J. Synchrotron Rad. (1999). **6**, 497–499

Extraction of phase fractions and compositions for bcc/fcc two-phase binary alloys from XANES data

Paul J. Schilling* and Roland C. Tittsworth

Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, Baton Rouge, LA 70803, USA. E-mail: pschill@lsu.edu

For two-phase binary alloys, pertinent information includes the fractions and compositions of each phase. We propose a method to obtain this information from X-ray absorption near edge structure (XANES) data. Tests of the procedure using Fe-Ni fcc and bcc standards indicate the method is accurate to within 5%. The method should be applicable to other two-phase binary systems, e.g. ball-milled Fe/Cu.

Keywords: XANES; iron; nickel; alloy; two-phase region

1. Introduction

A critical factor in the characterization of two-phase binary alloy systems is the determination of the phase fractions and compositions of each phase. In non-equilibrium systems, e.g. ball-milled Fe-Cu, these are sometimes difficult to attain (Hong & Fultz, 1998). A method is presented here to obtain these quantities indirectly from XANES data collected at the two relevant absorption edges, and tested using standards in the Fe-Ni system. Linear combination (LC) fitting of the XANES spectra can give, for example, the fraction of the total iron atoms which are in the bcc (or fcc) phase. From the LC-fits at both edges, along with the overall composition, the phase fractions and compositions can be extracted.

2. Definitions of parameters and relevant relationships

We will define a two-phase binary system consisting elements *A* and *B*, forming phases, α and β. We assume the overall composition is known:

X_A , X_B - the mole fractions of *A* and *B* atoms

From least squares fitting of XANES spectra as linear combinations of standard spectra for phases α and β at the absorption edge of element *A*, we obtain:

f_α^{A} - the fraction of *A* atoms which are in the α phase

f_β^{A} - the fraction of *A* atoms which are in the β phase

From similar fitting at the absorption edge of element *B*, we obtain values for f_α^{B}, f_β^{B}.

The quantities we wish to determine are:

f_α , f_β - the phase fractions for the system

X_{A}^α, X_{B}^α - the composition of the α phase

X_{A}^β, X_{B}^β - the composition of the β phase

Based on conservation of matter, the following relations were

$$f_\alpha = f_\alpha^{\mathrm{A}} X_{\mathrm{A}} + f_\alpha^{\mathrm{B}} X_{\mathrm{B}} \qquad (1)$$

$$X_{\mathrm{A}}^\alpha = \frac{f_\alpha^{\mathrm{A}} X_{\mathrm{A}}}{f_\alpha^{\mathrm{A}} X_{\mathrm{A}} + f_\alpha^{\mathrm{B}} X_{\mathrm{B}}} \qquad (2)$$

derived to express the desired quantities in terms of the known parameters and those obtained from the XANES fitting:

Similar equations can be written for the other four quantities of interest.

3. Experimental

As a test of the applicability of this method, we have measured combinations of bcc and fcc Fe-Ni alloys. This system was studied because the target system motivating this study is a bcc/fcc system (Fe-Cu) and suitable standards could be obtained. These included $Fe_{80}Ni_{20}$ (bcc, 10.2 μm) and $Fe_{20}Ni_{80}$ (fcc, 10.2 μm) transmission EXAFS foils (graciously loaned by Dr. Joe Wong) and $Fe_{64}Ni_{36}$ (fcc, 8.0 μm), Fe (bcc, 1.0 μm and 3.0 μm), and Ni (fcc, 3.0 μm) foils (from Goodfellow Corporation, Berwyn, PA). Pseudo-two-phase Fe-Ni alloys were made by combining one fcc and one bcc foil. Transmission XANES measurements were then performed through the pair of foils. The overall composition (X_{Fe}) and phase fraction (f_{bcc}) for each pair of foils were calculated based on the thickness and density of each foil. The composition of each phase in a particular pseudo-two-phase Fe-Ni alloy is simply the composition of the constituent foil. The samples and relevant parameters are summarized in Table 1.

Transmission XANES spectra were recorded at the K edges of Fe and Ni using Si(400) crystals at the DCM1 beamline at the CAMD synchrotron light source at Louisiana State University. Ionization chambers filled with air were used for all measurements. Each scan covered a large pre-edge region (200 eV) and extended 800 eV past the edge to provide a good basis for background removal. The first inflection point in each spectrum was chosen as E_0. Data analysis, including least squares fitting of the XANES spectra as a linear combination of standard bcc and fcc spectra, was performed using the WinXAS software package (Ressler, 1997).

