

SEMI F60-0306 (Reapproved 0611)

TEST METHOD FOR ESCA EVALUATION OF SURFACE COMPOSITION OF WETTED SURFACES OF PASSIVATED 316L STAINLESS STEEL COMPONENTS

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NOTICE: This document was reapproved with minor editorial changes.

1 Purpose

1.1 The purpose of this document is to define a method for testing passivated 316L stainless steel components being considered for installation into a high-purity gas distribution system. Application of this test method is expected to yield comparable results among components tested for the purposes of qualification for this installation.

1.2 This document defines a method of testing the interior surfaces of stainless steel tubing, fittings, valves, and other components to determine the surface composition and chemistry, as a measure of the effectiveness of passivation processes.

1.3 The objective of this method is to describe a general set of instrument parameters and conditions that will achieve precise and reproducible measurements of important surface chemistry within the chromium-enriched oxide layer.

2 Scope

2.1 This document describes a test method to characterize “as received” surface composition and chemistry encompassing all chromium-enriched stainless steel surfaces in tubing, fittings, valves, and other components. This procedure involves measurement of total Cr/Fe ratios, CrOX/FeOX oxide species ratios, and the surface elemental compositions by electron spectroscopy for chemical analysis (ESCA), also called x-ray photoelectron spectroscopy (XPS).

2.2 This document also describes the test method for a compositional ESCA depth profile measurement for Cr, Fe, Ni, O and C from the as-received surface, through the oxide layers, and extending into the base metal. The depth profile measurement evaluates the oxide thickness and the relative composition throughout the modified surface layer as a result of the passivation process.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 This test method is intended to be used by ESCA analysts familiar with the instrumentation and technique. The ESCA instrument must be calibrated and maintained to pertinent manufacturer’s specifications. The method is not intended to preclude the use of any particular brand or model of surface analysis equipment. While most of the test methodology has been developed using specific instrumentation, this method can be adapted to most surface analytical instrumentation.

3.2 The effects of the depth of analysis of the technique and surface contamination affect the results of this test method. These are discussed in the attached appendix. Surface roughness, non-planarity of the surface, and differential sputtering rates for the different chemical species also cause measurement uncertainties in this test method.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI F19 — Specification for the Surface Condition of the Wetted Surfaces of Stainless Steel Components

4.2 ASTM Standards¹

- | ASTM A276 — Standard Specification for Stainless Steel Bars and Shapes
- | ASTM A751 — Standard Test Methods, Practices, and Terminology for Chemical Analysis of Steel Products
- | ASTM E673 — Standard Terminology Relating to Surface Analysis
- | ASTM E902 — Standard Practice for Checking the Operating Characteristics of X-ray Photoelectron Spectrometers
- | ASTM E1078 — Standard Guide for Specimen Handling in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

4.3 NIST Standards²

- | NSIT SRD20 — NIST X-ray Photoelectron Spectroscopy Database

4.4 Other Documents

- | Physical Electronics — Handbook of X-ray Photoelectron Spectroscopy³

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Abbreviations and Acronyms

- 5.1.1 *Cr/Fe* — ratio of the total chromium to total iron in the passive oxide layer.
- 5.1.2 *CrOX/FeOX* — ratio of the chromium oxide to iron oxide in the passive oxide layer.
- 5.1.3 *ESCA* — electron spectroscopy for chemical analysis
- 5.1.4 *eV* — electron volts
- 5.1.5 *FWHM* — full width at half maximum
- 5.1.6 *SPC* — statistical process control
- 5.1.7 *TOA* — take-off angle
- 5.1.8 *XPS* — x-ray photoelectron spectroscopy (an equivalent name for ESCA)

5.2 Definitions

5.2.1 *chromium enriched layer thickness* — the depth within the oxide passive layer for which the chromium concentration is greater than the iron concentration, determined from the depth profile analysis as the depth from the surface to the point where chromium concentration = the iron concentration, if the chromium concentration is > the iron concentration at the surface. If an iron enriched oxide layer is present then the chromium enriched layer thickness is the depth at which the chromium concentration, decreasing from a maximum value, intersects the iron concentration, which is increasing to its maximum (bulk) value, minus the iron enriched oxide layer thickness. (See Figure 1).

