Applications of Phase Diagrams in Metallurgy and Ceramics

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G.C. Carter

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Experimental Determination of Phase Diagrams with the Electron Microprobe and Scanning Transmission Electron Microscope

A. D. Romig, Jr. and J. I. Goldstein
Department of Metallurgy and Materials Science
Lehigh University, Bethlehem, PA 18015

ABSTRACT

Within the past dozen years the electron microprobe (EMP) has proven itself a valuable tool in the determination of phase diagrams (solid phase regions). A literature survey indicates that over thirty (30) metallic systems have been determined with this instrument.

An important advantage of this technique is that one can determine equilibrium tie lines even when the bulk phases themselves are not in equilibrium. This advantage is best realized when one is considering a system where diffusion rates are so slow that the bulk equilibrium condition cannot be reached in a reasonable time period, or where the phase diagram contains a metastable phase that will decompose if heat treatments long enough to produce homogeneous phases are used.

Several factors affect the accuracy of the EMP measurements: (1) spatial resolution; (2) X-ray absorption; and (3) X-ray fluorescence. Even under optimum conditions it is not possible to generate X-rays from a volume with a diameter less than 1 μm and interface compositions must be determined by extrapolation to the interface position. This is a reasonable procedure, unless the concentration gradient is too steep. The use of the EMP technique is illustrated by its application to the Fe-Ni-Co and Fe-Ni-C systems.

The newly developed scanning transmission electron microscope (STEM) will allow X-ray excitation from regions less than 0.10 μm in diameter. The technique requires thin foils which are transparent to the incident electron beam (typically 80/100 kV). The use of thin foils and high excitation voltages usually eliminates the fluorescence and absorption problems present in microprobe analysis, thus permitting the application of a relatively simple matrix correction technique. The STEM methods have now been developed to the point where phase diagram determination is possible. Measurements of the Fe-Ni-Co system using this technique are presented and agreement with the accepted diagram is demonstrated.
Introduction

The experimental determination of solubility limits and tie lines in the solid regions of multicomponent phase diagrams is difficult. The phases which are present are often small, and sometimes the bulk specimen is not even equilibrated. In addition the necessary heat treatment cycles are usually lengthy and a large number of specimens are usually required. Many experimental techniques have been employed including X-ray diffraction, metallography and differential thermal analysis. All of these techniques require well equilibrated samples for analysis. The electron microprobe (EMP) has been used since the mid-1960's to determine the composition of the equilibrated phases directly. One specific advantage of the EMP technique is the spatial resolution which approaches 1 µm. This technique enables one to obtain tie line compositions directly, even in alloys with three or more components. Composition-distance profiles can be used in special cases even when bulk equilibration has not been attained.

The purpose of this paper is to describe the use of the EMP in the determination of multicomponent phase diagrams. Heat treatment cycles, EMP spatial resolution, and the accuracy of tie line measurements will be discussed. Examples of the use of the EMP in determining isothermal sections of ternary phase diagrams will also be discussed. In addition a description of the newly developed scanning transmission electron microscopy (STEM) technique for phase diagram analysis will be given.

Sample Analysis Techniques

Two techniques have been developed to obtain suitable samples for EMP analysis: 1) diffusion couple and 2) heat treatment. The diffusion
couple technique requires the bonding of two pieces of single phase material (a pure metal or alloy) and the subsequent annealing at a desired temperature.\textsuperscript{2} The resulting concentration gradient is then measured. The composition gradient will vary continuously through solid solutions and exhibit a sharp discontinuity at the boundary of a two phase region. As long as the two phases at the interface are in local equilibrium,\textsuperscript{2} the compositions at the interface correspond to an equilibrium tie line. The diffusion couple technique is applicable to binary, ternary, and higher order systems. The basic requirement is that the interface compositions be resolved with the EMP. The concentration gradients which result must not be too steep or accurate extrapolation to the two phase interface cannot be accomplished.

The second technique involves the heat treatment of an alloy within a 2 or 3 phase field at a desired temperature. The sample is usually one phase and compositionally homogeneous before heat treatment. A second or third phase is obtained by a specified heat treatment cycle.

