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Further insights into the mechanisms involved in the corrosion of 316L(N) austenitic steel in oxygenated liquid sodium at 550 °C

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22 Abstract

23 316L(N) austenitic steel was corroded at 550 °C in liquid sodium containing ca. 200 µg g⁻¹ dissolved 24 oxygen from 242 h to 7704 h. NaCrO₂ is formed for all immersion times, O and Na from liquid metal 25 and Cr from steel. The oxidation front is located at the chromite / steel interface and in the steel grain 26 boundaries. M₆C carbides (M = Mo and Fe) are also formed, C from liquid sodium. NaCrO₂ is dissolved 27 until the saturation of liquid sodium in Cr is reached. The Cr solubility is higher than that of pure Cr due 28 to the presence of dissolved oxygen. 29

30 Keywords

- 31 A. Stainless steel;
- 32 C. High temperature corrosion; interfaces; oxidation;
- 33
- 34

35 1. Introduction

Liquid sodium was chosen as the reference heat transfer fluid for the 4th generation of French nuclear 36 37 reactors because of its neutron and thermal properties, its excellent flow properties (low viscosity and 38 low density) and its compatibility with structural materials at high temperatures [1]. The temperature of 39 the reactor structure ranges from 400 °C to at least 550 °C with a low dissolved oxygen content (< 10 µg g⁻¹) under normal operating conditions. Although corrosion phenomena have limited effects under 40 41 these operating conditions, they must be well identified and predicted to ensure the service lifetime of 42 reactor structures. Indeed, some components such as the reactor vessel cannot be replaced and determine 43 the overall service lifetime of the reactor unit. The nominal lifetime is 60 years [2]. Similar corrosion 44 phenomena are expected for the fuel cladding operating at higher temperatures (650 °C at least) or for 45 the receivers in concentrated solar power plants (700 °C) [3]. 46 The reference material for structures in contact with liquid sodium is the low carbon nitrogen-enriched

47 austenitic steel of the grade 316L(N) (18Cr-12Ni-2Mo) [4]. Liquid sodium corrosion of austenitic steels
48 has been extensively studied but until now these studies have not been critically reviewed. That is why
49 we started our study with a state of the art on liquid sodium corrosion.

50 Liquid sodium corrosion of austenitic steels includes the following two phenomena: 1) dissolution of 51 alloying elements (section 1.1) and 2) chemical reactions with impurities, such as oxidation (section 1.2) 52 and carburisation [5,6].

53

54 **1.1. Dissolution of alloying elements**

55 The dissolution of alloying elements in liquid sodium has been extensively studied in sodium loop 56 systems made of austenitic steel [7-14]. In these systems, the dissolved oxygen content was maintained at less than about 10 μ g g⁻¹ through a continuous purification unit. The sodium loop is divided into the 57 58 high temperature section, heat exchanger units and low temperature section. Chemistry control was 59 achieved by bypassing a fraction of the main flowrate to heterogeneous crystallisation units maintained 60 at low temperature, near the melting point, known as cold traps. These units are capable of reducing the 61 hydrogen and oxygen content to levels down to their solubility limits at 110 °C, while maintaining the 62 amount of alloying elements dissolved from the structural components at a constant level [15]. As the 63 solubility of alloying elements increases with temperature, mass transfer can occur from the hot section 64 where dissolution takes place to the cold section where precipitation of corrosion products takes place, 65 including those activated under the neutron flux (Co-60, Mn-54) leading to component contamination 66 [16]. Usually, the specimen to be investigated for corrosion was placed at the inlet of the hot isothermal 67 section, or downstream, provided that a specific correction was applied to take into account the alloying 68 elements into liquid sodium that reduces the dissolution rate [10,11].

69 1.1.1. Empirical dissolution laws (dissolved $O < 10 \ \mu g \ g^{-1}$)

70 After the dissolution or reduction of the native oxides, leading to wetting, a first step of corrosion begins, 71 the initial corrosion. Since some alloying elements, such as nickel, have a higher solubility than others, 72 selective leaching occurs, depending on temperature, hydrodynamics and oxygen content, first removing 73 nickel and then chromium and manganese. The result is a surface layer depleted in austenite stabilisers. 74 Under certain conditions (e.g., high temperature, degree of depletion), a ferrite layer composed mainly 75 of iron (> 95 wt.%) of a few µm thick is observed [6,8-14,16]. Liquid metal penetrations within some 76 grain boundaries are also observed [11,14], as well as a depleted austenitic layer below. Corrosion 77 kinetics appear to be high at first and decrease over time to a constant steady-state corrosion rate [6], 78 reflecting the change from a power law to linear kinetics.

A total mass loss, Δm (in mg dm⁻²) after 1 year of corrosion (during the initial step) can be calculated by the following empirical relation for this steel grade [16]:

81
$$\Delta m = 7.8 \cdot V_{Na}^{0.435} \cdot w_{0,ppm}^{Na} \cdot \exp\left(-\frac{150.5}{\theta - 544}\right)$$
 Eq. (1.1)

where V_{Na} is the sodium velocity (in m s⁻¹), $w_{0,ppm}^{Na}$ is the oxygen concentration of sodium (in µg g⁻¹) and θ is the temperature (in °C). θ is between 544 and 720 °C. This mass loss is significant only above 544 °C. The mass loss amounts to 641 mg dm⁻² for 7.6 m s⁻¹, 600 °C and 5 µg g⁻¹ of oxygen. It corresponds to a dissolution thickness of 8 µm, assuming that the dissolution is uniform and neglecting the degraded surface layer composed of ferrite and depleted austenite, thus underestimating slightly the actual corrosion affected thickness. During steady-state corrosion, generally for an immersion time of more than several thousand hours [16], the ferrite layer initially formed on stainless steels is homogeneously dissolved [6]. The thickness or the mass loss are computed by two types of empirical models.

- 91 The first one takes into account the effect of oxygen concentration $(w_{0,ppm}^{Na}, \text{ in } \mu \text{g s}^{-1})$ and temperature
- 92 (*T* in K), as proposed in Eq. 1.2 [9,13,17-21]:

93
$$\log R_c = A_c + 1.5 \cdot \log w_{0,ppm}^{Na} - \frac{Q_c}{\ln 10 \cdot RT}$$
 Eq. (1.2)

94 where R_c is the corrosion rate (in μ m year⁻¹), A_c is a constant equal to 3.85 according to Thorley and 95 Tyzack for a Na velocity of 7.6 m s⁻¹ and an oxygen content between 5 and 200 μ g g⁻¹ [13] (these values 96 show some dispersions in the recent literature, probably due to some conversion errors), Q_c is an 97 activation energy (in J mol⁻¹ K⁻¹, usually $Q_c = 75,000$ J mol⁻¹ K⁻¹) and R is the gas constant (R = 8.31498 J mol⁻¹ K⁻¹). For comparison, the thickness dissolved amounts to 2.6 μ m year⁻¹ (201 mg dm⁻²) for 600 99 °C and 5 μ g g⁻¹ of oxygen.

100 The second type of model takes into account two different corrosion mechanisms: (i) dissolution 101 depending on temperature only and (ii) reactions with oxygen depending on oxygen concentration and 102 temperature [19]:

103
$$R_m = A_m \cdot \exp\left(-\frac{Q_{m_1}}{RT}\right) + B_m \cdot w_{O,ppm}^{Na} \cdot \exp\left(-\frac{Q_{m_2}}{RT}\right) \qquad \text{Eq. (1.3)}$$

where R_m is the mass loss rate (in mg cm⁻² year⁻¹), A_m and B_m are constants ($A_m = 1.2 \cdot 10^{11}$ mg cm⁻² year⁻¹, $B_m = 3.8 \cdot 10^2$ mg cm⁻² year⁻¹), Q_{m_1} and Q_{m_2} are activation energies ($Q_{m_1} = 203,000$ J mol⁻¹ K⁻¹) $P_{m_2} = 58,600$ J mol⁻¹ K⁻¹). Brissonneau [16] reports that the first term of Eq. 1.3 should be related to the preferential dissolution of Ni while the second term should be related to generalized corrosion. For comparison, the thickness of dissolved steel amounts to 0.85 µm year⁻¹ (68 mg dm⁻²) for 600 °C and 5 µg g⁻¹ of oxygen.

In conclusion, whatever the corrosion step (initial or steady-state) and the empirical model considered, the assessments of corrosion remain in the same order of magnitude and dissolved oxygen appears to be one of the most important parameters of corrosion kinetics, even if its influence on dissolution is far from obvious.

115 **1.1.2.** Oxygen effects on dissolution (dissolved $O < 10 \ \mu g \ g^{-1}$)

As shown in Section 1.1.1, the initial and steady-state corrosion rates of alloys depend on dissolved oxygen. In general, the higher the oxygen concentration, the higher the corrosion rate (Eqs. 1.1, 1.2 and 1.3), with even a change from uniform to intergranular attack [22]. This is why in all systems containing liquid sodium, dissolved oxygen is kept as low as possible. In general, the proposed corrosion rate depends on the oxygen concentration according to a *n* power law, where *n* is 2 for pure iron, 1 for pure chromium and 0 for pure nickel [6,11-13]. Only pure nickel (which does not form stable oxygen compounds in liquid sodium) exhibits an oxygen-independent corrosion rate.

