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ISS-SIMS SURFACE CHARACTERIZATION OF SMUT ON STAINLESS STEEL

MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

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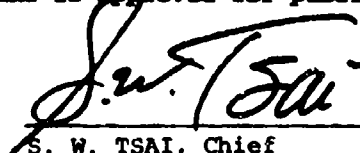| REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Chemical treatments such as acid pickling on stainless steels frequently leave behind more contamination than was originally present. This contamination can be deleterious to further pro-cessing or the use of stainless steels in such applications as adhesive bonding. This chemical residue that is left behind following treatments such as acid pickling is usually called smut. Smut is formed in this work on 304 stainless steel by treatment in sulfuric acid. The smut formed on the stainless steel is

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characterized by ion scattering spectrometry (ISS) and secondary
ion mass spectrometry (SIMS). It was found that the majority of
the smut formed on 304 stainless steel was not carbon or graphite
but rather silicon in an oxidized form. This silicon rich smut
was effectively removed by a further chemical treatment with sul-
furic acid and chromic acid, a similar mixture to that often used
for cleaning glass. This cleaning procedure is shown by the sur-
face chemical analysis methods to produce a clean surface compar-
able to that obtained by abrasion.

FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project 2419, "Nonmetallic and Composite Materials" and WUD No. 44, "Improved Materials, Processes, and Life Prediction Methodology of Adhesive Bonding" monitored by T. W. Haas.

This report covers work conducted inhouse during the period July 1978 - July 1979.

The careful experimental work which provided negative SIMS data is appreciated on the part of J. S. Solomon. G. Hamner is thanked for the XPS data.

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TABLE OF CONTENTS

AFML-TR-79-4138

LIST OF ILLUSTRATIONS

AFML-TR-79-4138

LIST OF TABLES

SECTION I

INTRODUCTION

There is an ever increasing demand for materials which can
operate at high temperatures with good corrosion resistance.
Such requirements are satisfied in many cases by stainless steel.
Conventional methods of joining stainless steels such as welding,
brazing, and soldering are used, but reliable methods of joining
stainless steels by adhesive bonding methods are also being
developed. Adhesive joints possess a more uniform stress
distribution, are lighter, and are better sealed than conven-
tional joints. Corrosion is also minimized in adhesive joints.
Also, in conventional methods which use heat such as welding
with stainless steel the alloy is subject to a structural change
resulting in intergranular precipitation of carbides which
impairs resistance to corrosion. Stainless steels following
final rolling are normally covered with a layer on the surface
containing processing aids and oxidation products. The surface
must undergo an etch or pickle for further processing. Allen and
Alsalim[1] have pointed out that generally this surface layer in
its original state has a deleterious effect on adhesive bond
strength. Unfortunately, following acid pickling the surface
can be even more contaminated than it was originally. This con-
tamination is called smut. Smut is a term used by metal processors
to denote an accumulation of a noticeable amount of relatively
nonadherent reaction products on chemically treated metal sur-
faces. Alloys containing copper, silicon, and carbon are particu-
larly susceptible to smut formation during processing. The usual
method for desmutting is wiping the workpiece following rinsing
while it is still wet or mechanical brushing by a wire or stiff
bristle brush after drying. However, Allen and Alsalim[1] found
only a portion of the smut is removed by these methods and that
chemical methods were required. This note will report the results
of surface characterization experiments on smutted or desmutted
surfaces of 304 stainless steel.

SECTION II
EXPERIMENTAL

The primary characterization techniques used for studying smut and removal of smut were ion scattering spectrometry[2,3] and secondary ion mass spectrometry.[4] This dual method uses a low energy noble gas ion beam (1-3 KeV) in ultra high vacuum to probe the surface. The ISS instrument (Model 520, 3M Co., St. Paul, MN) measures the energy loss when the probing ion scatters from the outermost layer of the surface. The SIMS technique measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. Positive SIMS was accomplished with a quadrupole mass spectrometer (Model 100C, UTI, Sunnyvale, CA) to which a simple energy analyzer was added. A drawing of the important parts of the instrument is shown in Figure 1. Negative SIMS and AES were performed in a separate UHV chamber as seen in the schematic of Figure 2.

Other instrumental methods of surface analysis used were x-ray spectroscopy (XPS), and scanning electron microscopy (SEM). Type 304 stainless steel which was used in this work is one of a group of standard iron-chromium-nickel alloys having an austenitic structure. The nominal composition of 304 stainless steel is seen in Table I. Chemicals used in this work were reagent grade. They were diluted in distilled water and all reactions were carried out in glass containers.

