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AUGER ELECTRON SPECTROSCOPY AND DEPTH PROFILE STUDY OF OXIDATION OF MODIFIED 440C STEEL

by John Ferrante

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Cleveland, Ohio 44135

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16. Abstract

Auger electron spectroscopy (AES) and sputtering were used to study selective oxidation of modified 440C, which is nominally a 77-wt% iron, 14-wt% chromium, and 4-wt% molybdenum bearing steel with carbon, sulfur, silicon, nickel, vanadium, phosphorous, and manganese making up the balance. The sample was polycrystalline. Oxidation was performed on initially clean surfaces for pressures ranging from 1×10^{-7} to 1×10^{-5} torr and temperatures ranging from room temperature to 800° C. AES traces were taken during oxidation. In situ sputtering depth profiles were also obtained. A transition temperature was observed in the range 600° to 700° C for which the composition of the outer surface oxide changed from iron oxide to chromium oxide. It was also found that heating in vacuum ($\sim5\times10^{-10}$ torr) to 700° C caused conversion of the iron oxide surface to chromium oxide.

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SUMMARY

Auger electron spectroscopy (AES) and sputtering were used to study the selective oxidation of modified 440C, which is a nominally 77-weight-percent iron, 14-weight-percent chromium, and 4-weight-percent molybdenum bearing steel with carbon, sulfur, silicon, nickel, vanadium, phosphorous, and manganese making up the balance. The sample was polycrystalline. Oxidation was performed on initially clean surfaces for pressures ranging from 1×10^{-7} to 1×10^{-5} torr and temperatures ranging from room temperature to 800° C. AES traces were taken during oxidation. In situ sputtering depth profiles were also obtained. A transition temperature was observed in the range 600° to 700° C for which the composition of the outer surface oxide changed from iron oxide to chromium oxide. It was also found that heating in vacuum ($\sim5\times10^{-10}$ torr) to 700° C caused conversion of the iron oxide surface to chromium oxide.

INTRODUCTION

The formation of oxides on alloy surfaces is important in modern technology, especially for corrosion and wear resistance (refs. 1 to 5). Most studies on the formation of these surface oxides have been both insensitive to the initial stages of oxidation and capable of detecting only thick (of the order of 10^{-7} m (1000 Å)) oxide films (refs. 1 and 2). It is possible that thin oxide films (one layer to 10^{-8} m (100 Å)) have desirable corrosion and wear properties (refs. 3 to 5). In addition, the formation of the oxides is dependent on initial surface conditions, the oxide already present, and the surface finish (ref. 6). Few studies have been performed on surfaces cleaned of oxides and with a well-defined analysis of surface composition as a starting point.

In the past 10 years, new tools have been developed for examining surfaces. AES (Auger electron spectroscopy) (ref. 7) is a technique for examining the elemental composition and, in some cases, the compound compositions of surfaces to a depth of 4 or 5 atomic layers. In addition, sputtering (ref. 8), a method for removal of material from a surface by positive ion bombardment, is a useful tool for surface cleaning. These tools in combination have been useful in creating a surface cleaned of oxides and in the subsequent examination of that surface (ref. 9).

The value in the types of experiments conducted in this investigation is that they isolate effects occurring in the initial stages of oxidation which may be related to the development of thicker oxides. The temperature dependence of the composition of oxide films could suggest processing procedures which would optimize either corrosion resistance or wear resistance. At present, industrial techniques are being put into practice where sputter cleaning and controlled reoxidation can be performed on a production-line scale. In wear applications, these studies may be more important than the study of heavy oxide scales in that they represent healing of disrupted surface oxides more accurately. The oxygen-starved conditions and flash temperatures attained with wear (ref. 3) may produce conditions similar to those used in these experiments. Certainly, the thinness of the oxide films is not detrimental, since thin films also have desirable properties in terms of resistance to wear. In reference 3, referring to the work of Rabinowicz, it was estimated that the spinel is the optimum oxide and a film thickness of 10^{-8} meter (100 Å) is the optimum thickness. In addition, in reference 10 it was found that thin films formed at 10^{-4} to 10^{-3} torr were more compact, adherent, and tenacious than films formed at atmospheric pressures.

This investigation was conducted to study, with the use of AES and sputtering, the oxidation of 440C, an iron-chromium alloy widely used in rolling-element bearings. The oxidation of 440C was studied for temperatures ranging from room temperature to 800° C and oxygen pressures ranging from 10^{-7} to 10^{-5} torr. The starting point for each oxidation study was a clean surface. In addition, the oxide surface compositions were examined by taking sputtering depth profiles, which involves simultaneous sputtering and AES surface analysis. A further objective of these studies was to analyze the composition of the films formed in the early stages of oxidation and to establish procedures for preparing protective films of known composition on 440C.

MATERIALS, APPARATUS, AND PROCEDURE

Materials

The sample of polycrystalline 440C HTST steel was cut from materials used in friction experiments. Its nominal composition in weight percent was 13 to 15 Cr, 0.75 Ni (max.), 0.15 V (max.), 0.1 Mn (max.), 1 Si (max.), 1 to 1.2 C, 3.75 to 4.25 Mo, 0.035 P (max.), 0.025 S (max.) and the balance Fe.

Research-grade argon was used for sputtering in obtaining depth profiles and for surface cleaning. Research-grade oxygen was used for oxidation studies. Purity of gases as bled into the vacuum system was checked with a quadrupole mass spectrometer.

Sample Preparation

The sample studied was a cylinder approximately 1 centimeter in diameter and 0.5 centimeter thick. It was cut from larger stock with a string saw. The specimen was then polished with varying grades of silicon carbide paper to a 600-grit finish. It was then polished with 3-micrometer diamond paste and given a final polish with 1-micrometer alumina. The procedure was chosen to simulate similar processing used in friction experiments. The surface was not electropolished. In preparing the surface for cleaning, the sample was outgassed at 700° C and cooled slowly to produce an annealed specimen.

Apparatus

The vacuum system used was a bakeable 250° C stainless-steel ultra-high-vacuum system. The chamber was evacuated by sorption, sublimation, and ion pumps. It was possible to clean the sample surfaces by ion bombardment, and it was also possible to bleed various adsorbent gases into the vacuum system. The base pressure for the system was 1×10^{-10} torr as measured with a nude Bayard-Alpert gage. The sample was heated by electron bombardment and radiation. Sample temperature was measured with a Chromel-Alumel thermocouple spot welded to its shank. The AES system used was a standard commercial retarding-field analyzer shown schematically in figure 1.