123 The solubility of iron appears to increase with dissolved oxygen content, resulting in a dissolution rate 124 that increases as dissolved oxygen content increases [1,9,23,24]. No oxygen and iron compounds are 125 expected to be stable in liquid sodium containing less than 10 μ g g⁻¹ of dissolved oxygen and at 126 temperatures less than or equal to 550 °C. However, a Na-Fe-O complex may be formed that would 127 explain the experimental observations [9]. A Na-Cr-O complex could also be formed [25], although 128 sodium chromite (NaCrO₂) is stable in this case, i.e, for a few μ g g⁻¹ of oxygen at 550 °C [26].

Finally, it was deduced from the overall results presented in Section 1.1 that the global dissolution kinetics is related only to the iron dissolution rate [8,9]. The potential influence of chromium dissolution on the steady-state dissolution has been ruled out, either because of its low solubility relative to iron solubility [23,24], or because of the fast sodium saturation in chromium due to the high ratio of sample surface area to sodium volume [25].

134 **1.2.** Oxidation in liquid sodium containing oxygen (dissolved $O > 10 \ \mu g \ g^{-1}$)

135 **1.2.1. Homogeneous oxidation**

In addition to increasing the dissolution rate of iron, dissolved oxygen can be responsible for a change in the corrosion mechanism: from dissolution to oxidation. Indeed, the formation of sodium chromite (NaCrO₂) has been reported by several authors [27-29], particularly for oxygen concentrations higher than ~15 μ g g⁻¹ [14,30,31]. Scanning electron microscope (SEM) observations of the oxidized surfaces indicate the formation of tetragonal crystals [14,32,33]. NaCrO₂ was characterised by X-ray Diffraction (XRD) on ferrous alloys [31] and austenitic steels [14,30,33]. In each observation, a preferential crystallographic orientation is reported along the [0001] axis. The oxide growth kinetic was measured at 600 and 675 °C using the [0003] XRD peak intensity [30]. The oxide growth kinetic appears as
parabolic with time (Eq. 1.4):

145
$$I_{XRD} = \sqrt{k_p \cdot t}$$
 Eq. (1.4)

where I_{XRD} is the [0003] XRD peak intensity (without unit), k_p is the parabolic constant of oxide growth (in s⁻¹) and t is time (in s). The parabolic constant equals to 5.10^{-3} h⁻¹ at 600 °C and ~ 2.10^{-2} h⁻¹ at 675 °C for 23 µg g⁻¹ of dissolved oxygen. The activation energy can be deduced by assuming an Arrhenius law of k_p as a function of temperature (Eq. 1.5).

150
$$k_p = k_{p_0} \cdot \exp\left(-\frac{Q_{k_p}}{RT}\right)$$
 Eq. (1.5)

where k_{p_0} is a pre-exponential coefficient, Q_{k_p} is the activation energy of the parabolic constant of oxide growth (order of magnitude 150,000 J mol⁻¹ [30]), *R* is the gas constant (R = 8.314 J mol⁻¹ K⁻¹) and *T* is the temperature (in K).

154 **1.2.2. Local corrosion and oxidation**

155 The formation of the NaCrO₂ oxide surface layer is not uniform. Pits are observed on the surface of 156 ferritic-martensitic steels [34,35] and intergranular corrosion is reported for ferritic-martensitic steels 157 [27,34-36] and austenitic steels at 650 °C [33] and 700 °C [37]. After 3100 h in flowing sodium at 710 °C containing 30 µg g⁻¹ of oxygen and after 2500 h in flowing sodium at 300 °C containing 8,000 µg g⁻¹ 158 159 ¹ of oxygen, i.e in oxygen saturated sodium, intergranular corrosion was observed for 304L steel over 160 an extent of 40 µm [22]. Cavities are also observed on ferritic-martensitic steels [34-36] and austenitic 161 steels [33] immersed in liquid sodium containing oxygen at 650 °C. At 550 °C, local corrosion is not observed for ferritic-martensitic steels immersed in liquid sodium containing 1 µg g⁻¹ of oxygen [36]. 162

163 **1.2.3. Chromium depletion**

Dissolved oxygen would also decrease the chromium composition of the steel surface layer [29,30,33-36]. Our previous results [33] show that the oxidation of chromium into sodium chromite is the driving force behind the diffusion of chromium to the steel surface. Cr depletion increases with time and temperature. In the case of austenitic steels, Cavell and Nicholas noted that the values of the activation energies of the parabolic constant of oxide growth and the diffusion of chromium in the grain boundaries are close [30]. Consequently, they concluded that the chromium diffusion in the grain boundaries could control the corrosion kinetics in sodium containing oxygen and then be the rate limiting step [30]. This hypothesis would be consistent with our team's previous observations on local chromium depletion around grain boundaries for the same grade of steel exposed under the same conditions except for the higher temperature (650 °C) in liquid sodium containing about 200 μ g g⁻¹ of dissolved oxygen [33].

174 **1.3. Summary and description of our experiments**

175 To conclude this short review, stainless steels and ferritic-martensitic steels are dissolved in liquid 176 sodium containing little oxygen. As oxygen concentration increases, the dissolution of iron and 177 chromium is enhanced by the formation of Na-Fe-O and Na-Cr-O complexes. These complexes increase 178 the corresponding solubility in liquid sodium. The formation of a soluble Na-Cr-O compound is a 179 hypothesis first proposed by Kolster and Bos [25]. For a slightly higher oxygen content, oxidation of 180 chromium into stable sodium chromite becomes possible. Previous literature has presented sometimes 181 contradictory observations on the actual formation of sodium chromite. The differences could be due to 182 competition from different mechanisms involved in such a system, or because of the somewhat different 183 operating conditions under which the tests were performed, or even the method applied to the storage 184 of specimens after the sodium tests. To our knowledge, there is no literature evidence of an observation 185 of NaCrO₂ oxide at the smallest scale currently available, nor of the observation of the dissolved Na-Cr-186 O complex, nor of any relation between the Na-Cr-O complex and the NaCrO₂ oxide potentially 187 dissolved in the liquid sodium. The equilibrium concentration of Cr into sodium with steels is of the 188 highest importance on the Cr dissolution kinetics because small variations in equilibrium concentration 189 greatly change the modelled kinetics [38].

One of the conclusions of this review is that the role of chromium in the corrosion of austenitic steels and its solubility in liquid sodium are not yet well understood. Our main objective is to study the formation of sodium chromite on austenitic steels and its dissolution in liquid sodium.

193 In particular, the role of Na-Cr-O complex will be evaluated.

To this end, corrosion tests in liquid sodium were carried out under conditions that promote the formation of sodium chromite and its dissolution. The ratio between the surface area of the specimens and the sodium volume is low, which avoids saturating the liquid metal with Cr too quickly. In addition, the test temperature was chosen at 550 °C to limit the iron dissolution, which would otherwise be too

- 198 severe to focus solely on the Cr oxidation [33]. The corrosion of 316L(N) austenitic steel was then
- 199 investigated at 550 °C in liquid sodium containing 200 μ g g⁻¹ of dissolved oxygen for duration ranging
- 200 from 242 h to 7704 h.

202 2. Materials, device, conditions and characterisation methods

203 2.1. Materials

204 In the study presented here, the corrosion tests were performed on 316L(N) stainless steel provided by 205 Industeel France. Table 1 gives its composition, measured by glow discharge optical emission 206 spectroscopy (GDOES) for carbon and inductively coupled plasma atomic emission spectroscopy (ICP-207 AES) for the other elements. The sample size was 30 x 20 x 1.5 mm³ and the grain size was 41 \pm 2 μ m 208 [33]. Before immersion in liquid sodium, all specimens were mechanically polished, the last step using a 1 μ m diamond suspension (average roughness obtained $Ra < 0.1 \mu$ m, Bruker Contour GT 209 210 interferometer). The influence of surface roughness was not studied because a previous study showed 211 that it had no effect on oxidation results [33].

The sodium used for the corrosion tests was supplied by Métaux spéciaux S.A. Sodium is 99.95 wt.% pure, containing $[Ca] < 2 \ \mu g \ g^{-1}$, $[Cl] = 4 \ \mu g \ g^{-1}$, $[Fe] = 1 \ \mu g \ g^{-1}$, $[K] = 4 \ \mu g \ g^{-1}$. It also contains C [33] and is initially covered with a thick sodium oxide layer. This layer is manually removed inside a glovebox filled with argon before the first melt.

216 **2.2. Corrosion test device**

217 The corrosion tests were performed in a static sodium device [33,39-41]. The stainless steel samples are 218 immersed in sodium (approximately 2.3 kg), contained in a molybdenum crucible. This crucible is 219 placed in a heat sink, the upper part of which opens inside a glovebox filled with purified argon. Sodium 220 is purified from its dissolved oxygen, first by removal of the floating oxides and then by hot trapping 221 [33]. Hot trapping consists of immersing a zirconium foil (200 x 300 x 0.1 mm) at 650 °C for 3 days. 222 The oxygen concentration is then estimated to be less than 1 μ g g⁻¹ [33]. Although this last purification 223 step is known to remove dissolved carbon from sodium, previous tests have indicated that the dissolved 224 carbon concentration remains high enough to cause the steel samples to carburize [33,39].

After purification, a precise amount of oxygen is added inside the liquid sodium by two methods. Either sodium oxide powder ($Na_2O + 14.1$ wt.% Na_2O_2 , provided by Alfa Aesar) is dissolved in molten sodium and the oxygen concentration is estimated assuming that the initial oxygen concentration in the liquid sodium is equal to zero and that Na_2O and Na_2O_2 are completely dissolved in liquid Na. Or an argonoxygen gas mixture is added by bubbling. For this second method, the volume of oxygen gas added is estimated from the measurement of the pressure variation in the Ar-O₂ bottle and the oxygen concentration in liquid sodium is estimated assuming total oxygen absorption (this is confirmed by measuring the partial oxygen pressure at the gas outlet). Uncertainties in the final oxygen concentration in sodium is related either to the uncertainty of the sodium oxide weight or to the measurement of the pressure variation of the bottle used for bubbling. Further details on the experimental setup are described elsewhere [33]. Oxygen concentrations were measured by using the hot trap purification method, by using the weight increase of the Zr foil that confirm the oxygen assessment within 20 %.

