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Dilatometric and thermal analysis of hipoeutectoid Zn-Al alloys

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The Zn-Al alloys containing different amounts of Al (4,8,12,22 and 27 wt. %) are very often found in certain applications. Microstructure changes and phase transformation of these alloys have been systematically characterized. The present paper is focused on the establishing activation energies for eutectoid transformations in the binary Zn (4,8,12,22) wt. % - Al systems, using the temperature values of correspondent peaks from experimental derivative dilatation curves. The increasing of aluminium contents determines a decreasing of activation energy value either for heating or cooling. The activation energy variation depends on aluminium content or eutectoid ratio in the alloy structure.

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1. Introduction

In the last years, Zn-Al alloy systems have been extended in different industrial applications. Certain composition contain 8, 12, 22, 27 and 40%wt. Al were standardized, their properties being well investigated [1-5].

Among other properties, these kinds of alloys reveal an excellent casting behaviour and good tribological properties, in terms of friction and wear. The main disadvantage of them is the long-time structural instability. In order to avoid this inconvenient, these alloys are heat treated, which contribute to increase the structural stability during service.

At the same time, certain composition with an Al content between 18 - 40% wt. present good super-plastic properties. Both the heat treatments recommended for these alloys and super-plasticity are correlated with solid-phase structural transformation.

If we consider the structural transformation, a very important task in this region is the thermodynamic aspects. Within the frame of this paper, a consistent experimental program regarding the eutectoid transformation of certain binary composition with 4, 8, 12, and 22% wt. Al is related.

For transformation analysis has took into account the Presnyakov's thermic equilibrium diagram Fig. 1 [6]. If we make a comparison with Hansen's diagram [7], the Presnyakov's diagram presents a supplementary β-phase (the intermetallic compound ZnAl).

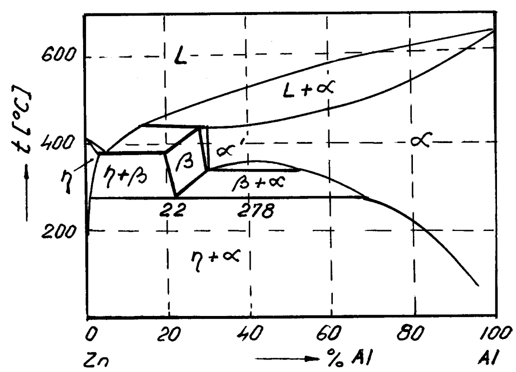

Fig. 1. Zn-Al equilibrium diagram.

Taking into account the binary system, during the cooling process, the eutectoid transformation appears at 278 ºC, according with the reaction:

$$\beta \rightarrow \eta + \alpha \quad (1)$$

and the inverse reaction is typically for the heating process. The activation energies both for heating and cooling have been established by dilatometric analysis.

The dilatometric study of solid phase transformations is possible only in certain cases, in which the transformation takes place with volume variation. A solid body, during the heating process, knows a dilatation, according to the relation:

$$L_t = L_0 (1 + \alpha T) \quad (2)$$

The dimensional variation (in length) can be estimated with the following relation:

$$\Delta L_{thermic} = L_t - L_0 = L_0(1+\alpha T) \quad (3)$$

If the metal (or alloy) presents solid phase transformations (e.g.: the eutectoid transformation), on the (length) dilatation caused by the increasing of temperature is overlapped the dilatation due to the phase transformation:

$$\Delta L_{total} = \Delta L_{thermic} + \Delta L_{phase} \quad (4)$$

The small length variation caused by the phase transformations are more dignified on the derivative dilatation curves.

2. Experimental procedures

For preparing the Zn - (4, 8, 12, 22) wt. % Al compositions, it has been used elementary metals.

The melting process has been achieved using an electric furnace (working with silit bar heating resistances), in a graphite crucible.

The over-heating temperature, before the casting, was 100 °C.

For thermal analysis, cylindrical samples having 30 mm in diameter and 60 mm height have been cast.

