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Introduction

A new chemical analysis technique has been developed that shows great promise in many areas of metallurgy. This technique, called Auger Electron spectroscopy, has been developed rapidly in the past three years and it has already demonstrated the capability to measure quantities previously un-measurable. It is the purpose of this paper to provide a basic understanding of the physics, history, experimental procedures, and application of this technique, with the primary emphasis being on the metallurgical applications.

Auger Electron Spectroscopy

Auger Electron Spectroscopy is a non-destructive method of surface chemical analysis which is accomplished by bombarding a target with a beam of electrons and then performing an energy analysis of the electrons ejected from the target. The electronic transitions involved in this technique are shown in Fig. 1. The incident electron beam with energy in the range of 2000 - 4000 eV can create a vacancy in an inner level such as the K level shown in Figure 1. The atom can then return to an equilibrium state by means of an Auger⁽¹⁾ radiationless transition. In this transition an electron from the M level fills the vacancy in the K level and an electron in the N level is ejected with energy $E_K - E_N$. The electron from the N level may then escape from the solid into the vacuum after losing the binding energy of that level and hence will be available for detection with an energy characteristic of the electronic energy levels of the host atom.

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Most elements will have a transition producing an ejected electron having an energy of less than 2,000 eV. Therefore, most studies to date have concentrated in the energy range of 0 to 2,000 eV.

The discovery of the phenomena on which Auger Electron Analysis is based dates back to the work of P. Auger⁽¹⁾ in 1925. Lander⁽²⁾ was the first to realize the potential of the technique for chemical analysis in 1953. However, it was not until the work of Harris⁽³⁻⁴⁾ in 1968 that the technique became a useful analytical tool. Harris used an electrostatic velocity analyzer on which he placed a small a-c perturbation voltage on the slowly swept deflecting voltage in order to obtain the derivative of the electron distribution curve. In addition, this a-c perturbation voltage enables one to use phase sensitive detection with a marked improvement in signal to noise ratio.

Experimental Procedures

A block diagram of the electronics developed by Weber and Peria⁽⁵⁾ with a four grid LEED electron optics unit to perform an energy analysis of electrons ejected from a target is shown in Fig. 2. An electron gun with a tungsten filament electron source is used to supply the incident beam of electrons with energy in the range from 2000 to 4000 eV. The primary current to the target is measured by the meter between V_3 and ground. This measures the current leaving V_3 and hence no corrections due to the secondary yield of the target are necessary.

The hemispherical grids subtend a full 180° angle to the target for maximum shielding of the electron trajectories and optimum collection efficiency. Grids G_1 and G_4 are connected and operated slightly positive with respect to the target. The retarding voltage and modulation (a-c perturbation voltage) are applied to grids G_2 and G_3 . A typical modulation frequency is 200 Hz and modulation amplitudes up to 10 volts peak-to-peak are used. The electrons with energy sufficient to pass over the potential barrier of the retarding grids reach the concentric collector and are observed by means of a phase sensitive detector.

Curves resulting from different modes of operation of this scheme are shown in Fig. 3. The top curve is the dc retarding potential curve which results when the dc component of the collected current is measured as a function of the retarding voltage applied to grids G_2 and G_3 . This curve is denoted by $I(E)$

and represents the number of electrons with energy greater than the retarding voltage-electronic charge product at every point on the curve. The inserts show in an amplified manner the structure due to Auger electrons superimposed on the background of secondary electrons.

The second curve in Fig. 3 shows the result of measuring the modulation frequency component of the collected current as a function of the retarding voltage. The energy of the incident electron beam is fixed at 700 eV as the retarding voltage applied to grids G_2 and G_3 is swept through the range. This curve represents the derivative of the retarding potential curve which is the differential electron energy distribution; $N(E)$. The structure due to the Auger electrons consists of peaks in the energy distribution superimposed on the large background of secondary electrons.

The third curve shows the derivative of the energy distribution which is the second derivative of the retarding potential curve. This curve is obtained by measuring the second harmonic component of the collected current and leads to more sharply defined Auger peaks on a smaller background. It is this curve which is most commonly used in Auger Electron Spectroscopy.

The spectra which will be discussed later have been obtained in ultra high vacuum environments. Because of the surface sensitive nature of the technique the vacuum environment must be sufficient to prevent accumulation of fractions of a monolayer of the residual gas during the time of the experiment. An oil-free pressure of 1×10^{-9} torr could ordinarily be expected to give one experimental times of up to one hour. The spectra to be discussed were obtained at pressures in the 10^{-10} torr range.

A vacuum system arrangement shown in Figure 4 has been used to study segregation in metals. Figure 4 shows the top view of the stainless steel vacuum system which is pumped by ion and titanium sublimation pumps. Rough pumping is accomplished by oil free cryosorption pumps. The system contains a four grid, complete hemisphere LEED electron optics unit shown in Figure 1. In addition provisions have been made for cooling, impact fracturing, and sputtering of the specimen. The specimen is moved by a rotatable feedthrough from the top of the system and can be rotated 360° to the various stations for sputtering, cooling, fracturing, or making Auger or LEED measurements.

