



Thermally grown oxide films and corrosion performance of ferritic stainless steels under simulated exhaust gas condensate conditions



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ABSTRACT

Five ferritic stainless steels are characterized in terms of thermally grown oxide films and corrosion performance under simulated exhaust gas condensate conditions. Oxide films developed at 300 °C show only little variation in microstructure and properties between the alloys, whereas those evolved at 600 °C exhibit clear differences. Especially in alloys with >11.5 wt.% chromium, the presence and distribution of such alloying elements as titanium, silicon, niobium and molybdenum are crucial for the film properties and the overall corrosion performance. The results may be exploited in the compositional optimization of the alloys for the cold-end components of automotive exhaust system.

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1. Introduction

Ferritic stainless steels are a nickel-free alternative to, e.g. austenitic stainless steels, for such demanding applications where resistance to corrosion, excellent thermal properties, good mechanical strength and competitive price are appreciated, such as energy conversion and exhaust systems [1]. Recently, ferritic stainless steels have gained interest particularly as an interconnect material for solid oxide fuel cells (SOFC) [2–13]. In the past, several commercial medium (16–19 wt.%) chromium grades were used as SOFC interconnect materials, although currently alloys with minimized impurity levels and possible additions of reactive elements, such as Ti, Zr, Ce and Y, and chromium contents ranging from medium (16–19 wt.%) to high (>25 wt.%) have been developed especially for SOFC applications. The new compositions have essentially aimed at a low elevated-temperature oxidation rate, low evaporation rate of chromium species and, in particular, low and constant electrical resistivity. [4,5,13] In turn, ferritic stainless steels used in the automotive exhaust gas systems [14–19] are an example of such an application area, where clearly less emphasis has been put on reporting in open literature on materials development and comparison, particularly from the viewpoint of corrosion performance. However, it is publicly recognized that too often too expensive materials are used in automotive exhaust systems [20].

An automotive exhaust system consists of several components, starting from an exhaust manifold at the engine side and ending in a tail end pipe. Typical operating temperatures near the engine, i.e., in the hot end, may be as high as 750–950 °C, whereas those in the other end, i.e., in the cold end, vary from 100–400 °C in the main muffler and the tail end pipe to 400–600 °C in the centre pipe. Hence, materials in the hot end need to exhibit excellent oxidation resistance, while those in the cold-end components should resist both internal corrosion by gas condensate and external salt corrosion. [1,20–22] Especially the inside of the cold end is subjected to harsh conditions: the condensation of combustion gases produces, e.g., sulphuric acid, H₂SO₄, and hydrochloric acid, HCl, that lead to essentially acidic pH values and enable the accumulation of chloride ions [23]. The most common alloys used in the cold-end components include those containing either 11–12 wt.% or 17–18 wt.% of chromium and being stabilized either by titanium or niobium [1].

The recently developed corrosion test VDA 230-214 for metallic materials intended for the use in exhaust gas carrying components by the German Association of the Automotive Industry (Verband der Automobilindustrie) first involves aging at elevated temperature, after which the test materials are subjected to the simulated exhaust gas condensate. The alternating cycle of these two steps is then repeated for six weeks [24]. Under the described test conditions, the oxide films developed during the first thermal aging phase naturally determine much of the behaviour under exposure to the exhaust gas condensate. Overall, it is generally

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acknowledged that particularly structural and electrical properties of the thermally grown oxide films play a crucial role in their protectiveness. Thermally grown oxide films on austenitic stainless steels, especially on the grade EN 1.4301 [25–29], have received much attention in terms of research effort. Recently, some papers have also reported the characteristics of thin thermally grown oxide films formed on some ferritic stainless steels [9,11,30], although the oxidation temperatures have typically been much higher than in the case of the cold end of the automotive exhaust system. Hence, it is important to obtain knowledge on the structural and electrical properties of the oxide films that evolve on ferritic stainless steels at temperatures corresponding to the cold end of the automotive exhaust gas system, since they play a key role in the performance of the materials.

In this study, thermally grown oxide films on five ferritic stainless steels that are or may be used in the cold-end components of automotive exhaust systems were characterized in terms of microstructure and electrical properties. The aging temperatures used to produce the oxide films were 300 and 600 °C, i.e., typical operating temperatures in the cold-end components of the exhaust system. The oxidized steel panels were then subjected to the simulated exhaust gas condensate following the VDA 230-214 test specification. The correlation between the characteristics of thermally grown oxide films and the corrosion performance under simulated exhaust gas condensate conditions of ferritic stainless steels is described and discussed in this paper. The results presented in this paper introduce unique and new information on the behaviour of ferritic stainless steels that may be used in, e.g., materials selection and alloy development for automotive exhaust gas components.

