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Initial Stages of Oxidation of Metals and Alloys

Progress Report

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Initial Stages of Oxidation of Metals and Alloys

Progress Report

Abstract

Studies of the oxidation kinetics of Ni-Fe alloys and of Be have been carried out over the past year. The majority of the alloy results are for the (100) surface of $\text{Fe}_{40}\text{Ni}_{60}$. Investigation of the clean surface over the temperature range up to $\sim 900^\circ\text{C}$ indicated only a slight enrichment in Fe relative to Ni compared to the bulk average composition. Under oxidizing conditions the situation is quite different; marked segregation of Fe occurs with the formation of iron oxide overlayers. The kinetics of this process have been studied using Auger spectroscopy and structural features of the overlayer observed by LEED. The LEED observations indicate the initial formation of (111) oriented FeO on $\text{Fe}_{40}\text{Ni}_{60}$ (100); at greater oxygen exposures a new oxide structure, probably Fe_3O_4 , develops with its (111) plane parallel to the (100) substrate. With Be the room temperature oxidation has been investigated over the pressure range 10^{-7} to 10^{-9} mm Hg. Auger lineshape studies indicate that most of the Be spectrum can be accounted for by contributions from clean Be and BeO. Data on the kinetics at 300 K have been obtained. A research ellipsometer with rotating analyzer has been installed and interfaced to a computer system.

Initial Stages of Oxidation of Metals and Alloys

This report describes work performed during the past 12 months under DOE support. The first progress report, dated April 1980, was mainly concerned with equipment set-up and preliminary experiments on both Fe-Ni alloys and on Be surfaces. During the past year we have largely concentrated on oxidation experiments on both these systems. The necessary Auger spectroscopy equipment, interfaced to a computer, is now operational and is being used for extensive data collection. The time investment in setting up this system seems to be well justified by the results now being generated. In order to construct a model of the oxidation kinetics during the initial stage, it is necessary to have data over wide ranges of both pressure and temperature. During the past 12 months we have installed a research ellipsometer with a rotating analyzer interfaced to a computer; this system will allow extension of our studies of oxidation kinetics to the thicker film region.

(i) Fe-Ni Alloy Studies

We have studied in detail the initial stages of oxidation of the (100) surface of an $\text{Fe}_{40}\text{Ni}_{60}$ alloy. The clean surface was first studied by LEED and Auger techniques. The diffraction observations showed no evidence of the bulk phase transition indicated on the Fe-Ni phase diagram in the neighborhood of 345°C . The high temperature f.c.c. solid solution is presumably retained as a metastable phase at low temperature even during repeated temperature cycling. We have however avoided annealing treatments between 100 and 345°C where there may be enough mobility to effect the transformation to b.c.c. $\alpha\text{-Fe}$ and FeNi_3 . Figure (1a) shows the LEED pattern obtained from the clean (100) surface at room temperature. By measuring the energies of the "Bragg" peaks in the intensity-voltage spectrum of the (00) beam and the angles of the non-specular beams, the lattice was determined

to be f.c.c. with a lattice constant of $3.70 \text{ \AA}$. This is in reasonable agreement with the value extrapolated from the lattice constants of pure Ni and of pure f.c.c. Fe. By measuring the relative heights of the Fe (47 eV) and Ni (61 eV) Auger peaks as a function of temperature, and normalizing the results against the ratio for the heavily ion bombarded surface, we obtained the data of figure (2). This shows that over the temperature range of our experiments there is only slight Fe enrichment in the surface region relative to the bulk, i.e., by a factor of 1.05. The starting condition of the surface for the oxidation experiments is thus similar to that for an average bulk plane. However, at this stage we are unable to say anything about the lateral distribution of the components in the surface plane or near surface region. Figure (3) shows the evolution of the low energy Fe and Ni Auger features during exposure to oxygen; this data is representative of the behavior over a range of temperature and O_2 pressure. The overall trend shown in figure (3) is that the Ni signal diminishes rapidly with exposure relative to that of the Fe. Figure (4) shows that, with higher resolution, one can also detect marked changes in the Fe Auger lineshape in the initial stages of the oxidation process; these changes are related to the development of new features in the valence band structure. Figures (5) and (6) show the kinetics of oxygen uptake at the $Fe_{40}Ni_{60}$ (100) surface. In figure (5) the oxygen signal is plotted versus exposure (in Langmuirs) at a particular pressure (2.5×10^{-8} Torr) for a range of crystal temperatures, while figure (6) shows data at 743 K for a range of gas pressures. These results indicated that at this stage of oxidation the rate of oxygen uptake is linear in pressure and essentially independent of temperature. There are no sharp breaks in the uptake curves which might signal changes in sticking coefficient as monolayers are completed. The mean composition of the surface changes dramatically during the initial oxidation. Figure (7)

