ANALYSIS OF PHASE TRANSFORMATIONS IN EUTECTOID Zn-Al ALLOYS

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Abstract: The paper concentrates on the phase transformations of $ZnAl_{22}$ and $ZnAl_{22}Cu2TiB$ eutectoid alloys obtained under various processing and cooling conditions. The results obtained by dilatometric (DIL) and differential calorimetric (DSC) analyses at various heating and cooling rates are presented. The presence of eutectic transformation in theses compositions indicates the intensity of the segregation processes during solidification. The analyses also aim at identifying the phase transformations specific for the two variants of thermal equilibrium diagrams for the analysed system.
Keywords: Zn-Al alloys, dilatometric analysis, differential calorimetric analysis, phase transformation.

1. INTRODUCTION

Vast amounts of literature are dedicated to the analysis of the structure of Zn-Al alloys [1-7]. This interest is explained by the complexity of the structural transformations in these alloys, as well as by the current tendency of promoting Zn-Al alloys with high aluminium contents (10 - 30 %). The complexity of structural transformations is amplified by the strong segregation tendency of these compositions. It needs be pointed out that because of the mentioned phenomena, scientific approaches to structural transformation analysis utilise two variants of thermal equilibrium diagrams, Fig. 1.
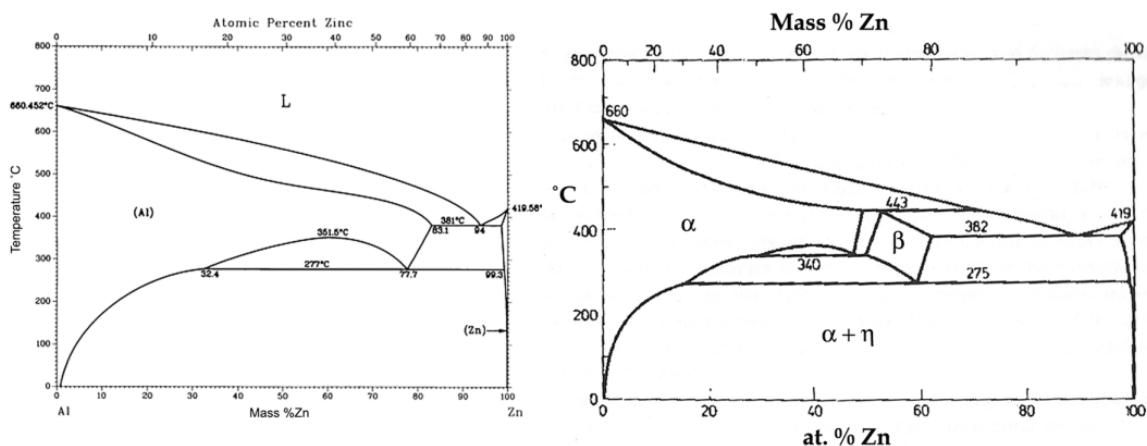

Figure 1: Variants of thermal equilibrium for the Zn-Al system [8,9]

The main difference between the two diagrams is the existence/absence of the peritectic transformation at 443 °C and the presence/absence of phase β, stable in the temperature interval of 275 - 443 °C and at Al concentrations of 17.2 - 29 %:

$$L_{14 \% Al} + \alpha_{30 \% Al} \rightarrow \beta_{28\% Al} \tag{1}$$

The paper analyses the structure of a series of eutectoid Zn-Al alloys, binary (ZnAl$_{22}$) and alloyed/modified with Cu – Ti + B (ZnAl$_{22}$Cu$_2$TiB).

A LINSEIS L75PT/1400 °C dilatometer and a DSC 200 F3 – Maia - Netzsch differential scanning calorimeter were used for the analysis of microstructure modifications determined by phase transformations as well as by the diffusion processes brought about by the thermodynamic tendency of restoring the state of equilibrium. The structural analyses were conducted by means of a Nikon – Omnimet - Buehler microscope.

2. EXPERIMENTAL DETERMINATIONS

The following primary metals were used for the two compositions: 99.95% pure Zn, 99.995% pure Al, Al-Cu$_{33}$ pre-alloy and AlTi$_5$B$_1$ for finishing the structure. The weight of the charges was of 2000 g. Melting was achieved in an electric furnace with silit bar heaters (electrical resistances) in a graphite crucible.

