Analytical electron microscopy of aluminium alloys

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Abstract. X-ray microanalysis and electron energy loss spectroscopy of thin foils constitute the important techniques of high resolution chemical analysis using the electron microscope. The technique of x-ray microanalysis is discussed in this paper with particular emphasis on the study of aluminium alloys using a dedicated scanning transmission electron microscope (STEM).

The principle of determining chemical composition from observed x-ray peak intensities including the absorption of x-rays and beam broadening in thin foils are considered. The accuracy of peak intensity measurement and detection limits in x-ray microanalysis are illustrated with reference to Al-Mn alloys. The Cliff-Lorimer (k) factors for manganese, iron and copper with respect to aluminium were obtained from standard samples. Identification of phases in 1100 and 1200 aluminium and 3008 (Al-Mn-Zr) alloy were carried out from measured intensities of x-ray peaks. The experimental results emphasize the value of developing techniques for extracting the particles from the aluminium matrix. The transition phases formed in Al-6 % Zn-3 % Mg and Al-4 % Cu were investigated by micro-diffraction and x-ray microanalysis.

Keywords. High resolution analysis; x-ray microanalysis; aluminium alloy; phase identification; metastable phases.

1. Introduction

High resolution chemical analysis of thin foils examined in the electron microscope is carried out by the detection and quantitative characterization of x-rays and inelastically scattered electrons. X-ray microanalysis involves the detailed study of the energy (or wavelength) and intensity of characteristic x-rays while electron energy loss spectroscopy is concerned with the determination of characteristic energy losses suffered by the primary electrons as they pass through the specimen. The energy loss arises from a number of excitation processes amongst which electrons causing plasmon excitation and inner shell ionization are useful in providing chemical information. The important parameters in chemical analysis are the intensity of signals arising from the interaction of the electron beam with the specimen and the volume of the specimen from which these signals are excited. The former influences the accuracy and sensitivity of analysis while the latter determines the spatial resolution. High sensitivity and high resolution chemical analysis, therefore, requires the use of a high intensity small diameter electron probe. This is obtained by the use of a scanning attachment to the TEM or a dedicated STEM. The use of a highly convergent probe also allows the formation of micro-diffraction patterns which provide crystallographic information from regions of the specimen illuminated by the probe.

Figure 1. Relationship between beam current and beam diameter in the HB5 STEM.

The dedicated STEM makes use of a field emission gun. The gun brightness of this source is high ($\sim 10^{13}$ A/m²/Sr) and it is thus possible to form an extremely fine probe carrying enough current to excite detectable signals from the specimen. The relationship between beam current and beam diameter in the VG HB5 STEM is shown in figure 1 (Williams 1980). A probe of ~ 2 – 5 nm diameter carries a current of ~ 5 nA sufficient to produce significant signal count rates. It should, theoretically, be possible to carry out chemical analysis with the same spatial resolution as the probe size. However, complications due to beam broadening (to be discussed later) affect the resolution. Microdiffraction patterns can be obtained from regions of ~ 2 nm diameter using the fine probe of the dedicated STEM. This topic has been covered at length by Cowley (1982) at this conference.

The principles of x-ray microanalysis are considered briefly in this paper followed by experimental results on phase identification and the nature of metastable phases in aluminium-base alloys.

2. Theoretical principles

2.1 The ratio technique

X-ray microanalysis involves the measurement of the intensity I_A of a characteristic x-ray peak and relating it to the total number of atoms, N_A , in the irradiated volume of the specimen exciting this particular radiation. I_A and N_A are related by the expression (Joy 1981),

$$I_A = I_0 N_A Q_A a_A w_A F, \quad (1)$$

where I_0 is the incident electron intensity, Q_A is the scattering cross-section for x-ray excitation, w_A is the fluorescent yield, a_A is the ratio of the number of $K\alpha$ (or $L\alpha$) x-ray photons to the sum of the total number of photons of the K (or L) series and F is the detection efficiency. It is assumed in (1) that the sample is so thin that absorption and fluorescence effects can be neglected. These two assumptions constitute the thin film criterion. N_A can be expressed in terms of the weight fraction C_A , atomic weight of A , A_A , thickness t of the foil and ρ the density of the foil—(1) can then be written as