237 2.3. Operating conditions

The corrosion tests were performed at 550 °C with three different liquid sodium melts containing approximately 200 μ g g⁻¹ of oxygen. The objectives of the study were to investigate the influence of immersion time (section 2.3.1) and to identify the reaction interfaces (section 2.3.2).

241 **2.3.1. Influence of immersion time**

The oxygen content of the first liquid sodium bath was set at $198 \pm 8 \ \mu g \ g^{-1}$ by dissolving the correct 242 243 amount of sodium oxide powder. Nine immersion times were chosen, namely 242, 584, 1276, 1924, 244 2395, 2830, 3842, 5304 and 7704 h, corresponding to nine samples. First, all nine samples were 245 immersed simultaneously in liquid sodium at 120 °C. Then, the sodium was heated to 550 °C at about 246 10 °C min⁻¹. After 242 h, the furnace was switched off, resulting in a temperature drop of 0.7 °C min⁻¹. 247 When the temperature reached 120°C, the first sample was taken out of liquid sodium. The exposure 248 time, 242 h for the first sample, is estimated from the moment when the temperature exceeds 97% of 249 the set temperature (i.e., 533 °C for a set temperature of 550°C). The furnace temperature is then raised 250 to 550°C to continue sodium corrosion of the remaining eight samples. To facilitate sample handling, all samples are removed one after the other from the liquid sodium at 120 °C. This means that the n^{th} 251 252 sample (1 < n < 9) undergoes *n* temperature increases from 120°C to 550°C and *n* temperature decreases 253 from 550°C to 120°C. The exposure time is the cumulative time spent by the sample at temperatures 254 above 533°C.

In short, the samples undergo several cycles of temperature rise and fall. To validate this approach, the corrosion mechanisms obtained were compared to the mechanisms obtained for samples immersed in and removed from the bath at 550°C. For this, a second liquid sodium bath with an oxygen content of 258 $200 \pm 8 \ \mu g \ g^{-1}$ obtained by dissolving sodium oxide powder was used. Two samples were immersed for 259 242 and 584 h (in two periods of 242 and 342 h) with the same experimental protocol as previously 260 explained (including temperature rise and fall cycles). Two other samples were immersed in liquid 261 sodium at 550 °C. Both of them were removed from liquid sodium at 550°C as well, the first after 239 262 h and the second after 239 and 339 h, for a total immersion time of 578 h. The second sample was 263 immersed twice because the two samples were held onto the same Mo bar, allowing samples to be 264 immersed and removed at 550 °C.

265 2.3.2. Reaction interfaces

The third test is intended to further investigate the reaction mechanisms using oxygen isotopes ¹⁶O and ¹⁸O to locate the reaction interfaces. We have implemented the so-called double oxidation technique, often used to study the growth of oxide films at high temperature. The principle is to oxidize the metallic substrate first under ¹⁶O₂ atmosphere then under an enriched atmosphere in ¹⁸O [42-44]. To our knowledge, this is the first time this technique has been used in the field of liquid sodium corrosion.

271 The experimental protocol is divided into four steps:

272 • In the first step, four samples were immersed at 120 °C in oxygen-free liquid sodium after purification 273 by zirconium hot trapping. The sodium was heated to 400 °C. Then, a gas mixture of argon and natural oxygen (Eurisotop, 99.757 vol.% isotope of ¹⁶O and 0.205 vol.% of ¹⁸O, this ratio corresponds to the 274 275 natural abundance of each isotope) was bubbled for one hour to obtain an oxygen concentration of 200 276 $\pm 20 \,\mu g \, g^{-1}$. After bubbling, the ¹⁶O-containing sodium was heated to 550 °C in 3 hours. The four samples 277 were maintained at temperatures greater than 533°C for 500 h. Then, the sodium was cooled to 120 °C to remove the four samples from liquid Na. In short, these first four samples were corroded in ¹⁶O -278 279 containing sodium for 500 h.

• The sodium was again purified to an oxygen concentration of less than 1 μ g g⁻¹ by Zr hot trapping. A gas mixture of argon and oxygen tracer (95 vol.% of isotope ¹⁸O) was bubbled for one hour. The oxygen concentration obtained was approximately 250 μ g g⁻¹ ¹⁸O, which corresponds to an equivalent ¹⁶O concentration of 280 ± 20 μ g g⁻¹. The difference with the oxygen concentration in the other two sodium baths is due to the difficulty of controlling the introduction of a precise amount of oxygen from the gas bubbling. • Three of the first four samples were re-immersed in this molten Na bath. The sodium was heated to 550 °C and the samples were removed one by one after 100, 500 and 960 h total immersion time with the same experimental protocol as previously explained (including cycles of temperature rise to 550°C and fall down to 120°C). These three samples were then immersed for 500 h in ¹⁶O -containing sodium and then for 100, 500 and 960 h in ¹⁸O -containing sodium.

291 **2.4. Characterisation techniques**

After corrosion in liquid sodium, all samples were immersed in 99.9 wt.% pure ethanol (provided by Carlo Erba) at room temperature for one hour. Interaction with ethanol removes sodium residues from samples surface. The samples are then characterized by complementary techniques.

Specimens were weighed before and after the corrosion test (AT20 precision balance, Mettler Toledo). The phases formed during corrosion on the surface of the samples were characterised by X-Ray Diffraction (XRD, Bruker D8 discover) in the θ -2 θ configuration with a copper cathode emitting X-rays of wavelength $\lambda = 1.5406$ Å. Scanning Electron Microscopy (SEM, Zeiss LEO 1460VP) combined with Energy Dispersive X-ray spectroscopy (EDX, SAMX DXP-X10P) was used to observe and analyse the surfaces and polished cross-sections of the specimens. All samples were weighed and observed by SEM and most samples were characterised by XRD.

302 For experiments using oxygen isotopes, mean elementary depth profiles were obtained on a 4 mm 303 diameter disk from the sample surface using Glow Discharge Optical Emission Spectroscopy (GDOES, 304 GD-Profiler 2, Horiba Scientific) under the same conditions as those presented before [33]. Each 305 analysis with GDOES was repeated at least twice. A precise calibration procedure with a set of standards 306 makes it possible to convert the element intensities into compositions with a fairly high confidence for 307 most elements, with the exception of oxygen and sodium whose variations are only qualitative. 308 Elementary depth profiles were also obtained by Secondary Ion Mass Spectrometry (SIMS, IMS7f, 309 Cameca). The incident beam ions used were Cs^+ for oxygen isotope and O_2^+ for metallic elements. The 310 incident beam energy was 15 keV and the secondary ion beam energy 5 keV. Only negative ions were 311 analysed. The analysis were performed on a 150 µm square divided in 128 x 128 pixels. The depth of 312 the craters at the end of the GDOES and SIMS analysis was obtained using an optical interferometer 313 (Contour GT, Bruker). Only the samples obtained during the corrosion test using the oxygen isotopes

- 314 were characterised by SIMS and GDOES. Only one of these samples (1460 h of cumulated immersion
- 315 time) was also characterized by Transmission Electron Microscopy (TEM) in scanning mode. The
- 316 instrument (Tecnai Osiris TEM, FEI) is coupled with an EDX detector (ChemiSTEM EDX, FEI). The
- 317 sample was prepared by Focused Ion Beam (FIB, Strata 400S FIB, FEI).

319 **3.** Corrosion test results

The mass gain of samples immersed in liquid sodium containing 200 μ g g⁻¹ of oxygen at 550 °C is given as a function of immersion time in Figure 1. All samples show a mass gain. Up to 3842 h of immersion, the mass gain appears almost negligible, although positive, and limited to about 0.5 10⁻³ kg m⁻² (the mass gain measured for a sample is divided by its total surface area including the 2 faces and 4 edges). This result is remarkably reproducible for all three tests up to 1460 h of immersion in liquid sodium. After a transition between 3842 h and 5304 h, the mass gain increased significantly to 2.2 10⁻³ and 2.5 10⁻³ kg m⁻² for 5304 h and 7704 h of immersion respectively.

As explained in the experimental protocol (Section 2.3), most samples underwent several cycles of temperature rise and decrease to facilitate sample handling. The mass gain of two samples immersed in and removed from the bath at 550°C was measured (@ in Fig. 1). The results obtained are in very good agreement with the other samples, thus validating our protocol and excluding significant precipitation on the specimen during the cooling stage.

The expected corrosion mechanisms for stainless steel in liquid sodium are (1) dissolution which would result in mass loss and (2) penetration of the liquid metal into the micro-porosities, diffusion of oxygen and carbon to their solubility limits in the matrix and then nucleation and growth of oxides and carbides on the steel surface and subsurface, which result in mass increase. The large increase in mass gain after several thousand hours should be the result of a change in corrosion mechanisms. This is why we will focus first on the characterization of samples immersed during 242 h to 3842 h (Section 3.1) and then on samples immersed during 5304 and 7704 h (Section 3.2).

