Journal of Thermal Analysis, Vol. 53 (1998) 785-795

THE Al–Zn–Ga PHASE DIAGRAM
Part II

E. Aragon, K. Jardet, P. Satre and A. Sebaoun

Laboratoire de Physico-Chimie du Matériau et du Milieu Marin, Matériaux à Finalité Spécifique (E.A. 1356), Université de Toulon et du Var, B.P. 132, 83957 La Garde cedex France

(Received August 8, 1997)

Abstract

The first part of this paper presented five experimental isopletic cuts in the Al–Zn–Ga ternary phase diagram. On these cuts, two isobaric ternary invariant reactions were determined and a significant retrograde miscibility of Ga in a α'_{ss} solid solution was observed.

In the second part, the two isobaric invariant reactions are studied more precisely. In particular, the composition of the invariant phases are given and the Ga miscibility in the α_{ss} ternary solid solution is studied. Isothermal sections are established. The results confirm the existence of a vanishing point in the liquidus area, conjugated with a ternary critical point at about 290°C. A general perspective shape of the equilibria in the diagram is proposed.

Keywords: Al–Zn–Ga system, isothermal section, ternary critical point, ternary invariant, ternary phase diagram, vanishing point

Introduction

The first results obtained with the isopletic cuts method by using DTA and X-ray diffraction at various temperatures [1, 2] have been supplemented by SEM observations and microprobe analysis.

The compositions of the invariant phases have been determined and isothermal sections of particular interest have been deduced from the results presented in the first part of this paper. These isothermal sections reveal important phenomena. First, they allow the evolution of the phase regions to be followed, and in particular the (α_{ss}+α'_{ss}+L) three-phase tie triangle evolution as a function of temperature.

The existence of a vanishing point in the liquidus area, conjugated with a ternary critical point, is confirmed. The critical temperature for which the (α_{ss}+α'_{ss}+L) three-phase tie triangle disappears on heating and the composition of the vanishing point have been determined. The isothermal sections demonstrate the miscibility evolution in the α_{ss}, α'_{ss} and Zn_{ss} solid solutions.

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

A study by SEM and microprobe analysis at room temperature on as-cast samples and samples quenched from different temperatures has been performed in order to supplement the miscibility data given by the isothermal sections.

The results are summarized in a schematic perspective representation which shows the evolution of the main monovariant lines in the ternary phase diagram.

Experimental

The eutectic and metatectic isobaric invariants at 23 and 123°C, respectively, were studied by using the enthalpic data obtained on the six isopleths [1, 2]. The Tammann method [3, 4], which allows determination on each isopletic cut of the limits of the invariant triangle, was extended to the equivalent determination on the Gibbs triangle at the invariant temperatures. The precision for the determination was ±2%.

The isothermal sections were established by using the data obtained by the isopletic cuts method, and by taking into account the general rules for adjoining phase regions in a ternary system [5] and in particular the law of adjoining phase regions due to Palatnik and Landau [6].

The rule of adjoining phase regions does not apply in the immediate neighbourhood of critical points in phase diagrams and their sections [7]. However, Palatnik and Landau [6] produced an empirical formula for determination of the dimension of a critical element. From this formula, the ternary critical point and the conjugated vanishing point in the liquidus area are zero-dimensional points. The temperature and the composition of the vanishing point were determined by using the liquidus data on the ZA15-Ga and ZA20-Ga isopletic cuts, which intercept the monovariant lines in the liquidus area, and the ZA40-Ga isopletic cut, which intercepts the $\alpha'_{ss}/(\alpha_{ss}+\alpha'_{ss})$ phase boundary in the neighbourhood of the ternary critical point. The precision of this determination was ±5% for the composition and ±5°C for the temperature.

In addition, electron microprobe analysis was used in the investigation. The relative precision varied as a function of the atomic mass of the analysed element, from about ±15% for Al to ±7% for Zn and Ga. Moreover, a statistical study on several measurements is needed for the low compositions (<10%) in order to evaluate the precision.

