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STRUCTURAL MATERIALS CANDIDATE FOR SUPERCRITICAL WATER-COOLED REACTOR

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The possibility of making a Supercritical Water-Cooled Reactor (SCWR) will be decided based on the selection of materials that will be able to withstand combined stresses (thermal, hydrostatic, and radiative) that arise from the operating conditions during the life of a reactor. Because supercritical water is a very aggressive corrosive environment, corrosion becomes a difficult problem for materials used in SCWR.

This paper summarizes the results of corrosion tests performed so far on promising structural materials for Generation IV water-cooled supercritical reactors. Austenitic stainless steels with Cr and nickel high are promising materials for reactor cladding, as they generally have satisfactory corrosion resistance in supercritical water at high temperatures.

Keywords: Supercritical Water-Cooled Reactor (SCWR), structural materials, oxidation, corrosion

1. Introduction

The greatest interest in achieving the Supercritical Water-Cooled Reactor concept (from now on mentioned as SCWR), results from the expectations of increasing the thermal efficiency (approximately 45% compared to 33% as in the case of LWR) by using water at supercritical temperature. This is due to the use of a wider range of operating temperatures, the high specific heat of the supercritical water which favors a higher heat transfer per unit volume thus allowing a lower flow rate compared to pressurized water. These factors considerably simplify the power plant by reducing the size of pumps, pipes and other associated equipment and increasing the economy of this concept. Indeed, the expected economy of SCWR is one of the points of interest [1].

Depending on the lines developed and the experience gained by the producers and users of water-cooled energy reactors, two feasible concepts of reactors with supercritical parameters have emerged: pressure vessel reactors (based on the evolution of BWR and PWR) and pressure tube reactors (developed initially by the former USSR from LGCWR reactors and recently by Canada, as a

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development of PHWR, ACR reactors) [2]. One of the key issues facing the engineering practice of a demo reactor is the selection of materials for core structure, such as fuel cladding, grid, water rod, and core shroud, which work under the condition of high pressure, high-temperature water, and high neutron flux. Owing to the thin cladding wall and corrosive environment of supercritical water, the most important test that must be done is to evaluate the general corrosion rate of candidate materials. Research to date has focused on the selection and qualification of candidate alloys for all key components of the SCWR. This includes general corrosion and stress corrosion cracking tests in autoclaves and loops as well as development work on test facilities, ionic irradiation tests of fuel cladding candidate alloy and development of novel alloys for fuel cladding.

Austenitic stainless steels [3], ferritic/martensitic steels [4], nickel-based alloys [5], oxide dispersion strengthened steels (ODS) [6], and modified zircaloys based on the PWR cladding compositions [7] have been studied and are considered structural or fuel coating materials for the supercritical water-cooled reactor (SCWR).

This paper focuses on the corrosion mechanism of SCWR candidate materials, based on data from the literature, in order to find or develop the most promising structural materials for SCWR.

2. Oxidation and corrosion of austenitic stainless steels in supercritical water

Stainless steels are widely used in industry due to their corrosion resistance. This strength is mainly due to the high Cr (> 11%) content of the alloy and the formation of surface protective layer [8]. According to the main elements of the phase structure, stainless steels are divided into three types (ferritic, martensitic and austenitic). Austenitic steels are the most resistant to corrosion at high temperatures. Compared to the other two types, they have a higher Cr content and added Ni. In order to maintain its resistance to oxidation and to preserve its mechanical properties, the temperature limit of these materials in the oxidizing environment is 1000^oC [9].