339 3.1. Immersion time less than 4000 h

For the samples immersed in liquid sodium containing 200 μ g g⁻¹ of oxygen at 550 °C for less than 4000

341 h, the mass gain is positive and low (Fig. 1). In most of the examples selected here, the results will be

342 presented for the sample immersed for 1460 h in the third liquid sodium bath (section 2.3). The results

for this immersion time are representative of all immersion times less than or equal to 3842 h.

344 3.1.1. Phases characterisation

345 The phases detected on austenitic steel in liquid sodium containing 200 µg g⁻¹ of oxygen at 550 °C are

346 identified by XRD. The diffraction pattern obtained for a 1460 h immersion time is plotted as the dark

347 line at the bottom of Fig. 2 and superimposed with the diffraction patterns of NaCrO₂ (PDF file # 00-

348 025-0819), austenite (PDF file # 031-0619) and Fe₃Mo₃C (PDF file # 00-047-1191).

- 349 The initial material corresponding to the austenite matrix is detected by the presence of the two most
- intense peaks (43.772°, 50.987°). The less intense peaks expected for austenite do not appear (24.858°,

351 35.438°, 57.531°).

- 352 Molybdenum-iron carbide (Fe₃Mo₃C) is identified by the following group of peaks, 35.087°, 39.598°,
- 42.112° and 46.047°, the less intense peaks (32.121°, 49.016°, 54.595°, 59.176°) being lost in the
- background noise. It should be noticed that all M₆C type carbides have about 3 Mo atoms and 3 M atoms
- which can be Cr, Mn, Fe and Ni in variable proportions. The best fit was found for Mo₃Fe₃C.
- 356 The theoretical peaks of $NaCrO_2$ are also plotted on the diffractogram, as they can correspond to the
- broadened peaks observed at 16.7° and 21.3°. The [0003] plane of NaCrO₂ should present a diffraction
- peak at 16.651°. However, the parallel cristallographic plane [0006] expected at 33.64° is not present,
- 359 nor are the other cristallographic planes (35.279°, 36.635°, 41.705°, 45.187°, 53.649°, 58.438°).
- 360 Crystallized NaCrO₂ is therefore not clearly characterised even if small amounts of an amorphous phase
- 361 (large peaks between 15 and 25°) could correspond to sodium chromite.
- 362 **3.1.2. External oxidation and carburization**

After corrosion in liquid sodium containing 200 μ g g⁻¹ of oxygen, the steel surfaces are characterised by 363 364 SEM. The backscattered electron images obtained at two different locations are shown in Fig. 3 for the 365 sample immersed for 1460 h. The contrast differences of these images give information about the 366 chemical composition of the phases (the brighter a zone appears, the higher its atomic number). The 367 steel surface is covered with dark grey particles about 200 nm in diameter. Their surface density varies 368 from place to place, possibly in relation to the orientation of the underlying austenite grains, forming 369 either discrete particles (Fig. 3a) or a continuous layer (Fig. 3b). The steel surface can be seen in light 370 grey between these dark grey particles (example of black arrow, Fig. 3a). White particles of about 1 µm 371 in diameter are also observed.

372 Chemical analysis were performed by EDS in the square area of Fig. 3b. Elementary maps of oxygen,

- 373 sodium, chromium, iron, nickel and molybdenum are given in Figs. 4a, b, c, d, e and f respectively.
- 374 Areas with a high concentration of the element appear in white. The layer of small particles 200 nm in

diameter contains O, Na and Cr (Figs. 4a, b and c). The white particles, shown in Fig. 3, are rich in
molybdenum (Fig. 4-f) and do not contained O, Na and Cr. Fe and Ni are detected almost everywhere
and correspond mainly to the steel matrix (Figs. 4d and e). The iron composition is higher in areas where
O, Na and Cr compositions are weak (top right for example), probably because the layer of corrosion
products is thinner.

Based on the results of these characterizations, the steel is coated with a thin, non-homogeneous corrosion layer, resulting in the low measured mass gain (Fig. 1). This layer contains sodium chromite in the form of dark grey particles 200 nm in diameter as can be deduced from their composition and shape [14,33]. White particles 1 μ m in diameter should correspond to M₆C carbide, characterised by XRD, since they are rich in Mo and C cannot be detected by EDX in our conditions.

To complete the surface characterisations, various techniques were used to measure the chemical evolution of the material under its surface: (1) mean composition as a function of the distance to the surface by GDOES (sections 3.1.3 and 3.1.4), (2) fine characterization of the Cr content around a grain boundary by TEM/EDX on a thin cross section extracted by FIB technique (3.1.4) and (3) position of the reaction interface by SIMS based on the analysis of ¹⁸O tracers (3.1.5).

390 **3.1.3. Internal oxidation and carburization**

Figure 5 shows the compositions of C, O, Na, Cr, Mn, Fe, Ni and Mo in log-scale as a function of sputtered depth from the steel surface up to 5 μ m depth, where the composition corresponds to the initial steel composition. The example chosen corresponds to the sample immersed for 1460 h at 550 °C in liquid sodium with an oxygen content of 200 μ g g⁻¹.

395 At the steel surface, the average composition is enriched in O, Na and Cr in a 0.75 µm-thick layer. For 396 the first 0.4 μ m, the sodium content exceeds 40 at.% while the oxygen content is steadily decreasing. 397 The chromium composition increases from the steel surface to 0.15 μ m, decreases from 0.15 μ m to 0.75 398 µm where it presents a local minimum. This surface layer rich in O, Na and Cr corresponds to the sodium 399 chromite zone. In this zone, the molybdenum content increases to a maximum located at a depth of 0.19400 μ m, while carbon presents a high content that decreases from the surface to 1 μ m. At this depth, a change 401 in slope of the C concentration profile is noticed and the Mo content reaches its bulk content. This 402 surface layer, enriched with Mo and C, should correspond to the zone where M₆C carbides are formed.

403 Iron and nickel compositions are steadily increasing from the steel surface, probably due to the 404 inhomogeneity of the corrosion zone and the roughness of the interface. It should be noticed that 405 chromium depletion is greater and deeper than iron depletion and that iron depletion is greater than 406 nickel depletion (this is clearly highlighted with the Fe/Ni ratio, not shown here). One corrosion 407 mechanism proposed in the literature is the preferential dissolution of nickel [1,6,8]. This is probably 408 not the case under our corrosion conditions, since, if nickel were preferentially leached from austenite, 409 Ni depletion would have been higher than that of Fe. In addition, it can be noted that the depletion in Cr 410 composition from 1 to 2.5 µm from the steel surface corresponds to the second peak of the sodium 411 profile. This second sodium peak could correspond to internal oxides formed at the grain boundaries (as 412 was the case at 650 °C [33], which shows significant similarities in the element profiles measured).

Finally, the corrosion zone consists of two parts: a surface layer composed of sodium chromite and carbides and a corrosion affected zone composed of austenite depleted in Cr. For this last reason, the role of Cr was further investigated and the results are presented in Section 3.1.4.

416 **3.1.4. Role of Cr**

417 In-depth characterization of the average Cr content of corroded steel

418 In order to evaluate the influence of the immersion time on the Cr depletion, three Cr concentration 419 profiles are plotted in Fig. 6 for 500, 1000 and 1460 h of immersion time. For the sake of comparison, 420 the interface between the corrosion zone (sodium chromite) and the steel matrix is chosen to be the 421 origin of the x-axis and is assumed to be located at the minimum chromium composition (1000 or 1460 422 h) or at a slope change in the Cr profile (500 h). With this procedure, negative depths (x < 0) correspond 423 to the zone where $NaCrO_2$ is formed. The extent of this corrosion zone increases slightly with exposure 424 time: 0.35, 0.43 and 0.67 μ m for respectively 500 h, 1000 h and 1460 h. At the same time, the extent of 425 the austenite zone depleted in Cr also increases. The low mass gain of the sample observed at the 426 beginning of the test corresponds to the formation of a thin layer of sodium chromite associated with the 427 chromium depletion zone.

- 428 Chemical composition in Cr around a grain boundary
- 429 A thin foil from a cross-section of the sample immersed for 1460 h at 550 °C in liquid sodium with 200
- 430 $\mu g g^{-1}$ of oxygen was obtained by FIB and observed by STEM in order to accurately characterise

chemical variations around the grain boundary. Fig. 7 gives a large field of view of the sample and the
inset image provides a larger magnification of the grain boundary emerging at the steel surface. Fig. 8
shows the elementary cartography of the enlarged zone for O, Na, Cr, Fe, Ni and Mo.

434 In order to protect the sample during the shaping of the thin foil, a layer of tungsten was deposited on 435 the surface exposed to sodium (at the top of the image, Fig. 7). Under the protective tungsten layer, a 436 thin layer of faceted particles (300 nm) is observed on the surface of the grains. Some of these particles 437 are darker than the alloy, others lighter. According to the elementary maps (Fig. 8), the dark particles 438 contain O, Na and Cr. The clear particles contain Fe and Mo. They correspond respectively to NaCrO₂ 439 in the form of a thin and non-homogeneous layer on the surface of the sample and to M_6C particles 440 (since they may contain Fe [33]). It is also noted that above the particle of M_6C , enrichments in O, Na 441 and Fe are detected: no candidate other than the Na₄FeO₃ ternary oxide can be proposed, although it 442 should not be stable in the test conditions.

