EXPERIMENTAL TECHNIQUES FOR STUDYING
GRAIN BOUNDARY CHEMISTRY

D. F. Stein, W. C. Johnson, and C. L. White

Department of Metallurgical Engineering
Michigan Technological University
Houghton, Michigan

ABSTRACT

A review of the techniques used to study the chemistry of near grain boundary regions is given. The traditional techniques of radiography, chemical etching, and microprobe are discussed and their limitations are pointed out. New techniques are presented such as ion scattering spectrometry, electron spectroscopy for chemical analysis, ion backscattering spectrometry, and Auger electron spectroscopy. The success of these new techniques indicates that they will prove most useful.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

The chemistry of the region adjacent to grain boundaries is of interest since a segregation of impurities to this region can have a marked influence on the properties of the material. Grain boundary fracture, grain boundary corrosion, and densification rates of powdered materials are all thought to be affected by grain boundary chemistry and therefore experimental techniques to measure the chemistry of this region would be useful.

It is reasonable to expect that the region adjacent to grain boundaries may be chemically different from the matrix or bulk chemistry. This expectation is reasonable because of the large elastic strains in the vicinity of the grain boundary which would be expected to attract impurity atoms having a larger or smaller atomic diameter than the host lattice. This attraction would be analogous to that of a foreign atom for a dislocation. Models have been proposed to quantitatively describe the segregation and the Gibb's¹ model will be briefly described now in order that a basis may be established for estimating the extent and amount of segregation that may occur to grain boundaries and the consequent requirements of instruments to measure this segregation.

Cahn and Hilliard² have estimated the segregation to grain boundaries starting with the Gibb's equation:

$$d\sigma = -\sum \Gamma_i du_i$$

where

σ = Grain boundary tension

μ_i = Chemical potential of i^{th} component

Γ_i = Excess amount of i^{th} component per
unit of grain boundary area

The excess quantity Γ is defined as the difference between the actual amount of the component in the system and that which would have been present in the same volume if the phases were homogeneous right up to the grain boundary. Defining $\Gamma_{2(1)}$ for a two component system as

$$\Gamma_{2(1)} = (\Gamma_2 - \frac{x}{1-x} \Gamma_1) \quad (1)$$

where x is the atom fraction of component 2 (solute) and denoting the measured value of $\Gamma_{2(1)}$ at an atom fraction of solute x_0 by $\Gamma_{2(1)}^0$, they have shown that for Gibb's adsorption

$$\Gamma_{2(1)}^0 < \frac{\sigma l}{kT} \left[1 + \ln \frac{x_e}{x_0} \right]^{-1} \quad (2)$$

for the range $0 < x_0 < x_e$ where x_e is the solubility limit of the solute. Thus, if the number of solute atoms is measured and plotted against the perpendicular distance from the grain boundary, the hatched area in Fig. 1 is equal to $\Gamma_{2(1)}^0$. The equilibrium theory thus predicts the number of atoms segregated, but it does not predict directly the concentration or width of segregation.

Denoting N_1 and N_2 as the number of atoms of the two components removed normal to a unit area of grain boundary, and if sufficient thickness has been removed from the boundary so that the remaining material is of bulk composition, then

$$\Gamma_{2(1)}^0 = \frac{1}{A} (N_2 - \frac{x_0}{1-x_0} N_1) \quad (3)$$

Since the right hand side of equation (3) vanishes at the composition x_0 of the grain interior, its value is independent of the depth of material removed for analysis, providing the depth exceeds the boundary thickness.

Using equation (3) we can estimate the total number of atoms segregated per cm^2 of grain boundary and from this estimate the concentration as a function of distance from the grain boundary. For the case of Sb segregation in Fe, using the following values in equations (2) and (3),

$$x_0 = 0.00018$$

$$x_e = 0.028$$

$$\gamma_{\text{Fe}} = 850 \text{ ergs cm}^{-2}$$

$$T = 750^\circ\text{C}$$

it is found that approximately 10^{15} atoms would segregate assuming the grain boundary energy went to zero. This suggests segregation profiles of the type shown in Fig. 2. Since there are about 10^{15} atoms in a monolayer, the width of the segregated region must be very narrow if the segregation is intense (on the order of a few atom distances). If the segregation is broad, then the enrichment at the boundary must be very low, because of the limited number of atoms segregated. Therefore, any experimental technique that is to measure equilibrium segregation must be very sensitive to a few numbers of atoms in a very small region.

