QUANTITATIVE X-RAY MICROANALYSIS OF PRECIPITATES IN ZINK-ALUMINIUM-COPPER ALLOYS

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ABSTRACT

The aim of the present study is to adapt the Cliff-Lorimer method for quantitative analysis of thin foils and to obtain information about the composition of fine metastable precipitates in Zn-Al-Cu alloys. The coefficients K_{alzn} and K_{alcu} were determined for accelerating voltage of 200 kV, about which there has no been data ever mentioned. Some applications of the method are given.

INTRODUCTION

Previous studies of Zn-Al-Cu [1] alloys have shown that the decomposition of the initial supersaturated solid solution down to the equilibrium α and η phases proceeds with the formation of zones G.P. and some metastable phases. These phases are usually regions of different composition as compared to the surrounding matrix with dimensions ranging from a few to 300 nm. Besides electron diffraction, which yields information on their structure, X-ray microanalysis with high spatial resolution may also be applied as regards to their composition. Resolution of thin films microanalysis in fact is limited generally from the sample thickness and normally the locality is about 50-100 nm. In previous our paper [2] the Cliff-Lorimer method for quantitative analysis of thin foils was adapted in order to obtain information about the composition of fine metastable precipitates in Zn-Al alloys. The aim of the present study is to adapt this method for quantitative analysis of thin foils of Zn-Al-Cu alloys.

EXPERIMENTALS AND DISCUSSION

The Cliff-Lorimer method [3] for the case of Zn-Al-Cu alloys is based on the expressions:

$$\frac{C_{al}}{C_{zn}} = K_{alzn} \frac{I_{al}}{I_{zn}}$$

(1)

$$\frac{C_{al}}{C_{cu}} = K_{alcu} \frac{I_{al}}{I_{cu}}$$

$$C_{al} + C_{cu} + C_{zn} = 100\% \qquad ,$$

where C_{al}, C_{zn} and C_{cu} are the concentrations in wt.% of Al, Zn and Cu in the analysed volume; I_{al}, I_{zn} and I_{cu} are the characteristic X-ray intensities, background-corrected for the same elements; K_{alzn} and K_{alcu} are proportional coefficients which are dependent only on the accelerating voltage.

In the present study we used the method for experimental determination of K_{alzn} and K_{alcu}, both because of the absence of any data related to an accelerating voltage of 200 kV, which we employed, and because of its greater accuracy. The specimen, thin foil of Zn-27w.%Al-2w.%Cu alloy aged 3

weaks at $250^{\circ}C$, was used as a standard. In zone of about 3x4 μm of α'-supersaturated solid solution we measured the composition by means of microprobe (EPMA) whith spot diameter 1 μm and accelerating voltage 20 kV, using the ZAPTEM PROGRAM of EG&G-ORTEC. The results are as follows: C_{al}=68w.%, C_{cu}=4w.%, C_{zn}=28w.%. The thickness of the investigated zone, measured by the contaminations, photographed by a TEM was 960 nm. At the same place with the help of EDS of TRACOR-NORTHEN, combined whith a TEM we measured the background-corrected characterisic intensities I_{al}=102383, I_{cu}=7698, I_{zn}=18327. On fig.1 is shown the TEM-EDS spectrum. The spot size is about 1 μm and the accelerating voltage is 200 kV. For the Cliff-Lorimer coefficients we obtaine:

$$K_{alzn}=0.76\pm0.05$$
$$K_{alcu}=1.28\pm0.9$$
$$K_{zncu}=1.68\pm0.11 \quad ,$$