At the same time, using the same load, were prepared samples, by casting both in graphite and firebrick forms.

Based on EBI-Winlog software, it has been recorded in a simultaneous mode the cooling curves. These samples used for structural and dilatometric analyses, were sampled from unfinished goods of 80x200x10mm, cast in steel ingots.

The structural analysis were performed both on heat-treated and non heat-treated alloys.

The microstructural aspects have been investigated using an inverse-metallographic microscope, Nikon type, with a magnification between 500 – 1000X.

The applied samples heat treatment supposed a heating to 350 °C, keeping at this temperature for 4 days (96 hours) and cooling in furnace.

According with the Presnyakov's thermal equilibrium diagram (fig.1), for Zn enriched alloys are characteristic three important transformations: the eutectic one at 381 ^{0}C, the eutectoid one from 278 ^{0}C and the peritectic one from 420 ^{0}C.

For the dilatometric analysis, small cylindrical samples with 6 mm in diameter and 16 mm in length have been used. The dilatometric tests were performed using a LINSEIS, L75/230 type dilatometer.

In order to establish the activation energy for eutectoid transformation of Zn-Al alloy systems, it has been used the temperature values corresponded of the tips from the derivative dilatation curves.

Kissinger's relation is used for establish the activation energy (E_a) [8]:

$$\ln\frac{v}{T_m^2} = -\frac{E_a}{R\cdot T} + M \quad (5)$$

where: T- temperature; v – the heating rate in [˚C/s]; R = 8,3144 [J/mol.K] – the gases constant; M - constant; T_m- maximum temperature [K] from the derivative dilatation curves.

3. Results and discussion

Table 1 presents the thermal parameters for cooling curves given in Fig. 2 and also for Zn. The cooling rates (in °C/min.), have been calculated for the temperatures interval situated before the start of phase transformation.

Table 1. The cooling rates and transformation temperatures associated of cooling curves from Fig 2.

Transformation and Transformation temperature for equilibrium conditions	The alloy					
	Zn		Zn-Al (12 wt. % Al)		Zn-Al (22% wt. % Al)	
	Casting in Graphite	Casting in firebrick	Casting in Graphite	Casting in firebrick	Casting in Graphite	Casting in firebrick
Start of solidification	420 (419)	28 (419)	465	28(456; 458)	1010	47 (500)
Eutectic transformation at 381 °C	-	-	60	7 (381)	110	10 (380; 381)
Eutectoid transformation at 278°C	-	-	17(248)	7 (251; 258)	17(252)	7 (253;254)

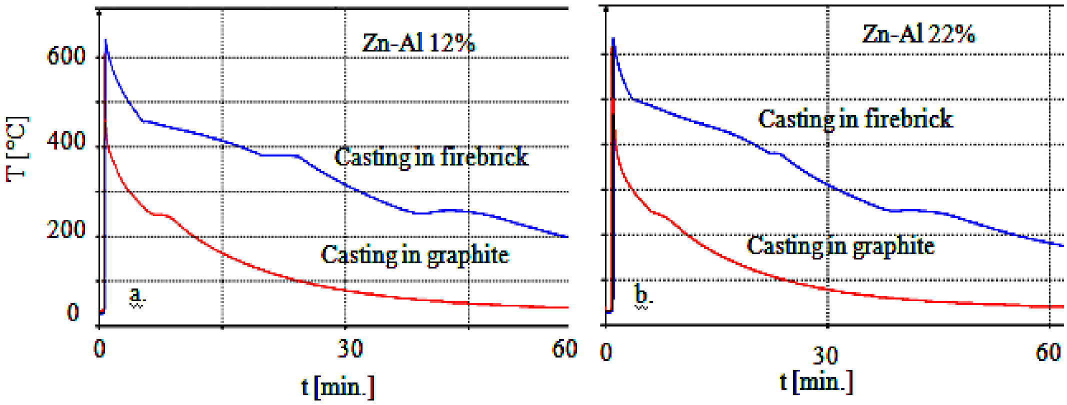

Fig. 2. Cooling curves typically of Zn-Al 12%: (a) Zn-Al 22% and (b) alloys, cast in graphite and firebrick.