EXPERIMENTAL TECHNIQUE

A. Traditional Methods

There have been several techniques used in the past in an effort to study grain boundary segregation. These include radiography, chemical etching, and the microprobe. Each of these techniques will now be discussed, with examples given of their usefulness and limitations.

1. Radiography

Auto-radiography would appear to be a very useful tool to study segregation to grain boundaries. In this technique a thin emulsion is brought into contact with a sample. This can be done either with the emulsion on a backing sheet or by painting the emulsion directly on the surface of the specimen. If the segregating species in the specimen is radioactive it will emit particles (beta or alpha are most common) and these particles will expose the film. This technique appears straightforward and intuitively appears to be a very powerful technique to study the chemistry of the grain boundary region.

Despite the apparent usefulness of the technique, it has had very limited success. In some cases it has proven useful, as shown in Fig. 3. In this microradiograph the segregation of nickel to a grain boundary in Al_2O_3 is demonstrated,³ but in general the technique is unsuccessful.

Stein⁴ examined the reasons for the limited success of this technique using a model system shown in Fig. 4. The model is of a semi-infinite bi-crystal with a single grain boundary perpendicular to the top face. The width of the grain boundary, W ,

is defined as the region to which segregation has occurred and it is assumed that the region is of constant composition. It is also assumed in the analysis that the measurement is not limited by the means of detecting the radiation (photographic emulsion) and the means of detecting the radiation is linearly sensitive to the radiation and has infinite resolving power.

The results using this model applied to β particle emission are shown in Fig. 5. In Fig. 5 the maximum percent increase in counting rate is plotted as a function of the segregation ratio, defined as the concentration at the grain boundary divided by the concentration in the bulk. In order to double the counting rate it is necessary that the segregation ratio be on the order of 1000 over a $30\text{\AA}$ wide region. Therefore, it is obvious that segregation of the Gibbs type will not be easily detected using radiography.

While the results depend on the radiation absorption coefficient, particle energy, grain boundary width and extent of segregation, it is expected that autoradiography will not be a generally useful technique to study grain boundary segregation. The basic problem is associated with the very small number of atoms segregated into the grain boundary region. If the concentration at the grain boundary of the segregating species is high, then the width of the segregation region must be small. Since the sampling volume is determined by the range of the alpha or beta particles which is usually on the order of 10^{-3} cm, the sample volume is very large in comparison to grain boundary volume and therefore difficult to detect. Only in cases where the range

of the beta or alpha particle is very low is there a reasonable expectation for success and in these cases very long exposure times must be used since there are very few particles reaching the surface to expose the emulsion or activate the counter.

2. Chemical Etching

Inman and Tipler⁵ have used a chemical etching technique to study the segregation of radioactive phosphorous to grain boundaries in iron. In this technique fracture was induced along grain boundaries and the grain boundary surfaces were then etched in a solution of 0.5 ml concentrated hydrochloric acid and 2.5 ml distilled water, in which was dissolved 1 mg each of potassium chlorate and sodium di-hydrogen phosphate. After the fracture surfaces were dipped in acid solution, the solutions were boiled to destroy the remaining potassium chlorate so they would not interfere with subsequent iron determination. The radioactivity of the solution was measured with a liquid counter, and the phosphorous contents determined by comparison of the measured activities with those of previously prepared standard solutions containing known quantities of radioactive phosphorous. Fig. 6 shows the results obtained for an iron that had been water quenched from 700°C and another that had been quenched from 1150°C. It is clear that the phosphorous content of the first 500Å is considerably greater than the bulk chemistry and the segregation is clearly demonstrated.

This technique requires great care in performing the etching experiment and in calibration, but it is clearly a useful tool to study massive segregation to grain boundaries.

3. Electron Probe Analysis

X-rays have been used since 1920 to identify chemical elements, but it was not until 1951 when Castaing developed electron probe analysis, that the technique became applicable to study microsegregation in solids. In recent years the development of the scanning electron microscope has resulted in a modification that allows this instrument to be used as a microprobe analyzer, but with certain limitations. The standard Electron Probe Microanalyzer will be discussed first and then the modifications necessary to make it compatible with a scanning electron microscope will be given.

a) Electron Probe Microanalyzer (EPM)

Fig. 7 shows the basic design of an EPM. Electrons are generated at a filament and focused on a specimen. The impinging electrons create electron vacancies in the lower lying energy levels in the atom as shown schematically in Fig. 8 and when an electron from an outer level fills this vacancy, an x-ray can be emitted. This characteristic x-ray then identifies the element emitting it and the chemical composition can be determined.

