The use of electron microbeam techniques in metallurgical analysis

by L. Andrews*

Journal Paper

Synopsis

Electron microbeam analysis of metallurgical samples covers a broad field and has applications in the areas of minerals processing, hydrometallurgy, pyrometallurgy, physical metallurgy and corrosion.

Some idea of the possibilities of microbeam techniques can be illustrated by examining the following example of a run of mine gold ore sample. Milling and bulk chemical analysis of the ore will provide major and minor element analysis as well as the gold grade. More detailed chemistry can also reveal the presence of trace elements that may be advantageous or deleterious to downstream processing. Electron microbeam analysis can provide additional information in the form of size, liberation, association and composition of the gold, the percentage of refractory gold, the size, liberation, association and composition of enclosing sulphide or arsenide phases and the levels and association of the trace elements that may affect processing. In most cases electron microbeam analysis complements bulk chemistry, and does not replace it. Both techniques should be used in parallel for maximum effect.

This paper touches on the origin and history of electron microbeam techniques, as well as the theory behind microbeam analysis and processing. The more common types of instruments and their applications will also be dealt with briefly.

Introduction

Mosely first discovered, in 1913, that the frequency of emitted X-radiation excited by an electron beam is a function of the atomic number of the analysed element. This discovery led to the development of spectro-chemical analysis. The forerunners of the electron microanalysers of today, however, were invented only during the nineteen fifties. The electron microprobe was developed in parallel by Castaing and Guinier in France and by Borovski in Russia, but Castaing's design was the basis of modern microanalysers. The initial area of analysis was brought down from over 1 mm^2 to less than 2 μm^2, as it is today. In 1956 Cosslett and Duncumb invented the scanning electron microprobe, where a beam of electrons could be scanned across an area of a sample. This, in turn, led to the development of the electron microprobe with both scanning and point analysis capabilities that we know today.

Essentially, all electron microbeam instruments operate by the production of a beam of electrons from a filament in a vacuum (i.e. an electron gun). The electron beam leaves the gun and is accelerated and focused by a series of electromagnetic lenses while passing down an evacuated column. The electrons eventually strike the surface of the sample to be analysed and may travel through a thin sample (transmitted electron microscopy) or react with a thicker sample to produce several kinds of reflected radiation.

Transmission electron microscopy involves imaging at high magnification and the use of high accelerating voltages. Although most commonly used for medical or biological applications, the transmission electron microscope (TEM) is also used for certain metallurgical applications. These include the examination of thin foils and surfaces reproduced as replicas. Occasionally energy dispersive X-ray analysers are attached to the TEM to allow phase identification (see EDX analysis).

When an electron beam strikes a solid sample too thick to allow electron transmission, secondary, backscattered and Auger electrons are excited close to the surface. In addition, characteristic X-radiation is generated to a depth of approximately 2 µm (depending on the sample composition and the accelerating voltage of the electron beam). Emitted radiation is shown in Figure 3.

Emitted radiation may be processed in point or scanning mode to provide information on the phase analysed, by imaging and/or microanalysis.

* *Anglo Research.*

© *The Southern African Institute of Mining and Metallurgy, 2007.* *SA ISSN 0038–223X/3.00 + 0.00. This paper was first published at the SAIMM Workshop,* Analytical challenges in Metallugy, *23–24 November 2006*

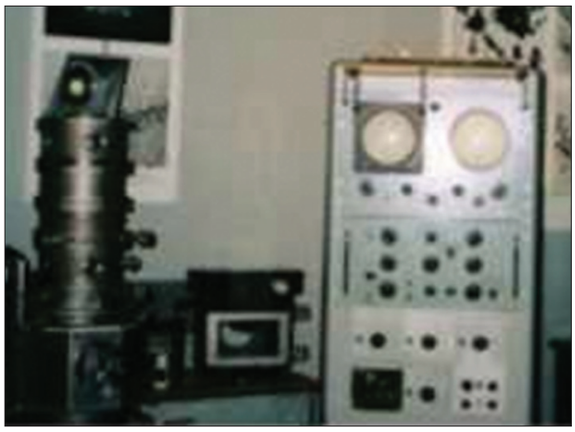

Figure 1—Early electron microprobe developed by Duncumb in 1956

Figure 2—The scanning electron microanalyser as produced by Duncumb and Metford in 1958

