



Influence of preoxidation on high temperature corrosion of a Ni-based alloy under conditions relevant to biomass firing



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ABSTRACT

Development of corrosion resistant materials in biomass fired power plants demands specific attention since the condensation of deposits rich in KCl on heat exchanger surfaces induces severe corrosion attack, which is different from corrosion in traditional coal fired plants. Therefore, the ability of preoxidized layers formed on a commercial Cr-Ti-Al-containing Ni-based alloy (Nimonic 80A) to withstand biomass-induced corrosion was investigated. Preoxidation treatments at 900 °C in O₂ and O₂ + 10 vol% H₂O, respectively, were conducted before samples were exposed to conditions that mimicked biomass firing. Complementary characterization methods were employed to study samples after preoxidation as well as after corrosion exposure. The oxides obtained by the preoxidation treatments protected the alloy during corrosion exposure at 560 °C for a period of 168 h. In contrast, non-preoxidized samples suffered corrosion attack and formed porous non-protective oxides containing the alloying elements, Ni, Cr, Ti and Al. The influence of the preoxidation layers on the corrosion mechanism is discussed.

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1. Introduction

High temperature corrosion is a serious problem for biomass fired power plants due to the condensation of corrosive KCl rich deposits on the heat exchanger surfaces (such as superheaters) [1–3]. This arises mainly from the high content of organically bound K and Cl in biomass, which during combustion, become devolatilized and condense as deposits rich in K and Cl [4,5]. To handle the corrosion problem in biomass fired plants, the maximum operation steam temperature is limited to low values (usually below 540 °C), thereby limiting the electrical efficiency of biomass fired power plants. Identification of materials with improved corrosion resistance for use as superheaters in biomass fired power plants is therefore of utmost importance [6].

Recent investigations have shown that without any dedicated surface modification, chromia and alumina forming alloys do not give adequate protection in the presence of alkali chlorides (see for example [6–12]). One of the principal factors responsible for this is the thermodynamic favourability of the reaction between alloying elements and chlorine, leading to formation of volatile metal chlorides which are then oxidized to form non-protective oxides [13]. Consequently, the protective ability of coatings containing possible protective elements have been

investigated under conditions related to biomass firing [14–19]. However, the inter-diffusion of alloying elements as well as the possibility of corrosive species to diffuse through the coating splat boundaries [18] are vital factors to be considered if coatings are to be applied for protection of superheaters against alkali chloride induced corrosion.

Surface modification employing the materials own alloying elements for the formation of protective oxides at the surface prior to corrosion exposure (i.e. preoxidation) provides an avenue for rendering protection to materials under aggressive conditions. This approach has been widely investigated under sulphidation conditions [20–24], and in a few cases, under conditions related to biomass firing [25–29]. With respect to investigations related to biomass firing, the effect of preoxidation for protection against corrosion depends on the composition and crystallography of the preoxidized layer, preoxidation conditions, as well as the corrosive environment [29]. In particular, a positive effect of preoxidation of pure Cr and Ni against HCl has been reported while pure Fe preoxidized under similar conditions suffered corrosion [29]. Similarly, the resulting Al₂O₃ from preoxidation of a commercial FeCrAl alloy has been reported to give some degree of protection against KCl induced corrosion attack [26]. Furthermore, an investigation with chromia forming alloys (EN 1.4982, EN 1.4301 and EN 1.4845) revealed a positive effect of preoxidation against attack by HCl at low temperatures (400 °C) [28]. On the other hand, no positive effect was reported for preoxidation of Fe-30Cr alloys in oxygen, when they were subsequently exposed to a gaseous KCl environment [27]. This implies that although Cr-oxide rich preoxidation layers may be resistant to attack by HCl [28,29], they can

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exhibit poor resistance to KCl-induced attack [27], possibly due to the reaction between KCl and Cr_2O_3 [30].

Investigations of the reactivity of a number of oxides and KCl under oxidizing conditions have indicated that KCl does not react with TiO_2 , ZrO_2 , Y_2O_3 , Ta_2O_5 , HfO_2 , Al_2O_3 , NiO , Fe_2O_3 , CeO_2 and Co_3O_4 [31]. These results suggest that alloys with the capability of forming such oxides may experience limited corrosion attack under biomass-firing conditions. Based on this and with the need for further exploration of preoxidation as an avenue for corrosion protection under biomass firing conditions, the present work reports on the influence of preoxidation on the corrosion resistance of a Cr-Al-Ti-containing Ni-based alloy (Nimonic 80A) under laboratory conditions mimicking biomass firing.

