



# The effect of temperature on mechanical properties of oxide scales formed on a carbon steel in a simulated municipal solid waste incineration environment



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## ABSTRACT

The effect of exposure temperature on the mechanical properties of scales in a carbon steel was investigated in a simulated waste incineration environment consisting of a gas mixture ( $N_2$ - $O_2$ - $H_2O$ - $HCl$ ) with samples immersed in a salt ( $K_2SO_4$ - $Na_2SO_4$ - $ZnCl_2$ - $KCl$ ) in the temperature range of 573 to 773 K. The microstructure, corrosion rate, elastic modulus ( $E$ ) and hardness ( $H$ ) of scales were determined by SEM, XRD, descaled weight loss and instrumented indentation technique. The results indicated that both the  $E$  and  $H$  decreased as a negative exponential function of temperature, thus obtaining a low mechanical and microstructural integrity of scales with high defect density between 673 and 773 K.

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## 1. Introduction

Municipal solid waste incinerators (MSWIs), also well-known as waste-to-energy plants, are facilities that burn municipal solid waste (MSW), which is nonhazardous solid waste collected from residential, commercial and institutional sources. In MSWI plants waste is burned under controlled conditions and heat is recovered to provide steam or hot water mainly for electricity generation. Although each system has some unique features, in most MSWI plants the as-received MSW is fed directly into the furnace and burned without pre-treatment such as material separation [1]. The flue gases produced during the combustion of MSW contain very aggressive gaseous acidic substances like HCl,  $SO_2$ , CO,  $Cl_2$  or  $NO_x$ , alkali and heavy metals able to form chlorides with high vapour pressures [2]. As a consequence heat transfer systems of MSWI often present serious corrosion problems. Numerous incidents of corrosion and erosion–corrosion of waterwall tubes, superheater tubes, and other parts under high pressure have been widely reported [3,4]. In general terms, the basic causes of lifetime reduction in MSWI boiler tubes are well known. Chlorine in MSWI flue gases is mainly originated by polyvinyl chloride (PVC) and sodium chloride contained in the household rubbish that feed the combustion chamber [5]. Concerning the MSWI boiler tubes, the most important corrosion factors are the composition of tube material, metal temperature, the difference between gas and metal temperatures, flue gas composition, deposit formation and reducing conditions, and the  $SO_2/HCl$  ratio [6,7]. In addition to

gaseous chloridation attacks, severe corrosion attacks can result from salt deposits that condense from the flue gas onto the metal surface [8], being the deposit formation, one of the main reasons for corrosion at relatively low temperatures of 473–573 K, which are present in evaporator tubes and membrane waterwalls. A lot of information on corrosion mechanisms, effects of temperature and deposit formation has been widely reported in literature [9,10]. Moreover, soft and sticky particles can adhere to the heat transfer surfaces [10,11]. These deposits contain salts like chlorides, sulfates, oxides, and unburned particles, thus resulting in low oxygen partial pressures at the metal surface [12]. Analyses of deposits have shown that, while outer scales present mainly sulfates like  $CaSO_4$ ,  $Na_2SO_4$ ,  $K_2SO_4$ ,  $ZnSO_4$  and  $PbSO_4$ , the inner scales at the scale–metal interface contain considerable amounts of chlorides like  $CaCl_2$ ,  $KCl$ ,  $ZnCl_2$ , and  $PbCl_2$  [13,14]. The presence of these low melting point compounds on metal walls can accelerate the corrosion process, due to the formation of volatile metal chlorides, thus promoting the dissolution of the metal surface and protective oxides [3,15].