Several researchers have studied the oxidation of austenitic steels exposed in SCW, under different conditions [10, 11]. For steels with a high Cr content, a complex layer of oxide composed of hematite, magnetite, Cr2O3 and FeCr2O4 can form on the metal surface. The inner layer is usually non-porous, protective and has a large amount of chromium. The composition of austenitic steels has enough chromium to form a protective layer rich in chromium oxide during the oxidation process at high temperatures of supercritical water [12, 13]. Fig. 1 shows the layered structure on 310 ODS austenitic stainless steel; However, there are significant differences in the oxidation performance of different steels, which largely depend on the concentrations of chromium and nickel in the steel, although minor elements such as silicon, manganese, titanium, molybdenum and probably Carbon may also be important in this report. Cr can lead to the formation of protective surface oxides, while Ni can improve the stability of the protective oxide. Thus, a higher amount of Cr and Ni in the composition of stainless steel can provide better performance at high temperature of this alloy in SCW [14].

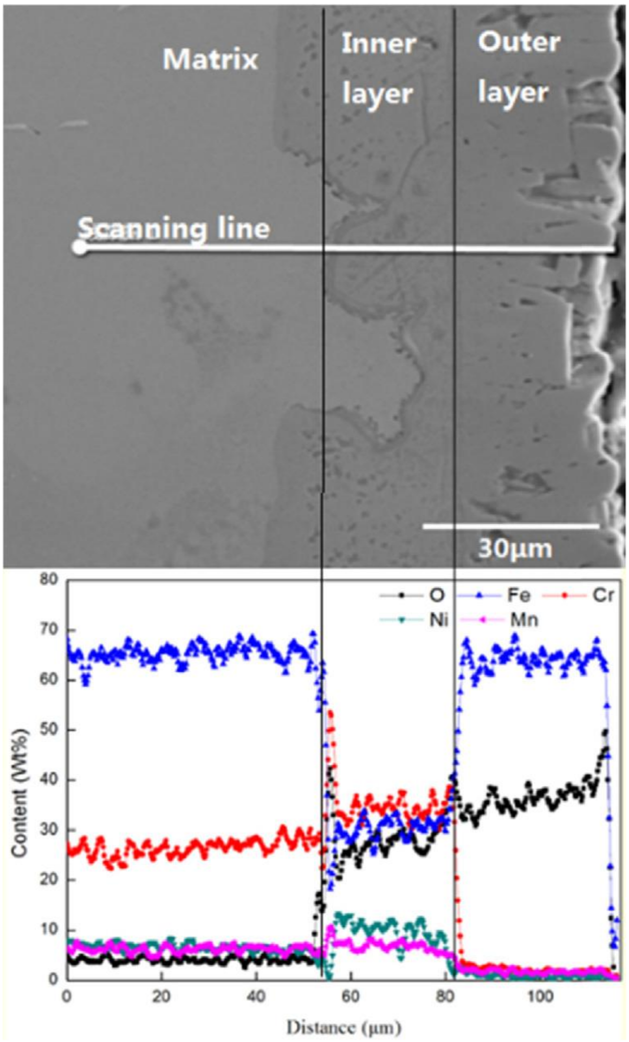

Fig. 1 Scanning electron microscope image showing the cross section of the 347H steel oxide film exposed to SCW for 1500 hours at 600°C. [15]

According to the research of Zhang et al. [14] and Was et al. [16] in Fe-Cr-Ni alloys, surface oxides increase predominantly through the external diffusion of metal atoms, especially Fe atoms, and through the internal diffusion of oxygen, which is significantly affected by short-circuit pathways, such as cracks, pores, gaps and grain boundaries. Because the structure of the oxide film formed on 310 steel (Fig. 2) is very compact, the excellent corrosion resistance of this material could be contributed by the formation of compact surface oxide films.

