LOCAL ELECTRON MICROANALYSIS IN MICROPROBE AND ELECTRON MICROSCOPES

V. Starý

Fac. of Mech. Eng., Czech Technical University in Prague, CZ121 35 Prague 2, Czech Republic
stary@fsik.cvut.cz

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Abstract

Electron microanalysis uses an electron beam to excite characteristic X-rays and to determine from their intensity the elemental composition of a material. As an analytical technique, it can be incorporated into an electron microscope to utilize the generation of X-ray photons for observing thin samples and bulk samples in various types of electron microscopes. A quantitative method for bulk samples was first used by R. Castaing [1] in France, and the method was improved by K.F.J. Heinrich and co-workers [2] in USA. The special devices used for applying this method are usually called "microprobes". The method is often called "electron probe microanalysis", though a microprobe is the name for a very thin electron beam used for local microanalysis. After some theoretical information on electron-matter interaction, the basic possibilities of the method are reviewed, and some practical examples are given. Some basic literature is reviewed in [3-8].

1. Introduction

Electron microanalysis enables the user to make a qualitative and quantitative analysis of element concentrations from measured intensities of the X-ray radiation of the atoms in a sample. Because radiation is created by excitation of the internal atomic levels, chemical bonds do not influence the X-ray spectra. The intensity of the emitted X-ray radiation does not depend not only on the atomic concentration. A relatively complicated calculation is needed for quantitative analysis. It has to take into account other elements present in the sample, the deceleration of the electron in the bulk sample, and the absorption and fluorescence of X-rays in the sample. Reasonable results are obtained in the range of tenths of one percent. Since a very thin electron beam can be used, very good lateral resolution can be obtained.

2. Interaction of electrons with matter

During the path of electron through matter, the electron interacts with atomic nuclei and with electrons. Interactions with phonons are omitted in the theory of microanalysis. The interactions are given by the electron cross-sections $_i$ or by their mean free paths $_i$, which are connected by the formula

$$\frac{1}{\ _i} \quad N_i \ _i, \tag{2.1}$$

where N_1 is number of atoms in the volume unity of a pure element,

$$N_i \quad \frac{N_A}{A}, \tag{2.2}$$

where N_A is the Avogadro number, A is the atomic mass and is the density. Both $_i$ and $_i$ depend on the type of atom and electron energy. When electrons interact with matter, the intensity of the electron beam decreases along the path x as

$$n(x) \quad n_0 \exp \quad \frac{x}{\ } \tag{2.3}$$

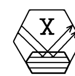
Both elastic and inelastic scattering appear.

3. Elastic and inelastic scattering

Due to the elastic scattering the electron beam mainly increases its width. Simultaneously, some of the electrons can change the direction and return to the surface. For a more complicated sample (an alloy), the elastic cross-sections can be added $_{el} \quad _{el,i}$.

Table 1. Some mean values for a free path and for the Bethe range R_B in several materials; $_{el}$ and $_{in}$ are the elastic and inelastic mean free path at given energy, respectively.

Material	C			Al			Cu			Au		
Energy [keV]	$_{el}$ [nm]	$_{in}$ [nm]	R_B m]	$_{el}$ [nm]	$_{in}$ [nm]	R_B m]	$_{el}$ [nm]	$_{in}$ [nm]	R_B m]	$_{el}$ [nm]	$_{in}$ [nm]	R_B m]
1	1.5		0.033	1.3		0.025	0.4		0.007	0.43		0.003
10	18	12.4	1.55	10	14.2	1.14	3.2		0.35	1.6	10.0	0.17
20	37		4.9	21		3.6	5.6		1.10	2.5		0.51
100	131.4	77.5		65.9	98.5					5.9	62.9	



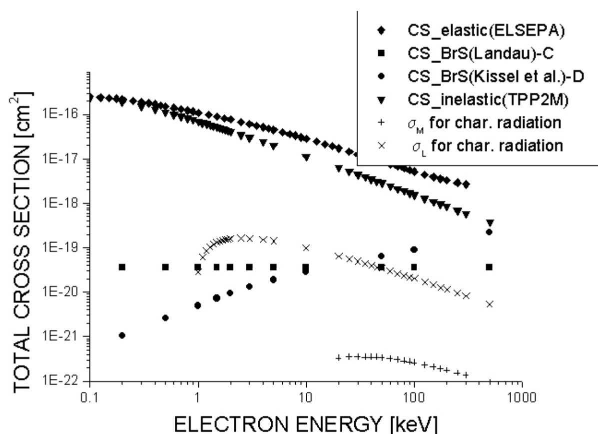


Figure 1a. Cross sections of elastic and inelastic scattering for Cu, including bremsstrahlung (BrS) and characteristic energy losses ($_K$ and $_L$).