$$I_A = \frac{(\text{Constant}) (C_A Q_A a_A w_A F)}{A_A}. \quad (2)$$

If the intensities of two peaks due to elements *A* and *B* are simultaneously measured, the intensity ratio can be expressed by the equation,

$$\frac{I_A}{I_B} = \frac{C_A Q_A a_A w_A A_B}{C_B Q_B a_B w_B A_A} = \frac{C_A}{C_B} (k_{AB})^{-1}, \quad (3)$$

where k_{AB} (commonly referred to as the Cliff-Lorimer factor) is a constant independent of sample thickness, orientation and composition but dependent on accelerating potential. Equation (3) forms the basis of the ratio technique for the determination of composition from observed intensity ratio of the peaks (Philibert and Tixier 1968; Cliff and Lorimer 1975).

2.2 Absorption of x-rays

The thin beryllium window, the gold contact layer and the inactive silicon layer on the detecting crystal can absorb a significant proportion of the incident x-rays (particularly the soft x-rays). A correction for absorption in the beryllium window can be made by using the expression,

$$\frac{I_A}{I_B} = \frac{C_A Q_A w_A a_A A_B}{C_B Q_B w_B a_B A_A} \left[\frac{\exp - (\mu/\rho)_{Be}^B \rho_{Be} t_{Be}}{\exp - (\mu/\rho)_{Be}^A \rho_{Be} t_{Be}} \right], \quad (4)$$

where $(\mu/\rho)_{Be}^A$ and $(\mu/\rho)_{Be}^B$ are the mass absorption coefficients of the characteristic x-rays in beryllium, ρ_{Be} is the density of beryllium and t_{Be} the thickness of the window (typically 7 μm).

When the thin film criterion is not valid, absorption correction can be made by the use of the expression (Tixier and Philibert 1969; Goldstein *et al* 1977)

$$\frac{C_A}{C_B} = k_{AB} (I_A/I_B)_{TK} \left[\frac{(\mu/\rho)_{sp}^A}{(\mu/\rho)_{sp}^B} \right] \left[\frac{1 - \exp - (\mu/\rho)_{sp}^B \rho t \cos \psi}{1 - \exp - (\mu/\rho)_{sp}^A \rho t \cos \psi} \right] \quad (5)$$

where $(\mu/\rho)_{sp}^A$ and $(\mu/\rho)_{sp}^B$ are the mass absorption coefficients of the characteristic x-rays in the specimen, ρ is the specimen density, t is the specimen thickness and ψ is the x-ray take-off angle. In the VG HB5 STEM ψ varies from 15 to 42 depending on the use of the non-tilt—or double tilt cartridge. The ratio $(I_A/I_B)_{TK}$ measured in thick specimens defines the constant K_{AB}^{thick} which is related to K_{AB} by the expression,

$$\frac{C_A/C_B}{(I_A/I_B)_{TK}} = K_{AB}^{thick} = K_{AB} \left[\frac{(\mu/\rho)_{sp}^A}{(\mu/\rho)_{sp}^B} \right] \left[\frac{1 - \exp - (\mu/\rho)_{sp}^B \rho t \cos \psi}{1 - \exp - (\mu/\rho)_{sp}^A \rho t \cos \psi} \right] \quad (6)$$

The ratio of K_{AB}^{thick} to K_{AB} is plotted in figure 2 for the compounds Al_6Mn , Al_2Cu and Al_3Fe using the data for mass absorption coefficients from Heinrich (Heinrich 1966). The absorption correction is significant when the thickness exceeds ~ 200 nm and also for low take-off angle.