Results

Figures 1 and 2 show the isobaric invariants at 123 and 23°C, which correspond to the reactions on heating:

– Ternary metatectic at 123±1°C	$Zn_{ss}+\alpha_{ss}+L_M \leftrightarrows \alpha'_{ss}$	$\Delta H>0$
– Ternary eutectic at 23±1°C	$Zn_{ss}+\alpha_{ss}+Ga_{ss} \leftrightarrows L_E$	$\Delta H>0$

The compositions of the invariant phases determined by the Tammann method [3, 4] are given in Table 1:

Table 1 Isobaric invariant equilibria: compositions of the invariant phases

Type	Phases	Composition/%* ±2%		
		Al	Zn	Ga
Metatectic	L_M	≈1	18	81
	α_{ss}	72	8	20
	α'_{ss}	13	66	21
	Zn_{ss}	2	94	4
Eutectic	L_E	≈3	≈3	≈94
	α_{ss}	84	2	14
	Zn_{ss}	≈1	97	2
	Ga_{ss}	≈1	≈1	≈98

* Compositions are all given as mass percentages

The Ga miscibility in the α_{ss} ternary solid solution at 23°C (about 14%, Fig. 2) was lower than that in the α_{ss} binary solid solution (about 20%) at 26°C [6].

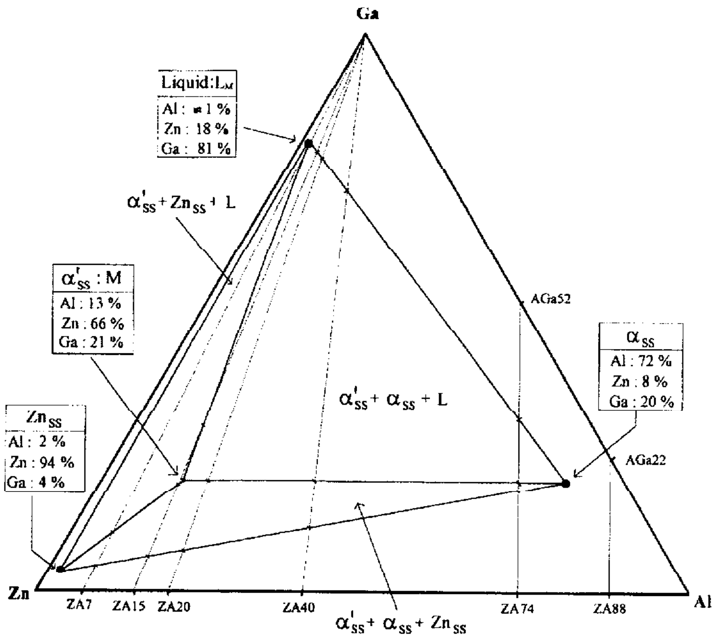


Fig. 1 Metatectic isobaric invariant at 123°C: composition of the invariant phases (obtained by the Tammann method)

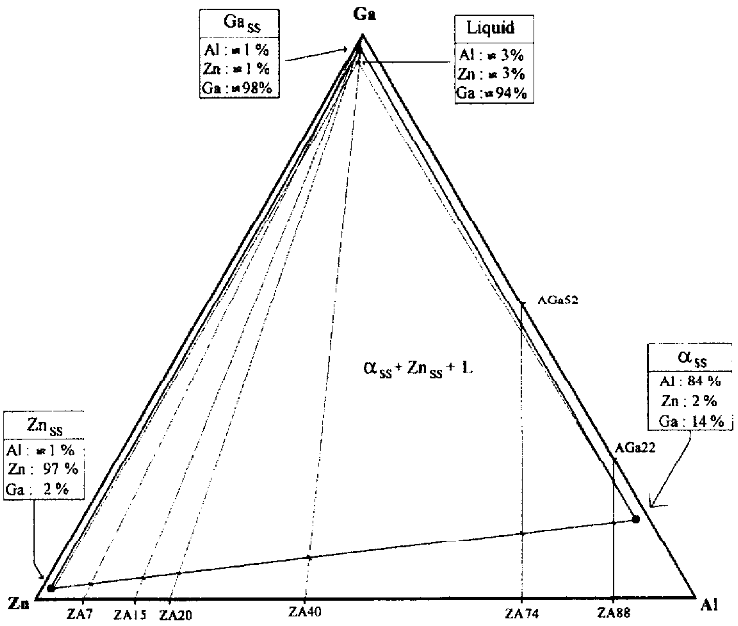


Fig. 2 Eutectic isobaric invariant at 23°C: composition of the invariant phases (obtained by the Tammann method)

Moreover, the miscibility evolved from 14% at 23°C to 20% at 123°C in the ternary diagram. On the other hand, the miscibility in Zn remained constant and at a low value.