Background removal was done using a two polynomial fit with a linear pre-edge (from -180 eV to -40 eV) and a cubic post-edge (from 45 to 790 eV) in the WinXAS package. This method proved successful in removing the strong Fe background

Table 1
Pseudo-two-phase Fe-Ni alloy standards.

Sample bcc + fcc	X_{Fe}	f_{bcc}	$X_{\mathrm{Fe}}^{\mathrm{bcc}}$	$X_{\mathrm{Fe}}^{\mathrm{fcc}}$
$Fe_{80}Ni_{20}$ + $Fe_{20}Ni_{80}$	0.49	0.48	0.8	.20
$Fe_{80}Ni_{20}$ + $Fe_{64}Ni_{36}$	0.73	0.55	0.8	.64
$Fe_{80}Ni_{20}$ + 3 μ Ni	0.61	0.76	0.8	0
3 μ Fe + $Fe_{20}Ni_{80}$	0.37	0.22	1	.20
3 μ Fe + $Fe_{64}Ni_{36}$	0.74	0.26	1	.64
1 μ Fe + $Fe_{20}Ni_{80}$	0.27	0.08	1	.20
1 μ Fe + $Fe_{64}Ni_{36}$	0.68	0.11	1	.64

contribution from the Ni XAFS spectra (as will be necessary for the binary alloy systems). This is demonstrated in Figure 1, which presents the superposition of several pure Ni spectra after the removal of backgrounds including various amounts of Fe.

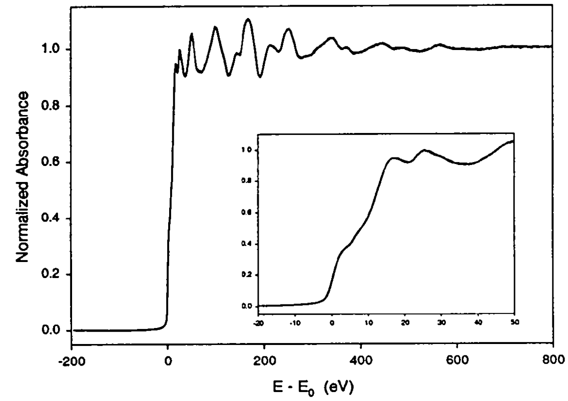

Figure 1
Spectra for (a) Ni XAFS of standard foil, (b) Ni XAFS of standard foil + 3 • m Fe, and (c) Ni XAFS of standard foil + 7.5 • m Fe, after background removal and normalization. The spectra overlap well.

