ANL/MCT/PP-- 72666

CORRECTION OF ENERGY SHIFT IN MEASUREMENTS OF SOLUTE SEGREGATION BY RUTHERFORD BACKSCATTERING SPECTROMETRY*

R. A. Erck

Materials and Components Technology Division
Argonne National Laboratory
Argonne, IL 60439 USA

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February 1991

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*Work supported by the Tribology Program, Office of Advanced Transportation Materials, U.S. Department of Energy, and the Materials Sciences Program, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38.

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Abstract

Rutherford backscattering spectrometry (RBS) is a sensitive technique for measuring the elemental composition of a specimen in the near-surface region. Studies of radiation effects in materials, such as radiation-induced segregation of solute elements to the external surface, often employ RBS to measure specimen composition because the high-energy ions can be used to produce radiation damage and also serve as the RBS profile ions. When small amounts of segregation are being measured, a shift in energy calibration renders the acquired data meaningless: the resulting edge shift in the spectra produces spurious contributions near the elemental leading edges that may greatly exceed the amount of segregation being measured. A simple method is proposed for correcting errors in measurement due to energy shift.

1. Introduction

When materials are subjected to high-energy irradiation, the resulting effects include not only microstructural changes, such as cavity formation and dislocation generation, but also changes in composition, such as solute segregation to defect sinks. A major effort has been made to understand radiation-induced changes on a microstructural scale because the mechanical properties of alloys are sensitively dependent on the presence of defects and the distribution of solute elements. It is known that radiation-induced segregation (RIS) is an important mechanism for compositional redistribution in alloys [1-3]. The resulting enrichment or depletion of solute elements near point-defect sinks may be large and can lead to the formation of second-phase precipitates [4, 5]. By measuring microcompositional changes during irradiation (e.g., by

measuring transport of solute to the external surface), point-defect production efficiencies and defect-solute interactions can be studied [6].

Rutherford backscattering spectrometry (RBS) has often been used for studies of radiation effects because the technique is sensitive to changes in composition in the near-surface region (≈ 200 nm). Because the high-energy ions can be used to both produce radiation damage and also serve as the RBS backscattering ions, compositional changes can be measured as a function of time or irradiation dose by comparing changes in successively acquired spectra.

When relative differences between successive RBS spectra are measured, it is important that the energy calibration of the detector and the associated electronics be very stable. If a change in energy calibration occurs, one spectrum is shifted in energy relative to the other. When small amounts of segregation are being measured, such shifts in energy calibration renders the acquired data meaningless: the resulting edge shift in the spectra produces spurious contributions near the elemental leading edges that may greatly exceed the amount of segregation being measured. Because small shifts in energy calibration commonly occur, due to changes in detector, electronics or beam energy, a method to remove error is needed. A method will be proposed for correcting errors in measuring solute segregation in a binary alloy.

2. RBS Technique

2.1 Description of Spectra

In the RBS technique, a collimated beam of monoenergetic ions impinges on a specimen. Some incident ions scatter at large angles from specimen atoms and are backscattered out of the specimen where they may be detected by an energy-resolving detector. Because ions lose energy in a continuously along the inward and outward paths, an ion that backscatters from deep in the specimen has less kinetic energy than one that backscatters from an atom near the surface. An RBS spectrum is obtained by plotting the particle backscattering yield as a function of the kinetic energy of recoil particles, allowing information about composition as a function of specimen depth to be determined. For a single-element target, the backscattered particles have a continuous range

of kinetic energies from zero energy, corresponding to a particle just able to escape from the specimen, to a characteristic maximal energy, corresponding to elastic scattering from atoms at the specimen surface. The channel numbers are proportional to the energy of the backscattered particles and are related to the depth in the specimen. From published stopping cross sections [7], determination of the relation between channel number and specimen depth can be straightforward.

An ion loses a certain fraction of its kinetic energy during the backscattering collision, depending on the masses of the colliding atoms. This loss permits identification of the elements in the specimen. The RBS spectrum of a binary alloy consists of two superimposed spectra of the individual constituents; the spectrum that is relatively higher in energy corresponds to ions backscattered from the heavier element. A detailed review of the analysis of RBS spectra can be found in ref. 8.

Figure 1 schematically depicts an RBS spectrum as might be acquired from a homogeneous A-B alloy. The slope of the spectrum (shown exaggerated in the figure) is due to changes in scattering cross section as a function of ion energy. The backscattering yield below the A-atom leading edge is proportional to the A-atom concentration in the near-surface region. At the B-atom leading edge and below, the B- and A-atom backscattering yields overlap; therefore compositional information cannot be uniquely determined in this representation. The leading edges are not vertical; this is due to the finite energy resolution of charged-particle detection systems.

Figure 2 is a schematic representation of an RBS spectrum of an A-B alloy enriched in A-atoms at the external surface. For consistency, the text and figures will depict A-atom enrichment in the near-surface region, and corresponding depletion in bulk. Figure 3, a superposition of the two spectra from Figs. 1 and 2, makes the differences more obvious. A-atom enrichment can be identified at and beneath the A-atom leading edge, and A-atom depletion can be identified in the subsurface region (lower in energy or channel number). The corresponding B-atom depletion at and just beneath the B-atom leading edge can also be identified, as can B-atom enrichment in the subsurface region. A more extensive description of the difference-spectra method of calculating segregation can be found in ref. 9.