The sample volume is defined by the diameter of the electron beam (1 - 10 μ) and the depth from which x-rays can escape without significant energy loss (1 - 10 μ). Therefore segregation must be on this scale to be detected.

Aaronson and Domain⁶ have used EPM to study the partition of alloying elements between the parent austenite and proeutectoid ferrite or bainite in high purity Fe-C-X alloys.

Fig. 9 shows the microstructure of an 0.11% C, 3.28% Ni steel formed by an isothermal reaction at 734°C. Figs. 9(b) and 9(c).

show an EPM trace across two different ferrite crystals in which the nickel is partitioned in the austenite, but in addition it is seen that a major enrichment in nickel occurs at one of the boundaries between the ferrite and austenite phase. Aaronson and Domain⁶ attributed this difference in behavior to the dislocation structure of the grain boundaries.

In general the problem with EPM is the large volume of material sampled and therefore it is insensitive to the very limited segregation of the equilibrium type.

b) Energy Dispersive Analysis (EDA)

The scanning electron microscope coupled with Energy Dispersive Analysis provides a technique to study grain boundary chemistry. In this technique the beam used to create the secondary electrons or backscattered electrons which in turn create the image in the scanning microscope is also used to generate the characteristic x-ray photons. Since this beam must be of extremely small diameter to produce fine spatial resolution, the current which is proportional to the $8/3$ power of the diameter is also reduced. In order to achieve beam diameter of $100\text{\AA}$ or less it is necessary to reduce the beam current to 10^{-11} to 10^{-12} amperes as compared to 10^{-6} to 10^{-9} in the conventional EPM. Since the signals produced are linearly proportional to the exciting current, this limits the sensitivity of EDA.

B. New Methods

In the past ten years there has been a rapid development of new techniques that either have proven or appear to be useful for study of the chemistry of near grain boundary regions. A

discussion of each of these techniques will now be given, with examples where possible, illustrating the use of the technique.

1. Ion Scattering Spectrometer (ISS)

In 1967, Smith⁷ showed that a technique based on scattering of noble gas atoms could be used to determine the chemistry of a surface layer. In this technique noble gas atoms having a primary energy of about 0.5 to 3.0 keV are scattered off the surface of the specimen. Using simple binary elastic collision theory, one would predict the energy loss to be given by the following expression:

$$E_1/E_0 = (M_S - M_O)/(M_S + M_O)$$

where

M_S = mass of surface atom

M_O = mass of bombarding ion

E_0 = energy of bombarding ion

E_1 = energy of the same ion when scattered at 90° angle

The experimental apparatus for application of ISS is shown in Fig. 10. The ion gun bombards the specimens from below and the ions are collected in an 127° energy analyzer. By displaying the number of ions collected as a function of the scattered ion energy ratio, E_1/E_0 , a spectrum such as the one shown in Fig. 11 is obtained. This spectrum shows traces of oxygen and sulfur on a clean copper surface, bombarded with He^+ ions. The resolution of heavy elements can be improved by using a heavier bombarding ion, since the mass ratio will be more nearly the same. This can be accomplished by simply interchanging the bombarding gas ions.

ISS is truly a surface chemistry analysis tool since only atoms lying in the outermost layer are detected. An ion penetrating deeper undergoes multiple scattering and disappears into the background. Under the appropriate conditions analysis for as little as one atom in 10,000 can be detected at the surface. Atoms are continuously sputtered from the surface during analysis, allowing determination of the chemistry of underlying layers.

Although this technique has not been used to study grain boundary chemistry, it would appear to be suitable for this application. Karasek⁸ has used the technique to study the electroplating of zinc on a steel electrode from $\text{Zn}(\text{CN})_2\text{-NaCN-NaOH}$ solutions. A dull dark film forms during the final coating operation and standard techniques had not been successful in determining its chemical composition. The results are shown in Fig. 12, showing contamination by oxygen and either sulfur or chlorine. By changing the probe gas from ^3He to ^4He it was possible to positively identify the impurity as chlorine.