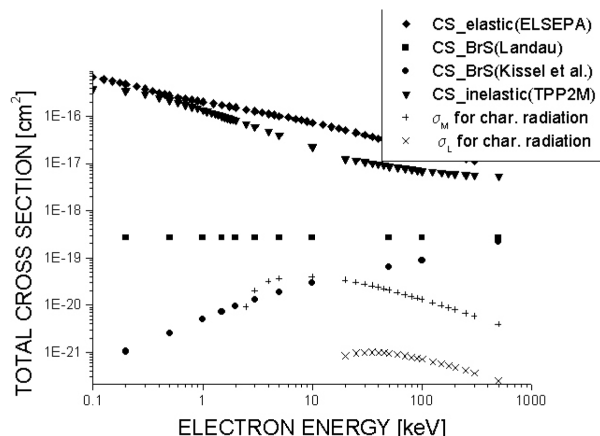


Figure 1b. Cross sections of elastic and inelastic scattering for Au, including bremsstrahlung (BrS) and characteristic energy losses ($_L$ and $_M$).

Inelastic scattering mainly causes energy losses. The angular deviations are much lower than for elastic scattering, but they do exist. Mainly in materials with "free electrons" there are energy losses in scattering due to plasmon excitations, or due to interband and intraband excitations. Generally, the energy decrease is due to the "stopping power" *-dE/dx=S*, a property, which can be calculated theoretically. The length of the electron path – range R_B (2.4), is limited to a few micrometers (Tab. 1). This is the maximum depth of the electron trajectory. Due to the directional changes, only a small number of electrons reache this depth.

$$R_B \quad \int_{E_0}^{0} \frac{1}{dE/dx} dE \qquad (2.4)$$

In a bulk sample, consequently, a thin beam creates a pear-shaped excitation zone in the material.

The probability of internal level excitations is relatively low (Fig. 1a,b).

4. EDX microanalysis

4.1. Advantages and disadvantages

A set of questions can be applied to show the suitability of a given analytical method. In the case of electron microanalysis, it is necessary to know:

- For which elements, compounds and alloys does the electron microanalysis give reasonable results, and for which elements, compounds and alloys does it not give reasonable results?
- What is the minimum content (concentration, number of atoms, mass) of the element that we are able to determine?
- Is the bulk material homogeneous (and we define the mean concentrations) or inhomogeneous (and we define the distribution of elements in sample)?
- Is the aim to determine the average element content, or the dependence of the concentration on the depth in the sample (especially in the case of films)?
- Is the method destructive (is there radiation damage, and/or disordering of material) or is it non-destructive?

4.1 Detection and analysis of X-ray radiation - devices

There are two basic systems for detecting and analysing X-rays from a sample: the first system separates the X-rays according to energy (energy dispersive spectroscopy - EDS), and the second system divides the X-rays according wavelength (wavelength dispersive spectroscopy - WDS). In EDS, solid state detectors, usually Si(Li) (Fig.2a) or silicon-drift (SDD) detector types are used. The EDS detector is located in the vacuum chamber of the microscope, the shortest distance away from the sample. The detector is cooled to a low temperature using liquid nitrogen or a Peltier cell. Older types of detectors were separated from the evacuated space of the microscope by a thin Be window. Nowadays, the window is usually made of plastics (UTW, Ultra Thin Window, Mylar PET polyester). Sometimes there is no window, and the detector is located directly in the space of the microscope. The Si(Li) detector is a pure silicon crystal doped with lithium. In this detector, the X-ray photons create electron-hole pairs, and the resulting charge is collected by gold electrodes on the crystal surface. The electric pulses are amplified by the field-effect transistor near the detector. The number of electron-hole pairs is proportional to the X-ray photon energy, with some uncertainty due to the statistics of electron-hole pair creation. The statistics gives the width of the energy peaks in the X-ray spectrum; the width depends on the photon energy, and determines the quality of the detector.

