Effect of nitric acid passivation on the surface composition of a mechanically polished type 316l sanitary tube

John C. Tverberg, PE (Professional Engineer) and Susan J. Kerber, PhD
Vice President Technology, Trent Tube, East Troy, Wisconsin, USA, and President, Material Interface, Inc., Sussex, Wisconsin, USA

Passivation has a profound effect on the chromium-to-iron ratios in mechanically polished Type 316L tubing. Pieces of the same tube were subjected to hot nitric acid for various passivation times and the passive layer was analysed using XPS (X-ray photoelectron spectroscopy). The changes in surface chemistry, especially with regard to the amount of elemental iron in the passive layer, were very measurable. There were significant differences in the Cr:Fe ratio and in the ratio of elemental chromium to chromium oxide. Other elements that exhibited anomalous behaviour were silicon and molybdenum. More elemental iron and chromium exist in the passive layer of the mechanically polished tubing than the equivalent electropolished tube, suggesting a more easily corroded surface for the mechanically polished tubing.

Type 316L Stainless Steel is the material of choice for most High-purity Water (HP) and Water for Injection (WFI) systems in the pharmaceutical industry. Two standard surface finish conditions are used for these systems in the USA: electropolished and mechanically polished. The tubing is usually ordered to the American Society for Testing and Materials' specification ASTM A 270 which, in its present format, requires a mechanical polish regardless of the existing surface smoothness.

Mechanical polishing takes one of two forms: swirl polishing or longitudinal belt polishing. Swirl polishing uses a rotating flapper wheel which moves up and down the length of the tube, removing only a thin surface layer of material, and creating a 'smeared surface'.

The longitudinal belt polish uses an abrasive belt that moves along the length of the tube, while the tube rotates and uses an air bladder to pressurise the belt to remove surface material. This technique removes a measurable amount of material, 0.0006-0.0008 inch (0.015-0.020 mm), and is a precursor to electropolishing to low Ra levels (<8 μ-in or 0.2 μm). Both methods remove the normal deep passive layer that is developed during production of the strip from which the tubing is made.

Occasionally, discoloration of the mechanically polished surface is seen, especially during hot, humid weather. This surface discoloration, which varies from light yellow to a light red, may be found with both types of mechanically polished tubing. It is readily removed by immersion in hot nitric acid followed with a water rinse.

Once the tube is acid-treated it does not discolour again providing the treatment takes place at an elevated temperature for a long enough period of time.

A study was initiated to determine what changes occur in the surface layer of mechanically polished tubing at several nitric acid passivation times. The acid concentration was that specified in US Military specification MIL STD QQ-P-35 and ASTM A 967 – Nitric Acid 3; namely, 20 per cent at the specified temperature of 120-140° F (50-60°C). This concentration and temperature provided the best results with the standard salt spray test used in the USA.

In this study the time at temperature was varied and the surfaces analysed using X-ray photoelectron spectroscopy (XPS). This paper presents the results of the passivation study.

Methodology

Reagent-grade nitric acid was diluted with deionised water to 20 volume per cent (v/o) and heated to a constant 136°F (58°C). Five samples of mechanically polished tubing were immersed in this solution, one each for 1, 5, 15, 30 and 60 minutes respectively. One sample was analysed in the 'as-polished' condition. After rinsing and drying, each of the treated mechanically polished samples was evaluated using XPS.

There was no visual difference among the six samples. All had identical surface lustres.

X-ray photoelectron spectroscopy is one of the newer analytical tools available and is also known as electron spectroscopy for chemical analysis, or ESCA. During XPS, a sample is irradiated with monoenergic soft X-rays and the

Corresponding author: John C. Tverberg, PE, Vice President Technology, Trent Tube, 2015 Energy Drive, PO Box 77, East Troy, WI 53120-0077, USA. Tel: (+1) 414 642 8210, fax: (+ 1) 414 642 8476.

emitted electrons analysed for energy response. In this study we used monochromatic Al Kα X-rays at 1,486.7 electron volts. These X-rays interact with the atoms on the surface and emit photoelectrons.

These photoelectrons are generated within approximately 30-50Å of the surface, with a resulting kinetic energy expressed as: $KE = hv - BE - \phi s$, where KE is the kinetic energy; hv is the energy of the photon; BE is the binding energy of the atomic orbital from which the electron originates, and ϕs is the spectrometer work function.

Each element and compound has a unique set of binding energies. Therefore XPS can be used to identify the concentration of elements on the surface being analysed and determine the binding energy of the surface species. From this binding energy inferences can be made to identify the chemical state of the element. This is an extremely useful function because we can identify changes in the passive layer composition as a function of passivation time.

Following each surface scan the surface was bombarded ('sputtered') with ionised argon to remove about 25Å of material, then the new surface was again analysed. This continued until we reached the maximum depth of oxygen penetration or until there were no further changes in composition.

For each sample at each depth, a survey scan, as illustrated in **Figure 1**, was made in the energy range of 1,200-0 eV to determine the elemental composition. Then, for each element of interest, a narrow window of about 20 eV around the central peak was analysed in a high-energy resolution mode to determine the binding energy of the surface species. Peak shifting in XPS may be considered a measure of covalency and the more

ionic compounds, such as intermetallic compounds, may or may not be shifted significantly from the pure element peak value.

The binding energy obtained for each element is compared to either published literature values of known standards or to theoretical arguments based on chemical bonding. The presence of overlapping, multiple-binding energies can make identification difficult. In our work we used data from the *Handbook of Photoelectron Spectroscopy*[1] and *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*[2] for the assignment of binding energy to compounds.