5.2.2 *Cr/Fe Ratio*

5.2.2.1 *total Cr/Fe ratio* — the ratio calculated from the peak areas of all species, elemental and oxides, of each element from the high resolution data of the as-received surface.

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² National Institute of Standards and Technology, 100 Bureau Drive, Stop 3460, Gaithersburg, MD 20899-3460, USA; Telephone: 301.975.6478, <http://www.nist.gov>

³ Physical Electronics, 18725 Lake Drive East, Chanhassen, MN 55317, USA; Telephone: 952.828.6200; Fax: 952.828.6176; <http://www.phi.com>

5.2.2.2 *max Cr/Fe ratio* — determined by inspection and calculation from the depth profile analysis as the maximum of the ratio of the Chromium concentration to the Iron concentration profiles.

5.2.2.3 *Cr/Fe ratio at 10 angstroms* — the ratio of the Chromium concentration to the Iron Concentration taken at 10 Angstroms from the initial surface from the depth profile analysis.

5.2.3 *CrOX/FeOX ratio* — the ratio calculated from the peak areas of only the oxide species of each element from the high resolution data of the as-received surface.

5.2.4 *depth profile analysis* — the atomic concentration of the elements present as a function of depth determined by surface analysis in conjunction with the removal of successive atomic layers by ion sputtering.