4. Standards for XANES fitting

The procedure to be followed here involves fitting each Fe K-edge XANES spectrum as a linear combination of a standard Fe bcc spectrum and a standard Fe fcc spectrum; and fitting each Ni K-edge XANES spectrum as a linear combination of a standard Ni bcc spectrum and a standard Ni fcc spectrum. This assumes, for example, a standard fcc Ni XANES spectrum which is valid across the compositional range of the Fe-Ni fcc phase. The error introduced by this assumption can be assessed by comparing the Ni K-edge spectra (after background removal and normalization) of pure Ni and $Fe_{64}Ni_{36}$, shown in Figure 2. The $Fe_{64}Ni_{36}$ XAFS spectrum exhibits a higher frequency, which was determined to be mainly due to an increased lattice parameter (in accordance with Vegard's law) through both EXAFS fitting and XANES simulations using FEFF7 (Rehr et al., 1991). To reduce the effect of this difference on the XANES fitting, fits were limited to the region from -10 to 30 eV (shown as an inset in Figure 2.) Over this XANES region, the $Fe_{64}Ni_{36}$ spectrum shows reduced amplitude. It is not clear whether this is due to a real effect of Fe substitution or is associated with the background removal. XANES simulations were performed (with FEFF7) for pure fcc Ni and for $Fe_{64}Ni_{36}$ (see Figure 3). For the $Fe_{64}Ni_{36}$ simulations a lattice parameter of 3.56 Å was used, which is consistent with both Vegard's law and results of fitting of the first coordination shell in the EXAFS spectrum from the $Fe_{64}Ni_{36}$ foil. These simulations clearly show the change in XAFS frequency associated with the increased lattice parameter. The two main features in the XANES region are reproduced, with the second showing a reduced intensity for the $Fe_{64}Ni_{36}$. This hints that the reduction in intensity of the XANES features in the experimental spectrum for $Fe_{64}Ni_{36}$ (see inset of Figure 2) may be due to the substitution of Fe atoms into the lattice, but this is not conclusive. Regardless, the difference in maximum intensity in this region is about 3 % and the shapes for the two spectra are basically the same. In particular these differences are slight when compared to the dramatic difference between the fcc and bcc XANES structures (see Figure 4) on which the fitting is based. It was therefore judged that, while the alloy composition does influence the XANES spectrum, a single fcc reference spectrum (and similarly a single bcc spectrum) can be used for the Ni K-edge (or Fe K-edge) XANES fitting. The Fe K-edge XANES data were fit using the spectra of Fe (bcc) and $Fe_{20}Ni_{80}$ (fcc) as standards (shown in Figure 4). The Ni K-edge XANES data were fit using the spectra of $Fe_{80}Ni_{20}$ (bcc) and Ni (fcc) as standards. Using these Ni standards, fitting of the $Fe_{64}Ni_{36}$ Ni K-edge XANES spectrum resulted in a best fit consisting of 98 % fcc and 2 % bcc. This further demonstrates that only a minor error is introduced by using a single fcc standard spectrum and ignoring the effect of composition (in the Fe-Ni system).

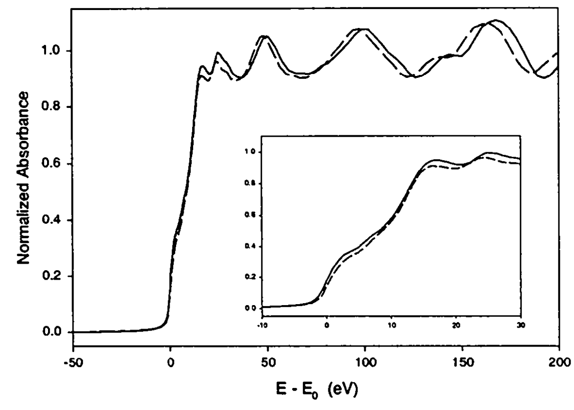

Figure 2
Comparison of Ni K-edge spectra of fcc Ni (solid line) and fcc $Fe_{64}Ni_{36}$ (dashed line).

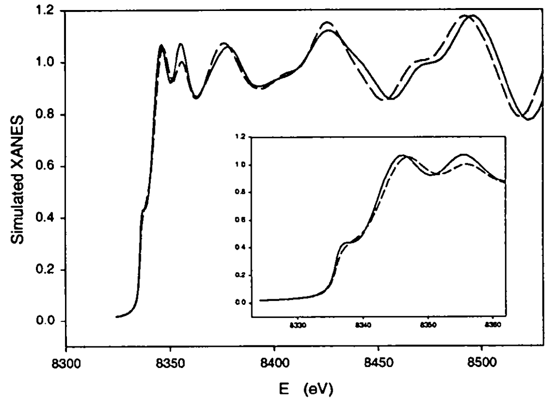

Figure 3
Comparison of FEFF7 simulations of Ni K-edge spectra of fcc Ni (solid line) and fcc $Fe_{64}Ni_{36}$ (dashed line).

5. Results of XANES fitting

The Fe K-edge XANES spectra of the pseudo-two-phase Fe-Ni

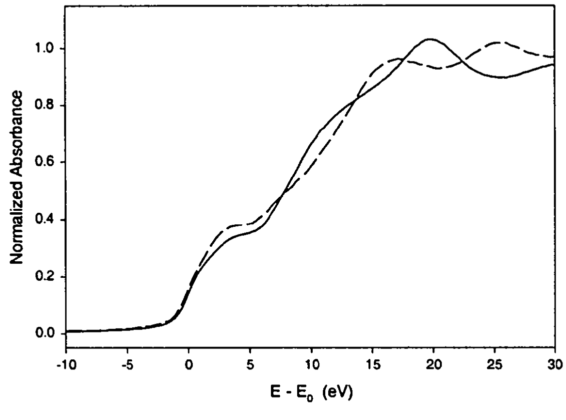

Figure 4
Fe K-edge standard spectra for Fe in bcc phase (solid line) and fcc phase (dashed line) taken from Fe and $Fe_{20}Ni_{80}$, respectively.