2.3 Beam broadening effects

The spatial resolution for x-ray microanalysis is influenced by the probe size and the broadening of the probe in the specimen. Goldstein *et al* (1977) have considered elastic scattering of a point source of electrons by atomic nuclei at the middle of the foil and

Figure 2. Relationship between $K_{AB}^{\text{thick}}/K_{AB}$ and thickness of the foil for Al_6Mn , Al_3Fe and Al_2Cu . The effect of varying the take off angle is illustrated for Al_6Mn .

arrived at the following expression for beam broadening (b)

$$b = 625 (Z/E) (\rho/A)^{1/2} t^{3/2} \quad (7)$$

where b and t are in cm and Z is the atomic number. A plot of beam spread against thickness is shown in figure 3 for aluminium. When the specimen thickness exceeds 200 nm, the spatial resolution for chemical analysis is ~ 30 nm. It is, therefore, clear that the advantage of using a fine probe as in the STEM may be counteracted by the use of relatively thick specimens. Beam spread has also been determined by using Monte-Carlo calculations (Keyser 1979) involving the simulation of individual electron trajectories. The results obtained are in excellent agreement with those predicted in (7) when the specimen thickness is less than 100 nm.

2.4 Precision and detection limits

The error in estimating the net intensity of an x-ray peak, I_A^n , can be expressed by the standard deviation, $\sigma(I_A^n)$, as

$$\sigma(I_A^n) = (I_A^t + I^b)^{1/2} \quad (8)$$

where I_A^t represents the total intensity collected in a predefined energy window and I^b is the background intensity. The relative error ε for 95% confidence limit can be expressed as

$$\varepsilon = \frac{2\sigma(I_A^n)}{I_A^n} = 2 \left[\frac{1}{I_A^n} \left(1 + \frac{2}{P/B} \right) \right]^{1/2}, \quad (9)$$

Figure 3. Variation of beam spread with foil thickness using the elastic scattering approximation.

where P/B is the net peak to background intensity ratio. The total relative error in the measurement of net intensities of two characteristic peaks ε_{AB} is then given by

$$\varepsilon_{AB} = 2 \left[\frac{1}{I_A^n} \left\{ 1 + \frac{2}{(P/B)_A} \right\} + \frac{1}{I_B^n} \left\{ 1 + \frac{2}{(P/B)_B} \right\} \right]^{1/2}. \quad (10)$$

The total relative error in the measurement of peak intensities of manganese and aluminium is plotted in figure 4 as a function of peak to background ratio, for two values of aluminium peak intensities. The relative error is large ($\sim 13\%$) for an aluminium count of 1000. A counting time of 100 sec gives rise to peak intensities of aluminium of ~ 10000 in the HB5 STEM; under these circumstances the error in peak intensity measurement is $\sim 4\%$.

The sensitivity limits for chemical analysis are defined by the minimum detectable mass (MDM) and minimum mass fraction (MMF). MDM represents the sensitivity in analyzing fine particles on extraction replicas or sputtered thin films. It is inversely proportional to the x-ray count time and electron current density. The electron current density in STEM is 10^4 A/cm² for a 10 nm probe (Oppolzer and Knauer 1979). This is about 2 to 3 orders of magnitude larger than that obtained with a conventional tungsten filament. Hence the MDM is much smaller in the STEM. The minimum mass fraction is a measure of the sensitivity of detecting one element in the presence of another. It is important in analyzing precipitates or composition gradient. MMF is limited by the continuous radiation arising from the excited volume. In order to distinguish a peak from the background the peak intensity I_A must be greater than

Figure 4. Dependence of the total relative error in the measurement of peak intensities on the peak to background (P/B) ratio. The mean value of 0.35 is used in the calculations for $I_{\text{MnK}\alpha}/I_{\text{AlK}\alpha}$.

$3(2I_A^b)^{1/2}$ where I_A^b is the background intensity in the energy region containing the peak of element A . Hence MMF can be expressed as,

$$(C_A/C_B)_{\min} = k_{AB} \frac{3(2I_A^b)^{1/2}}{I_B^n}. \quad (11)$$

Assuming that $I_B^b \approx I_A^b$ (i.e. a constant background in the energy interval containing the peaks due to A and B),

$$(C_A/C_B)_{\min} = 3(2I_B^n \cdot P/B)^{-1/2} k_{AB}. \quad (12)$$

Using (12) the minimum weight fraction of manganese detectable in aluminium is plotted in figure 5 for total counts of aluminium of 5000, 10000 and 50000 as a function of peak to background ratio. A value of 0.97 is used in the calculations for $k_{\text{Mn-Al}}$. For typical P/B values of 50–100 and total aluminium counts exceeding 10000, the minimum detectable weight fraction of manganese in aluminium is ~ 0.2 – 0.4% .