After heat treatment, the composition of the resulting phases is measured with the EMP. In some cases the bulk alloy may not be equilibrated. Even so appropriate tie line measurements can be obtained if local equilibrium is maintained at phase interfaces\textsuperscript{2} and if composition gradients in the various phases measured with the EMP are small. The heat treatment technique has been applied to a large number of alloy systems and is used more often than the diffusion couple technique.

For ternary two phase alloys the measured tie line need not go through the bulk alloy composition unless the sample is completely equilibrated after heat treatment. This effect is illustrated in Figure 1 where the 650°C isothermal section of the iron rich portion of the FeNiCo phase diagram\textsuperscript{3} is given. The measured $\alpha + \gamma$ tie lines do
not pass through the bulk composition of the alloys but are displaced to higher Co contents. The requirements of interface mass conservation and local equilibrium in ternary systems permit phase growth to occur by continuous adjustment in the tie line selected and in the rate of growth of the precipitate. Note that in the low Co alloy #9, equilibrium has been achieved in the heat treatment time allotted.

**Specimen Preparation**

Usually sample preparation involves melting an alloy of appropriate composition from either pure elements or master alloys of known composition. Induction melting, arc melting, resistance furnace melting, and other methods may be used depending on the specific alloy or oxide system. After melting, the sample should be homogenized to insure uniform composition throughout the sample. The time and temperature required for homogenization will again depend on the alloy or oxide system. Homogenization can be established by mounting-polishing selected samples and by using standard EMP analysis techniques. In some cases the as-cast alloy is used directly for the heat treatment cycle without prior homogenization. This procedure is not recommended in that the EMP data obtained from the sample will vary from place to place across the alloy.

Diffusion couples can be produced by standard techniques. Usually the interfaces between the two single phase samples are polished and are clamped together by an appropriate device until bonding is achieved. The clamp is often removed before the final diffusion treatment.

The number of heat treatment samples necessary for a phase diagram study can be minimized by use of the EMP technique. The same samples may be used to determine several isotherms. In addition for ternary systems
only one sample is necessary to determine the outline of an entire 3 phase field. A few strategically located alloys may in fact serve to determine an entire isothermal section.

Several heat treatment cycles are available for a given sample. These heat treatment cycles are:

(A) Annealing cycle. The sample (usually one phase) is rapidly cooled from a high temperature directly to the temperature of interest (usually in a two or three phase field) and held at that temperature until sufficient phase growth occurs. This type of cycle is used to avoid unwanted phases from forming during heat treatment and to promote nucleation.

(B) Quench and anneal cycle. The sample (usually one phase) is quenched from a high temperature to a low temperature and is reheated to the temperature of interest (usually in a two or three phase field). The sample is held at that temperature until sufficient phase growth occurs. This type of cycle is often used to promote nucleation of the phases of interest. In some alloy systems a martensitic structure is formed during the quench.

(C) Controlled cooling cycle. In this scheme the sample (usually one phase) is cooled from a high temperature to the temperature of interest (usually in a two or three phase field) by some continuous and/or step cooling sequence. The sample is maintained at this temperature for a specified time period. This type of cycle controls the amount of nucleation of a second phase during cooling and increases the amount of growth of the phases which form.
In all of these heat treatment cycles the sample is quenched immediately after removal from the final isothermal treatment.

Cycles (B) and (C) were used in the determination of the $\alpha + \gamma$ tie lines of the FeNiCo system. The quench and anneal technique (B) (heated up cycle--Fig. 1) yields fine platelets of $\gamma$ which have precipitated from a martensitic $\alpha_2$ structure and whose compositions can be measured directly with the EMP. The controlled cooling cycle (C) (cooled down cycle--Fig. 1) yields $\alpha$ grain boundary allotriomorphs in a $\gamma$ matrix. The $\alpha$ phase composition can be measured directly. However a steep Ni concentration spike was measured in $\gamma$ making a measurement of the $\gamma$ tie line composition impossible using cycle C.