where the error is a sum of the errors of the determination of the concentrations with ERMA ($\pm5\%$) and the statistical errors ($\pm2\%$) whith 3σ confidence interval.
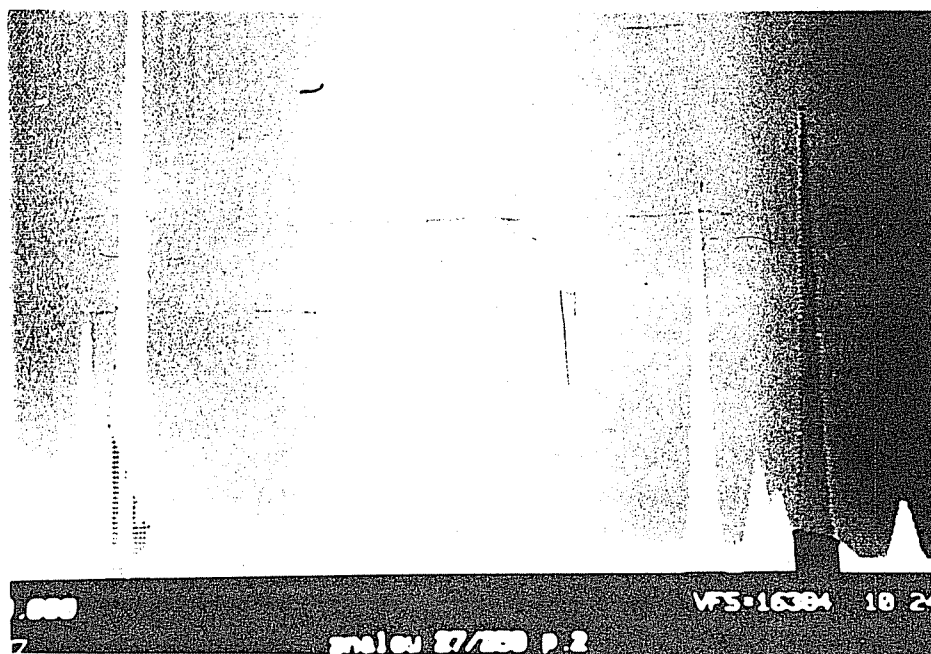

Fig.1. TEM-EDS spectrum of the α' zone used as standard.

It could be seen that K_{alzn} coinsides in the frame of the error whith data from our previous study [2], where we obtaine K_{alzn}=0.73$\pm$0.05.

This is known as the "thin film approximation method" and is corrected for absorption in case the coefficients K correction is greater then the error of the method. For the zone in which we determined K we obtained a correction coefficient CF=1.005, which lead to a difference for K of under 1% and would not be taken into account. Since the absorption correction CF, calculated for used foil thicknesses and concentrations, leads to an error not so considerable as the one of the method, we use the thin film approximation.

In the cases when an analysis of precipitates which are compleately surrounded by a matrix of a different composition is performed, the results must be corrected for matrix contribution. So, it is necessary to know the matrix composition C_{matr} and the excited volumes of the precipitate V_{ppt} and the matrix V_{matr}, normalized to 100%.

The quantitative microanalysis of precipitates made by this method is limited generally by the foil thickness t. The precipitate dimensions must

be near to t, but not less than 1/2 t, because the matrix correction lead to an error greather than the error of the method.

