Analysis of micronic phases containing light elements by quantitative backscattered electron microscopy and Image Analysis

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Abstract. — A new microanalytical method for phases containing both heavy and very light elements has been developed. Its principle is the quantitative Image Analysis of Scanning Electron Microscopy images of backscattered electrons (BSE), coupled with X-Ray microanalysis. The BSE measurement over a large population of the same phase provides a very good precision on the result ($\pm$ 0.1 atomic unit). This method requires a simple analytical configuration, and allows great ease of use by automation. The identification of a Al Li$_x$ Si phase by this method is presented.

1. Introduction.

In order to answer the continuous challenge for improving the performance of materials, many new metallurgical solutions are regularly developed; among them, an increasing proportion is based on light elements compounds. Typical examples can be given, as new Al-Li alloys; oxides, nitrides or borides for bulk ceramics, composites and surface layers; Fe-Nd-B magnets,... In each case, a precise characterisation of the microstructure — especially the nature and composition of often small phases — is a main condition for a good understanding of the metallurgical mechanisms that govern the development of these materials. In a such frequent context of multielement diagrams, one can observe the presence of several phases of adjacent nature, so global analytical techniques, as X-Ray diffraction, are inefficient to precise the location of each specific population. As a consequence, microanalysis of such small phases containing light elements is now an analytical problem we often have to solve.

Although several existing techniques are applicable (EPMA, PIXE, SIMS, AUGER,...), none of them is providing a real comfortable compromise in terms of efficiency and ease of use; main advantages and disadvantages of each one are given in table I.

In this context, we decided to take profit of our new Analytical Scanning Electron Microscope (ASEM) configuration by implementing, in a completely new and automated way, an already old method based on the quantitative interpretation of the backscattered electrons (BSE) signal.

Table I. — *Comparative capabilities of 4 techniques for the analysis of micronic phases containing light elements. (+) Advantages of the technique. (−) Limitation of the technique.*

Microprobe technique →	Electron (EPMA)	Ionic (SIMS)	Nuclear (PIXE)	AUGER
Spatial resolution	X,Y,Z : 1 to 3 µm ⊕(+)	X,Y 1 µm Z 0,005 µm ⊕(+)	X,Y ≥ 5 µm Z a few µm ⊙(-)	X,Y 0,2 µm Z 0,003 µm ⊕(++)
Phase localisation	with BSE detector ⊕(+)	⊕(±)	⊙(·)	with BSE detector ⊕(+)
Light element sensitivity	B, C, N, O : ⊕(+) Li ⊙(-)	⊕(++)	⊕(+)	all elements but Li ⊕(+) Li ⊙(-)
Quantitative analysis	⊕(±)	⊙(·)	⊕(++)	⊕(+)

⊕(+) : advantage of the technique

⊙(-) : limitation of the technique

2. State of the art.

The BSE signal provides unique information on the local mean atomic number of the specimen, with two main advantages:

– sensitivity to both heavy and light elements,

– good spatial resolution (i.e. 0.1 μm).

These two points explain a large development of this BSE option, but only in a qualitative mode; only rare papers in the litterature suggest a more efficient interpretation of the information, based on manual and local measurements of the grey level; the most complete work was probably published by Ball [1]. At this time, i.e. 5 years ago, we did similar experiments on a conventional SEM; but this manual method was extremely tedious and unreliable: after focussing the beam on each phase, the local BSE signal was obtained with a voltmeter at the output of the BSE detector amplifier, and an accomodation time of about one minute was necessary before obtaining a stable value; this procedure was sequentially applied to a maximum of phases, because of the cristallo-graphic effect, which is responsible of very significant BSE variations, even for optimal conditions (large aperture, low working distance, i.e. convergence angle 10^{-2} rad); as a consequence, during such a long routine, the unavoidable beam current shift cannot be neglected, and regular verifications on a reference specimen has to be adopted: quite often, unreliable measurements had to be done again.

3. Towards a new solution.

3.1 THE ASEM CONFIGURATION. — This configuration is composed of three different systems:
- a digital SEM (ZEISS DSM 950), equipped with a high brightness LaB$_6$ gun, a BSE detector (semi-conductor technology), a motorised stage, and an ion gun for *in-situ* cleaning the most reactive phases;
- an EDX microanalysis system (TRACOR TN 423), with a 30 mm^2 Be window detector and a complete software package for both driving all functions of the SEM and assuming quantitative microanalysis;
- an image analysis system (KONTRON IBAS), with a parallel processor, a powerful SEM interface, a complete software package (SEM management, grey-tone image enhancement, mathematical morphology algorithms,...) with a quite user friendly menue; this system is able to drive all the functions of the 2 former units.

