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The effect of high-temperature water chemistry and dissolved zinc on the cobalt incorporation on type 316 stainless steel oxide

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ABSTRACT

Oxidation tests on Type 316 stainless steel were performed under hydrogen water chemistry and normal water chemistry for 500 h with continuous injection of a ⁵⁹Co solution with and without 5 ppb of Zn injection. The present paper identifies the resultant oxides, analysed using analytical electron microscopy and complementary surface microstructural characterisation techniques. Zn injection has been shown to reduce Co incorporation in the inner oxide layer under both water chemistry conditions. The secondary effects of Zn injection on the oxide film growth have also been investigated and discussed.

1. Introduction

The major contributor to the radiation dose received by workers within nuclear power plants (NPPs) is radiation fields brought about by the highly radioactive ⁶⁰Co. The non-active ⁵⁹Co cation is contained within corrosion products suspended/ dissolved in the coolant; however, boiling processes in the core can lead to deposition on the fuel cladding, upon which activation through neutron capture occurs, yielding ⁶⁰Co containing corrosion-related unidentified deposits, known as CRUD [1,2]. During operation, the CRUD can be released through erosion and dissolution processes from the cladding surface and deposit on reactor internals causing activity build-up [3–7]. Although there are continued efforts to reduce the amount of cobalt in reactor components by the replacement of cobalt-chromium based Stellite™ alloys, ⁶⁰Co deposition still dominates the out of core radiation fields.

The consideration of the oxide growth mechanism under high-temperature aqueous conditions is fundamental to the phenomenon of activity build-up associated with ⁶⁰Co. The mechanism proposed by J. Robertson in 1991 [8] by which a duplex oxide forms is accepted for oxide growth on stainless steels whereby the inner layer exists as a thin, dense, fine-grained Cr enriched spinel layer and the outer layer is coarse-grained, loosely packed Fe enriched spinel reprecipitated at the oxide-solution interface.

The inner layer forms by the process of non-selective oxidation where the formation of the expected passive Cr₂O₃ layer decreases as the oxide growth rate exceeds the Fe-dissolution rate. Therefore, the

oxide growth is now limited by diffusion of elements through the oxide. The location of each alloying element in the oxide is controlled by its corresponding diffusion rate in the spinel-type oxide. This results in Cr remaining in the inner layer due to its strong preference to occupy octahedral sites in spinel; thus, diffusion rates through the oxide are slow. Meanwhile, the relatively faster diffusion of Fe and Ni through the oxide to the outer layer leads to the preferential dissolution of the steel. The outer layer forms at the oxide surface and is precipitated to relieve the supersaturation from the surrounding dissolution of metal ions [8–10].

Activity build-up occurs when ⁶⁰Co ions dissolved in the coolant are incorporated into the tetrahedral lattice sites of the spinel oxide where they replace Ni and Fe cations [3,11]. The rates of Co incorporation are, however, dominated by oxide structure and composition, which, in turn, depends on electrochemical conditions [3,12,13].

Under NWC the oxidising potential is high in the order of + 150 mV vs. Standard Hydrogen Electrode (SHE) due to radiolysis of H₂O yielding oxidising species such as H₂O₂ and O₂. Resultantly, a hematite (α-Fe₂O₃) over ferrite (MFe₂O₄) based oxide film is formed [13–16]. Since α-Fe₂O₃ is not a spinel but belongs to the hexagonal crystal group, it has no lattice sites for cations like Co resulting in lower Co pick-up rates [17,18] compared to HWC. Secondly, the inner layer under NWC is composed of fine grains of Ni_xFe_{3-x}O₄, and Co incorporation to form CoFe₂O₄ from a thermodynamic consideration is less stable than CoCr₂O₄ formed under HWC [4,14]. Furthermore, an inherent Cr enriched spinel-type inner layer fails to form due to further oxidation of

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Table 1
Chemical composition of the 316 SS test specimens.

Elements	C	Si	Mn	P	S	Co	Ni	Cr	Mo	Fe
Amounts (wt. %)	0.04	0.63	0.93	0.031	0.001	0.14	10.22	16.81	2.06	Balance

Table 2
Water chemistry conditions for the NWC and HWC oxidation tests with/without Zn injection.

	ECP vs. SHE	DH	DO	Co	Zn
HWC	−400 mV	50 ppb	< 5 ppb	0.1 ppb	0 ppb
HWC + Zn	−400 mV	50 ppb	< 5 ppb	0.1 ppb	5 ppb
NWC	100-200 mV	0 ppb	200 ppb	0.1 ppb	0 ppb
NWC + Zn	100-200 mV	0 ppb	200 ppb	0.1 ppb	5 ppb

Cr^{3+} to the soluble Cr^{6+} in the form of HCrO_4^- [3].

