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INITIAL STAGES OF HIGH-TEMPERATURE METAL OXIDATION*

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I. INTRODUCTION

The study of the initial stages of passivation and high temperature oxidation presents a number of experimental problems. In the case of passivation, the rate of the reaction can be measured precisely by electrochemical techniques. However, the composition and microscopic structure are extremely difficult to determine. The optical techniques including ellipsometry reflectance, Raman and IR have been utilized in an effort to obtain this type of information but they have met with only very limited success.[1] Mossbauer spectroscopy[2] has been used to study passivated iron surfaces in situ but the data-collection time required for these experiments is too long for it to be relevant to the initial stages of the reaction. It is possible, however, to freeze the sample in its initial state and then use Mossbauer to study it.

There have been a large number of efforts to study passive films on iron as well as a number of its alloys using surface analytical tools. The techniques used are primarily x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).[1] There has been little or no use of ultraviolet photoelectron spectroscopy (UPS). Although these techniques provide useful information about the composition and electronic properties of the passive film, again very little structural information is obtained.

The high temperature oxidation experiments, on the other hand, pose a different set of difficulties. In this case, a sample is held at a high temperature while it is exposed to oxygen which is being leaked into the vacuum system. Under such conditions, the surface of the sample is oxidized immediately, and surface analysis on this fully oxidized surface is straightforward. However, it is extremely difficult to control the reaction so that the initial stages can be observed. The reason is that the controlling of the oxygen activity at the metal surface in a well-defined manner can not be easily achieved. In this paper we report our efforts to carry out high temperature oxidation reactions using electrochemical techniques to control the oxygen activity.

The important feature of the oxidation experiments carried out in this study is the utilization of electrochemical cells based on yttria-stabilized zirconia (YSZ). This material is an ionic conductor over wide ranges of oxygen partial pressure at elevated temperatures[3] and the conduction mechanism is by mobile oxygen ion vacancies. Any perturbation in the oxygen activity at the surface will give rise to an electrochemical potential difference which can be measured. Conversely, when an external potential is applied the oxygen activity at the surface can be modified. This control of the oxygen activity given by the applied potential and the measurement of the reaction rate given by the observed current are extremely sensitive, hence the addition or removal of a fraction of a monolayer of oxygen can easily be achieved. Standard electrochemical techniques such as cyclic voltammetry, potential and current steps have been applied in this study. It should be pointed out that while these techniques are commonly used in liquid electrochemical studies, they have rarely been applied to solid electrolyte systems. A few studies of metal-oxygen interactions using cyclic voltammetry techniques have been reported.[4,5]

An important fact is that the solid electrolytes have essentially no vapor pressure, therefore they are ultra high vacuum (UHV) compatible. This fact makes it possible to perform in situ characterizations of the reactions using surface spectroscopic techniques. Thus, the electronic properties, chemical bonding behaviors and structural variations can be determined during the oxidation processes.

In this paper, two types of experiments will be discussed--the electrochemical studies of metal oxidation and the surface characterization of the electrochemically oxidized surfaces.

II. EXPERIMENTAL

Fig. 1a shows a schematic representation of the three-electrode cell configuration that was used for the studies of metal oxidation carried out in an inert atmosphere. The electrolyte was an 8 wt% YSZ disc, 1 cm in diameter and 0.3 cm thick. The metal to be studied is represented by M, which may either be a metal foil or evaporated metal film. The purity of the metals was 99.9% or better. The counter electrode, a disc of mixed metal-metal oxide, was spring loaded against the other side of the electrolyte. The counter electrode should be a good oxygen source and sink, so that any perturbation to the gas environment caused by electrochemical reactions at the counter electrode (e.g., O_2 evolution or decomposition of the residual H_2O) is reduced to a minimum when a potential is applied to the cell. A

A platinum paste electrode or another disc of mixed metal-metal oxide was used as a reference electrode. Since very sensitive variations of oxygen activity are involved in these studies, it is necessary that a reference electrode be used to determine the oxygen activity at the electrolyte/electrode interface on an absolute thermodynamic scale. At a temperature of 500°C, an increase of 38 mV corresponds to an order of magnitude increase in the equivalent oxygen partial pressure at the surface following the Nernst equation. This cell was enclosed in a tubular furnace with flowing inert gas. The inert gas was purified to remove CO_2 and H_2O and the purity was monitored with two oxygen meters, one before and one after the cell. For a typical experiment at 1000°C, the oxygen partial pressure in the inert gas was on the order of 10^{-13} atm.

The cell used for the UHV experiments is shown in Fig. 1b. The heating of this cell was achieved by resistance heating of a filament behind the counter electrode. The cell was enclosed in a heat reflector made of tantalum foil. The front surface of the cell was not enclosed in order to allow the surface analysis measurements. As a result of the exposure of the front surface, a temperature gradient existed across the cell. All temperatures were monitored with Pt/Pt-Rh thermocouples.

The electrolyte used in the UHV experiments was a rectangular piece of 8 wt% YSZ cut from a 2.5 cm diameter, 0.3 cm thick disc. The metals to be studied (Fe and Ni) were evaporated onto the front face of the cell. Since electrical conductivity in the film is necessary for running the electrochemical reactions, the thickness of the film is quite critical. The films were prepared in two ways. In the first, a grid of Pt was laid down on the surface and then the Fe and Ni films of 50 to 100 Å were evaporated over the Pt. The experiments with these thin films were not successful because of the metal segregation at high temperature and the subsequent loss of electrical continuity. A second set of samples was prepared without the grid but with thicker continuous films of Fe and Ni (∿ 1000 Å).