2.2 Integral Amount of Segregation

To quantitatively measure RIS, Sethi and Okamoto defined the amount of segregation as the amount of solute transported to or away from the surface; they determined it by integrating the excess (or deficit) of the solute concentration in the near-surface region [10]. The amount of A-atom enrichment (or depletion) is expressed as

$$M = \int_0^d [C_A(x) - C'_A(x)] dx,$$

where $C'_A(x)$ is the initial A-atom concentration as a function of specimen depth x , and $C_A(x)$ is the final concentration. The value of d is the depth of the A-atom-enriched region, i.e., d is the crossover between the enriched and deficient regions. This is shown schematically in Fig. 3. The amount of segregation is thus proportional to integral changes in backscattering yield near the A-atom leading edge. If the high-energy ions are used to produce radiation damage and also serve as the RBS profile ions, the amount of segregation is calculated in an identical fashion, but M becomes functionally dependent on ion dose. The case of nonlinear dependence of segregation on ion dose is treated in detail by Averback et al. [11].

The energy calibration of the Si solid-state detectors commonly used for RBS measurements strongly depends on temperature [12]. Temperature variations affect the width of the band gap in Si and therefore change the number of electron-hole pairs produced for an ion of given energy. Thus, the problem of energy shifts may be difficult to avoid in high-temperature work, such as in-situ studies of segregation in refractory metals and ceramics, where radiant heat from the specimen impinges directly on the solid-state detector.

When a change in energy calibration occurs, one spectrum is shifted in energy relative to the other. When the differences between the two spectra are integrated, the shifted leading edge contributes an incorrect measurement of the amount of segregation. Figure 4 is a representation of two identical spectra; one displays an energy shift. No segregation has occurred, but the extra

counts near the A-atom leading edge make a spurious addition to the measurement of the amount of segregation.

In segregation experiments where no loss of solute occurs (such as by preferential sputtering from the external surface), solute must be conserved, and any excess solute near the surface must be accompanied by a corresponding decrease in bulk. If a net excess (or deficiency) of atoms is measured, an energy shift has occurred, and it will be shown that it is possible to extract the correct value of M and the relative energy shift. The proposed error-correction method is based on conservation of solute; thus it cannot be used if significant removal of material from the specimen surface by sputtering has occurred.

2.3 Integral Backscattering Yield

To calculate the integral amount of segregation, the integrated backscattering yields from regions of interest in each spectrum are selected, normalized, and compared (see Fig. 3). The three regions are (a) a normalization region, (b) the B-atom near-surface region, and (c) the A-atom near-surface region. The following paragraphs show the principles for measuring the amount of segregation, and how the effects arising from a shift in energy calibration can be corrected.

Let $Y(E) dE$ denote the number of particles backscattered from a specimen (backscattering yield) between energy E and $E + dE$. The integral yield, Y_{ab} , between energies E_a and E_b is

$$Y_{ab} = \int_{E_a}^{E_b} Y(E) dE.$$

For a linear change in energy calibration

$E'_a = E_a(1+\Delta)$ and $E'_b = E_b(1+\Delta)$, thus

$$\begin{aligned} Y'_{ab} &= \int_{E'_a}^{E'_b} Y(E) dE \\ &= \int_{E'_a}^{E_a} Y(E) dE + \int_{E_a}^{E_b} Y(E) dE + \int_{E_b}^{E'_b} Y(E) dE \end{aligned}$$

$$= \int_{E'_a}^{E_a} Y(E) dE + Y_{ab} + \int_{E_b}^{E'_b} Y(E) dE.$$

If the regions of interest are chosen so that the slope of $Y(E)$ is small at the region boundaries (as is the case for Channels b, a1, and a2 in Fig. 3), or if Δ is small, then $Y(E'_a) \approx Y(E_a)$.

$$\begin{aligned} \int_{E'_a}^{E_a} Y(E) dE &\approx Y(E'_a)(E_a - E'_a) \\ &= Y(E'_a) [E_a - E_a(1 + \Delta)] \\ &= -Y(E_a) E_a \Delta, \end{aligned}$$

and

$$\int_{E_b}^{E'_b} Y(E) dE \approx Y(E_b) E_b \Delta.$$

Thus,

$$Y_{ab} = Y'_{ab} + \Delta[Y(E_a)E_a - Y(E_b)E_b]. \quad (1)$$

The corrected backscattering yield from a region between E_a and E_b will be the measured yield, Y'_{ab} , plus a correction term.

2.4 Measured Integral Backscattering Yield

The integral backscattering yield in the previous section has been expressed in terms of the continuous backscattering yield. During acquisition, the particle energies are digitized and recorded by a multichannel analyzer (MCA). Because the analog-to-digital converter has finite resolution, the digitized spectrum is a discrete approximation of $Y(E)$. We denote the number of counts in channel number n as x_n , and the relation between backscattering energy and channel number is $E = kn$, where k is a constant. We will adopt a convention for indexing MCA data such that

$$\int_0^k Y(E) dE = x_1.$$

That is, Channel 1 contains counts from particles with energy equal to or below $E = k$, and so on.