In the multichannel analyzer, the pulses are separated according their size and assigned to the intended number of channel, i.e., to the position in spectrum. The result of X-ray aquisition is a spectrum, i.e., the dependence of the intensity of X-ray phonons on their energy *E*, see Fig. 2b. For this reason, the system is classified as an energy dispersive system (EDS). This way of detection is called parallel, because the whole spectrum is acquired simultaneously. The spectrum is composed of peaks of characteristic radiation on a background given by bremsstrahlung.

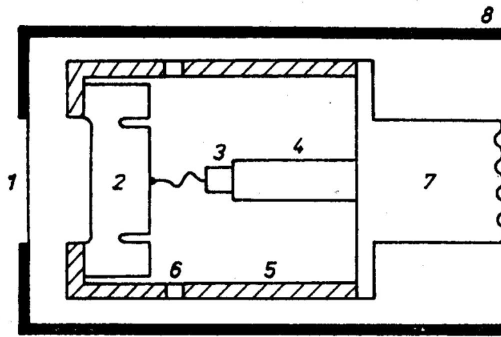


Figure 2a. EDS detector; 1 - window (Be or plastics), 2 – Si(Li) crystal, 3- input tranzistor, 4 – signal output, 5 – detector holder, 6 – evacuation holes, 7 – freezing contact, 8 – cover.

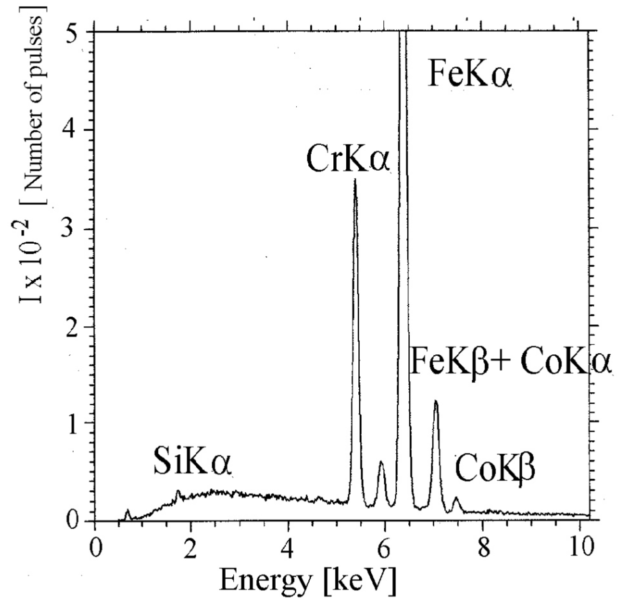


Figure 2b. EDS spectrum of duplex Cr steel.

Moreover the detector and the analyzer are connected together. In the presence of a Be window, the intensity of X-ray radiation for energy $E < 3$ keV is partially absorbed by window, at 1 keV about 90 %, so elements with Z > 10 (Ne) can be reasonably detected. The spectrum also contains some artefacts – intensive peaks can create a peak with sum of thier energies (or doubling energy of one intensive peak) and also an escape peak with energy decreased by excitation of silicon X-ray radiation, i.e., lower for SiK energy (1740 eV). When Be window is replaced by plastics (usually supported by a plastic mesh), light elements C, N, O can be also analyseded. Quantitative methods are complicated by peak overlapping, and by the presence of a background.