The vacuum system used was a Varian 200 ℓ/sec ion pump system. It also has an auxiliary 110 ℓ/sec turbomolecular pump. The surface analytical capability of this system includes Auger, XPS, UPS, LEED and mass spectrometry. In this study, the principal method used was XPS which is based on a Vacuum Generators Clam electron analyzer and X-ray source. The electron analyzer is preceded by an electron focusing lens, hence the sample was between two to three inches from the lens aperture. This physical configuration makes the XPS experiments possible. Under normal circumstances the high temperature sample would be in very close proximity to the analyzer which could cause dimensional changes in the analyzer leading to a loss of sensitivity and resolution.

The base pressure the system achieved was 5 x 10^{-10} torr with the cell at 500°C. It took approximately three weeks with the cell operating to achieve this pressure. This was due to the outgassing of the ceramic material from which the cell holder was constructed. The residual gases were primarily H_2O and H_2 and the ratio of H_2/H_2O was in the range of 0.5 to 10.

The electrochemical experiments were conducted with a Princeton Applied Research potentiostat (PAR 173) and a function generator (PAR 175). Data was recorded on a Nicolet Explorer III digital storage oscilloscope.

III. RESULTS AND DISCUSSION

An electrochemical cyclic voltammogram of a nickel foil at 815°C is shown in Fig. 2. The electrode potential was varied between -780 and -640 mV at a sweep rate of 20 mV/sec. The potential has been normalized with respect to air so that the equivalent oxygen partial pressure can be easily converted. Anodic and cathodic peaks were observed indicating that a well-defined oxidation and reduction reaction took place. The reversible potential of the redox reaction (at about -700 mV which is equivalent to $P_{O_2} \sim 10^{-14}$ atm) agrees within 20 mV of the tabulated value[6] of the standard free energy of NiO formation. Therefore, a surface oxide is electrochemically formed and reduced at the electrode/electrolyte interface. It is interesting to note that the integrated charge under the anodic curve is within 3% of that under the cathodic curve. This is usually indicative of an adsorption[7] process (adsorption at an electrode/electrolyte interface rather than at a gas/metal interface). It should be noted that the charge found for the surface oxide in Fig. 2 is less than that required to form a complete monolayer of oxide (280 $\mu C/cm^2$). Furthermore, the peak current is proportional to the square root of the sweep rate[4] instead of the first order dependence which is required for a simple one-step adsorption process.[7] The square root behavior is normally representative of an an electrode process involving diffusion.[8] Hence, it appears at this time that the observed electrochemical reaction is a more complicated process than either of the simple adsorption- or diffusion-limited process.

The rate of oxidation of Ni with time in UHV at 500°C is monitored (Fig. 3) after stepping the potential to −760 mV vs air (50 mV anodic to the NiO formation potential). The time scale in this plot is much greater than that in the cyclic voltammetry curves and the oxidation has progressed beyond the monolayer stage. Two reaction sequences or mechanisms are observed in Fig. 3. The first step occurs between 0 and 170 sec and has a charge equivalent to an oxide thickness of $\sim$100 Å. After 170 sec, a break in the curve occurs indicating that a different process or oxide growth mechanism is taking place. This observation is in general agreement with the previous findings that the oxidation of Ni follows two growth laws.[9]

Shown in Fig. 4 are cyclic voltammograms of an iron foil at 740°C. Several peaks are present in Fig. 4a, which indicates a sequence of discrete reaction steps. By varying the upper and lower limit of the potential sweep, one can identify some of the peaks corresponding to different stages of iron oxidation. For example, Fig. 4b shows the redox pair of the $Fe \rightleftarrows FeO$ reaction which corresponds to the peaks B and E in Fig. 4a. Similarly, Fig. 4c shows the redox pair of the $FeO \rightleftarrows Fe_3O_4$ reaction which corresponds to the peaks C and D in Fig. 4a. The upper limit of anodic sweep is −670 mV vs air which is 200 mV cathodic to the thermodynamic potential of Fe_2O_3 formation. Hence, the formation of Fe_2O_3 is not expected to be observed. The small but reproducible peak A can not be associated with any single oxidation state of iron. One can speculate that it corresponds to a precursor state of oxide in the initial stages of the iron oxidation processes. The cathodic peak F is also very interesting. This peak only appears after the potential is swept anodically beyond peak C (around -800 mV). It is speculated that as the potential is swept beyond peak C, certain transformations, such as lattice reconstruction, take place. The redox potentials for different oxide formations at different temperatures, as determined by cyclic voltammetry studies, agree within 25 mV of the published data[6] of thermodynamic potentials of iron oxide formation. As mentioned before, similar good agreements are found for nickel. Therefore, one can easily apply cyclic voltammetry techniques to obtain important thermodynamic properties such as the standard free energies of metal oxide formation. One can also use the position of the redox potential as a reference similar to using a mixed metal-metal oxide as the reference electrode.

It is shown that the application of cyclic voltammetry techniques reveals many interesting characteristics of the studied metals, in particular their initial oxidation behaviors. It appears that at the initial stages of oxidation, a complicated process, possibly involving interfacial adsorption, diffusion and lattice transformation, is taking place.[4] In order to resolve the detailed reaction mechanism, it is necessary to investigate the electronic properties and structural properties of the metal-oxygen system under controlled conditions. It is with this thought in mind that the in situ surface analytical experiments have been carried out.

Shown in Fig. 5 is the cyclic voltammogram of an evaporated nickel film obtained in UHV (∿1000 Å thick, 1.2 cm^2 area) at 500°C. The redox peaks are basically similar to those obtained in an inert gas environment (cf. Fig. 2). The cathodic sweep was limited to about -1050 mV vs air because, beyond this point, the potential at the counter electrode (where the anodic reaction was taking place) built up to the point where oxygen evolution began. Therefore, the complete cathodic sweep was not recorded. One also notes there is more than one peak on both the anodic and cathodic sides of the voltammogram. This is a result of the temperature discontinuities (on the order of 75°C) which were measured on the nickel sample due to non-uniform heating. The separations of the peaks are consistent with the oxide formation potentials at different temperatures. This problem was corrected for the iron sample discussed below.