The alloy melted at 650° C was cast in metal chills, such as to obtain ingots of 14x160x80 mm size. Cylindrical samples of 40 mm diameter and 50 mm height were cast in refractory brick moulds, Fig. 2. Temperature was recorded by means of K – TPN - 101 coaxial thermocouples of 0.6 mm diameter protected by means of a refractory paste.
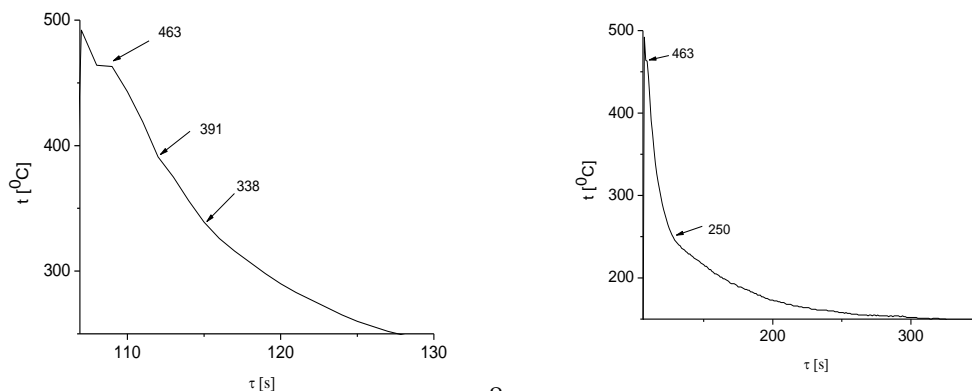

Figure 2: Casting moulds and assembly for cooling curve recording

Figs. 3(a) and 3(b) show the solidification curves obtained for the two compositions cast in metal moulds (OL).
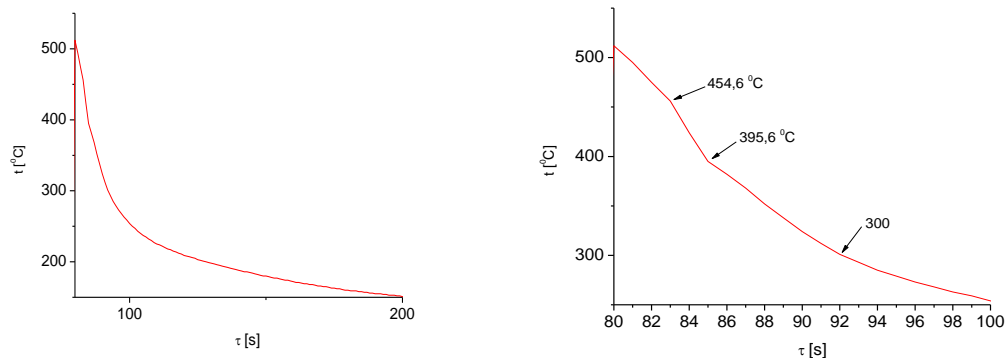
Figure 3: (a) Cooling curves for Zn-Al 22 alloy cast in a metal mould

Figure 3: (b). Cooling curves for Zn-Al 22-Cu2-TiB 22 alloy cast in a metal mould

The points of inflexion on the cooling curves were considered as corresponding to phase transformations. Table 1 shows the cooling rates for the two compositions cast in metal moulds. The cooling rates were computed prior to each phase transformation and the transformation temperatures indicated on the cooling curves of Fig. 3 (a) and Fig. 3 (b) respectively, are given in brackets.

Cooling rates and transformation temperatures corresponding to the points of inflexion of the cooling curves of Fig. 3.

Table 1: Cooling rates for $ZnAl_{22}$, $ZnAl_{22}Cu_2TiB$ respectively

Alloy	Cooling rate ($^\circ$C/s) and transformation temperatures ($^\circ$C)			
	Beginning of solidification	Eutectic transformation	Unidentified transformation	Eutectoid transformation
$ZnAl_{22}$	18.45 (454,6)	30.34 (395.5)	10 (300)	-
$ZnAl_{22}Cu_2TiB$	29.24 (463)	26 (391)	18.22 (338)	4.3 (250)

The samples taken from the cast ingots were subjected to DIL, DSC and structural analyses. H_2SO_4+HF +H_2O reactive was used for highlighting the structure.

Table 2 presents the parameters of DIL, DSC and structural analyses and the corresponding codes of the samples.