In wavelength dispersive systems (WDS – Fig. 3a), the X-ray photons are separated by diffraction on a single crystal with a known interplanar distance before being detected. According to the Bragg equation, the angle of the maximum reflection depends on the interplanar distance, the order of reflection and the wavelength of the actual X-ray radiation. Therefore the radiation wavelength can be determined from the reflection angle, and in this way the type of emitting atoms can also be determined. During the measurement, the crystal and detector slit move along the Rowland focusing circle. For example, LiF, PET (pentaerythritol $C(CH_2OH)_4$, plane (002)) and TAP (thalium pthalan $TlHC_8H_4O_4$, $(10\bar{1}0)$ plane crystals are used. X-ray radiation is detected by an ionisation chamber or by a proportional detector. The spectrum (Fig. 3b) is the dependence of the intensity on the angle of declination , (or directly on sin(/2), see Fig. 3b). The mechanical parts are relatively complicated. The energy/wavelength resolution of WDS is much better than the energy/wavelength resolution of EDS, thus the ovelapping of the peaks is very rare; in addition, a high signal-to-noise ratio is obtained. Due to the higher intensity of the electron beam in the microprobe, peaks with Z > 4 can be measured. Due to serial detection, the wavelengths are detected sequentially

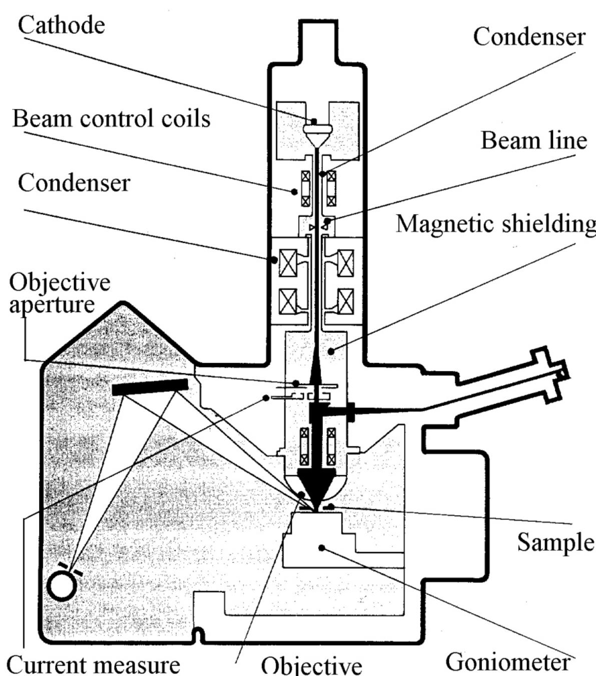


Figure 3a. Microprobe with a crystal spectrometer

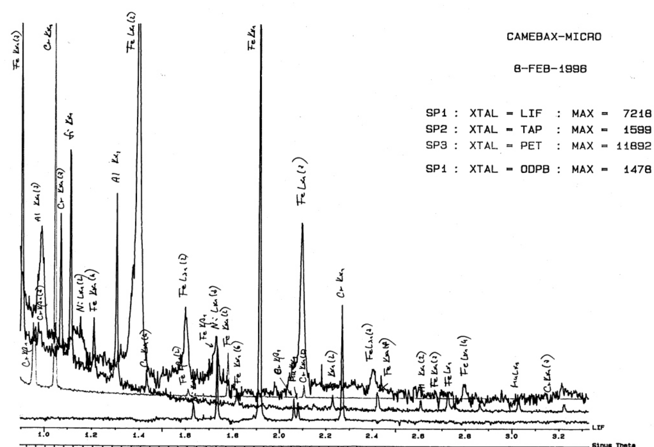
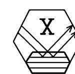


Figure 3b. WDS spectrum of Cr-Ni steel.



and the spectrum collection requires much longer acquisition times than for EDS. The presence of high order reflections also complicates the evaluation of WDS spectra. Usually, several spectrometers with various crystals are employed in the system to decrease the acquisition time.

4.2. Qualitative analysis

From the peak energy in EDS spectrum or from the angle of the maxima in WDS spectrum, we can make a quantitive determination of the elemental composition of the measured sample (with the limitations given above). In order to make a quantitative determination of the concentration of each element, some limits have to be specified. In particular the critical value, the minimum detected amount, and the minimum measurable values need to be defined for each element. In addition, the presence of several series K, L, M of one element in the spectrum and the presence of several lines in each series (, , etc.) must be taken into account. It is also necessary to check the possibility of escape and multiple peaks in the spectrum.