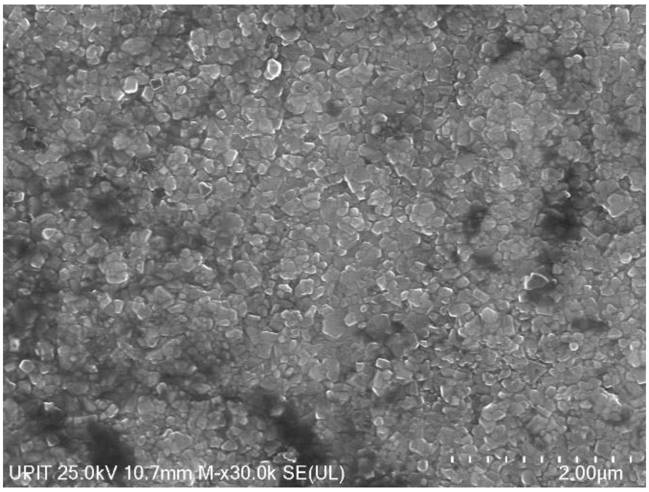

Fig. 2. Morphology of surface oxide on 310 stainless steel after exposure to SCW for 1560 hours [17]

3. Oxidation and corrosion of Ni-based alloys in supercritical water

Nickel-based alloys are characterized by high temperature resistance and hardness. Therefore, nickel-based components are widely used to withstand harsh environments, such as gas turbines, nuclear power plants and chemical processes. At high temperatures, it has good creep resistance, high surface stability and excellent oxidation and corrosion resistance.

To date, several studies have been conducted on nickel-based alloys in supercritical water (SCW) [18, 19, 20, 21]. Oxide films formed on the surface of nickel-based alloy exposed to pure SCW generally have a duplex structure of Ni and Fe in the outer layer and Cr in the inner layer, which effectively prevents the outer diffusion of the alloying elements and the inner diffusion of ion ions. The oxygen, thus reducing the corrosion rate of the substrate [22, 23].

Fujisawa et al. [24] found that some nickel-based alloys (including 625 alloy), have lower corrosion rates than austenitic 316 stainless steel when exposed to supercritical water. Zhang et al. [25] reported that a variety of nickel-based alloys, after being exposed to supercritical water at 550°C and 25 MPa for 1000 hours, had only a slight increase in weight.

For alloy 625, the weight gain was three times lower than that of 316 steel [26]. Fig. 3 shows the weight gain of alloy 625 below one subcritical temperature and two supercritical temperatures for different exposure times. The weight gain for alloy 625 at the subcritical temperature of 360°C is greater than the weight gain at the supercritical temperature; the effect of higher water density (under subcritical conditions) could be the reason for weight gain. The oxide layer proved to be very thin and the presence of holes on the surface of the Ni-based alloy was also observed.

The weight gain for alloy 718 would be expected to be higher than alloy 625 due to the increased Fe content found in alloy 718 compared to alloy 625 (19% for alloy 718 and 5% for alloy 625) [27, 28].

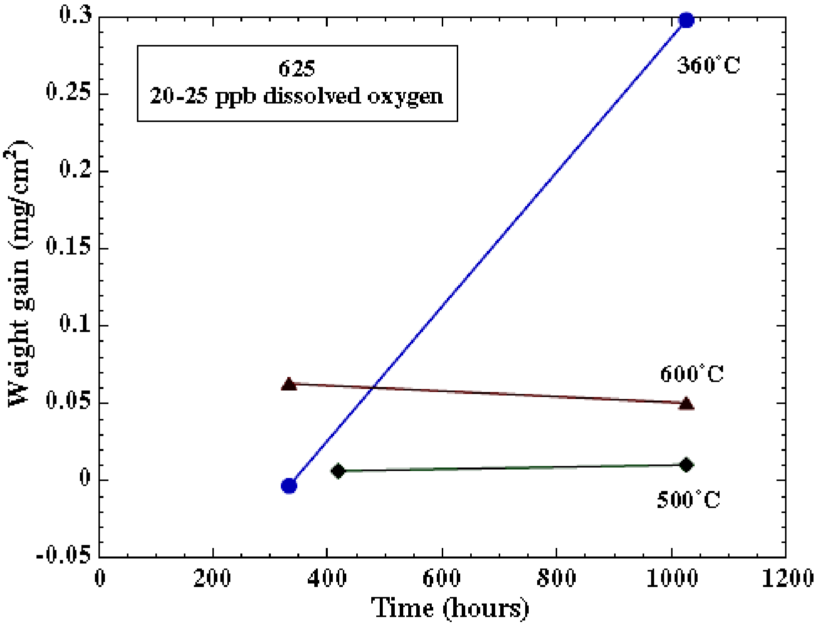

Fig. 3 Weight gain as a function of exposure time for IN 625 in low oxygen water at 360°C, 500°C, and 600°C [27]

