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Phase Transformations in the Heat Treated and Untreated Zn-Al Alloys

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Abstract: Microstructure changes and phase transformations of Zn-Al based alloys have been systematically studied, using XRD, SEM and TEM techniques. The paper presents the results of experimental research concerning the eutectoid transformation in the Zn-Al system. The paper focuses on the determination of the activation energy for the eutectoid transformation in the binary Zn- (4, 8, 12, 22, 27) % Al system, using the values of the temperatures corresponding to the peaks on the derivatives of the dilatation curves.

Keywords: Zn-Al alloys, eutectoid reaction, dilatometric analysis, activation energy.

1. Introduction

Over the last years the category of industrial alloys of the Zn-Al system has been extended by the standardizing of compositions with 8, 12, 22, 27 and 40% aluminium, respectively. Their properties have been thoroughly researched and documented [1]. Alloys of the Zn-Al category have excellent castability and good wear and friction strength. The disadvantage of such materials is their instability in time. In order to avoid this disadvantage Zn-Al alloys are exposed to heat treatments designed to contribute to an increased structural stability during deployment [2], [3].

At the same time compositions with 18 – 40% aluminium have super-plastic properties [4], [5]. The heat treatments applied to these alloys, as well as super-plasticity are based on structural transformations in the solid phase. The thermodynamics of the process is of highest relevance to an analysis of the structural transformations. The paper approaches the study of the eutectoid transformation for binary compositions with 4, 8, 12, 22 and 27 % aluminium, respectively. During cooling the eutectoid transformation occurs at a temperature of 278 ºC according to the reaction:

$$\beta \rightarrow \eta + \alpha,$$

while during heating the reaction unfolds in the opposite direction.
The activation energies for heating and cooling were determined by dilatometric analysis.

2. Experimental determinations

Primary metals were used to melt of Zn-(4, 8, 12, 22, 27) % Al compositions. Melting was achieved in an electric furnace with silit bar heaters (electrical resistances) in a graphite crucible. The over-heating temperature prior to casting was of 100 °C. Billets of 80x200x10 mm were cast in steel ingot moulds.

Test pieces were machined from the cast billets, to be used for determining chemical composition and hardness for the structural analyses conducted on heat treated and untreated alloys, as well as for dilatometric analysis. The applied heat treatment consisted of heating to 350 °C over 4 days (96 hours) followed by furnace cooling. Structure analysis took into account Presnyakov's thermal equilibrium diagram, *Fig. 1*.

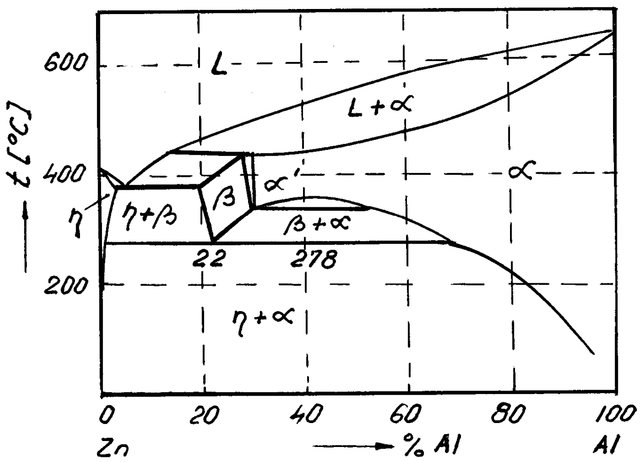

Figure 1: Zn-Al thermal equilibrium diagram.

Figure 2 shows obtained significant microstructures observed by means of a Nikon microscope for increase of 200 – 1000 times.