The XPS results for a nickel film (∿ 1000 Å) at 500°C are shown in Fig. 6. Fig. 6a corresponds to a reduced surface which is at a potential of -880 mV vs air. The potential was then stepped to -680 mV vs air where it was held for 30 mins. The XPS spectrum is shown in Fig. 6b. At 500°C and -680 mV the Ni should be substantially oxidized. A difference spectrum is shown in Fig. 6c. Here it can be seen that there is a decrease of the Ni metallic peaks coupled with an increase of the oxide peaks. The oxide peaks are very small indicating that only a fraction of the surface has been converted to oxide whereas a gross oxidation of the surface was expected. This behavior has several possible explanations:

1. The small amount of oxide observed is due to the formation of the chemisorbed oxide phase which reaches saturation coverage at a fraction of a monolayer.[10]
2. At 500°C the diffusion of Ni and consequently the oxide growth is very slow and the oxide observed is all that can be formed during the given time span.
3. There was a significant amount of hydrogen in the vacuum system during this experiment, a competitive reaction between the electrochemical formation of the oxide and the chemical reduction of the oxide by the hydrogen was taking place.

Although all three explanations are possible, there is direct evidence which favors explanation 3. When the oxidized sample was allowed to sit in the system at open circuit potential, i.e., at the potential where no net electrochemical reaction was occurring (-810 mV vs air), the oxide XPS signal was found to disappear over a period of time.

Shown in Fig. 7 are the XPS results for an iron film (∿1000 Å) at about 350°C. Fig. 7a is the open circuit data which corresponds to a well-reduced metallic iron film. Fig. 7b is the result of applying a potential of 200 mV anodic to the oxide formation potential for 80 mins. At 350°C, FeO is not stable; the first stable oxide is Fe_3O_4. Indeed the spectrum shown in Fig. 7b corresponds to the standard Fe_3O_4 spectrum.[11] If the electrode potential is further biased anodically, Fe_2O_3 is formed.

Therefore, one can electrochemically oxidize the entire metal film with controlled oxygen activity. Under the experimental conditions here, the competitive reduction of oxide by hydrogen was not a dominating reaction for the case of iron. This is in contrast to nickel and is consistent with the fact that the free energy of formation is greater for FeO_x than NiO. The spectra of completely reduced and oxidized iron were reproduced back and forth by stepping the electrode potential, similar to earlier reports.[10,12]

IV. SUMMARY

It is demonstrated that high temperature oxide electrolyte cells are extremely useful in studying the metal oxidation reactions. With the oxide electrolyte cells, one can simultaneously control the oxygen activity and measure the reaction rates with great precision. It is shown that the initial stages of metal oxidation studied here are a complicated process possibly involving interfacial adsorption, precursor states, diffusion and time-dependent transformations. Model simulation studies are needed to resolve these contributions. The redox potentials, easily measured by cyclic voltammetry techniques in this study, agree remarkably well with the standard potentials of oxide formation. This suggests that from a thermodynamic point of view, the oxide layers formed at the electrolyte/metal electrode interface are the same as those formed in the gas phase. Strictly speaking, the kinetic conditions may be different between the solid electrolyte and gas phase formed oxides. For example, oxygen dissociation and surface diffusion are two reaction steps most likely to occur in the gas phase oxide formation, but not in the electrochemical oxide formation (assuming perfect contact at the electrolyte/electrode interface). However, these differences may be insignificant when porous metal thin films are used or when the two aforementioned steps are not the rate limiting steps in the metal oxidation processes. Finally, the feasibility of performing in situ high temperature electrochemistry in a surface analysis chamber is successfully demonstrated. This adds another dimension to the investigation and understanding of the interactions between metal and oxygen.

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FIGURE CAPTIONS

Figure 1. a. Oxide-electrolyte cell arrangement used in an inert gas environment.

b. Oxide-electrolyte cell arrangement used in a UHV system. CE = counter electrode, RE = reference electrode, TC = thermocouple and lead wires. The dotted line indicates the tantalum reflector.

Figure 2. Cyclic voltammogram of a nickel foil. Temperature, 815°C; sweep rate 20 mV/sec. P_{O_2} in inert gas environment $\sim 10^{-15}$ atm.

Figure 3. Plot of current vs time for a Ni film in a UHV system; temperature 500°C; background pressure 2×10^{-8} torr.

Figure 4. Cyclic voltammograms of an iron foil; temperature 740°C; sweep rate 5 mV/sec. P_{O_2} in inert gas environment $\sim 10^{-17}$ atm.; a., b., and c. correspond to different potential sweep range. The arrows of $E_1°$ and $E_2°$ indicate the tabulated values (ref. 6) of standard potentials of FeO and Fe_3O_4 formation, respectively.

Figure 5. Cyclic voltammogram of a nickel film in a UHV system; temperature 500°C; sweep rate 50 mV/sec; background pressure $\sim 2 \times 10^{-8}$ torr.

Figure 6. XPS spectra of a nickel film; temperature 500°C; background pressure $\sim 2 \times 10^{-8}$ torr.

a. At open circuit potential which corresponds to a well-reduced metallic film.

