THE USE OF X-RAY MICROANALYSIS IN THE STUDY OF DIFFUSION

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Summary

This paper reviews the use of electron probe microanalysis, scanning electron microscopy and analytical electron microscopy in the measurement of compositional data obtained from diffusion couples. Methods to obtain x-ray spatial resolution as low as 1 nm with the AEM are described. In addition, techniques for improving the detection and for increasing the accuracy of compositional analyses are summarized. Sample preparation techniques for AEM are also discussed. Examples of the use of the above methods for materials problems such as Cu-Sn-Pb-Au solders, Ni-Cr-Al coatings, N diffusion in Fe and Ni-Nb diffusion couples are given.
The interdiffusion process is studied with various objectives in mind. One objective is to measure chemical or interdiffusion coefficients. Single or multiple phase diffusion couples can be used and binary or ternary coefficients can be measured. Another objective is to study phase or interface formation in multiphase diffusion couples. Rates of growth of the various phases formed in the diffusion couple can be measured and the formation of planar or non-planar interfaces can be studied. In addition, it is often possible to measure interface concentrations between phases which directly relate to tie lines on binary and ternary phase diagrams. Examples of these various applications of diffusion couples will be given later in this paper.

To study interdiffusion in a concentration gradient it is necessary to measure composition as a function of distance in a "diffused" sample. Electron optical techniques such as the electron probe microanalyzer (EPMA) and scanning electron microscope (SEM) provide the capability to measure composition gradients with spatial resolutions for chemical analysis of 1 to 2 um. The analytical electron microscope (AEM) provides the capability to measure these gradients at much better spatial resolutions of 0.02 um (20 nm, 200 Å) or better. These capabilities have permitted the study of diffusion over very short distances, such as those encountered in systems processed at low temperatures or for short times. In addition, one can characterize the initial bond interface before diffusion. This paper discusses the diffusion process, describes the electron optical instruments used in measuring the chemical composition variation in diffusion couples, and also gives several examples of the application of the EPMA, SEM and AEM.

II. Process of Interdiffusion and Its Measurement

1. Characterization of the Diffusion Process

When two semi-infinite bars containing different amounts of elements i and j, are joined together to form a binary diffusion couple, the resulting composition gradient will be driven to the average bulk composition. The diffusion of components i and j can be described by the chemical diffusion coefficient, or interdiffusion coefficient, D. The description of the diffusion process with D is entirely phenomenological and applies to diffusion by a vacancy (substitutional) or interstitial mechanism. In a polycrystalline material, the chemical diffusion coefficient describes the sum of both volume diffusion and short circuit (grain boundary, dislocation pipe, etc.) diffusion. D varies exponentially with temperature according to D = D₀ exp (−Q/RT) where D₀ is a constant, Q is the activation energy, R is the gas constant and T is absolute temperature.

The basic experimental scheme requires making a diffusion couple, heat treating the couple under an appropriate atmosphere for a specified time and temperature and then measuring the resulting chemical concentration profile with one or more electron optical techniques. From the concentration profiles measured in binary and ternary single phase as well as multiphase couples, it is possible to determine the chemical diffusion coefficient(s) as a function of composition. If Kirkendall markers are used, it is also possible to determine the intrinsic diffusion coefficients. The mathematics developed from the late 1940's through the mid-1960's to analyze concentration profiles are directly applicable to the determination of diffusion coefficients from concentration profiles measured by electron optical techniques. These mathematics are given in detail in the texts by Jost (1) and Crank (2) or in papers by Kirkaldy and co-workers (3 - 6).
For ternary single phase couples, four ternary coefficients can be determined if the appropriate concentration distance profiles are obtained (7, 8). To solve for the four diffusion coefficients, two diffusion couples whose diffusion paths cross at a common concentration \( C_1 \), \( C_4 \) are necessary. Unfortunately, at this time, multiphase ternary diffusion couples cannot be used to determine ternary diffusion coefficients.

2. Experimental Techniques

Because electron optical techniques have spatial resolutions of 1–2 um or better for chemical analysis, it is critical that the diffusion bond adhere across the interface. In addition, the bonding process should not provide a source for the formation of grain boundaries and dislocation substructure or a place for impurities to enter the system.

Several different techniques have been used to assemble solid state diffusion couples. One of the simplest techniques is the window-frame technique (9, 10) in which the two end member couples are ground and polished flat and mechanically clamped together. Since the surfaces are ‘perfectly’ clean the couples should diffusion bond very quickly. In some materials a natural oxide layer may form on the surface and make diffusion bonding difficult. In some cases, a short heat treatment at high temperatures is used to facilitate bonding. After a good bond is achieved, the couple is given its intended diffusion anneal. If a high temperature bonding treatment is used, the couple must be analyzed prior to the diffusion anneal to determine if any significant diffusion occurred during the bonding process. The smaller the diffusion profile, the more carefully the initial bonding treatment must be controlled. The formation of a fine oxide film at the bond interface is not necessarily undesirable since the fine oxides may serve as in-situ Kirkendall markers.

It is difficult to use the window-frame technique when materials have dissimilar melting points and/or crystal structures. For metals, inertia welding may be used (11). In this process, melting could extend over large distances or deformation structures could be imposed at the bond interface. For some metallic alloys, various electrolytic and electroless plating techniques (12, 13) can also be used to fabricate diffusion couples. One half of the couple is typically a piece of a bulk alloy. The second half of the couple is formed by plating the second alloy onto the bulk alloy substrate. The principal disadvantage of plated layers is the high defect density (14) (high vacancy concentration, voids, grain boundaries, impurities).

