# STAINLESS STEEL

*AES and XPS analysis of the passivation layer on stainless steel can help determine how well it will resist corrosion.*

*Susan J. Kerber**
*Material Interface Inc.*
*Sussex, Wisconsin*

*John Tverberg***
*Trent Tube Inc.*
*East Troy, Wisconsin*

**A**uger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are valuable techniques for analyzing the surface of stainless steels to establish their ability to resist corrosion. AES identifies the atoms in a layer by measuring the characteristic Auger electron energy, which is emitted in steps from an inner atomic shell. XPS (also known as ESCS, electron spectroscopy for chemical analysis) measures the energy spectra of electrons emitted when the surface is exposed to X-rays.

Both of these techniques have an analysis depth of approximately 2 to 4 nm (20 to 40 angstroms, or about ten atom layers); shallower measurements can be made under specially designed experimental conditions. AES can have a very small analysis diameter, down to 20 nm (200 angstroms), and its primary function is to provide elemental identification. XPS has a larger diameter of analysis (about ten microns), and is mainly used to determine the chemical state of near-surface elements. Both techniques can detect elements above atomic number two, with a limit of approximately 0.1 atomic percent. Standard AES and XPS instruments have the ability to sputter argon ions to depth-profile the surfaces of interest, yielding composition as a function of depth. For stainless steel analysis, the total depth of analysis is typically 15 nm.

AES and XPS data can be quantitatively analyzed by means of elemental sensitivity factors, normalization values that are based on yields for pure elements. Because of these factors, analysis of the same surface with AES and XPS can yield slightly different quantified compositions. When precise

*Member of ASM International
**Life member of ASM International
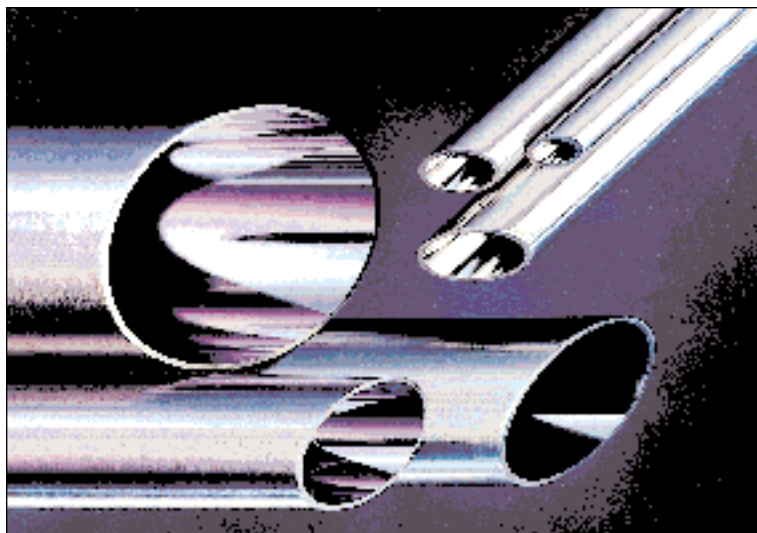
*Stainless steel is rendered resistant to corrosion because of the development of a chromium-rich chromium oxide passive layer on the surface.*

quantification is required, standards similar to the unknown should be the benchmarks.

This article explains how AES and XPS analysis of stainless steel surfaces treated by various chemicals can provide valuable information about passivation layer composition and depth, and its ability to protect against corrosion.

### The surface of stainless steel

Analysis of "clean" metallic samples exposed to the atmosphere typically shows levels of 10 to 20% carbon and 30 to 50% oxygen. The carbon (commonly called adventitious carbon) is present primarily because of adsorbed hydrocarbons and carbon oxides; the oxygen is from instantaneous oxide formation, as well as adsorbed water vapor and carbon dioxide. A clean metallic surface is very reactive and adsorbs more water vapor and atmospheric contaminants than a ceramic or a contaminated surface. Figures 1 and 2 show AES and XPS survey scans of mechanically polished 316 stainless steel that has been exposed to the atmosphere.