Semiquantitative analysis

If the number of collisions of electrons with atoms in a thin sample is low (e.g., in average one collision per electron) the energy losses are relatively low and the electron energy is relatively constant. The X-ray intensity of a given element *x* in a thin film of thickness *z* is proportional to the number of atoms $N_{1,x}$ and is consequently proprotional to the atomic fraction c_x. The X-ray intensity is expressed by the following equation

$$I_x \quad I_0 \;{}_x\; c_x \frac{N_A \;{}_{smp}}{A_x} d, \tag{4.1}$$

where I_o is the beam current, ${}_x$ is the cross section of X-ray production, is the fluorescent coefficient, ${}_{smp}$ is sample density, A_x is atomic mass and N_A is the Avogadro number. It is seen that I_o, N_A and *z* is the same for all elements, ${}_x$, A_x a are tabulated values. The cross section ${}_x$ (in cm^2) can be calculated according to the formula

$${}_x \quad 6.51 \quad 10^{20} \frac{n_s b_s}{U E_c^2} \ln(c_s U), \tag{4.2}$$

where n_s is the number of electrons at a given level (e.g., n_s = 2 at K series), b_s a c_s are the constants for a given level, E_c is the ionization energy for the series (in keV) and *U* is the so-called overvoltage ($U=E/E_c$, for a thin film $E=E_o$, E_o is primary electron energy); according to the literature, the recommended values for K series are b_s=0.9 a c_s=0.65.

In the case of a sample containing one element, the number of atoms in a volume unit is given by (2.2), while samples containing more than one element the number of given atoms in a volume unit is given by

$$N_{1,x} \quad c_x \frac{N_A \;{}_{smp}}{A_x}, \tag{4.3}$$

${}_{smp}$ being density of sample.

For calculating the elemental concentration of two elements in a thin sample, *x* and *y*, a simple equation reflecting the proportionality between the intensities of the X-rays and concentrations is used

$$\frac{c_x}{c_y} \quad k_{xy} \frac{I_x}{I_y}, \tag{4.4}$$

where k_{xy} is a coefficient given by measurement of standards (the so-called the Cliff-Lorimer factor). In the case of more elements, the obvious condition $c_i = 1$ must be taken into account.

4.3. Quantitative analysis

When a quantitative analysis of a bulk material is made, the concentration (mass fraction c_x) of given element *x* from the measured intensity of the characteristic X-ray radiation I_x has to be calculated. The underlying physical processes are following:

1. elastic scattering at atoms, connected with change of direction, including the possibility of backscattering;
2. slowing down of electrons;
3. ionisation of atoms with possible emission of X-rays;
4. fluorescence, i.e. ionisation of atoms by both characteristic and bremsstrahlung radiations;
5. absorbtion of the generated X-ray radiation in the path through the sample to the detector.

The generated intensity of X-ray radiation during the active movement of an electron in an sample is given by

$$I_x \quad {}_{0}^{R_B} c_x \frac{{}_x \; N_A \;{}_{smp}}{A} ds \quad c_x \frac{N_A \;{}_{smp}}{A} R \;{}_{E_0}^{E_c} c_x \frac{{}_x}{dE/ds} dE \tag{4.5}$$

where R is a correction for backscattering, *s* is the path in sample. Two methods, ZAF and Phi-Ro-Zet., are widely used for calculating concentrations.

ZAF Method

This method is used for calculating mass fractions with the use of standards, usually pure elements or chemical compounds with exact stochiometry. ZAF stands for the corrections used when calculating from the intensities. The calculation proceeds in a number of steps:

- first, the concentration is determined exactly from the ratio of the intensity from the sample and from the standard: $c_x/c_{x,s} = I_x/I_{x,s}$, I_x is the intensity from the sample, $I_{x,s}$ is the intensity from the standard under the same measurement conditions (energy and electron current, specimen tilt, specimen position to detector, etc.), $c_{x,s}$ is the element concentration in the standard (for a pure element $c_{x,s}$ = 1); $k = I_x/I_{x,s}$ is the so-called k-ratio, for a pure element standard c_x = k.
- second, corrections are included that reflect:
- 1. the difference of electron scattering and slowing down in the sample and in the standard, i.e., the