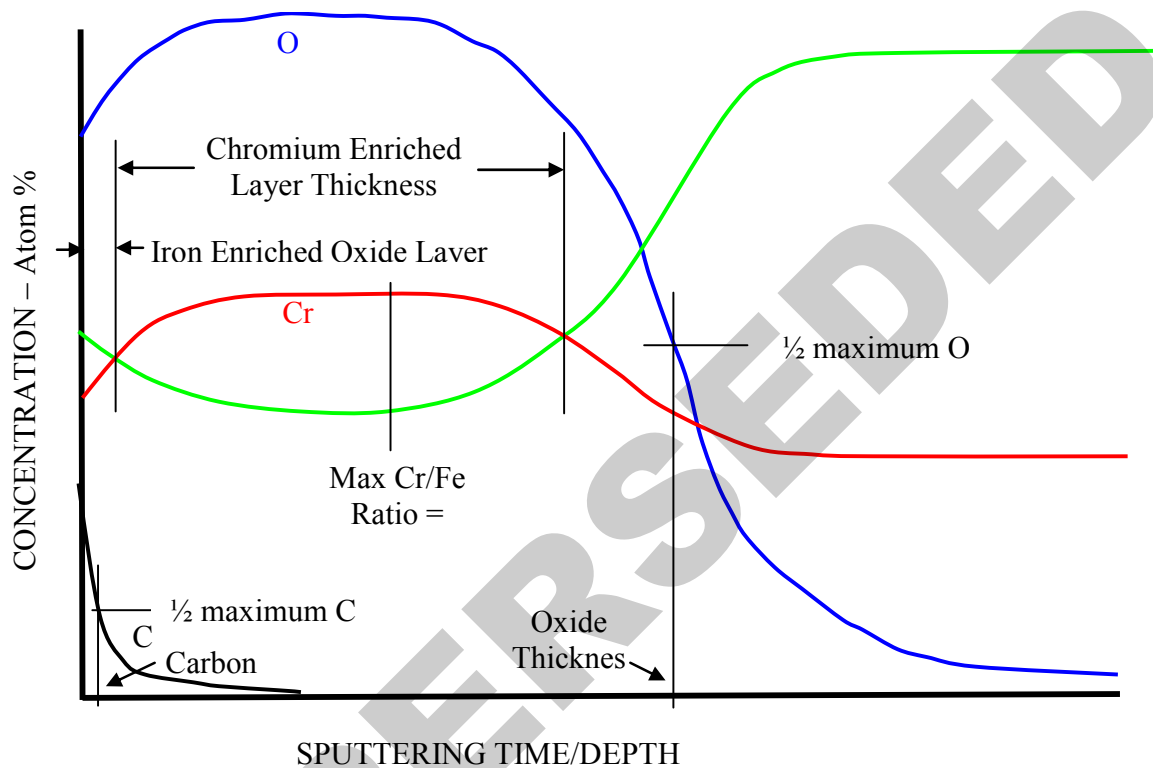


Diagram of Depth Profile Analysis of Stainless Steel Illustrating Definitions

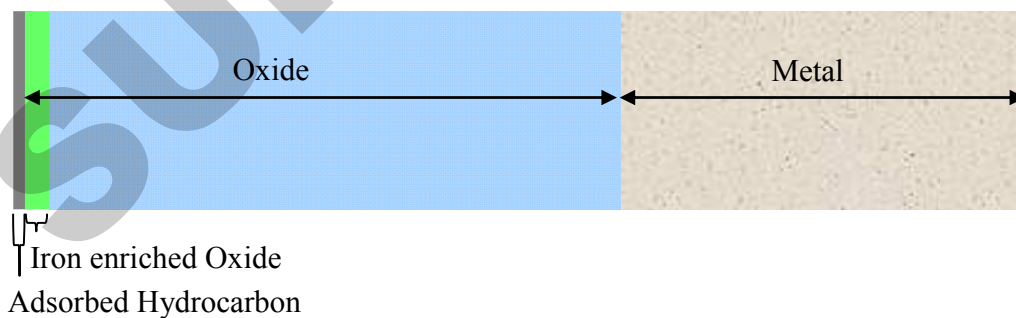


Illustration of Surface Layers on Stainless Steel Corresponding to the Depth Profile

Figure 1
Diagram of Depth Profile Analysis Corresponding to the Surface Layers on Stainless Steel

5.2.5 *iron enriched oxide layer thickness* — the depth from the initial surface for which the iron concentration is greater than the chromium concentration in the depth profile analysis of the passive oxide layer. Sometimes also called a *Detached Iron Oxide layer*. (See Figure 1.)

5.2.6 *oxide thickness* — the thickness of the passive oxide layer on the surface. Generally determined from the depth profile analysis as the sputter depth at which the oxygen concentration decreases to $\frac{1}{2}$ its maximum value. (See Figure 1.)

5.2.7 *passivation* — the chemical treatment of a stainless steel surface with an oxidizing solution for the purpose of enhancing the corrosion resistant surface film.

5.2.8 *passive oxide layer* — the chromium enriched oxide adherent surface film resulting from the passivation process that gives stainless steel its enhanced corrosion resistance.

5.2.9 *sampling volume* — the volume from which photoelectrons are detected. The x-ray spot size and/or the lens and aperture system of the electron analyzer determine lateral dimensions. A length of three times the photoelectron mean free path is considered the maximum depth sensitivity. Sampling volume is dependent on the sample material and TOA. The acceptance angle of the analyzer will also influence the distribution of the depth information.

5.2.10 *sputtering* — removal of successive atomic layers from the surface by bombardment with ions.

5.2.11 *take-off angle (TOA)* — the angle that the collection lens forms with the sample plane.

5.2.12 *wetted surface* — surfaces of the components that are in contact with the contained gases and/or liquids used in semiconductor manufacturing processes.

6 Summary of Method

6.1 Data Acquisition

6.1.1 Acquire elemental survey and calculate elemental composition of “as received” wetted surface.

6.1.2 Acquire chromium and iron regions at high resolution of “as received” wetted surface. The total Cr/Fe ratio and CrOX/FeOX ratios are calculated from these data.

