

## Characterization of Pt nanoparticle decoration of oxide layers on stainless steel



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### ABSTRACT

Pt particles, injected into the feed water of boiling water reactors, are used to mitigate stress corrosion cracking in austenitic stainless steels of the primary water cooling circuit, but the mechanism behind this mitigation process is still not well understood. This feasibility study was performed, in order to get first insights and understanding on the deposition mechanism of the Pt particles, their shape and spatial distribution, with respect to stainless steel oxide crystals and their composition. The Pt particles and oxide crystals were characterized by electron microscopy, namely scanning electron microscopy, high-resolution transmission electron microscopy, and scanning transmission electron microscopy coupled to energy dispersive X-ray spectrometry. It appears that the surface of the stainless steel is covered by polyhedral crystals, which consist of oxide of mainly Fe, mixed with Ni and Cr. Fe is rather homogeneously distributed within the crystals, while Ni concentrates in their centre relative to the Cr that segregates towards their surface. The Pt particles, with an average diameter of 14 nm, stick to the oxide crystal's surfaces and are rather evenly distributed without preference to oxide composition. The particles are consisting of pure metallic Pt with a round to faceted or rhombohedral morphology.

### 1. Introduction

Stress corrosion cracking (SCC) is one of the major ageing mechanisms in boiling water reactors (BWRs), causing tremendous economic losses and sometimes even challenges safety [1,2]. Therefore, different techniques have been developed over the past decades to mitigate it. In BWRs, the radiolysis of water with subsequent partitioning of the H<sub>2</sub> into the steam is at the origin of highly oxidizing conditions which may promote SCC [3]. Mitigation was attempted firstly by injecting H<sub>2</sub> into the feed water, a method termed hydrogen water chemistry (HWC) [4]. H<sub>2</sub> injection reduces the electrochemical corrosion potential and therefore lowers the SCC susceptibility, but has a problematic side-effect. The high H<sub>2</sub> content favours the partitioning of reduced <sup>16</sup>N species into the steam and thus significantly increases the steam line radiation dose rates.

Therefore the HWC has been further developed by adding a catalyst that improves the recombination efficiency of the injected H<sub>2</sub> with the reactive species O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> [5,6]. Consequently the amount of H<sub>2</sub> needed could be significantly reduced, which in turn substantially decreased the amount of <sup>16</sup>N in the steam. This catalytic technology, developed by General Electric to mitigate SCC, uses noble metals as

catalysts, typically Pt. Na<sub>2</sub>Pt(OH)<sub>6</sub> solution is injected into the feed water during operation (“Online NobleChem™”, OLNC) [6–8]. Under the influence of the elevated temperature, the injected noble metal compounds decompose to a fine dispersion of nanometric metallic Pt particles, which may deposit on all water-wetted surfaces of the reactor system and stay there electrocatalytically active over extended periods, thus providing SCC mitigation if a stoichiometric excess of H<sub>2</sub> is present [9]. For the efficiency of the OLNC technology, it is known that smaller Pt particles are advantageous with respect to SCC mitigation [6], under the assumption that the larger surface coverage provided by smaller particles for the same total amount of injected Pt is favourable to it. There is however still a lack of knowledge on the shape, distribution, chemical composition, and mechanism by which these Pt particles incorporate onto the steel surface under nuclear power plant operative conditions.

The aim of this work is to gain first insights on the deposition mechanism of the Pt particles, their morphology and dispersion, with respect to oxide crystals and their chemical composition formed during the process, investigated using advanced electron microscopy.

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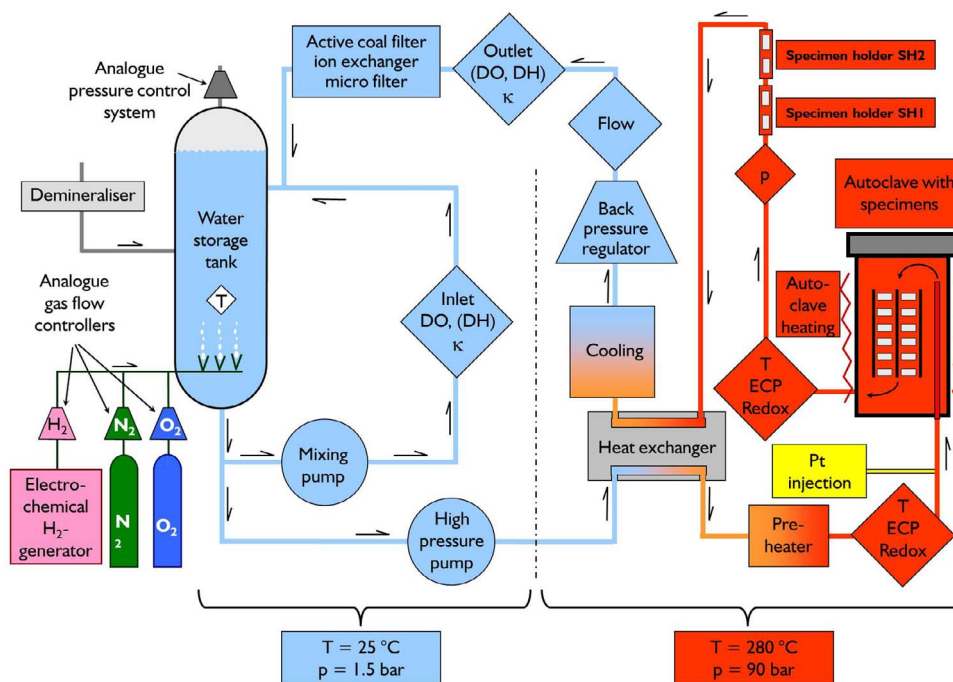


Fig. 1. Schematic of the experimental setup (high-temperature water loop/autoclave) used to reproduce the water chemistry conditions of a BWR, but without irradiation.

