Corrosion mechanism of a Ni-based alloy in supercritical water: Impact of surface plastic deformation

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A B S T R A C T

Ni–Fe–Cr alloys are expected to be a candidate material for the generation IV nuclear reactors that use supercritical water at temperatures up to 600 °C and pressures of 25 MPa. The corrosion resistance of Alloy 690 in these extreme conditions was studied considering the surface finish of the alloy. The oxide scale could suffer from dissolution or from internal oxidation. The presence of a work-hardened zone reveals the competition between the selective oxidation of chromium with respect to the oxidation of nickel and iron. Finally, corrosion mechanisms for Ni based alloys are proposed considering the effects of plastically deformed surfaces and the dissolution.

1. Introduction

Interest in supercritical water (SCW) is growing both for organic waste decomposition and for energy production [1,2]. The use of SCW for the supercritical water-cooled reactor (SCWR), one of the Generation IV nuclear reactor concepts, is of particular interest due to the relationship between steam temperature and boiler efficiency. The SCWR is an evolution of the light water reactors presently in service. The present design concept for the SCWR requires the materials to withstand a core coolant temperature of between 280 °C and 620 °C at a pressure of 25 MPa. In such conditions, the selection of corrosion resistant materials is one of the key issues for the development of the SCWR concept [3,4]. One of the critical issue remains with the selection of the fuel cladding material, where the material must withstand the greatest temperature and pressure conditions. Consequently, studies on the corrosion properties of metallic alloys at the extreme conditions at 600 °C and 25 MPa are of significant importance for the SCWR concept.

Several studies on the corrosion of Fe–Ni–Cr alloys have been carried out for the SCWR concept. These have focused on the fol-lowing aspects: the effect of the test water's chemical composition [6–8], the alloy's chemical composition [9–11], the effect of surface finish [12], the alloy's microstructure [5,9,10], and the effect of stress for studying the alloy's stress corrosion cracking resistance [13,14].

The characterization of the corrosion properties of nickel-based (Ni–Cr–Fe) and iron-based (Fe–Ni–Cr) alloys has largely been focused on in studies conducted for the SCWR reactor. Comparing the oxide scale that forms on nickel-based and on iron-based alloys after exposure to similar SCW conditions typically reveals a significant difference of thickness. For nickel-based alloys, the oxide layer is much thinner [8,15–17] than in the case of steels [5,13]. These observations agree with the significantly lower weight gains on nickel-based alloy samples compared to the gains for steel samples. The difference in the oxide thickness and weight gain when comparing these two alloy classes is believed to be due to the higher chromium content within studied nickel-based alloys. Indeed chromium rich oxides, such as α-chromia or mixed chromites are expected to form the protective part of the oxide on Ni–Cr–Fe alloys. These alloys thus appear more corrosion resistant.

More details on the oxide composition are necessary to propose mechanism describing the different oxide morphologies. Guzonas et al. [16] used Raman spectroscopy to describe the oxide layer composition. They performed SCW corrosion tests at 450 °C and 23 MPa during 483 h on many Fe–Ni–Cr alloys. The oxide layer typically
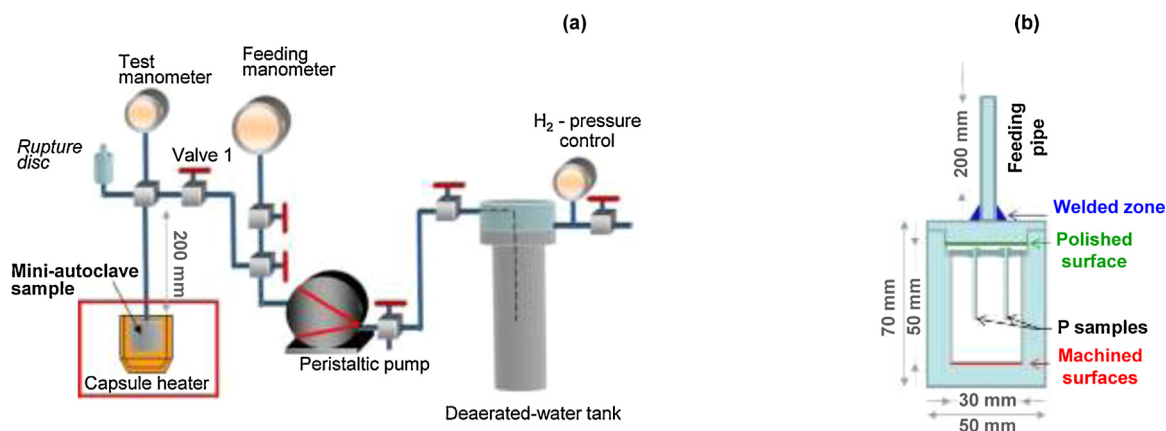
Fig. 1. (a) Scheme of the experimental set-up and (b) scheme of a mini-autoclave.