6.1.3 Acquire a compositional depth profile to determine the relative abundance of carbon, oxygen, chromium, iron and nickel. Additional elements may be included as desired (i.e., molybdenum, silicon and nitrogen). If minor elements are included in the profile the instrument parameters should be chosen to allow for a detection limit of 1 atomic percent (at%) or better.

6.2 *Reporting* — Data is provided consisting of:

6.2.1 A survey spectrum extending from at least 0 to 1100 eV.

6.2.2 The high-resolution Cr ($2p_{3/2}$) and Fe ($2p_{3/2}$) spectra from the as-received surface.

6.2.3 A compositional depth profile plot including C, O, Cr, Fe and Ni as a function of sputtering time.

7 Possible Interferences

7.1 *Mo (3d) and S (2s)* — Use S (2p) for quantification of sulfur. Molybdenum will appear as a doublet; quantity may be overestimated.

7.2 *Fe (2p_{3/2}) and Ni Auger* — Ignore.

7.3 *Mo (3p) and N (1s)* — The ability to accurately quantify the nitrogen will depend upon the chemical state of both the nitrogen and molybdenum. In some cases the nitrogen will be overestimated from a survey scan quantification.

8 Apparatus

8.1 *Instrumentation* — Any ESCA instrument with definable area of analysis approximately 1 mm or less and sufficient count rate to provide detection of low level contaminants at one atomic percent or greater. A count rate of at least 100,000 counts per minute for clean Au ($4f_{7/2}$) should indicate sufficient sensitivity.

8.2 The instrument should have peak resolution of 1 eV FWHM Au ($4f_{7/2}$) or better (i.e., <1 eV) to ensure species separation of metallic and oxide forms of chromium and iron.

8.3 If the instrument is of a variable take-off angle (TOA) design, the geometry should be set to a TOA of approximately 35° . Instruments with geometries significantly different from this, or with magnetic electron collection lens may provide analysis from a different sampling volume. The angle of the incident X-ray irradiation with respect to the sample plane and TOA must be recorded.

8.4 Data reduction software must have the ability to select an iterated Shirley-curve background.

9 Reagents and Materials

9.1 *Instrument Calibration Materials* — Refer to instrument manufacturer recommendations or ASTM E902.

9.2 *Statistical Process Control Material* — A nominal 316L material with a composition range within the guidelines of ASTM A276. The composition of the bulk material should be determined by methods consistent with ASTM A751.

10 Safety Precautions

10.1 This test method does not purport to address the safety considerations associated with use of high voltage, vacuum, and X-ray producing equipment. The method assumes an ESCA analyst with knowledge of instrumentation and associated safety precautions.

11 Test Specimen

11.1 Specimens are to be sectioned to appropriate size for the particular ESCA instrument using a clean, dry hacksaw or dry low speed bandsaw. Any sample preparation shall avoid introducing contamination onto the surface to be measured. In addition, preparation must avoid excessive heating of the sample, that is, the surface temperature shall not exceed 50°C , to avoid oxide growth or change in surface composition.

11.2 Sample preparation should preferably be done by the component manufacturer. Following sectioning the sample(s) are to be cleaned and packaged per the manufacturer's standard final cleaning and packaging procedures.

11.3 If sample preparation is done by other than the manufacturer, the sample(s) may be cleaned in deionized water and dried using clean dry air or filtered nitrogen. If the sample(s) are not to be analyzed immediately they should be packaged by wrapping in clean metal foil or sealing in cleanroom quality nylon bags.

11.4 If sample preparation is done by other than the manufacturer this shall be stated in the report narrative and the analytical results are not to be interpreted as indicative of the manufacturer's quality of cleaning and packaging procedures. A note to this effect shall be included in all tables of reported results of the composition of the surface.