3.2 THE BASIC ADVANTAGES OF ASEM. — The quantitative interpretation of the BSE signal is one of the most typical examples of application of this analytical "trilogy", with two main advantages:
- firstly, the use of an Image Analysis System, for the densitometric treatment of a real 2D grey level image: as compared with local measurements, such a large scale information is expected to limit the influence of undesired parameters (crystallographic contrast, local defects,...) and thus give access to a better precision,
- secondly, the use of simultaneous and complementary X-Ray microanalysis for the heavier elements, to provide a more complete and reliable chemical microcharacterisation of unknown phases.

3.3 SCALING BSE SIGNAL VERSUS ATOMIC NUMBER Z. — From this step on, we really took profit of the Image Analysis System with large 2D information to get rid of the main factors (crystallographic effect, polishing artefacts) which limited up to now the precision of the mean grey level of each phase nature. In each case, a large number of phases were investigated in an automatic way; a standard algorithm (median filter, size 5×5) was adopted to get rid of noise within the phases; then a delineation routine could rebuild sharp edges around each phase.

Considering the approximative atomic number of the unknown phase to be determined later ($11 < Z < 12$), we focussed on this local Z window, and we used Mg, Al and Si pure specimens for scaling BSE signal *versus* Z. The experimental results are given in table II. Several details have to be pointed out:
- Within this narrow Z window, a quite linear regression curve could be obtained ($r = 0.9994$),
- As a direct consequence of the consistent 2D information treated by image analysis, very small confidence interval is obtained for the mean atomic number: ± 0.1 unit at 5% risk,
- A dedicated amplification of the signal provides a favorable grey level coding of Z : 70 levels for one atomic number unit.

As a comment, the linear regression has to be considered as pure hasard, because it is strongly dependant of the energy sensitivity of our BSE detector at the time of the measurements; thus, such a scaling routine has to be done for each analytical system, and even checked before each measurement sequence.

3.4 VERIFYING Z CALCULATION FOR MULTIELEMENT PHASES. — The next scaling step is to find a good mathematical calculation giving the mean atomic number of a multielement phase as a

Table II. — *Experimental signal (G) and Z calculations, validating formula (1).*

Element/phase	Z	G	mean grey level	I.C.**	Z ***
Mg	12	68,4		5,3	11,9
Al	13	136,6		2,5	13,0
Si	14	202,3		2,0	13,9
Al$_2$LiMg	11,9 *	65,9		4,3	11,9
SiC	11,6 *	47,0		4,4	11,6
AlLi Si		77,9		2,0	12,1

*   Calculated with formula (1).
**   Confidence intervall (risk 5%).
***   Calculated from regression obtained with Mg, Al, Si results :

$$Z = 0,014^9 G + 10,97 \quad \left(r = 0,9999^4\right)$$

function of its chemical composition; of course this relationship has to be in agreement with the former scaling curve.

We chose first well known and stoechiometric phases, containing both heavy and light elements, in order to provide a more discriminant method, and clearly point out the best calculation; the experiments were done on both SiC and Al$_2$LiMg phases. The results clearly show that only a second order formula, proposed first by Danguy and Quivy [2] in 1956, was valid to calculate a very reliable mean atomic number in our context (Tab. II).

$$Z = \frac{\sum a_i Z_i^2}{\sum a_i Z_i} \tag{1}$$

a_i : stoechiometry coefficient for element i within the phase,

Z_i : atomic number of element i.

It has to be mentionned that this calculation is expected to be valid only *for energy sensitive BSE detectors*; on the other hand, the simpler first order formula, proposed by Castaing [3] for BSE current measurement in a microprobe, and recently confirmed by Herrmann and Reimer [4], remains the best choice in this particular context.

4. An example of industrial application of the method.

4.1 THE ANALYTICAL PROBLEM. — A few years ago, in the context of a challenge based on the development of industrial Al-Li alloys for aerospace applications, several new phases were discovered within the microstructure; a precise identification of these phases was of prime importance

for a better understanding of the metallurgical phenomena involved during the thermomechanical treatments, thus governing the final properties of the material; such a context was at once considered as a typical opportunity for checking a simple analytical solution based on the method presented before.

