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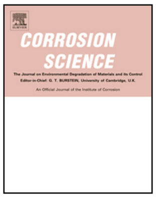

Microstructure and chemical composition of the oxide scale formed on the sanicro 25 steel tubes after fireside corrosion

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ABSTRACT

The Sanicro 25 austenitic steel is foreseen as a potential material for steam superheaters and reheaters in ultra-supercritical power plants. The aim of investigation was to characterize in detail an oxide scale grown on the Sanicro 25 tube after fireside oxidation at 650 °C. The morphology of the oxide scale and the microstructure of the bulk material were investigated using advanced electron microscopy methods. A multilayered and multicomponent oxide scale containing mainly Cr_2O_3 was found on the surface exposed to combustion gases. Directly under the oxide scale, a chromium-depleted zone with no $M_{23}C_6$ carbides was observed.

1. Introduction

Despite the significant spread of non-conventional sources of electricity (e.g., photovoltaic cells, wind turbines), fossil-fueled coal-fired power plants are still the major source of energy, what is inextricably linked with emission of the carbon dioxide to the atmosphere, which has major detrimental impact to climate change.

The most viable way to reduce the amount of CO_2 emission by conventional coal-fired plants is therefore to increase their thermal efficiency, which can be achieved by increasing the temperature and pressure of the steam at the turbine inlet. In order to construct elements able to withstand the highest temperature and pressure (e.g., superheaters, steam lines, high-pressure turbines) materials with sufficiently high creep- and corrosion resistance should be used [1–3]. Additionally, good weldability and fabricability of the materials are also required. Modern, A-USC (Advanced Ultra-Supercritical) technology, allowing power plants with efficiency exceeding 50% to be built, entails use of Ni-based alloys [4]. Due to the fact that nickel is already on the list of scarce metals and is very expensive, further attempts to apply them on a larger scale in the conventional power industry would increase the prices of tubes.

Noteworthy, high-Cr austenitic stainless steels, such as the Sanicro 25, produced by SANDVIK [5,6] are a cheaper alternative to Ni-based alloys. This steel in form of thin-walled, seamless tubes is used for superheaters and reheaters in power plants operating up to 680 °C [5]. Good oxidation resistance is obtained due to the high Cr content (22.5 wt%). Numerous alloying elements (e.g., W, Nb, Mn, Si, Cu, N, C) are responsible for both solid solution- and precipitation strengthening of the austenitic matrix by carbides, nitrides and intermetallic phases.

During service, the inner surface of the superheater tubes, comes into a contact with high pressure steam, which has a strong oxidizing and erosive properties. On the other hand, the outer surface of the tubes is exposed to combustion gas and ashes. The material used for the steam superheater must thus possess high oxidation resistance in both environments [7–14].

In the flue gas environment present inside a coal-fired boiler, in addition to approx. 70 vol.% of nitrogen and several percent of oxygen, also other aggressive gas components (such as H_2O, SO_2, CO_2, CO, HCl) are present. In addition to corrosive gases, also ashes consisting of solid oxides and liquid sulfates are present. They cause the so-called Type II hot corrosion [15–19] at temperatures between 600 and 800 °C. Carbon dioxide (several vol.%) is another important factor that adversely affects the ability of alloys to develop the protective Cr_2O_3 scale [20,21]. This means that the corrosion degradation rate of the steel under operating conditions of the power boiler is primarily influenced by the type of combusted coal. Intiso

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and Tassa [22] demonstrated that in a combustion gas inside the boiler, the corrosion product on the outer surface of the Sanicro 25 tube after more than 15 000 h of exposure at temperature not exceeding 600 °C was approx. 80 μm thick and was several times thicker than the scale formed on its inner surface in a steam environment.

Usually, the corrosion test in an exhaust gas environment is carried out for large sections of tubes that are "implanted" to a boiler for a period of several to several thousand hours, i.e., the time between boiler overhauls. In this case, it should be kept in mind, that the boilers operating parameters and the chemical composition of the fuel may vary over this period. Such an experiment thus provides very valuable information on the corrosion degradation of the material, but only in relation to particular energy installations. Comparing of these data with those obtained by others, always involves the risk of error.

In the present work, a corrosion test was carried out in a manner that allowed greater control of all parameters that significantly influence the corrosion degradation of the material. The aim of this study was to investigate the microstructure, chemical- and phase composition of corrosion products formed on the Sanicro 25 tubes during fireside corrosion, conducted at 650 °C with a total exposure time of 1000 h. Microstructural studies were performed mainly using advanced electron microscopy methods.

2. Material and methods

The chemical composition of the Sanicro 25 steel, measured by optical emission spectroscopy (OES) method (WAS Foundry-Master spectroscope), is given in Table 1.

The samples were delivered by RAFAKO S.A. in the form of head-on welded tube with an inner diameter of 38 mm and a wall thickness of 8.8 mm. Welded joints were the subject of a separate study.