Table 1

Chemical composition of the AISI 304L (DIN no. 1.4306) stainless steel, in wt.%.

C	Si	Mn	P	S	Cr	Mo	Ni	Co	Cu	N	Nb	Ti
0.024	0.35	1.49	0.026	0.005	17.9	0.247	10.00	0.088	0.305	0.059	0.001	0.001

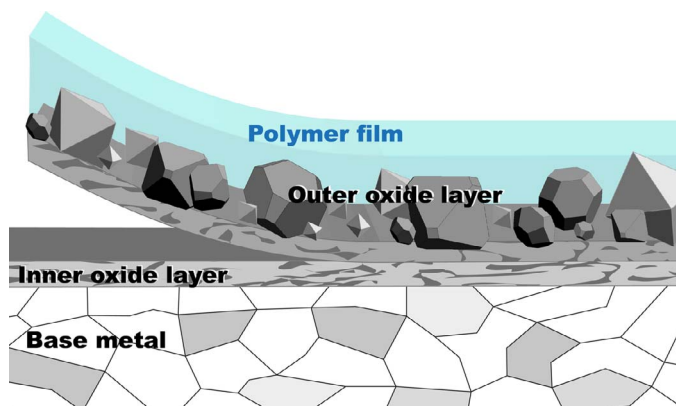


Fig. 2. Schematics of the extraction preparation of the TEM/STEM specimens.

## 2. Experimental procedure and analytical techniques

### 2.1. Specimen OLN treatment

To produce specimens for electron microscopy investigations, stainless steel coupon specimens were exposed in a sophisticated high-temperature water loop and autoclave system (Fig. 1). The loop reproduces the water chemistry of a BWR, but without irradiation. The water chemistry can be precisely adjusted in terms of  $H_2$ ,  $O_2$  and Pt content. The dissolved  $H_2$  and  $O_2$  concentrations, conductivity, electrochemical corrosion potential and fluid flow are closely monitored.

Coupon specimens  $13 \times 10 \times 4 \text{ mm}^3$  in size and made of AISI 304L stainless steel (Table 1), were pre-oxidized in the loop prior to the Pt application experiment. Pre-oxidation was performed for two weeks in

a high-temperature water loop at  $275 \text{ }^\circ\text{C}$  with 170 ppb dissolved  $H_2$  in high-purity water. For the experiment with Pt application, the pre-oxidized specimens were suspended in the water-filled autoclave under quasi-stagnant flow conditions (water velocity of a few  $\text{mm s}^{-1}$ ). Concentrations for the dissolved gases  $H_2$  and  $O_2$  were 80 ppb and 320 ppb, respectively, giving a molar ratio of  $H_2$  to  $O_2$  of about 4. The loop, loaded with the specimens, was pre-conditioned at  $280 \text{ }^\circ\text{C}$  for 8 days under these BWR-HWC conditions prior to the start of the injection of Pt as a solution of  $\text{Na}_2\text{Pt}(\text{OH})_6$  ( $90 \mu\text{g kg}^{-1} \text{ Pt}$ ). The Pt injection lasted for 450 h at a rate of  $1.60 \mu\text{g h}^{-1}$  ( $0.3 \text{ mL min}^{-1}$  @  $90 \mu\text{g kg}^{-1} \text{ Pt}$ ) into a water stream of  $10 \text{ kg h}^{-1}$ , resulting in a maximal Pt concentration in the loop water of  $0.16 \mu\text{g kg}^{-1}$ . The coupon specimens stayed in the loop for a total of 524 h. More details about the experimental conditions can be found in [10,11].

### 2.2. Analytical techniques

Pt loading on the specimen surfaces was quantified by laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS). Calibration curves were established using in-house made stainless steel standards with known surface loadings of Pt, namely to 0.14 and 1.4 nm thick layer, corresponding to 0.3 and  $3 \mu\text{g cm}^{-2}$  Pt surface loading, respectively.

The Pt-treated stainless steel coupons were first studied by field emission gun scanning electron microscopy (SEM) at PSI on a ZEISS ULTRA 55 that has an ultimate resolution of 1 nm. To better understand the bonding of the Pt particles to the oxide film, the spatial distribution and the morphology of Pt nanoparticles were further studied by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) as well as by scanning TEM (STEM) on a FEI Tecnai F30 operated at 300 kV located at ScopeM ETH Zürich. Chemical imaging and

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