Factors that influence the release of metals from stainless steels exposed to physiological media

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Abstract

Release rates of chromium, nickel and iron from grade 304 stainless steel with three different surface finishes, BA, 2B and 2D, have been determined after exposure to artificial lysosomal fluid. Metal release rates are discussed in relation to corrosion resistance, compositional changes of the outermost surface film of the stainless steel and to measurements of the effective surface area and roughness. The total metal release decreased in the following sequence: 2D > 2B ≈ BA, and was primarily related to the electrochemically active surface area. No direct correlation was observed between corrosion resistance and metal release rates.

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1. Introduction

The corrosion resistance of stainless steel has been extensively investigated in various media [1], whereas relatively few studies exist in the literature on rates of release of
individual alloy constituents [2–4]. It is important to obtain reliable data that can be used when assessing whether there is any potential for risk of adverse effects arising from exposure to the metals contained in stainless steel. Previous work in this laboratory has shown that there is no simple quantitative relationship between the bulk alloy composition or corrosion resistance and metal release rates from stainless steels of various grades exposed to environmental or physiological media that are relatively mild from the point of view of corrosivity, though there may be some correlation with the degree of chromium enrichment of the outermost surface film of the alloy [2,5–7]. In order to investigate further the factors that may influence the rate of metal release, a study of metal release rates and their correlation with various surface parameters has been made with grade 304 stainless steel (typically 18% chromium and 8% nickel) with three different surface finishes.

Stainless steel can vary significantly in appearance and performance depending on how the surface is finished. Different surface finishes are required by users with different needs for appearance and/or corrosion resistance, depending on factors such as the intended application, environmental conditions and the expected length of life of the product. A wide range of surface finishes is available on the market, ranging from mill rolled surfaces to highly decorative coloured and textured finishes [8]. Variations in surface roughness are common between different producers and depend on factors such as equipment and mode of operation during rolling. Properties such as corrosion resistance and cleanability are related, at least partly, to the surface roughness. This is recognized by the European standard EN10088, Part 2, that stipulates, for example, a maximum surface roughness of <0.5 mm (Ra, i.e. the average surface roughness or deviation of all points from the mean surface level [9]) for marine and external architectural applications [8]. International, national or industry standards often stipulate the required surface finish for certain applications, such as food processing or medical devices [10–12]. Some surface finishes, e.g. 2D, are designed for industrial and engineering applications but are not widely used for architectural applications where the 2B surface finish is more commonly used. Both 2D and 2B have a dull grey appearance but if a highly reflective surface is required, surface finish BA is recommended [11]. There are some studies in the literature on the influence of surface finish on the corrosion resistance, cleanability and fouling of stainless steel [13–15]. Results from these investigations show the 2B surface finish to be less smooth than surface finish BA and the latter to have a higher wettability compared to 2B and 2D [13,15].

Three different surface finishes of stainless steel grade 304 have been investigated in the current study, 2B, 2D and BA. The 2B finish involves cold rolling, heat treatment, pickling and skin passing and provides a smoother surface than the 2D surface finish, where no skin passing is performed. The BA surface finish provides a very smooth and bright surface as a result of cold rolling and bright annealing [10]. Hence, the surface roughness usually decreases in the following order: 2D > 2B > BA.

The aim of this study is to provide quantitative data on release rates of metallic alloy constituents from stainless steel grade 304 with these surface finishes into a synthetic body fluid, and to investigate if differences in surface area and/or surface roughness of each surface finish have any correlation with metal release rates. In addition, compositional changes in the passive film after exposure and corresponding changes in corrosion resistance have also been evaluated and related to the observed metal release rates.
2. Experimental

2.1. Stainless steel samples

Panels of stainless steel grade 304, approximately 0.8 mm thick, with three different surface finishes, 2B, 2D and BA were supplied by ThyssenKrupp Nirosta, Germany. The composition of grade 304 is shown in Table 1. The different surface finishes represent three commonly used surfaces: 2B is cold rolled, heat-treated, pickled and skin passed, 2D is cold rolled, heat treated and pickled and BA is cold rolled and bright annealed.

