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Comparison of damaging behavior of oxide scales grown on austenitic stainless steels using tensile test and cyclic thermogravimetry

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ABSTRACT

Two austenitic stainless steels, AISI 304L and AISI 303, were submitted to cyclic oxidation and to static mechanical loading after isothermal oxidation at 1000 °C. Alloy 303 contains ten times more S than 304L and some Mn addition. During the steel process, it formed manganese sulfides that lead to the formation of a less resistant oxide scale. Both alloys showed similar behavior during thermal cycling but breakaway oxidation and intensive spallation occurred much sooner for alloy 303 than for alloy 304L. A correlation could be drawn between tensile test on preoxidized samples, isothermal and cyclic oxidation.

1. Introduction

Maintaining good adhesion of the protective oxide layer on the surface of heat-resistant alloys is crucial for long-term cyclic oxidation resistance. Negative effect of S on the adherence of oxide scales grown on alumina or chromia forming alloys after high temperature isothermal or cyclic oxidation have been widely studied and are known to be a major cause of protective layer failure [1–5]. It was shown that S segregates to free surfaces of voids and cavities formed beneath the oxide scale, further promoting the weakening and consequently the delamination of the metal/oxide interface [6]. On the other hand, calculations and experimental investigations demonstrated the presence of S segregations also at intact interfaces [4,7] and at oxide grain boundaries, which affects the oxide growth mechanism [8]. For chromia scales, the prevailing effect of scale failure appeared to be the interfacial morphology associated with growth stresses, whereas S segregation at the interface is only a secondary effect [1,8].

Most industrial stainless steels contain S to improve steel machinability. S is considered as a detrimental element not only for oxide layer adhesion but also for hot ductility which is essential for forging and rolling. Therefore Mn is added in steels to avoid iron sulfide formation (FeS) which are non-deformable harmful inclusions. S is then trapped by Mn and precipitates as Mn sulfides in the liquid state and during solidification. These inclusions exhibit a lower hardness than Fe sulfides at high temperature and are elongated during hot rolling. At high temperature, the equilibrium between S in sulfides and S in solid solution in the Fe–Ni–Cr matrix is established, this controls the concentration of “free” S. During the high temperature oxidation of steels, oxidation of Mn sulfides can also free some additional S which can diffuse to the metal surface. This can change the metal/oxide interfacial behavior and decrease the adherence of the growing oxide layer. A more subtle mechanism was recently proposed in a companion paper [9]. Indeed, it was shown that when MnS precipitates are oxidized, some S is released and reacts with Cr to form Cr oxysulfides. Therefore the quantity of Cr available for the formation of a protective chromia scale becomes insufficient. Consequently, an accelerated

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Table 1
Chemical composition of austenitic stainless steels AISI 304L and AISI 303 (wt.%).

Steel	Ni	Cr	Mn	Mo	Si	C	S	N	O	Ca
AISI 304L	8.96	18.0	1.13	0.40	0.46	0.021	0.025	0.048	0.010	0.005
AISI 303	8.28	17.1	1.75	0.40	0.44	0.055	0.295	0.035	0.015	0.013

oxidation of the depleted alloy occurs (breakaway), leading to an oxide scale with poor mechanical properties.

To predict oxide scale lifetime before spallation, it is necessary to know the oxide/metal interface adhesion and the oxide scale mechanical behavior. The methods used to measure them are similar to the ones developed for brittle film on ductile substrate. Some of them are very simple to perform because they do not require any sample preparation, like indentation [10] or scratch test [11–13]. Nevertheless, those methods often lead to semi-quantitative information. Moreover, the oxide surface roughness can be an issue. Other methods called "sandwich specimen" methods, such as 4-point bending tests [14] for example, lead to more accurate measurements of the oxide/metal adhesion but they require more sample processing. In particular, a dummy substrate has to be glued onto the surface of the oxide. This bonding can become prohibitive: sometimes no measurement can be obtained because decohesion occurs in the adhesive bond instead of the oxide/metal interface. Finally, some adhesion measurements consist in imposing uniaxial tensile strain on the oxide film while observing the oxide surface with a microscope [15,16]. During such in situ SEM, mechanical tests the oxide scale can exhibit transverse cracks and/or spallation areas. Based on the quantification of those damages, the mechanical properties of the oxide scale such as toughness and adhesion, can be evaluated [17,18]. Nevertheless, like in all the other techniques described here, the knowledge of the residual stress in the oxide scale due to its growth is needed to accurately quantify those properties [19].