2. Electron Spectroscopy for Chemical Analysis (ESCA)

In 1946 Siegbahn⁹ reported on a technique in which high energy x-rays were used to produce emission of inner shell electrons. Since these electrons are characteristic of the atom emitting them, their emission can be used for chemical analysis.

The kinetic energy of the emitted electron is approximately equal to the energy of the incident x-rays minus the binding energy of the inner shell electron. The major advantage of the technique is its ability to define absolute electron energy levels, thereby identifying the chemical state of the emitting atom provided that

the incident x-rays are mono-energetic. Fig. 13 illustrates the experimental arrangement used in the commercial Dupont ESCA instrument. After excitation of the sample by x-rays the energy of the emitted electrons are analyzed and displayed as shown in Fig. 14. The principle benefit of the technique is its sensitivity to the chemical state of the atom in addition to identifying the elements present. The technique has not yet been used to study grain boundary chemistry.

3. Ion Backscattering Spectrometry (IBS)

IBS has been known to nuclear physicists for more than 20 years and they have regularly used the technique in nuclear experiments. However, the technique has not been extensively used in non-nuclear applications as pointed out in a review article by Nicolet, Mayer, and Mitchell.¹⁰ In recent years Guttman et al^{11,12} have made use of the technique to study grain boundary segregation in steels with good success.

The IBS technique is based on the scattering of high energy ions by the Coulomb repulsion of the nuclei of atoms in the solid (i.e., Rutherford scattering). In this type of scattering an energetic ion is on a path that will take it near the atom core, but because of its interaction with the atom core, the ion is backscattered along a hyperbola as shown in Fig. 15.

The experimental layout for a backscattering system is shown in Fig. 16. The high energy ion beam impinges on a sample placed in a vacuum chamber and the energy of the backscattered ions is analyzed and stored in a pulse light analyzer. Fig. 17 shows the spectrum taken from a thin film of Au, Ag, and Cu

using a 2.5 M.E.V. He ion beam.

The position of a peak is determined by the mass of the target atom, since the loss in energy of the impinging ion is proportional to a factor K defined as

$$K = \left(\frac{M-m}{M+m} \right)^2$$

where m is the mass of the impinging particle and M the mass of the scattering atom. Although the thin film had approximately equal quantities of Au, Ag and Cu it is noted that the signal obtained from the Au is much stronger than that obtained from the copper. This is due to the effectiveness of each atom in scattering the incident ion beam. Based on an analysis of Rutherford scattering it can be shown that the scattering cross section, σ , is related to the beam energy, E_0 , and the atomic numbers of the incident ion (Z_m) and substrate atom (Z_M).

$$\sigma \propto \left(\frac{Z_m Z_M}{E_0} \right)^2 \frac{1}{\sin^4(\theta/2)}$$

Therefore it is clear that the sensitivity increases rapidly with increasing atomic weight and the approximate Z_M^2 dependence is shown in Fig. 17.

Guttman et al^{11,12} have used IBS to study the segregation of antimony to grain boundaries during the temper embrittlement of a 0.15% C, 2% Mn, 600 ppm Sb (i.e., 300 at. ppm) steel. The analysis was performed using $^{12}\text{C}^+$ as the impinging ion and the results are given in Figs. 18 and 19 for non-embrittled and embrittled specimens respectively. By subtracting these two curves the peak shown in Fig. 20 is obtained. This peak is symmetrical about 1.1 M.E.V. and corresponds to that obtained

from a thin antimony reference layer. On this basis it was estimated that the excess antimony was within $250\text{\AA}$ of the grain boundary. From the peak ^{shape} height it was estimated that in this region the antimony was about six times greater than the bulk concentration.

IBS has proven its usefulness as a tool to study the chemistry of grain boundaries. Its principle strengths are its sensitivity to heavy elements and since it allows analysis over many atomic layers, it does not require the careful fracturing conditions of other techniques. However, it is limited in providing information on light elements, and its depth resolution is at present no better than about $100\text{\AA}$. The technique can detect concentrations on the order $10^{-2} - 10^{-3}$ of a monolayer under the proper conditions.