Immersion experiments were performed for 8 and 168 h in 7 mL of a synthetic body fluid (see below) using duplicate stainless steel samples (≈7 cm²) for each surface finish. Thus, the surface area/solution volume ratio was approximately 1.0 cm²/mL. Prior to exposure, all samples were cleaned in RBS solution to remove any organic residues on the surface. The RBS solution is an alkaline detergent that contains cationic and non-ionic surface-active agents but without phosphates. It is commonly used in hospitals and medical laboratories to clean glass and plastic containers from blood serum and protein residuals and also for decontaminating radioactive surfaces. Each sample was immersed in a 2% (volume) RBS solution at 50 °C for 10 min and carefully rinsed in ultra pure water (18.2 MΩ cm) followed by ultrasonic cleaning in ultra pure water for 3 min, rinsing again with ultra pure water and drying with room-temperature nitrogen gas. Clearly, stainless steel in the massive form cannot be inhaled, but as a large number of stainless steel grades are available in sheet form, and the surface finishes are well understood from the point of view of corrosion resistance, it was considered valuable to conduct “screening tests” on these products so that the magnitude of the release from the different grades could be assessed and compared.

2.2. Exposure conditions

To help ensure the reliability and reproducibility of the metal analyses, all vessels used for solution preparation and for the immersion experiments were cleaned with 10% HNO₃ for a minimum of 24 h and then rinsed in ultra pure water (18.2 MΩ cm) to remove any metal-containing contaminants. The sealed vessels containing the stainless steel samples and the medium were placed into a bi-linear shaking incubator (30 rpm) and kept in dark conditions at 37 ± 1 °C for 8 and 168 h. Reference vessels, without stainless steel, were exposed for the same time periods under the same conditions.

2.3. Physiological medium

Artificial lysosomal fluid (ALF) is analogous to the fluid with which inhaled particles would come into contact after phagocytosis by alveolar and interstitial macrophages

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>0.05</td>
<td>0.3</td>
<td>1.1</td>
<td>0.03</td>
<td>0.002</td>
<td>18.1</td>
<td>0.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>
within the lung. The chemical composition of ALF is given in Table 2 [16]. ALF differs from some other commonly used artificial body fluids in that it is relatively acidic (pH 4.5). Previous studies in this laboratory have shown that metal release from stainless steel exposed in this medium gives concentrations that, while low, are consistently above the limits of detection for the analytical method used [6]. Citrate is used to take the part proteins have in real lysosomal fluid and acetate to replace organic acids. All chemicals were of analytical grade and were dissolved in ultra pure water (18.2 MΩ cm). ALF has previously been used to investigate the durability of man-made mineral fibres following their phagocytosis by cells [17] and to study the bioaccessibility of a range of cobalt-containing materials including metallic cobalt powder and a cobalt-chrome alloy [18].

2.4. Metal analysis

After immersion in ALF, the concentrations of the released metals (Fe, Ni, Cr) were measured using inductively coupled plasma/mass spectrometer-dynamic reaction cell (ICP/MS-DRC) (Perkin-Elan 6100). All measurements of released metals were performed at the Environmental Research Laboratory, Swedish University of Agricultural Sciences, Umeå, Sweden. The detection limits were 44, 2.5 and 3.8 μg L⁻¹ for Fe, Ni and Cr, respectively. The metal concentrations of the reference ALF samples (without exposure to stainless steel) were all less than 5% of the concentrations of the samples exposed to the stainless steels.