The data obtained by the isopletic cuts method [1, 2] allowed the establishment of isothermal sections. Figure 3 shows some characteristic isothermal sections at 150, 200, 250, 280, 300 and 360°C in the diagram. On those cuts, from 123 to 360°C, it was possible to observe the following features:

– At 150°C, a small limited equilibrium field of the α'_{ss} solid solution, which originates from the metatectic point (*M*) at 123°C (Fig. 1).

– At 200°C, the field increases. The coherence with the isopletic cuts results leads to a crescent-shaped α'_{ss} one-phase region.

– Between 200 and 280°C, the expansion of the two α_{ss} and α'_{ss} solid solution regions corresponds to an increase in the Al miscibility in α'_{ss} as the Ga miscibility in α_{ss} decreases. At the same time, the (α_{ss}+α'_{ss}+L) three-phase tie triangle becomes smaller.

– Between 280 and 300°C, this three-phase tie triangle disappears.

– At 300°C, we observe a continuous solid solution field containing from 10 to 100% of Al and from 11 to 31% of Ga. This solid solution region presents a miscibility gap up to the temperature of the binary critical point (352°C, from [8]).

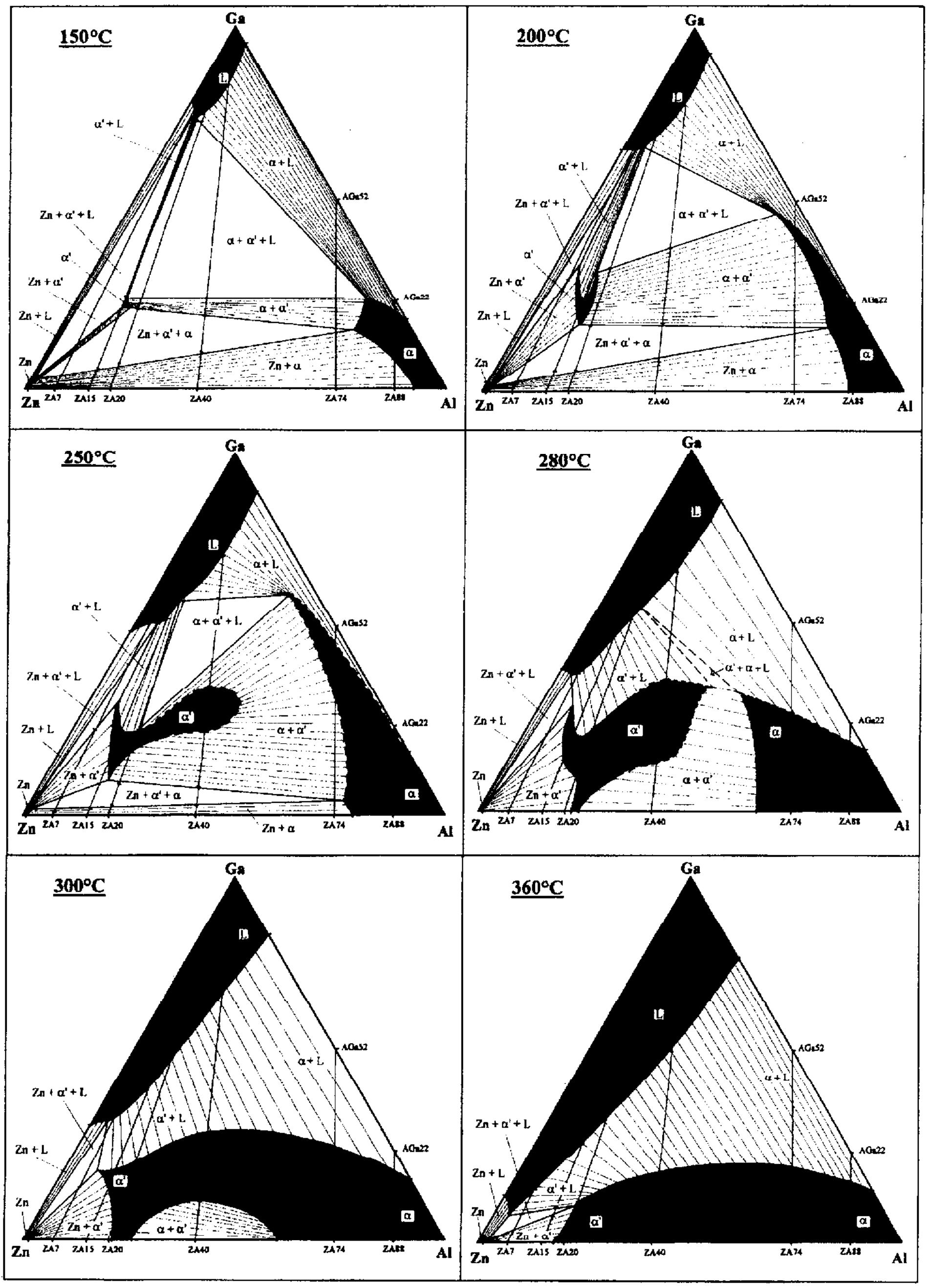


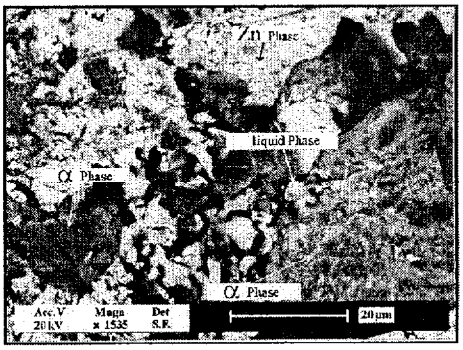
Fig. 3 Isothermal sections at different temperatures

