INTERVAL OF HOMOGENEITY OF THE ε-PHASE AND ANOMALIES IN THE RELATIVE DILATATION OF ALLOYS IN THE COMPOSITION INTERVAL 95-99 wt.% Zn OF THE Sb-Zn SYSTEM*)

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Abstract: The results of dilatometric investigations as well as the investigations by the qualitative dynamical differential calorimetry(DDC) method on the Sb-Zn alloys in the composition interval 40-43,5 wt.% Zn indicate a shift of the ε-phase composition interval towards the lower Zn compositions (between 41 and 41,72 wt.% Zn), in comparison with the phase diagram. This conclusion is in agreement with the earlier metallographic investigations of these alloys at room temperature

The thermal-dilatation analysis of homogenized (400 hours at 300°C) Sb-Zn alloys in the vicinity of the eutectic composition, 97,4 wt.% Zn, shows an anomalous change in the relative dilatation $\Delta l/l$, owing to the presence of the eutectic (η + Zn) in the alloys at the temperatures below 409°C. The metallographic examinations of microstructures at room temperature confirm the presence of this eutectic in the alloys investigated.

1. INTRODUCTION

The phase diagram of the Sb-Zn system of alloys, shown on Fig. 1, is rather complicated in the composition interval 35-50 wt.% Zn and characterized by a presence of several intermetallic phases, a number of which are formed during the cooling of alloys[1,2].

The earlier investigations[2,3] are rarely concerned with the concretisation of the homogeneity intervals of different phases in that system. Some results in this direction show the systematic thermal investigations of the Sb-Zn alloys[4,5]. They offer valuable informations concerning different phase transformations and have also pointed to the fact that some anomalies in dilatation behaviour of the alloys in the vicinity of the eutectic (η + Zn) composition have appeared. 97,4 wt. % Zn corresponds to the eutectic composition[2,3].

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The present investigations have been undertaken in order to examine the interval of ϵ-phase homogeneity, which, according

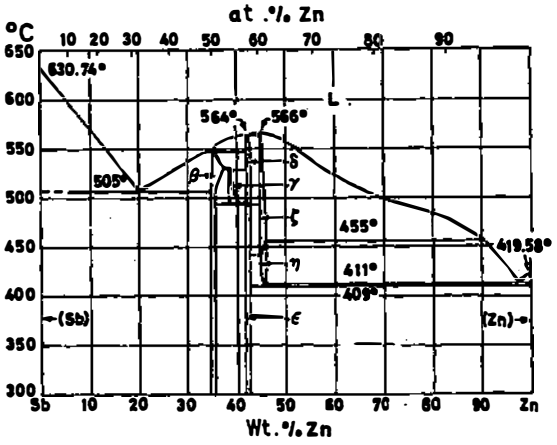

Fig. 1. The phase diagram of the Sb-Zn system.

to the phase diagram (Fig. 1), is located between the compositions 41,8 and 42,75 wt.% Zn, as well as to examine the reasons of the anomalies in the thermal-dilatation behaviour of the alloys in the vicinity of the eutectic composition 97,4 wt.% Zn.

For that purpose, the measurements of the alloys in the composition interval 40-43,5 wt.% Zn were taken by the methods of dilatometry and DDC, and dilatometric as well as metallographic investigations of the alloys in the composition interval 95-99 wt.% Zn have also been done.

2. EXPERIMENTAL PROCEDURE

The alloys were prepared by melting in evacuated pyrex tubes, placed in a ferrous cylinder that was filled with quartz sand in order to prevent rapid cooling of the alloys. The liquid alloys were cooled spontaneously out of the furnace.

After casting, cylindrical samples were homogenized for 400 hours at 300°C, and then slowly cooled to room temperature, as was the furnace.

The dilatometric and the DDC-measurements were taken using the "Netzsch" electronic high-temperature dilatometer type 402E and DTA-aparature type 404. A heating rate of 5°C/min was used for the dilatometric measurements, while the DDC-measurements were taken at a heating rate of 2°C/min. All measurements were carried out in an inert-argon atmosphere.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In Figs. 2 an 3 the temperature dependence of relative dilatation $\Delta l/l$ for investigated alloys is shown. A common scale for the $\Delta l/l$ axis is used, so the zero of the scale has to be shifted to the horizontal line in the beginning of each diagram. The compositions of the alloys are given in weight percentages of Zn.