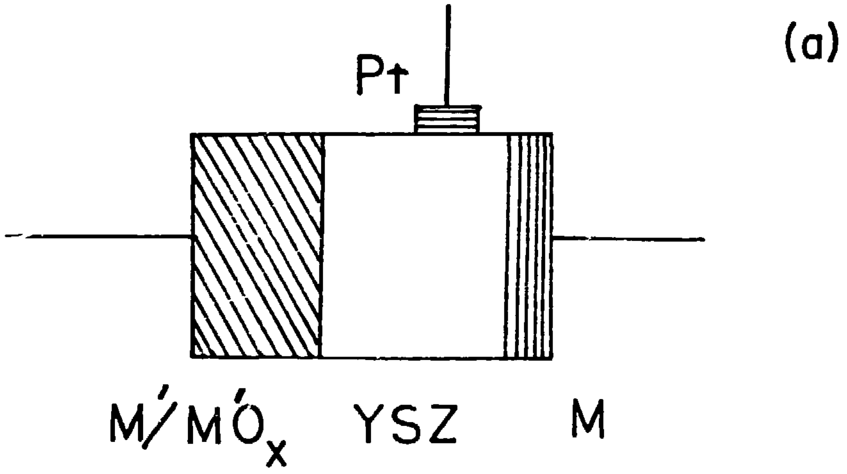
b. After 30 mins of at a potential 200 mV anodic to the oxide formation potential.

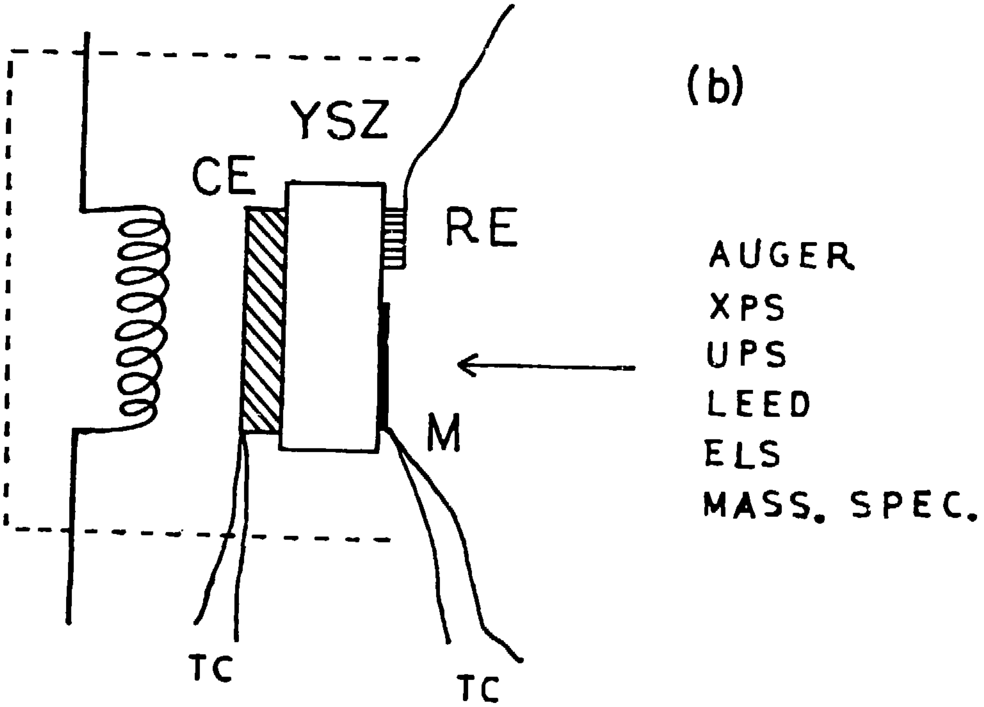
c. Difference spectrum (B-A).

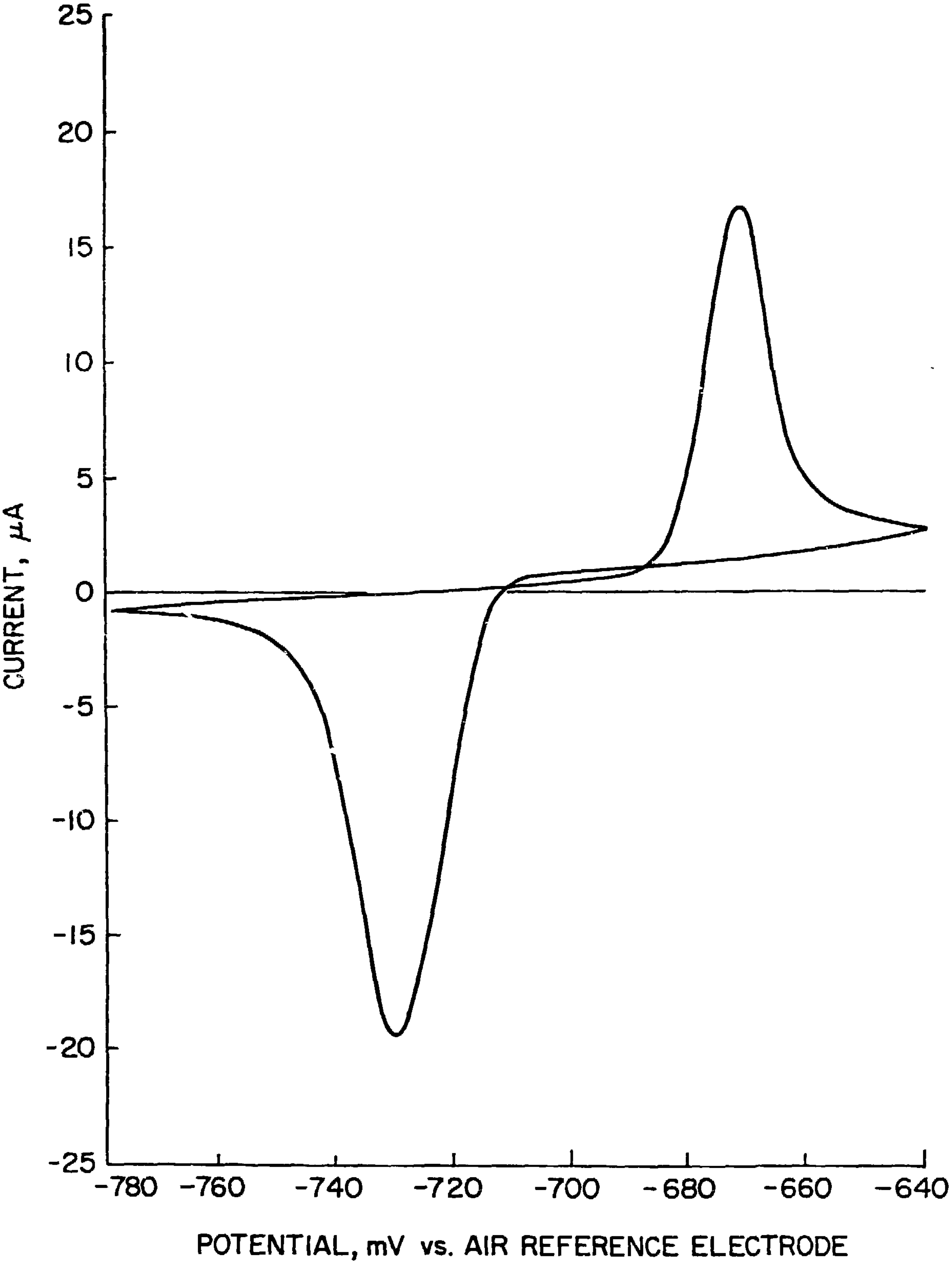
Figure 7. XPS spectra of an iron film; temperature 370°C; background pressure $\sim 4 \times 10^{-9}$ torr.