The XPS system used for the analyses was a Physical Electronics Model 5700. The binding energy values were calibrated with an internal standard, carbon from atmospheric exposure, set to 284.7 eV. Quantitative values for the data were obtained by the use of sensitivity factors which are based on the calculated yields for pure elements.[2] The analytical information should be taken as semi-quantitative at best and so most properly should be used for comparisons only.

Experimental results

Since all specimens were taken from the same tube and within one inch (25 mm) of each other, only one of the samples was analysed in the as-received state, after an isopropanol rinse to remove contamination from handling. Each surface of the acid-treated samples was analysed with XPS. In addition, the as-received sample and the 30- and 60-minute passivated samples were sputtered to determine elemental composition and oxidation state as a function of depth.

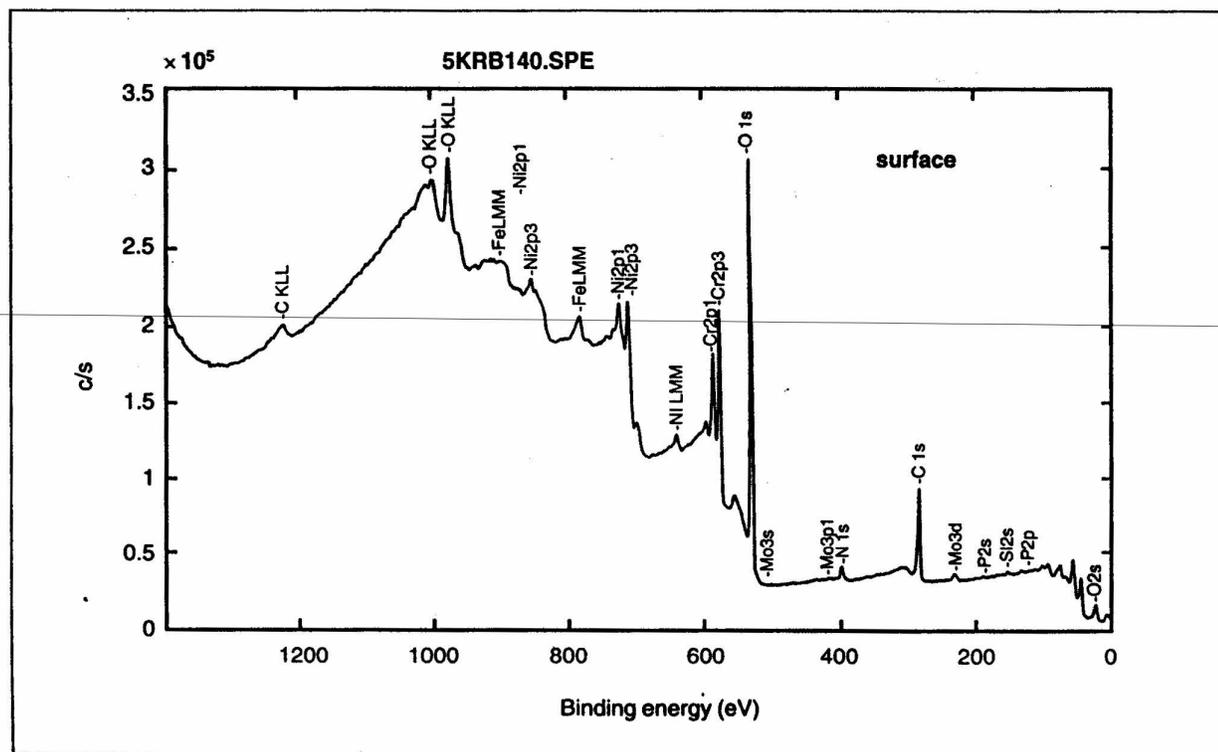Table 1 summarises the surface chemistry of the Type

Figure 1: Typical binding energy surface scan

Table 1: Elemental surface composition as a function of nitric acid passivation time

Passivation time (minutes)	C	N	O	Na	Mg	Al	Si	P	S	Ca	Cr	Fe	Ni	Mo
0	41.8	2.4	39.9	0.4	–	–	1.8	–	0.3	–	2.6	9.4	0.5	0.2
1	24.3	2.3	47.3	0.1	0.2	0.4	1.8	0.7	0.4	0.1	10.6	9.7	1.4	0.7
5	24.1	2.3	48.6	0.4	–	0.1	0.8	0.7	0.2	0.2	11.8	8.6	1.5	0.7
15	23.3	2.6	47.7	0.2	0.2	0.4	0.8	0.7	0.3	0.2	12.2	9.1	1.7	0.7
30	25.1	1.6	51.4	–	–	0.3	0.9	0.8	–	0.1	13.0	5.7	0.7	0.3
60	28.8	1.8	49.9	–	–	–	1.1	0.4	–	–	10.5	6.7	0.5	0.3

316L Stainless Steel samples after the different times in hot nitric acid. The data represent the atomic per cent composition of the elements above atomic number 3 within 40Å of the surface. **Figure 2** is a plot of the atomic surface concentration as a function of passivation time, and **Figure 3** is a plot of the metals only.

The data illustrate that chromium and oxygen concentrations reach a maximum after 30 minutes of passivation and that iron has its lowest value. When the data are compared as the ratio of metal to iron, as in **Table 2** and **Figure 4**, the maximum Cr/Fe ratio occurs after 30 minutes' passivation.

For some unexplained reason, both 15- and 60-minute passivation show a decrease in the Cr/Fe ratio. Both the Ni/Fe and Mo/Fe ratios reached a maximum at 15 minutes and began to decrease after 30 minutes of passivation.

The 0-, 30- and 60-minute passivated specimens were sputtered with ionised argon and the elemental composition as a function of depth was determined. The data are summarised in **Table 3** for the as-received specimen, **Table 4** for the 30-minute passivated specimen and **Table 5** for the 60-minute passivated specimen.