Experimental Procedure

Several initial steps were pursued in preparing the sample for oxidation. The specimen was outgassed at 700° C until the pressure in the vacuum system could be maintained in the 10^{-10}-torr range at temperature. The sample was then cleaned by argon ion bombardment at 2 kilovolts and approximately 3.5 $\mu A/cm^2$. A typical trace following argon ion bombardment is shown in figure 2. The sample was annealed for 30 minutes at 700° C following bombardment. The AES spectrum of an annealed surface is shown in figure 3. In all cases phosphorous, sulfur, and nitrogen segregated at the surface upon annealing. It should be noted that relative peak height is not an accurate measure of the amount of material present. Phosphorous and sulfur, which have high Auger yields, could give relatively large peaks for small surface concentrations.

A series of studies were performed involving adsorption, oxidation, and surface oxide depth profiles. The general procedure followed for the adsorption and oxidation studies was first to sputter clean the surface and then to anneal at 700° C for 30 minutes. The surface was then exposed to oxygen at pressures between 1×10^{-7} and 1×10^{-5} torr. The sample temperature during exposure ranged from room temperature to 800° C. During the adsorption and oxidation studies, significant Auger peaks (Cr, O, Fe) were monitored as a function of time. In addition, following oxidation, surface depth profiles were obtained by observing the appropriate portion of the AES spectrum during argon ion bombardment. A diffusion study was also performed by heating the sample in vacuum at 700° C following oxidation of the sample at 700° C and 1×10^{-6} torr and by observing the oxygen, chromium, and iron peaks as a function of time.

In order to obtain depth profiles of the surface oxide films, the sample surface was bombarded with argon ions at approximately 3.5 $\mu A/cm^2$ and 2 kilovolts while AES spectra were simultaneously taken. This procedure was used for films formed for three separate experiments. Following sputter cleaning and annealing in each case, (1) the sample was heated at 700° C in 1×10^{-6}-torr oxygen for 30 minutes, (2) the sample was heated at 600° C in 1×10^{-6}-torr oxygen for 60 minutes, and (3) the sample was heated at 500° C in 1×10^{-6}-torr oxygen for 30 minutes. In these cases the sample was not moved; therefore, the results represent analysis at the same spot on the surface. However, several spots on the surface were examined in order to establish that the results were not local. In order to estimate the time needed to sputter a layer of oxide, the surface was exposed to oxygen for 30 minutes at room temperature and a pressure of 1×10^{-6} torr. This was sufficient time for saturation of the oxygen peak-to-peak height and was assumed to represent one layer of surface oxide.

The principal AES peaks observed for the oxidation studies were the Cr(487 eV), O(511 eV), Cr(527 eV), Fe(596 eV), Fe(646 eV), and Fe(702 eV). However, in all cases the spectrum from 100 to 1000 electron volts was checked for effects from other alloying materials.

In order to ensure oxygen purity during oxidation, the ion pump was given repeated argon instability treatments (ref. 11). The ion pump was operating during all oxygen exposures. In order to determine whether the electron beam from the Auger electron gun was influencing the oxidation, oxidation was performed with the beam on and off. Introduction of oxygen did not appreciably affect the electron-beam current (~5 percent or less). In processing the data, the oxygen peak-to-peak heights were divided by the peak-to-peak height of the 703-electron-volt iron peak obtained after annealing the clean surface in order to normalize the data. The high-energy (527 eV) chromium peak was normalized by dividing by the peak-to-peak height of the 527-electron-volt chromium peak following annealing. For the depth profiles, the peaks plotted were not normalized but represent raw data in order to make direct comparisons simpler. There also was less reason for normalizations in these cases since analysis of the surface was performed under fixed geometrical conditions.

RESULTS

Room-Temperature-Exposure Studies

In order to compare adsorption and oxidation, oxygen was first adsorbed on the 440C surface at room temperature and a pressure of 1×10^{-6} torr until saturation of the oxygen peak occurred. The oxygen was then pumped out of the vacuum system. The AES trace following saturation is shown in figure 4(a). The interesting feature of this spectrum is the complete disappearance of all peaks except the iron peaks and the oxygen peak, indicating that iron was selectively oxidated at low temperature. Heating this surface to 700° C for 5 minutes with the system evacuated converted the AES spectrum to that of figure 4(b). Heating at this temperature caused replacement of the iron by chromium in the oxide surface. Lower temperatures did not cause the rapid conversion to chromium oxide.

It is also interesting to compare the growth of the oxygen peak at 1×10^{-6} torr for room-temperature adsorption with those for heating at 500° C and at 600° C. These results are shown in figure 5. It can be seen that for this case the oxygen peak height was much larger for the room-temperature exposure than for exposures at 500° C and 600° C.

High-Temperature-Exposure Studies

The general results observed in the oxidation studies are summarized in table I, showing the conditions under which certain states were obtained. The important result is that, at temperatures of 600° C and below, the outermost layer of the oxide surface was iron oxide; whereas, at temperatures of 700° C and above, the outermost layer of the oxide was completely chromium oxide. Figures 6 and 7 are examples of AES traces obtained for these two cases. Figure 6 is an example of the first case, where there are iron and oxygen peaks present but no chromium. Figure 7 is an example of the final AES traces for the second case, where there are chromium and oxygen peaks but no iron.

Figure 8 gives some examples of the behavior of the chromium AES peak height. At 600° C and 1×10^{-6}-torr oxygen pressure, the chromium peak decreases with time and indeed disappears. At 700° C and oxygen pressures of 1×10^{-6} or 1×10^{-7} torr, the chromium 537-electron-volt peak grows and then decreases and saturates.

An exception to the general result is obtained at 800° C and an oxygen pressure of 1×10^{-6} torr. At this pressure there was no oxidation of the surface; a small oxygen peak and all the characteristic peaks seen in figure 2(b) for high-temperature annealing were present. When the pressure in the system was raised to 1×10^{-5} torr, increasing the oxygen arrival rate, the surface proceeded to oxidize to chromium oxide. Figure 9 shows the behavior of both the chromium and oxygen peaks under these conditions.

In agreement with the room-temperature studies the iron oxide outer layer could be converted to chromium oxide by heating the oxidized surface in vacuum. Following oxidations for long times, ~1 hour, the iron oxide surface was converted to chromium oxide by heating at 700° C.

Diffusion Study

Observations were made to determine whether chromium was diffusing to the surface. Figure 10 is an example of chromium diffusion through the surface oxide layer. The sample was heated for 40 minutes in 1×10^{-6}-torr oxygen at 700° C, forming a completely chromium oxide surface. The oxygen supply was then cut off while heating at 700° C was continued. Figure 10 indicates that the chromium peak height increased with time by at least 50 percent in 30 minutes. There was no evidence of iron peak growth in this time.

Depth Profiles

Figures 11 to 13 show the results of sputtering depth profiles performed with an argon ion beam with an energy of 2000 electron volts and an approximate current density of 3.5 $\mu A/cm^2$. A calibration performed by determining the time required to sputter away a film formed by room-temperature exposure to oxygen indicated that it took roughly 13 minutes to remove one layer of oxide.