2. Experimental procedures

2.1. Sample preparation, preoxidation and high temperature corrosion exposures

The investigated material was a Ni-based alloy (Nimonic 80A). Its chemical composition as determined by energy dispersive X-ray spectroscopy (EDS), is as follows (in wt%): Al-1.3, Ti-2.2, Cr-20.6, with Ni as balance. Using fusion thermal conductivity detection units, LECO CS230 and LECO TN500, the carbon and nitrogen contents of the alloy amounts to 0.070 wt% C and 0.014 wt% N [7]. Arc shaped samples having an external arc length of 23.6 mm were obtained from the tube material with a precision cut-off machine (Struers, Accutom-50). The samples were ultrasonically cleaned and dried in acetone and ethanol, before they were subjected to the various heat treatments, which are summarized in Table 1. The various heat treatments consist of preoxidation or annealing in inert gas atmosphere and subsequent corrosion exposure. Preoxidation in oxidizing atmospheres was carried out in either O_2 (preoxidation-I) or O_2 with the addition of 10% water vapour (preoxidation-II) to form surface oxides. Annealing in inert atmospheres aimed to investigate possible temperature induced changes of the bulk microstructure. Finally, corrosion exposure of the different samples was carried out under conditions that mimic the environment experienced by superheaters in biomass fired power plants. To this end, a slurry of KCl in isopropanol was used to obtain an about 1 mm thick KCl deposit on each sample before its exposure to the corrosive gases in a dedicated corrosion test rig (for details about the test rig, see [32]). The KCl deposit together with the applied gas mixture containing HCl, SO_2 , CO_2 , O_2 , H_2O and N_2 according to Table 1 mimics biomass firing. All experiments were conducted isothermally and samples were subsequently allowed to cool under their respective gaseous atmospheres applied for the treatment. At least three samples in either the as-received, preoxidized or annealed condition have been exposed to high temperature corrosion and investigated afterwards.

2.2. Characterization of samples

Light optical microscopy (LOM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were employed for sample characterization.

Cross sections of the as-received, preoxidized and annealed samples were mounted in an epoxy resin and prepared by grinding and polishing down to 1 μm diamond suspension according to standard

metallographic procedures. For characterization of the bulk microstructure of the as-received (non-preoxidized), preoxidized and annealed samples, prior to and after corrosion exposures, cross sections of these samples were etched with glyceric acid before microstructure analysis using LOM (OLYMPUS GX 41). The cross sections of all samples exposed to the corrosive conditions were carefully prepared under water free conditions. Details of this procedure are described elsewhere [32]. These cross sections were analysed with SEM (Inspect S or Quanta ESEM FEG, FEI) and EDS (Oxford instruments) using an acceleration voltage of 15 keV. SEM investigations were conducted with both backscattered electron (BSE) and secondary electron (SE) detectors to obtain information on variations of both chemical composition and morphology. From the obtained SEM images, the thicknesses of the preoxidation layers and corrosion products were measured using the image analysis software ImageJ. Over 50 measurements were carried out for each set of samples to meet statistical requirements for the thickness distribution of the formed surface layers.

In addition to the conventional mapping of cross sections by EDS, an elemental re-quantification method (previously described in [33]) was employed to obtain an averaged one-dimensional representation of depth-profiles of relevant chemical elements. This involved subdivision of the mapped regions into strips of meshes in directions parallel to the sample surface, and subsequent re-quantification (from the acquired EDS map data) of the average composition of elements in these meshes using the INCA software (Oxford instruments). Generally, the length of these meshes (in the direction parallel to the surface of the sample) was over 100 μm , corresponding to the length of the micrograph. However, due to the difference in thickness of the oxides obtained from preoxidation, and the reaction products obtained after corrosion exposures, different widths of the meshes were employed. For the relatively thick oxides on the preoxidized samples, a mesh width of 1.5 μm was applied, while a 0.5 μm wide mesh was used to properly capture the chemical variations in corrosion products observed on non-preoxidized samples. The elemental profiles were then obtained by plotting the re-quantified averaged compositions from each strip of mesh, as a function of distance in the direction perpendicular to the interface between the oxide (or corrosion product) and the alloy.

Plan view investigations using SEM, EDS and XRD were also carried out to supplement the analysis of the cross sections. For corrosion exposed samples, plan view investigation involved careful successive removal of the corrosion products, starting from the deposit/gas interface, and characterization of the exposed interfaces (for details, see [34]). In all the plan view investigations, a diffractometer (Bruker AXS, D8 Discover) equipped with Cr-K α radiation was applied for XRD measurements. To limit the X-ray penetration depth, measurements were carried out in grazing incidence geometry (GI-XRD) using a fixed incidence angle ($\gamma = 2^\circ$ for analysis of preoxidation layers, and 5° for corrosion product analysis). A counting time of 10 s per detector step of $0.03^\circ 2\theta$ was employed for all XRD measurements.

3. Results

3.1. Morphology and composition of preoxidation layers

Results of microscopy and chemical analysis of the oxide surfaces after preoxidation of Nimonic 80A at 900 $^\circ\text{C}$ in O_2 (preoxidation I),

Table 1

The different heat treatment conditions applied in the present study.

Experiments	Temperature ($^\circ\text{C}$)	Time (h)	Atmosphere
Preoxidation I	900	168	O_2
Preoxidation II	900	168	$\text{O}_2 + 10 \text{ vol}\% \text{H}_2\text{O}$
Annealing	900	96	Ar
Corrosion exposures ^a	560	168	KCl deposit + 400 ppmv HCl, 60 ppmv SO_2 , 12 vol% CO_2 , 6 vol% O_2 , 3 vol% H_2O , N_2 -balance

^a With the exception of H_2O , gas compositions are given on a dry basis.

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