– At 360°C, above 352°C, the $(\alpha_{ss}+\alpha'_{ss})$ two-phase region is no longer observed. On this isotherm, the three one-phase fields correspond to liquid, Zn and α/α' hyper-critical solid solution. The three two-phase equilibria are

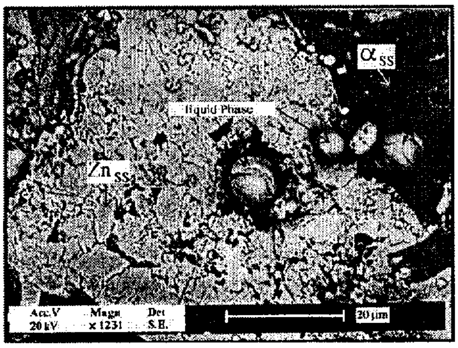
$$L \leftrightarrows Zn_{ss}, \qquad L \leftrightarrows \alpha_{ss}/\alpha'_{ss} \qquad \text{and} \qquad Zn_{ss} \leftrightarrows \alpha_{ss}/\alpha'_{ss}$$

The last three-phase tie triangle observed is $Zn_{ss}+\alpha'_{ss}+L$.

In the first part of this paper [2], we demonstrated the existence of a liquid phase (Ga-rich eutectic liquid) at room temperature, whose composition was determined by the Tammann method (about 94% of Ga, Fig. 2). This liquid phase was observed and analysed by electron probe microanalysis (Fig. 4). However, the sample temperature under the electron beam cannot be controlled. As a consequence, the composition of the analysed liquid phase (Al 2%, Zn 1%, Ga 97%) cannot be exactly that of the eutectic liquid. On the other hand, the sample heating and the Ga wettability lead to a superficial repartition of the liquid phase in the sample area for the high Ga compositions and for both as-cast and quenched samples. It may be observed from Fig. 4, however, that the number and the dimensions of the droplets increase as the Ga composition increases from 5 to 20% on the ZA7-Ga isopletic cut.