2.5. Surface area measurements

Electrochemical impedance spectroscopy (EIS) was used to measure the electrochemically active surface area. Impedance measurements were made using an electrochemical interface, Solatron 1287, and a frequency response analyser, Solatron 1250 controlled by Zplot software (Scribner Associates, Inc.). The measurements were performed at the open circuit potential at room temperature, with a perturbation amplitude of 10 mV and a frequency range from $1 \times 10^4$ down to $5 \times 10^{-3}$ Hz. The impedance data was fitted by using the least square method.
Table 3
Composition of PBS-solution (g/L)

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>Na₂HPO₄</th>
<th>KH₂PO₄</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.77</td>
<td>1.42</td>
<td>2.72</td>
<td>6.4 (not pH adjusted)</td>
</tr>
</tbody>
</table>

A three electrode electrochemical cell with a Pt-mesh as counter electrode and an Ag/AgCl reference electrode was used. All EIS measurements were performed in a phosphate buffered saline (PBS) solution (see Table 3 for chemical composition). PBS was used instead of ALF since it is much less corrosive but has good conductivity. The chemicals used were all of analytical grade and were dissolved in deionised water (1–10 MΩ cm). From the results of the impedance measurements the corrosion resistance was evaluated.

Surface area measurements were performed on six samples of each surface finish prior to exposure to ALF. Single samples were investigated after exposure to ALF. All the samples tested were ultrasonically cleaned in acetone for 3 min to remove any fatty substances from the sample surface that could affect the effective area, exposed samples were tested in the post-exposure condition.

Measurements of the surface area were also performed using profilometry. These measurements were performed at the Institute for Surface Chemistry, Stockholm, using a New View 5010 Zygo Ltd. (USA) instrument with a 20X lens, a lateral resolution of 1.1 μm, a vertical resolution on a nanometer scale and a maximum angle between pixels of seven degrees. The surface area of triplicate samples of each surface finish was measured before and after exposure to ALF. All surfaces were tested in an as-received condition, i.e. without any cleaning procedure. The results are presented as the ratio between the geometric area and the measured area, including all surface features such as peaks and valleys, and corresponding root-mean-squared value ($I_q$) of all vertical deviations from the mean surface level [9].

2.6. Surface film composition

The chemical composition of the outermost surface film was investigated using XPS, X-ray photoelectron spectroscopy (Kratos AXIS HS), on unexposed and exposed (ALF, 168 h) samples with each surface finish. Wide scans and detailed scans (pass energy of 80 eV) of Cr 2p, Ni 2p, Fe 2p, C 1s, O 1s were obtained with a monochromatic AlKα X-ray source (1486.6 eV) operated at 300 W (15 kV/20 mA). The area of analysis was approximately 0.4 mm². Sensitivity factors (Cr 2p—2.3 and Fe 2p—3.0) supplied by Kratos were used to estimate the chromium content of the surface film defined as the ratio (Cr/(Cr + Fe)). No distinction was made between metals in different chemical states.

3. Results and discussion

Release rates of chromium, nickel and iron from stainless steel grade 304 with three different surface finishes (2B, 2D and BA) are presented and discussed in relation to surface film composition (XPS) and surface area (profilometry, EIS). The metal release rates were obtained upon exposure of the stainless steel samples in a synthetic biological medium (ALF).
3.1. Metal release rates from three different surface finishes of stainless steel grade 304

Release rates of nickel, chromium and iron from stainless steel grade 304, when exposed in the acidic medium ALF, are presented in Fig. 1 for each surface finish and exposure period. All rates have been recalculated to a total weekly release rate and are expressed as \( \mu g \, cm^{-2} \, week^{-1} \). A general observation is that iron is preferentially released for all surface finishes and exposure periods. Samples with surface finish 2D show generally higher release rates of chromium and iron compared to surfaces with a 2B and BA surface finish for both exposure periods. All surface finishes show similar release rates of nickel.

The release rate for each element is higher during the early part of the exposure and decreases during the subsequent exposure time, in agreement with previous findings of time-dependent release rates from metals exposed in different fluids [2,19-21].