4. Auger Electron Spectroscopy (AES)

In AES, an electron beam of moderate energy (1000-3000 eV) impinges on the specimen and creates electron vacancies in the inner electron levels. When an electron from an outer level fills the vacancy, a photon or an Auger electron is emitted, depending on the relaxation time for photon emission. The relaxation time for Auger electron emission is nearly independent of the transition energies and therefore for light elements (i.e., for transition below about 2000 eV) Auger emission is the major relaxation mechanism. An illustration of the electronic transition involved in an Auger electron emission is presented in schematic form in Fig. 21. The incident electron beam creates a vacancy in an inner level such as the K level shown. If the

atom returns to the ground state by Auger emission, an electron from the M level fills the vacancy in the K level and an electron from the N level is ejected from the atom, carrying away the excess energy. This Auger electron has an energy characteristic of the levels that participated in the transition and this energy is approximately equal to $E_K - E_M - E_N$. The presence of energy bands due to solid state binding and the work function of the detection apparatus modifies the observed energy somewhat, but it can be seen that the energy measured will be characteristic of the levels and hence the type of atom involved in the electron emission.

The discovery of the Auger emission dates back to the work of Pierre Auger¹³ in 1925. Lander¹⁴ first demonstrated the possibility of using the Auger emission for chemical analysis in 1953. However, until Harris^{15,16} developed techniques in 1967 that markedly improved the signal-to-noise ratio, the technique was not useful for chemical analysis. Weber and Peria¹⁷ improved on the Harris design by using LEED optics to detect Auger electrons and this technique has been widely used. In 1969 Palmberg, Bohn and Tracy¹⁸ developed the cylindrical electrostatic energy analyzer and it is now the most commonly used analyzer. In this technique either a coaxial (normal incidence) or grazing incidence electron gun is used and the electrons from the specimen are collected by a velocity selector (Fig. 22). The outer cylinder is biased negatively and is swept over the voltage range of interest. Electrons of the correct energy are focused through the exit slit and collected by an electron multiplier. The

derivative of the electron distribution is then taken electronically and the plotted signal is the second derivative of the current being emitted by the specimen. Fig. 23 shows a spectrum from a maraging steel to illustrate the type of data one obtains in AES.

The technique is sensitive to all elements except H and He and it is particularly sensitive to the light elements. The peak heights are roughly proportional to concentration, but absorption correction must be taken into account if accurate quantitative analysis is desired. Since the energies of the Auger electrons are usually in the 50 eV to 1000 eV range the probability of Auger electrons from atoms lying more than 2 or 3 layers below the surface escaping without energy loss is small. Therefore the technique gives chemical information almost entirely from the outermost 2 or 3 atom layers.

AES provides only surface chemistry and because it is often of interest to know the chemistry below the surface, the AES technique is often combined with inert ion sputtering. In inert ion sputtering an inert gas ion beam is used to etch a surface (analogous to microscopic sand blasting). This allows controlled removal of angstrom thick layers of substrate. Alternate use of sputtering and AES yields a profile of chemical composition perpendicular to the original surface.

Because it is desirable to keep the fracture surfaces free from contamination it is necessary to fracture the specimen in an ultra-high vacuum system (10^{-10} - 10^{-11} torr), perform AES analysis, and sputter the surfaces without removal from the vacuum system. A schematic of a system used for this purpose is presented in Fig. 24.

AES has proven to be a valuable tool to study grain boundary chemistry in solids.¹⁹⁻²⁷ For example, it had been thought that the brittle behavior of polycrystalline tungsten was associated with oxygen segregation to grain boundaries.

Joshi and Stein²⁰ studied samples of powder metallurgy tungsten having a wide variation in ductile-to-brittle transition temperatures. The results of AES of these materials are shown in Fig. 25. A wide variation in phosphorous concentration is observed on the surface and it was shown that the phosphorous peak heights correspond well with the ductile-brittle variation in transition temperature. By using inert ion sputtering in conjunction with AES it was shown that the phosphorous was segregated over a very narrow region (on the order of 3-5 atom layers). (Fig. 26.)

A number of investigations^{19,22,24-26} have studied the temper embrittlement of low alloy steels using AES. Fig. 27 shows a AES spectrum comparing a non-embrittled and an embrittled steel containing 0.39 at. % C, 3.5 w/o Ni, 1.6 w/o Cr, 0.003 w/o Mn and 620 wt. ppm Sb. This steel exhibited a shift in the ductile-brittle transition temperature for a fully embrittled condition of nearly 700°C and the embrittled fracture surface showed a substantial enrichment of Ni, Cr and Sb.