443 One of the M_6C particles is located at the top of the grain boundary on the sample surface. Along the 444 grain boundary and below the surface, we see a first phase rich in Mo and Fe and then a large phase rich 445 in O, Na and Cr (300 nm wide, 1 µm long), which corresponds to an internal NaCrO₂ oxide. The NaCrO₂ 446 particle presents slip bands, cracks and cavities that were filled with sodium during immersion in liquid 447 sodium. Further below the enlarged area, a black area 0.5 µm long contains Si and O (indicated by an 448 EDS point analysis not shown here) that may correspond to silicon oxide (SiO₂), indicating that internal 449 oxidation may occur. This issue will not be discussed further. Further down the grain boundary, small 450 clear particles, corresponding to carbides, are observed, but their precise chemical characterizations has 451 not been possible. Finally, the grain boundary ends with a triple grain boundary at a depth of 16.3 μm. 452 It can be noted that these observations, although local, are consistent with the GDOES mean 453 measurement (Figs. 5 and 6) as well as with the SEM observations (Fig. 3). Indeed, the surface corrosion 454 layer containing chromite and carbides presents a thickness of 300 nm in accordance with the 200 nm 455 crystallites observed with SEM. The area affected by corrosion below the surface layer corresponds to 456 grain boundaries that contain carbides and oxides to a depth of about 2 µm. This depth is in fairly good 457 agreement with the GDOES mean measurement of 2.5 µm for the Cr depleted zone.

458 In order to accurately quantify the extent of chromium depletion along this specific grain boundary, 459 several chromium EDX profiles were measured at different locations shown by the arrows in Fig. 7. 460 Profiles 1, 2, 3 and 4 were measured in the direction perpendicular to the grain boundary, at an increasing 461 distance from the sample surface of 0.52, 4.26, 7.67 and 12.79 µm respectively. The chromium profiles 462 obtained, expressed in at.%, are plotted in Fig. 9. The origin of the abscissa corresponds to the grain 463 boundary position. Cr profiles close to the sample surface exhibit a higher chromium depletion 464 compared to profiles located at a greater distance. The chromium composition is always minimal at the 465 grain boundary. This minimum gradually increases from 2.7 at.% close to the sample surface to 7 at.% 466 and 10.5 at% deeper. The Cr depletion in profile 1 appears to be asymmetric: it extends over 75 nm from 467 the left grain boundary while the depletion of the right grain extends up to 440 nm. These observations 468 are reproduced on profiles 2 and 3 with shorter depletion distances and higher minimum compositions. 469 On profile 4, the asymmetry is no longer visible. Depletion along the grain boundary and asymmetry 470 between the grains are typical of the consumption of an element diffusing to the interface. Diffusion in 471 grain boundaries is faster than volume diffusion, because the grain boundaries present a higher degree 472 of disorder [45]. Similarly, the asymmetry may be explained by the fact that the bulk diffusion 473 coefficient depends on grain orientation or other mechanisms such as grain-boundary migration.

474 **3.1.5. Interface reaction**

475 In order to study the oxidation mechanism, the oxygen tracer technique was used in the third test (section 476 2.3.2). For this test, oxygen was added to the liquid sodium by bubbling a gas either composed mainly of ¹⁶O (99.757 vol.%) and 0.205 vol.% of ¹⁸O or composed of 95 vol.% of the stable isotope ¹⁸O. Three 477 478 samples were successively immersed in liquid sodium containing 200 μ g g^{-1 16}O for 500 h, then in liquid sodium containing 250 µg.g^{-1 18}O (corresponding to 280 µg g^{-1 16}O) for 100, 500 and 960 h. A fourth 479 sample that has only been immersed for 500 hours in liquid sodium containing 200 μ g g⁻¹¹⁶O is used as 480 481 a reference. The SIMS technique using mass spectroscopy makes it possible to differentiate the ¹⁶O and 482 ¹⁸O signals. In addition, it provides the intensities of the detected elements in all three directions of 483 space, allowing isotope mapping as a function of sputtered depths.

484 Fig. 10 provides cartographies of the relative intensities of ¹⁸O (Fig. 10, top) and ¹⁶O (Fig. 10, bottom)

485 at several depths from the sample surface. The chosen example was obtained for an immersion time of

486 1460 h (the same results were obtained for the lower immersion times studied). The cartographies are 487 squares 150 µm wide, composed of 128 pixels in each direction. In Fig. 10, at 0.02 µm depth, near the surface, the ¹⁸O signal is high, implying that the surface is covered with oxide, some areas had a weak 488 489 18 O signal, such as the upper left corner which appears free of oxide. At 0.6 µm below the surface, 490 heterogeneities of oxide thickness appear: some areas are covered with oxide while others are not. At 491 depth, the free oxide zones extend and delimit the alloy grain boundaries (1.4 µm deep). The evolution 492 of the ¹⁶O concentration as a function of depth is identical. It seems that the concentration of ¹⁸O is higher than that of 16 O at a depth of 1.4 µm. 493

494 In Fig. 10, two square areas (20 µm x 20 µm) are visible, one above one grain and the other including a grain boundary. For each of these square areas, the ¹⁶O and ¹⁸O concentration profiles were measured as 495 496 a function of corrosion time. Fig. 11 presents the results obtained in the grains (left column, Fig. 11a, 497 11c and 11e) and at the grain boundaries (right column, Fig. 11b, 11d and 11f) for 600 h (Fig. 11a and 498 11b), 1000 h (Fig. 11c and 11d) and 1460 h (Fig. 11e and 11f). The oxygen profiles are compared with the ¹⁶O profile obtained in the first corrosion step (500 h in ¹⁶O containing liquid sodium, black dotted 499 line). For each corrosion time, the oxygen (¹⁶O and ¹⁸O) concentration and oxidation depth are higher in 500 the grain boundaries than in the grains. The ¹⁸O concentration increases with corrosion time both in the 501 grains and at the grain boundaries. The ¹⁶O concentration is of the same order of magnitude as that 502 503 obtained for the reference case but it seems to increase slightly with corrosion time. As the second 504 corrosion step involves only ¹⁸O, this increase is probably due to a slight progressive pollution of liquid Na in ¹⁶O. 505

506 From the measurements of 16 O and 18 O, the relative abundance of 18 O can be calculated as a function of depth from the surface (Fig. 12). The relative abundance of ¹⁸O is calculated as the ratio of the intensity 507 of ¹⁸O signal I(¹⁸O) to the sum of the intensities of the ¹⁶O and ¹⁸O signals I(¹⁸O) + I(¹⁶O). The same 508 509 measurements were performed at the different immersion times (600, 1000 and 1460 h). Fig. 12 shows 510 the relative abundance profile of 18 O from the surface to 2.5 μ m deep in a grain (Fig. 12a) and on a grain 511 boundary (Fig. 12b). As the intensities of the measured signals decrease with depth, the ends of the 512 relative abundance profiles are noisy. In the grain (Fig. 12a), depths between 0 and 0.1 µm are enriched in ¹⁸O. This peak in ¹⁸O abundance increases and widens with immersion time. Between 0.1 and 0.3 μ m 513

514 deep, the ¹⁸O abundance also increases with immersion time. For depths greater than 0.3 µm, the 515 intensity of the oxygen signals is too low, resulting in a noisy relative abundance profile. At the grain boundary (Fig. 12b), the ¹⁸O abundance profiles show a peak that extends to 0.3 µm and increases in 516 517 height with immersion time (as in the grain, Fig. 12a). From a depth of 0.5 µm, ¹⁸O becomes more and more abundant over time to a depth of 1.7 µm. As reminded above, the volume fraction of ¹⁸O compared 518 to ¹⁶O in the gas mixture was low (0.205 vol.%) during the first 500 h and then higher (100 vol.%). This 519 520 means that if the relative abundance of ¹⁸O is greater than 0.00205, the diffusion of ¹⁸O into the steel 521 occurred after the first 500 h of immersion in sodium. As shown in Fig. 12, the relative abundance of 522 ¹⁸O is greater than 0.00205 in both the grain and the grain boundary.

Most of the time, the double-oxidation technique is used to study the transport mechanism during the oxide scale growth at high temperature [42-44]. In our case, the oxide scale remained very thin for immersion times of less than 4000 h and the oxide was mainly located at the grain boundaries. This case is much less documented in the literature [46]. Two mechanisms determine the oxygen isotope distribution in the material, namely diffusion transport and oxygen isotope substitution in already formed oxide particles.

Fast oxygen diffusion along the austenite grain boundaries is clearly visible throughout the immersion period (Fig. 12b). Much of ¹⁸O passes through the region of the ¹⁶O-oxides previously formed along the grain boundaries that serve as fast oxygen transport channels through the internal precipitate zone, resulting in an increased amount of ¹⁸O-oxides near the oxidation front. This behavior has also been observed in the case of selective oxidation of model ternary iron-based alloys containing Mn and Al, Cr or Si at 700°C for 60 min in Ar / H₂ / H₂O gas mixture [46].

At the sample surface, a peak of ¹⁸O relative abundance can be observed. This could be explained by two mechanisms. For the first mechanism, when diffusing into the materials, ¹⁸O comes into contact with ¹⁶O-containing oxides. This could cause a tracer exchange and near the sample surface, the exchange time is longer, leading to a ¹⁸O maximum concentration. The ¹⁶O isotope would then be pushed further inside the steel giving the shape of the ¹⁶O profile measured after 1000 h of corrosion time (Figs. 11c to 11f). This interpretation should be taken with caution due to the slight ¹⁶O pollution mentioned above. The second mechanism involves the formation of a new oxide scale due to Cr diffusion to thesteel surface.

543 **3.2. Immersion time more than 5000 h**

544 The mass of samples immersed for 5304 and 7704 h increased 5 times more than that of samples

545 immersed for a shorter period of time (Fig. 1). The sharp increase in mass gain after several thousand

546 hours is the result of a change in corrosion mechanisms.