Was et al. [29] noted that on the surface of the material, oxygen and chromium were enriched at the granule boundaries and there was a lack of nickel (Fig. 4). While in the layer below the oxide surface, chromium was depleted at the granule boundaries, where a small enrichment of nickel was found. Granule boundaries are the main route of chromium delivery to the surface, leading to the preferential formation of high Cr oxides above the granule boundaries and the limits of Cr-deficient granules at the metal surface.

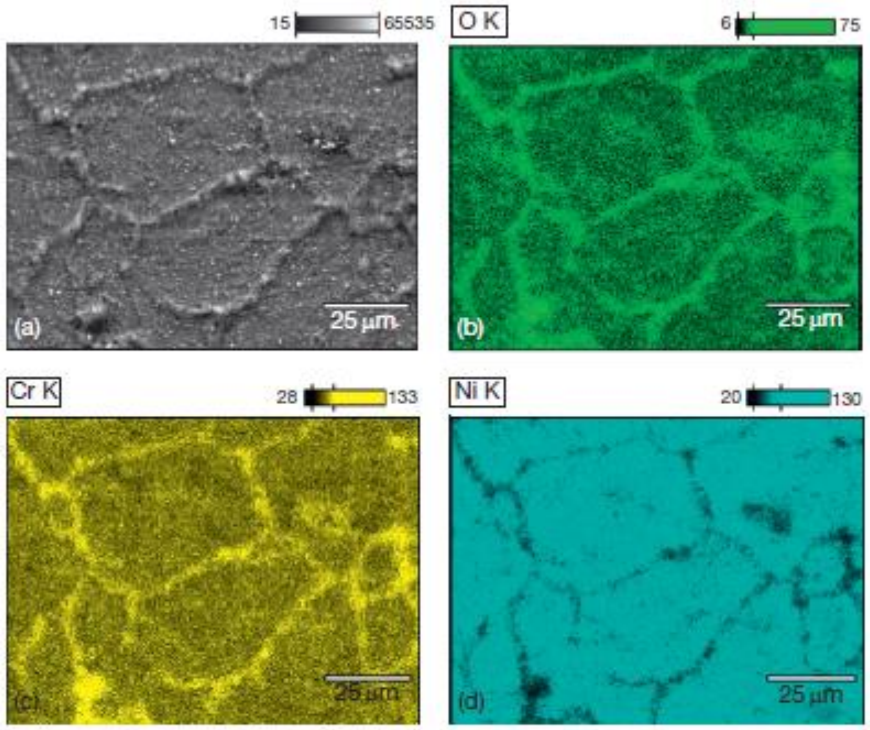

Fig. 4 Interganular corrosion observed in alloy 625 after exposure to supercritical water at 600°C for 1026 hours [30]

4. Oxidation and corrosion of ferritic-martensitic steels in supercritical water

Ferritic-martensitic steels with Cr content up to 18 have been tested in SCW at temperatures up to 650°C, the surface oxide film has a double-layered structure. The outer layer of the oxide film is structure Fe_3O_4, containing nearly no Cr. The inner oxide layer is Cr-rich spinel $FeCr_2O_4$-type protective oxide. The internal oxidation layer in matrix metal reveals that the oxide film cannot prevent the penetration of oxygen in supercritical environment. Ferritic / martensitic steels have a high weight gain rate and a thick oxide film on the surface.

For ferritic-martensitic steels, increasing the bulk chromium concentration reduces the weight gain due to oxidation. An example of this correlation is shown in Fig. 5 where the 9 at.% Cr alloy NF616 has a greater weight gain than the 12 at.% alloy HCM12A [31].