The controlled cooling cycle (C) may be required when one is attempting to determine phase equilibria with a metastable phase. For example, when attempting to determine the composition and temperature range over which (Fe$_3$Ni)$_3$C, cohenite, can exist in the Fe-Ni-C system it was discovered that the carbide cannot be grown by either cycles (A) or (B). The cohenite is metastable with respect to metal plus graphite and the conventional heat treatment cycles, (A) and (B), produced the stable assemblage. However, cohenite precipitates, up to 5 microns in size, which are sufficiently large for EMP analysis, have been grown with the controlled cooling cycle technique.

**Electron Microprobe Analysis**

After the heat treatment cycle the sample is mounted and polished with standard metallographic techniques. Etching, surface marking, and repolishing may be necessary if the microstructure cannot be seen in the as-polished condition. The sample is then coated with a thin conducting layer to prevent charging during EMP analysis.
To obtain the most meaningful results from the probe analysis the operating conditions must be optimized. Operating potential, sample current, and counting time are perhaps the most critical parameters. The optimization of these parameters have been discussed in detail\textsuperscript{5} and will only be described briefly in this paper.

A ratio of operating voltage to excitation potential for the measured characteristic X-ray lines of approximately 2 to 3 is desirable in order to maximize peak to background ratios and minimize the X-ray source size-resolution. Hence, if the characteristic X-rays being detected vary greatly in excitation potential, a multiple analysis at more than one operating potential may be necessary. The sample current is chosen so that X-ray counts are maximized for a statistically meaningful analysis without greatly increasing the electron beam size. Count times must be sufficiently long to allow the collection of enough X-ray counts for statistically meaningful results. The total number of counts accumulated is the critical variable in determining the detectability limit and sensitivity for each element in the analysis. The X-rays generated may be detected by either wavelength dispersive or energy dispersive spectrometers. Both systems have specific advantages and the choice will depend on the alloy system. For example, in systems containing light elements and/or overlapping spectra the wavelength dispersive spectrometer would most likely be selected. In many modern EMP systems both types of spectrometers can be used simultaneously.

Accuracy of Phase Diagram Determination

The accuracy of phase boundary measurement with the EMP is limited by three main factors: X-ray spatial resolution, X-ray absorption and
X-ray fluorescence. These factors are discussed in turn in the following paragraphs.

The X-ray source size or X-ray spatial resolution in which primary X-rays are produced is much larger than the size of the electron beam. The X-ray source size is defined by the amount of elastic scattering which occurs in a solid sample and is almost always 1 μm or larger in diameter even under optimum conditions. Therefore the direct measurement of the phase boundary composition is impossible within a distance equivalent to the X-ray source size of the analyzed phase. Typically then, the interface composition is determined by extrapolation to the interface position. The extrapolation procedure can only be used if the concentration gradient is small. Deconvolution techniques have been developed to account for "smeared" interface gradients. These techniques are not very useful when compositional accuracy of the type necessary for phase diagram measurements is desired. In most cases, the necessity for extrapolation is the most serious limitation of the EMP technique.

The X-ray absorption effect occurs when X-rays produced at one point within the specimen travel through material of different composition, and perhaps different mass absorption coefficients on their way to the spectrometer. To avoid such an absorption effect, it is necessary to orient the interface perpendicular to the surface of the specimen and the interface parallel to the X-ray path to the spectrometers.

The X-ray fluorescence effect occurs when characteristic lines of a given element are excited by the continuum and the characteristic spectrum of other lines at a distance away from the electron beam (> 5 μm). In this case additional X-ray excitation may occur on one side of the two phase interface even though the electron beam and the analysis point is on the
other side of the interface. In such a situation, it is best to determine how large the effect is by using undiffused couples and to correct the data accordingly.

In addition the measured X-ray counts from the EMP must be converted to composition (weight percent). The most common method used in solid materials applications is the (ZAF) matrix correction technique. The X-ray counts from the point of beam impingement are ratioed against the counts obtained from a homogeneous standard of known composition. Weight percent are obtained from these ratios after correcting for effects of atomic number, absorption, and fluorescence.