Conversely, under HWC, the reducing conditions and hence low oxidising potential (−500 mV vs SHE) results in a more spinel-based oxide [1,19]. The inner oxide composition is markedly different to NWC with a thick Cr enriched inner layer consistent with FeCr_2O_4 (chromite). The outer layer is composed of large octahedral crystallites of Fe_3O_4 (magnetite) [14,15,19]. The location of Co incorporation under HWC is known to be in the inner layer the formation of CoCr_2O_4 is more favourable than CoFe_2O_4 [20]. The different oxide structures and compositions are observed when switching between NWC and HWC and leads to differences in radiation fields attributed to ^{60}Co .

Radiation field mitigation technologies involving the injection of soluble Zn species is in operation across many plants. The Zn stabilises the oxide and prevents the incorporation of other species, namely ^{60}Co into the oxide due to its strong preference for tetrahedral sites in the oxide [3,18,21]. Furthermore, Zn also has the effect of replacing the ^{60}Co previously incorporated into the oxide during standard operation. Rejected ^{60}Co in the coolant can then be removed by the Reactor Water Cleanup (RWCU) system [22].

In the present work, the oxide films formed on Type 316 SS exposed to a simulated functional hot test in a BWR coolant under both NWC and HWC with/without Zn injection are investigated by advanced

electron microscopy techniques. The amount of ^{59}Co and Zn incorporation and their localisation within the oxide has been analysed using surface analytical and morphological analysis, analytical electron microscopy combined with energy dispersive x-ray spectroscopy (EDXS) analysis and Laser Raman spectroscopy (LRS). ^{59}Co was used because it is chemically identical to ^{60}Co but, being non-radioactive, facilitates the safe handling of the coupons and the subsequent microstructural characterisation. The present research is relevant to a hot functional test with an aqueous Zn injection, and it was not aimed at simulating post-fuel cycle Zn injection operations to reduce the shut-down dose rates attributed to ^{60}Co .

2. Experimental details

2.1. Sample preparation and oxidation

The material used in this study was type 316 L SS with a composition depicted in Table 1. The samples ($L = 15 \text{ mm} \times W = 8 \text{ mm} \times T = 1.5 \text{ mm}$) were mechanically polished with 600-grit silicon carbide abrasive paper wetted with deionised water, then cleaned in an ultrasonic ethanol bath to remove surface contaminants.

The samples were subsequently exposed to simulated BWR operating conditions using a recirculating flow loop autoclave with wetted components was constructed of Type 316 SS, (equivalent to the material of the tested samples). The design of the loop consisted of two separate flow circuits both being supplied by a 200-litre feed tank. The first loop was the high temperature and pressure loop and the second was a low-pressure loop containing the demineralised (nuclear grade mixed bed ion exchange resins) and water chemistry analysis apparatus (dissolved oxygen and hydrogen sensors, conductivity and pH sensors). The feed tank water chemistry was controlled by bubbling H_2 , O_2 and

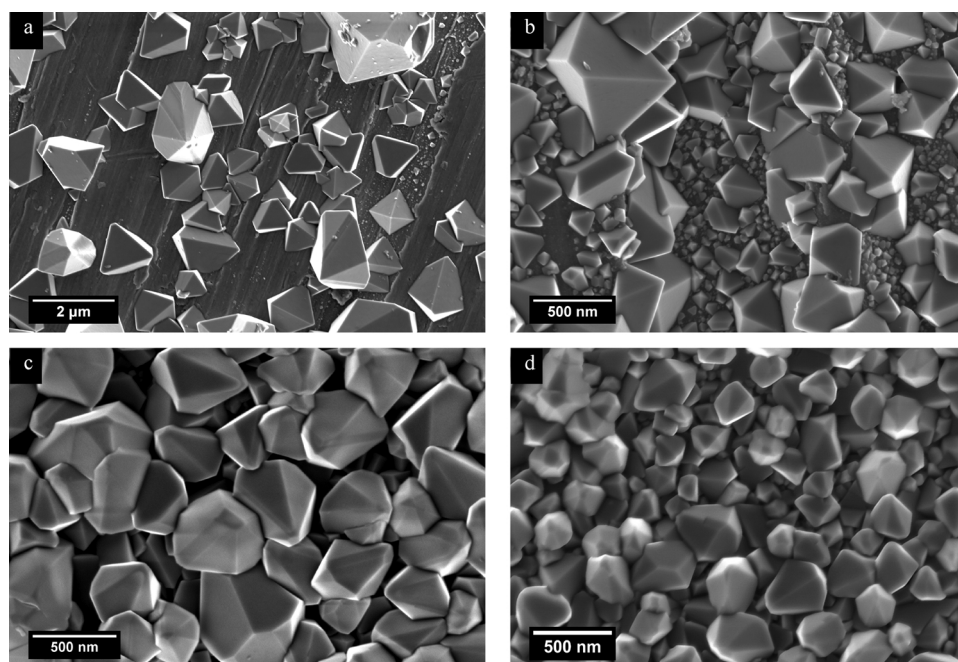


Fig. 1. SE images of the typical oxide morphology formed on a surface prepared with a 600 grit surface polish under a) HWC with no Zn injection; b) HWC with a 5 ppb Zn injection; c) NWC with no Zn injection; d) NWC with a 5 ppb Zn injection.

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