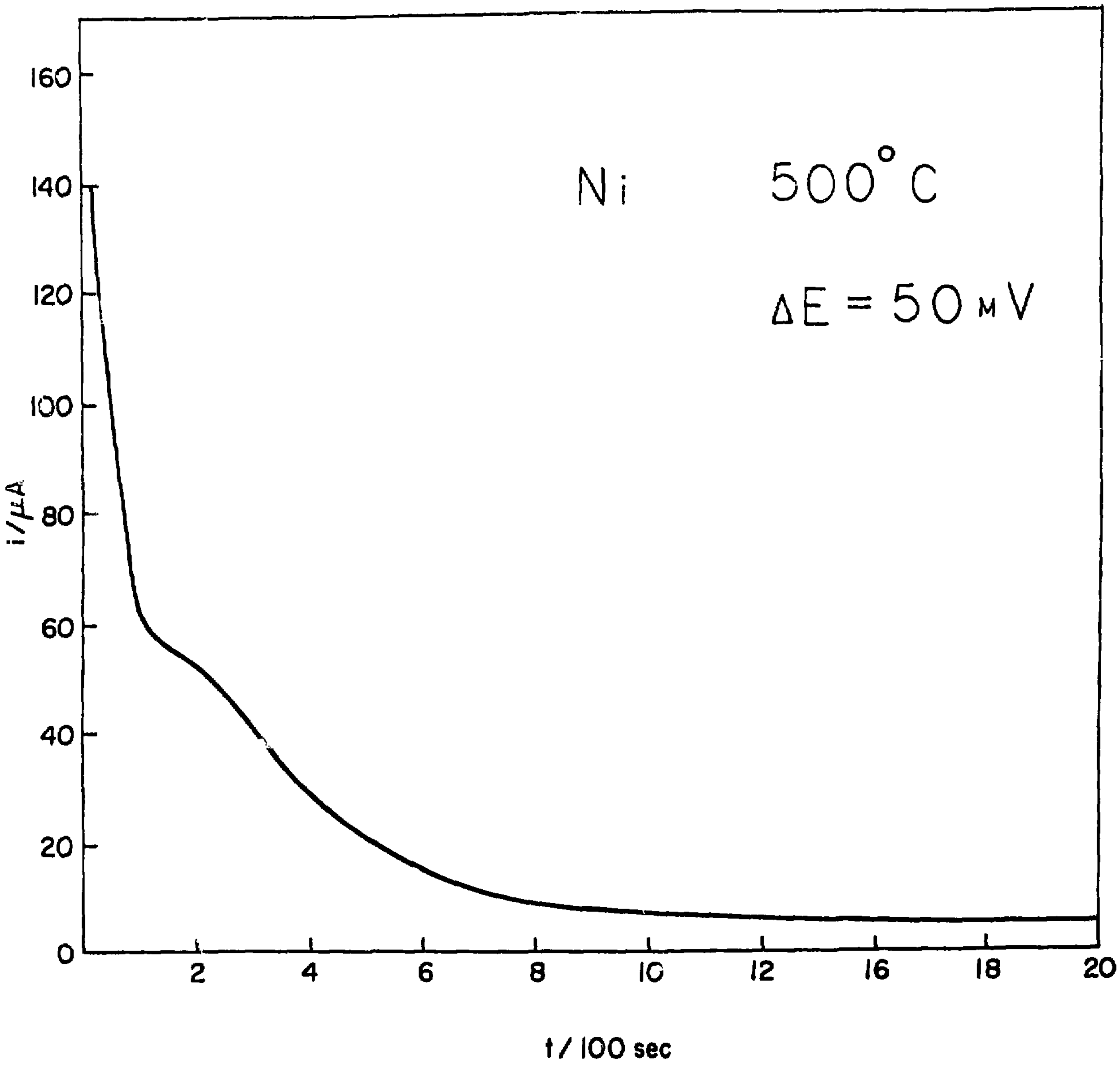
a. At open circuit potential which corresponds to a well-reduced metallic film.

b. After 80 mins at a potential 200 mV anodic to the oxide formation potential.