12 Preparation of Apparatus

12.1 Instruments shall be routinely tested in accordance with manufacturer recommendations to assure proper performance. The instrument vacuum shall be $1.0\text{E}-7$ Torr or better during the analysis.

13 Calibration and Standardization

13.1 Proper instrument calibration is necessary to provide the most accurate and reproducible results, particularly if results are compared among different laboratories. Instrument calibration for sensitivity factors and binding energies shall be performed in accordance with the instrument manufacturer recommendations or other accepted method, such as that provided in ASTM E902.

13.2 A measurement of the binding energy difference between the Au ($4f_{7/2}$) at 84.0 eV and Cu ($2p_{3/2}$) at 932.6 eV is an acceptable method of calibrating analyzer linearity. A value of $\pm 3\sigma$ based upon a minimum of 10 historical measurements of less than ± 0.25 eV is acceptable.

13.3 The general ESCA calibration procedures described above are suitable for most analyses and provide reasonably accurate relative quantitative information regarding the surface chemistry. However, in order to establish the most accurate measurement practical and to maintain the desired level of reproducibility over time, an application-specific statistical process control (SPC) shall be established for this test method to determine the appropriate sensitivity factors for chromium, iron, nickel and molybdenum in 316L stainless steel. The bulk

composition of the SPC material should have an assay consistent with the acceptable composition range of 316L for Chromium, Iron, Nickel and Molybdenum, as set forth in ASTM A276. The bulk composition of the SPC material should be determined by methods consistent with ASTM A751. The relative sensitivity factors established for the quantification of data should reflect the nominal composition of the bulk 316L SPC standard after a sputter cleaning sufficient to remove any surface contamination and the oxide passive layer. A $\pm 3\sigma$ relative precision should be established from a minimum of 10 SPC measurements with the following tolerances:

- Cr — $\pm 10\%$
- Fe — $\pm 10\%$
- Ni — $\pm 25\%$
- Mo — $\pm 30\%$

As referenced from ASTM A276-97, a typical 316L material has a composition range in terms of wt% of:

- Cr — 16 to 18
- Ni — 10 to 14
- Mo — 2 to 3
- C — < 0.03
- Mn — < 2.0
- P — < 0.045
- S — < 0.03
- Si — < 1.0
- N — < 0.1
- Fe — Balance

Note that ESCA data is reported in atomic percent.

13.4 The sputter conditions established for the SPC surface cleaning shall be the same as those established for the ESCA depth profile measurement part of this standard. A minimum sputtering etch cleaning of the SPC sample of ≥ 10 nanometers is recommended in order to remove surface contamination, the oxide passive layer and establish equilibrium. Note that the degree of preferential sputtering and other ion etching artifacts are a function of the matrix material and the ion gun conditions.

13.5 Calibration frequency of the application specific SPC should be designed to establish a record of the reproducibility and accuracy of the measurement, as reflected by the nominal composition of the 316L standard. A minimum frequency of one per week is recommended, or immediately prior to performing a measurement in accordance with this test method.

13.6 A sputter rate calibration shall be performed prior to an ESCA profile measurement conducted in accordance to this test method. The ion sputter rate determination shall be made using standard thin films of 100 nanometers or less of SiO_2 on Silicon. The method of determining the thickness of the oxide film shall be based upon the oxygen concentration profile. The oxide – substrate interface shall be specified as the point at which the oxygen concentration decreases to $\frac{1}{2}$ its maximum value in the SiO_2 film, ignoring the first sputter cycle.

13.7 Multiple samples may be analyzed following a single sputter rate determination if the ion gun parameters have not been adjusted and the ion gun performance is documented as stable over the period in question.

14 Procedure

14.1 *As-Received Surface Analysis* — The sample is to be mounted in accordance with manufacturer's recommendations and in a manner consistent with ultra-high vacuum surface analytical procedures. Some of these practices are detailed in ASTM E1078. The area to be analyzed should be mounted parallel to the sample holder surface so that TOA is well known.