Journal of Nuclear Materials 457 (2015) 266–272

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

# Effect of ultrasonic impact peening on the corrosion of ferritic–martensitic steels in supercritical water

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ARTICLE INFO

*Article history:*
Received 22 October 2013
Accepted 9 November 2014
Available online 14 November 2014

ABSTRACT

Ferritic–Martensitic (F/M) steels are important candidate alloys to be used in the next generation (Generation-IV) SCWRs. In this work, two F/M steels with the same Cr content of around 12 wt.% and varied Si content from 0.6 wt.% to 2.2 wt.% were evaluated in supercritical water (SCW) at 500 °C and 25 MPa for up to 1000 h. The effect of ultrasonic shot peening on the oxidation behavior of these F/M steels have been investigated. The results showed that the oxidation was affected by the Si content as well as the surface modification. The F/M steel with low Si concentration exhibited higher corrosion resistance than that of the alloy with high Si content. Shot peening, which could modify the microstructure at the surface, showed significantly beneficial effect to improving the oxidation resistance. A thin, uniform oxide layer formed on the peened sample could be attributed to the enhanced diffusion of Cr induced by the surface modification.



## 1. Introduction

Due to greenhouse effect and recent climate change, more efforts have been devoted to develop some advanced $CO_2$-free power plants with much improved energy efficiency [1]. Supercritical water-cooled reactor (SCWR) is one of the most promising next generation nuclear concepts proposed by the Generation IV International Forum (GIF) [1]. Compared with current water-cooled nuclear reactors (WCRs), SCWRs offer the following advantages: (1) Higher thermal efficiency (45–50% vs. 30–35%); (2) Simplified plant design and reduced capital costs; (3) Significantly improved safety and reduced risks [2–4]. High-temperature, high-pressure supercritical water (SCW) ($T > 374.1$ °C, $P > 22.1$ MPa) will be used as the coolant in SCWRs to achieve these advantages, which inevitably brings some challenges for materials selection for the SCWR. Corrosion of materials is one of the key issues that needs to be addressed, since both alloys and ceramics can suffer severe corrosion in SCW environments, especially when large amounts of oxidants, such as oxygen, are present [5–7]. Therefore, identifying methods to improve the corrosion resistance of candidate materials in SCW becomes an essential task for developing SCWRs.

It is well known that the corrosion of materials is dependent on the material surface state and can hence be modified by applying suitable surface treatments [8,9]. Shot impact peening has attracted considerable attention for improving the surface properties of materials, thereby optimizing the material properties, such as corrosion, wear and fatigue [10–12]. Shot-peening is a cold-working process that uses shot media (metallic, ceramic particles) to bombard the surface of materials, introducing large residual compressive stresses on the surface and changing the grains structure by producing ultrafine grains in the near-surface region [10,13]. The investigation of the effect of shot-peening treatment on corrosion has been reported in numerous publications. However, the investigation of shot-peening on the corrosion behavior of steels in SCW is quite limited. Warzee et al. [14] investigated the effect of surface treatment, including electrolytic polishing, mechanical polishing, milling, lathe-turning and grinding on the corrosion of AISI 304 and 410 steels in superheated steam between 400 °C and 600 °C. Their results indicated that the corrosion kinetics of the steels was significantly reduced by the surface cold-work treatment. Tan et al. [15] examined the effect of shot-peening on the corrosion of Alloy 800H exposed to SCW at 500 °C and 25 MPa. They found that shot-peening effectively improved the oxidation resistance and also suppressed oxide exfoliation. In this study, the effect of ultrasonic shot-peening on the corrosion behavior of two Ferritic–Martensitic (F/M) steels was investigated. The

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http://dx.doi.org/10.1016/j.jnucmat.2014.11.028
0022-3115/

beneficial effect of shot-peening on the corrosion and its mechanism were discussed.

## 2. Experimental

Table 1 lists the chemical compositions of the two Ferritic–Martensitic (F/M) steels evaluated in this study. The two F/M steels were denoted as FM-1 and FM-2. The Si contents varied from 0.6 wt.% to 2.2 wt.% and the Mn content was at the same level at around 1.7 wt.%. The as-received F/M steels were cut into rectangular coupons with dimensions of 20 mm × 5 mm × 2 mm. All the coupons were then ground by using emery papers from 240# to 1200# grit, which was followed by an ultrasonic cleaning for 30 min prior to shot-peening and SCW testing. Two groups of samples were prepared in order to compare the effect of peening on corrosion in SCW. Samples in the first group were the as-received samples which were denoted NP-FM-1 and NP-FM-2. Samples in the second group were the samples that received shot-peening treatment, which were denoted P-FM-1 and P-FM-2. The ultrasonic shot-peening process was conducted using a HJ-III, Sunbow Technology ultrasonic peening machine with the main parameters listed in Table 2.