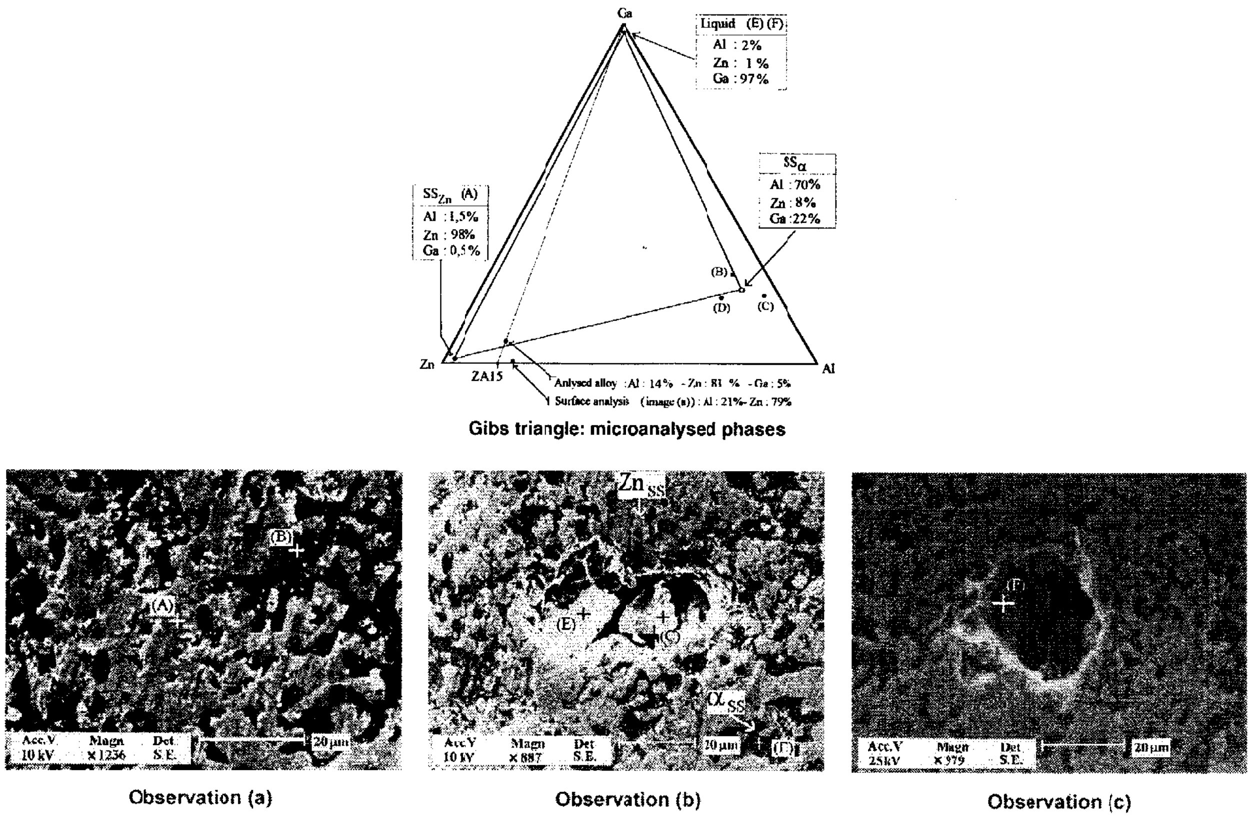


Alloy of 5% Ga on the isopleth ZA7-Ga



Alloy of 20% Ga on the isopleth ZA7-Ga

Fig. 4 Zn_{ss}, α_{ss} and liquid phase observed by SEM



Gibs triangle: microanalysed phases

Observation (a)

Observation (b)

Observation (c)

Fig. 5 Microanalysis of the ${}_{ss}\alpha$ and liquid phases: alloy of 5% Ga on the isopleth ZA15-Ga

Figure 5 shows a specific localization of the liquid phase in cavities for a sample with a low Ga composition (5% on the ZA15-Ga isopletic cut). Microanalysis allows identification of the eutectic liquid. Surface analysis, which does not identify Ga, confirms this localized repartition. On the other hand, various analysed spots of the α_{ss} phase lead to the mean composition Al 70%, Zn 8%, Ga 22%. This result is in accordance with the data obtained by the Tammann method (Figs 1 and 2), taking into account the microanalysis precision (about 15%) and also the evolution of the Ga miscibility in the α_{ss} ternary solid solution as a function of temperature, which increases under the electron beam.