Figure 11 shows that the oxide formed by heating at 600° C for 60 minutes at an oxygen pressure of 1×10^{-6} torr has a thin (one layer) iron oxide outer crust covering a thicker film that may be a mixture of iron and chromium oxides or a spinel. Finally, this thicker crust (~6 layers) covers another even thicker film (~20 layers) of oxides and possibly free metal with varying composition.

Figure 12 shows the results of examining the same spot on the sample surface after oxidation for 30 minutes at 700° C in 1×10^{-6}-torr oxygen. In this case it can be seen that the surface has a relatively thick chromium oxide film (~6 layers and 20 percent of the oxide film). Beneath this film is a thick oxide film (~30 layers) of varying composition which is different from that presented in figure 11. A longer oxidation time was used at 600° C to compensate for slower diffusion at the lower temperature.

Figure 13 shows the surface oxidized at 500° C and 1×10^{-6} torr for 30 minutes. The oxide film in this case again has an outer crust of iron oxide, but the entire film is much thinner and of much less homogeneous composition.

DISCUSSION

Comparison with Other Results

The principal observations in this study are that the composition of the oxide film varies with temperature and that an iron oxide surface layer can be converted to chromium oxide by heating in vacuum. A summary of the results observed is presented in table I and in figures 4, 11, 12, and 13. It would be interesting to compare these results with other oxidation studies performed on iron-chromium alloys.

The studies reported in references 2, 3, 6, 12, and 13 are in disagreement with the present results. References 2 and 3 summarize the work of Moreau (ref. 12) in which iron-chromium alloys of varying composition (2.6 to 30 wt% Cr) were oxidized in oxygen at a pressure of 1 atmosphere at temperatures of 800° to 1250° C. The results of Moreau's study indicated that the surface films consisted of an outer layer of iron oxide covering a lower layer of a spinel of iron and chromium, which, in turn, covered a third layer of a mixture of FeO and spinels. Isherwood and Quin (ref. 6), using lower oxidation pressure (50 torr) and a lower temperature range (200° to 700° C) with glancing angle X-ray scattering as a diagnostic tool, came to similar conclusions. Chattopadhyay and Wood (ref. 13), using an atmosphere of oxygen, a temperature of 600° C, and chromium compositions varying from 5 to 30 percent but short oxidation times (~15 min), also came to similar conclusions about the oxide structure. In all cases, these studies reported only iron oxide as the outer layer.

The results of the present study agree with those of Wood and Whittle (ref. 10), even though their oxidation conditions (atmospheric conditions) were considerably different. The samples, however, in their studies were given a preoxidation treatment at 10^{-4} to 10^{-3} torr and 1200° C, which created a thin, highly adherent chromium oxide film. This preoxidation created an initial surface condition similar to the results obtained in the present study at temperatures above 700° C. Wood and Whittle's low-temperature studies (below 700° C) agree with our results. The surface layer is iron oxide and the lower layers are either a mixture of oxides or spinels, agreeing with the low-temperature (≤600° C) results of this report.

The differences between our results and those of references 2, 3, 6, 12, and 13 are not surprising. In this report the oxygen pressures were considerably lower ($\leq 10^{-5}$ torr) than used elsewhere. In addition, the surface at the inception of oxidation in our studies was atomically clean of oxygen, whereas the surfaces used in the cited references had oxide layers present. Isherwood and Quin (ref. 6) point out that the state of oxidation of the surface and/or its finish before oxidation can radically affect the composition of the final surface oxide. The oxides examined in our study are also much thinner than those observed in the other studies; they are more like tarnish films than scales.

Possible Mechanisms for the Formation of Observed Oxide Films

Two principal results are observed in film formation: a temperature dependence of film composition, and the conversion of the iron oxide film to chromium oxide (fig. 4). The two results suggest that the film formation is diffusion controlled. At the low temperature (~600° C), iron diffuses faster than chromium (ref. 10), resulting in an outer layer of iron oxide and an inner layer of a mixture of oxides or spinels. At higher temperatures (~700° C), the chromium diffusion rate becomes sufficiently great to reduce the outer layer of iron oxide and to promote the buildup of an outer layer of chromium oxide. This interpretation agrees with the results and interpretations of references 14 and 15, where the nature of the surface oxides for Fe-Cr-Al, Ni-Cr-Al, and Fe-Al alloys are examined. In these experiments the composition of the oxide layer was temperature dependent. The results of reference 15 suggest that steady-state oxidation conditions may have been achieved in parts of our study. Steady-state conditions are defined in reference 15 as the formation of a continuous oxide film of a single alloy constituent, as occurred for the conditions in figures 11 and 12. The results of the sputtering study (figs. 11 and 12) suggest that at 600° C a steady-state iron oxide outer layer was forming and above 700° C a steady-state chromium oxide outer layer was forming. As further substantiation of this interpretation, figure 8 shows the transient behavior of the chromium peak. It can be seen that at 600° C the chromium peak is disappearing with time and that at 700° C it is approaching a stable value which depends on oxidation pressure. It may be possible, however, for long oxidation times that sufficient chromium diffusion would occur at 600° to cause conversion to chromium oxide. Under these conditions we would be observing a "frozen in" transient state at 600° C.

Winograd, Baitinger, Amy, and Munarin (ref. 16) observed effects similar to the conversion of the iron oxide to chromium oxide shown in figure 4 of our study. In reference 16, aluminum was evaporated onto a nichrome alloy which had been selectively oxidized to chromium oxide. The more chemically active aluminum reduced the chromium oxide to chromium and oxidized the aluminum to aluminum oxide.

Some further comment should be made concerning the temperature dependence of surface oxide composition observed in this study. It has been previously postulated in this study that a temperature-variable diffusion rate for chromium was responsible for the differences in composition observed. It should be pointed out that in complicated alloy systems such as 440C, phase changes can occur which may affect oxide composition. For example, reference 17 shows that for iron-chromium-carbon alloys with compositions similar to 440C, phase changes do occur near 700° C. The causes of the increased availability of chromium are not pursued in the present study.

Other Effects of Pressure and Temperature on Film Composition

Table I and figures 11 to 13 indicate that differences in surface composition do exist as a result of temperature and pressure. At this stage it is not possible to identify the chemical composition of surface oxides. For example, the iron oxide films (table I) differ in the iron-to-oxygen peak height ratios as a function of temperature; however, there is only a weak pressure dependence. The chromium oxide films, in contrast, show both a strong pressure and temperature dependence (table I and fig. 9). These differences in peak height ratios could represent different oxides, such as Cr_2O_3 and Cr_3O_4, possibly because the films were mixtures of more than one oxide.