By definition, stainless steel contains a minimum of 50% iron and 10.5% chromium. Corrosion resistance is the result of protection conferred by a chromium-rich passive layer, which is typically on the order of 3 to 5 nm thick, or about 15 layers of
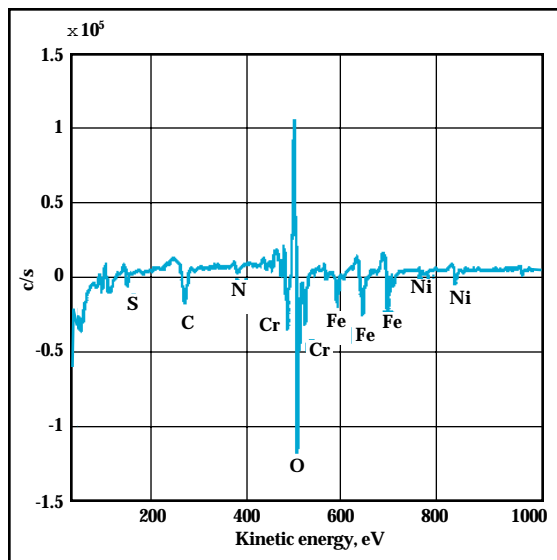
*Fig. 1 — This auger electron spectroscopy scan shows the distribution of elements above atomic number three within five nanometers of a 316 stainless steel surface that has been exposed to the atmosphere.*
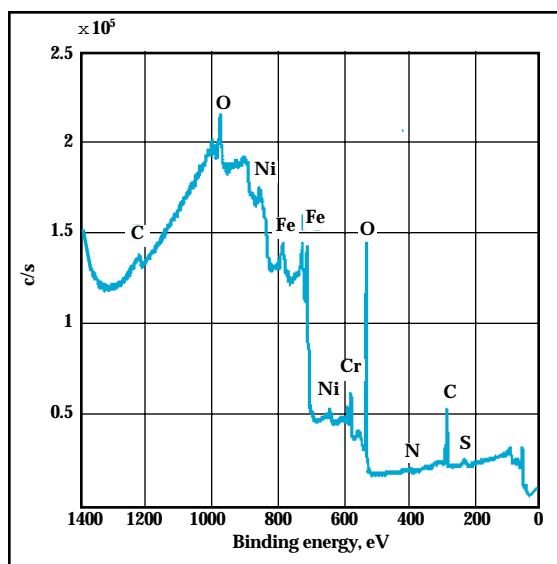


*Fig. 2 — This is an X-ray photoelectron spectroscopy scan showing the distribution of elements above atomic number three within 5 nm of a 316 stainless steel surface that has been exposed to the atmosphere.*

## Table 1 — Ratio of chromium to iron*

| Passivation time, minutes | Cr/Fe, atomic percent |
|---|---|
| 0 | 0.28 |
| 1 | 1.09 |
| 5 | 1.37 |
| 15 | 1.35 |
| 30 | 2.30 |
| 60 | 1.58 |

*As a function of nitric acid passivation time (20% nitric at 58°C) as determined with XPS.*

## Table 2 — Ratio of iron and chromium oxide to metal for various passivation times

| Time, minutes | 0 | 1 | 5 | 15 | 30 | 60 |
|---|---|---|---|---|---|---|
| Iron oxide/Fe$^0$ | 1.0 | 0.5 | 0.4 | 0.3 | 1.5 | 3.8 |
| Chromium oxide/Cr$^0$ | 3.2 | 4.5 | 4.5 | 4.5 | 8.5 | 13.0 |

atoms. The passive layer is formed by an oxidation-reduction reaction in which the chromium and iron are oxidized, and the passivating agent is reduced. If this layer is not allowed to form, or if the layer is broken, rapid general and/or galvanic corrosion can follow.

The surface chemistry of stainless steel ultimately depends largely on the chemical or mechanical processing of the surface. Studies show that air oxidation at most temperatures results in a two-layer oxide structure. The outermost layer ($\alpha$-Fe$_2$O$_3$) forms before the inner iron-chromium oxide. At reduced oxygen pressures, a chromium-rich oxide forms first.

AES and XPS studies of aqueous corrosion indicate that the chromium concentration rises as the passivating potential is approached, due in part to selective dissolution of iron from the mixed oxides. Additionally, the outer layer is significantly hydrated, including the presence of mixed iron-chromium oxyhydroxide. The thickness of these layers is on the order of several atom distances.