(a)
Pt
M′/M′O$_x$
YSZ
M


(b)
YSZ
CE
RE
AUGER
XPS
UPS
LEED
ELS
MASS. SPEC.
M
TC
TC


25
20
15
10
5
0
-5
-10
-15
-20
-25
CURRENT, μA
-780
-760
-740
-720
-700
-680
-660
-640
POTENTIAL, mV vs. AIR REFERENCE ELECTRODE


Ni
500°C
ΔE = 50 mV
i/μA
0
20
40
60
80
100
120
140
160
2
4
6
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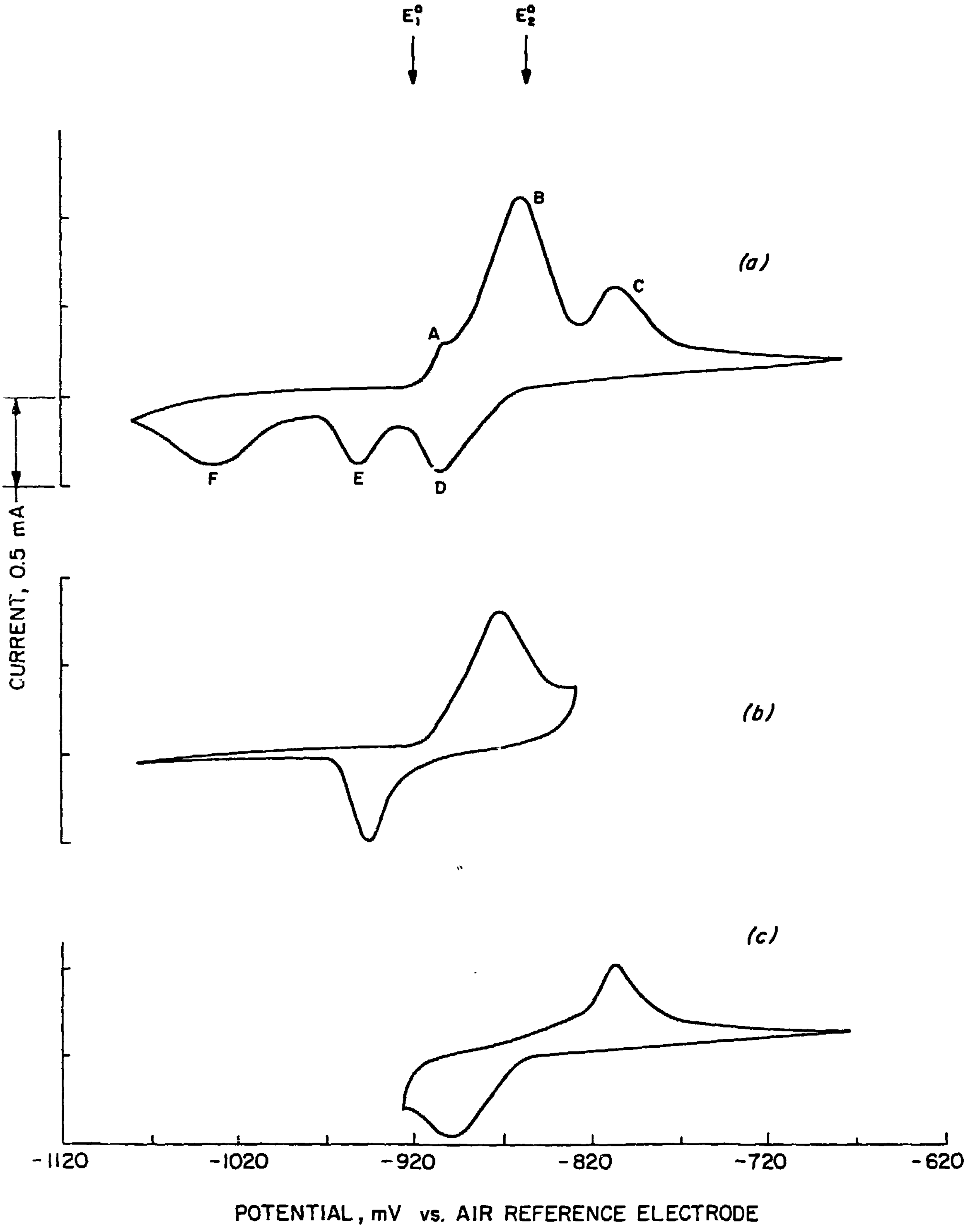
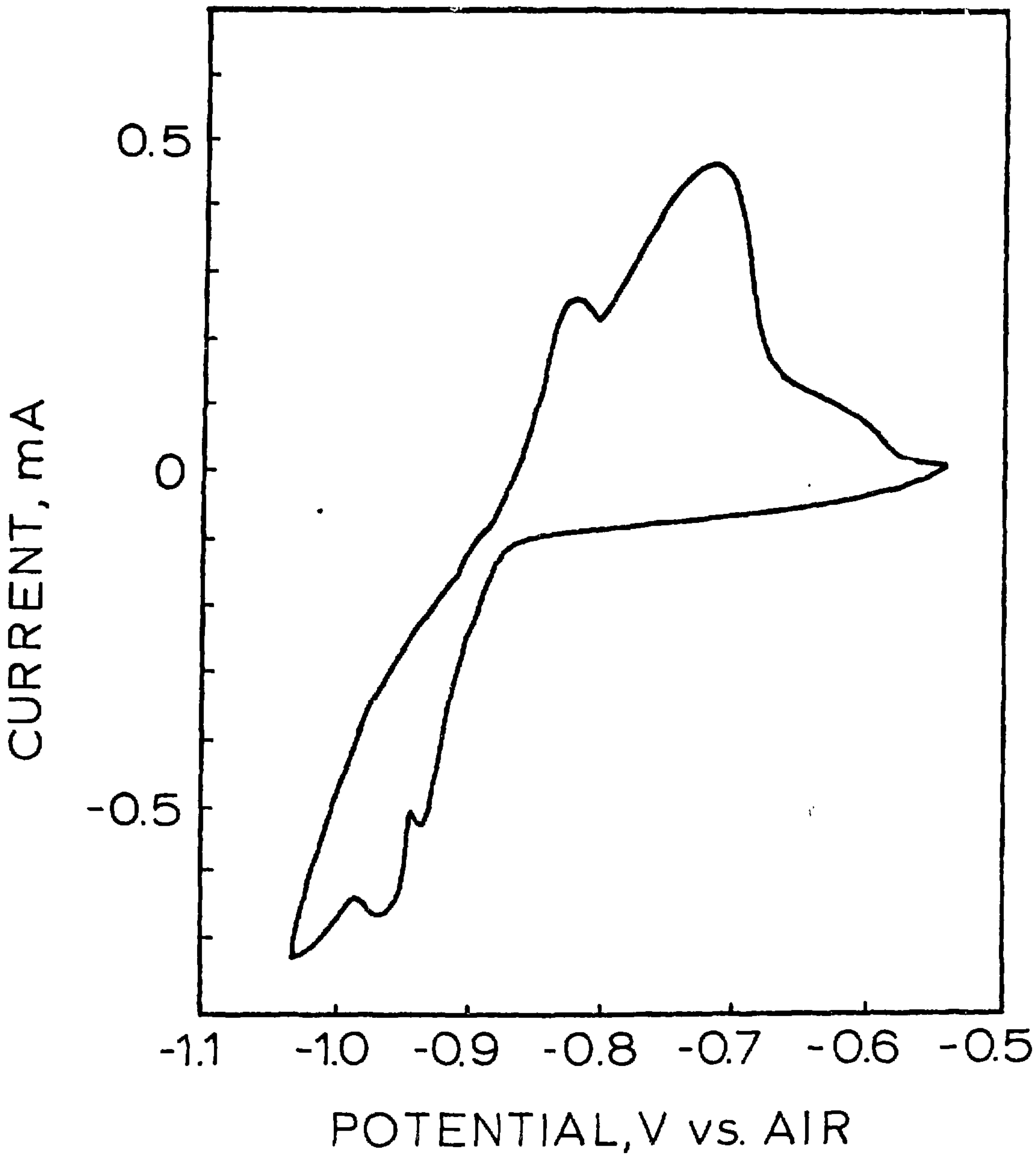
10
12
16
18
20
t/100 sec