Other nonsolution plating techniques have also been used including plasma spraying and chemical vapor deposition (CVD). These techniques are suitable for both metals and nonmetals. The process typically involves the deposition of a layer by spraying or CVD onto a bulk substrate, although it is possible to deposit both materials by spraying or CVD. The principal disadvantage of these techniques is sample heating which could produce interdiffusion during couple preparation. Thermal evaporation, electron beam evaporation, or laser evaporation can also be used to deposit a second alloy layer onto a bulk substrate. Depending on the specific experimental design, sample heating may or may not be a concern. Deposition from the liquid by dipping has also been used successfully. The dipping procedure is commonly used to form diffusion couples between the noble metals (Cu, Ag, Au) and fusible alloy compositions. In these alloys, reactions often occur between the liquid and solid substrate.
It is clear that all of the techniques used to produce the initial bond interface (window-frame, inertia welding, plating, plasma spraying, CVD, evaporation and dipping) may introduce initial chemical gradients, grain boundaries, dislocation substructure or impurities. It is, therefore, very important to characterize the bond interfaces prior to interdiffusion. As discussed later, AEM techniques are very useful for establishing the presence of any of these effects.

III. Electron Optical Techniques

1. Instrumentation

The scanning electron microscope (SEM), the electron probe microanalyzer (EPMA) and more recently the analytical electron microscope (AEM) have become useful tools for the measurement of interdiffusion profiles on a very fine scale. Figure 1 shows the electron optical systems of the conventional SEM/EPMA and AEM (15). The only real distinction between the SEM and EPMA at this time is the number of x-ray detectors and the sophistication of the x-ray compositional analysis equipment. We will consider them as one instrument. SEM/EPMA and AEM instruments require a high energy source or gun. Most SEM/EPMA's operate between 10 and 25 keV for x-ray analysis while most AEM's operate between 100 and 400 kV for x-ray analysis. Typical electron sources are tungsten filament, LaB₆ filament or field emission gun (FEG) (16).

The SEM/EPMA and the AEM utilize a system of probe forming lenses placed after the electron source in the column. These lenses focus the electron probe to a diameter of less than a nanometer to a few hundred nanometers. To form a scanning image, electrostatic scan coils raster the electron beam over the surface of the sample. To analyze a specific point, the raster is stopped and the beam positioned on that point. The incident high-energy electrons interact with the bulk solid to produce signals, including secondary electrons, backscattered electrons, and characteristic x-rays. These signals are detected electronically and processed to produce an image.

The AEM may also operate as a transmission electron microscope (TEM), see Figure 1b. Conventional TEM pictures can be obtained as well as diffraction patterns from selected areas on the specimen. Other capabilities of the AEM include energy loss spectrometry and other specialized diffraction techniques (15).

The major difference between the SEM/EPMA and AEM is the type of specimen which is investigated. Solid specimens are analyzed in the SEM/EPMA while thin foil specimens, transparent to the high energy electron beam, are analyzed in the AEM. The source size of the characteristic x-rays, which are used to measure chemical composition, are determined by the type of specimen which is analyzed. In solid specimens the characteristic x-ray signal comes from a volume determined by elastic scattering of the electrons which produce x-rays in the sample. This volume is typically 1 to 2 μm in diameter (see Figure 2). Even though the electron probe size is 10 to 100 nm, the x-ray source size is much larger. In thin specimens, the characteristic x-ray signal comes from a volume determined by the probe size and the elastic scattering of the electrons which produce x-rays in the sample. Since the specimen is thin, only a small amount of elastic scattering occurs before the electron beam passes through the specimen. Hence, in the AEM, the x-ray source size is much closer to the electron probe size. We will discuss spatial resolution in more detail in a following section.
Figure 1. Comparison of electron optical columns for electron microscopy; (a) SEM/EPMA, (b) AEM.

Figure 2. Comparison of electron beam spreading in (a) thin foils and (b) bulk targets.
The x-ray signal from the specimen must be detected and corrected for matrix effects in order to perform quantitative analysis. Two different x-ray detectors, wavelength dispersive spectrometer (WDS) and energy dispersive spectrometer (EDS) are used to collect x-ray spectra from samples analyzed in modern electron optical instruments. All electron probe microanalyzers are equipped with a WDS x-ray detection system. The WDS system uses an x-ray diffracting crystal and discriminates x-rays according to Bragg's Law. In order to detect all characteristic energies of potential interest, several crystals with varying interplanar spacings are needed. The diffracted x-rays are collected by a proportional counter and then electronically processed. A modern EPMA has several crystal spectrometers so that characteristic x-rays of various energies can be detected simultaneously. Some of the characteristics of the WDS system which are important with respect to the quantitative analysis of diffusion couples include: (1) elemental detection for atomic numbers \( \geq 4 \), (2) x-ray energy resolution as good as 5 eV, which allows one to discriminate between x-ray lines of very similar energy and (3) a high count rate and low background which gives detectability limits on the order of 100 ppm. Although the cornerstone of EPMA x-ray microanalysis, WDS systems are currently not used on an AEM because of the low probe currents and therefore the low x-ray intensities available in a 20 nm electron probes and the low detection efficiency of WDS systems. With the use of FEC, a WDS in an AEM has been proposed (17).