Molybdenum is often added to stainless steel to improve chloride corrosion resistance. However, little molybdenum is detected on the surfaces of these alloys, and its absence cannot be explained by selective dissolution. One possible mechanism for the improved corrosion resistance of molybdenum-containing stainless steel alloys is that hexavalent molybdenum reacts with active sites where the oxyhydroxide cannot form. Subsequent activity at these sites is therefore reduced, leading to the formation of a more uniform chromium-rich passive layer. In this way, molybdenum complexes may stabilize active sites and prevent the formation of gaps in the passive layer.

### Passive layers

Corrosion resistance in stainless steel may be enhanced by electropolishing and/or chemical treatments. Electropolishing increases the chromium/iron ratio near the surface; chemical passivation treatments further increase this ratio.

Many types of acids are commonly chosen for stainless steel passivation. These include nitric acid, hydrofluoric acid, phosphoric acid, citric acid, and ethylenediamine tetra-acetic acid (EDTA). Various combinations and concentrations of these solutions applied at different temperatures and for different lengths of time yield different chromium/iron ratios in the near-surface region of 300-series stainless steels.

It is important to note that chemical passivation is necessary to significantly increase the Cr/Fe ratio in the near surface region; simple passivation by atmospheric exposure does not form the necessary surface compounds for enhanced corrosion protection.

The changes in the surface layer of mechanically polished 316L tubing have been evaluated after passivation with nitric acid for various lengths of time. The mechanical method chosen was swirl polishing, which removes only a thin layer of material from the surface and may leave some original processing oxide in place. The acid concentration was

that specified in MIL STD QQ-P-35 and ASTM A 967 — Nitric Acid 3; namely, 20% at the specified temperature of 50 to 60°C (120 to 140°F). This concentration and temperature provided the best results with the standard salt spray test. In this study, the time at temperature was varied (0, 1, 5, 15, 20, and 30 minutes) and the surfaces were analyzed by XPS and AES.

No visual difference was seen among the six samples, but SEM examination indicated some slight topography changes. In addition, AES and XPS showed substantial changes in the surface chromium/iron ratio as a function of passivation time (Table 1). In many corrosive environments, a Cr/Fe ratio between 1.5 and 2.0 is advantageous. The highest Cr/Fe ratio (2.3) was calculated for a 30 minute passivation time. Although the data in Table 1 can nominally be measured with either XPS or AES, slightly different ratios are often detected with the two techniques. Experiments at our facility demonstrated that Cr/Fe ratios determined with XPS are usually closer to standardized values than those achieved with AES.

Electropolishing has been shown to increase the Cr/Fe ratio near the surface. However, even if surfaces are electropolished, welding can generate an area within which the alloy chemistry is not balanced for optimum corrosion resistance. For example, weld chemistries can have high manganese, and have Cr/Fe ratios as low as 0.11. To prevent corrosion in these areas, it is necessary to passivate to remove the manganese and to raise the Cr/Fe ratio over one. Unless the surface is passivated chemically, accelerated corrosion can develop in vulnerable areas, and galvanic corrosion may develop if the environment contains electrolytes.

**Depth profile analysis**

The thickness of the passive layer is just as important as its surface chemistry. The composition as a function of depth can be analyzed by in-situ argon ion beam sputtering (found on most surface analytical equipment). Figure 3 illustrates the concentration as a function of depth of oxygen, chromium, and iron in mechanically polished 316L stainless steel. The concentration of iron is substantially higher than chromium at all of the depths analyzed.

Figures 4 and 5 illustrate the change in composition with passivation times of 30 and 60 minutes, respectively, as described above. The data indicate that in the near-surface region, the concentration of chromium is higher than the concentration of iron after passivation. Because of the original polishing method, the total oxygen content was somewhat elevated for a relatively deep displacement depth into the material. For materials initially polished to a greater depth, the oxygen often decreases to 1 to 2% in about 4 nm (40 angstroms). One measure of the passivation thickness is the intersection of the iron and oxygen traces in Fig. 3-5.