Between the brackets are presented the real transformation temperatures and possible re-heating processes.

In the case of casting in graphite forms, the cooling curves revealed only the eutectoid transformation. For the alloy with an Al content of 22 wt. %, for casting in firebrick forms, supplementary appears the eutectic transformation, which means that the alloy's solidification may appear also for these cooling rates in non-equilibrium conditions. Fig. 3 presents the suggestive micrographs, for magnifications of 500X and 1000X.

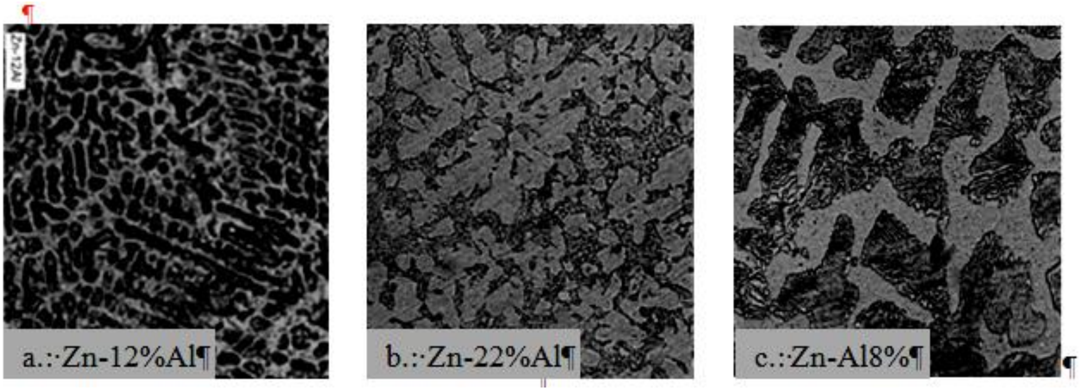

Fig. 3. Structural aspects of Zn-Al alloys: (a) Zn-12%Al cast (X500); (b) Zn-22%Al cast (X500); (c) Zn-8%Al heat treated (X1000).

For hipoeutectoid composition alloys, it could be observed the dendritic structure, which contains phase - η in the case of hypoeutectic alloys, and phase - α in the case of hypereutectic ones. For the sample with a eutectoid composition, it could be observed the peritectic reaction effect; this effect is revealed by the typical placement of the eutectoid at the boundaries of α solid-solution.

Anyway, it has to be mentioned that, the achieving of an equilibrium structure supposes long-time heat treatments.

In the Figs. 4 and 5 are presented the diagrams used for establishing of activation energy of eutectoid transformation (in the case of Zn-Al 4 % alloy) for heating and cooling respectively.

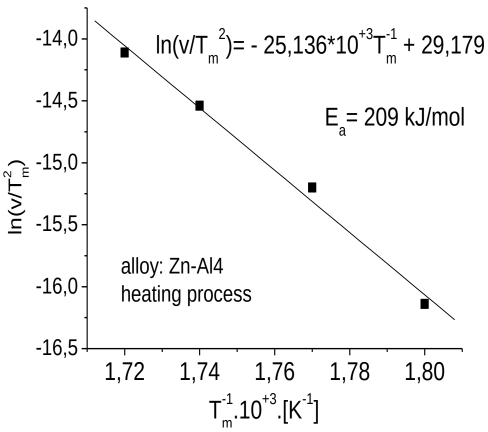

Fig. 4. The establishing of heating activation energy, for Zn-Al 4% alloy.