**Application of the EMP to the Determination of the Fe-Ni-C Phase Diagram**

In the Fe-Ni-C system equilibrium occurs between the f.c.c. (γ) phase, b.c.c. (α) phase, and the metastable line compound (Fe,Ni)\textsubscript{3}C. Figure 2 shows the metallography of an Fe-3.75 wt% Ni-1.0 wt% C alloy obtained by continuous cooling from 1000°C at 25°C/hour to 730°C with an isothermal 24 hour hold at that temperature. The matrix of the alloy is now martensite, produced at the end of the heat treatment when γ was quenched from 730°C to room temperature. The grain boundary precipitate is (Fe,Ni)\textsubscript{3}C. Microprobe traverses were made across the carbidos. One such traverse is shown in Figure 3. The interface compositions are indicated on the figure and the corresponding tie line is plotted on the 730°C isotherm, Figure 4. Several other measured tie lines are shown in this Figure. It should be noted that the tie lines in the γ + Fe\textsubscript{3}C phase field do not go through the bulk alloy compositions.
Summary - EMP Technique

The method of phase diagram determination with the EMP is well developed and has been used to determine phase diagrams in over 30 systems. Table 1 lists several systems where the EMP has been used to determine at least part of the phase diagram.

The utility of the technique has been fully described in this work, yet it is not without its shortcomings. One area where improvement is possible is in spatial resolution. Errors attributable to extrapolated interface compositions could be minimized and steeper gradients could be measured if a small excitation volume could be obtained.

Application of STEM Techniques to Phase Diagram Determination

In the last few years the scanning transmission electron microscope has been developed. It is now possible to focus the primary electron beam of this instrument to ≤ 100 Å spot size on the specimen. Similar to the EMP, the excited characteristic X-rays can be measured in a suitable detector and used for localized chemical analysis. The major advantage of this technique is that, by using electron microscope thin films and operating voltages of 80 to 200 kV, little electron scattering occurs in the sample. The X-ray source size obtained is < 0.1 μm, a factor of 10 better than the EMP. With sufficiently thin samples, the X-ray source size may be < 0.01 μm. In addition, the use of thin films at high electron beam excitation voltages eliminates, in most cases, the need to correct for absorption and fluorescence effects in the conversion of X-ray data to composition.
As an example of the use of the STEM technique for phase diagram determination the Fe-Ni-Co system will be considered. The phase diagram has recently been redetermined by microprobe analysis at several temperatures. The 650°C isotherm is given in Figure 1. The alloy samples used for this isotherm were heat treated for times of up to 6 months and analyzed with the EMP techniques previously described. The 6 month treatment time was necessary to produce γ plates ≥ 5 μm in width for EMP analysis. To evaluate the applicability of the STEM to phase diagram determination an Fe-8.96 wt% Ni-7.92 wt% Co alloy was prepared using a quench and anneal cycle (B). The alloy sample was heat treated at 650°C for only 2 weeks and the γ plates produced were 0.3-0.5 μm in width.

A thin foil transmission microscope sample was prepared from the specimen by ion etching.

Figure 5 shows a scanning transmission image of the γ plates and α matrix prior to data acquisition. A Philips 300 STEM instrument was used with an operating potential of 80 kV and with the specimen tilted at 36°. Data was taken across the γ platelets and the α matrix with an electron beam ~ 320Å in diameter. The position of the beam during analysis are visible due to sample contamination as shown in Figure 6.

X-ray data was collected on a solid state X-ray detector with a counting time of 60 sec. per point. The Fe$_{Kα}$ and Ni$_{Kα}$ integrated peak intensities were measured and the continuum background was subtracted. A plot of $I_{Ni}/I_{Fe}$ vs. distance was constructed and is shown in Figure 7. The circles represent data points as measured on the STEM. The 2 σ error bars were calculated from the accumulated X-ray counts on the specimen. The bulk alloy $I_{Ni}/I_{Fe}$ value was determined by scanning the electron beam over the entire area of Figure 5.
The diameter of the X-ray generation region is indicated on Figure 7 by \( R(x) \). For the EMP, \( R(x) \) is a nominal 1 \( \mu \)m and represents the diameter of the X-ray excitation volume. For the STEM, \( R(x) \) represents the 320A beam diameter plus an estimate of the amount of beam spreading in the specimen, about 200A for a 1000A iron thin foil.\(^6\)