The major segregation was of antimony and Fig. 28 shows how the antimony builds up during the embrittling treatment. Therefore even in a complex steel AES has proven to be a useful tool to study grain boundary chemistry.

AES can also be used to study segregation in ceramic materials and the work of Marcus and Fine²⁷ on the role of Mg in the densification of Al_2O_3 will be used as an example. Coble²⁸ had shown that small amounts of Mg could markedly improve the densification of Al_2O_3 during sintering and this result has been explained on the basis of Mg segregation to Al_2O_3 grain boundaries. However, Marcus and Fine²⁷ clearly demonstrate that Ca and not Mg is segregated to the grain boundaries (Figs. 29 and 30).

AES has proven a useful tool to study the chemistry of the grain boundary region. The power of the technique rests in the ability to detect segregation on the order of a fraction of a monolayer of all the elements but hydrogen and helium. When combined with inert ion sputtering it can be used to determine the chemistry of moderately thick layers (on the order of 1000 - 10,000 atom layers).

SUMMARY

A brief survey has been given of some techniques that have proven to be or appear to be useful for chemical analysis of grain boundaries. In the introduction, a calculation was made to estimate the extent of grain boundary segregation and it was found that for equilibrium segregation the extent of segregation was very limited. From the subsequent discussion of the techniques for determining grain boundary chemistry, it was found that the traditional methods such as radiography, chemical etching, and microprobe would not be expected to be sensitive to this limited segregation.

New analytical techniques were then discussed that are more sensitive to grain boundary segregation. At the present time Auger Electron Spectroscopy and Ion Backscattering Spectrometry have been used successfully to study grain boundary segregation, but two other techniques, Ion Scattering Spectrometry and Electron Spectroscopy for Chemical Analysis appear to hold promise. Table I briefly summarizes and compares each technique.

TABLE I

Technique	Excitation	Emission	Elements Detectable	Sensitivity Atomic Layers Ideal Conditions	Approximate Cost	Major Advantage
Radiography	--	α -rays β -rays	Low energy α or β emitter	≈ 2 Very limited	Low	Cost
Chemical Etching	--	--	All elements	≈ 5	Low	Cost
Microprobe and Energy Dispersion	Electrons 25 keV	x-rays	Good for elements $Z > 11$ Can detect $Z = 5$	≈ 5	\$70,000	Versatility
Ion Scattering	Ions 0.5 to 3.0 keV	Ions	$Z > 2$	$\approx .001$	\$50,000	Analysis of first Atomic layer
Electron Spectroscopy for Chemical Analysis	x-rays	Electrons	All elements	$\approx .01$	\$50,000	Obtain Chemical State Information
Ion Backscattering Spectrometry	Ions 0.5 to 3000 keV	Ions	Best for Heavy Elements Element $Z < 10$ probably not detectable	$\approx .01$	\$50,000?	Use with atmosphere contaminated samples
Auger Spectroscopy	Electrons 2-5 keV	Electrons	Good for Light Elements. Can detect all elements with $Z > 2$	$\approx .001$	\$50,000	Analysis of outer layers. Analyzes all Elements simultaneously

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the Atomic Energy Commission under Grant No. AT(11-1)-2166.

For Additional Information

Radiography

D. F. Stein, TRANS. AIME, Vol. 239 (1967 p. 1721.

Chemical Etching

M. C. Inman and H. R. Tipler, Acta Met., Vol. 6 (1958),
p. 73.

Electron Probe

L. S. Birks, Electron Probe Microanalysis, 2nd ed.,
Wiley-Interscience, New York, (1971).

A. J. Tousimis and L. Morton (eds.), Advances in Electronics
and Electron Physics, Electron Probe Microanalysis,
Academic Press, New York (1969).