Figure 5. Variation of the minimum weight fraction of Mn detectable in Al with the peak to background ratio.

3. Experimental procedure

Cliff-Lorimer factors have been measured on a set of standard Al-Mn, Al-Fe and Al-Cu alloys supplied by the Alcan Laboratories, Kingston. Phase identification has been carried out on cold-rolled ($\sim 90\%$) and annealed (at 873 K) 1100 Al, 1200 Al and 3008 aluminium alloy. The composition of these alloys and the treatments given are shown in table 1. The nature of metastable phases has been studied in Al-6% Zn-3% Mg and Al-4% Cu alloys. Details of thermal treatments to which these alloys were subjected are also shown in table 1. The samples were chemically thinned in a mixture of orthophosphoric acid, sulphuric acid and nitric acid followed by electropolishing in a Struers Tenupol unit using methanol (90% by vol) and perchloric acid (10% by vol). They were heated for 300 sec at 373 K in the prevacuum of the STEM prior to examination. X-ray spectra were obtained from the phases using a typical count time of 100 sec.

The results of x-ray microanalysis can be complicated by surface films on thin foils or the appearance of 'systems peaks'. Surface films lead to abnormal intensity ratio near the edge of the foil. This effect has been observed in a number of aluminium-base alloys.

Table 1. Composition and thermal treatment of aluminium alloys.

System	Composition	Treatment
1100 Al	Fe 0.55 % Si 0.15 % Al 99.0 % min.	Hunter cast — Cold rolled 90 % annealed at 873 K for 1 h
1200 Al	-do- + small amount of chromium	-do-
3008 alloy	Mn 1.38 %, Fe 0.46 % Si 0.12 %, Zr 0.29 % Cu 0.09 %, Ti 0.016 % balance Al.	-do-
Al-Zn-Mg	Al-6 % Zn-3 % Mg	Solution treated at 748 K 1 hr quenched to 473 K for 1 min. and then maintained at 294 K for 1 min., aged at 448 K
Al-Cu	Al-4 % Cu	Solution treated at 798 K for 24 hr in vacuum, quenched in water and aged at 513 K for 4 h.

Careful examination of the standard samples and commercial aluminium alloys reveal no significant difference in intensity ratio at the foil edge. The origin of 'systems peaks' and the methods of minimizing them are discussed in detail by Zaluzec (1979), X-ray counts from holes present in the particles show that the total hole count is less than 1% of that measured in the thinnest region of the particle—consequently complications due to system peaks can be ignored.

4. Results

4.1 Determination of K values

The microstructure of the standard Al-Mn and Al-Cu alloys and the x-ray spectra from the particles are presented in figures 6 and 7. The Al-Mn alloy reveals irregularly-shaped particles while those in Al-Cu are in the form of discs or are irregularly shaped. The intensity ratio, $I_{\text{MnK}\alpha}/I_{\text{AlK}\alpha}$ is constant in the various regions of the particle and also for a large number of particles. The mean value of the intensity ratio is 0.35 ± 0.01 . Selected area diffraction patterns obtained in the TEM and STEM reveal that these particles are Al_6Mn . These two results are used to obtain a k value (the Cliff-Lorimer factor) of 0.97 ± 0.03 . The results obtained from the Al-Cu and Al-Fe alloys show considerable scatter possibly because of the fact that the particles do not occupy the entire thickness of the foil. Analysis of selected area diffraction patterns indicates that the particles are CuAl_2 and FeAl_3 . The k values obtained in this study are presented in table 2 along with other available data based on theoretical calculations and experimental measurements. The results are in good agreement with the theoretical calculations by Goldstein *et al* (1977) and Zaluzec (1979) and experimental measurements of Cliff and Lorimer (1975) and Woods *et al* (1981).