Over the last decades, a lot of technical literature on corrosion mechanisms, effects of temperature and deposit formation in carbon, low-alloy and stainless steels, and Ni-alloys has been reported [4–11]. However, there is little specific information about the effect of temperature and chloride content on the mechanical properties of oxide layer formed on carbon steels, which can be associated to the corrosion kinetics and resistance [16,17]. Ideally, an oxide layer should be dense, continuous and have a good adhesion to the surface, as long as possible, without forming cracks or pores to protect against metal corrosion [18]. In order to better understand the oxide growth mechanism and kinetics,

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the scale microstructure, the mechanical integrity and optimal applications, the mechanical properties of the oxide scale should be widely investigated. An instrumented indentation technique, also known as nanoindentation when the indentation depth is lower than 1000 nm, is a suitable method to determine the evolution of the mechanical properties in different corrosion and degradation processes of steel scale [19,20]. This technique allows one to study locally these properties on small structural features in different types of materials as ceramics, metallic alloys, etc. Its small measurement length scale (micrometric or nanometric) and quasi-non-destructive nature allows one to obtain the elastic modulus ( $E$ ), hardness ( $H$ ) and fracture toughness ( $K_{IC}$ ), in bulk [21], thick and thin-films [22] and multilayered materials [23].

The present work is focused on the study of mechanical properties of oxide scales formed on DIN 17175 Grade St. 35.8 carbon steel that is typically used for both the evaporator tubes and the membrane water-walls in worldwide MSWI. Special attention was paid to the influence of temperature on the elastic modulus and hardness of formed oxide scales in order to better understand the relation between these mechanical properties and the microstructural morphology, resistance, kinetics and mechanisms of corrosion as well as the protection effectiveness of formed scales.

## 2. Experimental procedure

The nominal composition of the DIN 17175 Grade St. 35.8 carbon steel for corrosion tests is shown in Table 1. Specimens of  $60 \times 20 \times 5 \text{ mm}^3$  were ground with SiC grinding paper, 1200 grit (in grains of SiC per square inch), which was supplied by Struers, in order to remove the previously metal oxide layers which adhered to the surfaces. Afterwards, the samples were weighed and cleaned in acetone in an ultrasonic bath. The specimens were subsequently exposed to a simulated waste incineration environment that consisted of a gas mixture (total flow rate =  $100 \text{ cm}^3 \cdot \text{min}^{-1}$ ) of  $\text{N}_2$ , 10 vol.%  $\text{O}_2$ , 5 vol.%  $\text{H}_2\text{O}$ , and 1000 vppm HCl, and with samples immersed in salt containing 5 wt.% KCl, 15 wt.%  $\text{ZnCl}_2$ , 40 wt.%  $\text{Na}_2\text{SO}_4$ , and 40 wt.%  $\text{K}_2\text{SO}_4$ .

Corrosion tests were carried out in a vertical Pyrex tube located into a furnace at different exposure temperatures: 573, 623, 673, 723, and 773 K, for 200 h. After corrosion tests, the scales and corrosion products were examined on a polished cross-section by a Leica Cambridge Stereoscan S360 Scanning Electron Microscope equipped with Energy-dispersive X-ray microanalysis (EDX). X-ray diffraction (XRD) was performed in a Bragg–Brentano Siemens D-500 powder diffractometer with CuK radiation in order to determine the crystalline phases of the corrosion products. The porosity of scales was determined from detachment scales using a Micromeritics model Tristar 3000 porosimeter. The effect of corrosion was determined by measuring the mass loss after 200 h, removing the corrosion products by chemical etching in a Clark solution with 50 g of  $\text{SnCl}_2$  and 20 g of  $\text{Sb}_2\text{O}_3$  in  $1000 \text{ cm}^3$  of 37% (v/v) HCl, at room temperature (around 298 K). Finally, it was cleaned with acetone in an ultrasonic bath [24]. In this study, each mass loss value is an average with the corresponding standard deviation of 5 measurements performed on 5 specimens in order to have statistical significance.