It was shown that cyclic continuous thermogravimetry analysis (CTGA) is a fast way to obtain an evaluation of the material resistance to cyclic oxidation and to compare the performance of different materials [20]. This technique combines the assessment of the oxidation kinetics and the assessment of the resistance to thermal cycling with associated stresses. It is therefore interesting to try to correlate CTGA results with isothermal oxidation kinetics as well as with the evaluation of the mechanical properties of the oxide/metal system. The main objective of the present study is to investigate the oxide/metal interfacial behavior during high temperature cyclic oxidation of austenitic stainless steels in relation with the static mechanical loading of pre-oxidized samples. The S content is used as a sensitive parameter influencing the growth kinetics and mechanical resistance of the oxide scale.

2. Experimental procedure

2.1. Materials and methods

Two austenitic stainless steels AISI 304L and AISI 303 provided by Ugitech were chosen as substrates. The alloys were produced by continuous casting and bars of 20 mm were made by hot rolling. These bars were then cold drawn with a 15% reduction of the section. The chemical composition of the investigated materials was controlled by Fluorescence Spectroscopy Analysis and Optical Emission Spectrometry equipped with a gas analyzer. The amount of minor elements in both steels was controlled to make sure their concentrations were similar. They were, except for S and Mn. AISI 304L contains 0.025 wt.% of S and 1.13 wt.% of Mn, whereas the AISI 303 steel contains 0.295 wt.% S and 1.75 wt.% Mn. A difference in carbon content can be noticed, with a higher concentration for alloy 303. Alloys compositions are given in Table 1.

In order to characterize the microstructure prior to oxidation testing, optical microscopy has been performed on the cross section of the samples. Samples have been electrolytically etched in an 85% nitric acid solution for 10 s at 20 mA cm^{-2} to reveal manganese sulfides MnS (in black in Fig. 1b, d) and residual δ-ferrite (in grey in Fig. 1b, d). They were etched in the same solution for 40 s at 20 mA cm^{-2} to reveal grain size (Fig. 1a, c). For AISI 304L, the mean grain size is around 30 μm, and around 22 μm for AISI 303. The main difference between the two microstructures lies in the presence of numerous inclusions of MnS in the AISI 303 due to its higher S content. After etching, Mn sulfides appear in black in Fig. 1. As these inclusions are highly deformable at rolling process temperatures, they also indicate the longitudinal axis of the sample. As the solidification starts in the δ-ferrite phase, we also observe some residual ferrite that has not transformed into austenite during solidification. These ferrite islands have also been deformed during hot rolling. AISI 304L shows slightly more ferrite (~2%) than AISI 303 (~1%) as a direct consequence of the chemical composition of the two grades.

2.2. Samples preparation

Specimens were obtained from 22 to 24 mm diameter rods. Rectangular plates were cut in the longitudinal direction by electrical discharge machining. Parallelepipedic samples with dimensions of 17 mm × 10 mm × 2 mm (Fig. 2) were machined for thermogravimetric tests. Prior to oxidation, all sides of the specimens were ground with SiC paper, down to a final grade of P1200. All samples were cleaned in an ultrasonic bath with acetone followed by high-purity alcohol. They were weighed with an accuracy to within 10 μg with a Sartorius ME balance before and after high-temperature exposures.

Flat specimens for in situ SEM tensile tests were machined from rectangular 1 mm thick plates using electrical discharge machining. Fig. 2 shows the specimen geometry presenting a gauge section of 2 mm width by 1 mm thick and a gauge length of 3 mm. Prior to oxidation, the tensile specimens underwent the same preparation route as TG samples.

2.3. Experimental conditions

Tensile specimens were isothermally oxidized in a tubular furnace at 1000 °C with a heating rate of 60 °C min^{-1}. Synthetic air flow rate was maintained at 0.6 l h^{-1} corresponding to a linear flow rate of 0.17 cm s^{-1} at RT.

Cyclic thermogravimetry analysis (CTGA) was applied to the cyclic oxidation at 1000 °C on the same thermobalance than for the isothermal thermogravimetry. A commercial SETARAM™ TAG 24S thermobalance ensuring a sensitivity better than 1 μg was used. The device has a double symmetrical furnace designed to compensate signal disturbances resulting from gas flow, buoyancy and convection. It is suitable for the accurate measurement of small mass variations occurring during short oxidation tests or induced by very slow-growing oxide scale such as alumina and chromia scales. Through air flow modulation during a dummy isothermal experiment, it was checked that the chosen synthetic air flow rate was sufficient to leave the oxidation kinetics unaffected. CTGA not only allowed the assessment of oxidation kinetics but also the measurement of any oxide scale spallation occurring during specimen