Figure 6. a. Typical STEM micrograph of Al_6Mn particle in the standard Al-Mn alloy. b. X-ray spectrum from the particle showing AlK, MnK α and MnK β peaks.

4.2 Phase identification

Commercially pure aluminium contains the following binary and ternary phases (Porter and Westengen 1981); Al_3Fe (monoclinic), Al_6Fe (C-centred orthorhombic), Al_mFe (body-centred tetragonal), Al_2Fe (unknown structure characterized by highly irregular diffraction patterns), $\alpha\text{-AlFeSi}$ (b.c.c.), $\alpha'\text{-AlFeSi}$ (hexagonal), $\alpha''\text{-AlFeSi}$ (tetragonal) and $\beta'\text{-AlFeSi}$ (monoclinic).

X-ray spectra from one of the particles and the matrix in 1200 aluminium are shown in figure 8. The particle shows prominent peaks due to Al, Si, Cr and Fe. Several particles show only Al, Cr and Fe peaks. The intensity ratios, viz $I_{\text{SiK}\alpha}/I_{\text{AlK}\alpha}$, $I_{\text{CrK}\alpha}/I_{\text{AlK}\alpha}$ and

Figure 7. a, b. Typical STEM micrograph of CuAl₂ particles in the standard Al-Cu alloy. c. x-ray spectrum from one of the CuAl₂ particles showing AlK α , CuK α and CuK β peaks; the small peak to the left of aluminium is probably due to noise in the system.

Table 2. Cliff-Lorimer (*k*) factor for Mn, Fe and Cu with respect to Al.

System	Present work	<i>k</i> values				
		Goldstein <i>et al</i> (1977)	Zaluzec (1979)	Schreiber and Wims (1981)	Cliff and Lorimer (1975)	Woods <i>et al</i> (1981)
Mn-Al	0.97 ± 0.03	1.17	1.23	0.67	0.86	1.20
Fe-Al	1.15 ± 0.1	1.19	1.28	0.78	0.89	1.16
Cu-Al	1.60 ± 0.15	1.42	1.60	0.96	1.11	1.42

Figure 8. X-ray spectra from **a.** a particle in 1200 aluminium showing AlK, SiK, CrK α , FeK α and FeK β peaks and **b.** the matrix showing only the AlK peak.

$I_{\text{FeK}\alpha}/I_{\text{AlK}\alpha}$ show considerable scatter possibly due to improper orientation of the foil with respect to the electron beam and due to the fact that the particles do not occupy the entire depth of the foil. This problem has been overcome by carrying out x-ray microanalysis on the particles sticking to the edge of the foil (figure 9). Analysis from these particles should minimize contribution from the aluminium matrix. The results of analysis from 4 different regions of the particle in figure 9 are summarized in table 3. The SiK α to AlK α and CrK α + FeK α to AlK α intensity ratio are about the same; it is to be noted that CrK α + FeK α to SiK ratio is also nearly the same. Another method of overcoming this problem is to extract the particles using a mixture of 8-hydroxy quinoline, methanol, chloroform and benzoic acid (Cogan *et al* 1978; Hodgson and Parker 1981). This method is currently being tried for the extraction of particles. Two typical x-ray spectra from particles in 1100 aluminium are shown in figures 10a, b

Figure 9. Typical STEM micrograph of a particle in 1200 aluminium sticking to the edge of the foil.

Table 3. Intensity ratio from various regions of the particle shown in figure 9.

Region	Ratio		
	$I_{\text{SiK}\alpha}/I_{\text{AlK}\alpha}$	$I_{\text{CrK}\alpha}/I_{\text{AlK}\alpha}$	$I_{\text{FeK}\alpha}/I_{\text{AlK}\alpha}$
1	0.13	0.05	0.43
2	0.12	0.05	0.44
3	0.14	0.07	0.43
4	0.16	0.10	0.46

revealing prominent peaks due to Al, Fe, Mn and Cu; convergent beam diffraction pattern obtained from the second particle is shown in figure 10c, the pattern corresponds to cubic AlFeSi . The intensity ratio obtained for particles showing Al and Fe peaks matches well with that obtained for Al_3Fe in the standard Al-Fe alloy. A few CuAl_2 particles have also been identified.