2. Experimental

2.1. Materials

Five ferritic stainless steels, EN 1.4512, EN 1.4510, EN 1.4521, EN 1.4509 and EN 1.4622, were examined in this work. The bulk alloy compositions are given in Table 1. The grade EN 1.4512 features the lowest chromium content, 11.5 wt.%, and is stabilized by titanium only, whereas the grade EN 1.4622 has the highest chromium level, 20.8 wt.% and both titanium and niobium for stabilization. The three other grades, EN 1.4510, EN 1.4521 and EN 1.4509, have basically the same chromium contents, varying only from 17.0 to 17.9 wt.%, but different molybdenum contents (2.03 wt.% in EN 1.4521 and 0.02 wt.% in EN 1.4510 and EN 1.4509) and stabilization by niobium and titanium (EN 1.4510 practically stabilized by titanium only, whereas EN 1.4509 and EN 1.4521 stabilized by both niobium and titanium). Silicon, a common element for elevated-temperature applications, is included in all five ferritic stainless steels (highest in EN 1.4622, 0.6 wt.%), while aluminium, another common element for elevated-temperature applications, is present at very low levels in all five grades.

All alloys exhibited a standard surface finish 2B. The alloys were hence first cold rolled and annealed, then picked and finally given a smooth surface by a further light rolling between highly polished

rollers, i.e., skin passed. The result is a semi-bright grey surface which has an R_a value between 0.1 and 0.5 μm . The alloys were supplied by Outokumpu Stainless Oy, Tornio, Finland, as sheets with a typical thickness of 2.0 mm. The panel specimens of the size of 50 mm \times 100 mm were laser-cut from the sheets. For the tests, the specimens were then ultrasonically cleaned for 3 min in a cleaning mixture consisting of 1/3 of acetone, denaturated ethanol and petroleum ether 40–60 DAB (Deutsches Arzneibuch, German Pharmacopoeia), and air dried.

2.2. Thermal oxidation and oxide film characterization

Oxidation of the ferritic stainless steel panel specimens was performed following the thermal aging step in the test specification of VDA 230-214 [24]. The freely hanging panels were oxidized for 5 h in a chamber furnace at the temperatures of 300 and 600 °C under atmospheric air, after which the panels were transferred to and maintained overnight at ambient temperature in air prior to weighing. Oxidation experiments were conducted using either two or three replicate specimens.

The specimens were weighed before and after the oxidation treatment, enabling the weight changes to be quantified. The morphology of the developed oxide films was examined with a field emission scanning electron microscope (FE-SEM) Zeiss ULTRApplus. FE-SEM examinations were conducted in different areas of the specimens, in order to provide a holistic picture of the formed oxide films. The compounds formed on the specimen surfaces during the oxidation treatment were characterized by Fourier-transform infra-red spectroscopy (FT-IR) using a Bruker Optics Tensor 27 spectrometer, enabling data collection in the wavenumber range of 4000–400 cm^{-1} . In all cases, three replicate FT-IR spectra were collected in different areas of the surface to ensure the reproducibility of the results.

The thermally grown oxide films were also investigated using electrochemical methods. Electrochemical properties of the oxide films were determined under non-aggressive conditions using electrochemical impedance spectroscopy (EIS), the measurements of which were conducted in a borate buffer solution (deionized water, 0.075 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 0.05 M H_3BO_3 , pH 9.1). Furthermore, electrical properties of the films were characterized using Mott–Schottky analyses that were also carried out in the borate buffer solution. Indeed, it is acknowledged in, e.g., [29,31,32], that understanding on the electrochemical and electrical properties of oxide films is best obtained when exposed to a non-aggressive electrolyte; for example, comparison between different oxide films in terms of the overall electrical resistance may be done because it is known that the observed changes are not due to corrosion. Especially electrical properties are considered to be crucially important in understanding the overall protective character of oxide films against corrosion [29]. Here, the protective properties of the oxide films under automotive exhaust system cold-end conditions are also of interest and were studied in a simulated exhaust gas condensate (deionized water, 0.075 M HNO_3 , 0.026 M H_2SO_4 , 0.028 M NaCl, pH 1.2) using EIS measurements. Open circuit potential (OCP) monitoring was also performed in

Table 1
Composition of the studied ferritic stainless steels, in wt.%, that are arranged with respect to increasing chromium content.

Grade	C	Si	Mn	Cr	Ni	Mo	Ti	Nb	Al	N
EN 1.4512	0.022	0.59	0.23	11.5	0.2	0.01	0.18	<0.01	0.01	0.018
EN 1.4510	0.020	0.46	0.55	17.0	0.2	0.02	0.37	0.03	0.02	0.012
EN 1.4521	0.014	0.49	0.51	17.5	0.3	2.03	0.12	0.37	0.01	0.024
EN 1.4509	0.018	0.45	0.50	17.9	0.4	0.02	0.11	0.38	0.01	0.018
EN 1.4622	0.019	0.60	0.35	20.8	0.2	0.01	0.15	0.25	0.01	0.024

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