Figure 5 shows a strong dependence of oxygen peak-to-peak height on temperature. It can be seen that a substantially larger quantity of oxygen is present on or near the surface for room-temperature adsorption. This is not too surprising, since for standard room-temperature chemisorption, oxygen forms the entire surface layer. In this present case, however, a rearrangement of the surface must have occurred, since the chromium peaks disappeared. It is plausible, however, that chromium is still in the vicinity of the surface. The higher temperature and associated reduced oxygen peak heights demonstrate diffusion of the oxygen into the bulk to form metallic oxides.

Figure 9 shows the results of an attempt to oxidize the surface initially at 800° C and 1×10^{-6} torr. Under these conditions the surface did not oxidize. This result indicates that either oxygen diffused into the bulk at too high a rate; the oxygen sticking coefficient was too low at this temperature; or other constituents of the alloy, namely, phosphorous and sulfur which segregated at the surface in large quantities at this temperature, were responsible for failure of the surface to oxidize. It is not improbable that these two elements formed volatile oxides and prevented the surface from oxidizing. Raising the pressure to 1×10^{-5} torr caused rapid oxidation of the surface to chromium oxide. At this pressure the oxygen arrival rate was sufficient to form the surface oxide.

Diffusion Effects

An attempt to observe diffusion of chromium at 700° C to the surface following oxidation of the outer layer to chromium oxide is shown in figure 10. As can be seen, the chromium peak height increased with time after the oxygen supply was cut off. The resulting curve indicates that the chromium was diffusing to the surface region at 700° C, supporting the explanation offered for the temperature dependence of film composition. In the time of observation, no iron diffusion was observed.

CONCLUSIONS

In the study of 440C stainless steel by Auger electron spectroscopy and sputtering, the following conclusions were drawn:

1. The composition of surface oxides on 440C is temperature dependent. At 600° C and below, the outer layer of oxide is entirely iron oxide with an underlying layer composed of a mixture of oxides and/or spinels. For oxidations performed at higher temperatures (700° C and above) the outer oxide layer is chromium oxide with an underlying layer composed of a mixture of oxides and/or spinels.
2. At 700° C the chromium in 440C will convert iron oxide to chromium oxide on the surface.
3. Chromium is the principal diffusing species at 700° C, following oxidation of the outer surface layer to chromium oxide.
4. Room-temperature oxidation of the 440C surface to iron oxide occurs at an oxygen pressure of 1×10^{-6} torr.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 29, 1974,
502-01.

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TABLE I. - SUMMARY OF RESULTS

Temperature, ^{0}C	Pressure, torr	Surface oxide	Metal-oxide ratio at saturation	Comments
Room	1×10^{-6}	Iron	0.165, 0.168	At equilibrium
Heated at 700° C and cooled following preceding step	------	Chromium	0.37, 0.38	-------------
500	1×10^{-6} 1×10^{-7}	Iron	0.2 .21	At equilibrium
600	1×10^{-6} 1×10^{-6}	Iron	0.19 .19	At equilibrium
700	1×10^{-7} 1×10^{-6}	Chromium	0.43 17	At equilibrium
800	1×10^{-5}	Chromium	0.24	At equilibrium. At 1×10^{-6} torr there was no appreciable oxidation of the surface.

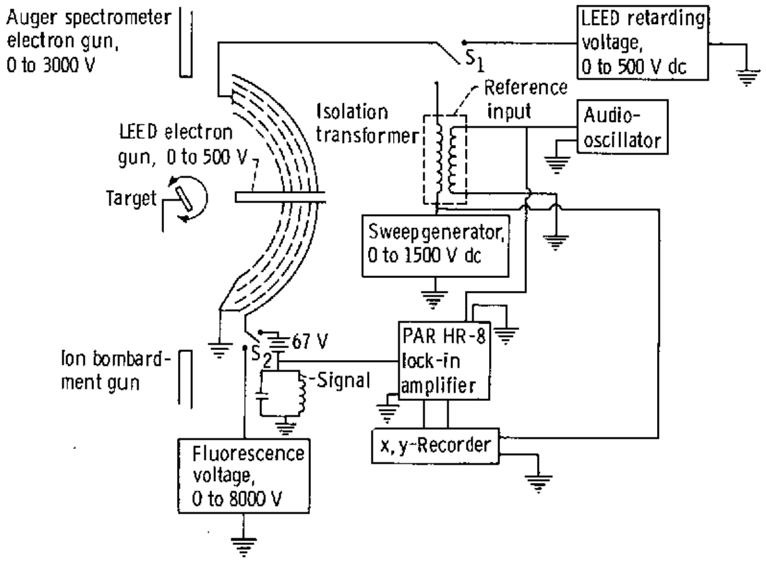


Figure I. - Schematic diagram of Auger electron spectroscopy (AES) apparatus.

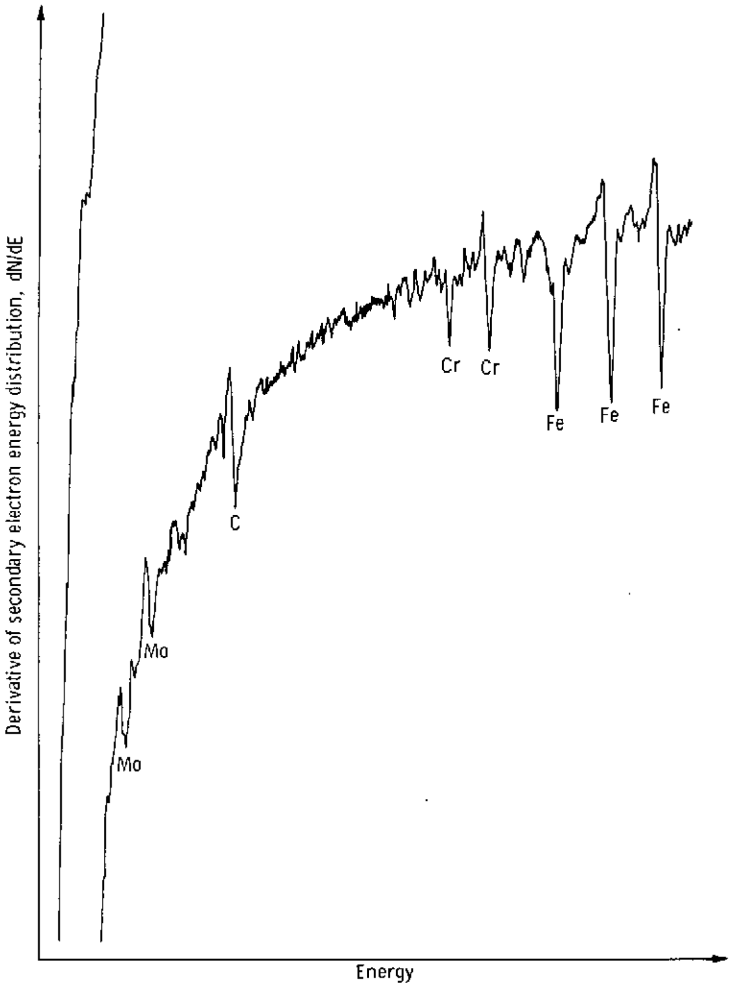


Figure 2. - Typical AES spectrum following sputter cleaning at ~3.5 μA/cm^2 and 2000 kV.