Ion Scattering Spectrometry

F. W. Karasek, Research/Development, Jan., 1973.

Electron Spectroscopy for Chemical Analysis

D. M. Hercules, Anal. Chem., Vol. 42 (1970) p. 20A.

Ion Backscattering Spectrometry

M. A. Nicolet, J. W. Mayer, and I. V. Mitchell, Science,
Vol. 177 (1972) p. 841.

Auger Electron Spectroscopy

C. C. Chang, Surf. Sci., 25, 1971, p. 53.

W. C. Johnson, D. F. Stein, and A. Joshi, Canad. Jour. of
Spec., 17 (1972) p. 88.

REFERENCES

1. S. Glasstone, "Thermodynamics for Chemists," Van Nostrand, New York, 1963, p. 244.
2. J. W. Cahn and J. E. Hilliard, *Acta Met.*, Vol. 7, 1959, p. 219.
3. P. J. Jorgenson and J. H. Westbrook, *J. Am. Ceram. Soc.*, Vol. 47, 1964, p. 332.
4. D. F. Stein, *Trans. AIME*, Vol. 239, 1967, p. 1721.
5. M. C. Inman and H. R. Tipler, *Acta Met.*, Vol. 6, 1958, p. 73.
6. H. I. Aaronson and H. A. Domain, *Trans. AIME*, Vol. 236, 1966, p. 781.
7. D. P. Smith, *J. Appl. Phys.*, Vol. 38 (1), 1967, p. 340.
8. F. W. Karasek, *Research and Development*, Jan., 1973, p. 25.
9. K. Siegbahn, C. Nordling et al., *ESCA*, Almquist and Wiksallg AB, Upsalla, Sweden, 1967.
10. M. A. Nicolet, J. W. Mayer and I. V. Mitchell, *Science*, Vol. 177, 1972, p. 841.
11. M. Guttman, P. R. Krahe, F. Abel, G. Amsel, M. Bruheaux and C. Cohen, *Scripta Met.*, Vol. 5, 1971, p. 479.
12. M. Guttman, P. R. Krahe, F. Abel, M. Bruheaux and C. Cohen, *Scripta Met.*, Vol. 7, 1973, p. 23.
13. P. Auger, *Comptus Rendus*, Vol. 180, 1925, p. 65.
14. J. J. Lander, *Phys. Rev.*, Vol. 91, 1953, p. 1382.
15. L. A. Harris, *J. Appl. Phys.*, 39, 1968, p. 1419.
16. L. A. Harris, *J. Appl. Phys.* 39, 1968, p. 1428.
17. R. E. Weber and W. T. Peria, *J. Appl. Phys.* 38, 1967, p. 4355.
18. P. W. Palmberg, G. K. Bohn, and J. C. Tracy, *Appl. Phys. Letters*, Vol. 15, 1969, p. 254.
19. D. F. Stein, A. Joshi and R. P. Laforce, *Trans. ASM*, Vol. 62, 1969, p. 776.
20. A. Joshi and D. F. Stein, *Met. Trans.*, Vol. 1, 1970, p. 2543.
21. A. Joshi and D. F. Stein, *J. Inst. Metals*, Vol. 99, 1971, p. 178.

22. A. Joshi and D. F. Stein, ASTM Tech. Pub. 499, 1972, p. 59.
23. D. F. Stein, W. C. Johnson and C. L. White, to be published in book, Grain Boundary Structure and Properties, Chadwick and Smith, eds., Academic Press.
24. H. L. Marcus and P. W. Palmberg, Trans. AIME, Vol. 245, 1969, p. 1664.
25. P. W. Palmberg and H. L. Marcus, Trans. ASM, Vol. 62, 1969, p. 1016.
26. R. Viswanathan, Met. Trans. Vol. 2, 1971, p. 809.
27. H. L. Marcus and M. E. Fine, J. Am. Ceram. Soc., Vol. 55, 1972, p. 568.
28. R. L. Coble, J. Am. Ceram. Soc., Vol. 41, 1958, p. 55.
29. L. S. Birks, Electron Probe Microanalysis, 2nd ed., Wiley-Interscience, New York (1971).
30. John C. Russ, Elemental X-ray Analysis of Materials EXAM Methods, EDAX Laboratories, International, Inc., 1972.
31. D. F. Stein, R. E. Weber and P. W. Palmberg, J. of Metals, Feb. 1971.