Typical microstructures of the constituents in the 3008 alloy are shown in figure 11a, b and the diffraction pattern from one of these particles in figure 11c. The pattern corresponds to Al_6Mn . It was not possible to identify any coarse zirconium-rich particles by diffraction. Typical x-ray spectra from the particles are shown in figure 11d, e with prominent Al and Mn or Al, Mn and Fe peaks. The ratio of Fe + Mn to Al intensity is constant within the limits of experimental error for a large number of particles irrespective of their morphology. The x-ray spectrum from the matrix shows only an aluminium peak (figure 11f). Careful examination of the sample reveals very fine zirconium-rich particles; a typical micrograph is shown in figure 12a and the x-ray spectrum in figure 12b revealing prominent $\text{AlK}\alpha$ and $\text{ZrL}\alpha$ peaks. The intensity ratio of zirconium to aluminium is 0.22.

Figure 10. X-ray spectra from particles in 1100 aluminium showing **a.** AlK α , FeK α and FeK β peaks and **b.** AlK α , SiK α , MnK α , FeK α , FeK β , CuK α and CuK β peaks, **c.** Convergent beam diffraction pattern from the particle in (b).

4.3 Formation of metastable phases

The transition phases formed in the Al-Zn-Mg and Al-Cu alloys were investigated by x-ray analysis and microdiffraction. Figure 13 is a bright field micrograph of metastable phases in Al-Zn-Mg formed by step quenching. The needles form along the $\langle 100 \rangle$ directions of Al. The selected area diffraction pattern from the area is shown in figure 13(a) while figure 13b, c, d represent microdiffraction patterns from the precipitate at approximate illumination half angles (α) of 8, 4 and 1.7 mrad respectively. The compositional difference between the metastable and equilibrium precipitates is clearly brought out in figure 14. The micrograph shows both needle-like metastable precipitates (marked as 2) and equilibrium precipitates (marked as 1) η -MgZn₂. The x-ray spectrum from the equilibrium precipitates shows ZnL α and AlK α peaks. The difference in the relative enrichment of the peaks is evident.

(a)

(b)

(c)

Figure 11. a, b. Microstructures of particles in the 3008 alloy. c. SAD pattern from one of the particles, Al_6Mn beam direction $[112]$. d, e. X-ray spectra from the particles showing $AlK\alpha$, $MnK\alpha$ and $K\beta$ and $FeK\alpha$ and $K\beta$ peaks. f. X-ray spectrum from the matrix showing only the $AlK\alpha$ peaks.

Figure 12. a. STEM micrograph of zirconium-rich particles in the 3008 alloy b. X-ray spectrum from one of the particles in (a) showing AlK α and ZrL α peaks.

Figure 13. Bright field micrograph of the metastable phase in Al-Zn-Mg alloys. **a.** SAD pattern from the precipitate. **b-d.** Convergent beam diffraction patterns with illumination half angles of 8, 4 and 1.7 mrad respectively.

Figure 14. X-ray spectra from the equilibrium (marked 1) and metastable (marked 2) precipitates in Al-Zn-Mg alloys.

Figure 15a.

Figure 15b.

Figure 15. a. θ' platelets in Al-Cu alloy; the inset shows micro-diffraction pattern from the region indicated with illumination half angle of 1.7 mrad. b. θ' precipitates viewed with beam direction close to matrix [110] and microdiffraction patterns from one of the platelets. c. θ' platelets viewed normal to the large faces; SAD pattern obtained from a region of ~ 10 nm diameter using zero objective lens excitation current.