E_1^0
E_2^0
B
(a)
C
A
F
E
D
CURRENT, 0.5 mA
(b)
(c)
-1120
-1020
-920
-820
-720
-620
POTENTIAL, mV vs. AIR REFERENCE ELECTRODE


0.5
0
-0.5
CURRENT, mA
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-1.0
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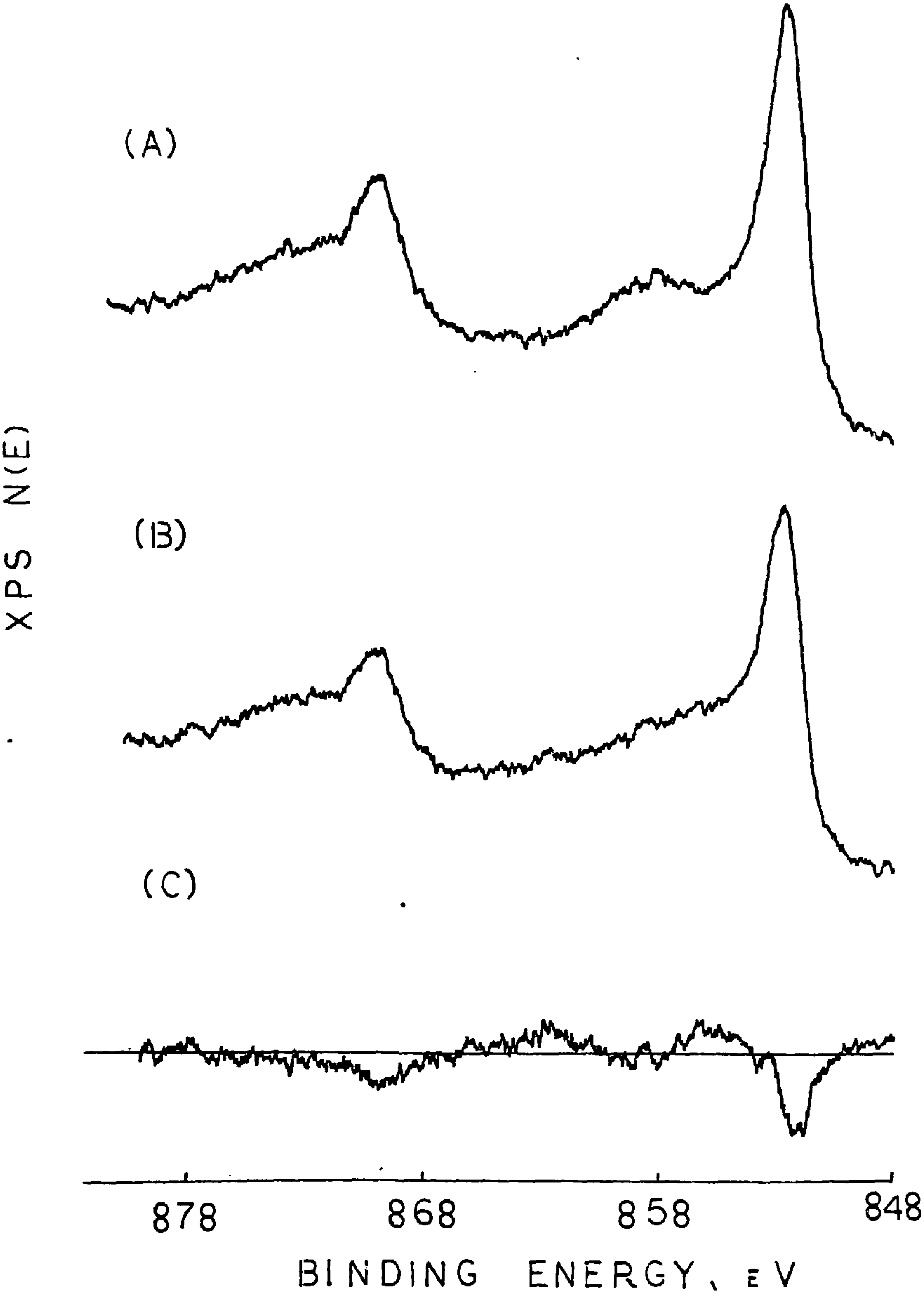
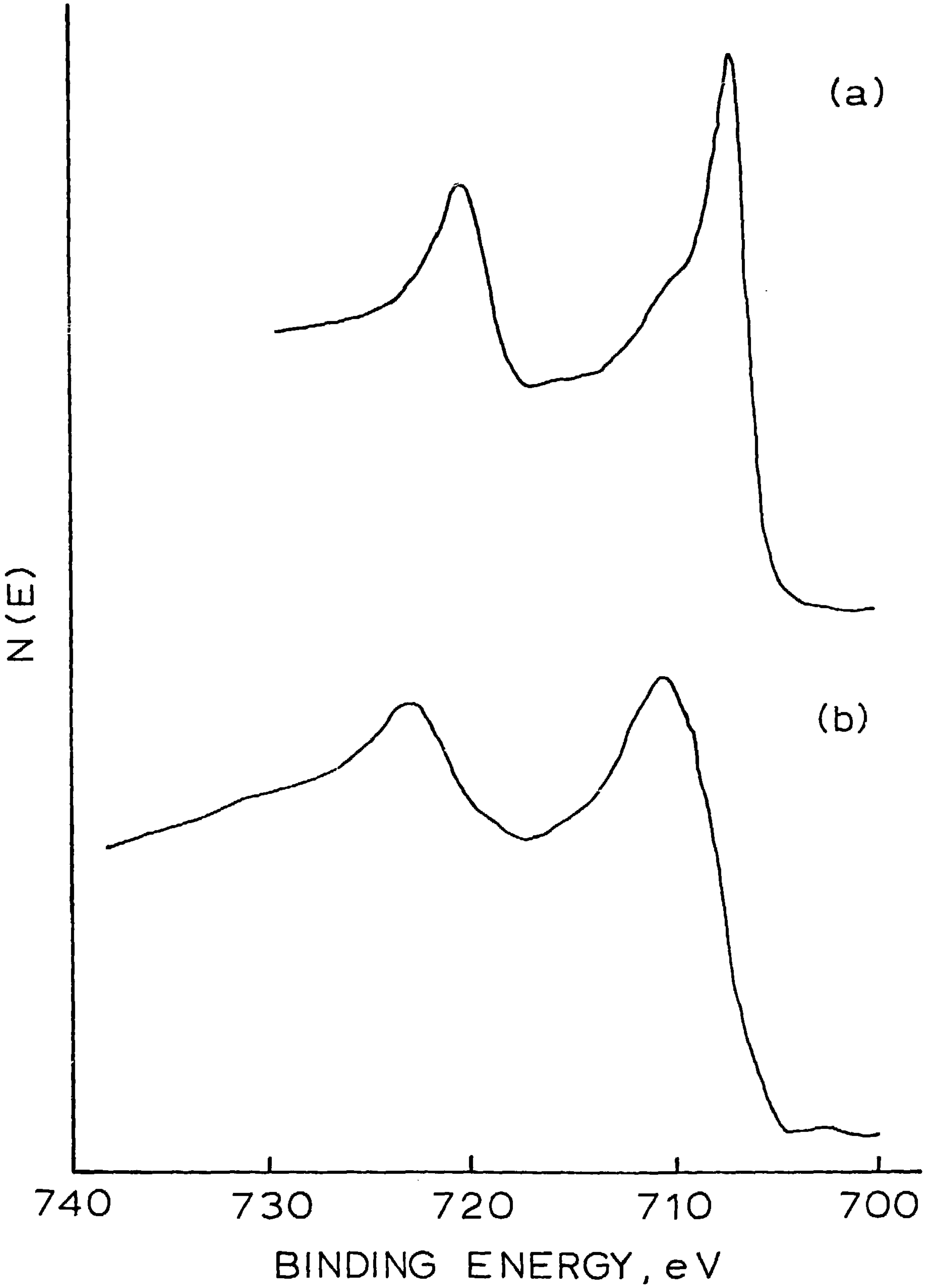
-0.8
-0.7
-0.6
-0.5
POTENTIAL, V vs. AIR


(A)
(B)
(C)
XPS N(E)
878
868
858
848
BINDING ENERGY, eV


(a)
(b)
N(E)
740
730
720
710
700
BINDING ENERGY, eV