An EDS x-ray detection system is used on most EPMAS and all AEMs. The detector is a cooled (liquid N\(_2\)) lithium drifted silicon chip. Conventional EDS detectors are isolated from the microscope environment by a thin (\( \sim 7.5 \) um thick) Be window. The impinging x-rays are absorbed in the detector and form electron-hole pairs. The number of electron hole pairs created is directly proportional to the energy of incident characteristic x-rays. Some of the characteristics of the EDS system which are important with respect to the measurement of composition in a diffusion couple are: (1) elemental detection for atomic numbers \( \geq 11 \), due to x-ray absorption in the Be window. Recently, windowless and ultrathin window (UTW) detectors have been introduced to allow collection of x-rays from elements with an atomic number \( \geq 6 \); (2) x-ray energy resolution approximately 150 eV, making it difficult to discriminate x-rays of similar energies; and (3) a low count rate and a relatively low peak to background ratio relative to the WDS system. Detectability limits of the order of 1000 ppm are obtained with the EDS. Recently, Ge detectors have been developed with energy resolution less than 150 eV (18). These detectors are now being interfaced to AEM instruments.

In order to determine concentration profiles in a diffusion couple with the EPMA or AEM, the measured x-ray intensities must be converted to chemical compositions. The procedures used for x-ray quantification are quite different. For the EPMA and bulk solid targets, the ZAF, or \( \Phi(\text{pz}) \) techniques are used to correct for matrix effects such as atomic number (Z), x-ray absorption (A) and x-ray fluorescence (F) in the samples and standards used. For the AEM and thin foil targets, the ratio technique is employed. For some thin foil samples, x-ray absorption corrections may also be necessary. Review papers outlining these quantification techniques are available (15, 16, 19-22).

2. X-ray Spatial Resolution and Minimum Detectability

A major driving force for the development of the AEM was the improvement in spatial resolution compared with the EPMA. This improvement arises for two reasons. First, the use of thin foil samples means that less elastic and inelastic scatter occurs as the beam traverses the sample.
Second, the higher beam energy (>100-400 keV in the AEM compared with 10-25 keV in the EPMA) further reduces beam scatter because the mean free path for both elastic and inelastic collisions increases with the electron energy. The net result is that increasing the accelerating voltage when using thin samples decreases the total beam-specimen interaction volume, thus giving a more localized x-ray signal source and a higher spatial resolution. With bulk samples in the EPMA, increasing the voltage increases the interaction volume thus degrading spatial resolution. In the EPMA, the physics of beam-specimen interactions, at the voltages used, means that spatial resolution never improves below 0.5-1.0 μm. Therefore, there is little interest in the theory of spatial resolution and little or no effort is routinely made to optimize this parameter. By contrast, much theoretical and experimental work has been carried out to both define and measure the spatial resolution in the AEM.

In the AEM field it is generally agreed that the x-ray source size, R, comprises some combination of the incident electron probe size (d) and the spreading of the probe (b) as it traverses the specimen, (23) for example:

\[ R = (b^2 + d^2)^{1/2} \]  

(1)

Usually, b is governed by the beam energy (E₀), sample thickness (t) and density (p) such that (24):

\[ b \propto \rho^{1/2} t^{3/2} E_0^{-1/2} \]  

(2)

It is obvious from equation (1) that to improve spatial resolution, both d and b must be minimized. Minimizing d reduces the input probe current. For thermionic sources, if d < 100 nm, count rates are unacceptably low. With a thermionic source, sample thicknesses have to be such that sufficient counts are generated for quantification but the net result is usually that b dominates in equation (1). For example, in an Fe foil, 100 nm thick, examined at 100 kV, a scattering diameter (b) of approximately 30 nm would be produced. With an electron probe diameter (d) of 20 nm, the total x-ray spatial resolution would be approximately 40 nm. Under these circumstances, much attention has been paid to increasing the accelerating voltage since, from equation (2), that is the only variable left for a given sample. The development of 300-400 keV instruments owes much to this perceived need for improved resolution.

With a FEG, sufficient current (<1 nA) can be generated in a 1 nm probe to permit quantitative analysis. As high brightness field emission gun (FEG) sources become available and higher voltage AEMs become commonplace, it will be easier to get quantitative data from thinner samples and then d will play a more dominant role in equation (1), and the expected combination of 300 keV and FEG will result in spatial resolutions < 1 to 5 nm.

However, spatial resolution and minimum detectability are intimately related. It is a feature of any microanalysis technique that an improvement in spatial resolution is balanced by a worsening of the detectability limit (all other factors being equal). This is because at higher spatial resolution the analyzed volume is smaller and, therefore, the signal intensity is reduced. This reduction in signal intensity means that the acquired spectrum will be noisier and therefore small peaks from trace elements will be less detectable. Therefore, in the AEM, the price that is paid for improved spatial resolution is a relatively poor minimum detectability.

The minimum mass fraction (MMF) represents the smallest concentration of an element that can be measured in the analysis volume. The MMF can be
decreased or improved by increasing the peak x-ray intensity (P) for the element of interest, by increasing the peak to background ratio (P/B) for the element of interest, and by increasing the analysis time (τ) (25). In general:

$$\text{MMF} \propto \frac{1}{(P \times P/B \times \tau)^{1/2}}$$

(3)

To increase P, we can increase the current in the electron probe and increase the thickness (t) of the specimen, while to increase P/B one can increase the operating voltage (E₀) and decrease instrumental contributions to the background. Improvements in AEM instrument design such as using a high brightness source, a high voltage gun, and a higher collection angle for EDS can increase P. To increase P/B, one needs a stable instrument with a clean vacuum environment to minimize or eliminate specimen deterioration and contamination. Improved AEM stage design, to minimize stray electrons and bremsstrahlung radiation, both of which contribute to the detected spectrum, could also help to increase P/B.

