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QUANTITATIVE ANALYSIS OF INTERMETALLIC PHASES IN Al-Li ALLOYS BY ELECTRON, ION AND NUCLEAR MICROPROBES

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Abstract.

Conventional microanalytical techniques (Optical Microscopy OM, Scanning Electron Microscopy SEM, Electron Probe Micro Analysis EPMA) were used in combination with new techniques (Secondary Ion Mass Spectrometry SIMS and Nuclear Microprobe NM) to visualise and identify unknown phases in ternary and quaternary Al-Li alloys. The limitations of each technique are compensated by the unique advantages of the others : spatial resolution, qualitative and quantitative analysis of light elements such as Li. Finally, the Nuclear Microprobe may be considered as a reference method by providing standard samples on which correction procedures for the quantitative analysis of light elements by conventional techniques (SEM and EPMA) can be tested and implemented.

Introduction.

Depending on the alloy composition, numerous constituent particles are likely to be present in complex ternary or quaternary Al-Li alloys for aerospace applications. Besides the phase recognition and the structure determination by X-ray and electron diffraction, the study of the composition of such intermetallic compounds for the establishment of complex equilibrium phases diagrams needs a combination of microanalytical techniques.

The conventional techniques (SEM, EPMA) using secondary X-ray emission are not able to detect Li due to the associated high wavelength. However, micrographs using backscattered electrons (BSE) in the SEM give a mean atomic number contrast and may indicate the possible presence of Li. This contrast can also be quantitatively exploited by densitometry.

New methods are necessary to detect, visualise and analyse Li in phases. Qualitatively, SIMS offers the ability to visualise Li in combination with any other element in solid solution or in intermetallic phases (1). Due to important matrix effects at high concentration (> 1%), the quantitation is difficult if standard samples of similar composition are not available. Quantitative microanalysis of major elements, particularly Li, can be performed with high accuracy (2) by the Nuclear Microprobe (NM). Nuclear reactions have already been used to determine the Li loss profile in the superficial region of Al-Li sheets (3-4), i.e. essentially in the solid solution. In this work, we shall extend the field of application of the Nuclear Microprobe to the determination of the composition of intermetallic phases.

The efficiency of combining conventional (OM, SEM, EPMA) and new (SIMS, NM) microanalytical techniques will be illustrated by the quantitative analysis of known and unknown intermetallic compounds in the Al-Li-Zn and Al-Li-Si systems.

1. Experimental procedure.

1.1. Samples.

Slices of ingots (18 mm in diameter) were prepared and polished after casting in steel molds with solidification times of approximately 1 minute. Areas of interest were located in the optical microscope (OM) by circular tracks for further characterisation. Two series of samples were analysed :

- standard samples : intermetallic alloys or solid solution in homogeneous ternary and quaternary alloys
- as-cast alloys with unknown primary polyhedral phases previously recognised by X-ray diffraction (5)

The quaternary (Al, Li, Cu, Mg) sample was chosen as reference material because its as-cast microstructure appeared to consist almost entirely of large crystals of cubic $R - Al_5 Cu (Li,Mg)_3$ phase in a preliminary investigation. The ternary (Al, Mg, Zn) reference sample was in an intermetallic alloy of $T - Mg_{32} (Al,Zn)_{49}$ phase in the as-cast condition. The third (Al, Li, Zn) reference sample was a solid solution prepared by the homogenisation for 24 h at 520 °C and water quenching of a dilute ternary alloy. The chemical composition of these 3 samples are given in Fig.1.

1.2. Microanalytical techniques.

A DSM 950 Zeiss digital SEM working at 15 kV in the BSE mode was coupled with a Kontron Image Processor in order to quantify the grey level of BSE micrographs. On the same instrument, a quantitative Tracor EDX system was used to perform the analysis of heavy elements (e.g. , Al, Si, Zn) with ZAF corrections.

For SIMS, the instrument used was a Cameca IMS 3f Ion Microanalyser equipped with 2 ions sources (Cs and duoplasmatron) and with an ultra-sensitive detector allowing single ion detection of every element from H to U (6). The spatial resolution in the imaging mode is typically 0.5 - 1.0 μm . Ion micrographs were taken by bombarding the sample with Cs ions of 5.5 KeV and by saturating the surface with an oxygen jet to maximise and stabilise the ion emission .