Table 2: Parameters of the DIL and DSC analyses

Sample state	$ZnAl_{22}$		Sample code	$ZnAl_{22}Cu_2TiB$		Sample code
	Parameters			Parameters		
	DIL	DSC		DIL	DSC	
Cast	-	-	a - 0	-	-	b - 0
One heating	$V_h = 20$ $V_c = 10$ $T = 420$ $\tau = 0.1$h	$V_h = 10$ $V_c = 0,3$ $T = 385$ $\tau = 2$h	a - 1 - 1	$V_h = 1$ $V_c = 1$ $T = 430$	-	b - 1 - 1
	-	$V_h = 10$ $V_c = 1$ $T = 510$ $\tau = 0.1$h	a - 1 - 2	$V_h = 20$ $V_c = 5$ $T = 430$ Softening (beginning of melting)	-	b - 1 - 2
Two heatings	$V_h = 1$ $V_c = 5$ $T = 430$ $\tau = 0.1$h Partially melted	-	a - 2	$V_h = 1$ $V_c = 1$ $T = 430$	$V_h = 10$ $V_c = 10$ $T = 510$ $\tau = 0.1$h	b - 2

V_h = heating rate [$^\circ$C/min]; V_c = cooling rate; T = heating temperature [$^\circ$C] and τ = maintaining time

The dilatometric analyses reveals significant dimensional modifications upon repeated heating of the $ZnAl_{22}$ samples cast in steel moulds, Fig. 4. Upon the first heating beyond the eutectoid temperature the sample contracts, what does not occur anymore upon the second heating. It can be noticed that the reverse eutectoid transformation in both heatings occurs at the same temperature but with different intensities, what indicates a modified share of eutectoid in the structure of the alloy. Both heatings were conducted at a rate of 1 $^\circ$C/min.
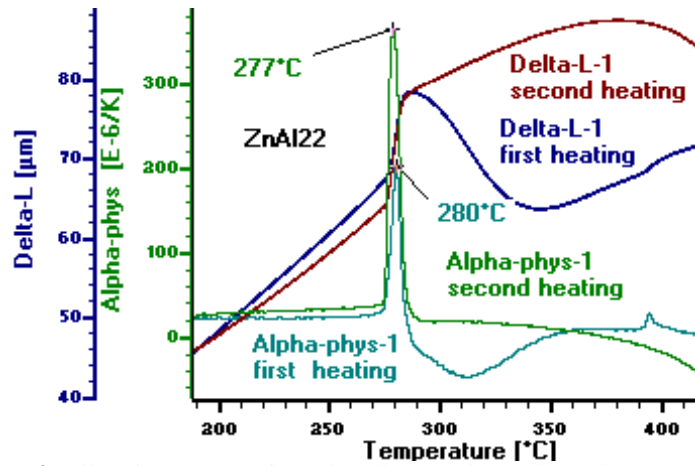
Figure 4: Dilatation curves of ZnAl$_{22}$ alloy cast in steel moulds, second sample

Figure 5 presents the dilatation curve for ZnAl$_{22}$Cu$_2$TiB alloy versus time as well as versus temperature, in order to highlight the dimensional modifications determined by the diffusion phenomena generated by both (eutectoid) phase transformations and the structure's tendency of achieving equilibrium.
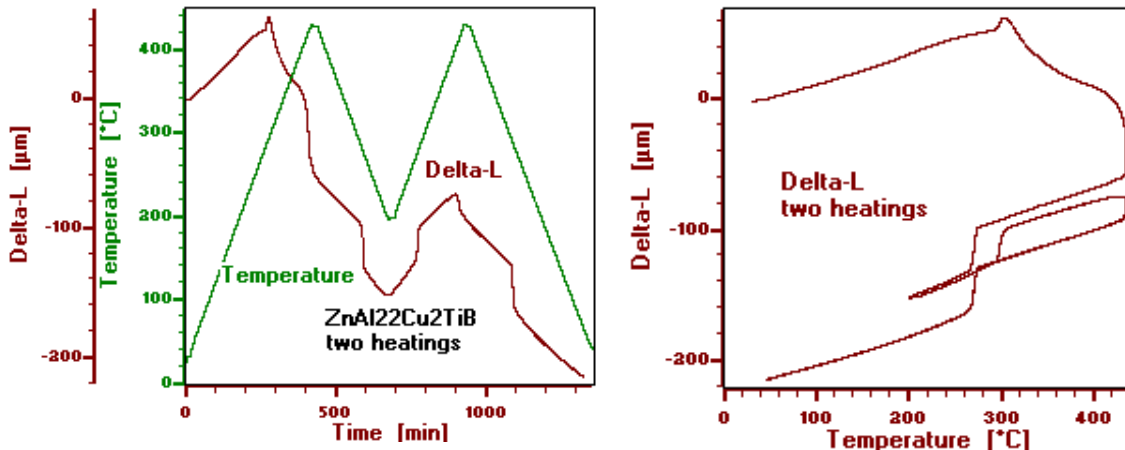