The best compromise in terms of improving MMF and x-ray spatial resolution is to use high operating voltages (300 to 400kV) and thin specimens to minimize beam broadening. The loss of x-ray intensity, P, a consequence of using thin specimens, can be compensated in part by the higher voltages and/or by using a high brightness FE electron source where a small spot the size of 1 to 2nm can still be maintained. In summary, optimum MMF and spatial resolution can be obtained by using a high brightness, intermediate voltage source with thin foils, perhaps of the order of t ~ 10nm. Under these circumstances, MMF values < 0.1wt% will become routine. This, of course, does not compare well with the EPMA, where MMF is routinely ~ 0.01wt%. But a more favorable aspect of detectability limits in the AEM is evident when we consider the absolute sensitivity rather than the mass fraction.

In summary, the x-ray spatial resolution obtained by using the AEM is at least 50 to 100 times better than that obtained by using the EPMA. Future AEM developments, where a spatial resolution of 1-2nm is possible, increases this ratio to 500 to 1000 times better than the EPMA. Such improvements have several important consequences for diffusion measurements. In order to perform a Boltzman-Matano analysis, 10 to 20 unique (spatially resolved) chemical analyses in the chemical concentration gradients are required. For data collected by EPMA, the diffusion gradient must be ~ 25um in length. Conversely, for data collected by AEM, the diffusion gradient must be ~ 250 to 500 nm in length, some 50 to 100 times less than that for the EPMA. Since the diffusion distance X is ~ √(Dτ), use of the AEM allows one to measure diffusivities as much as 10⁶ times smaller than those obtained with the EPMA when diffusion experiments are run for the same heat treatment time. Conversely, the AEM allows one to perform diffusion experiments using heat treatment times, at the same diffusion temperature, 10⁻⁶ times those necessary when employing EPMA as the analysis technique. With future developments in AEM instrumentation and specimen preparation, diffusivities as must as 10⁶ times less than those obtained with the EPMA for the same heat treatment time can be obtained. The diffusion gradient need be only ~ 25 to 50nm in length. In this case, initial bonding effects, as discussed earlier in this paper, will be very significant. In addition, the AEM has another special advantage in that grain boundaries can be observed and any potential effects of grain boundary diffusion can be avoided in the composition measurement.

3. Specimen Preparation

Successful microanalytical investigation, using EPMA or AEM, depends
strongly on careful specimen preparation. Recently, an entire volume (26)
has been written concerning these preparation techniques for TEM and AEM
studies. The problem of specimen preparation becomes critical when trying
to thin and measure composition across multiphase interfaces such as might
be encountered in applications involving metal-semiconductor, metal-ceramic,
or ceramic-ceramic interfaces.

For the particular case of the preparation of diffusion couple samples
which are to be analyzed in the EPMA or the AEM, one must be certain not to
introduce any specimen preparation artifacts into the experimental data. In
preparing bulk samples for analysis in the EPMA, several factors must be
considered. It is essential that the concentration profile be measured
perpendicular to the diffusion interface and parallel to the diffusion
direction. This orientation requirement must be satisfied for both single
phase and multiphase diffusion couples. Final mechanical polishing must be
done perpendicular to the diffusion direction (parallel to the diffusion
interface) to prevent "smearing" of the concentration profile. The surface
to be analyzed must be flat. Single and multiphase couples should be
anodized prior to ion beam thinning will introduce surface relief which could
generate errors in the measured concentration profiles. It is also
important that the profile should be measured away from any grain
boundaries, especially if the diffusion anneals were carried out at low
temperatures. If large grained starting materials are available, the
avoidance of grain boundaries in the diffusion couple analysis will be
simplified. It may be necessary to etch the sample to see the grain
boundaries. If this is necessary, the sample should be marked with a
micro hardness indenter, photographed and the etching relief polished off
prior to EPMA analysis. The microhardness indentations will allow proper
orientation of the sample for analysis.

The preparation of diffusion couples for the AEM may be quite
difficult. Rarely do two different materials, such as those which might be
used to make a diffusion couple, thin at equal rates in an electrochemical
polishing solution or in an ion beam thinner. Combinations of
electrochemical thinning solutions and/or ion beam thinning may be required.
Off-center sample positioning and masking may be useful "tricks" for ion
beam thinning. Following electropolishing, it is often advisable to clean
the thin foil in an ion beam thinner for a few minutes to remove any
potential chemical residue. Since the electron transparent thin area is
often limited, it is usually impossible to measure concentration profiles
much more than 1 to 2 um in length.