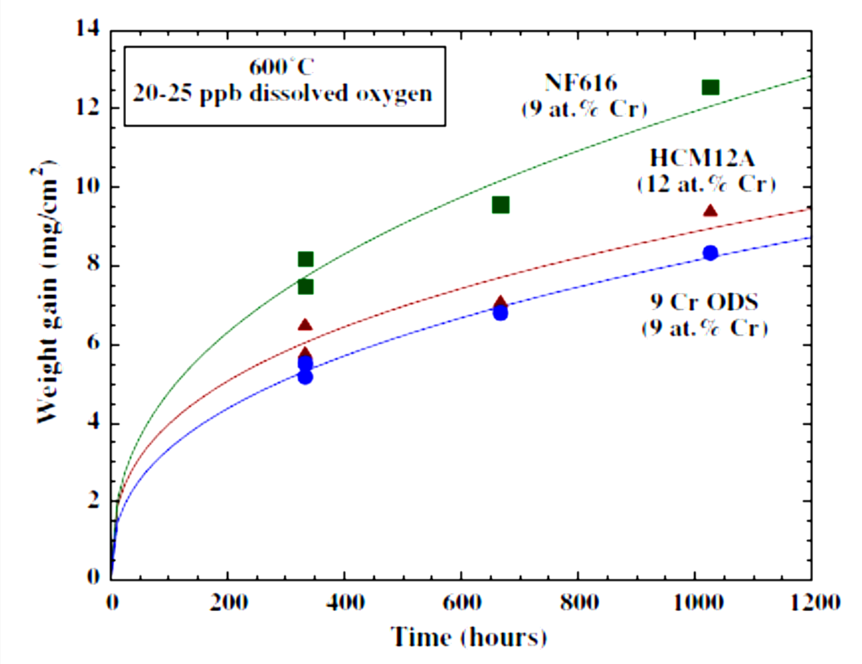

Fig. 5 Weight gain over time of materials exposed to a low concentration of oxygen in supercritical water at 600 °C [31].

Therefore, Cr content and temperature appear to be the key factor determining the weight gain of F / M steels, and the weight gain increases significantly with the exposure temperature.

5. Oxidation and corrosion of ODS steels and Zr based alloys in supercritical water

ODS steels are produced by mixing small amount of ultrafine Y2O3 oxide particles in heat-resistant steel mechanically or chemically. High creep strength at elevated temperature is achieved by the uniform dispersion of oxide particles within base metal. Avoiding contamination by air, milling balls and container are crucial for the performance of these alloys. Oxide dispersion-strengthened (ODS) steels may be an alternative to replace austenitic steels at high operating temperatures, but key challenges in manufacturing processes need to be solved.

Zr based alloys, which have a low neutron capture cross-section, are the preferred materials for the fabrication of reactor core components for the current generation of WCRs. However, these alloys exhibit unacceptably high corrosion rates and poor mechanical properties in SCW.

6. Conclusions

The service condition of cladding materials in SCWR is very aggressive. Tests on the corrosion behavior of candidate cladding materials in SCW and out-of-pile data base buildup is of great importance. The weight gain of materials in SCW after relatively long time exposure (1500 h) is used to evaluate the corrosion resistance of candidate cladding materials.

Various SCWR programs have shown that austenitic stainless steels and nickel-based alloys exhibit much better corrosion performance compared to other alloy classes. This led to the selection of several alloys, including 347H, 310S Alloy 800H, Alloy 625 and Alloy 214, as primary candidates for fuel coverage. Based on a survey of available corrosion data in SCW and superheated steam, a detailed corrosion assessment was conducted and predictive models for the corrosion rate as a function of time and temperature formulated. Austenitic stainless steels and Ni-based alloys are predicted to meet the corrosion performance requirement and have the potential to be used as the fuel cladding in the SCWR concept due to their high chromium content. Testing in an inreactor loop is required to address most of the remaining knowledge gaps.

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