The mechanically polished surface has an oxide layer that is approximately 2 nm thick. The 30 minute passivation treatment yields an oxide layer that is about 19 nm thick; the 60 minute treatment
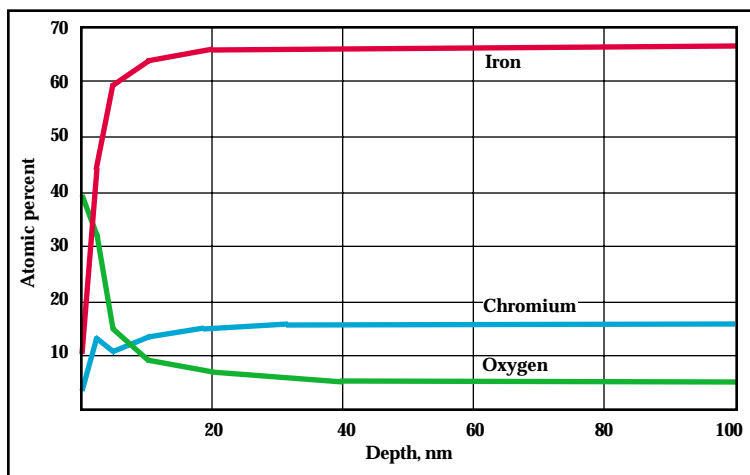


*Fig. 3 — This depth profile analysis of mechanically polished 316 stainless steel results from X-ray photoelectron spectroscopy.*
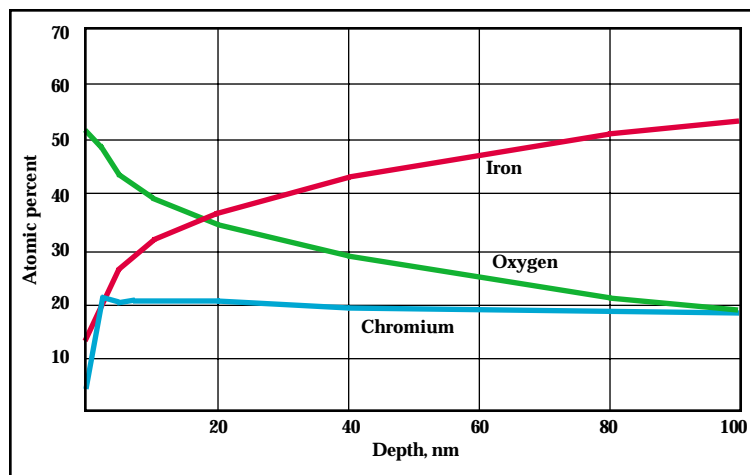


*Fig. 4 — Depth profile analysis of mechanically polished 316 stainless steel passivated with nitric acid for 30 minutes.*
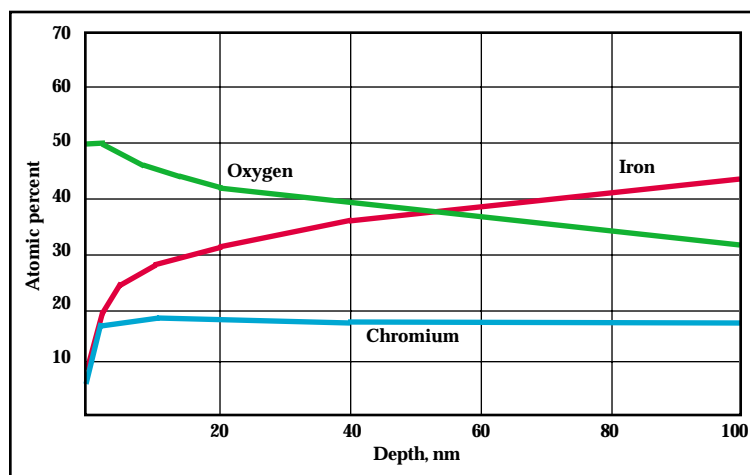


*Fig. 5 — Depth profile analysis of mechanically polished 316 stainless steel passivated with nitric acid for 60 minutes.*

produces a 50 nm oxide layer. Figure 6 shows the Cr/Fe ratio as a function of depth for 0, 30, and 60 minutes of passivation. The Cr/Fe ratio is consistently higher in the outer 10 nm for the 30 minute treatment.