FIGURE CAPTIONS

- Figure 1. Schematic of segregation to grain boundaries
Joshi and Stein, Ref. 22.
- Figure 2. Variation in Ni and Sb concentration with distance
from intergranular fracture surface of embrittled
Ni-Cr-C-400 ppm Sb steel.
Joshi and Stein, Ref. 22.
- Figure 3. (A) Microstructure of Al_2O_3 with 0.03 wt. % NiO
containing ^{63}Ni and (B) autoradiograph of same
specimen (X50).
Jorgenson and Westbrook, Ref. 3.
- Figure 4. Model showing bicrystal having a single grain
boundary perpendicular to top surface. W is
width of pure segregant, y is the distance from
grain boundary to the point at which radiation
is being measured, and x is the integration variable.
Stein, Ref. 4.
- Figure 5. The maximum percentage increase in counting rate
as a function of grain boundary width and differing
values of the segregation ratio. For β particles only.
Stein, Ref. 4.
- Figure 6. Histogram showing distribution of phosphorous as a
function of distance from grain boundary for two
irons. (a) Water quenched from 700°C. (b) Furnace
cooled from 1150°C.
Inman and Tipler, Ref. 5.
- Figure 7. Schematic diagram of electron probe microanalyzer.
Birks, Ref. 29.
- Figure 8. Electron transitions giving rise to x-ray emission.
Russ, Ref. 30.
- Figure 9. Ferrite crystals with concentration profiles. (b)
and (c) Concentration profiles through two
different ferrite crystals formed by isothermal
reaction of .11% C, 3.28% Ni steel at 734°C.
Aaronson and Domain, Ref. 6.
- Figure 10. Schematic of essential components of ISS instrument.
Karasek, Ref. 7.
- Figure 11. ISS analysis of clean copper surface showing oxygen
and sulfur contamination.
Karasek, Ref. 7.

- Figure 12. Expanded portion of ISS spectrum of dark film covering electroplated zinc coating on steel reveals presence of zinc, oxygen and either chlorine or sulfur. Karasek, Ref. 7.
- Figure 13. Schematic of essential components of ESCA instrument. Karasek, Ref. 7.
- Figure 14. Two prominent zinc peaks are shown in portion of ESCA spectrum. Karasek, Ref. 7.
- Figure 15. Deflection of an α -particle by a nucleus. Ion other than α -particles may be used.
- Figure 16. Layout of IBS system. An accelerator (not shown) generates an atomic beam of high energy and the backscattered ions are energy-analyzed by detector. Nicolet, et al. Ref. 10.
- Figure 17. IBS spectrum of a thin film of approximately equal parts of copper, silver, and gold. Note Z_M^2 dependence of peak heights. Nicolet, et al. Ref. 10.
- Figure 18. IBS spectrum from non-brittle low alloy steel. Guttman, et al. Ref. 11.
- Figure 19. IBS spectrum of brittle fracture surface of low alloy steel. Guttman, et al. Ref. 11.
- Figure 20. Observed peak after subtraction of spectrum from non-brittle steel from brittle spectra. Peak corresponds to antimony. Guttman, et al. Ref. 11.
- Figure 21. Electron energy diagram illustrating a transition giving rise to an emission of an Auger electron. Stein, et al. Ref. 31.
- Figure 22. Scheme for measuring Auger spectrum with cylindrical analyzer. Stein, et al. Ref. 31.
- Figure 23. AES spectrum of maraging steel.
- Figure 24. Layout of apparatus in bell jar for fracturing specimens in vacuum, for sputtering, and performing AES analysis.

Figure 25. Comparison of AES spectra of various tungsten specimens. (a) Zone refined tungsten. (b) Moderately brittle powder metallurgy tungsten (T.T. $\approx 250^{\circ}\text{C}$). (c) Brittle powder metallurgy tungsten (T.T. $\approx 700^{\circ}\text{C}$). Joshi and Stein, Ref. 20.

Figure 26. Variation in phosphorous concentration with distance from the intergranular fracture surface in tungsten. Material (c) in Fig. 25. Joshi and Stein, Ref. 20.

• Figure 27. AES spectra of non-embrittled and embrittled Ni-Cr-C-620 ppm Sb steel. Joshi and Stein, Ref. 22.

Figure 28. Variation in Sb concentration as a function of distance from intergranular fracture surface of steel after various stages of embrittlement. Joshi and Stein, Ref. 22.

Figure 29. AES spectrum of Mg doped Al_2O_3 taken from grain boundary fracture. Marcus and Fine, Ref. 27.

Figure 30. Sputter profile showing calcium concentration normal to grain boundary fracture surface. Marcus and Fine, Ref. 27.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Fig. 18

Fig. 19

Fig. 20

Fig. 21

Fig. 22

Fig. 23

Fig. 24

Fig. 25

Fig. 26

Fig. 27

Fig. 28

Fig. 29