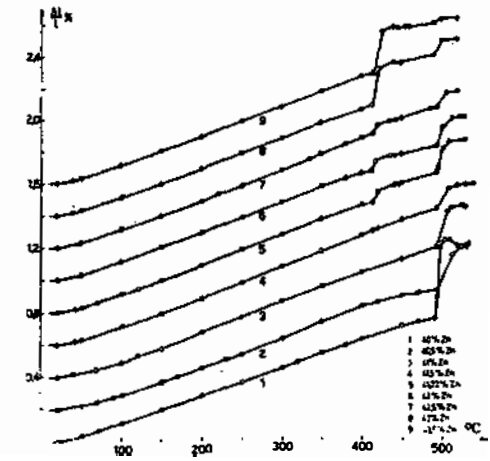

Fig. 2. Relative dilatation vs temperature for alloys of 40-43,5 wt.% Zn.

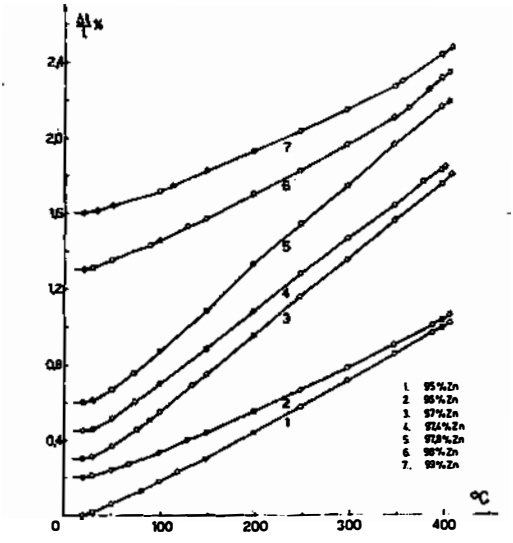

Fig. 3. Relative dilatation vs temperature for alloys of 95-99 wt.% Zn.

A. From the diagrams $\Delta l/l$ -temperature (Fig. 2), it can be seen that in the alloys containing 40 to 41,72 wt.% Zn $\Delta l/l$ increases continuously with the rise of temperature, until the transformation at 493°C. That transformation is followed by an abrupt increase in $\Delta l/l$, which is maximal for the alloy with a composition of 40 wt.% Zn. In the alloys that contain more than 41,72 wt.% Zn, in addition to this transformation, an abrupt change in $\Delta l/l$ at ~409-412°C and a smaller change at 440°C can be observed, which correspond to the eutectoid transformations at 409°C an 440°C. The temperatures at which these abrupt changes of $\Delta l/l$ begin are marked by rings on the equilibrium phase diagram[1] and shown in Fig. 4 a).

The results of DDC-measurements show that the transformations already mentioned are followed by remarkable heat absorption effects during the

heating. The temperatures at which these effects appear are also marked by rings on the phase diagram and shown in Fig. 4 b).

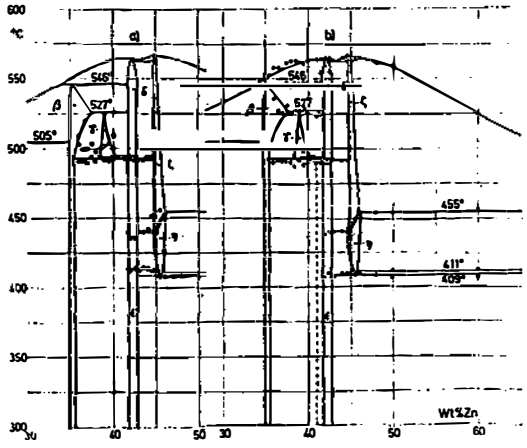

Fig. 4. The temperatures (shown by rings) at which the transformations in the alloys begin.
a) Dilatometric measurements, b) DDC-measurements.

The maximal increase in $\Delta l/l$ during the transformation at 493°C that takes place for the alloy of 40 wt.% Zn may be referred to the effects occurring in the alloys with compositions over 40 wt.% Zn. Namely, the occurrence of the eutectoid transformations at 409°C and at 440°C in the alloys with compositions over 41,72 wt.% Zn points to the fact that the right-hand ϵ-phase limit line is at 41,72 wt.% Zn, which is in slight disagreement with the conclusion of Takei[3], but in real conflict with the results of Vuillard and Piton[6].

From the results of present measurements and using the results of metallographic analysis of these alloys[5] at room temperature, which have pointed to the fact that the alloys between 41 and 41,72 wt.% Zn have single-phase composition, while the alloys on both sides of this composition interval have two-phase compositions, it can be concluded that the interval of ϵ-phase homogeneity may be located between the compositions 41 wt.% Zn and 41,72 wt.% Zn.

