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Corrosion of uncoated and alumina coated steel X20CrMoV12-1 in H_2O–CO_2–O_2 and air at 600 °C

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ABSTRACT

Future coal power plants will in case of oxyfuel combustion be operated with altered atmospheres. Hence, corrosion attack might become more severe and steels have to be protected. An alumina-sol was used to coat X20CrMoV12-1 (X20) with alumina to test the protection. Testing was performed at 600 °C in flowing H_2O–CO_2–O_2 and static laboratory air for 1000 h. Oxidation under air is minor compared to exposure in oxyfuel atmosphere. In both cases a multilayered oxide (hematite, magnetite, spinel) was formed on uncoated steels. Carburization appeared on uncoated X20 in H_2O–CO_2–O_2. The coating demonstrates a high protection.

1. Introduction

The need for more efficient power generation results in more aggressive corrosion, if oxyfuel combustion power plants are considered [1]. A typical oxyfuel power plant flue gas mainly consists of CO_2, H_2O, O_2 and SO_2/SO_3 [1–3].

9–12% chromium steels are used as superheater tubes in coal-fired power plants [4,5]. Such steels provide a good corrosion resistant behaviour at high temperatures in several atmospheres [6,7]. The oxidation in steam or in water containing atmospheres is heightened compared to the oxidation in dry air [8–11]. Hünert et al. [8,9] investigated X20CrMoV12-1 (X20) under flowing synthetic air at several temperatures and oxidation times and Schulz et al. [12] tested X20 under static laboratory air at the service temperature of 600 °C for 1000 h. In both cases a thin oxide layer composed of hematite, magnetite and spinel was formed. Atmospheres containing oxygen, steam and CO_2 led to the formation of a thick multilayered oxide composed of hematite, magnetite, $FeCr_2O_4$ precipitates and an internal corrosion zone [13]. The resulting compositions of scales are compared in Fig. 1.

Additionally, 9–12% chromium steels exposed in CO_2 containing environments demonstrated a strong carburization zone beneath the oxide scale after keeping at 600 °C for 1000 h [9,13,14].

To guarantee the necessary service life of high temperature parts protective coatings made of heat resistant ceramics may be a technical solution. Alumina has proven to withstand harsh environments [15,16] and is producible as coating by the sol–gel method [17–21]. Dressler et al. [22] presented an effective protection of Inconel-718 by a sol–gel alumina layer even after exposure for 4000 h at 800 °C in static laboratory air. Therefore, this type of coating was tested on a typically power plant steel X20 under static laboratory air at different temperatures and exposure times [12]. Generally, the alumina layer on X20 was intact, but local defects became visible. Chromium and manganese diffused into the alumina scale resulting in the formation of mixed oxides. The mass gain after exposure to 650 °C for 500 h in static laboratory air of the coated sample was negligible compared to that of the bare steel.

Because of these promising results, the well known superheater material X20 was selected to study the effect of such type of coating under oxyfuel conditions, too. Uncoated and coated X20 samples were investigated after exposure in laboratory air and H_2O–CO_2–O_2 for 1000 h at the service temperature of 600 °C. The paper is focussed on surface reactions and phase formations during the corrosion in both atmospheres. Diffusion of alloying elements into the coating, as well as the protective action of the alumina will be discussed.

2. Experimental details

2.1. Sample preparation

Disks of X20 (diameter: 20 mm, thickness: 2 mm) were cut from a rod by wire eroding and afterwards ground as well as

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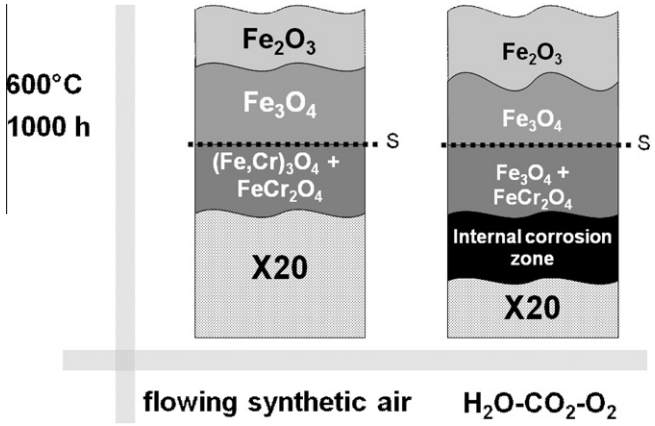

Fig. 1. Scheme of the oxide scales formed on X20 after 1000 h exposure time in flowing synthetic air [8,9] and H_2O–CO_2–O_2 [13] at 600 °C. "S" denotes the original substrate surface.