TABLE I

Compositon of 304 Stainless Steel

Element	Percent	Element	Percent
Carbon	0.08 max	Chromium	18.00-20.00
Manganese	2.00 max	Nickel	8.00-11.00
Silicon	1.00 max	Iron	Remainder

SECTION III
RESULTS AND DISCUSSION

Allen and Alsalim[1] showed that it is essential that smut be
removed because its presence on surfaces to be bonded reduces
bond strength by about 50 percent. They found in their work on
martensitic base stainless steels that all the treatment solu-
tions which effectively attack the steel leave a deposit of what
they termed graphite on the surface. It seems unlikely that smut
produced by Allen and Alsalim consists only of carbon, particu-
larly in the graphite form because the alloy they used contains
significant amounts of other materials which show serious smutting
characteristics such as silicon, manganese, and copper. It was
desired in this work to find the magnitude and chemical identity
of any smut which formed on a typical 18-8 stainless steel,
which in this case was 304 stainless. Type 304 stainless steel
was etched for varying periods of time in warm 1 molar H_2SO_4.
Smut appeared on the surface and was especially evident in those
samples etched for long periods of time. The smut usually forms
very uniformly on the surface, and sometimes it is necessary to
wipe a portion of the surface while it is still wet to increase
visibility of the smut. The wiping increases the detectability
by introducing a contrast change in color and reflectivity of the
smutted and wiped surfaces. The ion scattering reference spectra
are shown in Figure 3 for 304 stainless steel sputtered clean by
positive ions. This data is from scattering of neon ions at
2500 volts and scattering of helium ions also at 2500 volts. In
the neon scattering spectra only chromium and iron are visible.
Nickel may be observed by spectrum subtraction methods or by
curve resolution methods. The helium scattering spectra shows
only a small amount of oxygen on the surface and the unresolved
chromium-iron doublet. The ion scattering spectrum from a sample
etched in sulfuric acid is shown in Figure 4. Here the spectrum

is obtained with [3]He and bears little resemblance to the original
clean 304 stainless surface. The primary elements which are
observed are silicon and oxygen. Some carbon is present on the
surface and only a very slight amount of the matrix material is
seen. The positive secondary ion mass spectra taken simultaneously
with the ISS data shows primarily silicon and fingerprint spectra
of silicon and oxygen along with a small amount of the matrix
material. Even when the surface of the 304 stainless steel
following rinsing was wiped and appeared visible clean, some
amount of smut remained behind as detected by both a positive
SIMS and ISS. This smutting of ferrous and other metals, particu-
larly in acid media, is well known and many recipes and processes
have been detailed for the removal of this smut.[5] It has been
reported that when the smut is largely carbon it is a finely
divided coating which is easily wiped off.[6] If an appreciable
amount of silicon is present in the alloy the silicon may remain
behind, and it is necessary to remove it by dipping the work in
hot caustic soda solution.[6] Also effective is the chromic acid
solution which had been recommended in the literature,[5] and con-
sists of the following: chromic acid, 500 g; sulfuric acid con-
centrated, 150 ml; and water to make up 1 liter. This solution
applied at room temperature is effective in producing a bright
smut-free surface. The ion scattering spectrum of a desmutted
surface, using [3]He, is shown in Figure 5. Compared with this
spectrum is one obtained by smutting a surface and then lightly
sanding the smut from the surface. It can be seen that the
spectra indicate that the two surfaces are virtually identical.
The positive SIMS spectra from the desmutted surface is also
shown in Figure 6. It can be seen that much of the silicon has
been removed; however, it is still detectable on the surface.
The origin of the large amount of sodium visible in both the ISS
and SIMS spectra is not known. It was shown in other experiments
using mild heating of stainless steels[7] that appreciable amounts