The specific behaviour of the alloy with 40 wt.% Zn during the transformation at 493°C might be ascribed to the eventual coincidence of this alloy with the peritectoid composition of the ϵ-phase; the invariant at 493°C might be a peritectoid line.

The possible location of the left-hand limit line of the ϵ-phase is represented by the dotted line in the phase diagram in Fig. 4 b).

B. As can be seen from the diagrams in Fig. 3, $\Delta l/l$ increases continuously with the rising temperature for all alloys in the region investigated. It can also be seen that the alloys of compositions 97; 97,4 and 97,8 wt.% Zn (diagrams 3, 4, 5) are characterized by a faster increase in $\Delta l/l$.

Fig. 5 represents the relative dilatation-composition isotherms. The corresponding temperatures (in °C) are shown on each diagram. In the same figure the portion of the phase diagrame (Fig. 1) in the investigated region is projected. An unexpected increase in $\Delta l/l$ is observed in all isotherms in the vicinity of the eutectic composition (97,4 wt.% Zn). Such behaviour of the alloys in the investigated region, according to the phase diagram (Fig. 1), is not normal.

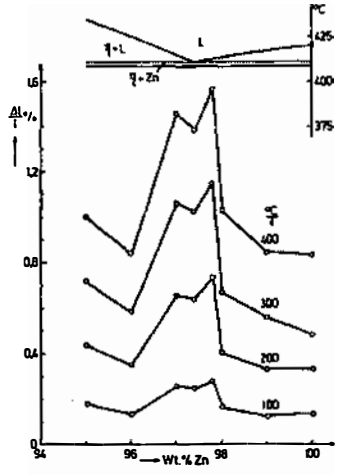

Fig. 5. Relative dilatation vs composition of the alloys.

In addition, the metallographic analysis of some alloys was performed, the results of which are illustrated by the micrographs in Fig. 6. In order to reveal the structures, the samples, after mechanical polishing, were etched with a solution (1:4) of $HNO_3+H_2O_2$ (the alloys of 80 and 99 wt.% Zn) and 5% alcoholic solution of HCl (the alloys of 97 and 97,4 wt.% Zn).

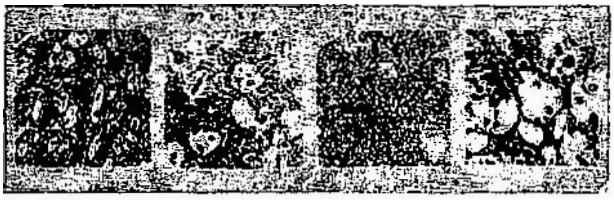

Fig. 6. Metallographic structures of some Sb-Zn alloys.

The micrographs show that, apart from the crystal grains of the ϵ-phase (which are gray) and Zn (which are white), a small-grained structure like a eutectic mixture can be observed, the amount of which is especially dominant in the alloys of compositions 97 and 97,4 wt.% Zn. As has already been mentioned, according to the phase diagram and the results of recent investigations[4,5]

the alloy of 97,4 wt.% Zn coincides with the eutectic composition of the eutectic (η + Zn), which crystallizes at 411°C.

The presence of this eutectic structure in the alloys may be due to the improper cooling regime of alloys at and below the eutectoid temperature of 409°C, which does not help the decomposition of eutectic (η + Zn). Namely, the eutectoid transformation, which has to take place only 2°C below the eutectic temperature of 411°C, cannot be completed. Furthermore, it does not take place after the additional heat treatment. Most probably an extremely slow cooling regime around 409°C could provide the transformation η + Zn $\rightarrow$ ϵ + Zn.

The unexpected high values of the relative dilatation $\Delta l/l$ (Fig. 5) are due to the presence of η-phase in the eutectic, the thermal expansion coefficient α of which has a very high value compared with the thermal expansion coefficients of other phases[5].

4. CONCLUSIONS

A. By dilatometric and DDC-measurements the eutectoid transformations at 409°C and 440°C are observed in the alloys with compositions over 41,72 wt.% Zn. From the existence of these transformations and the results of previous metallographic analysis we may conclude that the homogeneity interval of the ϵ-phase is located between 41 wt.% Zn and 41,72 wt.% Zn.

B. The dilatometric measurements on Sb-Zn alloys of compositions in the vicinity of the eutectic composition 97,4 wt.% Zn show that an unusual variation in $\Delta l/l$ is observed. This variation is ascribed to the presence of eutectic (η + Zn) in the alloys, which is retained at temperatures below 409°C. Additional heat treatment does not eliminate it. Metallographic analysis confirms this conclusion.

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