- (5) MA 956 exhibited the lowest corrosion rate due to its high Cr and Al content which help the formation of a protective film. However, surface spalling and nodular corrosion are also found on the sample exposed in flowing SCW.

#### 5. Acknowledgement

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#### 6. References

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