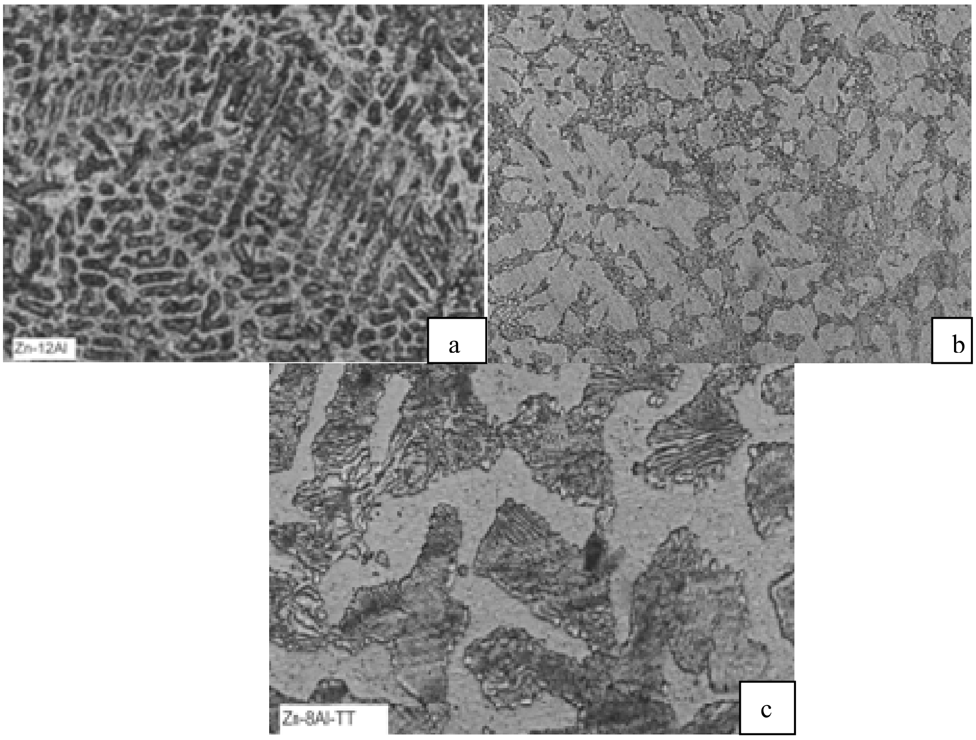

Figure 2: Structure of Zn-Al alloys
a.) Zn-12%Al, cast, x500 b.) Zn-22%Al, cast, x500 c.) Zn-8 %Al heat treated, x1000.

In alloys of hypoeutectoid composition a dendritic structure can be observed, consisting of η phase in the hypoeutectic alloy and phase α in the case of hypereutectic alloys, embedded in the η + α. eutectic. In the test sample of eutectoid composition reveal the effect of the peritectic reaction can be observed from the location of the eutectoid at the margins of the α solid solution dendrites. It has to be remarked that achieving the equilibrium structure requires long term heat treatment, as only under such conditions is the structure is in accordance with the nature and proportion of phases indicated by the thermal equilibrium diagram.

For dilatometric analysis round test pieces of 6 mm diameter and 15 – 17 mm length were machined. Dilatometric analysis was conducted by means of a LINSEIS, L75/230 device, *Fig. 3*.

Phase transformations in solid state can be studied with a dilatometer only when volume variations during transformation are also involved. Any heated metallic body dilates according to the equation:

Figure 3: LINSEIS, L75/230 dilatometer.

$$L_t = L_o\,(1 + \alpha.t). \tag{1}$$

The variation in length is computed by the equation:

$$\Delta L_{Thermal} = L_t - L_0 = L_o\,(1 + \alpha.t). \tag{2}$$

In case the metal (alloy) presents phase transformations in solid state, as the eutectoid one, a variation in length determined by the phase transformation is added to the one determined by temperature increase:

$$\Delta L_{Total} = \Delta L_{Thermal} + \Delta L_{Phase} \tag{3}$$

Variations in length determined by phase transformations are more visible on the derivatives of the dilatation curves, *Fig. 4*.
The value of temperature corresponding to the peaks on the dilatation curves derivative was used to determine the activation energy in the case of the eutectoid transformation in the Zn-Al system.

The activation energy (E_a) is calculated by Kissinger's equation written in the form below:

$$\ln\frac{v}{T_m^2} = -\frac{E_a}{R \cdot T} + M \tag{4}$$

where: T - temperature;

v – heating rate in ˚C/s

R – constant of gases, R= 8.3144 [J/mol.K];

M - constant;

T_m – maximum point on the dilatation curves derivatives, in degrees Kelvin.