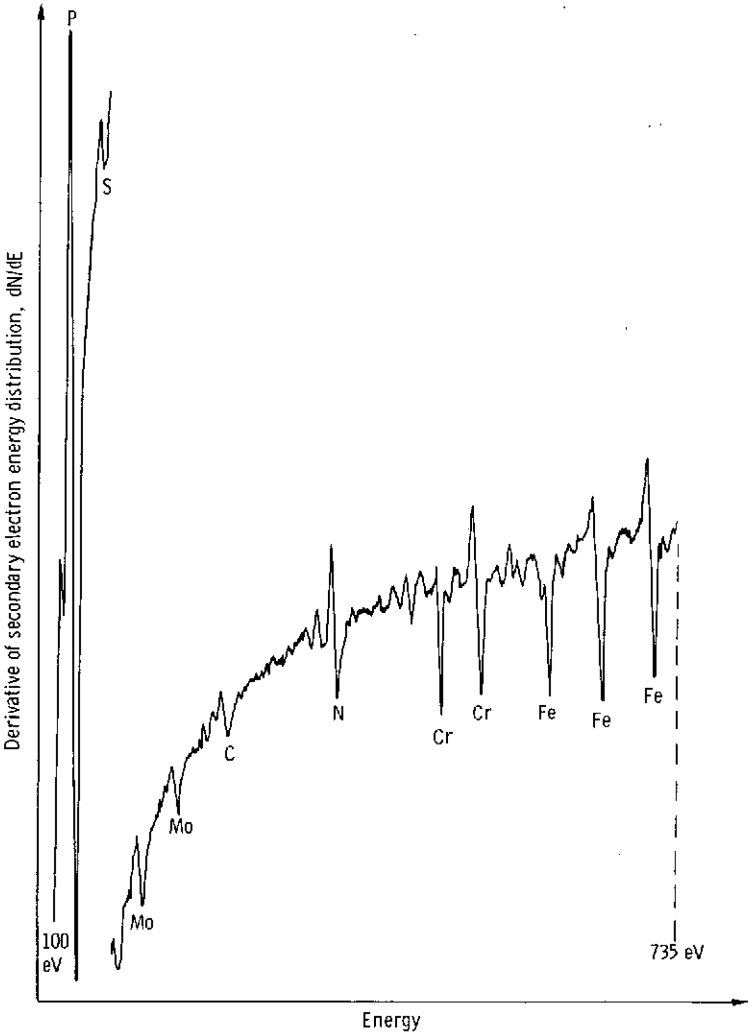
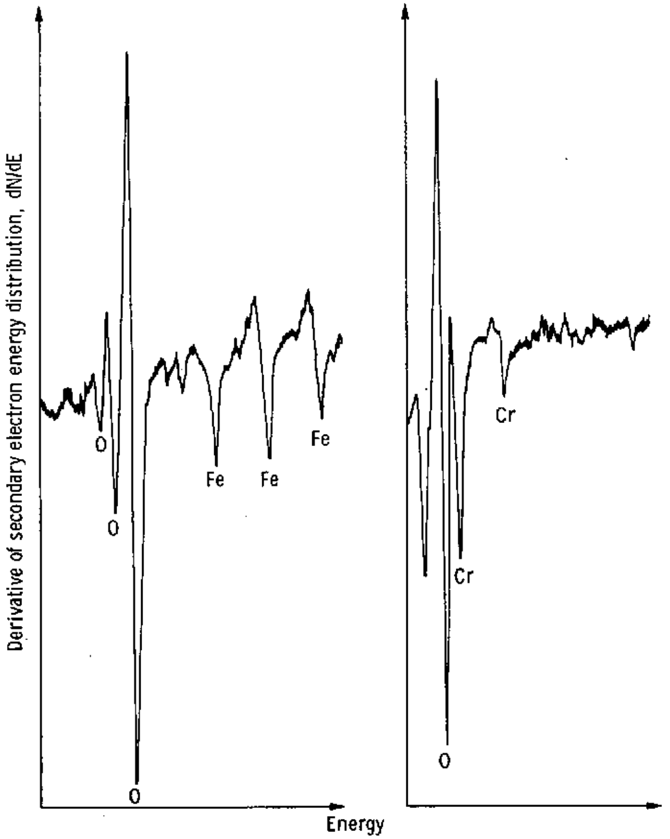


Figure 3. - Typical AES spectrum following annealing for 30 minutes at 700° C.



(a) Spectrum directly following adsorption.

(b) Spectrum following heating for 5 minutes at 700° C.

Figure 4. - AES spectrum following room-temperature adsorption of oxygen for 30 minutes at 1x10^{-6} torr.

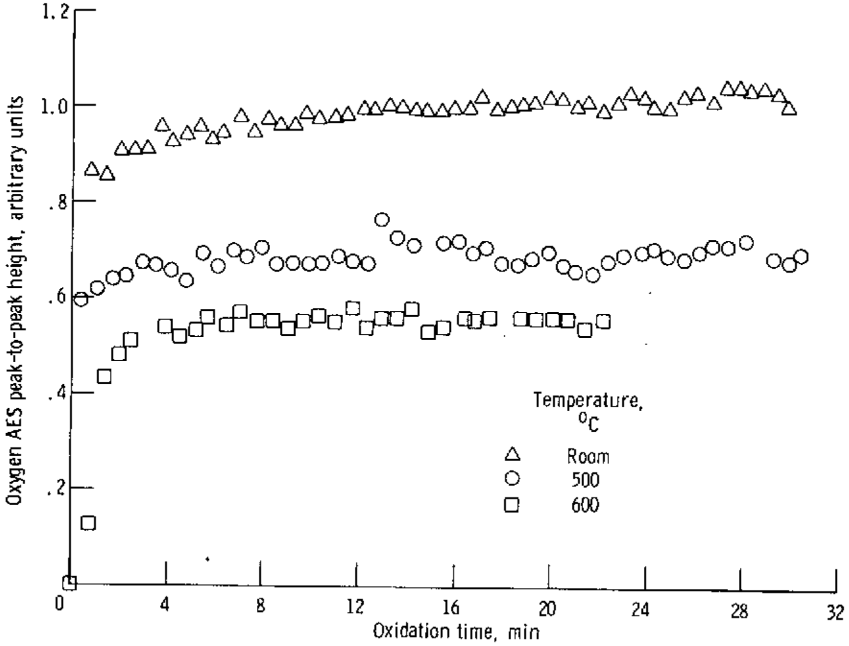


Figure 5. - Oxygen AES peak-to-peak height as function of oxidation time for three temperatures - room temperature, 500° C, and 600° C - at an oxidation pressure of 1x10^{-6} torr.