547 First, the XRD phase characterisation of the 5304 h immersed sample (blue line in Fig. 2) shows the

 $548 \qquad formation of M_6C \ as \ for \ shorter \ immersion \ times. \ In \ addition, \ NaCrO_2 \ diffraction \ peaks \ are \ also \ present$

549 at angles $2\theta = 16.651^{\circ}$, 33.64° , 35.279° , 36.635° , 41.705° , 53.649° and 58.438° . Two other peaks are

observed at $2\theta = 12.49$ and 22.68° , which could not been explained. This characterisation proves the

551 formation of crystallized NaCrO₂ after 5304 h of immersion in liquid sodium.

552 This is confirmed by the characterization of cross-section samples. For example, the cross-section of a sample immersed for 7704 h in liquid sodium containing 200 µg g⁻¹ of oxygen at 550°C is given in Fig. 553 554 13. It shows the secondary electron image of the cross-section and the elementary EDX mapping of O, 555 Na, Cr, Fe and Mo. At the top of Fig. 13a, the mounting resin appears in black, at the bottom stainless 556 steel appears in grey. At the interface, a dark grey phase and a light grey phase are visible. These two 557 phases extend to a depth of 4 μ m. According to the EDX analysis, the dark grey phase is NaCrO₂ and 558 the lighter phase is M₆C containing Mo and Fe. Compared to the results obtained after 1460 h of 559 immersion (Fig. 7), the corrosion products are thicker and continuous at longer immersion times: the 560 surface is covered by NaCrO₂ and M₆C.

562 4. Discussion on corrosion mechanisms in liquid sodium

563 4.1. Formation of sodium chromite

- 564 Two oxidation behaviours were observed with mass gain measurements (Fig. 1).
- 565 For short immersion times (less than 4000 h), a small mass increase is measured. SEM and TEM
- analyses show the formation of NaCrO₂ (Figs. 3, 4, 7 and 8): in this condition, NaCrO₂ is formed below
- the surface at the grain boundaries and a very thin and discontinuous layer probably forms on the steel
- 568 surface. X-ray diffraction does not detect it, probably because of the small amount formed (Fig. 2).
- 569 For longer immersion times (more than 4000 h), a larger mass increase is measured and NaCrO₂ is
- 570 detected by all characterisation methods.
- 571 Two hypotheses can be formulated and tested: NaCrO₂ is formed for all immersion times but, for the
- 572 short immersion times, it dissolves as it is formed.

573 4.1.1. Consistency of the NaCrO₂ formation hypothesis

- 574 Thermodynamic stability under the selected experimental conditions
- 575 Thermodynamic calculations of oxide stability in the same system as used here can be found in ref. [33]
- 576 (Ellingham diagram, Fig. 10 [33]). In particular, for the same austenitic steel, i. e. the same Cr activity,
- 577 it can be seen that NaCrO₂ is stable at a temperature above 350°C if the composition of the liquid sodium
- 578 in dissolved oxygen is of the order of 200 μ g g⁻¹ (precisely 189 μ g g⁻¹ in the publication). These
- 579 thermodynamic data therefore predict that NaCrO₂ can be formed on the austenitic steel considered here
- 580 in liquid sodium containing 200 μ g g⁻¹ of oxygen at 550°C.
- 581 Consistency with experimental results obtained at short immersion time
- For an immersion time of 3842 h or less, SEM observations show that NaCrO₂ forms a discontinuous layer of 200 nm large crystals (Fig. 3). For these immersion times, the mass gain of the samples varies little and is equal to $\Delta m_s = (2.0 \pm 0.3) 10^{-4}$ kg m⁻². Assuming that the mass variation of the samples is due only to the formation of NaCrO₂, the thickness of a continuous oxide layer corresponding to this mass gain can be calculated using Eq. 4.1.

587
$$e_{NaCr_{2}} = \frac{1}{\rho_{NaCro_{2}}} \Delta m_{s}$$
 Eq. (4.1)

where ρ_{NaCrO_2} is the sodium chromite density ($\rho_{NaC}_2 = 4,360 \text{ kg m}^{-3}$ [33]). A thickness of $e_{NaCrO_2} = 46 \pm 7 \text{ nm}$ is obtained. This calculation overestimates the continuous oxide layer thickness equivalent to the mass gain of the samples, since it does not take into account the M₆C formation which also contributes to the mass gain. In conclusion, the size of the crystals (200 nm) combined with their dispersion is consistent with the order of magnitude of the equivalent thickness of the oxide found.

593 4.1.2. Consistency of the NaCrO₂ dissolution hypothesis

As shown in Figs. 5 and 6, the austenitic steel is depleted in chromium below its surface: the surface oxide corresponds to the chromium peak associated with the high Na and O composition. As the distance to the surface increases, the Cr composition decreases until a minimum concentration, corresponding to the depletion zone, is reached and then increases to the bulk composition measured at 17 at.%. Consequently, the Cr concentration profiles obtained are compatible with Cr selective oxidation, i.e. the diffusion of Cr to the steel surface and its oxidation into NaCrO₂.

Using the shape of the concentration profiles obtained by GDOES and assuming that there is no receding of the interface, we can estimate the amount of Cr that has left the austenitic steel in this process. The measurements give the chromium composition in mole fraction (x_{Cr}) as a function of depth (z) from 0 (corresponding to the minimum Cr concentration) to ∞ (corresponding to the initial composition x_{Cr}^0) (Fig. 6). The total amount of Cr consumed in steel per unit area (mol m⁻²), $\frac{\Delta n_{Cr}}{s}$, can be calculated by Eq. 4.2:

606
$$\frac{\Delta n_{Cr}}{S} = \int_0^\infty \left(x_{Cr}^0 - x_{Cr}(z) \right) \frac{\rho(z)}{M(z)} dz$$
 Eq. (4.2)

where $\rho(z)$ is the density of the material at depth z and is given by GDOES, M(z) is the molar weight at depth z, such that $M(z) = \sum_i x_i(z) M_i$, where $x_i(z)$ is the mole fraction of element i at depth z and M_i is the molar mass of element i. In practice, $\rho(z)$ and M(z) are almost constant and equal to $\rho(z) =$ $(7.5 \pm 0.2) 10^3$ kg m⁻³ and $M(z) = (54 \pm 2) 10^{-3}$ kg mol⁻¹.

611 This amount of released Cr corresponds to an equivalent thickness of oxide that can be formed, given 612 by Eq. 4.3. It should be noted that, due to the increase in Cr depletion (Fig. 6), the thickness of the oxide 613 formed is expected to increase over time, which is contradicted by short-term mass gain measurements.

614
$$e_{NaCrO_2} = \frac{\Delta n_{Cr}}{S} \frac{M_{NaC_2}}{\rho_{NaCrO_2}}$$
Eq.(4.3)

615 where $M_{NaCrO_2} = 107 \ 10^{-3} \text{ kg mol}^{-1}$ is the molar weight of NaCrO₂.

616 The NaCrO₂ thickness calculated with Eq. 4.3, i.e. assuming that the Cr released from the steel is 617 completely oxidized into a compact NaCrO₂ layer, is between at least 138 nm for 242 h of immersion 618 in liquid sodium and 670 nm for 3842 h. The equivalent oxide thickness obtained by mass gain is $46 \pm$ 619 7 nm at most (section 4.1.1). Since the oxide thickness possibly formed by the Cr released from the steel 620 is greater than the measured oxide thickness, it can be concluded that only part of the chromium from 621 the steel reacted on the surface to form sodium chromite and that the remaining part of Cr was released 622 into the liquid sodium. As the Cr solubility in liquid sodium is far too low to justify any selective 623 leaching, it must be concluded that the Cr was released into the liquid sodium under a specific but 624 unidentified chemical compound.

625 4.1.3. Proposed reaction mechanisms

As explained above, the shape of the Cr composition profiles confirms the transport of chromium from the steel bulk to its interface with liquid sodium (Fig. 6). In addition, the shape of Cr depletion around grain boundaries (Fig. 9) is typical of the diffusion of type B regime according to Harrison's classification [47], which implies that grains and grain boundaries participate in the diffusion mechanisms [48-52]. This type B diffusion regime explains the presence of thicker oxide within the grain boundaries than at the grain surface. This chromium which diffuses towards the surface of the steel can form NaCrO₂ or dissolve in liquid sodium (section 4.1.2).

The formation of NaCrO₂ crystals may result (i) from heterogeneous precipitation of dissolved Cr or
 compounds containing Cr in liquid sodium or (ii) from selective oxidation of Cr diffusing from the steel

- 635 bulk to the steel/oxide interface.
- 636 In the first case, the driving force for heterogeneous precipitation is the chemical supersaturation of
- 637 liquid sodium into Cr or compounds containing Cr. Under our conditions, supersaturation can only be
- 638 achieved during the cooling phase (from 550 °C to ambient temperature), which implies that NaCrO₂
- 639 formation would only occur during cooling. If this were the case, the samples that undergo this cooling
- 640 phase would present a larger mass gain than a sample taken from liquid sodium at 550 °C without such

a decrease in temperature in liquid sodium. Experiments show that the mass gain for samples taken directly from liquid sodium at 550 °C (\oslash in Fig. 1) is close to that of samples subjected to temperature transients (• in Fig. 1). It therefore appears that mass gain is not affected by temperature transients and that NaCrO₂ formation does not result from heterogeneous precipitation of Cr or a compound containing Cr, from liquid Na.

