Evaluation of exfoliation issues in the fossil-fueled power plant

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ABSTRACT

Purpose: of this work is to evaluate the differences in corrosion behavior and the susceptibility to exfoliation between two steels that are used in fossil-fueled power plants.

Design/methodology/approach: The X6CrNiMo17-13-2 and X10CrNiCuNb18-9-3 steels were exposed at supercritical water conditions (600°C, 25 MPa). Behavior of these steels was evaluated and compared. The nature of oxide scales formed on their surface was evaluated by SEM-WDS, XPS, Raman spectroscopy and impedance measurements.

Findings: In comparison with the Super 304H steel the 17341 steel showed higher oxidation rate which resulted in higher oxide scale thickness which subsequentially tends to exfoliate more easily. From the microstructural and chemical point of view the oxide scales formed on both steels were very similar. Due to the oxidation kinetics differences the replacement of the 17341 steel by shot-peened Super 304h steel can be advised. However, owing to its high content of carbon, the Super 304H steel is very susceptible to sensitization to intergranular corrosion.

Practical implications: The exfoliation phenomenon cannot be fully avoided in the case of austenitic stainless steels. Therefore, the processes carrying out in the power plants need to be carefully monitored in order to prevent the potential system failure. During the service of the fossil-fueled unit the perforation of operations removing the exfoliated oxides is advised.

Originality/value: Nowadays in some fossil-fueled power plants where the supercritical regime is introduced the X6CrNiMo17-13-2 austenitic stainless steel suffers severe exfoliation issues. According to the newest trends in material engineering this steel is being currently replaced by shot peened X10CrNiCuNb18-9-3 steel. The value of this work is the evaluation of exfoliation issues of those steels in the fossil-fueled power plant.

Keywords: Austenitic stainless steel; Exfoliation; Fossil-fueled power plant

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PROPERTIES

1. Introduction

Nowadays the old fossil-fueled units are being renovated in order to increase their total efficiency, reduce the emissions of harmful gases and to prolong their life-time. The increased total efficiency is achieved by raising the working parameters of the cooling medium. One of such renovation concerned Czech fossil-fueled power plant Tusimice II. The new working parameters of this power plant are summarized in Table 1. The renovation increased the power plant total efficiency from 34% to 39% that in a result means 14% savings in lignite. At the same time the emissions of NO_x, SO_2 and solid air pollutants were decreased by 70%, 79% and 87%, respectively. T [1,2].

Table 1.
Tusimice II power plant working parameters

Superheated steam temperature	575°C
Reheated steam temperature	580°C
Superheated steam pressure	18.1. MPa
Reheated steam pressure	3.72 MPa

Unfortunately, during the early stages of service of the renovated power plant there were observed problems regarding oxide exfoliation taking place on superheater internal surfaces. Due to the oxide exfoliation, the superheater piping bends are clogged and subsequently overheated because of the restricted flow of the cooling media.

Originally used X6CrNiMo17-13-2 (1.4918, AISI 316H, CZ 17341) austenitic non-stabilized and creep-resistant steel does not comply the required oxidation resistance of max. 0.1 $mm.a^{-1}$ at 600-650°C (which is 150 μm of oxides over the whole service period). In order to enhance the oxidation resistance the content of Cr needs to be increased. The positive effect in this sense is also achieved by stabilization of austenitic stainless steels by Nb or Ti and increasing the stability of austenitic phase by Ni and N. Based on these findings the new Nb-stabilized steel Super 304H SP (X10CrNiCuNb18-9-3) with higher chromium content was developed in 1980s. The SP stands for Shot Peening which delivers fine-grained surface of high corrosion resistance therefore some of the anticorrosion properties of Super 304H SP steel can be compared even to that of the highly alloyed HR3C (X6CrNiNbN25-20, AISI 310) steel [3].

2. Experimental

The samples of X6CrNiMo17-13-2 (hereafter denoted as 17341) and X10CrNiCuNb18-9-3 (hereafter denoted as Super 304H) steels were supplied by Tusimice II power plant owner, the CEZ Group. These materials were supplied as pipes in state ready to be installed in the power plant operational structure. These pipes were then cut into samples with dimensions of 50 x 18 x 2 mm. In the case of the Super 304H SP steel the shot peened surface (inner surface of the pipe) was preserved. Other surfaces were ground up to the grinding paper P200. The samples composition was verified by optical emission spectrometry (Arcmet 8000 SL MobileLab, Oxford Instruments).