A schematic of the TEM-AEM preparation technique is given in Figure 3.
After the diffusion couple is removed from the furnace and quenched, it is
electro-spark discharged machined (EDM) with the interface parallel to the
brass electrode. The resulting 3 mm diameter cylinder must be carefully
checked for discontinuities and if present, removed by hand filing. The
cylinder is then glued to a metal support and disks up to 4 mm thick are
saved off using a diamond blade as seen in Figure 3. Experience has proved
that these precautions are necessary, for stresses due to the diamond wheel
are sufficient to cause the bond interface to tear apart. This is
particularly true when a) too thin a slice is taken, b) no support was given
to the cylinder or c) if cracks, or discontinuities, acting as stress
concentrators, are present at the interface. The 3 mm disks are then ground
down to a thickness of about 80 um on 600 grit paper, using ethanol as the
wetting agent. After proper cleaning and drying, the specimens are electro-
jet polished and/or ion milled. In nearly all cases, the thin area will not
be located at the bond interface. The sample is then ion milled until the
thin area is present at the diffusion interface. In some cases, specimen
preparation must be done completely by ion milling. The advent of a new
generation of ultramicrotomes capable of cutting metal foils thinner than 30 nm may also prove to be important for AEM applications.

Figure 3. Schematic of specimen preparation procedure for AEM starting with a bonded diffusion couple. Note location of bond interface during the various states of specimen preparation.

The thinning of a heterogeneous multilayer structure is a particularly difficult problem. Electrochemical jet thinning has been used for the preparation of Al-Ag (27) and Al-Zn (28) foils where concentration gradients have been measured and diffusion calculations made at grain boundary solute depleted regions, and a combination of electrochemical jet thinning and ion-thinning has been used to prepare edge-on multilayer Ni/Ni_3Al/NiAl foils (29) from bulk diffusion couples. Baxter, et al. (30) have used a method proposed by Newcomb and Stobbs (31), to examine layered Au/Ag/Au and Ag/Pd/Ag films edge-on. This method involves cementing the layered material between two steel hemicylinders and inserting this cylindrical sandwich into a brass tube which is thin sectioned perpendicular to the tube axis and then ion-thinned. Selvarian, et al. (32) have used cross-cut and multiple samples to study layer growth on Al-Zn-S hot dip coated Fe sheet. Edge-on TEM foils of semiconductor devices involving impurity-doped Si on SiO_2 or Al_2O_3 have also been noted in the recent literature (Roberts, et al. (33), Booker (34). Finally, ball-cratering (Zoung Yong-An, et al. (35) and precision ion-milling techniques (36) should both provide promising approaches for edge-on thinning or multilayer foils, but are just now being developed.

Thinning of interfacial regions in ceramic-metal and ceramic-ceramic systems are particularly difficult, but the careful use of ion-thinning techniques has helped greatly to overcome difficulties in thinning of heterogeneous materials. Recently, TEM and AEM studies have been performed which examine the diffusion growth of Ti_3Al by reaction to Ti on sapphire substrates (37), and the formation of TiN and TiAl_N by reaction of Ti on AIN substrates (38, 39). Ion beam thinning has also been used to prepare specimens of directionally solidified zirconia eutectics for HREM and AEM
specimens of directionally solidified zirconia eutectics for HREM and AEM examination (40, 41).

Once a suitable thin foil has been obtained, certain precautions must be observed during data analysis. The profile must be measured parallel to the diffusion direction and if the sample is a multiphase couple the phase interface(s) must be oriented parallel to the incident beam. If x-ray absorption is a concern, the specimen must also be oriented so that the direction of the x-rays from the analysis point to the EDS detector is parallel to the diffusion front and the foil thickness at each analysis point must be known. It is also very important that concentration profiles not be measured in the vicinity of grain boundaries so that only the bulk diffusion contribution is obtained.

4. **Comparison of Electron Optical Techniques**

Although the EPMA and AEM have distinct advantages and disadvantages relative to one another, they are complimentary techniques in the analysis of diffusion couples. For example, EPMA can be used for high temperature diffusion couples and AEM for low temperature diffusion couples in the same system (42, 43). The prime advantage of the EPMA is high relative accuracy (< 1.0% relative), a low elemental detectability limit (100 ppm), the ability to analyze low atomic number elements, and ease of sample preparation. The prime disadvantage of EPMA analysis is the lower spatial resolution (~1 to 2 μm), and the necessarily long diffusion fields, (~25 μm). The prime advantage of the AEM is high spatial resolution (~50 nm), allowing for the accurate analysis of diffusion concentration gradients only 250 to 500 nm in length. Improvements in instrumentation will further improve AEM spatial resolution. The prime disadvantages of the AEM include the inability to obtain quantitative analysis of elements with atomic numbers <11, a relatively low accuracy of 3-5% (relative) and very difficult sample preparation. Use of FEG instruments and UTW EDS detectors will help improve the capabilities of the AEM. The following section gives some examples of diffusion couple analyses using EPMA and AEM.

IV. **Examples of Diffusion Couple Measurements by Electron Optical Techniques**

1. **Diffusion Coefficient Measurements (Single Phase) — EPMA**

The electron probe microanalyzer has been used since the early 1960's to measure diffusion profiles in binary and ternary single and multiphase couples. There are literally hundreds of studies which have employed the EPMA. The following examples serve only to illustrate the use of the EPMA. Figure 4 illustrates electron probe data taken across incremental single phase binary diffusion couples in Y Fe-Ni system (44). The Y Fe-Ni couple has a gradient ~100 μm in length. The couples contained W Kirkendall markers and the initial grain sizes of the alloys were ~ 0.03 cm. In the Fe-Ni couples progressive recrystallization was observed at 1000°C, ~ 0.7 of the melting point of the couple. Short circuiting paths such as grain boundaries were produced. The effect of grain boundary diffusion led to measurements of diffusivity at lower temperatures above those extrapolated from the exponential variation of log D with 1/T.
The EPMA has been employed to measure concentration gradients in ternary and higher order systems as well. For example, in ternary couples in the $\gamma$ phase of the Fe–Ni–P system at 1100°C (45), or in the $\gamma$ phase of the Ni–Cr–Al system at 1100 and 1200°C (46). The composition gradients were determined by EPMA and the four ternary diffusion coefficients were evaluated at the intersection of two diffusion paths. Other researchers, such as Dayananda (47) have used this type of data to obtain the zero flux planes rather than to evaluate the four or more diffusivities in such multicomponent systems.