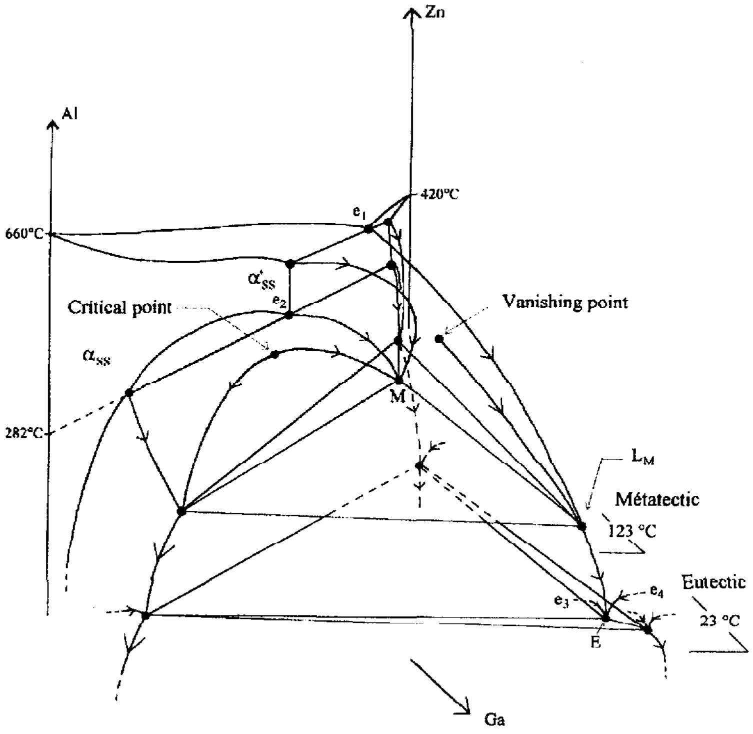


Fig. 6 Monovariant lines and ternary invariant reactions

A general perspective shape of the ternary diagram, taking into account the overall results, is presented in Fig. 6. The main monovariant solid–solid and liquid–solid lines in the Al–Zn–Ga ternary phase diagram, and particularly those which reach the ternary metatectic invariant from the Al–Zn binary diagram are drawn.

Figure 6 also shows the vanishing point in the liquidus area, which is conjugated with a ternary α_{ss}–α'_{ss} critical point. The temperature of these two points is about 290±5°C. Between 280 and 300°C, Fig. 3 shows the characteristic evolution of the phase regions. The isothermal section at 280°C (Fig. 3) demonstrates a small hypothetical three-phase tie triangle (α_{ss}+α'_{ss}+L), which disappears at the critical temperature. At 300°C (Fig. 3), this three-phase region is no longer observed.

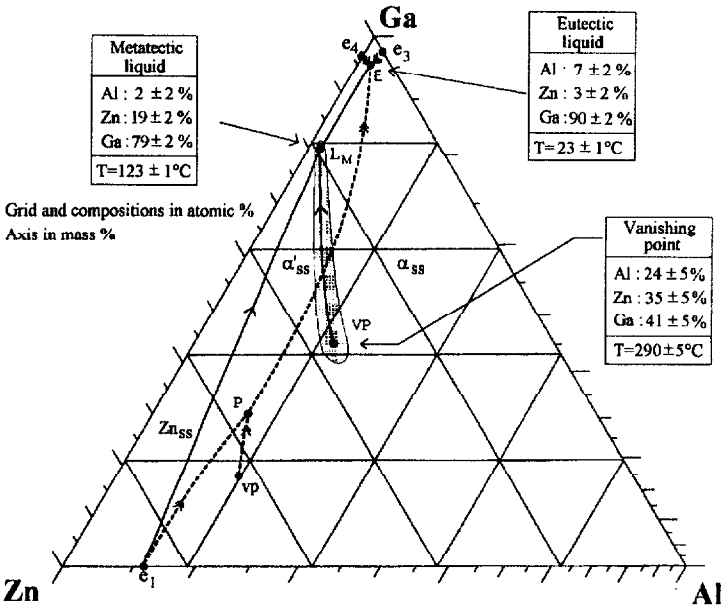


Fig. 7 Monovariant lines in the liquidus area: ···· calculated from [9], — this experimental work