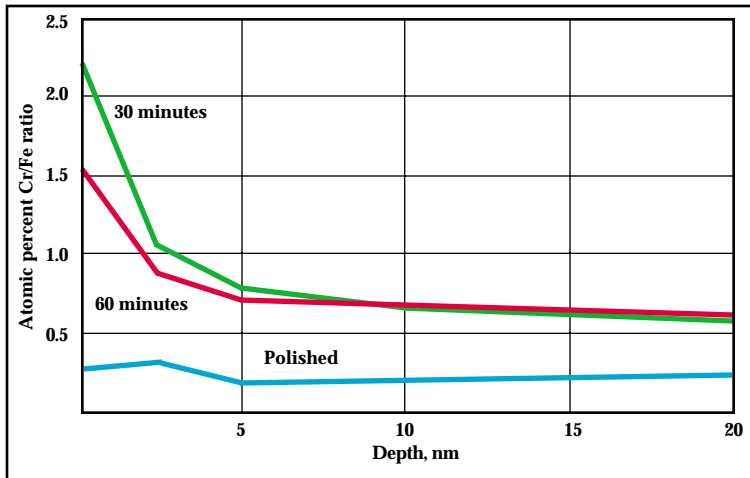**Oxidation state analysis**

When XPS is conducted in a high-energy reso-

*Fig. 6 — The Cr/Fe ratio as a function of depth for nitric acid passivating times of 0, 30, and 60 minutes.*



*Fig. 7 — XPS high energy resolution scan of iron, showing the presence of iron and iron oxides.*

lution mode, each of the peaks of interest in Fig. 2 is scanned individually to measure a more precise value of the energy of the peak. Comparison of this peak location to literature standards may indicate which compound is present. For the most part, oxides can be differentiated from metallic species, and identification of specific oxide compounds is usually possible. A high-energy resolution iron peak is shown in Fig. 7. Through this additional analysis, the ratio of metal-to-oxide for each of the elements can be determined by deconvoluting the peaks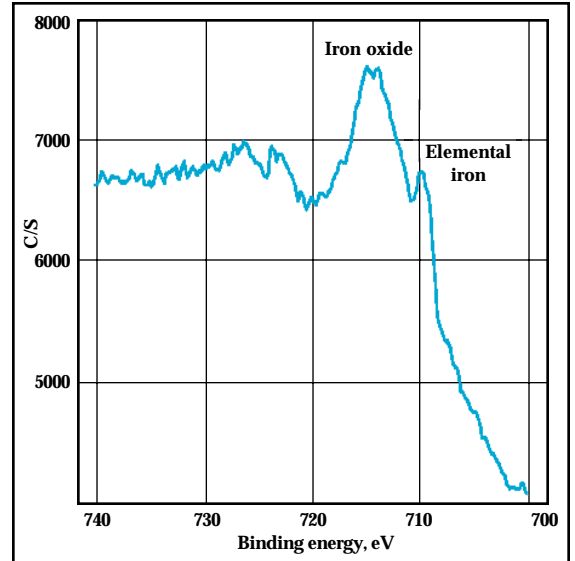 and measuring their area. Table 2 summarizes the ratio of iron and chromium oxides to their metals for various passivation times.

The data in Table 2 confirm that the concentration of metallic species of both elements drops substantially after 30 minutes of treatment, showing that at least this much time is necessary for the successful oxidation of the surface.

**Test results**

Salt spray testing data indicate that for a nitric acid passivation procedure, 30 minutes of treatment gives the best corrosion resistance. The surfaces were analyzed by AES and XPS to investigate the cause for this behavior. Results showed that the maximum near-surface chromium/iron ratio develops with 30 minutes of treatment time, and the surfaces are almost fully oxidized shortly thereafter.

New passivation processes that are more environmentally friendly are currently being designed, and analysis with AES and XPS will be an integral part of direct research and routine quality control. ■

1/4
proto

**References**
1. S. Hofmann, in ASM Handbook, Volume 5, *Surface Engineering*, ASM International, Materials Park, Ohio, 1994; pg. 669-678.
2. *Practical Surface Analysis*, D. Briggs & M.P. Seah, ed., Volume 1, Second Edition: J.W. Wiley & Sons, Chichester, 1990.
3. N.S. McIntyre and T.C. Chan, in Ref. 2, pg. 509-514.
4. S. Jin and A. Atrens, *Appl. Phys. A,* 50; 287-300, 1990.