Figure 5: Dilatation curve versus time and temperature for heating and cooling rates of
1 °C/min, sample b - 2

Figure 6 presents the processed dilatation curves with indication of the transformation temperatures on their derivatives, actually representing the variation of the physical dilatation coefficient versus temperature. The heating rates applied while conducting the dilatometric analyses are written on the curves, namely 1 and 20 °C/min, respectively.
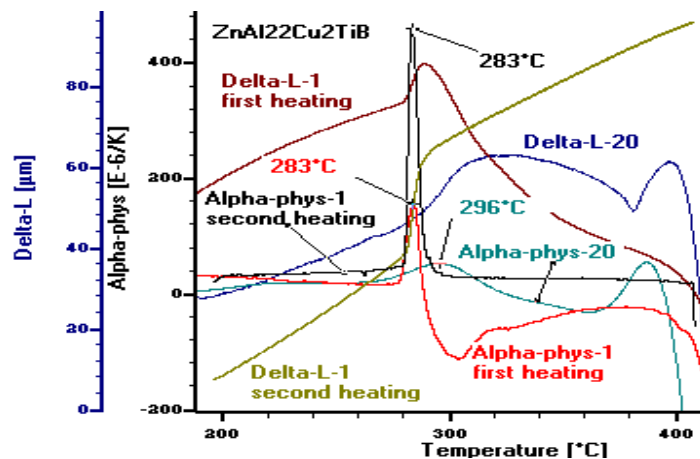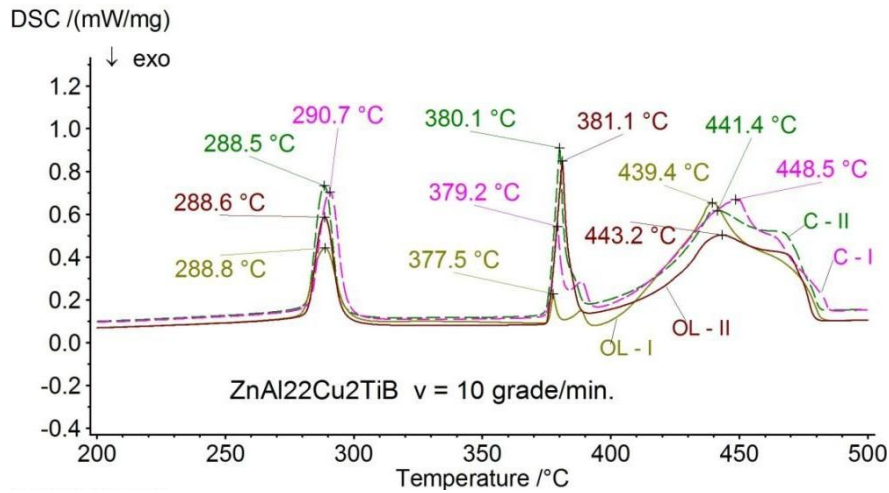

Figure 6: Dilatation curves of ZnAl$_{22}$Cu$_2$TiB alloy cast in steel moulds, samples b - 1 - 2 and b - 2

The dilatometric measurements were further completed by DSC analyses. These determinations allowed tracing of the phase transformations until the melted phase is reached.

Figure 7: DSC curves for the heating of the samples cast in steel moulds (OL) - sample b - 2, brick moulds (C), heated once (I) and heated twice (II)

At heating rates of 10°C applied in DSC analysis the peaks corresponding to the eutectoid, eutectic transformations and to melting by liquid solution appear on the heating curves, Fig. 7. The peak corresponding to the melting interval has the characteristic shape of melting with liquid solution [10]. It needs be pointed out that the 3 transformations occur at different intensities for the two heatings, what explains the thermodynamic tendency of restoring the state of equilibrium. It can be noticed that in the first heating the peak corresponding to the eutectic transformation is less obvious and is followed by a peak that suggests the existence of yet another solid state phase transformation prior to the beginning of melting through solid solution. For the second heating the first peak of the eutectic temperature becomes significantly more obvious, while the immediately subsequent peak disappears.