Examination of the specific binding energy peaks for each element indicate that both oxide and metal are

Table 2: Ratio of key elements to iron as a function of nitric acid passivation time

Passivation time (minutes)	Si/Fe	Cr/Fe	Ni/Fe	Mo/Fe
0	0.191	0.277	0.055	0.024
1	0.188	1.088	0.141	0.068
5	0.089	1.367	0.176	0.075
15	0.090	1.351	0.186	0.078
30	0.165	2.299	0.131	0.050
60	0.166	1.578	0.073	0.039

present; that is, metal with a valency of zero. In the case of iron, both the oxide and elemental iron are present in significant quantities. This is especially the case for elemental iron at passivation times less than 30 minutes. **Table 6** and **Figure 5** present the ratios of the iron and chromium to their respective oxides.

These data indicate that the iron oxide abruptly decreases after one minute and continues to drift downward until the chromium oxide reaches a near-saturation point at somewhere between 15 and 30 minutes. After 30 minutes both ratios increase,
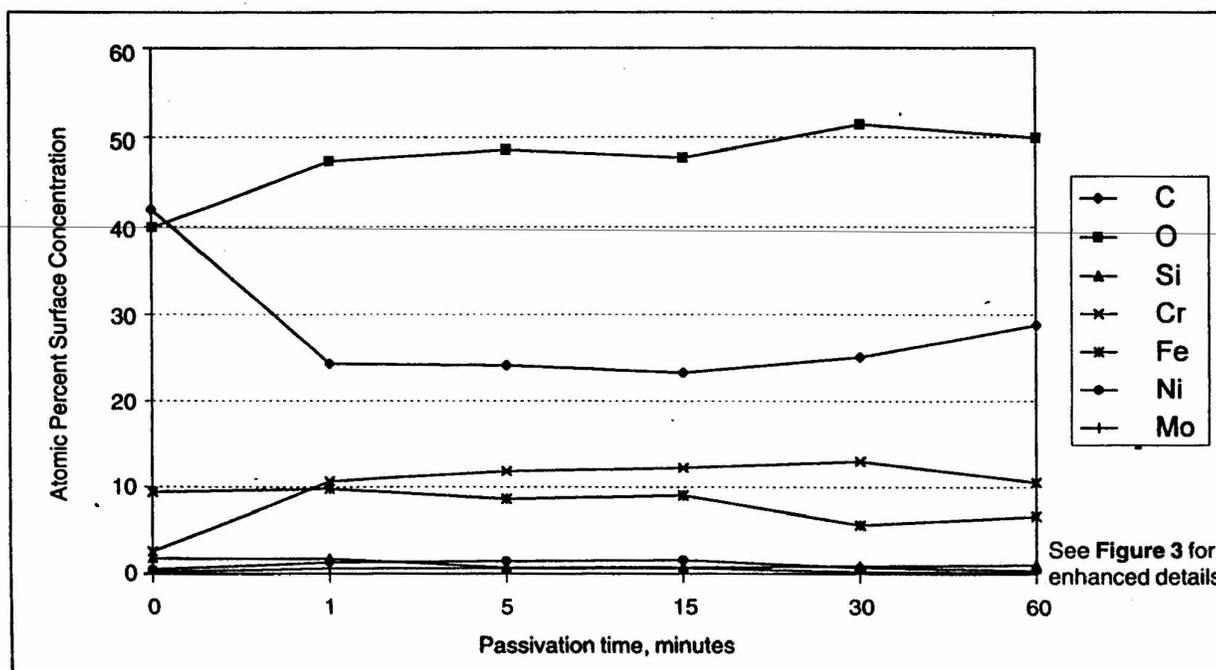
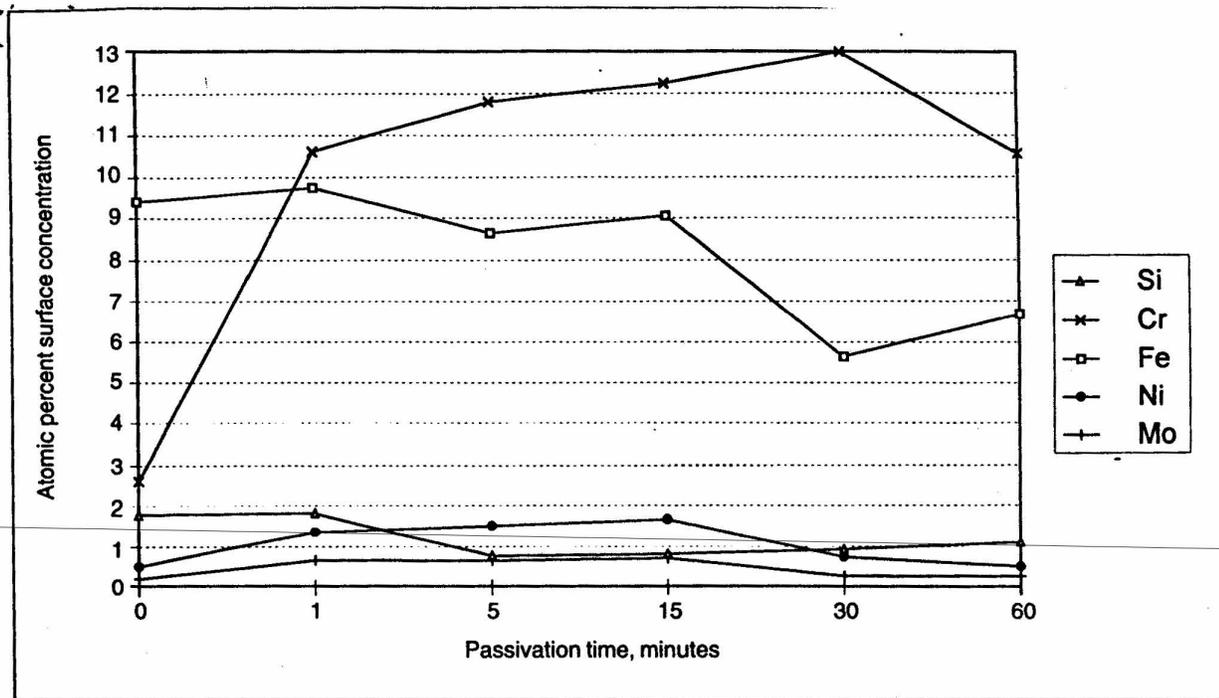**Figure 2:** Plot of surface composition as a function of passivation time