In the Nuclear Microprobe of the LARN, a proton beam of 2.8 MeV (15 x 15 μm in size) induced emission of photons (PIGE) for Al and Li and X photons (PIXE) for Zn. Images of the repartition of these elements could also be obtained by scanning the sample surface to check the validity of any local analysis in a phase.

2. Calibration results.

2.1. Nuclear microprobe signals.

We have chosen the 472 keV γ -rays from Li nucleus excitation, the 843 and 1013 keV γ -rays for Al and the 8.6 and 9.6 keV K X-rays from Zn (all induced in the first 5 to 8 μm under the irradiated surface) as characterization signals. The depth at which they are produced and their energies allow to certify the negligible absorption of these photons in this light Al matrix. Even for heavier matrices (like Au) corrections are minor and can be easily calculated (7).

For 3 standard samples, Fig.1 illustrates the variation of the normalised signals $Li(\gamma)/Al(\gamma)$ and $Zn(X)/Al(\gamma)$ versus the corresponding concentration ratios. As theoretically expected, the γ signals vary linearly with concentration. The line passes through the 2 experimental points and through the origin. A linear variation is also observed for Zn.

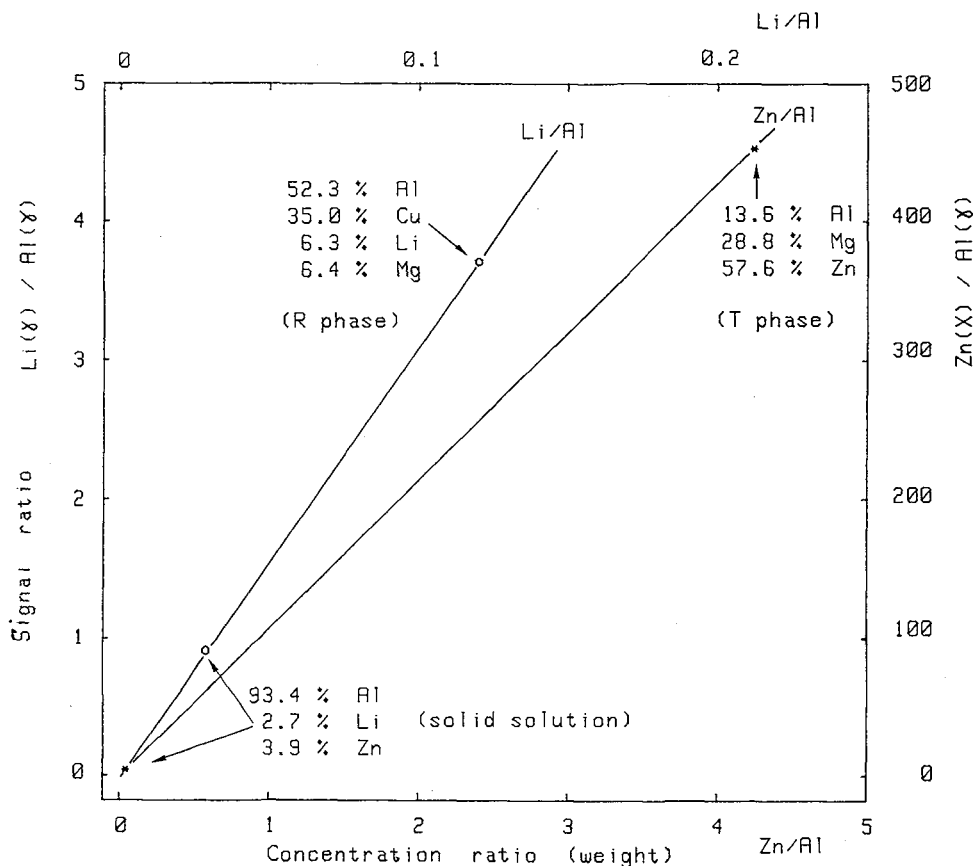


Fig. 1. Linear variation of the signals detected in the Nuclear Microprobe versus concentration ratio. The bulk composition is given for each experimental point.