![Fig. 1. Release rates of nickel (top), chromium (middle) and iron (bottom) from three different surface finishes of stainless steel grade 304 exposed in ALF for 8 (striped) and 168 (filled) h.](image-url)
behaviour has been thoroughly discussed previously and will not be addressed any further herein.

Total metal release rates are displayed in Fig. 2 for each surface finish and are also compiled in Table 4 together with corresponding release rates of individual alloy constituents after 1 week of exposure to ALF.

Panels with a 2D surface finish show higher total 1-week average release rates of alloy constituents compared to surfaces with a 2B and BA surface finish, the latter two having similar rates. The main difference in weekly release rates from the 2B and the BA surface finish is a somewhat lower rate of chromium for the BA surface. Observed total weekly release rates from the 2B surface finish are in close agreement with other recent findings when stainless steel grade 304 (2B surface) was exposed in AlF [6]. Thus, the total release rate decreases according to the following sequence: 2D > 2B ≈ BA.

Compositional analysis of changes of the chromium content of the outermost surface film was performed by means of XPS for all surface finishes after 1 week of exposure to ALF. The results are illustrated in Fig. 3. The chromium content of the passive film before exposure to ALF decreased in the order 2B > 2D > BA. All samples showed an increase in the chromium content of the outermost surface film following exposure to ALF for 168 h.

A small enrichment in chromium compared to the unexposed surface condition can be seen for the 2B surface whereas the chromium enrichment is more pronounced, but of the same order of magnitude, for the 2D and BA surfaces. The passive film on stainless steel consists of an inner barrier film enriched in chromium oxides and iron oxides and an outer hydroxide film (mainly Cr(OH)_3) [22]. Since XPS only measures the composition of the outermost surface layer, corresponding to a thickness of a few nanometers (10^-9 m), the presence of iron and chromium in their metallic state provides a qualitative measure of

<table>
<thead>
<tr>
<th>Surface finish</th>
<th>Cr (µg cm^-2 week^-1)</th>
<th>Ni (µg cm^-2 week^-1)</th>
<th>Fe (µg cm^-2 week^-1)</th>
<th>Total (µg cm^-2 week^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>0.105 ± 0.004</td>
<td>0.026 ± 0.002</td>
<td>0.987 ± 0.078</td>
<td>1.118 ± 0.084</td>
</tr>
<tr>
<td>2B</td>
<td>0.087 ± 0.001</td>
<td>0.016 ± 0.001</td>
<td>0.615 ± 0.039</td>
<td>0.719 ± 0.041</td>
</tr>
<tr>
<td>BA</td>
<td>0.047 ± 0.005</td>
<td>0.023 ± 0.001</td>
<td>0.628 ± 0.017</td>
<td>0.698 ± 0.020</td>
</tr>
</tbody>
</table>

Table 4
Release rates of individual alloy constituents and corresponding total metal release rates from stainless steel grade 304 with different surface finishes after 1 week of exposure to ALF.
the film thickness. Metallic iron was observed in the surface film on both unexposed and exposed samples, which indicates a relatively thin passive film. The passive film thickness decreased in the following order: BA > 2D > 2B for unexposed surfaces, and 2B ≈ 2D > BA for samples exposed in ALF for 1 week, Table 5 (decreasing fraction of metallic iron with increasing surface film thickness).

An increased chromium content in the surface film is generally believed to increase the corrosion resistance of stainless steel, the surface film then acting more effectively as a barrier against corrosion and metal release. Measurements of corrosion resistance were therefore performed prior to and after exposure to ALF for 1 week in order to investigate if a higher chromium content of the passive film (2B > 2D > BA, see Fig. 3) would improve the corrosion resistance. The results for each surface finish are presented in Fig. 4.

