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Kinetics of the oxidation of stainless steel in hot and concentrated nitric acid in the passive and transpassive domains

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ABSTRACT

Oxidation of 304L stainless steel was studied in 4 mol/L nitric acid solution at 100 °C over a wide potential domain. For different potentials, long-term chronoamperometry experiments coupled with mass loss measurements were performed until steady-state was reached to characterize the corrosion kinetics of the passive and transpassive domains. With EIS and XPS measurements, the passive domain was characterized by the formation of a thin film, the thickness of which was potential dependent.

1. Introduction

In France, reprocessing of spent nuclear fuel is based on the PUREX chemical process (Plutonium and Uranium Refining by EXtraction) [1]. The preliminary steps consist in the shearing of fuel clads, the dissolution of spent fuel in nitric acid, and the recovery of insoluble solids by clarification. Then the PUREX process uses an organic solvent (tributylphosphate) to extract uranium and plutonium, to recover fission products in nitric acid phase, to extract plutonium from the uranium/plutonium solution by reduction of plutonium, and to purify, concentrate and chemically transform uranium and plutonium. The products are plutonium, which can be used with depleted uranium for MOX fuel manufacturing, and uranium enriched at the level of the spent fuel. As a consequence of the use of nitric acid to dissolve oxide spent fuel, various nitric media are met throughout the process. Nitric acid is at concentrations almost up to the azeotropic level (14.4 mol/L) and at temperatures up to its boiling temperature (120 °C for 14.4 mol/L HNO_3). These nitric media, processed at pressures not higher than atmospheric, may be more or less renewed, depending on the equipment (e.g. fuel dissolver, fission product concentrators, acid recovery evaporators, fission-product storage tanks). In order to properly contain these very acidic and very oxidizing media, metallic materials have been chosen according to their corrosion limits, optimized and qualified before the building of the plants [2]. They are mainly very low carbon austenitic stainless steels, SS, (AISI 304L, 316L and 310Nb) for the major part of the equipment; a special stainless steel with 4% silicon, for the fission product evaporators; zirconium, chosen for the construction of the most critical equipment in term of corrosion, such as fuel dissolvers and nitric acid recovery concentrators. It is therefore of great importance to have a precise knowledge of the corrosion mechanisms of these materials in nitric acid media.

Concerning SS (more specifically 304L), the corrosion potential is in the passive domain where SS oxidation corresponds to the formation of Fe(III), Cr(III) and Ni(II) [3]. The oxidation rate is low due to the existence of a metastable [4] chromium-rich-oxide layer at the surface [5–7]. In addition, any increase of nitric acid temperature or concentration can lead to an increase of the SS corrosion potential, which could thus be shifted into the transpassive domain, where corrosion is severe [5,6,8]. In this potential range, Cr is possibly oxidized to Cr(VI) that rapidly dissolves [3] and intergranular corrosion (IGC) is also observed [5,6,9]. IGC results from a preferential corrosion at grain boundaries, which generates triangular grooves at grain boundaries. The progression of these grooves inside the steel can induce grain dropping. Some authors proposed

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that this IGC morphology results from the existence of two different dissolution rates: a dissolution rate at the surface of the grains, V_s, and a dissolution rate at the grain boundaries, V_{gb} [10–14]. Based on this phenomenology, a model shows that the total mass loss of the steel is thus ascribable to two contributions: steel oxidation/dissolution and grain dropping [13].

In addition to metal oxidation, nitric acid reduction occurs in a large potential range that partially superimposes the anodic domain of SS [2,14]. The complex reduction phenomena of nitric acid have been widely studied and the reduction mechanisms at the surface of an inert electrode are now well established [15–23]. These mechanisms depend mainly on the potential and on the concentration of the nitric acid. For a small over-potential a first autocatalytic process was shown firstly by Vetter [24–26]. This mechanism is based on the adsorption and reduction of NO_2 (valence IV of nitrogen) to NO^+ or HNO_2 (valence III of nitrogen). Then NO^+/HNO_2 can be oxidized by HNO_3 (valence V of nitrogen) to form again NO_2. For higher over-potential a second autocatalytic process occurs as proposed by Schmid [27–31]. This mechanism is based on the adsorption and reduction of NO^+/HNO_2 to form NO (valence II of nitrogen), which in turn reacts with HNO_3 to form again NO^+/HNO_2. Both mechanisms correspond to an autocatalytic kinetics and it should be mentioned that the potential dependency of these processes was demonstrated by Razygraev [32,33], who also showed that other mechanisms occur for larger cathodic over-potentials. Moreover for both mechanisms, it is not HNO_3 that directly exchanges the electrons with the steel, but a lower valence product such as NO_2 or NO^+/HNO_2.