In this paper, we will focus on one specific problem, involving phase determination within the Al-Li-Si diagram; let us write the chemical formula as $Al\,Li_x\,Si_y$, corresponding to a rather reactive phase.

4.2 RUNNING THE METHOD.

4.2.1 First step, EDX Microanalysis.

— In the context of these unknown phases containing two "heavy" and one light elements, we first determined the atomic ratio $y = Si/Al$ by EDX microanalysis, considering for ZAF correction the Li element as being the complementary part to 100%. This first step could determine the y ratio as equal to unity, with a reasonable precision.

But the problem is more difficult for the x parameter, especially for three reasons:

– small differences in the Li content separate the three chemical formulae proposed in the litterature, i.e. $AlLi_x Si$ with $x = 1.0$, 1.5 and 2.0, corresponding to 11.2, 15.4 and 20.0 wt% Li, respectively; the associated Z values are 11.5, 12.0 and 12.5 calculated by relation (1)

– by principle, indirect estimation of Li content (by difference to 100%) is not precise, because this value is affected by the cumulative uncertainties of the other concentrations, i.e. Al and Si;

– on such reactive phase, the sum of the weight contribution of the three elements cannot be expected at exactly 100%, but rather between 95% and 100%, because of unavoidable corrosion products at the surface of the polished specimen.

As a consequence, no reliable phase determination can be done with only EDX (and probably WDX) technique.

For this reason, we had to take profit of the parallel BSE result, to provide a more precise information on Li content.

4.2.2 Second step: BSE measurements.

— Most of the advantages of image analysis were used to provide the most reliable routine for mean grey level measurements; the main points of the analytical sequence are the following:

– SEM conditions:

* For light materials, a low primary energy ($E = 10\,keV$) is a good compromise between limited in depth information (especially for micronic phases), BSE sensitivity and EDX efficiency (excitation of X-Ray lines),

* A small working distance (10 mm) is expected for BSE efficiency and a smaller crystallographic contrast, but simultaneous quantitative EDX microanalysis may require larger values to stand at the focus point,

* The larger diaphragm (another compromise with resolution!), for the larger convergence angle and also a smaller crystallographic contrast,

– Image acquisition:

* 256 × 256 pixels for "large" phases at the field scale, 512 × 512 for smaller ones, 256 grey levels (8 bits),

* Noise reduction at the pixel scale (MEDIAN filter, size 3 × 3 or 5 × 5 pixels),

* Grey level opening, to reconnect parts of the same phase separated by small cracks or scratches,

* "Contour" reconstruction, to provide sharper edges around the phase,

* Segmentation of all the phases observed in the field ($\Rightarrow$ binary image),

* Erosion algorithm on this binary image, in order to get rid of two kinds of unreliable zones: both the too small phases, and the peripheral part of the larger ones.
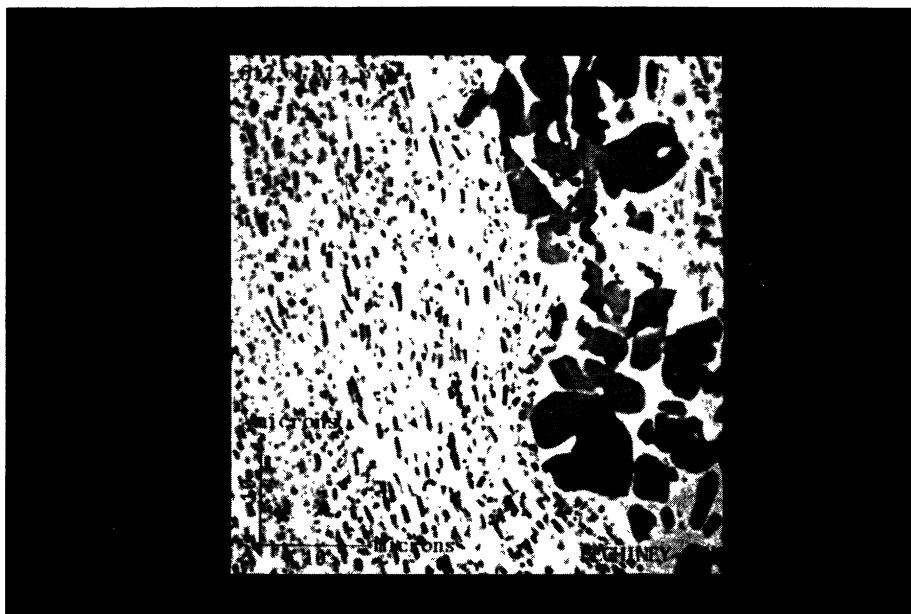
Fig. 1. — "As received" image (45 × 45 μm) containing both large (right side) and micronic phases to be analysed. Resolution is 512 × 512 pixels.