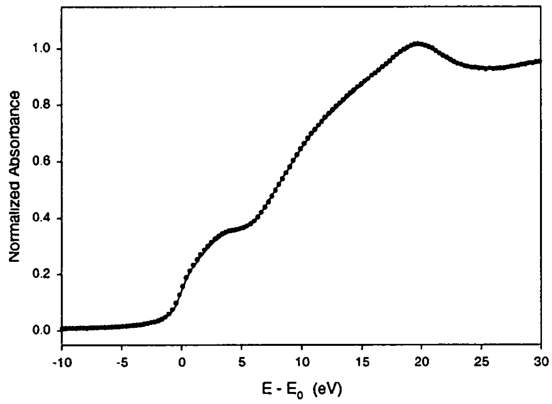

Figure 5
Result of XANES fitting at the Fe K-edge for the $Fe_{80}Ni_{20}$ + $Fe_{20}Ni_{80}$ sample. The sample spectrum (line) is compared to the fit result (dotted).

alloys were fit as linear combinations of the Fe K-edge bcc and fcc standards (an example is shown in Figure 5) to obtain the fraction of Fe atoms in each phase, e.g. f_{bcc}^{Fe}, and similarly for the Ni K-edge, f_{bcc}^{Ni}. Substituting these values, along with the overall composition, X_{Fe} (from Table 1), into equations (1) and (2), we obtain the desired parameters: the phase fraction f_{bcc} and the compositions of each phase X_{Fe}^{bcc} and X_{Fe}^{fcc}. These results are shown in Table 2. The values for phase fraction and composition of each phase obtained from XANES fitting can be compared to the expected values shown in Table 1. A comparison of the phase fractions obtained from the XANES data (f_{bcc} in Table 2) to the correct values (f_{bcc} in Table 1) shows excellent agreement. The largest error was 0.05, with an average difference (between measured and expected values) of 0.03. Similar comparison of the phase compositions obtained from the XANES data (X_{Fe}^{bcc} and X_{Fe}^{fcc}) also showed excellent agreement. For these values, the maximum error observed was also 0.05, with an average difference of 0.02. The results demonstrate that the phase fractions and phase compositions can be determined to within about 5 % over the ranges covered by these standards.

Table 2
Results of XANES fitting.

Sample bcc + fcc	f_{bcc}^{Fe}	f_{bcc}^{Ni}	f_{bcc}	X_{Fe}^{bcc}	X_{Fe}^{fcc}
$Fe_{80}Ni_{20}$ + $Fe_{20}Ni_{80}$	.78	.20	0.49	0.79	0.21
$Fe_{80}Ni_{20}$ + $Fe_{64}Ni_{36}$	.64	.48	0.60	0.78	0.65
$Fe_{80}Ni_{20}$ + 3 μ Ni	1.00	.36	0.75	0.81	0.00
3 μ Fe + $Fe_{20}Ni_{80}$	.62	.02	0.24	0.95	0.19
3 μ Fe + $Fe_{64}Ni_{36}$	.40	.03	0.30	0.97	0.63
1 μ Fe + $Fe_{20}Ni_{80}$	.35	.00	0.10	1.0	0.18
1 μ Fe + $Fe_{64}Ni_{36}$	.22	.02	0.16	0.96	0.62

6. Conclusions

XANES analysis can be used to obtain phase fractions and compositions in some two-phase binary systems. The results obtained from standards in the bcc/fcc Fe-Ni system indicate the accuracy of the technique to be approximately 5 %.

References

Hong, L.B., & Fultz, B., (1998). *Acta mater.* **46**, 2937-2946.

J. J. Rehr, J.J., J. Mustre de Leon, J., S.I. Zabinsky, S.I., and R.C. Albers, R.C. (1991). *J. Am. Chem. Soc.* **113**, 5135.

T. Ressler, T., *J. Physique IV* (1997). **7**, C2-269.

(Received 10 August 1998; accepted 26 January 1999)