shows the value of the low energy Ni:Fe Auger peak ratio as a function of O_2 exposure at different temperatures. For high temperature oxidation there is a rapid decrease in the Ni:Fe ratio even though the rate of oxygen uptake is not significantly temperature dependent [see figure (5)]. Furthermore by annealing at 600°C the surface which was oxidized to 60 L at 100°C produced a Ni:Fe ratio similar to that for oxidation at 600°C . The interpretation appears to be that at low temperature a mixed oxide layer (e.g. $\text{NiO} + \text{FeO}$) grows on the alloy surface while at higher temperatures, where mobility is increased, there is a marked preference for iron oxide formation. This trend is in accord with the relative thermodynamic stability of FeO and NiO . The behavior of the Ni:Fe Auger ratio at low temperature exposure is very interesting. The initial increase in Ni:Fe ratio may be due to initial preferential adsorption and dissociation at the Fe sites of the alloy surfaces; this could happen whether or not there is clustering or random distribution of the components. [We are considering the possibility of XAFS measurements to investigate this point.] As exposure proceeds the relative decrease of the Ni:Fe ratio is probably due to NiO formation. The structure of the oxide overlayer is extremely interesting. As shown in figure (1b) a $\text{C}(2 \times 2)$ superlattice first forms on the $\text{Fe}_{40}\text{Ni}_{60}$ (100) surface. The maximum in the intensity of the $(\frac{1}{2}, \frac{1}{2})$ beam with exposure at half a monolayer has been useful in providing a calibration of the oxygen uptake data. With increased exposure a structure with average lattice spacing approximately that of FeO forms with $\text{FeO}(111)$ parallel to $\text{Fe}_{40}\text{Ni}_{60}(100)$. The exact location of the FeO overlayer relative to the substrate is not yet known with any certainty. The diffraction pattern of this stage is shown in figure (8). The overlayer pattern has (overall) 3 fold symmetry as expected from the f.c.c. oxide surface provided it is at least 3 layers thick. There is a marked splitting of the diffraction beams which

we cannot yet explain in a totally satisfactory way. It may be due to double diffraction effects or conceivably may be associated with periodic deviations from stoichiometry of the type reported by Mitchell and Hobbs* from electron microscopy studies of relatively thick FeO layers. At a later stage the oxide structure gives the diffraction pattern shown in figure (9). The overlayer is still epitaxial and at this point appears to have the Fe_3O_4 (111) structure; this identification is tentative at this stage.

A detailed write-up and interpretation of the results is now underway and we have samples available to extend the work to other alloy compositions and surface orientations. The sequence of overlayers is particularly interesting when compared with the structure seen in high temperature, high pressure (vmm Hg) oxidation studies. Copies of manuscripts prepared from this work will be communicated to DOE whenever they are available.

(ii) Be Oxidation Studies

So far we have studied the room temperature oxidation characteristics of Be(0001). The evolution of the Be Auger spectrum during the initial stages of oxidation is shown in figures (10), (11) and (12), while figure (13) is a spectrum taken under the same conditions from a (bulk) BeO crystal. The Be lineshape at any intermediate exposure during the oxidation can reasonably be represented as a linear combination of the initial cleaved surface spectrum and that of the BeO spectrum. This suggests that there is no intermediate state of Be which is electronically distinguishable from clean Be or clean BeO. In contrast with results on Zn and those described for Fe-Ni the rate of oxygen uptake is not independent of pressure as indicated on figures (14a,b,c,d,e). There is also considerable structure in the plot of oxygen signal versus exposure and corresponding features in the variation of the contribution from BeO in the Be signal. We

* Private communication.

have now accumulated a large amount of data over a wide pressure range (10^{-6} - 10^{-9} Torr) for room temperature oxidation and are beginning further series of experiments at higher temperatures. At this stage our preliminary LEED observations indicate that there is no oxygen superlattice which occurs before BeO formation. The kinetics do not indicate a linear dependence on pressure, perhaps implying that place exchange may be controlling even in the initial stages. The structure in the uptake curves is suggestive of the importance of nucleation in initiating successive layers. With more extensive data we hope to answer many of these questions over the next few months.

$[001]$
 $[010]$

(a)

(b)

Figure (1)

FIGURE (2)

FIGURE (3)

Figure (4)

Figure (5)

Figure (6)

$\text{NiM}_{23}\text{M}_{45} / \text{FeM}_{23}\text{M}_{45}$

FIGURE (7)

$[001]$

$[010]$

Figure (8)

Figure (9)

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FIGURE (10)

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FIGURE (11)

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FIGURE (12)

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FIGURE (13)

Cleaved Be w/ $1.00\text{E}-07$ torr O_2

Δ - Be 'CLEAN', scale = 1.0 , zero = 0.00
 $+$ - Be 'OXIDE', scale = 1.5 , zero = $2.67\text{E}-04$
 $\times$ - Oxygen, scale = 1.5 , zero = 0.00

FIGURE (14a)

Ion B. Be w/ 1.00E-07 torr O₂

Δ - Be 'CLEAN', scale = 1.0 , zero = 0.00
+ - Be 'OXIDE', scale = 1.5 , zero = 4.00E-04
x - Oxygen, scale = 1.5 , zero = 0.00

FIGURE (14b)

Cleaved Be w/ 1.37E-07 torr C

△ - Be 'CLEAN', scale = 1.0 , zero = 0.00
+ - Be 'OXIDE', scale = 1.0 , zero = 4.00E-04
X - Oxygen, scale = 1.0 , zero = 0.00

FIGURE (14c)

Ion B. Be w/ 3.00E-07 torr O₂

△ - Be 'CLEAN', scale = 1.0 , zero = 0.00
+ - Be 'OXIDE', scale = 1.0 , zero = 4.00E-04
x - Oxygen, scale = 1.0 , zero = 0.00

FIGURE (14d)

Ion B. Be w/ 3.56E-09 torr O₂

Δ - Be 'CLEAN', scale = 1.0 , zero = 0.00
+ - Be 'OXIDE', scale = 1.5 , zero = 4.00E-04
X - Oxygen, scale = 1.5 , zero = 0.00

FIGURE (14e)