Cliff and Lorimer\(^7\) have outlined a simple technique to carry out the quantitative analysis of thin foils with the STEM analytical electron microscope. For very thin foils where X-ray absorption and fluorescence can be neglected, the following expression may be used:

\[
\frac{I_A}{I_B} = (k_{AB})^{-1} \frac{C_A}{C_B}
\]

where \( I_A \) and \( I_B \) are the measured characteristic X-ray intensities, and \( C_A, C_B \) are the weight fractions of two elements A and B in the thin film. The constant \( k_{AB} \) varies with operating voltage but is independent of sample thickness and composition if the two intensities are measured simultaneously. This method has been often referred to as the standardless method in that pure bulk standards are not needed for the analysis.

These \( k_{AB} \) values can either be measured or calculated. The value of \( k_{NiFe} \) used in this experiment was calculated using the expressions developed by Goldstein et al.\(^6\) A value of \( k_{NiFe} = 1.081 \) for 80 kV operating potential was calculated using the method of Goldstein et al.\(^6\) which corrects for the absorption of the Be window in the detector and the relativistic nature of the electron beam.

**STEM - Discussion**

Using Equation 1 and the calculated \( k_{NiFe} \) value one can calculate the expected \( I_{Ni}/I_{Fe} \) ratios for the \( \alpha \) and \( \gamma \) phase compositions using measured \( C_{Ni}, C_{Fe} \) values obtained from a tie line drawn through the bulk
composition of the Fe-8.96 wt% Ni-7.92 wt% Co alloy at a temperature of 650°C (Figure 1). The solid lines of $I_{Ni}/I_{Fe}$ plotted on Figure 7 for the $\alpha$ and $\gamma$ phases were determined by this procedure. The bulk alloy intensity ratio was calculated similarly. It is apparent that excellent agreement has been obtained between measurements of tie line compositions by EMP and STEM techniques.

It is clear from this example that phase diagram determination by STEM techniques has a promising future. The increased spatial resolution will allow analyses of phases 0.5 µm in size and possibly smaller. Growth times for precipitates will also be greatly reduced by this technique. A major advantage will be the extension of phase diagram analysis to lower temperatures than have been possible to date. Problems of contamination, X-ray absorption, and thin film preparation in STEM analysis have yet to be completely solved, however.

Acknowledgements

The authors wish to thank D. Richards for the preparation of the STEM sample and R. Korastinsky for assistance with the STEM analysis work. We thank D. Williams and S. Widge for helpful discussions and suggestions. This work was supported by NASA Grant NGR 39-007-056.
REFERENCES