5

of sodium appeared on the surface, apparently due to grain
boundary migration. The smutted and desmutted surfaces were
also examined by several other methods of surface characteriza-
tion. The results of these experiments are shown in Table II
where the species which were found on 304 stainless steel are
listed for each of the surface characterization techniques. Each
of the techniques has its strong points. In AES, for instance,
both sulfur and chlorine are readily detected in the AES spectra;
while in the ISS spectrum, neither of these elements was detected,
probably because they occur in an area of high scattered ion back-
ground. The effectiveness of the chromic acid solution desmutting
method is shown in Figure 6 where the AES spectrum in the region
of silicon (LMM) is shown for both the smutted and desmutted sur-
faces. Although SIMS suffers from widely varying and ever chang-
ing secondary ion yields, it still provides a useful complementary
technique for the other methods shown here. In addition to the
extremely high sensitivity for some elements, such as the alkali
metals, the appearance in the spectrum of fingerprint or cluster
spectra make this technique useful for deduction of the chemical
bonding on the surface. The method generally used for chemical
bonding, XPS, showed that the carbon 1s peak appeared at approxi-
mately the correct energy for graphite, but that some amount of
splitting in the band suggested that perhaps it was also present
in a second valence state. A detailed examination of the silicon
peaks in the photoelectron spectra of the smutted surface shows
that silicon is in the oxide form, which probably should be
expected from its formation in an oxidizing media. Apparently
the silicon does not go into solution during the etching in the
sulfuric acid but does oxidize. Probably this change in oxida-
tion state provides even further resistance to normal methods
of removal.

TABLE II.   Species Found on 304 Stainless Steel

by Surface Analysis Techniques

	Smutted in Sulfuric Acid	Desmutted in Sulfuric-Chromic Acids
AES	Si, O, S, Cl, C, Cu, Fe, Cr, Ni	O, C. S, Fe, Cr, Ni
ISS	Si, O, C, Cu Fe, Cr	O, Na, Fe, Cr
+SIMS	Si^+, Na^+, SiO^+, S, OH^+, Cu^+, CH_n Fe^+, Cr^+, Ni^+, Cu^+	Na^+, K^+, Si^+, S, OH^+ CH_n^+, Fe^+, Cr^+, Ni^+
-SIMS	$C_nH_n^-$, O^-, OH^- Cl^-, SiO^-, SiO_2^- SiO_3^-, SiF^-, $SiOF^-$ SiO_2F, FeO_2^-	$C_nH_n^+$, O^-, OH^-, Cl^- SiO_n^- (greatly reduced) CrO^-, CrO_2^-, CrO_3^- FeO_2^-
PES	C^*, O, S, Si^{**}, N, Cu, Fe, Cr, Ni *more than one form **oxide form	C, O. Fe, Cr, Ni

SECTION IV
CONCLUSIONS

Examination of surfaces of 304 stainless steel smutted in sulfuric acid show that the smut is primarily silicon in an oxidized form with many impurities present. The same analysis methods show that the smut is readily removed in a chromic acid solution.