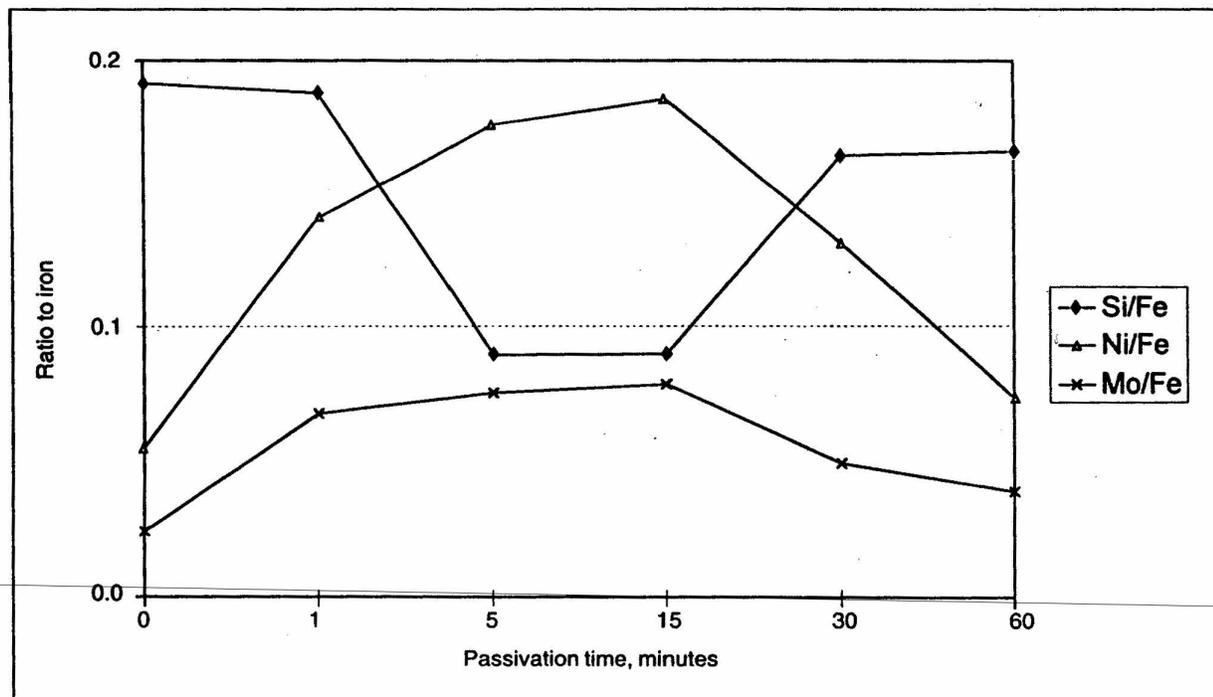**Figure 3:** Change in surface composition as a function of passivation time

Figure 4: Metal to iron ratio as a function of passivation time

although the rate of increase is greater for chromium oxide than for iron oxide. This would indicate that the surface is becoming more passive with longer exposure to the hot nitric acid.

Discussion

A passivation treatment of mechanically polished Type 316L stainless steel appears necessary to enhance its corrosion resistance. Mechanical polishing destroys the passive layer formed during manufacture of the strip and tube. The passive layer is quite thin, in the order of 50-400Å, or 12-150 atoms thick.