Such prepared samples were then put into SuperCritical Water Autoclave with circulating demineralized water of conductivity below 10 $\mu S.cm^{-1}$ and flow 3 $ml.min^{-1}$. The conditions in autoclave were maintained at 600°C and 25 MPa. The exposure took 1000 hours. The precise (error 0.00001 g) weights of the samples before and after exposure were recorded. After exposure, the samples were prepared for the metallographic observations, SEM analysis and electrochemical experiments. The metallographic observations took place in UJV in Rez and the electrochemical experiments were carried out in Institute of Chemical Technology in Prague.

The metallographic observations were performed by Nikon Epiphot 300 microscope equipped with imaging analyzer NIS-Elements 3.0 and MHT Anton Paar 4 micro-hardness tester. The detailed microstructure of the oxide scales, created during the exposure in supercritical water, was observed and their chemical and phase composition was analyzed by scanning electron microscope TESCAN VEGA TS 5130 XM equipped with WDX, EDX and EBSD detectors.

The oxide scales were analyzed by means of surface analysis; Electron spectrometer ESCAProbeP (Omicron Nanotechnology Ltd.) provides the analysis of photoelectron spectroscopy (XPS) which allows acquiring information about chemical composition of the surface layers. The source of X-rays is an aluminum anode (Al Kα – line 1486.6 eV) with monochromator. The XPS measurements are performed under high vacuum. The analyzed area is 1 mm^2 and the analyzed depth is about 5 nm. The device allows sputtering of the surface by bombarding by the ions of argon. The Ramans spectra of the oxide scale were measured by Raman dispersive spectrometer Labram HR (Jobin Yvon) with laser parameters of 532 nm wavelength and 40 mW of input power. As a detector, a multichannel air-cooled CCD camera is used. The oxide scales are measured on area of about 1 μm^2.

The electrochemical impedance spectroscopy spectra were measured in three-electrode arrangement. The surface of the working electrode was 1.21 cm^2. The measurement was carried out in the environment of borate puffer

(pH = 8.41). The amplitude of sinus signal applied on working electrode was 10 mV. The frequency of the alternating current was from 60 kHz to 6 mHz. The devices Solatron 1287 and Solatron FRA1250 were used to realize these measurements.

3. Results and discussion

The as-received 17 341 steel possessed austenitic microstructure with finely dispersed carbides (not shown). The as-received Super 304H steel possessed austenitic microstructure as well as the finely dispersed carbides (not shown). In the case of Super 304H steel the carbides are observed along the austenitic grain boundaries and the tiny precipitates of niobium carbonitrides are present as well. The chemical composition of as-received samples (see Table 2) complies the corresponding standards. The microhardness of the as-received materials was 151 HV0.1 for 17341 steel and 199 HV0.1 for Super 304H steel. The increased microhardness of Super 304H steel is caused by higher content of carbides in the steel structure, given by higher content of carbon in this steel, and by the presence of hard niobium carbonitrides as well.

The microstructure of examined alloys after exposure in SuperCritical Water (SCW) at 600°C, 25 MPa for 1000 hours is shown in Figures 1 and 2. Owing to the exposure, high amount of carbides precipitated preferentially along the grain boundaries in the microstructure of both materials. The current carbides probably underwent coarsening, as did the niobium carbonitrides. The increase of the amount of carbides (and carbonitrides in the structure of Super 304H steel) is followed by hardening of the examined materials. The microhardness of the 17341 steel increased from 151 to 170 HV0.1 and the micro-hardness of the Super 304H steel increased sharply from 199 to 250 HV0.1.

After the exposure in SCW at 600°C, 25 MPa for 1000 hours the samples surface was covered by dense layer of oxides of several tens of μm thickness (see Figure 3). The corrosion rate of the samples was evaluated as their weight gain in milligrams per reaction surface in square centimeters. The corrosion rate was therefore 1.176 mg.cm^{-2}

for Super 304H steel and 1.958 mg.cm^{-2} for 17341 steel. These values can be converted into standardized corrosion rates in mm per year, which are 0.0006 mm.y^{-1} for Super 304H steel and 0.001 mm.y^{-1} for 17341 steel.
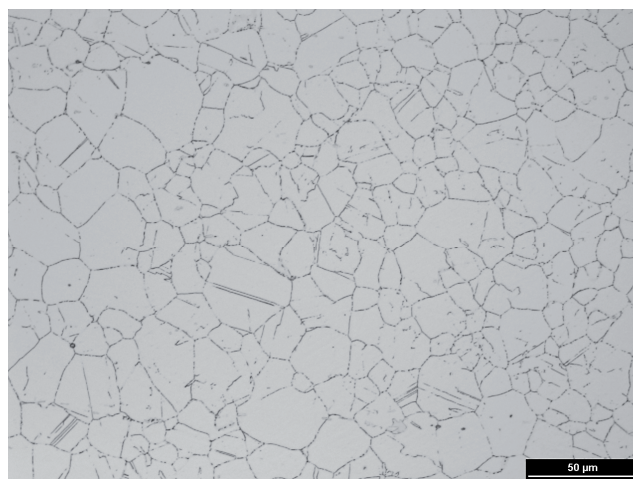