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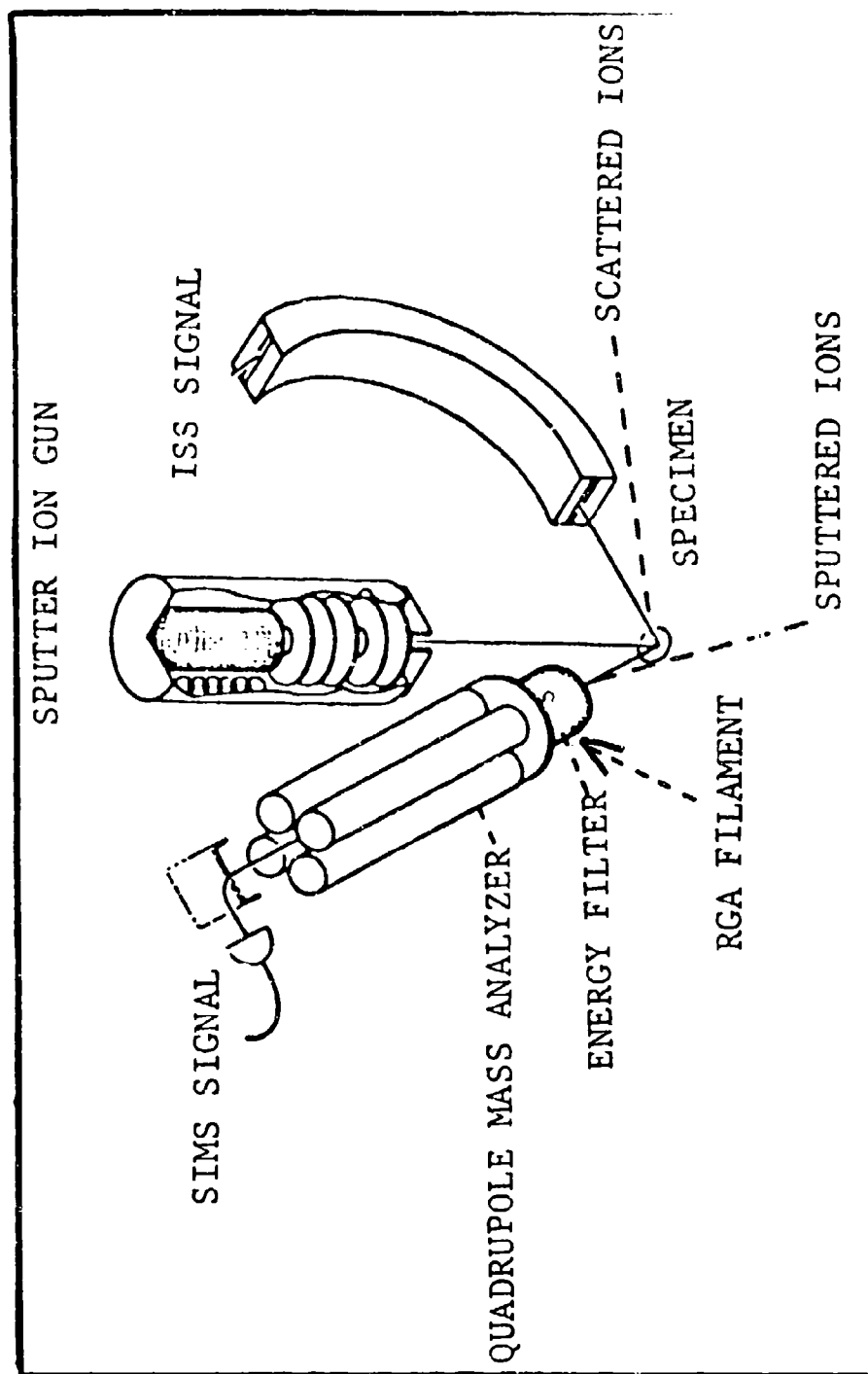
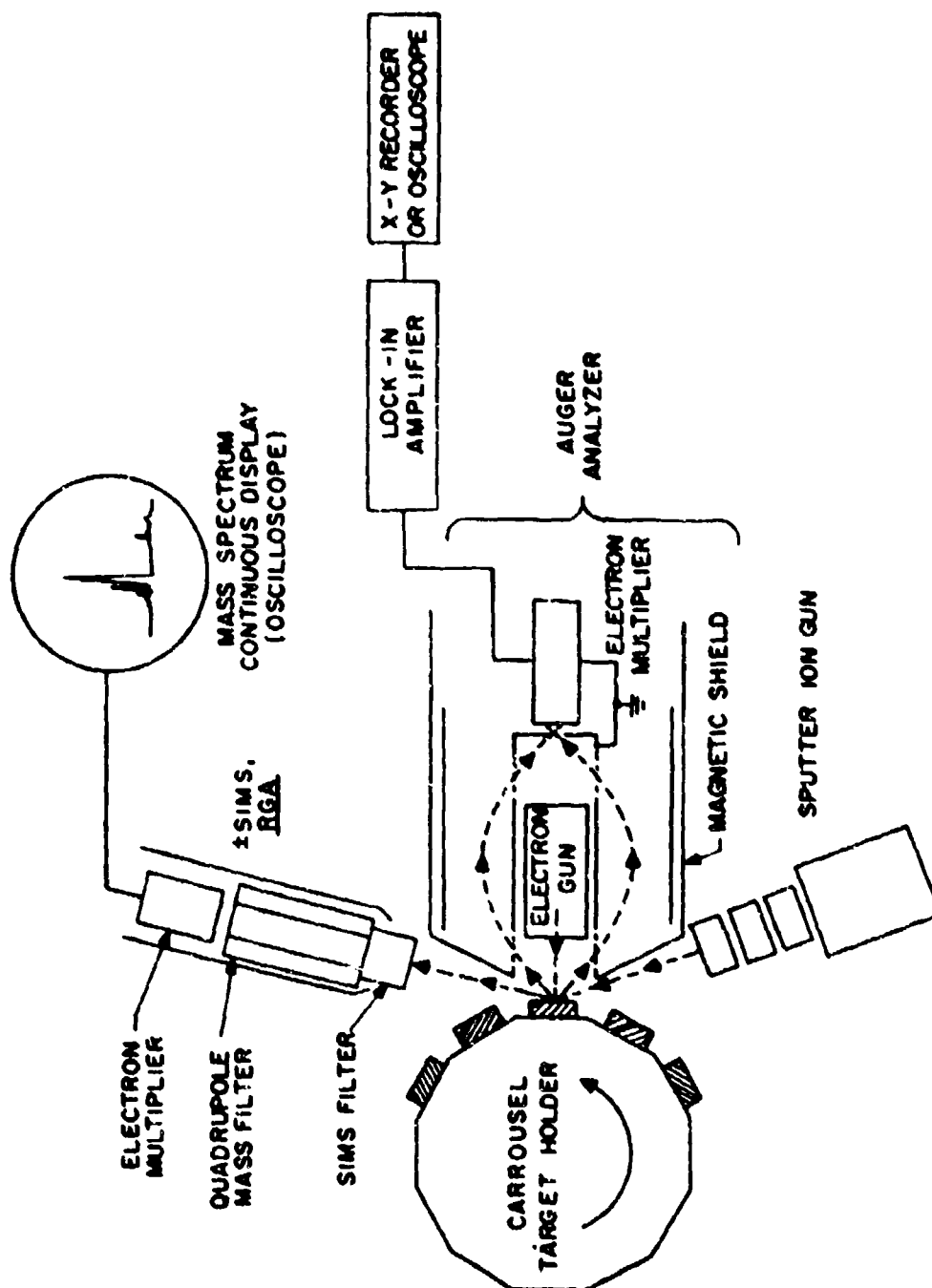Figure 1. Components in Ultra High Vacuum for Ion Scattering Spectrometry and Secondary Ion Mass Spectrometry.