Despite these very complex processes, it is often assumed that the reduction current is mainly due to the reduction of acid nitric into nitrous acid [15–19] according to:

$$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O \qquad (1)$$

Conversely to the corrosion behavior of 304L SS in sulfuric acid solution which is well documented [34–49], the oxidation behavior of SS in hot and concentrated nitric acid has been poorly discussed in the literature [5,6,50–55], and it has mostly been studied through electrochemical methods only [5,6,51–55]. In this case, the use of usual electrochemical techniques may not be sufficient since only a global current is measured, which results from the addition of both anodic (oxidation of the SS) and cathodic (reduction of nitric acid) currents. It is thus intricate to separate these two contributions especially in the cathodic domain for which the anodic contribution is masked by a large cathodic current. It should be mentioned that such a behavior has already been shown for other materials, *e.g.* by Haupt and Strehblow for the corrosion of chromium in diluted sulfuric acid [56]. In this case, they were able to separate the anodic and cathodic contributions by measuring both the global current and the chromium release in solution with a rotating-ring disk electrode (RRDE) technique.

Even though electrochemical techniques are techniques of choice for the investigation of corrosion kinetics, a crude limitation is that only redox phenomena can be detected. For instance, in the case for SS in nitric acid in the transpassive domain, the corrosion process involves metal dissolution (detectable by electrochemistry) but also grain losses that cannot be detected by electrochemistry and which requires the concomitant use of other analysis techniques. Moreover for most of the authors [5,51–55] the oxidation behavior of SS in such an aggressive solution was studied with dynamic electrochemical methods (cyclic voltammetry) [5,51–55] and the stabilization time before measurement (when it is mentioned) was restricted to the range 10 min–5 h [5,50,52–55]. For these experiments, the extrapolation of the results to longer time is questionable, as it will be shown in the following.

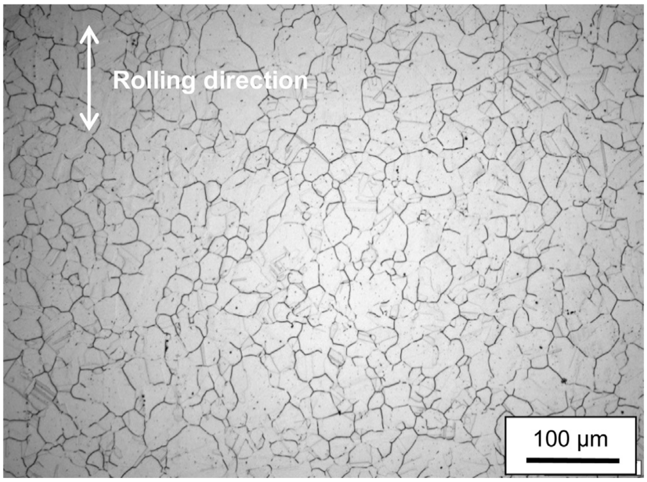

Fig. 1. 304L SS surface after a 5 s immersion in a solution composed of ⅓ H_2O – ⅓ H_2O_2–⅓ HCl.

Table 1
304L stainless steel composition (in weight%).

Cr	Ni	Fe	Mn	Si	Al	P	C	S
17.95	8.45	Bal.	1.45	0.61	0.005	0.036	0.015	0.025

Therefore, this work aims at studying the oxidation behavior of a 304L SS in nitric acid 4 mol/L and at 100 °C. These conditions were chosen in order to be representative of the operation of some devices in a reprocessing plant for spent nuclear fuel. The variation of the corrosion kinetics of 304L SS and its surface properties (aspect, composition, thickness of passive film...) were studied as a function of the potential from the passive to the transpassive domain. A particular attention has been paid to characterize the steady-state of the system. For that purpose, chronoamperometry experiments were carried out at different potentials and for durations as long as 150 h and different surface analysis techniques were used.

2. Experimental

2.1. Materials

The samples were obtained from a solution-annealed and quenched 304L stainless steel, in the form of a hot-rolled sheet provided by Tonnetot (65% deformation ratio). This SS is an austenitic steel with a low ferrite content (the ferrite to austenite ratio is 1.8%), and, from SEM image analysis as shown in Fig. 1, its average grain size is of about 45 µm. Its nominal composition is given in Table 1.

A cuboid sample ($6 \times 20 \times 30\,mm^3$) was used for weight loss measurements. It was cut from the steel sheet by spark machining and machined to be mounted on a steel axis that was connected to the electrochemical workstation.

Before any experiment, the surface of the sample was prepared with an automated polisher (Struers Abramin), using silicon carbide papers with successive grades from 800 to 4000 for 2 min and then with a 3-micron diamond paste for 1 min. The sample was rinsed with demineralized water and ethanol and dried with compressed air. As expected, complementary surface chemical analysis (X-Ray Photoelectron (XPS) analysis—see below for a description of the technique) showed that the steel surface is partially oxidized during the surface preparation process, resulting from polishing, rinsing and/or contact with ambient air. This initial oxide film is some nanometers thick and it is composed of Fe and Cr.

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