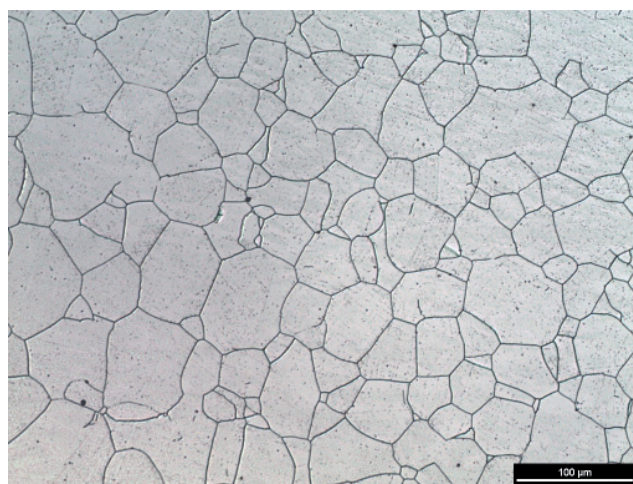Fig. 1. Structure of Super 304H steel after exposure in SCW (LM)

Fig. 2. Structure of 17341 steel after exposure in SCW (LM)

Table 2.
Chemical composition of received samples (OES) in weight %

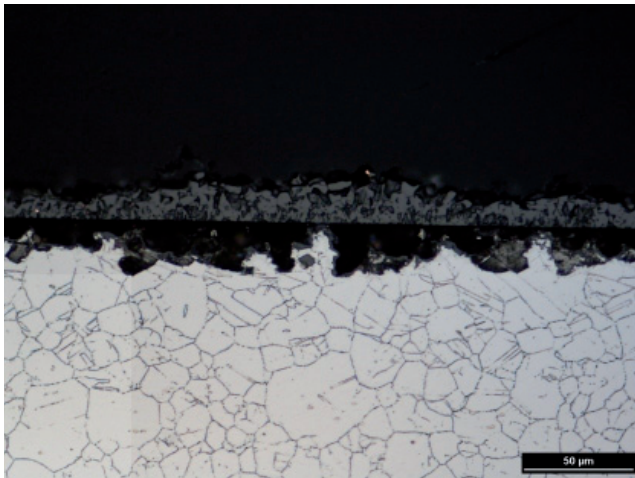| Sample	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Nb	N
17341	0.047	0.49	0.71	0.018	0.012	17.2	12.1	2.0	0.33	-	-
Super 304H	0.09	0.23	0.8	0.03	0.01	18.1	8.4	-	2.9	0.4	0.05

Fig. 3. Oxide scales formed on Super 304H steel after exposure in SCW (LM)

The uniform corrosion rate is given mainly by the content of chromium, stabilization of austenitic steels by niobium or titanium and stabilization of austenitic phase by nickel and nitrogen. The alloying by the molybdenum (17341 steel has 2 wt.% of Mo) has no effect on formation of protecting chromium-based spinels or oxides [3]. Even the one percent difference in chromium content caused that the uniform corrosion rate of 17341 steel is higher than that of Super 304H steel.
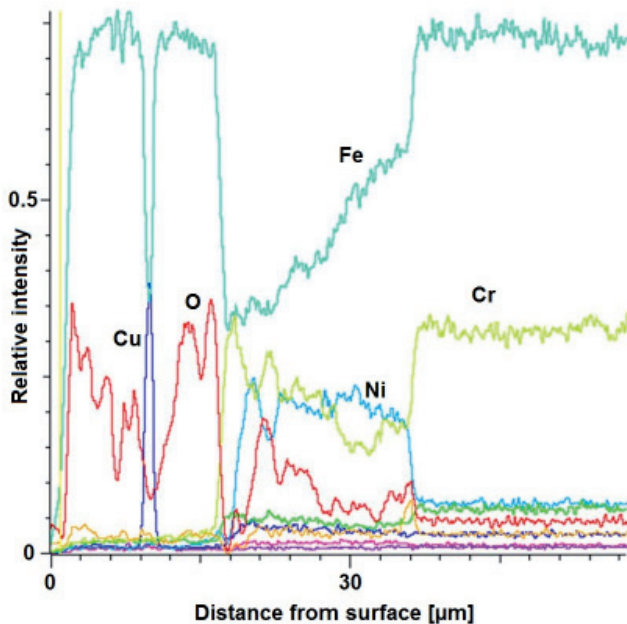