Experimental Results

Fig. 5-9 show typical spectra from pure metals that have been carefully cleaned. It is observed that one or more strong peaks are observed for each of the metals studied. A strong characteristic line has been present for all materials studied to date, so it appears that it will be possible to detect all materials using Auger spectroscopy.

Fig. 10-11 show the spectra for metals that have not been carefully cleaned. It is observed that strong peaks occur at the various energies characteristic of oxygen, carbon, and sulfur. This demonstrates the capability of Auger Electron Analysis to detect the light elements in contrast to the insensitivity of x-ray fluorescence techniques to these elements. Actually Auger spectroscopy is more sensitive to the light elements than to the heavy elements.

Weber and Johnson⁽⁶⁾ have pointed out the quantitative nature of the measurement by calibrating the Auger peak for K on Ge(111). They found that the height of the K peak was proportional to the total amount of K on the surface. This was in agreement with theoretical prediction and therefore it is expected that this linear relation between peak height and amount present will be followed. However, it will be necessary to have a pure metal spectra of the element of interest for comparison order to determine the amount present. Figures 12-13 show the spectra for a stainless steel and a low alloy steel. A fair estimate of the amount of Ni and Cr present in the iron can be made by comparing the height of the peaks of each element. However, this is true only because the height of the major peaks of each of these elements is approximately the same in the pure metal.

The study of fracture surfaces by Auger Electron Emission spectroscopy is particularly attractive because of the two unique characteristics of the technique. The sensitivity to light elements and the ability to sample a very thin layer. Palmberg and Rhodin⁽⁷⁾ have shown the mean escape depth of an Auger electron is on the order of 15 Å in Ag.

Figure 14-15 show results of Marcus and Palmberg⁽⁸⁾ and of Stein, Joshi, and Laforce⁽⁹⁾ on a low alloy steel that had undergone temper embrittlement and another that had been de-embrittled. The lower curve is for the embrittled steel and it shows a strong antimony doublet at about 470 e.v. indicating that segregation of these elements had taken place during embrittlement. The

remarkable reproducibility of the results by separate groups of people using different apparatus clearly demonstrates the reliability of Auger Electron Spectroscopy.

Marcus and Palmberg⁽⁸⁾ have shown that the layer of segregation is very small by sputtering thin layers of the fracture surface. Figure 16 shows the results of Marcus and Palmberg⁽⁸⁾ on the segregation of Sb in a low alloy steel.

Potential Applications

There are several areas which have not been explored that appear promising for investigation using Auger Electron Spectroscopy. It is recognized that the adherence of either plated or sputtered surface coatings varies considerably. This may be due to small chemistry changes on the surface to be plated and it would be of interest to determine the relation between surface chemistry and adherence.

Auger spectroscopy would appear to be a useful tool in studying corrosion. For instance many materials are attacked more readily at the grain boundary than in the bulk. This may be due to chemistry differences at the grain boundary similar to those producing the brittle fractures previously discussed. Also the phenomena of passivation of surfaces by certain chemical treatments should be amenable to study by Auger spectroscopy.

It would be possible to study bulk or surface diffusion using Auger spectroscopy. It would be most valuable in studying the diffusion of slow moving species and for measurements at low temperatures because of the very sharp profiles (on the order of atomic spacing) that can be measured. There are already people active in surface diffusion using Auger spectroscopy (Gjostein at Ford Scientific Labs).

These are examples of a wide number of problems that could be studied using Auger Electron spectroscopy. Other would be in the area of powder-metallurgy, thin film devices, electronic structure of solids, phase identification and surface segregation.

Summary

Auger Electron Emission Spectroscopy shows promise in many areas of metallurgical research. The advantage of the technique is its ability to sample

very thin layers and its sensitivity to all of the elements, including the light elements. The technique is developed at the present time such that it gives reproducible and accurate measurements. The application of the technique should be widespread and lead to much new information in developing our understanding of materials.

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- Fig. 1 Electron energy diagram illustrating a transition giving rise to an emission of an Auger Electron.
- Fig. 2 Block diagram describing the electronic circuit used for Auger Electron Analysis.
- Fig. 3 Comparison of the signals received depending upon the mode of operation.
- Fig. 4 Layout of apparatus in bell jar for fracturing specimens in vacuum, for sputtering, and performing Auger Electron Analysis⁽⁹⁾
- Fig. 5 Spectra of clean zinc⁽¹⁰⁾
- Fig. 6 Spectra of clean Indium⁽¹⁰⁾
- Fig. 7 Spectra of pure Iron
- Fig. 8 Spectra of pure Molybdenum
- Fig. 9 Spectra of pure Tungsten
- Fig. 10 Spectra of uncleaned Zinc⁽¹⁰⁾
- Fig. 11 Spectra of uncleaned Indium⁽¹⁰⁾
- Fig. 12 Spectra of 304 Stainless Steel
- Fig. 13 Spectra of 3340 Steel
- Fig. 14 Spectra of embrittled and De-embrittled 3340 steel
 (Marcus and Palmberg)
- Fig. 15 Spectra of embrittled and non-embrittled 3340 steel
 (Stein, Joshi, and Laforce)
- Fig. 16 Antimony concentration as a function of layers removed from fracture surface.

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Fig. 1

COMPARISON OF THREE MODES OF OPERATION