2. Diffusion Coefficient Measurements (Multiple Phase) — EPMA

Multiphase binary couples have also been analyzed using the EPMA. Figure 5 shows an EPMA composition profile ~200µm in length from a multiphase couple between Ni and Nb diffused at 850°C for 2,000 hours (11). Two intermediate phases NiNb and Ni$_3$Nb formed at this temperature. Diffusion coefficients for these two phases and the Ni and Nb rich end member solid solutions were obtained.

Joining these couples was especially difficult since the end members had such dissimilar melting points (Ni, 1455°C vs Nb, 2471°C). To overcome this difficulty, inertia welding was used. In order to make sure that the bonding process did not introduce diffusion gradients during high temperature processing an AEM analysis of the initial bond interface was made. Figure 6 shows the composition gradients across the interface. The total apparent gradient is 125nm (0.125µm). The x-ray source size (equation 1) is approximately 40 to 50nm so that within the spatial resolution of the AEM, no interdiffusion was measured. It appears that initial characterization of bond interfaces should now be routinely made by AEM techniques.
Figure 5. Electron probe microanalyzer scan from a multiphase couple between Ni and Nb diffused at 850°C for 2000 hours (11).

Figure 6. Analytical Electron Microscopy (x-ray) scan across an initial bond interface in a Ni-Nb diffusion couple.

3. **Diffusion Coefficient Measurements (Single Phase) -- AEM**

The AEM has only recently been used for analysis of diffusion couples. Although the advantages of the improved spatial resolution of AEM have been known for some years, the difficulty of specimen preparation has slowed the application of the technique. The first known application of the AEM technique was to the Fe-Ni system (48). Figure 7 shows a TEM photomicrograph of a typical diffusion zone and a Ni profile over a 2 micron diffusion field in a Fe-20 Ni vs. Fe-25 Ni ternary diffusion couple heat treated to 650°C for 4 months. The error resulting from the best fit concentration gradient was estimated as ± 2% (note figure 7). This small error allowed the diffusion coefficient to be determined to within an error of ± 15%.
Figure 7a. TEM photomicrograph of a ternary 20 Ni vs. 25 Ni diffusion couple containing ~0.25 wt% P (F2ON-F25NP) diffused at 650°C for 121 days. The diffusion couple bond interface is shown along with contamination spots indicating the positions of the point analysis during the generation of a Ni concentration profile. The smallest size between points is 50 nm (48).

Figure 7b. Experimental Ni concentration gradient from F2ON-F25NP ternary couple diffused at 650°C for 121 days. Error bars for individual points and for the best fit profile are given. 4 traces were obtained from the couple (48).

Figure 8 shows the binary Fe-Ni diffusion coefficients measured between 900°C and 600°C in the austenite phase. The binary diffusion coefficients follow the curves of the Goldstein et al. data (44) extrapolated from high temperatures (1288 to 1000°C) for varying Ni contents. Figure 9 shows a diffusion profile in another thin area of the 650°C sample (Figure 7) where a grain boundary is present. The distortion of the volume diffusion profile is easily observed, thereby demonstrating that the effect of grain boundary diffusion can be avoided using the AEM technique. Measurements of Fe-Ni
diffusion below 1000°C by EPMA have yielded higher diffusivities than those shown in Figure 8.

Figure 8. Experimental results of binary Y interdiffusion coefficient as a function of temperature. Range 900°C to 610°C. The error bars on $D$, binary at 610°C indicate the possible range of $D$, values at that temperature (48).

One can compare the results of the Dean and Goldstein (48) AEM study of Fe-Ni diffusion with that of the Goldstein et al. (44) EPMA study of Fe-Ni diffusion. The lowest temperatures and the lowest measured diffusivities in these two studies were 650°C, $1.2 \times 10^{-17}$ cm$^2$/sec and 1000°C, $1.0 \times 10^{-19}$ cm$^2$/sec for the AEM and the EPMA study. The respective diffusion times were 121 days vs. 9 days. If one compares the products of $D$ for the two temperatures, the $D$ product for the AEM data is $\sim 10^{-4}$ that of the EPMA data. This decrease in $D$ is due to increased spatial resolution as discussed previously. In this specific case, by using the increased spatial
resolution of the AEM and a heat treatment 13 times longer, the measured diffusivity was almost 5 orders of magnitude smaller and the measurement occurred 350°C lower than was previously obtained.

In another early study using AEM, Romig and Cieslak (43) obtained both intrinsic and chemical coefficients in the Ta-W system. Diffusion was investigated in the temperature range 1300 to 2100°C with single phase diffusion couples prepared by CVD. Small oxide inclusions present at the original interface served as Kirkendall markers. The movement of the markers and the concentration profiles were measured by imaging and x-ray compositional analysis with the electron microprobe and/or the AEM. The concentration profiles determined in the study by Romig and Cieslak are shown in Figure 10. Measurements at 2100 and 2000°C were made with the EPMA. After annealing at 1300°C for 220 days, the interdiffusion distance was approximately 1500 nm. A concentration gradient of such limited extent can be measured only with AEM techniques. In all three couples, the Kirkendall marker plane corresponded to the composition plane of approximately 70 at.-% W. The intrinsic diffusion coefficients were determined for this composition. This study is the first reported in the literature in which both chemical and intrinsic coefficients have been determined from diffusion couples analyzed by the AEM.