The aim of the corrosion experiment was to evaluate the influence of the conditions inside the boiler on the formation and morphology of the oxide scale.

The two-stage corrosion experiment was conducted at University of Stuttgart (IFK) and described in detail in Ref. [23]. During the first stage, Sanicro 25 was placed between the radiative and convective zones of the 500 kW pulverised fuel combustion test rig, where samples were exposed to the fireside corrosion for 30 h [23]. Afterwards, during the second stage, initially oxidized samples, covered by deposit layer were moved to laboratory corrosion test set-up, consisting of the electrical furnace and a gas mixing station, and further oxidized for 970 h. Chemical composition of the laboratory gas atmosphere was corresponding to one occurring inside the combustion test rig (Table 2) [23].

In experiment designed in this way it is possible to freely determine the duration of each of the stages—to combust only a particular type of coal in the first stage, and to strictly control parameters such as temperature, composition and the flow rate of the gas mixture in the second stage, etc.

After the corrosion experiment, the ash deposit (Fig. 1) was removed from the sample and analyzed. Results are given in Table 3 [23].

Table 1
Chemical composition of Sanicro 25 (wt%) measured by OES.

Element	Fe	Ni	Cr	W	Cu	Co	Mn	Nb
wt%	balance	25.1	22.5	3.45	2.95	1.08	0.56	0.52
Element	Si	Mo	C	Pb	Ti	P	Al	S
wt%	0.21	0.20	0.08	0.05	0.03	0.03	0.02	0.02

Table 2
Chemical composition of combustion and laboratory gas used during the corrosion test [23].

Constituent	Combustion atmosphere	Laboratory gas atmosphere
SO_2	0.03%-vol.	0.1%-vol.
O_2	2.5%-vol.	4.5%-vol.
CO_2	15.5–16%-vol.	16%-vol.
H_2O	7–8%-vol.	7%-vol.
N_2	balance	balance
CO	~250 ppm	none

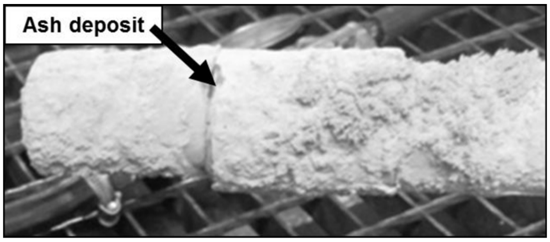

Fig. 1. Fragment of a Sanicro 25 tube after 30 h of exposure in the test rig [23].

The microstructure of the oxidized sample was then investigated using advanced electron microscopy methods. Circular saw was utilized to cut the tube into sections, which were further used in order to prepare metallographic cross-sections for scanning electron microscopy (SEM). Scanning transmission electron microscopy (STEM) was performed on lamellae, prepared by means of the Focused Ion Beam (FIB) NEON CrossBeam 40EsB (ZEISS). Before cutting out the lamellae, a thin protective layer of platinum was deposited on the oxide scale surface. The lamellae had dimensions of 10 × 7 μm, thickness of about 80 nm and was oriented perpendicular to the outer tube surface.

Micro- and nano-structural analyses were conducted using a high resolution scanning electron microscope (Merlin Gemini II of ZEISS), equipped with the FEG electron gun and EDX detector with the Quantax 800 microanalysis system of Bruker as well as high resolution transmission electron microscope S/TEM Titan Cubed G2 60-300 with ChemiSTEM system (FEI). The ChemiSTEM, consisting of the modern field emission electron source (X-FEG), a probe Cs corrector and four coupled silicon drift diodes (Super-X detector), allows to perform chemical composition analyses in nanoareas, even with atomic resolution.

During STEM studies, the signal was detected by high angular annular dark-field (HAADF) as well as bright-field (BF) detectors. The chemical composition was examined using energy dispersive X-ray spectrometry (STEM-EDS). Elemental distribution maps were made both for the matrix and the oxide scale formed on the steel surface.

Phase identification was performed by selected area electron diffraction (SAED) supported by EDS and JEMS software [24]. In order to study the microstructure of the oxide scale, high-resolution transmission electron microscopy (HRTEM), assisted by a Fast Fourier Transform (FFT) was also used.

Table 3
Chemical composition of ashes deposited on the surface of Sanicro 25 steel during corrosion test [23].

Constituent	Total carbon		Al_2O_3	BaO	CaO	Fe_2O_3	K_2O	MgO
	Organic	Inorganic						
H_2O free wt%	0.032	0.061	27.1	0.20	9.47	2.87	0.828	1.44
Constituent	MnO_2	Na_2O	P_2O_5	SO_3	SiO_2	SrO_2	TiO_2	
H_2O free wt%	0.060	0.232	1.426	5.38	48.5	0.292	1.64	