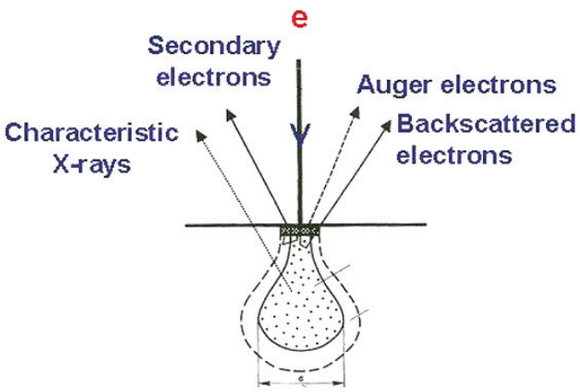

Figure 3—Radiation emitted from a solid sample when struck by an electron beam. Adapted from Viljoen and Johnson (1983)

Secondary electron imaging (SEI) is used to produce topographic images, which provide information on surface contours or crystal morphology. Backscattered electron imaging (BEI) or 'compo' mode reveals the relative density of the phases imaged because the BEI intensity is proportional to the atomic weight of the phase under the beam. Examples of SEI and BEI scans are shown in Figures 4 and 5.

Auger electron spectroscopy (AES) is a surface technique performed under very high vacuum. Solid samples can be analysed by removal of thin layers of sample by ion sputtering, electron beam irradiation, and processing of emitted Auger electrons. This is known as a depth profile. The detection limit of trace elements analysed by this technique is very low. Metallurgical applications in this area are mainly flotation or leaching related.

The characteristic X-radiation produced by electron-specimen interaction can be processed in point mode by energy-dispersive or wavelength-dispersive X-ray analysis.

Energy-dispersive X-ray (EDX) analysis is the most commonly used electron microbeam technique in metallurgy and finds applications in the fields of minerals processing, hydrometallurgy, pyrometallurgy, physical metallurgy, corrosion studies and forensics.