### Table I

Summary of Phase Diagrams

Tabulation of systems where the EMP has been used in the determination of solid solubility limits, tie-lines, tie-triangles, and phase identification.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature Range (°K)</th>
<th>Technique*</th>
<th>Measured Parameter (Phase Relationship)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Mo</td>
<td>1673-1873</td>
<td>D.C.</td>
<td>solubility limits: Al$_3$Mo$_3$, Al$_6$Mo$_3$ Mo AlMo - AlMo$_3$ - Mo</td>
</tr>
<tr>
<td>Cr-Fe</td>
<td>1123-1373</td>
<td>HTB</td>
<td>tie-lines: α + γ</td>
</tr>
<tr>
<td>Cr-Pt</td>
<td>970-2133</td>
<td>HTB</td>
<td>tie-lines: γ + β, β + α, γ' + β</td>
</tr>
<tr>
<td>Fe-Mo</td>
<td>1073-1773</td>
<td>HTB</td>
<td>tie-lines: α + γ</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>773-1073</td>
<td>HTB, D.C.</td>
<td>tie-lines: α + γ</td>
</tr>
<tr>
<td>Fe-P</td>
<td>1133-1273</td>
<td>D.C.</td>
<td>solubility limits: α - Fe$_3$P</td>
</tr>
<tr>
<td>Fe-PbTe</td>
<td>1073-1195</td>
<td>HTB</td>
<td>solubility limits: Fe-PbTe</td>
</tr>
<tr>
<td>Fe-W</td>
<td>1173-1813</td>
<td>HTB, D.C.</td>
<td>tie-lines: α + λ, λ + μ, α + μ, μ + 'ω'</td>
</tr>
<tr>
<td>Mo-Ni</td>
<td>1073-1568</td>
<td>D.C.</td>
<td>tie-lines: (Mo) + ζ, (Ni) + ζ, ζ + γ (ζ = MoNi, γ = MoNi$_3$, β = MoNi$_4$)</td>
</tr>
<tr>
<td>Nb-Zn</td>
<td>1293-1393</td>
<td>HTB</td>
<td>compound identification: NbZn$_3$, NbZn$<em>2$, NbZn$</em>{1.5}$, NbZn</td>
</tr>
<tr>
<td>Pt-V</td>
<td>1173-1973</td>
<td>HTB</td>
<td>tie-lines: ζ + β, α + β, γ + β (β - V$_3$ Pt, ζ - VPt)</td>
</tr>
<tr>
<td>Al-B-Ti</td>
<td>923</td>
<td>HTB</td>
<td>compound identification: Al$_3$Ti, AlB$_2$, TiB$_2$</td>
</tr>
<tr>
<td>Al-Fe-Zn</td>
<td>723</td>
<td>solid-liquid equilibration</td>
<td>phase and compound identification: FeAl, FeAl$<em>2$, FeAl$</em>{15}$, 61, ζ, two ternary phases 2 Al$_2$O$_3$, 61, ζ, two ternary phases 2 Al$_2$O$_3$, 61, ζ, two ternary phases 2 Al$_2$O$_3$, 61, ζ, two ternary phases 2 Al$_2$O$_3$, 61, ζ, two ternary phases 2</td>
</tr>
<tr>
<td>Al-Nb-Ni</td>
<td>1073-1473</td>
<td>HTA, D.C.</td>
<td>solubility limits: γ' - Nb tie-lines: γ + γ'</td>
</tr>
<tr>
<td>Al$_2$O$_3$-Cr$_2$O$_3$-FeO</td>
<td>1923-2073</td>
<td>HTB</td>
<td>solubility limits: FeO - Cr$_2$O$_3$ - FeO - Al$_2$O$_3$ quasi-binary</td>
</tr>
<tr>
<td>Au-In-Pb</td>
<td>432-706</td>
<td>HTB</td>
<td>phase identification: AuIn, AuIn$_2$</td>
</tr>
<tr>
<td>System</td>
<td>Temperature Range (°K)</td>
<td>Technique*</td>
<td>Measured Parameter (Phase Relationship)</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------------------</td>
<td>------------</td>
<td>-----------------------------------------------------------------</td>
</tr>
<tr>
<td>Au-Ni-Pt(^{23})</td>
<td>1085-1533</td>
<td>HTB</td>
<td>tie-lines: solid 1 - solid 2 miscibility gap</td>
</tr>
<tr>
<td>C-Fe-Mn(^{24})</td>
<td>1163-1373</td>
<td>HTB</td>
<td>tie-lines: γ + M(_3)C, phase identification: M(<em>3)C, M(</em>{15})C(<em>4), M(</em>{23})C(_6), e</td>
</tr>
<tr>
<td>C-Fe-Ni(^{25})</td>
<td>773-1003</td>
<td>HTB, HTC</td>
<td>tie-lines: α + γ, γ + (Fe,Ni)(_3)C, α + (Fe,Ni)(_3)C</td>
</tr>
<tr>
<td>Co-Be-Cu(^{26})</td>
<td>673-1373</td>
<td>HTB</td>
<td>solubility limits: α - (Fe,Ni)(_3)P</td>
</tr>
<tr>
<td>Co-Fe-Ni(^{3})</td>
<td>926-1073</td>
<td>HTB, HTC</td>
<td>solubility limits: α - β, α - γ(_2), α - γ(_1)</td>
</tr>
<tr>
<td>Cr-Fe-Ni(Al,Nb,Si,Ti)(^{27})</td>
<td>1089-1533</td>
<td>HTB</td>
<td>solubility limits: α' - γ, tie-lines: α' + γ</td>
</tr>
<tr>
<td>Cu-Al-Ag(^{28})</td>
<td>848-898</td>
<td>HTB</td>
<td>solubility limits: terminal regions (α(_1) - (Ag), α(_2) (Cu))</td>
</tr>
<tr>
<td>Fe-Mn-Zn(^{29})</td>
<td>893-1273</td>
<td>HTB</td>
<td>tie-lines: α + γ</td>
</tr>
<tr>
<td>Fe-Mo-W(^{11})</td>
<td>1373-1578</td>
<td>HTB</td>
<td>tie-lines: α + γ, α + μ, α + R</td>
</tr>
<tr>
<td>Fe-Ni-P(^{30})</td>
<td>823-1373</td>
<td>HTB, HTC</td>
<td>tie-lines: α + (Fe,Ni)(_3)P, γ + (Fe,Ni)(_3)P, α + γ, α + liquid, γ + liquid</td>
</tr>
<tr>
<td>Sb-Te-Tl(^{31})</td>
<td>483-518</td>
<td>HTB</td>
<td>phase identification: α (Tl(_2)Te(_3)), δ (Sb(_2)Te(_3)), ε (SbTlTe(_2)), δ (Te)</td>
</tr>
<tr>
<td>Ti-V-Zr(^{32})</td>
<td>1073</td>
<td>HTA</td>
<td>tie-lines: α + γ, β + γ, δ + β, γ + δ</td>
</tr>
<tr>
<td>C-Cr-Ni-Si(^{33})</td>
<td>1173</td>
<td>HTB</td>
<td>phase identification: Cr(_3)C(_2), solubility limit: γ - Cr(_3)C(_2)</td>
</tr>
</tbody>
</table>