**Table 1**  
Nominal composition of DIN 17175 Grade St. 35.8 carbon steel.

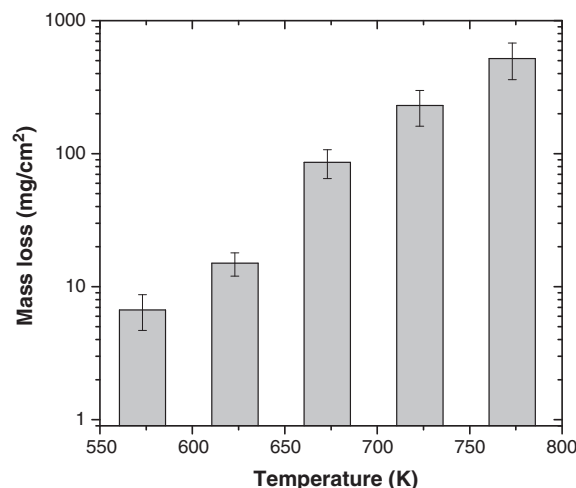
Composition	wt.%
Fe	Bal.
C	0.17
Mn	0.40–0.80
Si	0.10–0.35
P	0.04
S	0.04

Afterwards, an instrumented indentation technique was used to record the surface changes at different exposure temperatures (573–773 K), thus obtaining the elastic modulus and hardness. Nanoindentation tests were carried out with a Nano Indenter® XP System (Agilent Technologies) equipped with Nanosuite 6.1 software. The mechanical tests were made by a three-sided pyramid Berkovich diamond indenter, where the area function of the indenter was calibrated using a fused silica standard ( $E_{\text{silica}} \approx 72 \text{ GPa}$  [25]). The frame stiffness was automatically corrected and the thermal drift during the experiments was maintained below  $0.05 \text{ nm} \cdot \text{s}^{-1}$ . First, an experiment series at room temperature were performed on the surface of each scale as a function of indentation depth, up to 2000 nm, in order to determine the mechanical properties of scales without the effect of the steel substrate. In other experiment series, both  $E$  and  $H$  of steels were measured in the cross-section after polishing in order to determine the influence of corrosion on the steel at the scale–steel interface. Both  $E$  and  $H$  were obtained using Oliver and Pharr's method [25]. Each  $E$  and  $H$  value present in this study is an average of 50 measurements performed on four different zones of the same sample, in order to have statistical significance.

## 3. Results and discussion

### 3.1. Corrosion tests

Descaled mass loss measurements as a function of exposure temperature for 200 h are shown in Fig. 1. Significant differences in corrosion rates were found for the samples exposed at different temperatures. So, it confirmed that the temperature had a strong effect on the corrosion kinetics in boilers under these conditions. It was related to both the used gas mixture that consisted of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and HCl, and the molten fraction of the salt mixture ( $\text{K}_2\text{SO}_4$ – $\text{Na}_2\text{SO}_4$ – $\text{ZnCl}_2$ –KCl). Salt mixtures, either chloride–chloride or chlorine–sulfate, can have relatively low melting temperatures, due to the formation of eutectic solutions. For instance, KCl has a melting point of 1050 K, but it can form eutectics in solution with several other substances at low temperatures. Thus, a binary mixture of 52KCl–48ZnCl<sub>2</sub> (wt.%) present a eutectic system at 523 K [26]. The adding of alkali sulfate salts increases the melting point of salt mixture. In our case, the molten fraction of the salt mixture was significantly augmented with the temperature from ~20% (573 K) to ~80% (773 K). The results of these corrosion tests were in agreement with previous studies for low-alloyed steels exposed in similar oxidizing and chloridizing environments [27,28]. Thus, for instance, Spiegel et al. [27] found values of mass loss between 10 and  $300 \text{ mg} \cdot \text{cm}^{-2}$  for 15Mo3 steel in  $\text{N}_2$  – 8 vol.%  $\text{O}_2$  – 2000 vppm, HCl – 15 vol.%,  $\text{H}_2\text{O}$



**Fig. 1.** Mass loss measurements at different exposure temperatures for 200 h.

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