θ' platelets in Al-4% Cu alloys are shown in figure 15. The matrix has a cube orientation with a single θ' precipitate viewed edge on. The inset microdiffraction pattern has been obtained from the region indicated using α of 1.7 mrad. An array of θ' precipitates viewed θ' with beam direction close to matrix $[110]_a$ is shown in figure 15b. The microdiffraction pattern obtained from an approximately 3 nm area centred on a θ' platelet at the portion indicated using α of 1.7 mrad is shown in the figure 15b. Figure 15c shows a stack of θ' platelets viewed normal to their large faces. The SAD pattern was taken at the position shown from an isolated θ' platelet using zero objective lens excitation. The beam diameter in the plane of the specimen in this mode is ~ 10 nm. The θ' reflections are seen near the forbidden (110) matrix reflections.

5. Conclusions

(i) The principles of x-ray microanalysis using the dedicated STEM are presented in this paper with particular emphasis on absorption correction to be applied when examining particles, beam broadening in foils of aluminium, precision of intensity measurements and detection limits; (ii) Hole count measurements indicate that the systems background effect can be ignored while examining the specimens in the VG HB5 STEM. (iii) The Cliff-Lorimer factor for converting the observed intensity ratio into weight fraction ratio has been measured for Mn, Fe and Cu with Al as the base as 0.97 ± 0.03 , 1.15 ± 0.1 and 1.60 ± 0.15 respectively. These values are in good agreement with other experimental measurements and theoretical calculations. (iv) The peak intensity ratio obtained from a number of particles show a wide scatter possibly due to the contribution from the aluminium matrix. However, consistent results are obtained when particles at the edge of the foil are considered. The results also focus on the necessity of carrying out x-ray microanalysis on extracted particles. (v) The following phases have been identified in 1100 and 1200 Al and 3008 alloys: Al_3Fe , cubic $AlFeSi$, $CuAl_2$, Al_6Mn and possibly $ZrAl_3$. (vi) Microdiffraction and x-ray microanalysis have been used to study the structure and composition of metastable phases in Al-Cu and Al-Zn-Mg alloys.

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References

- Cliff G and Lorimer G W 1975 *J. Microsc.* **103** 203
- Cogan S F, Gayle F W, Klein J D, Cocks F H and Shepard M L 1978 *J. Mater. Sci.* **13** 2687
- Cowley J M 1982 *National Seminar on high resolution and analytical microscopy* (Kalpakkam)
- Goldstein J I, Costley J L, Lorimer G W and Read S J B 1977 (ed) O Johari (Chicago: IITRI) p. 315
- Heinrich K F J 1966 *The electron microprobe* (eds) T D McKinley, K F J Heinrich and D B Wittry (New York: Wiley) p. 296
- Hodgson P and Parker B A 1981 *J. Mater. Sci.* **16** 1343
- Jones I P and Loretto M H 1981 *J. Microsc.* **124** 3
- Joy D C 1981 *J. Microsc.* **124** 37

- Keyser D F 1979 *Introduction to analytical electron microscopy* (eds) J J Hren, J I Goldstein and D C Joy (New York: Plenum Press) p. 199
- Oppolzer H and Knauer V 1979 *Scanning electron microscopy* (ed) O Johari (Chicago: SEM Inc) 111
- Philibert J and Tixier R 1968 *J. Appl. Phys.* **1** 685
- Porter D A and Westengen H 1981 *Quantitative microanalysis with high spatial resolution* (London: Metals Society) p. 94
- Schreiber T P and Wims A M 1981 *Ultramicroscopy* **6** 323
- Tixier R and Philibert J 1969 *Proc. 5th int. conf. on x-ray optics and microanalysis* (eds) G Mollestedt and K H Garukler (Berlin: Springer Verlag) p. 180
- Williams P M 1980 *Chem. Phys. Solid Sur.* **8** 84
- Woods J, Williams D B and Goldstein J I 1981 *Quantitative microanalysis with high spatial resolution* (London: The Metals Society) p. 24
- Zaluzec N J 1979 *Introduction to analytical electron microscopy* (eds) J J Hren, J I Goldstein and D C Joy (New York: Plenum) p. 121