2.2. Densitometry in backscattered electron micrographs.

Fig.2 illustrates the variation of the grey level of 3 pure metallic samples (Mg, Al, Si) versus their atomic number Z ; the results correspond to the mean of 5-7 images. Due to the narrow range in atomic number ($11 < Z < 14$) on one hand and to the dynamic range of 256 levels on the other hand, the sensitivity of the method is very high: 70 grey levels represent 1.0 Z unit. The linearity of the curve appears to be excellent (correlation coefficient of 0.9994). For complex compounds of the type $A_{a_1}B_{a_2}N_{a_i}$, it appeared that the mean atomic number Z could be estimated by the following formula previously proposed by Danguy and Quivy(8):

$$Z = (\sum a_i Z_i^2) / (\sum a_i Z_i) \quad (1)$$

where a_i represent the stoichiometry coefficients. The validity of this assumption is illustrated for the compound SiC in Fig.2.

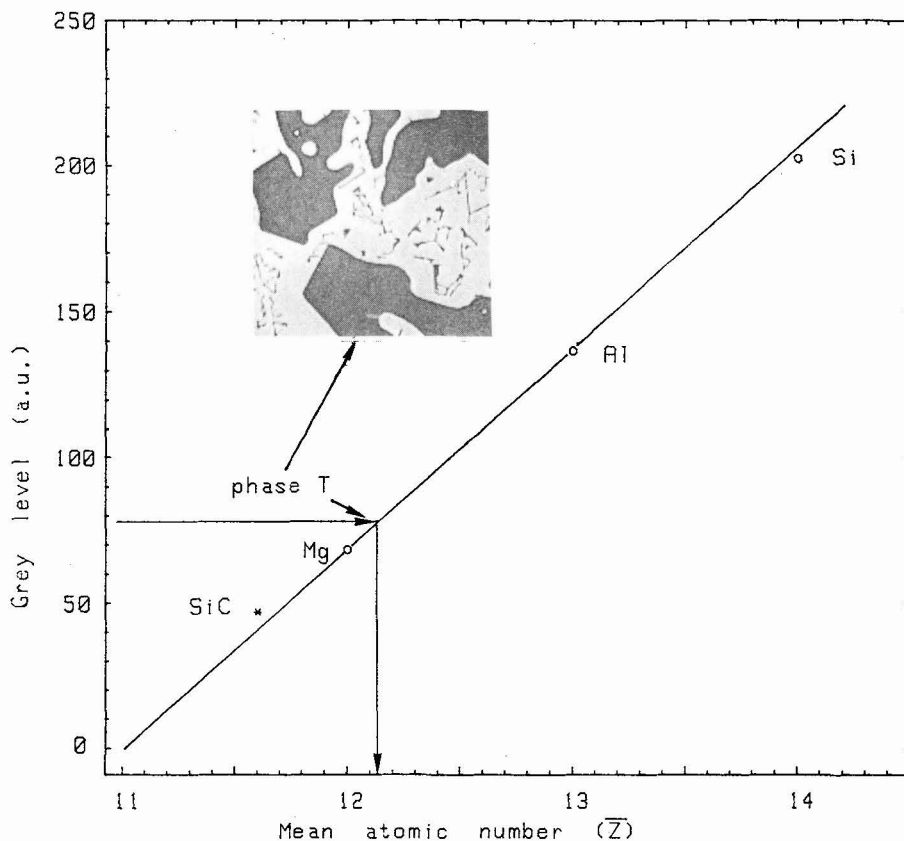


Fig.2. Linear variation of the grey level of 3 pure samples (Mg, Al, Si) and 1 compound (SiC) versus the mean atomic number. Determination of the composition of an unknown phase "T" visualised in the SEM in the backscattered electron mode.

3. Chemical microanalysis of complex Li bearing intermetallic compounds.

3.1. Phase " τ " in the Al-Li-Zn system.

In the course of our study on the constitution of ternary Al-Li-X alloys, a new intermetallic compound, designated by τ was found to crystallise in Al-Li-Zn alloys within a narrow composition range ($2 < \text{Zn/Li} < 4$ by weight). Unlike the T - $(\text{Al}, \text{Zn})_2 \text{Li}$ cubic compound previously reported by Cherkashin et al (9) in this system, it exhibits a quadratic structure (5). Its chemical composition was determined in the following manner for the investigated alloy (the global composition is given in column 2 of Table 1).