Fig. 4. Elements distribution in profile of oxide scale formed on Super 304H steel after exposure (SEM-WDS)

The chemical composition of the oxide scales formed on the surface of examined specimens was evaluated by SEM-WDS (see Figure 4), by XPS (not shown) and Raman dispersive spectrometry (not shown). Figure 4 shows elements distribution in profile of oxide scale formed on Super 304H steel after exposure in SCW. The oxide scale is formed by two layers (see Figure 3), the topotactic oxide that has lattice coherency with the metal matrix and therefore is very stable and does not tend to exfoliate. The second, outer, layer is an epitactic oxide that has no lattice continuity to metal matrix nor the topotactic layer and therefore tends to exfoliate due to the stresses induced mainly by the thermal cycling during piping service. The topotactic oxide is traditionally formed by spinel with some amount of hematite ($FeCr_2O_4.2Fe_3O_4$). The epitactic layer is formed by non-protective magnetite (preferentially Fe_3O_4). The very similar situation occurred in the case of the 17341 steel (not shown). The only difference was the thickness of the oxide scales, especially the epitactic oxide, which was significantly thicker in the case of 17341 steel.

The XPS spectra (not shown) confirm the above stated results concerning the composition of oxide scales formed on the surface of the examined steels during exposure in SCW. On the very surface of the exposed specimen of 17341 steel the high content of carbon was detected. It refers to a high carbon contamination of the sample surface. Even though, the iron- and chromium-based oxides were detected. After 10 minutes of sputtering by argon ions, the oxide scales composition was revealed further (not shown). The concentrations of main cations of oxide scales, iron and chromium, have grown significantly. Iron was detected in a form of Fe_3O_4 and Fe_2O_3, chromium in oxidation states Cr^{3+} (Cr_2O_3) and (marginally) in Cr^{6+} (CrO_3). There were no molybdenum cations detected in the scales. The XPS spectra of Super 304H steel (not shown) indicated similar results. The oxidation states of iron and chromium did not differ significantly. Owing to some content of niobium in the alloy, Nb_2O_5 was detected in the scales formed on the Super 304H steel.

Raman spectra of 17341 steel after exposure in SCW (not shown) resemble the Raman spectrum of chromite which contains 20.0 wt. % of FeO and 55.5 % of Cr_2O_3 [4]. The Ramans spectra of Super 304H steel (not shown) confirms similarly the composition of the top oxide scale.

The electric behavior of oxide scales formed on both alloys during exposure in SCW was evaluated by the Mott-Schottky characteristics that is derived from the impedance measurements results. These characteristics indicate that the oxide scales formed on both alloys behave very similarly and have both the P type and N type semiconductor characteristics. It is probably caused by the non-stoichiometric

composition of the oxide scale. In its outer layer the Fe cations dominate, therefore the N type semiconductor behavior is expected. Contrarily in the inner layer of the oxide layer dominate the Cr cations, the composition is close to that of chromite, which is the reason why the P type semiconductor behavior is expected [5].

The results showed that the oxide scales formed either on 17341 steel or Super 304H steel have more or less same composition (WDS, XPS, Raman) and properties (Mott-Schottky). The only result in oxidation behavior between these two examined materials is their uniform corrosion rate, which is higher in the case of the 17341 steel. As stated before, the uniform corrosion rate is mainly given by the content of chromium, which is higher in the case of the Super 304H steel. Above all, the thickness of the oxide scale determines whether it will exfoliate or not. The higher thickness of the oxide scale, the higher the internal stresses caused by different oxide and metal molar volume and by different oxide and metal thermal expansivity. The exfoliation then occurs in the case of the outer, epitactic, layer which has low adhesion to the metal substrate.