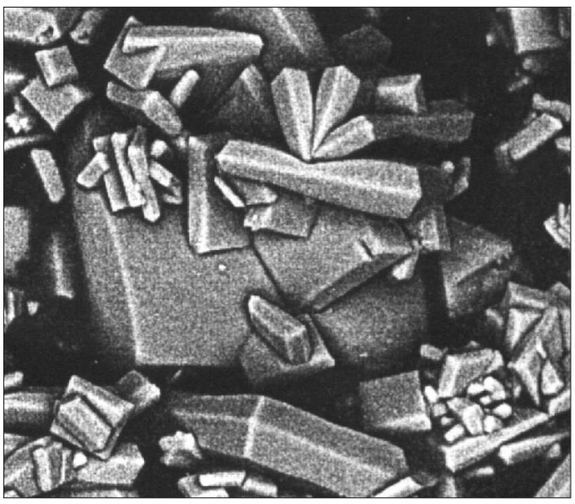

Figure 4—SEI showing crystal form

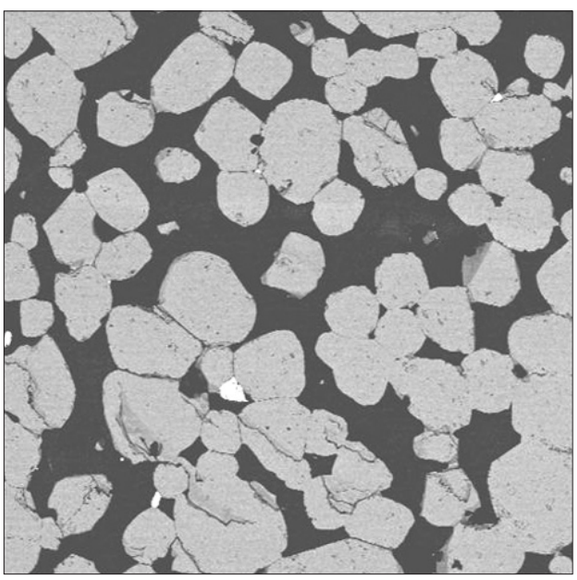

Figure 5—BEI of chromitite showing relative phase density by intensity

EDX analysis involves the rapid simultaneous acquisition of all elements present under the beam heavier than lithium. This is the most easily available form of electron microbeam analysis, and is similar to bulk XRF determination, but phase specific. EDX detectors are found on most scanning electron microscopes (SEM's) and were historically identified by the attached liquid nitrogen dewar. Modern detectors, however, are liquid nitrogen free. The advantages of EDX analysis are speed—especially important for quick phase identification, and for automated techniques —and versatility. An SEM (or microprobe) can be set up to run qualitative EDX analysis, or quantitative EDX analysis when standards are used. The main limitations of EDX analysis are relatively poor spectral resolution and high detection limits (see later).

Examples of a SEM and automated instrumentation using EDX are shown in Figures 6 and 7.

Wavelength-dispersive X-ray (WDX) analysis is geometry based using reflection of X-rays from a crystal of specific d-spacing, which travels on a Rowland circle inside a spectrometer. Light element spectrometers can quantify oxygen and carbon using gas flow detectors. WDX spectrometers form the basis of the electron microprobe and are sometimes attached to the scanning electron microscope (WD-SEM). The advantages of WDX analysis are good spectral resolution and lower detection limits when compared to EDX analysis (see below). WDX analysis involves calibration on standards, so highly accurate results can be obtained. This, and the fact that element acquisition is sequential, however, means that this type of analysis is relatively slow and phase analysis is usually restricted to a maximum of twelve elements. WDX spectrometers attached to a microprobe and to a WD-SEM are shown in Figures 8 and 9.

Spectral resolution is a measure of peak separation, and this is generally greater in WDX than EDX analysis. The best-known peak overlap in EDX is that of Pb-M with S-K. Although modern EDX software can correct for the overlap, problems are encountered when one of the two elements is present in minor to trace amounts. The two peaks are separate and therefore measurable using WDX techniques. Other overlapping peaks in EDX include Ru with Cl, Mg with As, Ti with O, Zr with Pt. Peak overlaps occur even in WDX spectra when dealing with the platinum group elements or the rare earth elements. Quantitative analyses of these elements should be run on WDX using PHA settings to remove high order peak interference. It may also be necessary to choose β rather than α peaks, and/or to employ certain software corrections.

The detection limit (DL), defined as the minimum detectable amount of an element at 99% confidence level, is important when trace elements have to be measured within a given phase. Detection limits may be lowered by playing with the accelerating voltage, the specimen current, and the spectral background settings but the limit is invariably lower in WDX than in EDX analysis as the following examples show:

Figure 6—A scanning electron microscope with an EDX detector attached

Figure 7—A QemSCAN with four EDX detectors. Detector multiplicity allows shorter analysis times

Palladium in pentlandite ($(Fe,Ni)_9S_8$)
EDX-DL = 0.5 %
WDX-DL = 100 ppm
Vanadium in chromite ($(Mg,Al,Cr,Fe)_3O_4$)
EDX-DL = 0.3 %
EDX-DL = 80 ppm