* Mean grey level measurement on each phase, then mean value over about 100 phases.
    A typical image is given in figure 1.

4.2.3 *Interpretation of the results.* — On the larger phases, i.e. several microns size, very reliable results were obtained on about 100 phases: a mean grey value of 79, affected with a 95% confidence interval lower than 2. One can see from figure 2 that such a precision provides an unambiguous determination of the phase nature, which is in fact $Al_2Li_3Si_2$ [5].

On the smaller phases, i.e. submicronic ones, a better lateral resolution was necessary, and even with a smaller beam current we had to use a smaller diaphragm; as a consequence, a larger contribution of the crystallographic contrast induced a significant spread of the grey values; if no strict phase effect determination was possible in this case, we could nevertheless notice that the mean value of the histogram is just corresponding to the reliable result obtained on the larger phases.

5. Conclusion.

The development of a new analytical configuration (ASEM = digital SEM interfaced with EDX microanalysis and Image Analysis System), could give rise to a simple, reliable and automated method for the microanalysis of phases containing both heavy elements and a light one. This original routine is measuring the mean atomic number $\bar{Z}$ on a large number of the unknown phases, by quantitative interpretation of the backscattered electron images with an Image analysis system; a precision of ±0, 1 atomic unit is obtained.

An industrial application on AlLiSi alloys could undoubtly indentify an unknown phase among three very close solutions (within 1 atomic unit); we could also estimate quite a reasonable limitation of the method in terms of phase size (i.e. 1 micron).
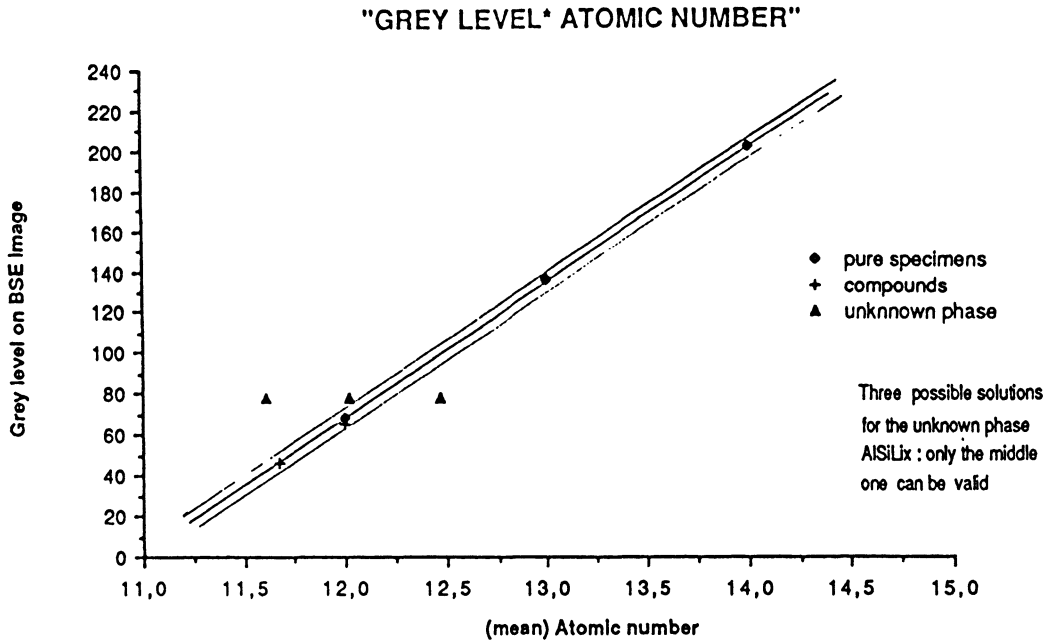
"GREY LEVEL* ATOMIC NUMBER"

Fig. 2. — Grey level *versus* atomic number.

References

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