Static capsule autoclaves were built to conduct the SCW corrosion tests as shown in Fig. 1. The autoclave was made of a section of 316L stainless steel tubing with an outer diameter of 9 mm and a wall thickness of 1.5 mm. The samples were separately placed in one capsule filled with a controlled amount of deionized water. The capsule was then heated in a tube furnace at 500 °C to conduct the SCW test. All the SCW tests were conducted at 500 °C and 25 MPa in SCW with an initial dissolved oxygen concentration of 8 ppm (the value measured at room temperature).

The SCW exposure time was 1000 h for all the samples tested. The weight of samples was measured by using a balance with five-decimal accuracy. The surface morphologies were characterized using a Zeiss EVO MA-15 Scanning Electron Microscope (SEM) equipped with a Bruker Energy Dispersive X-ray Detector. X-ray diffraction (XRD) analysis was performed using a Rigaku Ultimate IV X-ray diffraction system. Micro-hardness tests were conducted on the cross-section of shot-peened samples to identify the depth of the peening-affected zone by using a Buehler IndentaMet 1100 micro-indentation hardness tester with a load of 100 g.

## 3. Results

### 3.1. Samples after ultrasonic peening

Ultrasonic shot-peening (USP) is an effective method to modify the surface of materials and hence to achieve improved properties. One significant feature of the surface after USP treatment is the evident grain refinement near the surface region of materials. Fig. 2 shows the morphology of the surface and a cross-section of Sample P-FM-2. It can be seen that the shot-peened samples exhibited a rough surface with overlapped dimples produced by the bombardment in the peening treatment. Cracks induced from severe deformation appeared at the peening surface. Evident grain refinement occurred and deformation texture, such as slip bands, formed underneath the peening surface.

**Table 2**
Parameters used for the ultrasonic shot peening treatment.

| Parameter | Value |
|---|---|
| Work frequency | 20 kHz |
| Work load | 10 g |
| Time | 180 s |
| Impact needle diameter | 4 mm |

**Table 1**
Chemical compositions of the F/M steels studied in this work.

| Sample identification | Alloy element (wt.%) | | | |
|---|---|---|---|---|
| | Cr | Si | Mn | Fe |
| FM-1 | 11.6 | 0.6 | 1.8 | Bal. |
| FM-2 | 11.7 | 2.2 | 1.7 | Bal. |

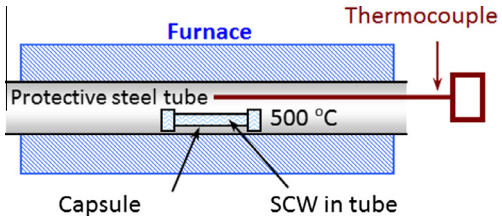


**Fig. 1.** Apparatus used for the supercritical water tests.

It has been reported that the ultrasonic shot-peening process could induce the formation of a nanocrystalline surface layer on steel plate [1,2]. The significant grain refinement observed by shot-peening was related to the production of a high density dislocations and small shear bands in the surface deformation layer [3]. The depth of the deformation layer induced by the USP treatment could be examined by hardness testing, since the hardness varied at different locations due to the change of structure. Micro-hardness tests were conducted on the cross-section of the sample at different locations (25 μm, 50 μm, 100 μm, 150 μm and 200 μm deep from the surface). Fig. 3(a) shows the results of the hardness tests on the cross-section of the as-received samples (NP-FM-1 and NP-FM-2). Two hardness values were obtained at different depths, which could be attributed to the duplex-phase structure of the F/M alloy. The higher hardness value (around HV300) represents the hardness of the hard martensitic phase in the duplex-phase steel. The lower hardness value (around HV 150) represents the hardness of the soft ferrite phase. Fig. 3(b) shows the hardness profile on the cross-section of the peened samples (P-FM-1 and P-FM-2). The hardness was measured at around HV 600 near the peening surface and decreased to HV300 at a depth of 150 μm. However, no obvious deviation of the hardness values was observed until reaching the depth of 200 μm, suggesting the existence of a peening-affected layer with a thickness of around 150 μm, which was consistent with the SEM observation.

### 3.2. Weight changes

Fig. 4 shows the oxidation kinetic plots determined by the weight gain measurements for the tests in SCW with a low oxygen concentration. The weight gains of the samples were fitted according to the generalized equation:

$$\Delta W = kt^n \tag{1}$$

and

$$k = k_0 e^{\left(\frac{-E_A}{RT}\right)} t^n \tag{2}$$

where $k$ and $k_0$ are rate constants, $E_A$ is the activation energy, $R$ is gas constant, $T$ is the temperature, and $n$ is an exponent to describe the time dependence of the weigh increase. Although weight gain is not an ideal measure of corrosion, under the constant conditions of these tests it is a reasonable measure.

The time exponents ($n$) determined by fitting were also shown in Fig. 4 which indicated that the oxidation kinetics of all the samples generally approached a parabolic oxidation behavior ($n$ = 0.5),