The measured integral backscattering yield of a region of the spectrum is denoted as N_{ab} , and

$$N_{ab} = \sum_{n=n_a+1}^{n_b} x_n = \int_{E_a}^{E_b} Y(E) dE = Y_{ab}.$$

For an energy shift Δ , $E = kn(1 + \Delta)$, and one obtains, from Eq. (1),

$$Y_{ab} = N'_{ab} + \Delta(x_a n_a - x_b n_b). \quad (2)$$

For purposes of measuring near-surface segregation, three regions of the spectrum are defined (see Fig. 3). The first region, N, bounded by Channels n_1 and n_2 , is a normalization region used to correct for differences in acquisition time. Region N (not shown) should be chosen far from where segregation is observed. Region B is bounded by Channels b and a_1 and should be chosen to contain B-atom enrichment and depletion and A-atom depletion. Because solute is conserved, the B-atom-enriched and -depleted regions effectively cancel. Region A is bounded by channels a_1 and a_2 and should be chosen to contain the A-atom-enriched region only, i.e., Channel a_1 is the crossover point between the enriched and depleted regions. Thus,

$$N = \sum_{n=n_1+1}^{n_2} x_n, B = \sum_{n=b+1}^{a_1} x_n, \text{ and } A = \sum_{n=a_1+1}^{a_2} x_n.$$

The amount of segregation is proportional to the difference in the normalized backscattering yields in Regions A and A', where A is the integral backscattering yield in Region A of the unprimed spectrum and A' is the integral backscattering yield in Region A in the primed spectrum. If N_0 is the normalization constant, the amount of segregation, M, is

$$M = \frac{A' N_0}{N'} - \frac{A N_0}{N}. \quad (3)$$

Conservation of solute requires that

$$-M = \frac{B' N_0}{N'} - \frac{B N_0}{N}$$

because Region B contains the A-atom-depleted region. If the unprimed spectrum experiences an energy shift Δ , the corrected expressions for A, B and N from Eq. (2) must be substituted, giving

$$M = \frac{A'N_0}{N'} - \frac{[A + \Delta(x_{a1}a_1 - x_{a2}a_2)]N_0}{N + \Delta(x_{n1}n_1 - x_{n2}n_2)} \quad (4)$$

and

$$-M = \frac{B'N_0}{N'} - \frac{[B + \Delta(x_{b1}b_1 - x_{b2}b_2)]N_0}{N + \Delta(x_{n1}n_1 - x_{n2}n_2)} \quad (5)$$

Equations (4) and (5) can be solved to obtain

$$\Delta = \frac{N'(A+B) - N(A'+B')}{(A'+B')(x_{n1}n_1 - x_{n2}n_2) + N'(x_{a2}a_2 - x_{b2}b_2)} \quad (6)$$

and

$$M = \frac{N_0[(B'N - N'B)(x_{a1}a_1 - x_{a2}a_2) + (A'B - B'A)(x_{n1}n_1 - x_{n2}n_2) + (N'A - A'N)(x_{b1}b_1 - x_{b2}b_2)]}{N'[N(x_{a2}a_2 - x_{b2}b_2) + (A+B)(x_{n1}n_1 - x_{n2}n_2)]} \quad (7)$$

M is the amount of segregation and is positive for enrichment of A atoms at the external surface in the primed spectrum relative to the unprimed spectrum.

This method was used to analyze the data in a study of the kinetics of solute segregation in irradiated Mo-Re alloys. Examples of error reduction in sample and actual data will be reported in a subsequent paper.

4. Summary

A simple method to correct errors arising from RBS spectrum edge-shifts that introduce errors into measurements of near-surface solute segregation has been presented. The method is based on the principle that any net increase or decrease in the total amount of solute must be an artifact arising from an edge shift. Although developed here for a binary alloy, the method could be extended to measurement of segregation in other alloy systems or to other analysis techniques.

Acknowledgments

This work was supported by the Tribology Program, Office of Advanced Transportation Materials, U.S. Department of Energy. The study began under the sponsorship of the Materials Science Division, Argonne National Laboratory, with the support of the Materials Sciences Program, Office of Basic Energy Sciences, U.S. Department of Energy. The author thanks Drs. P. R. Okamoto and H. Wiedersich for helpful discussions, and Dr. M. K. Kwong for assistance with the mathematics.

Figure Captions

- Fig 1. RBS spectrum from a homogeneous A-B alloy.
- Fig 2. RBS spectrum from an A-B alloy with A-atom segregation to the external surface.
- Fig 3. Superposed RBS spectra from Figs. 1 and 2, showing regions of enrichment and depletion, regions A and B, and amount of enrichment.
- Fig 4. Two superposed identical RBS spectra, one displaying an energy shift.

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Fig 1.

Fig 2.

Fig 3.

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