This observation is in agreement with the results of the dilatometric analyses that reveal the closeness of the real structure to the equilibrium one by disappearance of the peak corresponding to the eutectic transformation. This observation is supported also by the DSC curve recorded for both heating and cooling of a $ZnAl_{22}$ sample cast in a metal mould, heated to a temperature slightly greater than that of the eutectic transformation, Fig. 8 (a). These curves obtained for sample a-1-1 are comparable to similar curves recorded for sample a-1-2, Fig. 8 (b) and 8(c).
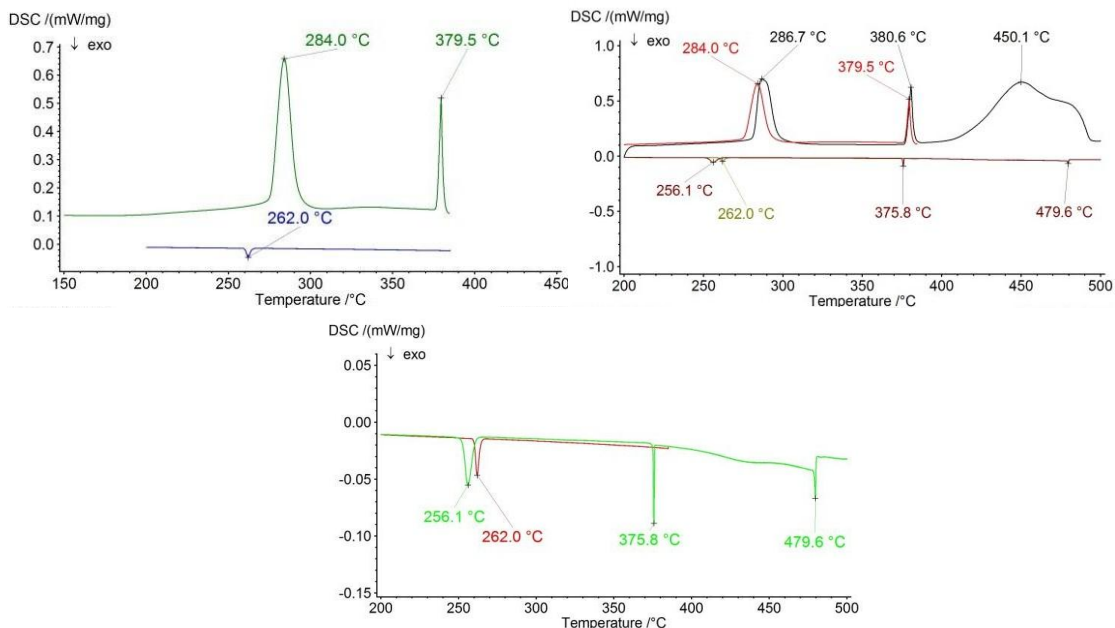
Figure 8: DSC curves for metal mould cast $ZnAl_{22}$ alloy (a) sample a - 1: heating + cooling; (b) samples a - 1 - 1 and a - 1 - 2 heating + cooling, overlapped and (c) samples a - 1 - 1 and a - 1 - 2 cooling, overlapped

11

The results of the DIL and DSC analyses are confirmed by the structural analyses conducted on the cast and heat treated samples (we considered that both analyses, when melting does not intervene, can be assimilated to homogenisation heat treatment). Figure 9 presents the structures observed in a binary alloy with 22 % Al.

Figure 9: Structure of steel mould cast ZnAl$_{22}$ alloy: (a) sample a - 0 - in cast state; (b.) sample a - 2 - DIL – partial melting, and (c) sample a - 1 - 1-DIL, no melting

3. CONCLUSION

The results of the DIL analysis reveal the intensity of the segregation processes during solidification.The results of the dilatometric analyses underline the importance of heat treatment in view of restoring the equilibrium structure such as to avoid dimensional modifications of components during operation.

Because of the high cooling rates during the liquid-solid phase transformation the point corresponding to the maximum solubility of aluminium in zinc at eutectic temperature is significantly displaced to the left, towards higher aluminium concentrations, what explains the presence of the eutectic structure (transformation) in alloys with 22% Al, in which, according to the thermal equilibrium diagram eutectic is not supposed to appear.

The cooling rate of 1°C/min does not ensure achievement of the equilibrium structure according to the thermal equilibrium diagram.

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