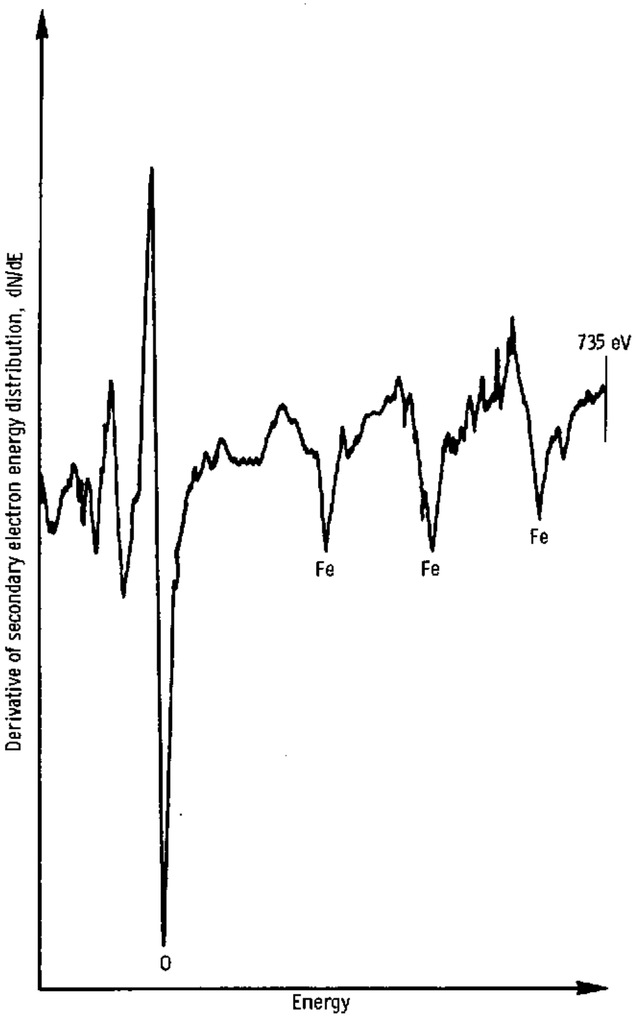


Figure 6. - AES spectrum following heating in oxygen for 60 minutes at 600° C and 1×10^{-6} torr.

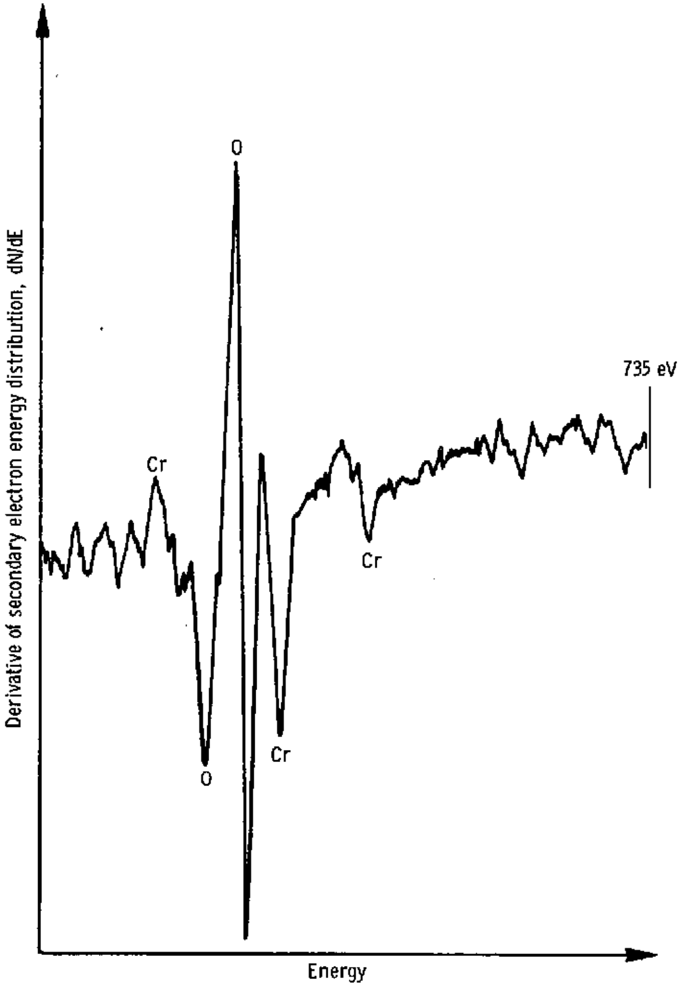


Figure 7. - AES spectrum following heating in oxygen for 40 minutes at 700° C and 1×10^{-6} torr.

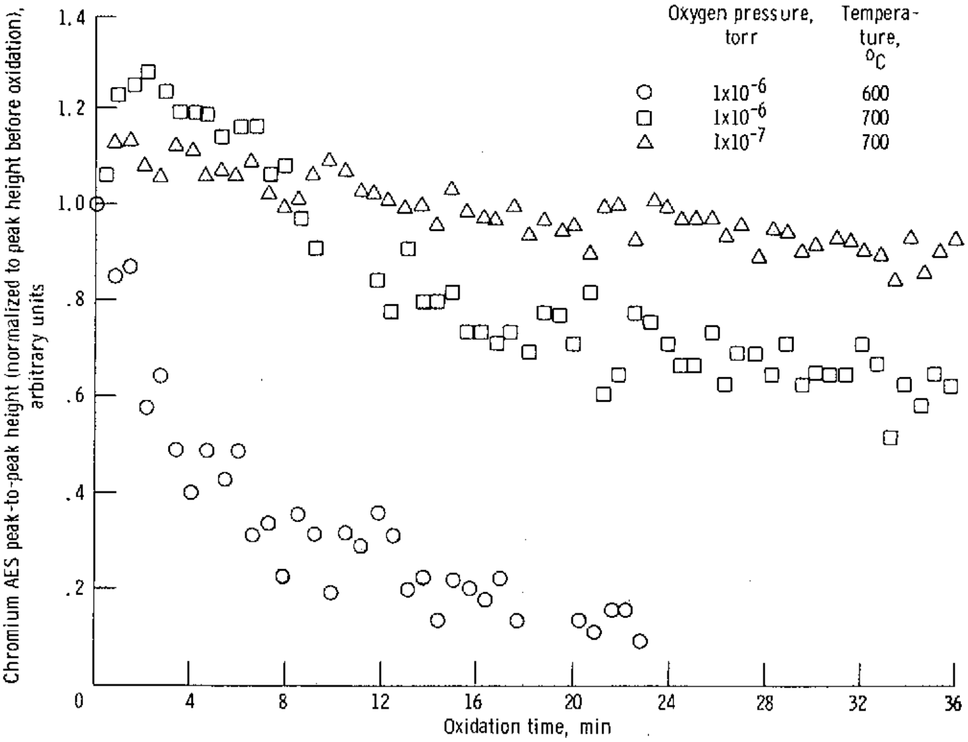


Figure 8. - Chromium AES peak-to-peak height as function of oxidation time for three oxidation conditions (1×10^{-6} torr, 600° C; 1×10^{-6} torr, 700° C; and 1×10^{-7} torr, 700° C).