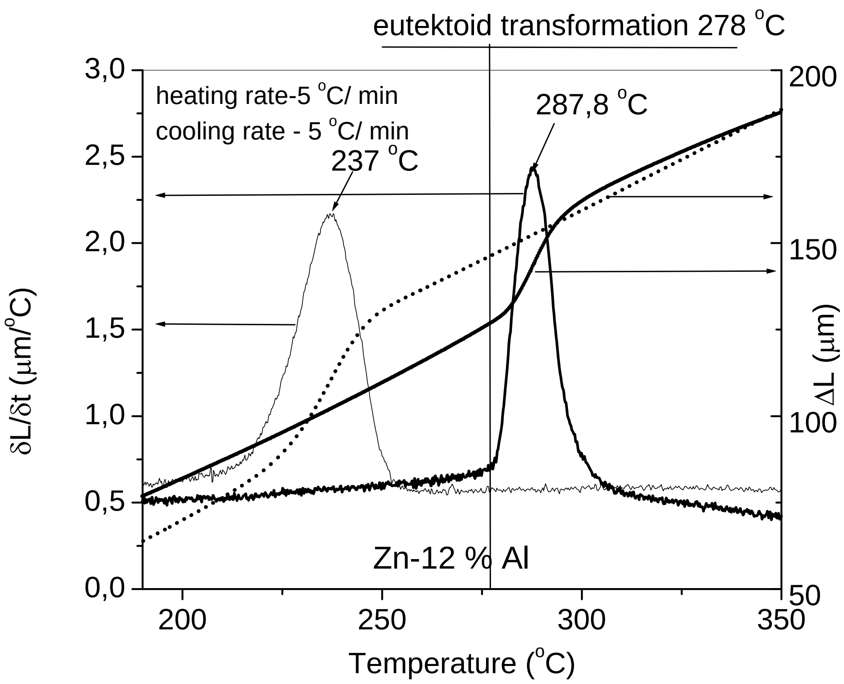

Figure 4: Dilatation curves for Zn-Al 12 % composition and their derivatives.

Figures 5 and *6* show the diagrams for determining of the activation energy of the eutectoid transformation during heating and cooling, respectively, for a Zn-Al 12 % composition.

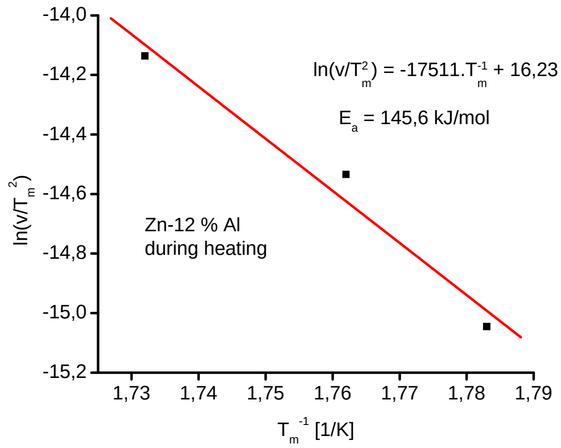

Figure 5: Determination of the activation energy during heating of the Zn-12 %Al %alloy.

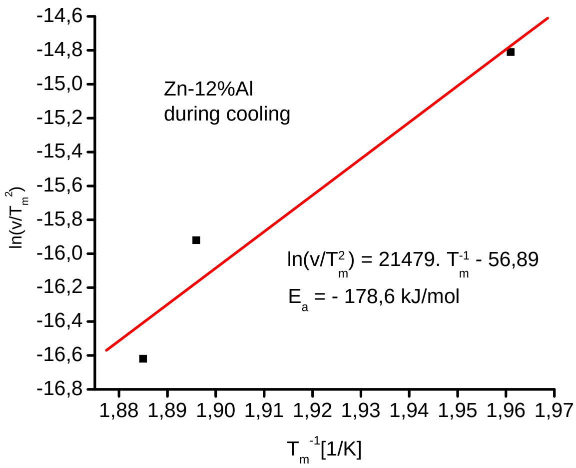

Figure 6: Determination of the activation energy during cooling of the Zn-12%Al alloy.

The diagram in *Fig. 7* presents the variation of the activation energy versus zinc concentration in the alloy, during heating and cooling, respectively. Relationships presented in the chart in *Figure 7* are valid for hypoeutectic compositions.

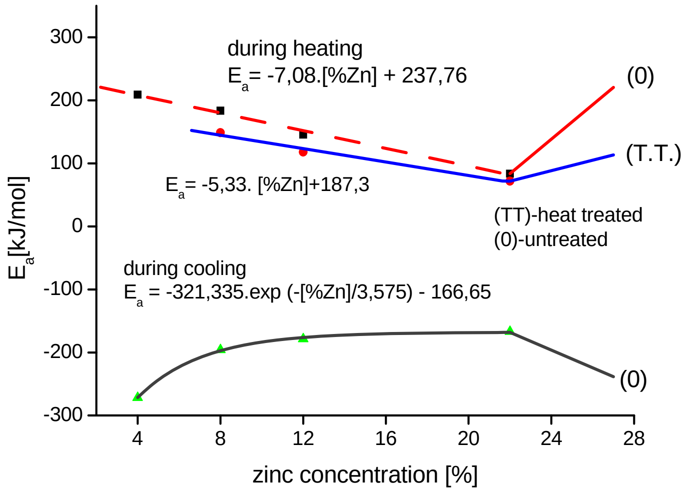

Figure 7: Variation of the activation energy versus zinc concentration during heating and cooling, respectively.

3. Conclusions

The degree of generating of the peritectic transformation significantly influences the structure of alloys at environment temperature.

In transformation processes during both heating and cooling the increase of zinc contents determines a decrease of the value of the activation energy.

The variation of activation energy depending on zinc or eutectoid concentration in the structure of the alloy is governed by different laws of constituent germination for the cases of heating and cooling of the alloy, respectively.

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