Although swirl polishing does not remove a measurable amount of metal, the passive layer is destroyed as evidenced by surface oxidation. When these oxidised surfaces are dipped in hot nitric acid the colours disappear, indicating removal of iron oxides. Thus, passivation following polishing is a necessary operation.
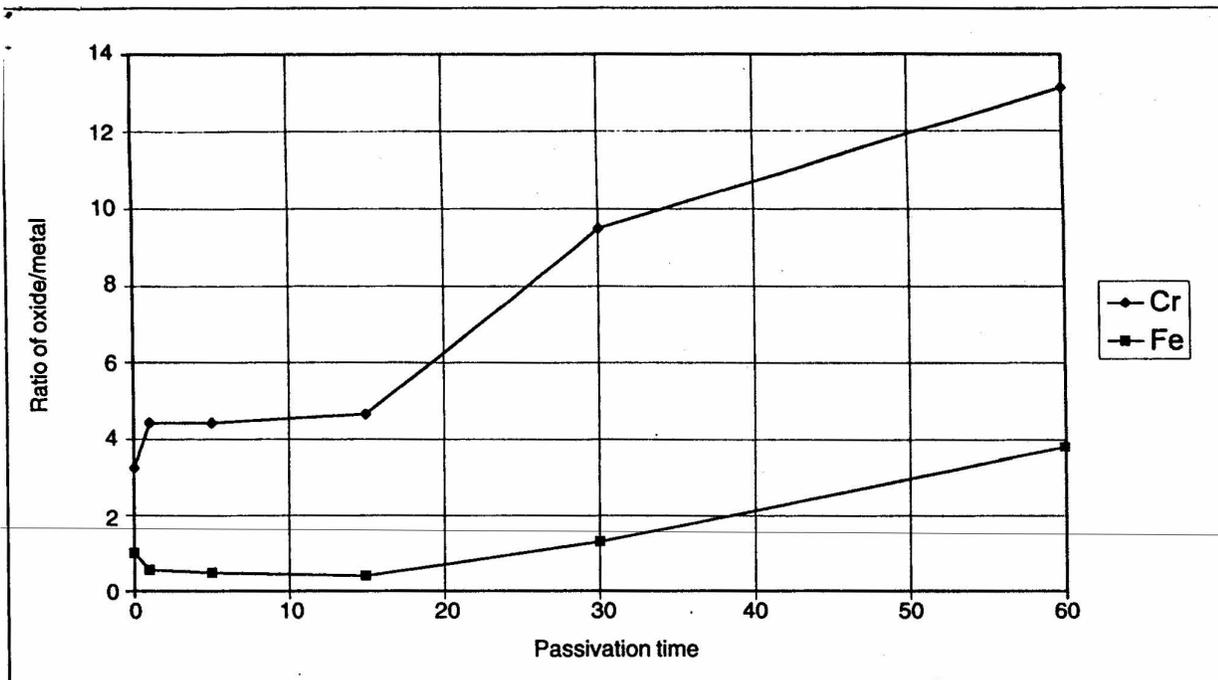
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Figure 5: Change in ratio of Cr_2O_3:Cr and Fe_2O_3:Fe as a function of passivation time
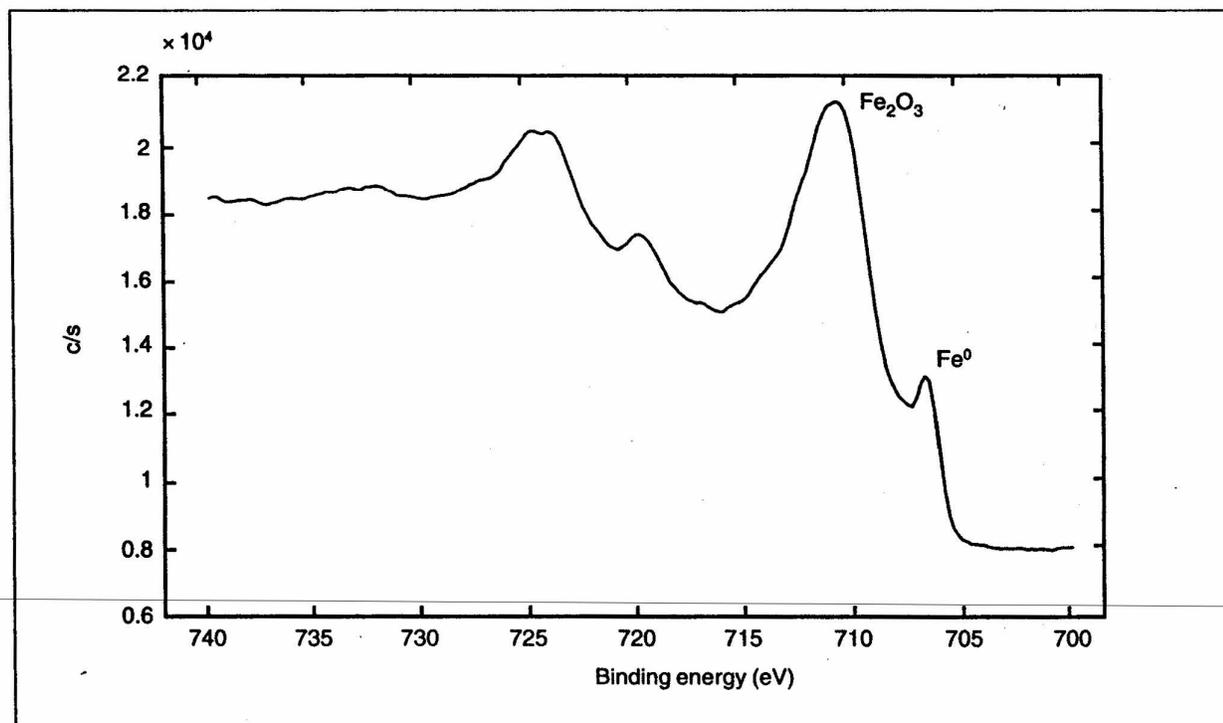

Figure 6a: Iron-binding energy scan of as-received material showing relative oxide and free iron levels

The most dramatic change in surface chemistry occurs after only one minute in hot nitric acid during which time the surface Cr/Fe ratios change from 0.26:1 to 1.1:1. Much of this change appears to be the dissolution of surface iron oxide as seen in **Figures 6a and 6b**. A careful examination of the binding energy curves for both iron and chromium (**Figures 7a and 7b**), shows that the metallic chromium (valency zero) steadily drops with increasing passivation time, and chromium oxide increases.

Metallic iron, however, remains a significant species even after 60 minutes' passivation, as seen in **Figure 8**. Electropolished material by comparison exhibits very little metallic iron[3], which suggests that it will have better corrosion resistance.