646 Consequently, NaCrO₂ formation results from the reaction of sodium and oxygen dissolved in Na with 647 chromium in steel. This mechanism is confirmed by the location of the oxidation reaction, in particular 648 in the steel grain boundaries, determined by the double oxidation technique with oxygen isotopes (Figs. 649 11 and 12, section 3.1.5). This is also supported by the constant Cr composition observed at the NaCrO₂/steel interface (x_{Cr}^i) independently of immersion time with $x_{Cr}^i = 9.6 \pm 0.5$ at.% (Fig. 6). This 650 651 composition should coincide with the Cr composition in equilibrium with NaCrO₂ if the GDOES 652 technique allowed a local value to be measured rather than the mean value over a large surface area [33]. 653 The Cr composition gradient measured in steel (Fig. 6) is representative of a positive diffusion flux of 654 Cr to the surface. Therefore, the oxide thickness was expected to increase over time. However, the mass 655 of oxide formed is almost constant during the first 3842 hours. This can be explained by the dissolution 656 of NaCrO₂ simultaneously with its formation or the dissolution of Cr in liquid sodium. This NaCrO₂ dissolution was demonstrated by the difference in the amount of Cr released by the steel and the Cr 657 658 contained in oxide (section 4.1.2).

So far, only Cr oxidation and depletion have been taken into account for the mass balances. In the next
 section, the dissolution of the alloying elements in Na will be evaluated.

661 4.2. Mass balance considering dissolution, oxidation and Cr depletion in steel

662 **4.**

4.2.1. Driving force for dissolution

According to previous studies [7-14], dissolution is recognised as the main corrosion phenomenon of austenitic steel in flowing liquid sodium. The driving force of dissolution is the difference between the concentration of the element in liquid Na and its solubility. The solubility of an element in liquid sodium is defined as the highest concentration of that element in dissolved form. The known solubilities are those of pure elements, such as C [1], O [53], Cr [54], Mn [55], Fe [56], Ni [57], Mo [1]. In the case of 668 Cr, solubility ($w_{Cr,ppm}^{Na,sat}$, in µg g⁻¹) is given for temperatures (*T* in °C) between 683 and 980 °C by [54]: 669 $\log w_{Cr,ppm}^{Na,sat} = 9.35 - \frac{9010}{T+273.15}$. By assuming that the solubility can be extrapolated at 550 °C, it is equal 670 to $w_{Cr,ppm}^{Na} = 25 \ 10^{-3} \ \mu g \ g^{-1}$. Similarly, the solubilities at 550 °C of Mn [55], Fe [56], Ni [57] and Mo [1] 671 are 0.75, 0.52, 1.45 and 1.16 $\mu g \ g^{-1}$, respectively.

672 A rough mass balance was established for the first liquid sodium bath (section 2.3.1), taking into account 673 the solubility of the elements, the total area of the immersed samples (9 samples, 1.206 dm²) and the 674 liquid sodium mass (2.3 kg). Assuming that all samples are dissolved in the same way, the maximum total mass of dissolved steel per surface unit ($\Delta m_s^{(d)}$) can be estimated at $\Delta m_s^{(d)} = 8.3 \ 10^{-4} \text{ kg m}^{-2}$. When 675 676 immersed in liquid sodium, the steel samples dissolve and a layer of NaCrO₂ is formed. The mass gain 677 obtained between the initial sample and the sample taken out of the bath includes the formation of the layer and the dissolution. Therefore, the mass gain due to formation of NaCrO₂ ($\Delta m_s^{(ox)}$) is given by: 678 $\Delta m_s^{(ox)} = \Delta m_s + \Delta m_s^{(d)} = 10.2 \pm 0.1 \ 10^{-4} \text{ kg m}^{-2} \ (\Delta m_s = (1.9 \pm 0.1) \ 10^{-4} \text{ kg m}^{-2} \text{ for the first liquid}$ 679 680 sodium bath only). This corresponds to a maximum oxide thickness of 230 ± 10 nm (Eq.4.1).

As a reminder, assuming that the decrease in Cr concentration of the steel is fully involved in the formation of NaCrO₂, the average thickness of this oxide would be 138 nm after 242 h of immersion time and 670 nm after 3842 h (section 4.1.2). For the shortest corrosion times, the maximum oxide thickness corresponding to Cr depletion is less than 230 nm. This means that the dissolution of the elements is incomplete, i.e. the liquid sodium bath has not reached saturation. The NaCrO₂ layer can therefore dissolve as it forms, as we have suggested in the reaction mechanisms above (section 4.1.3).

687 4.2.2. Discussion on the solubility of the elements in the liquid sodium bath

For long immersion times, the rough mass balance described above leads to a maximum oxide thickness of 230 nm while the thickness estimated from Cr depletion reaches 670 nm. This means that the dissolution of the elements estimated from the solubility of the pure elements is underestimated.

691 The measurements in the first liquid sodium bath are used here to estimate an order of magnitude of the

- 692 Cr solubility in sodium under our operating conditions. Nine samples were immersed in this sodium
- 693 bath, respectively for 242, 584, 1276, 1924, 2395, 2830, 3842, 5304 and 7704 h. The change of
- 694 corrosion mechanisms occurs after about 4000 h (Fig. 1). Our interpretation is as follows: the sodium

695 bath is gradually enriched with Cr and reaches saturation after the first 4000 hours of our tests. The solubility of Cr in liquid sodium containing 200 μ g.g⁻¹ oxygen at 550°C can then be estimated from the 696 697 Cr profiles measured by GDOES for the samples immersed from 242 h to 3842 h (method presented in 698 Section 4.1.2). The amount of Cr released during the first 3842 h for samples immersed for 5304 and 699 7704 h cannot be measured. It is assumed to be equal to the amount of Cr released by the sample 700 immersed for 3842 h. Finally, the quantity of Cr released is then estimated at 2.09 10⁻⁴ mol, or 10.9 mg. 701 The proportion used for oxide (considering a maximum thickness due to dissolution) is subtracted to obtain the proportion of Cr released in the liquid sodium: $n_{Cr}^{Na} = 1.08 \ 10^{-4}$ mol, or 5.62 mg. For the first 702 test, the Cr concentration is then estimated at $w_{Cr,ppm}^{Na} = 2.44 \ \mu g \ g^{-1}$ at 3842 h (2.3 kg of liquid sodium). 703 704 This concentration is 98 times higher than the solubility of pure Cr in liquid sodium found in the 705 literature [54].

Such a high solubility of Cr in liquid sodium could result from the influence of other elements in solution, such as Mn, Fe, Ni and Mo, which could increase the apparent solubility of Cr due to the formation of intermetallic compounds. However, such compounds involving Cr have not yet been reported in the literature to our knowledge. Another explanation could be the influence of oxygen on Cr solubility that has already been observed [33,54] or the formation of a Na-Cr-O complex [25] but no specific data were measured.

712 If this high value of Cr solubility in sodium is confirmed, its effects on corrosion modelling is of primary 713 importance. Indeed, the solubility is involved in the driving force of corrosion and only a small variation 714 of this parameter could lead to large changes in the corrosion modelling of steels [38] in liquid sodium 715 heat exchangers that could be used in future nuclear power plants. This new data shows the importance 716 of taking Cr selective oxidation into account when modelling corrosion.

717 With a longer immersion time (t \geq 5304 h), NaCrO₂ is characterized by XRD (Fig. 2) and the mass gain

of the samples increases significantly (Fig. 1). This change in behavior can be explained by the saturation

of liquid sodium with corrosion products containing chromium (Cr and NaCrO₂ or Na-Cr-O complex).

720 4.3. Formation of M₆C and Na₄FeO₃

721 In all tests, surface characterizations by XRD (Fig. 2) and SEM (Figs. 3 and 4), depth observations by

GDOES (Fig. 5) and STEM (Fig. 7) indicate the formation of M_6C carbides, where M is Mo and Fe.

Thermodynamic calculations confirmed the stability and composition of these carbides at 550 °C [33]. Since the surface of the steel is enriched with C when compared to the bulk, it can be concluded that the carbon comes from liquid Na (carburization) [33]. The steel is slightly depleted in Mo under the corrosion layer (depth > 1 μ m in Fig. 5). This depletion is a sign of the formation of M₆C with the Mo contained in the steel, although Mo may be present in liquid Na due to the dissolution of the crucible (Mo structure). More anecdotally, a particle containing O, Na and Fe is observed by TEM coupled to EDX (Fig. 8). This

⁷²⁵ More anecuotany, a particle containing O, Na and Pe is observed by TEW coupled to EDA (Fig. 8). This 730 particle could be Na₄FeO₃ which is the most stable compound containing Na, Fe and O [33,58] to our 731 knowledge. Thermodynamic calculations show that Na₄FeO₃ is stable in liquid sodium containing 200 732 $\mu g g^{-1}$ at a temperature below 350 °C [33,58]. This implies that Na₄FeO₃ was formed during the liquid 733 Na cooling step and not at 550°C. The observation of Na₄FeO₃ is unusual in our experiments (which 734 minimizes the impact of this artefact in our experimental protocol).

735 During immersion in liquid sodium, the mass of the samples increases through the formation of $NaCrO_2$

but also M₆C and Na₄FeO₃. However, the quantities of M₆C and Na₄FeO₃ formed are unknown and their

effects on mass gain cannot be calculated, although they are probably negligible. If a possible effect of

738 their formations were taken into account in our calculations, the calculated NaCrO₂ thickness would be

reduced, which would imply a higher unexplained amount of dissolved Cr, making no change in the

740 previous conclusions.