No significant difference in polarization resistance (a measure of corrosion resistance) was seen between samples with different surface finishes prior to exposure, even though there were significant differences between the samples in relation to chromium content of the passive film (2B > 2D > BA). However, after exposure for 1 week in ALF, the corrosion resistance varied considerably, despite similar chromium content of the surface film as measured by XPS (Fig. 3). The corrosion resistance was substantially improved for samples with a 2B surface finish compared to unexposed samples, whereas samples with a 2D surface finish showed reduced corrosion resistance. No difference in corrosion resistance was seen between unexposed and exposed samples of surface finish BA. The reduced corrosion resistance of samples with surface finish 2D parallels the fact that these surfaces show the highest metal release rates of all alloy constituents, Fig. 1.

Overall, the differences in total metal release rates (2D > 2B ≈ BA) cannot be explained by changes in the chromium content of the outermost surface film or by its thickness. This

Table 5
Fraction of metallic iron (%) of total iron (metallic + oxidized iron) measured by means of XPS in the surface grade 304 of different surface finish before and after 1 week exposure to ALF.

<table>
<thead>
<tr>
<th>Surface finish</th>
<th>Unexposed (%Fe)</th>
<th>Exposed (%Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td>2B</td>
<td>24</td>
<td>27</td>
</tr>
<tr>
<td>BA</td>
<td>11</td>
<td>37</td>
</tr>
</tbody>
</table>
implies that the release process is governed also by other surface parameters such as the uniformity of the passive film. Previous investigations have suggested the release of Ni and Fe to occur non-uniformly over the chromium-enriched surface film, probably at locations of, for example, defects, metallic inclusions, imperfections, etc. [2] and have shown the importance of surface finish on the corrosion resistance [13].

3.2. Surface area measurements

To further evaluate the possible reasons for observed differences in release rates of alloy constituents from stainless steel grade 304 with different surface finishes, the influence of surface area was considered. The surface area and surface roughness were evaluated with two different techniques, (i) profilometry, which provides a measure of the average surface topography with a lateral resolution in the micrometer range and (ii) electrochemical impedance spectroscopy, EIS, which provides a relative measure of the electrochemically active surface area.

Visually, the BA surface finish is more shiny than the 2B and 2D finishes. The latter have a more dull appearance, which may be a result of differences in surface roughness or surface area that, in turn, will influence the surface area available for contact with the liquid medium. This observation was confirmed with results from the profilometry investigation that measures the surface area that can be accessed by light. The results are presented in Table 6 for samples of each surface finish before and after exposure to ALF for 1 week. Differences between the geometric area and measured area (expressed

Table 6
Surface area measurements by means of profilometry

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>2D</th>
<th>2B</th>
<th>2R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unexposed</td>
<td>Exposed</td>
<td>Unexposed</td>
</tr>
<tr>
<td>Area: geometric area (µm²)</td>
<td>0.375</td>
<td>0.375</td>
<td>0.373</td>
</tr>
<tr>
<td>Area: measured (geometric)</td>
<td>+2.1%</td>
<td>+2.1%</td>
<td>+7.1%</td>
</tr>
<tr>
<td>( l_{r} ) (rms)</td>
<td>0.199</td>
<td>0.192</td>
<td>0.361</td>
</tr>
</tbody>
</table>

The measured area is based on the average height and depth of surface features and \( l_{r} \) the corresponding root mean squared value.
as the average height and depth of peaks and valleys and other surface features) are presented together with the root-mean-squared value ($I_q$).

The results show no significant difference between the geometric area and the measured area for samples, both unexposed and exposed, with surface finish BA, i.e. the bright annealed (shiny) surface. Samples with a 2D surface finish show a minor, but statistically significant, difference between the geometric and the measured area, both before and after exposure to ALF. Of the unexposed samples, the largest measured area and also the highest $I_q$ value were obtained for samples with the 2B surface finish. Exposure to ALF resulted in a slight but statistically significant increase of the measured surface area for these samples. The measured surface area decreases according to the following sequence: $2B > 2D > BA$, for both unexposed and exposed samples. These findings are contradictory to the general observation that a skin passed 2B surface finish would have a smoother surface than a 2D surface finish. The reason is unclear, but could be related to limitations in the lateral resolution of the measurement technique, hence, further investigation is needed.