consisted of mixed spinel oxides $Ni_xFe_yCr_zO_4$ whose compositions depended on the alloy composition. They identified, especially on Alloy 690, $NiFe_2O_4$ and assumed the presence of chromia. Maslar et al. [18] similarly used Raman spectroscopy to identify the sole presence of $NiFe_2O_4$ within the oxide scale that formed on a polished (alumina gel finish) alloy 600 (Ni–15Cr–8Fe–Mn–Ti–Si) sample after testing at 543 °C and 25.4 MPa. Maslar et al. [18] also investigated the influence of surface finish on the phases present with the oxide layer. It was determined that polishing alloy 600 with a coarse grain SiC paper induced the formation of both $NiFe_2O_4$ and traces of α-chromia. In the same way, in different conditions of temperature and pressure, the oxide morphology or the corrosion kinetics [19–21] has been shown to be dependent on the surface finish of the alloy sample. In subcritical condition (325 °C and 15 MPa), i.e., in simulated primary media of a pressurised water-cooled reactor (PWR), Lefaix-Jeuland et al. [20] showed that the chromia morphology was dependent on the crystallographic defect structure present near the surface of the sample prior to testing. A high content of subsurface defects leads to a high density of chromia nodules at the oxide/alloy interface. In contrast, a low defect density induces fewer chromia nodules at the same interface. Moreover, Lefaix-Jeuland et al. reported that the evolution of oxidation kinetics exhibited by these two types of samples (high and low defect densities) differed strongly. Here, the corrosion behavior of Ni base alloys in supercritical water has been studied taking into account the alloy surface finish.

The physical state of the corrosion medium must also be taken into account when studying corrosion of nickel-based and iron based alloys in SCW conditions. Dissolution is specific of corrosion in a liquid phase, whereas, volatile compounds can be formed within gaseous environment. At 600 °C and 25 MPa, supercritical water is expected to have a behavior close to the vapor phase, according to its physical properties [22,23]. Nevertheless, Guzonas and al. [16] mentioned some dissolution in supercritical conditions at 500 °C and 25 MPa corresponding to a liquid behavior, whereas, a vapor behavior could also be expected.

In this present work, the generalized corrosion of the Ni-based Alloy 690 was studied in SCW conditions at 600 °C and 25 MPa. As these temperature is not sufficient to produce volatile compounds of chromium, particular attention was focused on the possibility of some dissolution in SCW. Moreover, these results compare a polished reference state to a machined surface (as described below) in order to investigate the corrosion behavior of nickel-based alloys in SCW as a function of the alloy's surface finish. The corrosion mechanisms taking both the dissolution and the effect of the surface finish into account have been discussed based on these results.

2. Material and methods

2.1. Corrosion test experiments

The present study focuses on corrosion in extreme SCW conditions, i.e., at 600 °C and 25 MPa, supposing that an alloy in these conditions would exhibit equal or greater resistance at less exacting conditions.

At 600 °C and 25 MPa, SCW is expected to behave similar to the vapor phase according to its physical properties (see Section 1). However, regarding the published data [16], some metal dissolution may occur in these conditions that could cause contamination of the test samples from the dissolution of the testing apparatus materials.

Consequently, a specific corrosion device had to be used in order to avoid any possible pollution of the test samples. This methodology also allows for accurate conclusions to be made about the alloy test sample's dissolution in SCW conditions. For these purposes and also to avoid any coupling effects during the corrosion test, this study used mini-autoclaves and coupons that were made of the same alloy. Thus, both the coupons and the mini-autoclaves were used as test samples. The mini-autoclave (Fig. 1) was a cylinder with a height of approximately 5 cm and a diameter of approximately 3 cm resulting in a working volume of 35 cm³. This corresponds to 2.5 mL of water in normal conditions of temperature and pressure.

The experimental set-up is presented in Fig. 1. It is composed of a high temperature part (a furnace containing the mini-autoclaves) and an ambient temperature part which allows the control and the adjustment of the pressure in the autoclaves. After evacuating the mini-autoclave until a primary vacuum was reached, it was introduced into the furnace at the test temperature. Feed water was introduced into the mini-autoclave from a tank with a peristaltic pump which permitted to reach the testing pressure. Afterwhich, the mini-autoclave was sealed for the duration of the test (Valve 1, Fig. 1).

The feed water consisted of ultrapure water (18.2 MΩ cm), deaerated by H_2 bubbling and maintained under a H_2 pressure of about 0.2–0.4 MPa in the tank. In these conditions, using Henry's law, the dissolved H_2 concentration does not exceed 10^{-3} molar ratio on H_2O used in the test. All corrosion tests were performed at 600 °C and 25 MPa, for three exposure times: 335 h, 840 h, and 1740 h.

2.2. Materials

Although the Alloy 690 does not have sufficient creep properties to be considered as a fuel cladding material for the SCWR,