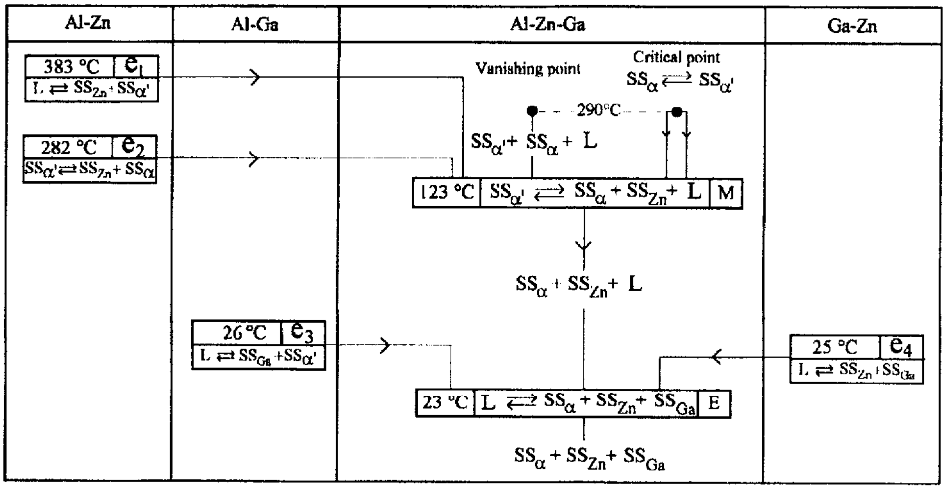


Fig. 8 Reaction scheme

Figure 7 shows the approximate composition at the vanishing point (*VP*:Al 11%, Zn 39%, Ga 50%) and the evolution of the monovariant lines in the liquidus area, compared with the data obtained by Ansara [9]. From the vanishing point (*VP*), the monovariant line in the liquidus area, for which the liquid is conjugated with the α_{ss} and α'_{ss} solid solutions, advances up to the metatectic liquid (L_M) at 123°C. In the liquidus area, the ZA15-Ga and ZA20-Ga isopleths cut across this monovariant line for Ga concentrations of 65 and 55% and T=200°C and T=280°C, respectively [1, 2]. The greyish area in Fig. 7 represents the dubiousness interval for its experimental determination and for the determined composition of the vanishing point (±5%). The ZA7-Ga isopleth cuts the monovariant line for which the liquid is conjugated with the Zn_{ss} and α'_{ss} solid solutions, for a Ga concentration of about 40% [1, 2]. This other monovariant line starts from the binary eutectic (e_1) in the Al –Zn diagram and reaches the metatectic liquid (L_M) at 123°C. At this temperature, these two monovariant lines give a third one (for which the liquid is conjugated with the Zn_{ss} and α_{ss} solid solutions), which goes to the eutectic point (E) at 23°C.

Finally Fig. 8 presents the reaction scheme of the Al–Zn–Ga ternary phase diagram.

Conclusions

This experimental study of the Al–Zn–Ga ternary phase diagram, conducted by DTA, X-ray diffraction at various temperatures and microprobe analysis, has shed light on some important phenomena in the diagram. First, a significant miscibility of Ga in the α'_{ss} solid solution has been observed. The existence of a vanishing point in the liquidus area, conjugated with a ternary critical point at about 290°C, has also been confirmed. Two identified invariants have been precisely studied. A study by SEM observations and microprobe analysis has demonstrated the difficulties due to the existence of a liquid phase at room temperature, which covers the sample surface. Microprobe analysis at equilibrium temperatures into solid-phase regions could be adapted to confirm the proposed isothermal sections. On the other hand, these experimental data might need an assessment by thermodynamic modellization.

* * *

The authors thank the D.G.A./D.C.N. (Délégation Générale de l'Armement/Direction des Constructions Navales) of Toulon for financial support during the thesis preparation by E. Aragon at Toulon University. In particular, the help of Mr. Giroud is gratefully acknowledged.

References

1 E. Aragon, Thesis, Toulon University, France (1995).
2 E. Aragon, K. Jardet, P. Satre and A. Sebaoun, J. Thermal Anal., (in press).

3 A. P. Rollet and R. Bouaziz, L'Analyse Thermique, Gauthier Villars, Paris (1972), Vol. 1, Chap. V.

4 Tammann, Z. anorg. allgem. Chem., 37 (1903) 303, 45 (1905) 24, 47 (1905) 289.

5 G. Masing, Ternary Systems, Reinhold, New York (1944).

6 L. S. Palatnik and A. I. Landau, Phase Equilibria in Multicomponent Systems, Holt, Rinehart and Winston, New York (1964).

7 A. Prince, Alloy Phase Equilibria, Elsevier Publishing Company, 1966.

8 J. L. Murray, Bulletin of Alloys Phase Diagrams, 4 (1983) 55.

9 I. Ansara, Al–Zn–Ga, G. Petzow and G. Effenberg ed., Ternary Alloys, 5 (1991) 552.