The mechanism for passivation appears to be related to the progressive oxidation of chromium as the first step. Once the free chromium is essentially consumed, iron begins to form its oxide. The atmosphere-formed iron oxide, which was dominant in
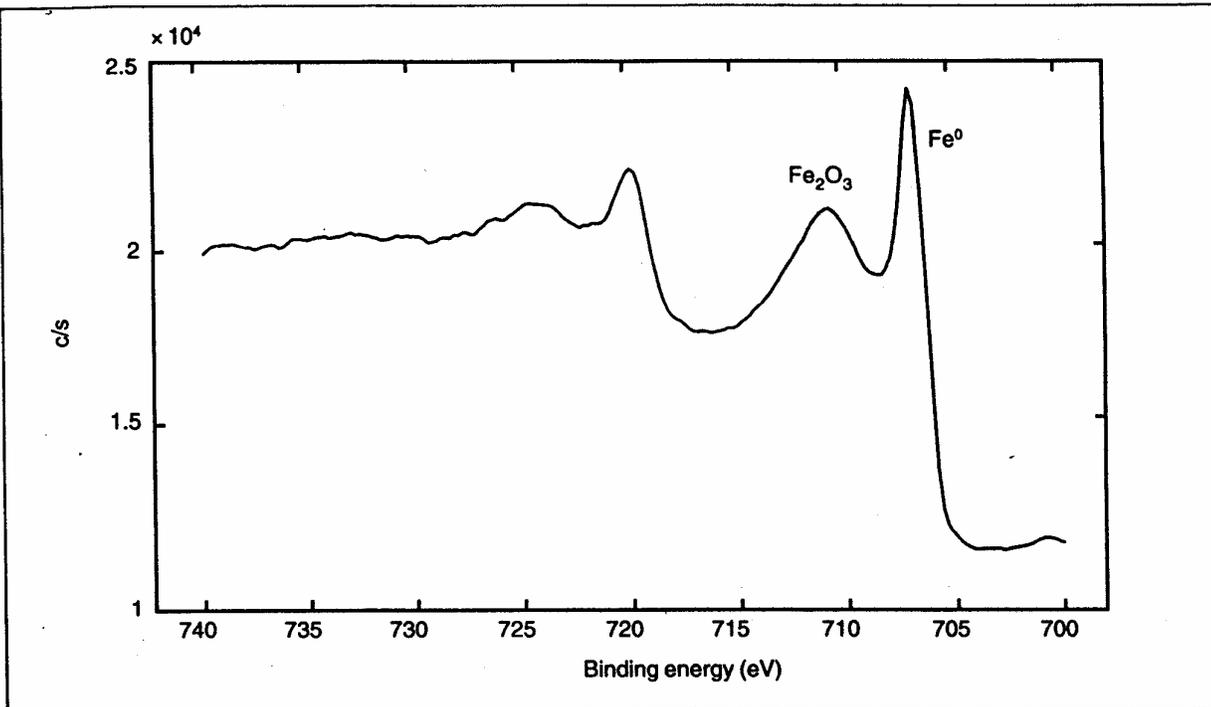
Figure 6b: Iron-binding energy scan after one minute passivation illustrating the decrease in oxide and increase in free iron
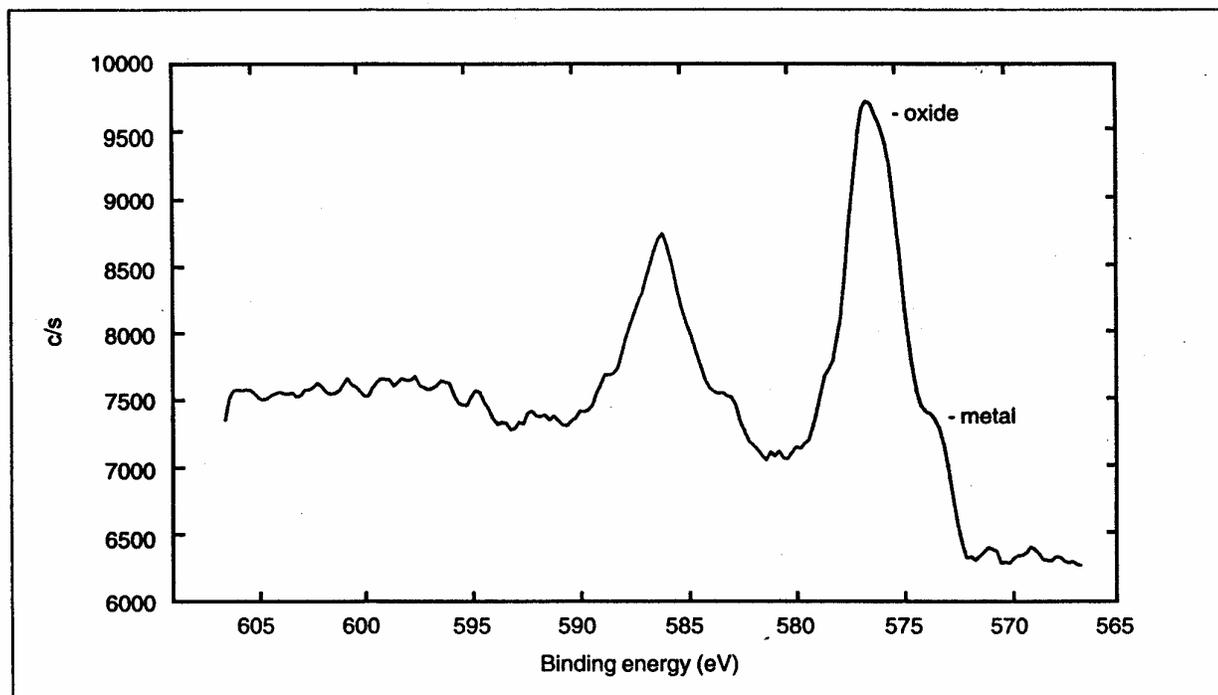

Figure 7a: Chromium-binding energy scan of as-received material showing relative oxide to free chromium levels

the as-received material, rapidly dissolves in the hot nitric acid and metallic iron remains the dominant species up to 30 minutes where the amount of oxide finally exceeds that of the metallic iron.