![Figure 10. Concentration profiles as measured in each single phase Ta-W diffusion couple following the diffusion anneal.](image-url)
Diffusion Coefficient Measurements (Multiple Phase) - AEW

Romig (49) has measured the diffusion coefficients in the U-Nb system from 1650°C to 800°C. Above 1000°C, U-Nb forms a continuous bcc solid solution. EPMA was used to analyze the couples except below 1000°C, where the spatial resolution was insufficient to investigate all the phases. Figure 11 shows the concentration profiles measured across a three phase U-Nb diffusion couple annealed at 900°C for 3000 hours. The concentration profile in the Nb rich phase cannot be resolved by EPMA (Figure 11a). The AEM data is necessary to study the α/γ interface. Analysis of these multiphase couples showed that the diffusivities determined from single phase bcc couples annealed at high temperatures were valid for all three bcc phases at lower temperatures. Coincidentally, the interface composition in the multiphase diffusion couple can also be used to determine new tie lines on the low temperature (<1000°C, portion of the U-Nb binary phase diagram.

Figure 11. Compositional analysis across a three phase U-Nb diffusion couple annealed at 900°C for 3000 hours. 1la) Electron Probe Microanalysis data of whole diffusion zone. 11b) AEM x-ray analysis data around the Nb rich phase.

Diffusion Couples - Application to Phase Formation

The major advantage in using the EPMA and AEM for multiphase couples is not only to measure the diffusivity but to study the early stage growth of intermediate phases or the development of concentration gradients at the multiphase interface. One of the earliest multiphase diffusion couple
studies by Glitz et al. (29) deals with the growth kinetics and the intermediate phase microstructure developed during early stage growth of Ni$_3$Al layers in NiAl/Ni diffusion couples.

Composition profiles obtained by the AEM across the diffusion interfaces are shown in Figure 12 for a specimen held at 1100°C for 15 minutes. The corresponding thickness profile taken across the thin foil is shown in Figure 12b. In order to obtain the final concentration profile (upper data set in Figure 12a) the data were corrected both for thickness and absorption effects. The equilibrium concentrations at the appropriate two-phase boundaries at 1100°C are shown in Figure 12a. Within the error of the present technique, the data obtained at the NiAl/Ni$_3$Al and Ni$_3$Al/Ni interfaces after 1100°C for 15 minutes appear consistent with the interface concentrations predicted from phase equilibria. It has been proposed in the literature that non-equilibrium conditions may exist at short times at the interfaces in a diffusing system. Unfortunately, the data obtained at the interfaces from the multiphase couples were not of sufficient sensitivity (Note Figure 12) to measure any non-equilibrium effects. The difficulty of obtaining such high quality data, when the foil thickness is non-uniform and x-ray absorption is a factor, cannot be minimized.

Figure 12. Sample diffused at 1100°C for 15 min. (29). a) AEM x-ray analysis across a Ni–NiAl diffusion couple; b) thickness of couple across the diffusion zone.
Another application of the diffusion couple approach is to investigate surface layer development in alloys. Metin et al. (50) have studied nitride layer growth in iron and titanium alloys by EPMA. Ion nitriding was used to produce metastable nitrides at the surface of the metallic specimen which subsequently decompose. For example, the Fe was nitrided at 600°C. Figure 13 shows an optical micrograph of an iron sample nitrided at 600°C for 2.5 hours. The intermetallic phases Fe$_{23}$N and Fe$_N$ form during the diffusion anneal as well as iron. Figure 14 shows the N profile, as measured by EPMA, of the 600°C sample shown in Figure 13. The outer Fe$_{23}$N layer was too thin to be properly retained during metallographic polishing. The linear concentration gradients are a consequence of steady-state diffusion and Metin et al. (48) were able to detect and measure quantitatively N with a modern EPMA and thereby obtain the diffusion coefficients. The modern EPMA is also capable of detecting and measuring quantitatively other light elements including B, C, and O.

Figure 13. Optical micrograph of Fe sample nitrided at 600°C for 2.5 h at N pressure of 10 torr. Phases shown on micrograph are those formed during diffusion anneal. Subsequent transformations occur on quenching that alter crystal structure but do not alter phase composition.

Figure 14. N profile, measured by the electron probe microanalyzer, in the sample shown in Figure 13.
Multiphase ternary diffusion couples cannot be used to measure diffusion coefficients. However, they can be used to understand interfacial stability and the origin of multiphase products. As an example, in a study by Merchant et al. (51, 52), solid-solid diffusion couples consisted of a common terminal β-NiAl end member and a series of γ-alloys containing Ni-10, 20, 30, 40 at% Cr and pure Ni. These couples were diffused at 1150°C for 49 hours and analyzed with the EPMA.

