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Full Length Article

Combined ToF-SIMS and XPS characterization of 304L surface after interaction with caesium iodide under PWR severe accident conditions

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ABSTRACT

In case of a severe accident (SA) occurring in a pressurized water reactor (PWR) fission products (Cs, I) are released from the degraded fuel and transported through the reactor coolant system (RCS). A part is deposited onto surfaces of the RCS and can be subsequently chemically re-mobilized, in case the atmosphere composition changes. In order to improve our understanding on the re-mobilization processes, it is important to describe the interactions between deposited fission products and surfaces representative of RCS in SA conditions (mainly oxidized SS 304L) and to identify the species formed after remobilization. In this study CsI aerosols were deposited on the surface of 304L coupons, which have been previously oxidized. The deposits were afterwards reheated (up to 750 °C) in either air or steam. At every step, the 304L coupons were analysed by a combination of surface analysis techniques (XPS, ToF-SIMS), Raman spectroscopy and SEM. It has been established that the initial surface state of the 304L coupons (i.e. oxidation in air or steam) has no effect on the release of caesium or iodine. However, the composition of the carrier gas during the re-heating phase influences significantly the release of caesium. Specifically, in air a significant amount of Cs remains on the coupon and forms mixed oxides with chromium, such as Cs_2CrO_4 and $Cs_2Cr_2O_7$. The results are then discussed and compared with literature data.

1. Introduction

In case of a severe nuclear accident occurring on a Pressurized Water Reactor (PWR), volatile fission products (FPs), such as caesium and iodine are released from the damaged fuel. They are transported through the reactor coolant system (RCS) and the containment building, and might be released into the environment by containment leakages, contributing to the radiological consequences for the population in the short term for iodine and long-term for caesium.

Most of the FPs, however, are deposited on the surface of the RCS [1] either by condensation or by thermophoresis (due to high thermal gradient), as well as by gravity deposition. The main pipes of the RCS are composed of AISI 304L and 316L austenitic stainless steel whereas the steam generator tubes are made of Inconel alloy. In the stringent conditions (high temperature, complex steam/hydrogen atmosphere) of a severe accident, such surfaces are significantly oxidized. The interactions of FPs with the RCS surface are a main issue in severe accident studies, since such interactions could play a role in delayed source term.

Previous studies [2–6] have already focused on the FPs-surface interaction, using a wide variety of analysis techniques (SEM-EDX, XPS, TEM, EPMA, XRF, Raman, XRD and SIMS). Particularly, Allen et al. [6] conducted a comprehensive multi-technique study of CsOH interaction with stainless steel at high temperature in presence of steam and hydrogen. The conclusion was that the diffusion of Cs through the oxide layer is temperature dependent. Also, at 750 °C the oxide has a double-layer structure: a thin outer layer rich in Fe and an inner thick layer rich in Cr.

Subsequent studies [1,7,8] have also shown that the FPs deposited on the RCS surface can be re-mobilized under certain conditions, particularly when the carrier gas composition changes. This work deals with the re-vaporisation of CsI aerosols deposits (natural isotopes) from pre-oxidized 304L stainless steel surface. The objectives were to address (i) interactions with the stainless steel surface and (ii) the nature of the revaporized species.

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The 304L stainless steel is one the main materials used in the RCS piping (particularly the primary loop hot leg and cold leg) [9]. Special attention was brought to the substrate and its preparation in order to obtain a surface state as similar as possible of RCS inner parts after several hours of oxidation in steam conditions [12]. The reason is that during the normal operation of a PWR and especially during a severe accident, the surface of the RCS evolves as a result of the chemical and physical environment (high-temperature, high-pressure liquid water containing hydrogen, boric acid, lithium hydroxide and radioactive corrosion products) [13]. Particularly during a severe accident the fluid in the RCS is at high temperature, mainly in gas state and represents a mixture of H_2/H_2O and possibly even air, for air-ingress scenario [14]. The gas mixture depends on the accident type and the delayed time after the beginning of the accident. The composition and the structure of the oxide layers (iron (III) oxide in low-temperature oxidation conditions and chromium (III) oxide at higher temperatures) formed during a severe accident have been discussed by Mamede et al. [12].

Both Cs and I are FPs and CsI is one of the main species which is expected to be transported and deposited on the RCS surface during a SA transient [1]. Thus CsI could be a potential source for the release of gaseous iodine compounds (I_2, HI, etc.). In this study, only CsI aerosols deposits were considered with amounts of about 1 mg/cm^2, which is consistent with previous studies [10,11].

The re-vaporisation tests were carried out at 750 °C, since Bottomley et al. [7] has observed that the re-vaporisation rate for Cs is greatly reduced above 800 °C. The carrier gas was either synthetic air or pure steam. While during a SA the atmosphere would be a mixture of steam, air and hydrogen, the choice of separate tests was done in order to study the impact of each gas components.

