The analytical electron microscope (AEM) incorporates an energy dispersive spectrometer (EDS) to detect x-rays from an electron-transparent foil. The combination of a thin foil and a focused high energy electron beam permits a nominal x-ray spatial resolution of $\sim 10-50$ nm. This resolution is two orders of magnitude better than that obtained with bulk specimens in the scanning electron microscope (SEM). In addition, quantification of the x-ray data is relatively straightforward using the ratio method, where the concentration ratio of elements A and B in the thin foil is directly proportional to the x-ray intensity ratio: 

$$\frac{C_A}{C_B} = k_{AB} \left( \frac{I_A}{I_B} \right)$$  \hspace{1cm} (1)

The constant $k_{AB}$ is independent of concentration but varies with the AEM operating voltage and may be determined using standards or by calculation from first principles. The AEM instrument is used in numerous materials applications. This paper will illustrate a wide variety of examples where the instrument is of particular use.

1. Study of Precipitate-Free Zones in Al-Ag (1)

The occurrence of precipitate-free zones (PFZ) around grain boundaries in aged Al-based alloys has been attributed to solute depletion due to grain boundary precipitation, or vacancy depletion. In Al-Ag alloys two distinct zones free of the metastable $\gamma'$ precipitate are observed (Fig. 1): a wide 'grey' PFZ (GPFZ), and a narrow ($\sim 500$ nm wide) 'white' PFZ (WPFZ) immediately adjacent to the grain boundary. A typical TEM microstructure of an aged alloy is shown in Fig. 1,

![Fig. 1: A typical microstructure of a Al-16 wt% Ag sample aged at 433 K for 50 hrs.](image)

![Fig. 2: (a) AEM concentration profile across a grain boundary WPFZ for a sample aged at 433 K for 50 hrs. (b) AEM concentration profile across a GPFZ in the grain boundary region.](image)
exhibiting a well-defined WPFZ and GPFZ. Solute concentration profiles were measured using an electron-beam diameter of 5 nm. X-ray data were analyzed using equation (1). The results (Fig. 2) indicate that the WPFZ is caused by marked solute depletion (Fig. 2a) and the GPFZ by vacancy depletion (Fig. 2b). The solute content of the GPFZ is equal to that of the bulk. Therefore both solute depletion and vacancy depletion mechanisms explain the formation of PFZ in this system.

2. Early Stage Growth of the Ni$_3$Al Intermediate Phase in Ni-NiAl Diffusion Couples (2)

The major experimental techniques used during the past decade to study the kinetics of interdiffusion and intermediate phase growth have been the optical microscope and the electron microprobe. Because both of these techniques have spatial resolution limits of $\sim 1 \mu m$, it has not been possible to examine early growth kinetics. For example there is little or no information available on the kinetics and/or morphology of Ni$_3$Al layer growth for times $< 3$ hrs.

Figure 3 is a typical microstructure showing the growth of Ni$_3$Al in a Ni-NiAl diffusion couple produced at 1100°C. The protrusions in the Ni$_3$Al phase are always associated with grain boundaries in the Ni$_3$Al layers since grain boundary diffusion significantly contributes to Ni$_3$Al layer growth below 1100°C.

AEM profiles obtained across the diffusion interfaces are shown in Fig. 4. To obtain the upper data set in Fig. 4 the data were corrected

Fig. 3: TEM micrograph of an Ni$_3$Al layer protrusion associated with a single Ni$_3$Al grain boundary.

Fig. 4: AEM profiles for a specimen held at 1100°C for 15 minutes.
for x-ray absorption effects (3). The equilibrium concentrations at the appropriate two-phase boundaries at 1100°C are shown in Fig. 4. The data obtained at the interfaces appears consistent with the interface concentrations predicted from phase equilibria. It thus appears that interfacial equilibrium is established even at very short times.

3. Chemical Identification of Submicron Particles in Steel Weld Metal

The complexity of the variables that affect the welding process make it difficult to determine the relationship between the microstructure and the mechanical properties of welds. Interpretation of the significance of microstructural differences has been limited by the lack of localized chemical information. However AEM, in combination with optical and scanning microscopy can overcome some of these problems.

The identification of submicron particles in pressure vessel steel weldments is of particular interest because of their effect on mechanical properties. Fig. 5a shows a TEM image of precipitates in such a weldment. The EDS spectrum of the precipitates, Figure 5b, taken in the AEM shows large amounts of Si and Mn indicating that the precipitates are silicates, responsible for poor impact properties. If such precipitates are analyzed in bulk specimens using the SEM the matrix Fe will so dilute the EDS spectrum that silicate identification is impossible.

Fig. 5:(a) TEM image showing the presence of precipitates characteristic of G80 weldments. (b) EDS spectrum from matrix precipitates in Fig. 5(a).

4. Low Temperature Diffusivity Measurements

In Fe-Ni alloys, a knowledge of the diffusivity of Ni in Fe-Ni (D_Ni) below 800°C is necessary to model the growth of ferrite in austenite. Experiments that report D_Ni values have been carried out only above 1000°C. Simulation of ferrite growth therefore requires a considerable downward extrapolation of high temperature diffusivity data. Diffusion distances obtained for temperatures < 1000°C and for times < one month are smaller than the spatial resolution of the EPMA. Because of the improved resolution of the AEM, diffusion profiles that are 40 times as small as those necessary for the EPMA technique can be measured at temperatures down to 750°C.
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Fig. 6 shows three profiles in an Fe-10.4 wt% Ni/Fe-15.5 wt% Ni diffusion couple. In Fig. 7 the measured $D_Ni^v$ values are compared with other high temperature data. The diffusivities agree well with the extrapolated values of the high temperature data.

In summary the AEM can be used for a large number of materials applications. With improved specimen preparation techniques higher beam currents and higher operating voltages, we may eventually have even better x-ray resolution than is available on our present AEM instruments.

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