Microstructure typical of the reaction diffusion zone produced in diffusion couples with various end-member compositions are shown in Figure 15. The β vs. pure Ni and β-Ni10Cr (Figure 15) couples showed an intermediate γ"-layer. The γ"-phase exhibits planar interfaces with both β and γ regions, except in the vicinity of Kirkendall pores and grain boundaries. The β-Ni20Cr (Figure 15b) and β-Ni30Cr couples did not contain any intermediate phases and these bonded producing a planar interface. The β-Ni40Cr couple (Figure 15c) showed an intermediate α-layer with an irregular α-γ interface. The α-phase tended to be laterally associated with regions of β, so that alternate layers of α+β were found touching the γ region. Microprobe data taken across a planar α-γ region in the reaction diffusion zone of the β-Ni40Cr couple (Figure 15c) are shown in Figures 16a and 16b.

Figure 15. Typical microstructures of reaction diffusion zone in β-α couples; heat treated at 1150°C for 49 hours: a) β-NiAl vs. Ni-20Cr, intermediate layer; b) β-NiAl vs. Ni-20Cr, planar β/α interface; c) β-NiAl vs. Ni-40Cr, intermediate layers of α and β (52).
Figure 16. Microprobe data taken across $\beta$ vs. Ni-40Cr diffusion couple annealed at 1150°C for 49 h: a) trace across entire region; b) region near interface (52).

The microprobe data have also been plotted on the 1150°C isothermal section of the Ni-Cr-Al system, Figure 17, to designate the reaction diffusion paths of $\beta$-$\gamma$ couples investigated. The transition from a stable or planar to an unstable or non-planar interface with the systematic variation in Cr-content of one of the end-members of the diffusion couple can be indexed by means of the diffusion paths and phase-equilibrium relationships.
Figure 17. Reaction diffusion paths of the $\beta$-Ni$_{50}$Al vs. $\gamma$-Ni-Cr binary alloy diffusion couples plotted on the 1150°C isothermal section of the Ni-Cr-Al system (52).

Diffusion couples containing Ni$_{20}$Cr and Ni$_{30}$Cr exhibit interfacial compositions that nearly coincide with the $\beta$ and $\gamma$ phase boundaries, indicating that the reaction path follows a tie-line within the $\beta\gamma$ region. Consequently, these couples form a planar interface. Electron microprobe data across the interdiffusion region of the $\beta$-Ni$_{40}$Cr couple (Figures 16, 17) indicate that the reaction path varies smoothly within the $\beta$-phase field, enters the $\alpha$-region and leaves it to vary again within the $\gamma$-phase field. This couple is unable to attain direct $\beta$-$\gamma$ equilibrium, unlike the preceding cases and, the system takes the easiest path available to approach equilibrium, namely through the $\alpha$-phase. A phenomenological description to explain this type of interfacial breakdown is given by Merchant et al. (52). It should be noted, however, that in producing these Ni-Cr-Al diffusion couples, Al transported in the vapor coats the surfaces of the diffusion couple before bonding takes place. In this example, there is a major effect of impurities (Al) during the bonding process on the subsequent diffusion behavior (52).

Roeder et al. (53, 54) have studied diffusion couples of Au-Cu vs. Sn (Cu$_3$Au, CuAu or Cu$_3$Au vs. Sn) to understand the formation of intermediate phases in solder connection in electronic packages. The diffusion couples were heat treated at 170°C for over 200 hours, and resulting Au, Cu and Sn compositions were measured with the EPMA. Two new ternary compounds were found, $\phi$ (25Au-55Cu-20Sn At%) and $\chi$ (33.3At% Au, Cu, Sn) in the diffusion couples.

As an example, Figure 18 shows a backscattered electron micrograph of the resultant Cu$_3$Au vs. Sn diffusion couple, the simplest morphology of the three diffusion couples studied. Two intermediate phases, $\phi$ and $\eta_1$, were formed as essentially planar layers. Perturbations in the layers appearing in the micrograph are attributed to the presence of voids. The EPMA trace along the Cu$_3$Au vs. Sn diffusion couple is shown in Figure 19 and the diffusion path for the couple as plotted onto the isothermal section of the phase diagram at 170°C is shown in Figure 20. The interfaces present between the ternary phase layers in this couple represent regions of two-
Figure 18. Back scattered electron micrograph of a Cu₃Au vs. Sn diffusion couple annealed at 170° for 256 hours.

Figure 19. Electron probe microanalyzer scan across Cu₃Au vs. Sn diffusion couple shown in Figure 18.
phase equilibria. Thus, the dashed portions of the diffusion path represent tie-lines.

The complexity and width of the diffusion zone were found to increase with increasing Au content of the Au–Cu end member. In relation to the application of Pb–Sn solders to Au–Cu alloys, the results indicate that limiting the amount of Au present in the base metal will reduce the number of intermetallic phases produced by elevated temperature service.

V. Summary

The advantages of using EPMA and AEM for compositional analysis of diffusion couples are clear. The techniques are nondestructive, they yield quantitative chemical analyses and can analyze various regions of the same diffusion couple. The analytical electron microscope has only recently been used for diffusion couple analysis. Its primary advantages are enhanced spatial resolution, 100 to 1000X that of EPMA, and the ability to observe the presence of grain boundary effects in the compositional analysis. The technique can yield data to obtain diffusivities as much as 4 to 6 orders of magnitude smaller than those determined with EPMA. Although the thin foil specimen preparation techniques for AEM analysis are very difficult and x-rays of elements below atomic number 11 cannot be routinely measured, it is expected that these problems will be overcome and that AEM will be used routinely for compositional analysis of diffusion couples.

Figure 20. Diffusion path of Cu$_3$Au vs. Sn diffusion couple shown in Figures 18 and 19.
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