In the present study the surfaces before and after deposits re-vaporisation processes were carefully determined by advanced surface analysis characterization combining high resolution X-Ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Additional analyses were carried by Scanning Electron Microscopy (SEM) and Raman Spectroscopy.

2. Materials and methods

2.1. Pre-oxidation of 304L

The 304L stainless steel coupons (8 × 15 × 2 mm), whose composition is presented in Table 1, with surface roughness Ra of 0.8 µm were cleaned in ethanol. Then they underwent a thermal treatment in a controlled atmosphere in a flow reactor to reproduce as close as possible the surface state of the RCS inner part in SA conditions. The thermal treatment consisted in exposing the coupons to a flow of either air or a mixture of argon/steam (v 50/50) at 750 °C during 24 h. The heating rate was 5 °C/min and steam was injected at 150 °C. The total gas flow rate was fixed at 1 L/min at standard conditions.

2.2. CsI deposition

CsI deposits were obtained by CsI aerosols impaction at room temperature on the oxidized coupons placed in an exposure cell connected to an aerosol generator (AGK 2000, Palas). Aerosols are generated by nebulization of a concentrated CsI aqueous solution (240 g/L of CsI powder 99.9%, Acros Organics). The generated aerosols are then dried in a high argon flow (10 L/min) and transported to the exposure cell where they are impacted on the coupons. About 3 h of generation are necessary to achieve a deposition of a few mg/cm^2. The homogeneity of the aerosol deposition was checked so that up to eight coupons can be loaded per batch. The deposited mass is determined after leaching the coupons in alkaline media (NaOH 0.1 M) for I and Cs recovery in solution followed by elemental I and Cs determinations by Inductively-Coupled Plasma – Mass Spectrometry (ICP MS –Varian 810 MS).

Table 1
Chemical composition of 304L alloy, in wt.%.

	Fe	Cr	Ni	Mn	Si	C	P, S
304L SS	base	18.21	8.02	1.64	0.46	0.02	< 0.03

2.3. Vaporization of CsI deposits

The vaporization of CsI deposits was monitored by thermogravimetric analysis (SETSYS EVO TGA instrument equipped with a type P thermocouple), allowing mass variation measurements with an accuracy of +/−1 µg during a thermal treatment (full mass variation range of +/− 20 mg) - after correction of buoyancy. A specific manufactured alumina tube (10 mm inner diameter) is inserted in the furnace chamber to protect it against corrosive deposition of Cs species. The samples are heated following a thermal cycle including a heating ramp (with a rate ranging from 1 °C/min up to 10 °C/min), up to a temperature plateau (750 °C) which is maintained for 1 h before cooling down by natural convection. During the thermal cycle, the sample is swept by a low carrier gas flow either composed of synthetic air (30 mL/min) or steam/argon (steam mixture featuring a flow rate of 30 mL/min; argon flow rate set at 70 mL/min). Steam was injected at temperature above 150 °C and switched off during the cooling phase (below 400 °C). After this thermal treatment, the residues (if any) on the coupons were analysed following the same procedure as for the initial deposited mass (see above).

2.4. Surface characterization techniques

The sample surface was characterized by combination of X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). XPS provides chemical composition of less than 10 nm depth scale of the surface while the ToF-SIMS was used in depth profiling mode to reach composition up to several micrometres in depth. Several samples were also analysed by Raman spectroscopy. The morphology of the surface before and after re-vaporisation was investigated by Scanning Electron Microscopy (SEM).

XPS measurements were carried out on a Kratos AXIS Ultra^{DLD} spectrometer equipped with a monochromatic Al Kα source (1486.6 eV). The analyser was operated in constant pass energy of 40 eV using an analysis area of approximately 700 µm × 300 µm. Calibration was done by using the C 1 s component of adventitious carbon at BE (binding energy) = 285.0 eV. Quantification and decomposition were carried out using CasaXPS software [15]. Quantification took into account a non-linear Shirley [16] background subtraction. Binding energy value uncertainty is +/−0.1 eV and uncertainty on quantitative elemental analysis is +/−10%.

ToF-SIMS analyses were carried out using a TOF.SIMS 5 instrument (IONTOF GmbH). Pulsed Bi_1^+ primary ions have been used for analysis (25 keV, ≈1 pA) and O_2^+ for sputtering (2 keV, ≈500 nA). While an oxidation of the metal is possible due to the use of an O_2^+ sputtering ion beam, it has been estimated that the effect was not significant since the analysed surface has already been oxidized in severe conditions, at high temperature and for long duration. The sputtering rate was calculated taking into account the sputtering parameters such as sputter beam current, sputtered surface, the density of the material and the ionization yield at 45° (data from the SurfaceLab software). For this calculation, the material was approximated as homogeneous chromium oxide Cr_2O_3. Given the sputter parameters, the sputter rate is estimated around 1.6 nm/s.

Mass spectra were recorded in positive polarity for each sample from an analysis area of 100 µm × 100 µm centred into a 300 µm × 300 µm sputtered area. Charging effects, due to analysis and sputtering ion beam, were compensated using low energy electrons