The exfoliation process is a thermodynamically stable oxidation accelerated by cyclical deformation changes. It cannot be fully surprised in the case of the austenitic steels even not in the case of the highly-alloyed (min. 24% Cr) steels. Besides increasing the content of chromium there are other ways to reduce the exfoliation. One of them is a fine graining and shot peening of a surface resulting in its hardening and chemical homogeneity (see Figure 5) [6-8].
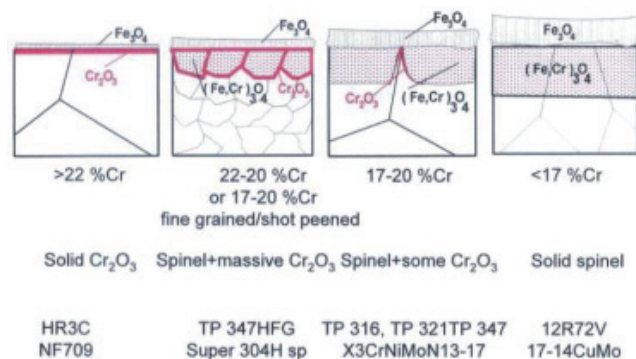

Fig. 5. The influence of the Cr content and surface treatment on the oxidation behaviour of austenitic steels in steam at 600-700°C [6]

The solution of the exfoliation issue in the Tusimice II power plant would be then replacing the currently used 17341 steel with shot peened Super 304H steel since its oxidation, due to the higher content of chromium and the surface hardening, proceeds slower. However, the Super

304H steel has significant drawback which is its high content of carbon. Even though it is stabilized by niobium it still undergoes very strong sensitization to intergranular corrosion. Figure 6 shows the potentiokinetic reactivation curves for the Super 304H steel in as-received and exposed states. It is evident that the level of sensitization of this steel is almost 100% (see also sharp hardness increase). The sensitization means chromium depletion of the grain boundaries due to its reaction with carbon and formation of stable $Cr_{23}C_6$ carbides. The chromium depleted grain boundaries are then susceptible to the localized intergranular corrosion. From this reason, the Super 304H steel needs to be properly heat-treated before introducing into service in the fuel plant. Another issue consists in welding of this alloy since this process could remove the surface hardening introduced by shot peening. Such spots would be then susceptible to the localized forms of corrosion. Proper post-welding treatment and reintroducing of the shot peened surface in these spots is therefore advised.
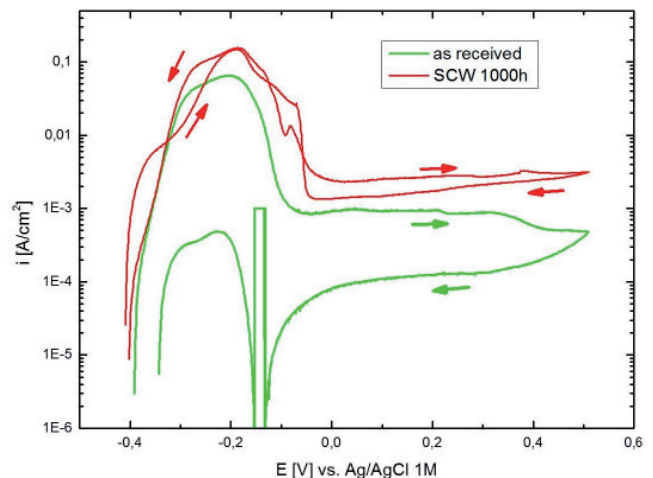

Fig. 6. Potentiokinetic reactivation curves of Super 304H steel before and after exposure in SCW

4. Conclusions

Exfoliation issue of 17341 steel in high-parameters fossil-fueled power plants is concerned in this paper. Currently it is being replaced by more resistant shot-peened Super 304H SP steel. In this paper, we focused on comparison of the corrosion behavior of these two steels in supercritical water and their susceptibility to exfoliation under such conditions. In comparison with the Super 304H steel the 17341 steel showed higher oxidation rate which

resulted in higher oxide scale thickness which subsequentially tends to exfoliate more easily. From the microstructural and chemical point of view the oxide scales formed on both steels were very similar. Due to the oxidation kinetics differences the replacement of the 17341 steel by shot-peened Super 304h steel can be advised. However, owing to its high content of carbon, the Super 304H steel is very susceptible to sensitization to intergranular corrosion.

Unfortunately, the exfoliation phenomenon cannot be fully avoided in the case of austenitic stainless steels. Therefore, the processes carrying out in the power plants need to be carefully monitored in order to prevent the potential system failure. During the service of the fossil-fueled unit the perforation of operations removing the exfoliated oxides is advised.

Acknowledgements

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