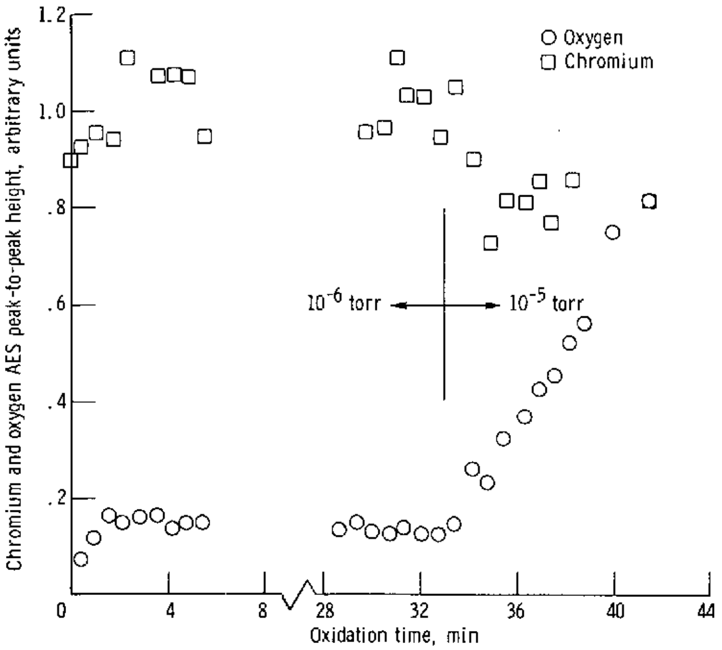


Figure 9. - Chromium and oxygen AES peak-to-peak height as function of oxidation time for two oxidation conditions (1×10^{-5} torr, 800° C; and 1×10^{-6} torr, 800° C).

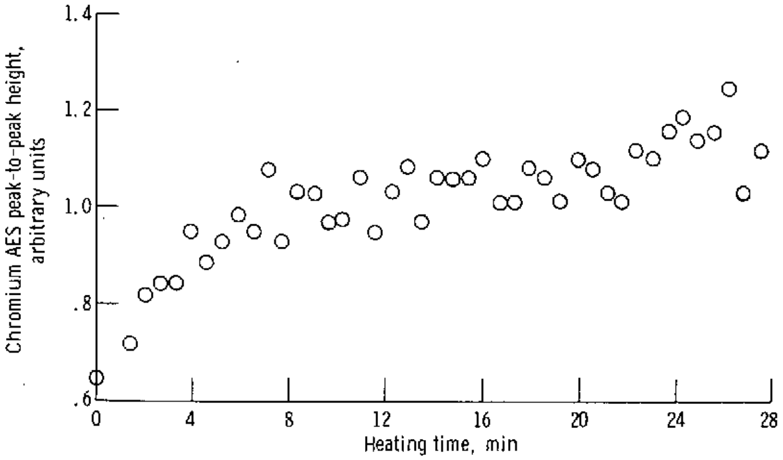


Figure 10. - Growth of chromium AES peak-to-peak height at 700° C after oxidation for 40 minutes at 700° C and 1×10^{-6} torr.

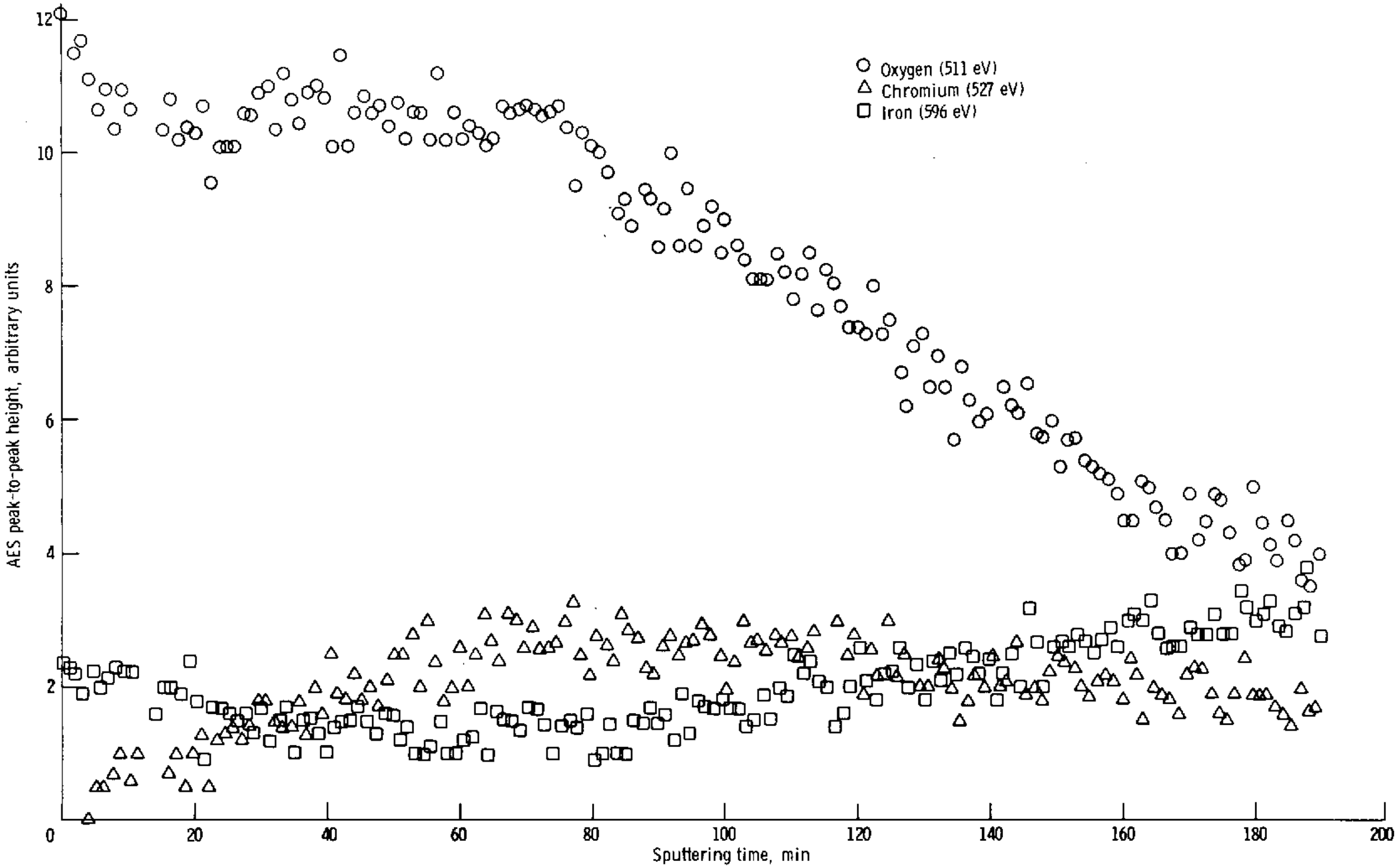


Figure 11. - Sputtering depth profile of 440C stainless steel oxidized for 60 minutes at 600^0 C and $1x10^{-6}$ torr.