As an application to the method we can determine the weight percentage o the ε-phase in η lamellas of Zn-27w.%Al-2w%Cu alloys. The samples are age to 250°C and 100°C for 1,2,3 and 4 weeks. Thin foils are prepared b electropolishing using the window technique. Using high localit microanalysis the observed in η lamellas accicular precipitates - fig.2 are characterized as Zn-Cu phase whith high content of Zn. Interpretatio of ellectron diffraction patterns indicates that they are ε-phase-CuZn [4]. Since the precipitates diameter is very fine for quantitative analysi (less than 1/10 t), the analysis was made in zones with diameter about 10 nm with both $\varepsilon-$ and η-phases. Using equations (1) for the case of $I_{\alpha l}=0$ i has been established that the Cu concentration changes in very wide rang in different lamellas and time of ageing, for samples aged at 250°C - fro 1 to 5%, and for the same aged at 100°C - from 1 to 9%. It has not bee found any dependence neither in the frame of one probe nor on time o ageing. The only thing that can be confirmed is that the ε-phase is stabl in all times of ageing investigated. Considering the ε phase i stoichiometric, we have calculated that the variation of ε in η-matrix is for ageing at 250°C - from 5 to 25% and for ageing at 100°C - from 5 t 45%.
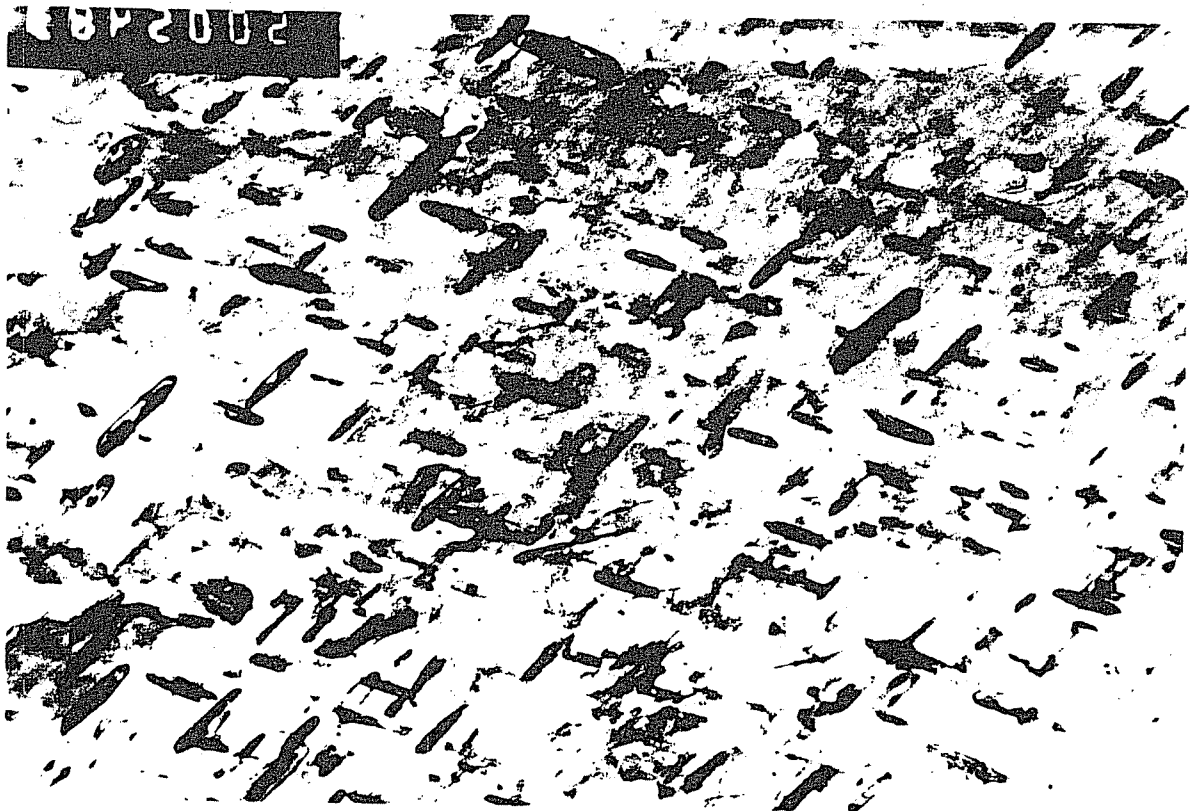

Fig.2. Acicular precipitates in η phase characterized as ε phase-CuZn4

As a future application to the method we expect to determine the process of T'-phase precipitations For the periods of ageing investigated it ha not been found T'phase, but we have data that for shorter ageing time (till 2 days) T' could be found.

REFERENCES

1. L. Terziev, J. Lecomte-Beckers, T. Greday, J. Wegria, Rapport Interne CRM (1985)
2. P. Rachev, L. Terziev, Phis. and Chem. of Sol., 98 (1987)
3. G. Cliff, G.W. Lorimer, J Microsc., **103**, 203 (1975)
4. J. Lecomte-Beckers, L Terziev, P. Rachev, G. Walmag, J. de Micr. et Spectr. Electr., in press.