742 **5. Conclusions**

We studied the corrosion of 316L(N) stainless steel in static liquid sodium containing about 200 µg g⁻¹ 743 744 of oxygen at 550 °C, for 239 h to 7704 h. Two additional specific tests were performed to locate the 745 oxidation reaction and measure the effect of transient temperature variations related to the handling of 746 samples. After the corrosion tests, the samples were characterized by techniques that provide 747 information on average corrosion behaviour, such as mass gain, XRD and GDOES. Local 748 characterizations were also performed such as EDX coupled to SEM on surfaces and cross sections, 749 STEM analysis of cross sections and SIMS analysis. These characterizations highlight reaction 750 mechanisms at the micrometric scale.

751 In our experiments, two different behaviors were identified as a function of immersion time in liquid 752 sodium, i.e. less than 3842 h or more than 5304 h. The transition was not precisely determined but falls 753 between these two experimental times examined.

754 First, for a time less than 3842 h, the samples have a low mass gain that remains constant over time. X-755 ray diffraction only detects M_6C carbides where M is Mo and/or Fe and the austenitic matrix. The steel 756 surface is covered with tiny NaCrO₂ crystals that are too small to be detected by XRD but visible in the 757 Cr enrichment at the steel surface with GDOES. Steel is depleted in Cr, in the grains and in the vicinity of the grain boundaries below the surface. The double-oxidation technique with ¹⁸O and ¹⁶O isotopes 758 759 coupled with a SIMS analysis revealed an oxygen enrichment in the grain boundaries of the steel at 760 depth. This means that the reaction interface for the NaCrO₂ formation is probably located at the 761 NaCrO₂/steel interface and in the grain boundaries, which act as short circuits of diffusion.

762 For longer immersion times ($t \ge 5304$ h), higher mass gains are measured corresponding to a thicker 763 sodium chromite layer, observed in cross section by SEM and detected by XRD. To explain these 764 experimental results, mass balances using the mass gain of each samples and the Cr depletion profiles 765 in the steel allowed us to propose reaction mechanisms for corrosion of the steel in liquid sodium: Cr 766 diffuses towards the surface of the steel and the O initially dissolved in the liquid sodium diffuses inside 767 the steel together with Na preferably through grain boundaries which are short diffusion circuits. They 768 react to form sodium chromite at the oxidation front located at the chromite/steel interface and in grain 769 boundaries. NaCrO₂ is formed for all immersion times but, at immersion times of less than 3842 h, a 770 significant difference (at least a factor of 100) between the amount of Cr present in the sodium chromite 771 actually observed on the samples and the amount of chromium leaving the metal estimated from the Cr 772 concentration profiles led to the conclusion that most of the chromium was dissolved in liquid sodium. 773 The increase in NaCrO₂ thickness at longer immersion times (t \geq 5304 h) is attributed to the saturation 774 of liquid sodium with corrosion products containing chromium (Cr and NaCrO2 or Na-Cr-O complex) 775 in our experiments. The immersion time at which this phenomenon is observed is related to our 776 experimental protocol and cannot be extrapolated to other facilities. However, this shows the importance 777 of the solubility of Cr in liquid sodium for the corrosion of austenitic steels. 778 Our study shows that the Cr solubility in liquid sodium is underestimated by the pure Cr solubility law 779 found in the literature. One explanation could be that the solubility of Cr increases with the presence of 780 O dissolved by the formation of soluble sodium chromite or a Na-Cr-O complex. An order of magnitude

 g^{-1} O at 550°C. The solubility of chromium could be the result of various contributions, pure Cr, NaCrO₂ and Na-Cr-O complex.

of the solubility of Cr evaluated with our experiments is 2.4 µg g⁻¹ in liquid sodium containing 200 µg

This new data shows the importance of taking Cr selective oxidation into account as well as its dissolution mechanism for the long term modelling of stainless steel corrosion, as well as on the oxygenenhanced dissolution mechanism of iron.

787

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792 Data availability

- 793 The raw/processed data required to reproduce these findings cannot be shared at this time due to
- technical or time limitations.

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- 944 **Table 1.** Composition in wt.% of stainless steel 316L(N) tested.
- 945 Figure 1. Mass evolution as a function of immersion time of 316L(N) stainless steel in liquid sodium
- 946 containing 200 μ g g⁻¹ of oxygen at 550 °C (first Na bath: \diamond , second Na bath: compared to \oslash where
- 947 the samples were immersed and removed at 550 °C, third Na bath: x). The mass gain of the steel samples
- 948 increases significantly after 4000 h of corrosion.
- 949 Figure 2. XRD diffraction patterns of 316L(N) steel immersed for 1460 h (bottom dark line) and 5304
- 950 h (top blue line) in liquid sodium containing 200 μ g g⁻¹ of oxygen at 550 °C, compared with the
- 951 diffraction patterns of NaCrO₂, austenite and Fe₃Mo₃C.
- 952 Figure 3. SEM observations of 316L(N) specimen immersed during 1460 h in liquid sodium containing
- 953 200 μ g g⁻¹ of oxygen at 550 °C (back-scattered electron mode). The steel surface is covered with dark
- grey and white particles. The surface density of the dark grey particles varies from place to place,
- 955 possibly in relation to the orientation of the underlying austenite grains.
- **Figure 4.** EDX elementary maps of the sample immersed during 1460 h in liquid sodium containing 200 μ g g⁻¹ of oxygen. The steel surface is covered with small particles rich in O, Na and Cr and larger particles rich in Mo.
- 959 Figure 5. Elementary composition profile measured by GDOES from the steel surface to a depth of 5
- 960 μ m for a 316L(N) specimen immersed during 1460 h in liquid sodium containing 200 μ g g⁻¹ of oxygen
- 961 at 550 °C: C (thin black line), O (light grey line), Na (grey line), Cr (dotted line), Mn (dark grey line),
- 962 Fe (thick black line), Ni (dashed line) and Mo (double thin line). The red dotted vertical line delimits
- 963 the oxide layer rich in O, Na and Cr.
- **Figure 6.** Chromium concentration profiles obtained by GDOES, after 500, 1000 and 1460 h of immersion in liquid sodium at 550 °C containing 200 μ g g⁻¹ of oxygen, the measurement uncertainties are calculated using at least two GDOES profiles.
- 967 Figure 7. HAADF images of a cross section of a sample immersed for 1460 h at 550 °C in liquid sodium
- 968 with 200 μ g g⁻¹ of oxygen. The sample surface is covered with a layer composed of two types of particles
- 969 (dark and light in appearance) and the grain boundary also contains different types of particles up to a
- 970 distance of 2 μm.

971 Figure 8. EDX elementary mapping of a cross section of a sample immersed during 1460 h in liquid sodium containing 200 µg g⁻¹ of oxygen (enlarged view of Fig. 7). Some particles are rich in O, Na and 972 973 Cr (probably corresponding to NaCrO₂) and others are rich in Fe and Mo (probably corresponding to 974 M₆C carbides).

975 Figure 9. Chromium EDX profiles along the grain boundary from the sample surface (profiles 1 to 4

976 shown by arrows in Fig. 7), specimen immersed during 1460 h in liquid sodium containing 200 μ g g⁻¹

977 of oxygen at 550 °C. Cr depletion is observed in the grain boundary and in the grains. This Cr depletion

978 decreases from the sample surface to the bulk. Cr profiles are also observed to be asymmetric.

Figure 10. Cartographies of ¹⁸O (top) and ¹⁶O (bottom) at several surface depths for a sample immersed for 1460 h in liquid sodium containing 200 µg g⁻¹ of oxygen at 550 °C. At 1.4 µm depth, oxygen is 980 981 located mainly at grain boundaries and ¹⁸O appears to be more present than ¹⁶O.

982 Figure 11. ¹⁶O and ¹⁸O concentration profiles obtained by SIMS in the grains (left column, Fig. 11a, 983 11c and 11e) and at the grain boundaries (right column, Fig. 11b, 11d and 11f) for 600 h (Fig. 11a and 11b), 1000 h (Fig. 11c and 11d) and 1460 h (Fig. 11e and 11f). The oxygen profiles are compared with 984 985 the ¹⁶O profile obtained in the first corrosion step (500 h in ¹⁶O containing liquid sodium black dotted line). The example chosen is corrosion in liquid sodium at 550°C containing 200 µg g⁻¹ of oxygen. For 986 987 each corrosion time, the oxygen (¹⁶O and ¹⁸O) concentration and oxidation depth are higher in the grain 988 boundaries than in the grains. The ¹⁸O concentration increases with corrosion time both in the grains and 989 at the grain boundaries.

Figure 12. Relative abundance profiles of ¹⁸O obtained by SIMS, from the sample surface along the 990 991 grains (a) and grain boundaries (b) for samples immersed in liquid sodium at 550°C containing 200 μ g 992 g⁻¹ of oxygen. Fast oxygen diffusion along the austenite grain boundaries is clearly visible throughout 993 the immersion period.

Figure 13. Cross section of a sample immersed for 7704 h in liquid sodium containing 200 µg g⁻¹ of 994

995 oxygen at 550°C. (a) secondary electron image, (b), (c), (d), (e) and (f) EDX mapping for, respectively

996 oxygen, sodium, chromium, iron and molybdenum.

997

998 Table 1. Composition in wt.% of stainless steel 316L(N) tested.

	Fe	Cr	Ni	Mo	Mn	С	Si	Ti	Al	Cu	Co
	Balanced	17.9	12.1	2.35	1.72	0.012	0.45	0.0015	0.0025	0.0025	0.0008
999											
1000											











Figure 4.



Figure 5.













1026 Figure 10.

1025



1032 Figure 11.









1038 Figure 13.