True passivation does not appear to occur until the metallic elements are totally converted to the oxide. For mechanically polished material this will be in excess of 60 minutes' passivation in hot nitric acid.

We did not investigate the role of citric acid or citric acid plus EDTA (ethylene diamine triacetic acid), therefore we cannot comment on their rate of metallic iron conversion to the oxide. This will be the subject of another study.

The question is often asked: Is passivation of the completed WFI system necessary, especially if nitric acid passivated tubing is used for the construction?

Table 3: Composition as a function of depth for an as-polished specimen

Depth, Å	C	N	O	SI	S	Ar	Cr	Fe	NI	Mo
0	41.8	2.4	39.9	1.8	0.3	–	2.6	9.4	0.5	0.2
25	4.1	–	32.7	0.6	0.2	1.2	13.4	42.2	4.6	0.7
50	4.2	–	14.9	0.8	–	2.1	11.0	59.2	6.5	1.2
100	3.8	–	9.4	0.9	–	2.5	13.4	63.5	4.8	1.6
200	2.1	–	7.2	0.6	–	2.5	15.0	65.7	4.8	1.9
400	1.5	–	5.4	0.9	–	2.5	15.8	66.1	5.7	2.0
800	1.6	–	3.8	0.5	–	2.4	16.1	68.4	4.9	2.2
1,600	1.4	–	3.1	0.3	–	2.5	16.6	68.8	4.8	2.2

Table 4: Composition as a function of depth for 30-minute nitric acid passivated Type 316L

Depth, Å	C	N	O	SI	Ar	Ca	Cr	Fe	NI	Mo
0	25.1	1.6	51.4	0.9	–	0.1	13.0	5.7	0.7	0.3
25	3.7	0.2	48.1	0.7	1.4	0.1	21.5	20.4	3.0	0.5
50	3.1	0.3	43.3	0.7	1.7	0.1	20.6	26.1	3.2	0.6
100	2.3	–	39.3	0.2	2.0	0.1	20.9	31.4	2.9	0.8
200	1.9	–	34.4	0.3	2.2	0.1	20.7	36.4	3.1	0.9
400	2.1	–	28.8	–	2.3	–	19.3	42.8	3.3	1.2
800	1.8	–	21.2	–	2.3	0.1	18.4	50.7	4.1	1.5
1,600	1.9	–	11.6	–	2.4	0.1	17.4	59.9	4.8	1.9

Table 5: Composition as a function of depth for 60-minute nitric acid passivated type 316l

Depth, Å	C	N	O	SI	P	Ar	Ca	Cr	Fe	NI	Mo
0	28.8	1.8	49.9	1.1	0.4	–	–	10.5	6.7	0.5	0.3
25	8.6	0.3	49.8	0.9	0.3	1.2	0.1	17.2	19.6	1.7	0.4
50	5.6	0.4	47.8	0.8	0.1	1.5	0.2	17.1	24.0	2.1	0.5
100	4.0	0.3	45.2	0.5	0.1	1.7	–	18.1	27.7	2.1	0.5
200	3.6	–	41.9	0.5	0.1	1.7	0.1	18.4	31.0	2.1	0.6
400	3.0	–	39.1	0.1	–	1.7	–	17.2	35.8	2.3	0.8
800	2.0	–	33.7	–	–	1.8	0.1	17.3	41.3	2.7	1.1
1,600	2.1	–	24.3	–	–	1.8	–	17.7	49.2	3.4	1.4
3,200	1.8	–	12.8	–	–	2.1	–	17.1	60.0	4.3	1.9

The answer is yes. Even if the tube surface is adequately passivated it is in the best interests of the end user to passivate.

Orbital welding results in an area within which the alloy chemistry is not balanced for optimum corrosion resistance. Typical weld chemistries have Cr/Fe ratios of 0.11:1 and high manganese.[4] It is necessary to passivate to remove the manganese and to change the Cr/Fe ratio to greater than 1:1. Unless this is done there will be an area where accelerated corrosion can occur, and in those environments containing electrolytes, galvanic corrosion may take place.

Conclusions

Rather dramatic changes occur in the surface chemistry of mechanically polished Type 316L during

Table 6: Ratio of iron and chromium oxide to the metal for various passivation times

	0 mins	1 min	5 mins	15 mins	30 mins	60 mins
Fe_2O_3/Fe^0	1.0:1	0.5:1	0.4:1	0.3:1	1.5:1	3.8:1
Cr_2O_3/Cr^0	3.2:1	4.5:1	4.5:1	4.5:1	8.5:1	13.0:1

passivation. Iron decreases as does silicon, nickel and molybdenum. Oxygen and chromium both increase. The Cr/Fe ratio increases with passivation time.

The passivation mechanism appears to be controlled by the oxidation of metallic chromium to the trivalent oxide. Iron does not begin to form appreciable trivalent oxide until chromium is satiated.