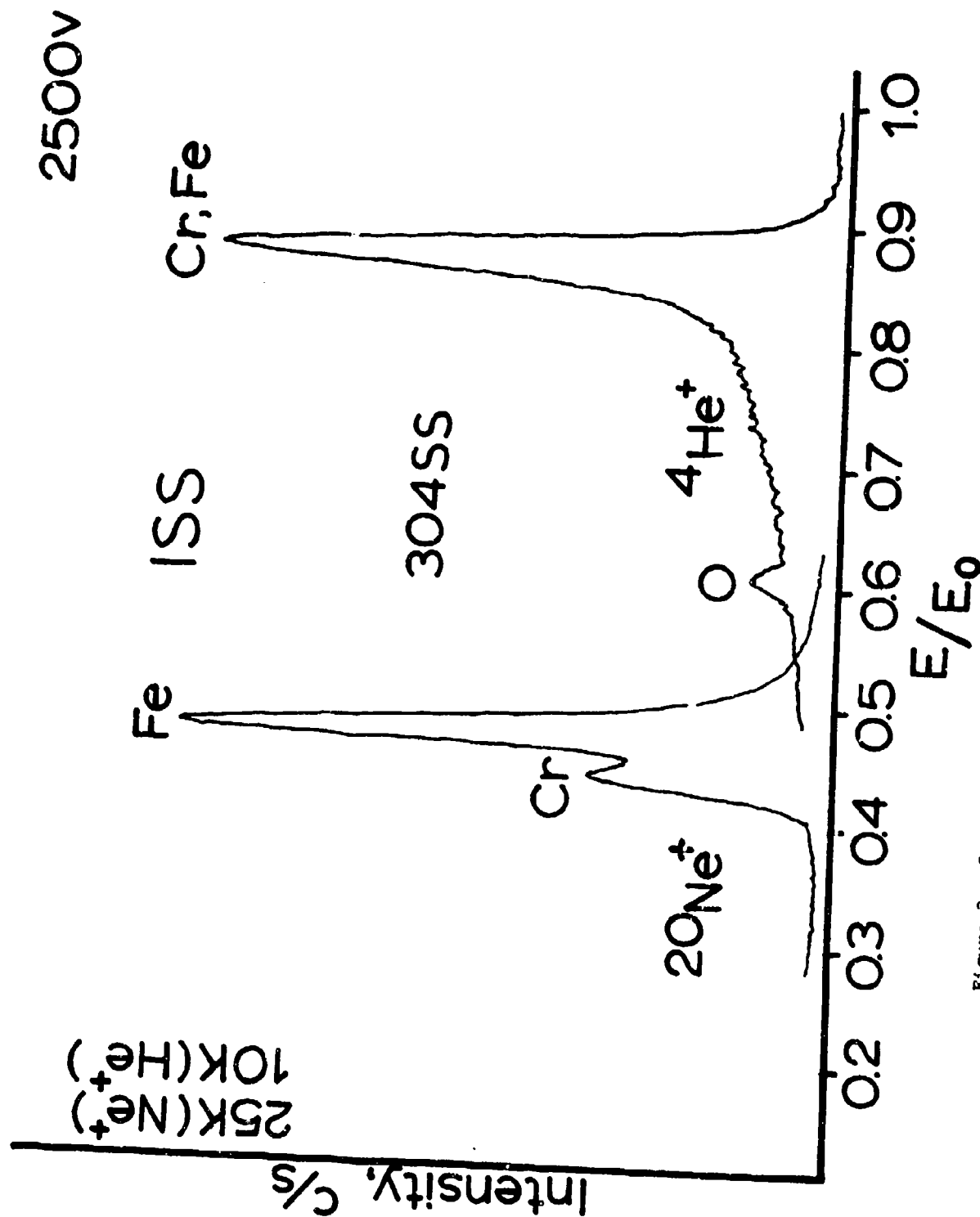Figure 2. Components in Ultra High Vacuum for AES and SIMS.