The $R_a$ value for all three surfaces was found to be less than 0.5 $\mu$m and since the resolution of the instrument was 1 $\mu$m, the complete area could not be evaluated. $R_a$ is the average surface roughness or deviation of all points from the mean surface level [9]. However, no correlation can be seen with the observed differences in total metal release rates following 168 h of exposure to ALF ($2D > 2B \approx BA$) which indicates that the surface area measured by profilometry is not the active surface area during exposure to ALF.

Further investigations were therefore made to estimate the electrochemically active surface area by using electrochemical impedance spectroscopy (EIS) measurements. This technique provides a measure of the surface area in contact with an electrolyte, whereas the surface area measured with profilometry is governed by the lateral resolution and the possibility for light to penetrate into smaller cavities such as pores. The investigated surface area is also significantly larger: 1 cm$^2$ with EIS compared to 0.35 $\mu$m$^2$ with profilometry. EIS does not result in any quantitative measure of the surface area, but allows relative comparison between samples of different surface finish, as the effective surface area is proportional to the capacitive response of a metal surface-electrolyte interface [23]. The polarisation resistance recorded during the EIS measurements is inversely proportional to the geometric surface area and the total interfacial capacitance, which is directly proportional to the effective area. The dielectric constant and the thickness of the oxide films on the different surface finishes were assumed to be the same since all surface finishes had native oxide films. The results are presented in Fig. 5 for each surface finish using the mean value for samples with a BA surface finish as the benchmark. A bode plot representative of all surface finishes is shown in Fig. 6.

Samples with a 2B and a 2D surface finish show larger effective areas compared to samples with a BA surface finish, $+19\%$ and $+20\%$, respectively. Relatively small variations in effective area were observed for samples with a 2B surface finish (six replicates) whereas samples with a 2D surface finish showed a significantly larger variation between the six replicates. This suggests that samples with surface finish 2B exhibit small variations in electrochemical activity whereas samples with surface finish 2D exhibit larger variations. The corresponding variation between replicates for samples with surface finish BA was significantly smaller compared to the 2D surface finish and comparable to the 2B surface finish. Taking into account the variation in results between replicates of each surface finish, the electrochemically active surface area decreases according to the following sequence: $2D > 2B > BA$. This correlates reasonably well with the sequence for metal release with...
highest metal release rates of all alloy constituents from samples with surface finish 2D and lower for samples with surface finishes 2B and BA.

In all, it can be concluded that release of metallic alloy constituents from stainless steel, under the present exposure conditions, varies with surface finish and seems to correlate best with the electrochemically active surface area. Other properties, such as passive film composition and thickness, are of lesser importance for metal release rates when comparing different surface finishes.

4. Conclusions

Differences in release rates of chromium, nickel and iron from stainless steel grade 304 with three different surface finishes, 2B, 2D and BA, have been investigated during
exposure to artificial lysosomal fluid, ALF, a synthetic body fluid that mimics the acidic (pH 4.5–5) intracellular milieu.

The following main conclusions were drawn:

- Average total metal release rates vary between 0.7 and 1.1 µg cm\(^{-2}\) week\(^{-1}\) from stainless steel grade 304 with 2B, 2D and BA surface finishes.
- The total weekly metal release rate decreases according to the following sequence of surface finishes: 2D $> 2B \approx BA$.
- Higher release rates of iron compared to chromium and nickel and a time-dependent metal release process were observed for all surface finishes and exposure periods, but all release rates were very low for all three surface finishes.
- The release rates of alloy constituents from the stainless steels with different surface finishes could be related most closely to variations in their electrochemically active surface areas, but not to variations in passive film composition and thickness, geometric surface area or surface roughness.

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