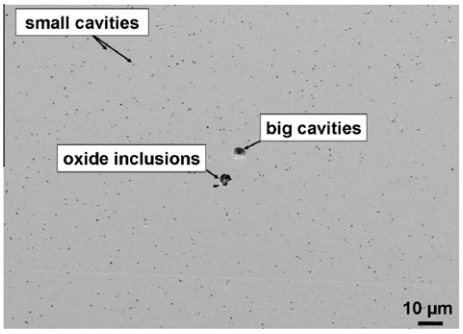

Fig. 2. SEM image of a polished substrate showing oxide inclusions as well as small and big cavities.

polished to a mirror-like surface (1 µm, water-based diamond suspension). After this treatment small (<1 µm) and big (up to 5 µm) cavities as well as oxide inclusions existed in the substrate as shown in Fig. 2. Size and distribution of the small cavities support the assumption that these are a result of pulling of $M_{23}C_6$ and perhaps other carbides which were precipitated along martensite laths and previous austenite grain boundaries as described in [23]. Because of the cavities mentioned before, the roughness of the polished X20 surface is about 1,2 µm. The inclusion in Fig. 2 is composed of aluminium and oxygen.

The composition of the used X20 as measured by spark emission spectrometry (Spectrolab of the company Spectro) is given in Table 1.

Preparation of sols and coatings followed the procedures given in [12,19,22] and is schematically shown in Fig. 3. At first an aluminium-nitrate solution was prepared and heated up to 87 °C. At this temperature aluminium-tri-sec-butylate dissolved in sec-butanole was added to this solution under vigorous stirring for up to 1 h. After cooling down to room temperature the sol was directly used for the spin-coating process. The sol was applied on rotating (4000 rpm) substrates and then the samples were dried at 350 °C for 2:30 min. This procedure was repeated for four times. Finally the coated samples were heat treated at 500 °C for 0.5 h to form a well adhesive alumina coating. The coating thickness amounted to 400 nm (see Fig. 8 below).

2.2. Corrosion testing

Corrosion tests were carried out in a corrosion facility [9] in H_2O–CO_2–O_2 (30-69-1 mol%) atmosphere for 1000 h at 600 °C and 1 atmosphere total pressure. The gas velocity is about 0.3 m/s. For comparison, samples were also tested in a Nabertherm L15/12 furnace for 1000 h at 600 °C under static laboratory air. The experimental conditions are listed in Table 2.

The samples exposed under laboratory air were taken out from the furnace every 250 h to measure the mass change and document the sample surface. In case of the corrosion under oxyfuel conditions, the samples were tested for 1000 h without interruption.

Table 1
Composition of X20 (material number 1.4922) in wt.% [12].

Ni	Cr	Fe	Mo	Cu	V	Mn	Si	Co	C
0.43	11.25	86.0	0.78	0.08	0.29	0.52	0.15	0.02	0.2

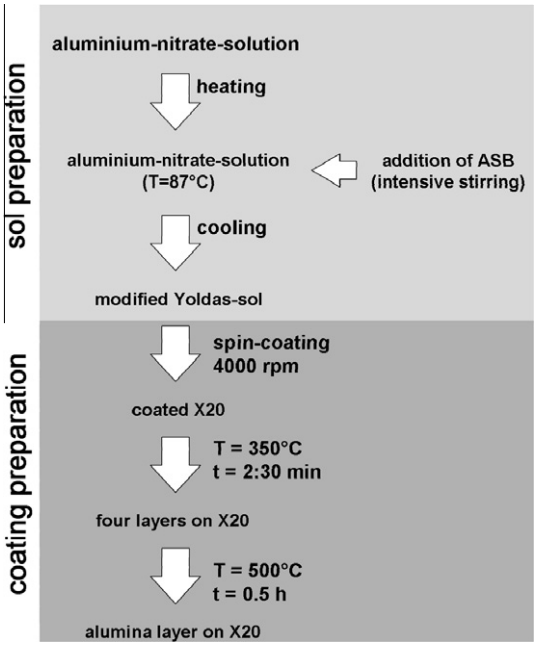

Fig. 3. Schematic description of sol and coating preparations.

Table 2
Overview of oxidation tests with X20.

Uncoated samples	Coated samples	Atmosphere
U-A	C-A	Laboratory air ("A")
U-F	C-F	H_2O–CO_2–O_2 ("F")

2.3. Microstructure analysis

Light (Jenapol) and scanning electron microscopies SEM–EDX (Leo Gemini 1530VP-10 kV) were used to image the sample surface and oxide sequence of the uncoated and coated X20. The oxide scale thicknesses of the uncoated samples were evaluated by light microscopic inspection of cross sections. In case of coated samples a focussed ion beam (FIB; StrataTM 200 xP TMP) cut was prepared due to the very thin coating layer of 400 nm. Phase identification was carried out by transmission electron microscopy (TEM; JEM-2200FS, JEOL, 200 kV) by using bright field imaging (BF), scanning transmission methods (STEM), electron diffraction and energy dispersive X-ray spectroscopy (EDX).