Figure 3. Ion Scattering Spectra from Clean (Sputtered) Stainless Steel, Using ^{20}Ne and ^{4}He.
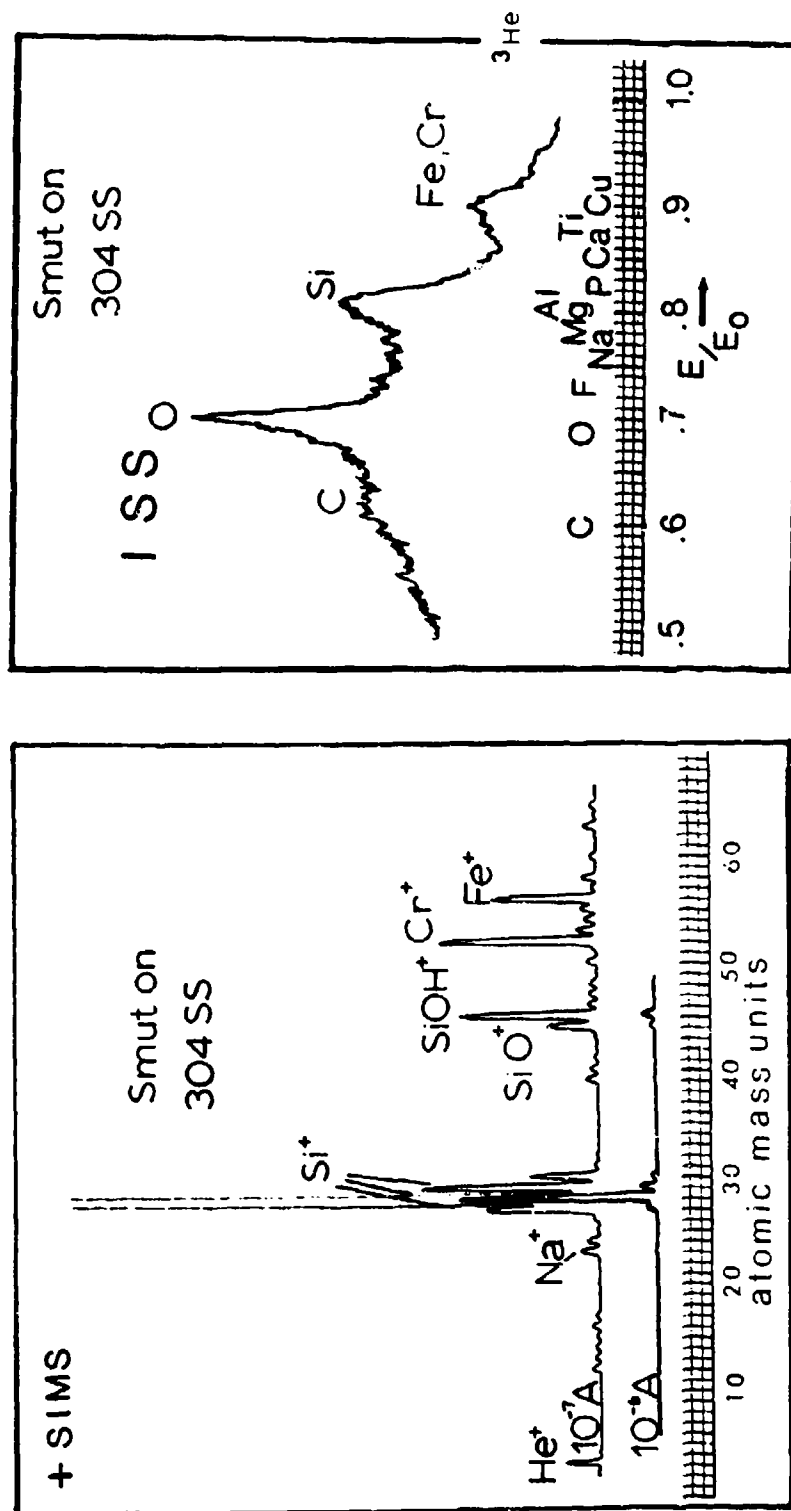
Figure 4. ISS Data for Smutted 304 Stainless Steel, Using 3He at 2500 Volts. Also shown are positive SIMS data obtained simultaneously.
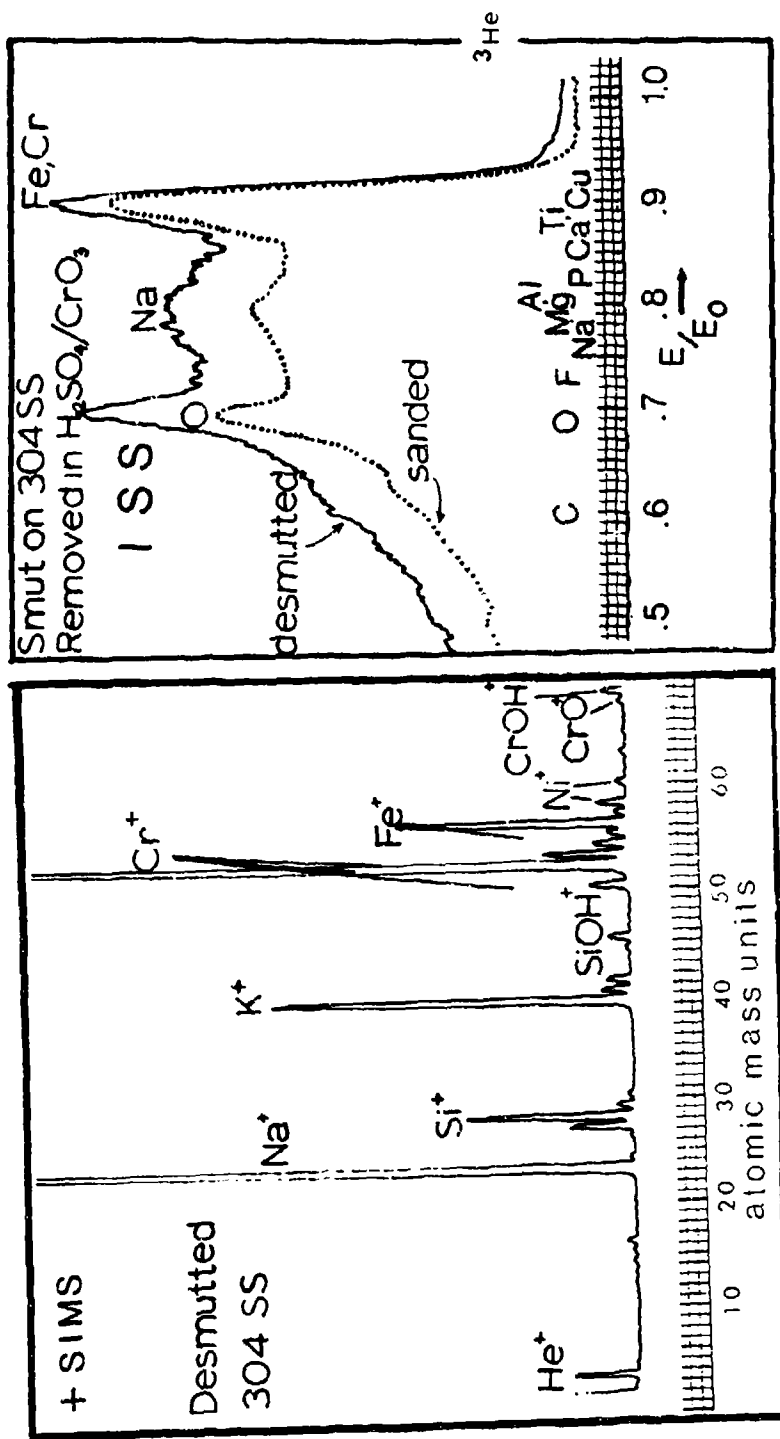