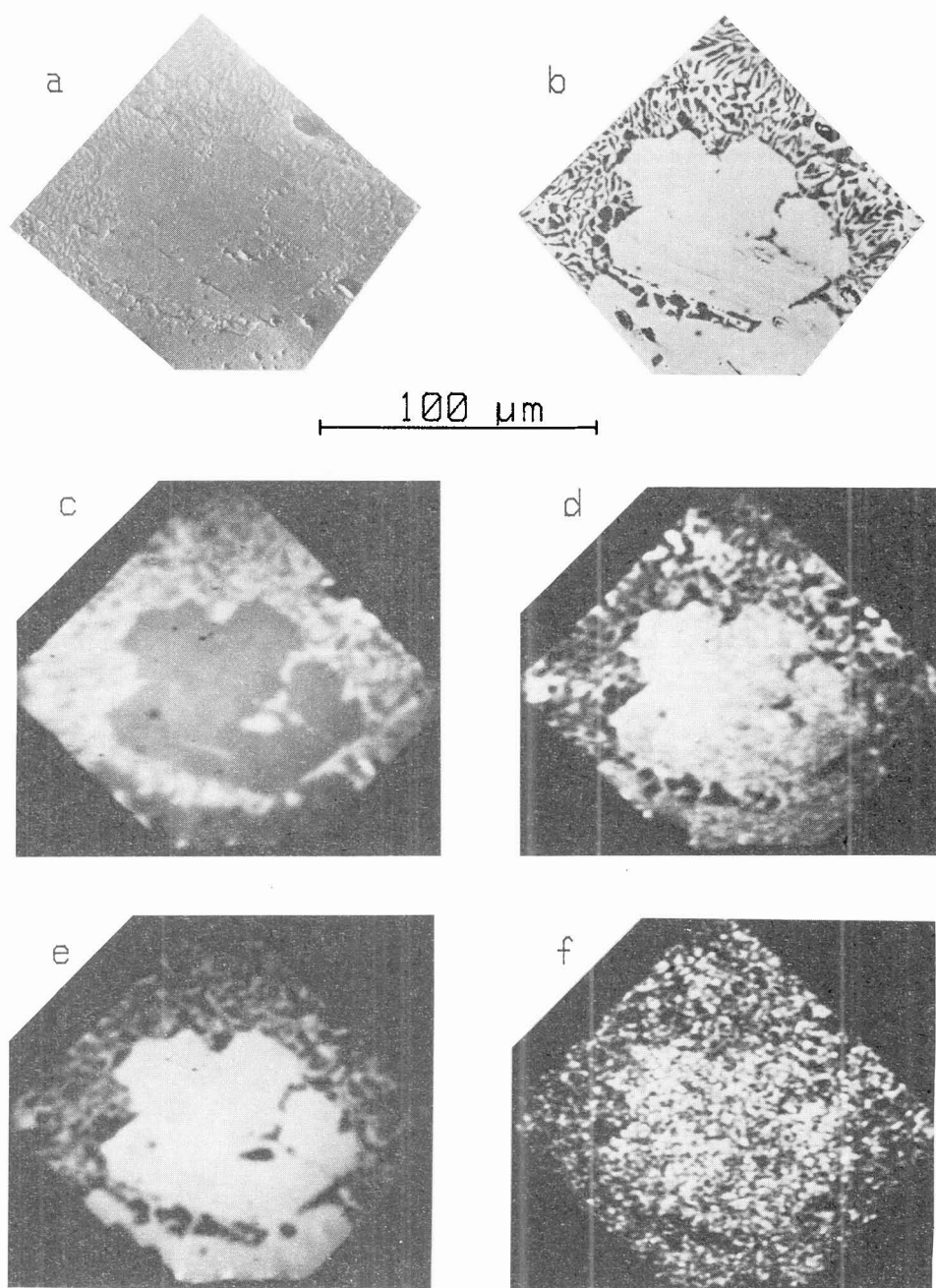


Fig.3. Micrographs of the same area containing an unknown τ phase. a : OM; b : SEM in the BSE mode, c : SIMS $^{27}\text{Al}^+$; d : SIMS $^{133}\text{Cs } ^{64}\text{Zn}^+$, e : SIMS $^7\text{Li}^+$; f : SIMS $^{64}\text{Zn } ^7\text{Li}^+$ ions.