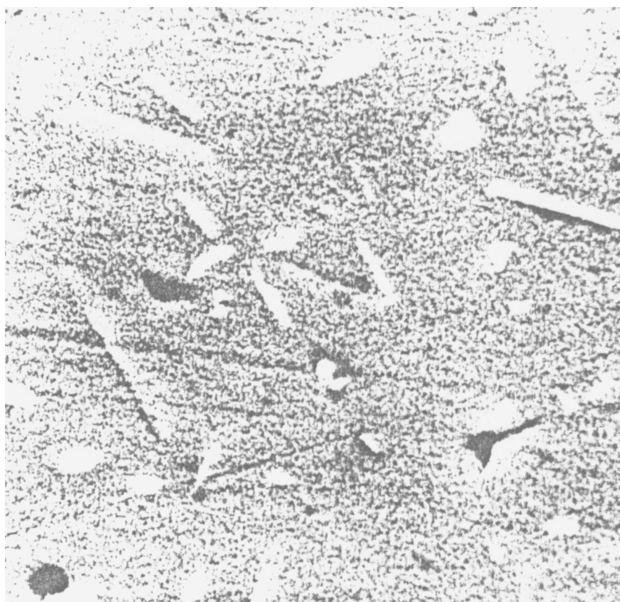


Figure 4a. SEM image of light alloy AlLiCuZr, in the bright particles there is an excess of Cu, Fe, Ni and Zr, in the dark particles there is an excess of Li, magnification 1000 .

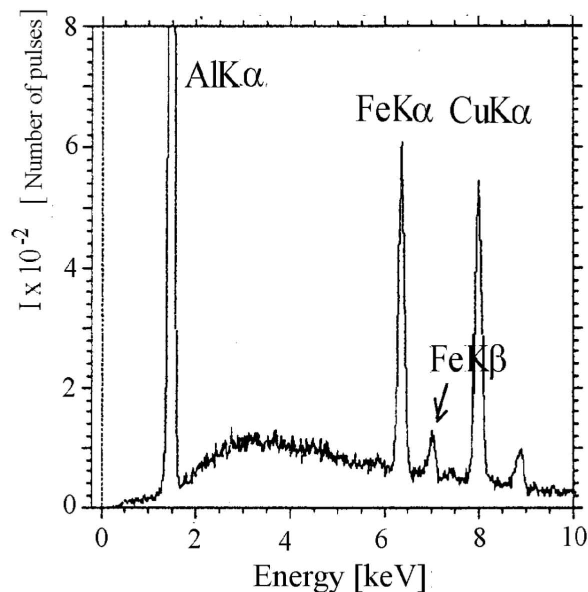


Figure 4b. EDS spectrum of the bright particles in Fig. 4a; in addition to Al, the particle contains Cu and Fe. The sample also contains particles with Zr and Ni.

atomic number effect – this is denoted as Z correction;

- 2. the difference in absorbtion of the X-rays generated in the sample and in the standard - this is denoted as A correction;
- 3. the difference in fluorescence in the sample and in the standard - this is denoted as F correction.
- The correction factors can be calculated according to the physical processes in the sample and in the standard, and are incorporated in the evaluation software. The calculation proceeds iteratively. In the next step, the first estimation of the concentrations calculated in the previous step is used for corrections to calculate the new values of concentration etc. The calculation is completed when differences in subsequent steps decrease below a defined level.
- The resulting composition is given for $c_{x,s} = 1$ as $c_x = k/(ZAF)_x$, ZAF being the product of the corrections that have been applied.

Finally we have both the mass and atomic fractions of the elements including their measurement errors - standard deviations calculated from peak intensities of characteristic radiation and spectrum background.

PHI-RO-ZET method

The distribution of X-ray generation in sample is used to determine the concentrations. No standards are used. The function (z) (i.e., Phi-Ro-Zet) describes the ratio of the intensity $I_{x,gen}$ of the generated X-rays from a thin film *d(z)* in mass depth *z*, being the mass density and *z* the physical depth in the sample and the intensity $I_{x,0}$ from a free thin film of the same thickness

$$(\quad z) \quad \frac{I_{x,gen}}{I_{x,0}}, \qquad (4.6)$$

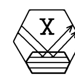
Let's assume a constant concentration of element. The generated intensity depends also on the primary electron energy E_o and on the density of the material. The depth dependence of (z) in parametric shape can be calculated as follows