Even after 60 minutes' passivation in hot nitric acid a definite metallic iron peak still remains, indicating that further passivation could occur.
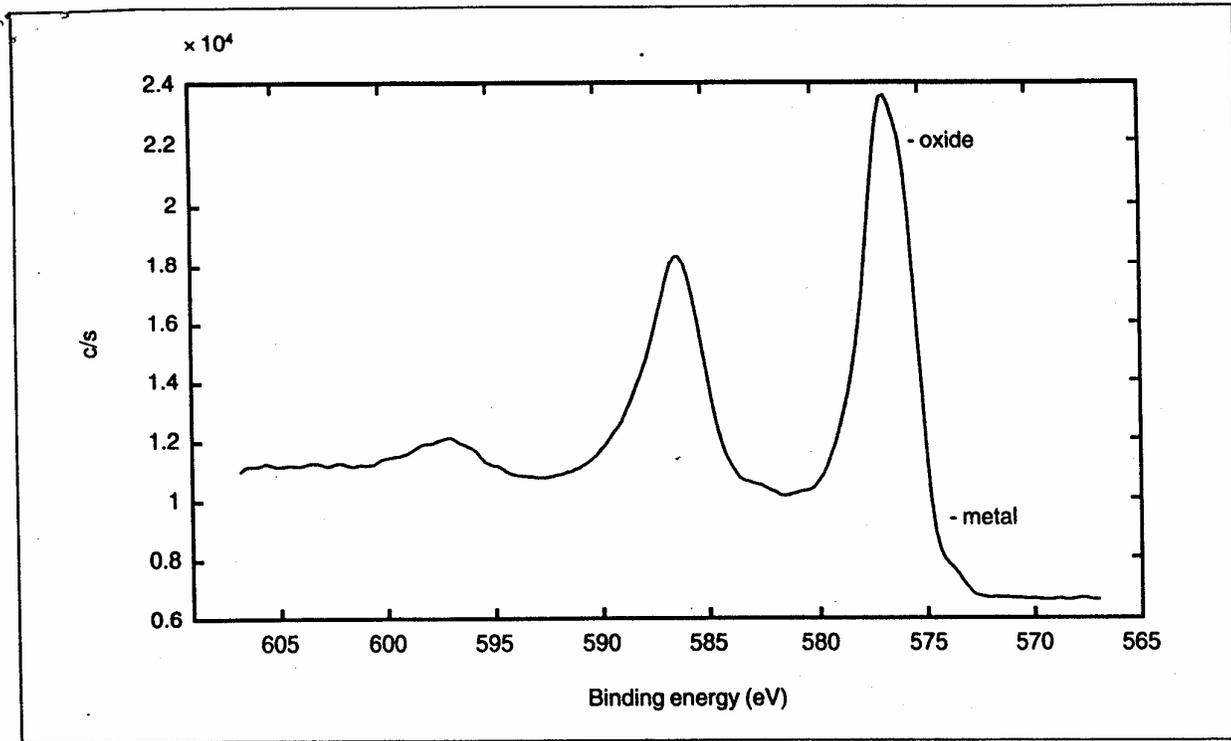
Figure 7b: Chromium-binding energy scan of the 60-minute passivated material showing decrease in free chromium
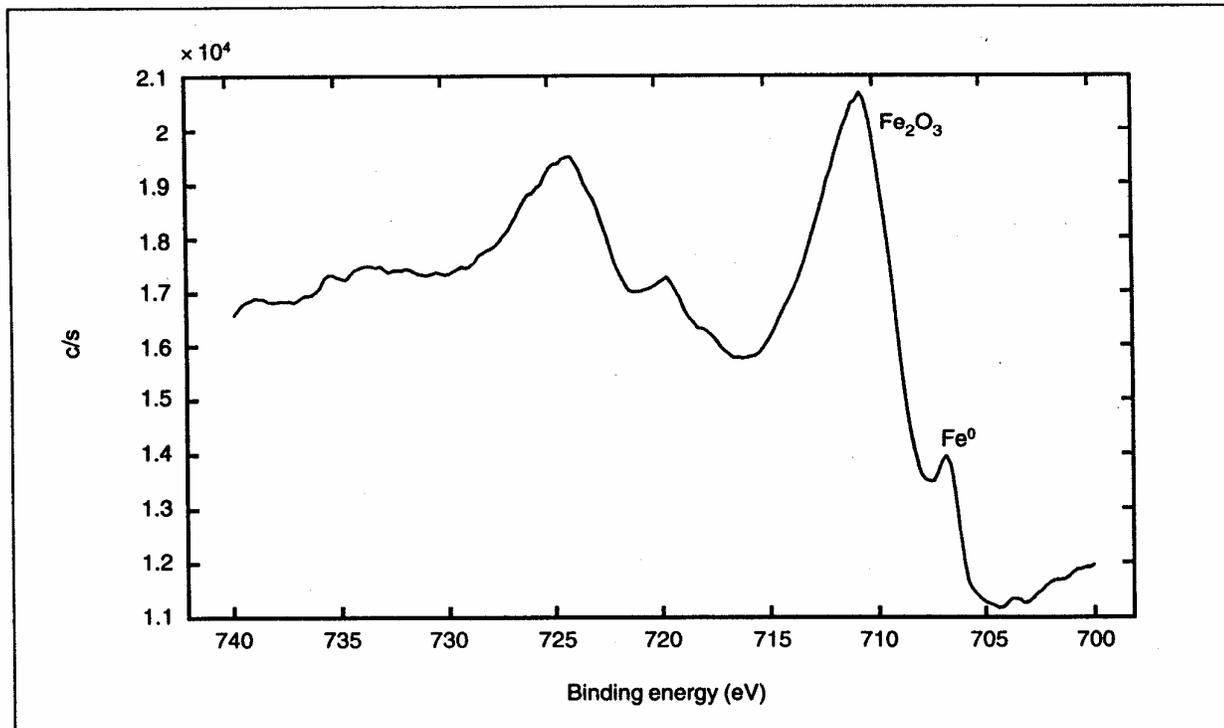

Figure 8: Iron-binding energy scan of 60-minute passivated material showing significant residual free iron

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3. Tverberg JC and Kerber SJ. *Colour Tinted Electropolished Surfaces: What Do They Mean?* Conference Proceedings, Interphex Philadelphia, April 15-17, 1997.

4. Kerber SJ. Report: *Analysis of Orbital Butt Weld with X-ray Photoelectron Spectroscopy.* June 22, 1996.