The micrographs of the same primary phase obtained, at the same magnification, by different techniques are given in Fig.3. Fig.3a and 3b allow the location by OM and SEM while Fig. 3c,d,e,f provide the certitude of the presence of Li (e) in combination with Al(c) and Zn through the molecular ion Cs Zn^+ (d). The intermetallic Zn Li^+ ion (f) provides evidence that the 2 elements Zn and Li are close neighbours in specific areas of the sample. The quantitative analysis by NM using the calibration line of Fig.1 gave the values of column 3 in Table 1. Analysis of this phase by EPMA, but taking into account the presence of Li, gave results given in column 4 of Table1. The concentration of the heavy elements Al and Zn are in good agreement, while that of Li, deduced by difference, presents the correct order of magnitude.

Table 1. Composition of the investigated alloy and of the intermetallic phase τ determined by Nuclear Microprobe (NM) and conventional EPMA (results in weight %).

Element	Bulk composition	NM	EPMA	Composition $\text{Al}_5 \text{Zn Li}_3$
Al	63.0 ± 0.9	61.3 ± 0.6	61.1 ± 0.6	61.0
Zn	28.0 ± 0.8	28.8 ± 0.2	30.2 ± 1.2	29.6
Li	9.0 ± 0.3	9.9 ± 0.2	(8.7) (by difference)	9.4

Hence, the phase τ is found to have a composition very close to that of a $\text{Al}_5 \text{Zn Li}_3$ compound given in column 5 of Table 1.

Provided that standard samples are available with homogeneous phases with dimensions greater than the spatial resolving power of the NM ($> 10 \mu\text{m}$), this technique is able to characterise any unknown Al-Li alloy. In the near future, it would be interesting to analyse these samples by conventional EPMA in order to propose and to implement systematically the correction procedures taking into account the presence of light elements.

3.2. Phase "T" in the Al-Li-Si system.

The presence of Si as an impurity in Al-Li alloys is known to promote the formation of intermetallic constituent particles of ternary compound. The latter, also designated by T, has been given a formula $\text{Al}_2 \text{Li}_3 \text{Si}_2$ according to Drits et al (10) and Kadaner et al (11). On the other hand, Hanna and Hellawell (12) used a formula Al Li Si for the T phase, in agreement with Novotny and Holub (13), who reported that this phase could be an extension of the $\delta\text{-AlLi}$ phase. The following analyses were undertaken to elucidate the actual composition of the T- (Al, Li, Si) phase.

The BSE micrograph of an area containing the ternary phase in an as-cast alloy (87.5 % Al, 4.7 % Li, 7.8 % Si) is shown in the Fig.2. Its identification was performed in 2 steps. First, the analysis by EPMA, including the correction for the presence of Li, gave an atomic ratio $\text{Al/Si} = 1$. The formula is then $\text{Al Li}_x \text{Si}$. Secondly, its mean atomic number deduced from the calibration line of Fig.2 has a value of $Z = 12.12 \pm 0.09$. Values of $x = 1, 1.5$ and 2 for the stoichiometric coefficient of Li would lead respectively to mean atomic number values of $Z = 11.61, 12.02$ and 12.47 according to relation (1). From a statistical interpretation, the experimental value corresponds without ambiguity to the value $x = 1.5$. The phase T is thus actually characterised by the formula $\text{Al}_2 \text{Li}_3 \text{Si}_2$.

This technique combining SEM and Image Processing appears to be a valuable routine tool for the microanalysis of alloy systems containing light elements.

4. Conclusion.

The combination of conventional (OM, SEM, EPMA) and new (SIMS, NM) microanalytical techniques allowed the quantitative analysis of all elements, including Li, in intermetallic phases of Al-Li alloys. The Nuclear Microprobe may be considered as a new reference method for the metallurgist. It provides standard samples on which correction procedures for the quantitative analysis of light elements by conventional techniques (SEM and EPMA) can be tested and implemented in the future.

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