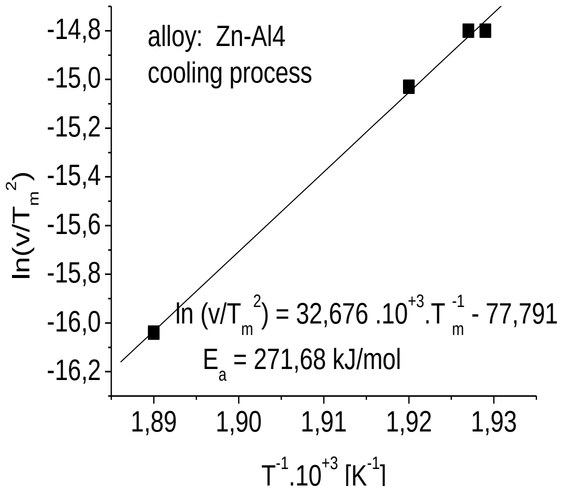

Fig. 5. The establishing of cooling activation energy, for Zn-Al 4% alloy.

Table 2 presents the over-heating and under-cooling processes, registered for different heating rates (the negative values of heating rate correspond to the cooling process), vis-à-vis on equilibrium temperature of eutectoid transformation (278 ºC).

Table 2. Undercooling and overheating rates registered for the Zn-Al alloys.

Heating rate [˚C/min.]	Al [% wt.]			
	4	8	12	22
-6	-32.8	-	-41	-52.6
-5	-30.4	-36.9	-	-31.8
-2	-23.2	-26.4	-33.5	-38.7
-1	-	-19.1	-20.4	-
2	4.4	-	-	-
5	14.4	10.5	9.8	8.9
10	23.7	16.8	16.6	17
15	30	25.5	26.5	24.9

In this case, the over-heating and under-cooling represent the temperature where the phase transformation takes place at a maximum rate. Table 3 and the diagram from Fig. 6 present the dependence between activation energy and Al concentration, for heating and cooling.

Table 3. Activation energy values - E_a, in kJ, for cast and heat treated alloys containing 4, 8, 12 and 22 wt. % Al.

Processing method		E_a [kJ]			
		4 wt. % Al	8 wt. % Al	12 wt. % Al	22 wt. % Al
Cast	At heating	209	183.5	145.6	83.71
	At cooling	-271.7	-196	-178.6	-167
Heat treated	At heating	-	148.7	117.9	71.7
	At cooling	-	-195.4	-238.6	-184.3

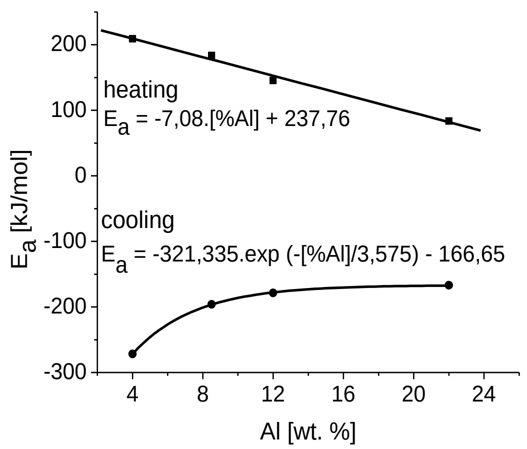

Fig.6. Variation of activation energy with the Al concentration, in the case of Zn-Al cast alloys, for heating and cooling processes.

Is important to note that, for eutectoid decomposition of β - phase, the activation energy value is negative because, this process is accelerated by the temperature decreasing.

4. Conclusions

The real structures of Zn-Al cast alloys present, at normal conditions of temperature, significant deviation from the equilibrium form ones (presented by the thermal equilibrium diagrams). This is the reason of applying of long-time heat treatments.

In the case of eutectoid transformation, increasing of Al concentration leads to decreasing of over-heating grade and increasing of under-cooling grade.

Both for heating and cooling transformation processes, the increasing of Al concentration determine a decrease of the absolute activation energy.

For the variation of activation energy with both the Al or eutectoid concentrations, both for heating or cooling, different laws are valid for constituent's nucleation process.

Taking into account the Zn-Al system, for the eutectoid transformation, the activation energies (absolute values) are significant higher in comparison with those ones from heating process. Thus, for achieving the mechanical mixture, the β – phase atoms arrangement involves higher energy than the inverse transformation, which entails under-cooling grades higher than over-heating grades.

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