$$(\quad z) \quad \frac{A \quad B\exp(\quad z/C)}{1 \quad \exp(\quad z \quad D)/E} \qquad (4.7)$$

the quantities A to E are polynoms of atomic number Z and overvoltage U ($U=E_o/E_c$); the formula for calculation takes into account the depth dependencies of the stopping power S and the coefficient of beam attenuation due to backscattering R. The intensity I_x from the sample is measured, and intensity $I_{x,s}$ is calculated. From the shape of function *(z)* in the sample and the standard and intensity ratio $I_x/I_{x,s}$ we can calculate the concentration c_x of the measured element x in the sample.

Local microanalysis and chemical mapping

X-rays are generated only in that part of the sample where the accelerated electrons move, i.e., in a very small part of the sample volume. The dimension of this "interaction volume" is given approximately by the electron range R_B (Tab. 1), and depends on the composition and density of the sample and the energy of the electrons. Thus the size of the interaction volume (depth and diameter) is in the order of tenths of one m for heavy elements and units of m for light elements. When the electron beam is focused on a defined position on the sample, information is obtained from a single "point" of the sample. Because we usually observe the image of the surface as a (secondary or backscattered) electron image, we can position the beam on areas which are of interest for the study. This way is referred to as "local microanalysis". In this type of local microanalysis of small-sized objects (particles or phases), it is always nec-



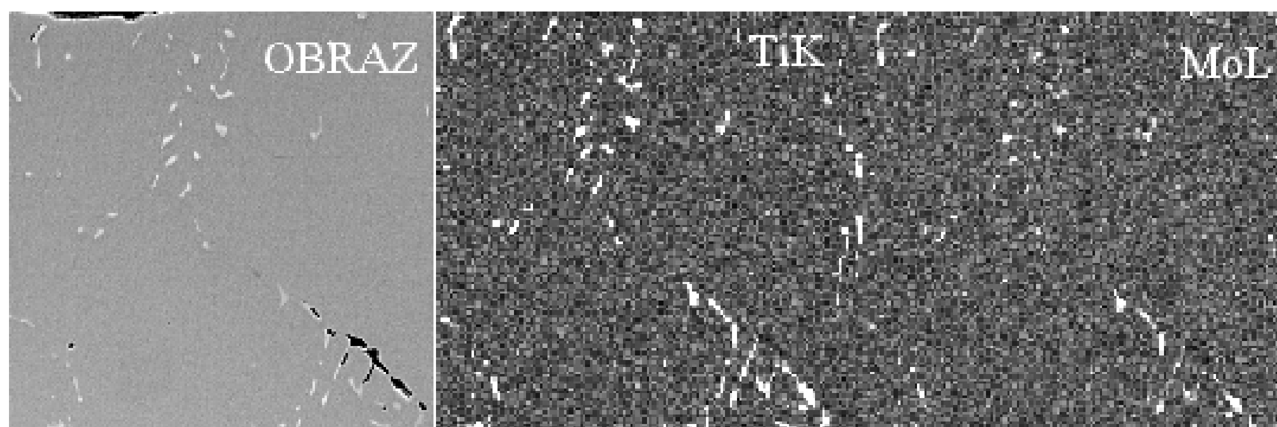


Figure 5. Chemical maps of several elements in a superalloy, magnification of original image 750 .

essary to compare the size of a particle (phase, etc.) with the size of the interaction volume that the information comes from.

The small size of the interaction volume means that the beam can be moved along a line (for example to cross the interface) or that the sample can be mapped by an electron beam over a selected area. This method is known as "elemental mapping", and is widely used in a large number of applications. The beam moves in an array of points, and a matrix is created (Fig. 5). At each point of the matrix the whole spectrum can be acquired, but this is time-consuming. Another way is to use only relatively narrow energy windows for selected elements (or for the background). In any case, the time of measurement in one point is much shorter than the time for spectrum measurement for qualitative or quantitative analysis, so the precision of the measurement is lower. However, using this method we obtain a survey of the distribution of a single element in the sample.

Conclusion

The X-ray nicroanalysis is a very suitable and important method for studying the composition of materials and biological objects.

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