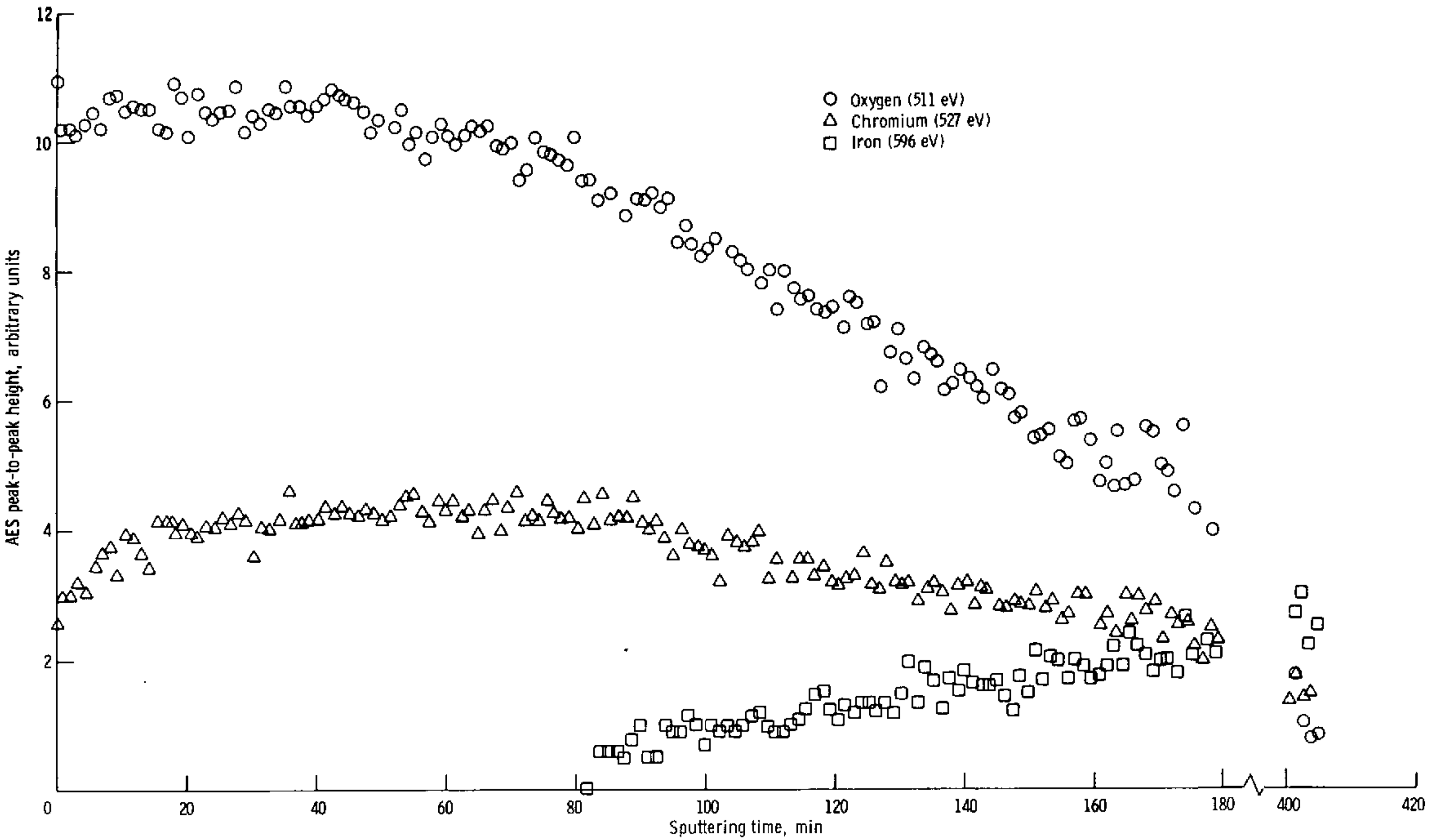


Figure 12. - Sputtering depth profile of 440C stainless steel oxidized for 30 minutes at 700° C and 1×10^{-6} torr.

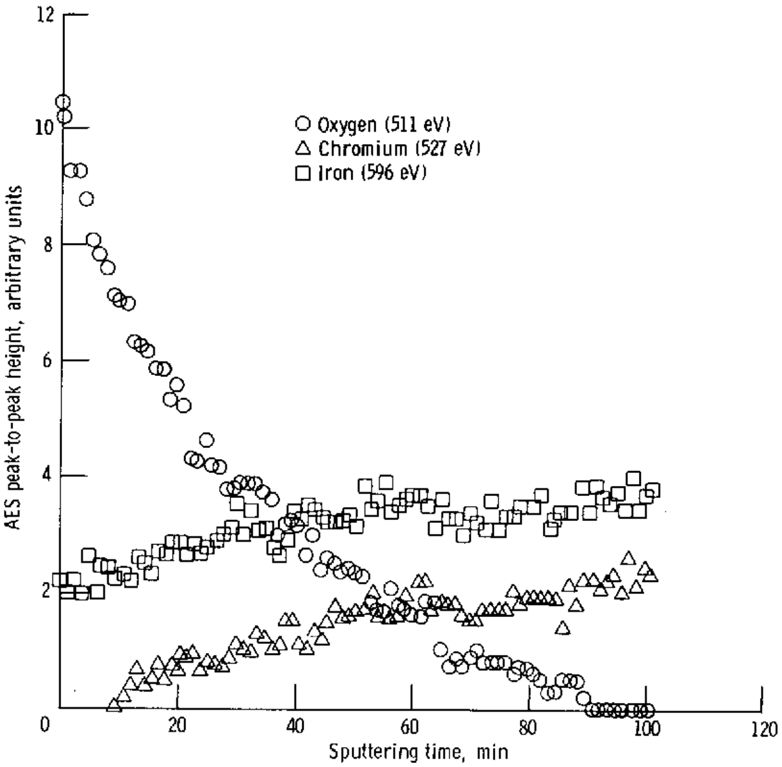


Figure 13. - Sputtering depth profile of 440C stainless steel oxidized for 30 minutes at 500° C and 1×10^{-6} torr.