Figure 5. Ion Scattering Spectra Using ^{3}He at 2500 Volts from a Desmutted and a Sanded Surface of 304 Stainless Steel. Also shown is a positive SIMS spectrum obtained from the same surface simultaneously with the ion scattering spectra for the desmutted surface.
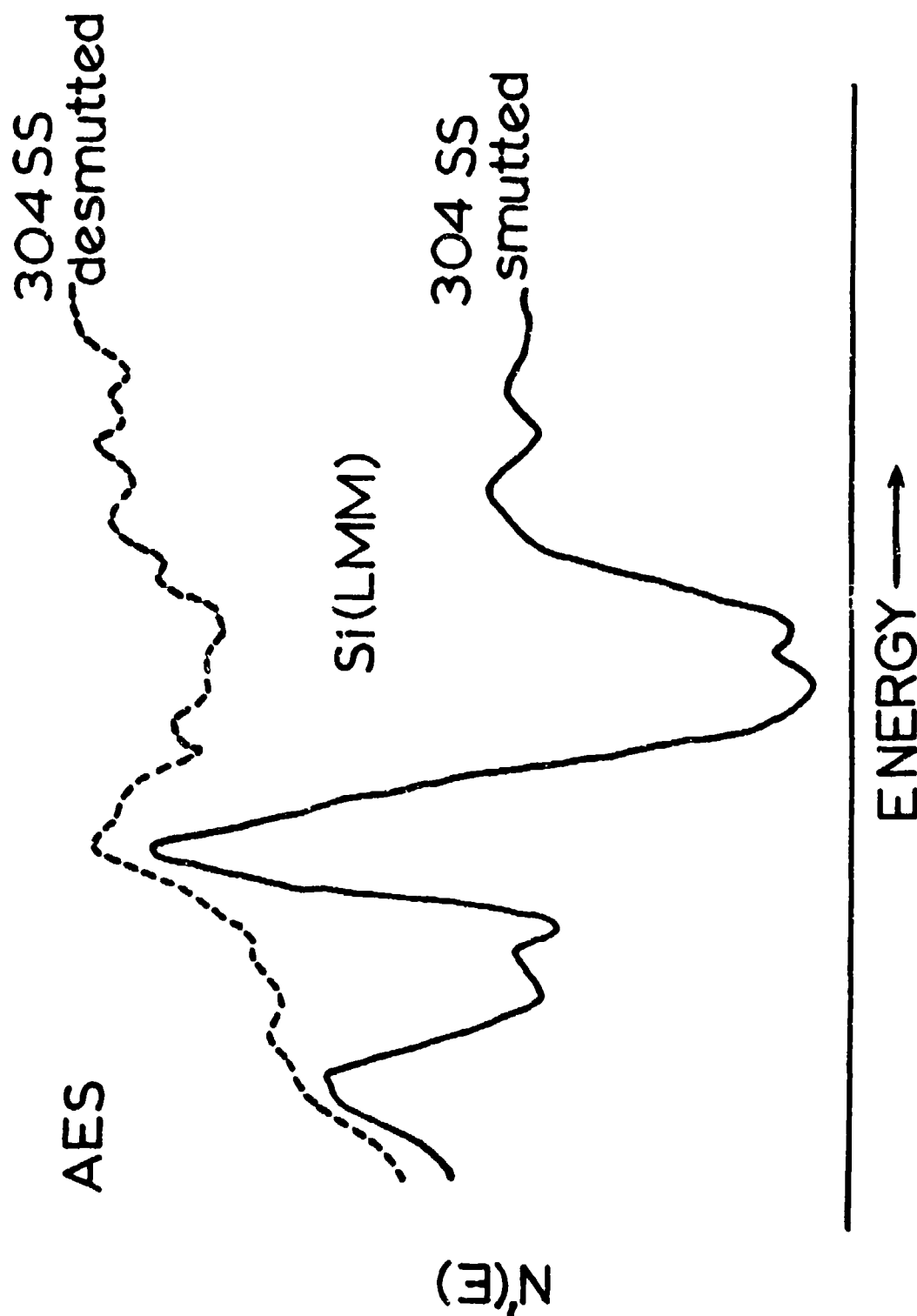
14

Figure 6. AES Spectra in the Si (LMM) Region from the Smutted 304 Stainless Steel Surface and the Desmutted Surface.