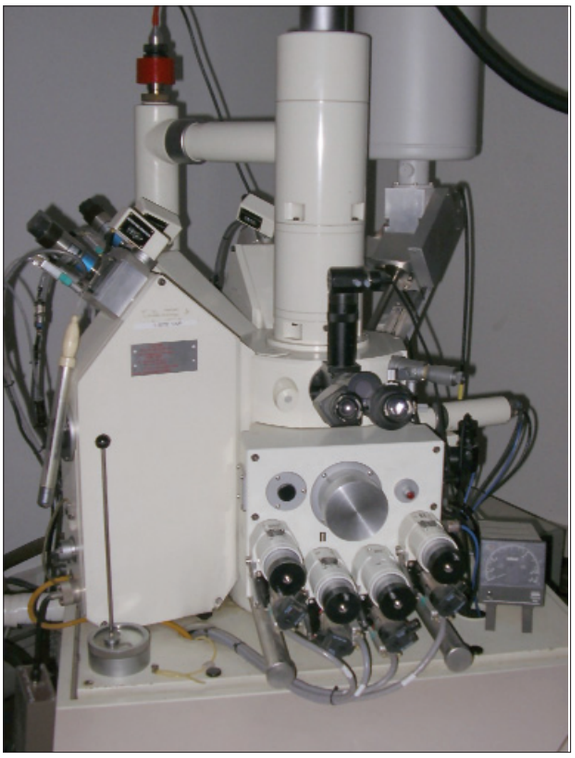

Figure 8—This electron microprobe is fitted with three vertical WDX spectrometers and one EDX detector

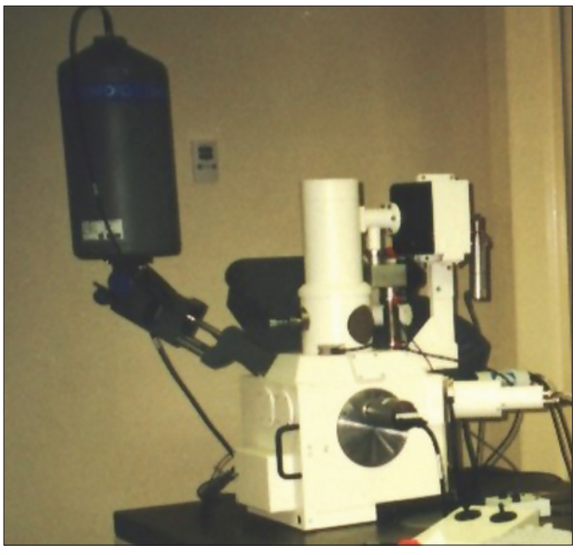

Figure 9—The WD-SEM has EDX capability and one horizontal WDX spectrometer (at the rear)

From the information provided thus far it is evident that instruments such as the electron microprobe, which runs in WDX mode, would be the most suitable choice to measure trace element distribution between phases, for multi-element quantification and for samples containing peak-overlapping elements. EDX is suitable for qualitative analysis, and quantitative analysis using standards. Most SEM-EDX quantification systems currently in use, however, require complex standards to closely match the unknown to be used, whereas WDX-EMP Quantification can be achieved using elemental standards or simple sulphides and oxides.

As mentioned earlier, the most valuable features of EDX analysis are speed and whole spectrum acquisition, and this is why the technique is used in automated analysis. Instruments such as the QemSCAN (quantitative evaluation of material by scanning electron microscopy) or the MLA (Minerals Liberation Analyser) utilize a combination of BEI and EDX for phase identification, followed by software processing.

Such instruments are capable of running many samples without operator input and the data can be processed later to produce accurate statistical information, even from tailings samples running at <1g/t values. A number of analysis modes may be used, singly or in combination. Phases may be identified according to their BEI intensity, by centroid EDX analysis, by linescan EDX or using EDX grids over mineral grains. Averaged data then define modal analysis, phase size distribution, liberation and association. Such information is obviously invaluable for beneficiation by milling and flotation. Less obvious, but extremely valuable, are the applications in exploration geology and pyrometallurgy. Processing of core samples taken during exploration using these techniques may influence mining and beneficiation practices, as well as financial planning. In smelting operations, the use of automated modal analysis in combination with EMP-WDX or SEM-EDX analysis can quantify losses to slag, and predict value recovery from furnaces and/or converters. This information can be used for process optimization.

The information presented in this paper is intended as an introduction to the application of electron microbeam techniques in metallurgical analysis. More detailed information, tailored to project requirements, can be obtained by approaching a microbeam technologist at an electron microscopy unit or a research organization.

References

VILJOEN, E.A. AND JOHNSON, J.A. Microbeam techniques in applied mineralogy. *Special Publications of the GSSA 7*, 1983. pp. 499–506.

GOLDSTEIN, J.I, NEWBURY, D.E., ECHLIN, P., JOY, D.C., FIORI, C., and LIFSHIN, E. *Scanning electron microscopy and X-ray microanalysis*. Plenum Press, New York and London. 1981. ◆