* Codes:  
  D.C. - diffusion couple  
  HTA - heat treatment A - quench from high temperature to temperature of interest (annealing cycle)  
  HTB - heat treatment B - quench from high temperature to low temperature, then reheat at temperature of interest (quench and anneal cycle)  
  HTC - heat treatment C - controlled cooling from high temperature to temperature of interest (controlled cooling cycle)
Figure 1
Isothermal section of Fe-Ni-Co ternary diagram at 650°C. Origin is at 95Fe-5Ni, and heat treatments are as indicated in the text.

Figure 2
Microstructure of an Fe-3.75 wt% Ni-1.0 wt% C alloy. Austenitized at 1000°C and then cooled to 730°C at 25°C/hour and isothermally treated for 24 hours. Matrix is martensite and grain boundary precipitate is (Fe,Ni)3C. 2% Nital Etch. Scale Bar = 200 μm.
Figure 3
Microprobe traces taken in an Fe-3.75 Ni-1.0 C alloy. x and o represent data points from two separate traces.

Figure 4
Fe-Ni-C 730°C isotherm.
Figure 5
Fe-8.96 wt% Ni-7.92 wt% Co alloy treated at 650°C using the quench and anneal cycle. STEM image of the thin foil prior to composition analysis. Scale Bar = 1 μm.

Figure 6
Fe-8.96 wt% Ni-7.92 wt% Co alloy treated at 650°C using the quench and anneal cycle. STEM image of the thin foil after composition analysis. Scale Bar = 1 μm.
The analysis points can be observed by the contamination spots left on the foil. The white dots are placed on the photograph to more clearly indicate the analysis points.
Figure 7
STEM trace across the $\alpha$ and $\gamma$ phases formed in a Co alloy annealed at 650°C for 2 weeks. Solid circles are data points and 2 $\sigma$ error bars are shown. The solid lines are calculated from the known Fe-Ni-Co phase diagram and the dashed line is calculated from the bulk alloy composition. The spatial resolution of the STEM and typical resolution of the EMP are also shown.