JOURNAL OF MATERIALS SCIENCE 29 (1994) 1711–1713

Phase equilibria in the $Ag_{2/3}Zn_{1/3}$–Te system

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Using differential thermal analysis, X-ray diffraction analysis and composite phase diagrams, the most probable form of the polythermal section $Ag_{2/3}Zn_{1/3}$–Te of the ternary system Ag–Zn–Te has been deduced. It was found to be non-quasi-binary with 14 phase fields and four isotherms of the non-variant equilibria. It is suggested that a phase with composition Ag_2ZnTe_2, stable at temperatures above 515 °C, is formed.

1. Introduction

The phase equilibrium in the ternary system Ag–Zn–Te was studied and the phase pattern of the polythermal section $Ag_{2/3}Zn_{1/3}$–Te, about which there are no data in the literature, has been built-up.

The partial binary systems comprising the ternary system, have been studied in detail [1–5]. Complicated physicochemical interactions were found to take place, resulting in the formation of intermediate phases with constant and variable composition.

The sections Ag–ZnTe [6] and Ag_2Te–Zn [7] of the ternary system Ag–Zn–Te have been examined previously. It was found that they were quasi-binary, a number of intermediate phases with constant or variable composition, as well as restricted solid solutions, on the basis of silver, zinc, Ag_2Te and ZnTe being formed in them.

In order to outline the fields of existence of the stable phases and the solid solutions in the ternary system Ag–Zn–Te, the polythermal section $Ag_{2/3}Zn_{1/3}$–Te needed to be investigated.

2. Experimental procedure

The starting alloy with a composition $Ag_{2/3}Zn_{1/3}$, as well as compositions of $Ag_{2/3}Zn_{1/3}$–Te, were synthesized by the technique described elsewhere [8]. The raw materials were silver, zinc and tellurium with a purity of 99.999%.

The phase transitions were investigated by differential thermal analysis (DTA), X-ray diffraction analysis (XDA) and composite state diagrams.

DTA was carried out with a "Paulik–Paulik–Erdey" (Hungary) apparatus at a heating rate of 20 °C and with an etalon substance – melted Al_2O_3. The diffraction patterns were recorded with a diffractometer TUR-M62 with CuK_α radiation (nickel filter).

The microhardness, HV, was measured by Vickers method, and the density, d, by the hydrostatic method in toluene as a working liquid.

Two types of etching solutions were used to reveal the microstructure of the samples – with an acidic (HNO_3, HF, H_3PO_4, H_2SO_4) or a basic (NH_4OH) character. The processing time was 30–150 s at 25 °C.

3. Results and discussion

The solid lines in Fig. 1 mark the sections investigated previously, and the broken line indicates the polythermal section investigated in the present work.

The area of the section $(Ag_{2/3}Zn_{1/3})_{1-x}Te_x$, where $0 \leqslant x \leqslant 1$, was found by X-ray diffraction analysis of the composition at point A, obtained by alloying appropriate quantities of the starting components $Ag_{2/3}Zn_{1/3}$ and tellurium. The $Ag_{2/3}Zn_{1/3}$–Te section was proved to be non-quasibinary, and the Ag_2Te–ZnTe section to be quasibinary. (The latter will be a subject of future investigations.)

The results from the X-ray diffraction investigations are presented as a Strich-diagram in Fig. 2. In the

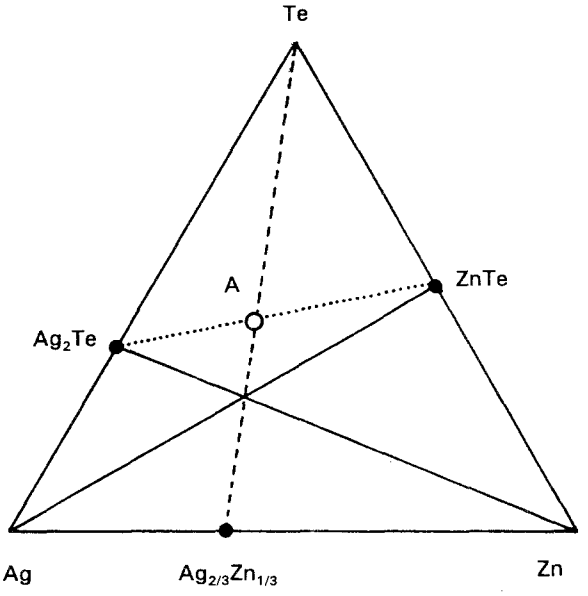

Figure 1 Gibbs concentration triangle of the three-component system Ag–Zn–Te.

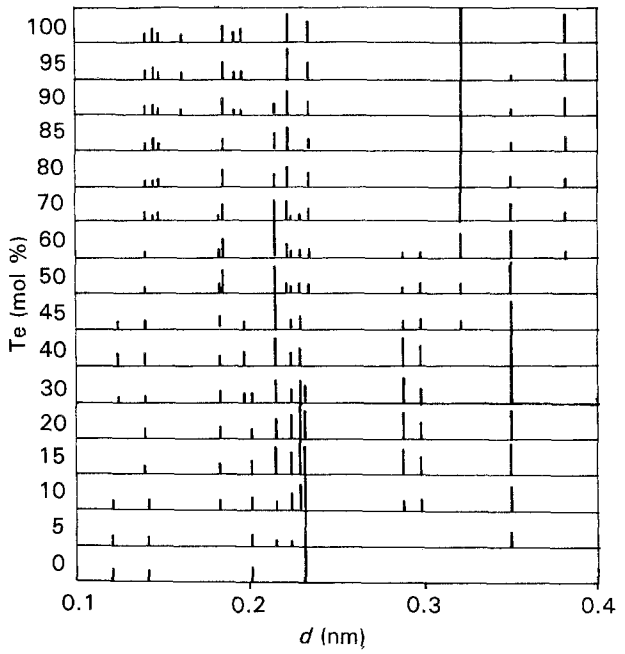

Figure 2 A strich-diagram of the $Ag_{2/3}Zn_{1/3}$–Te system.

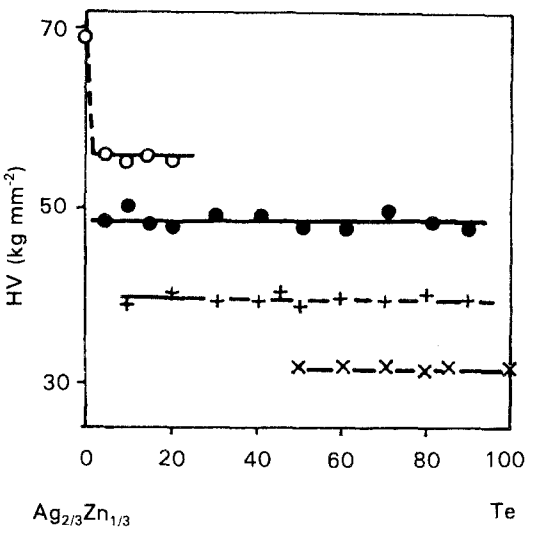

Figure 3 Microhardness versus composition dependence of samples from the $Ag_{2/3}Zn_{1/3}$–Te system.

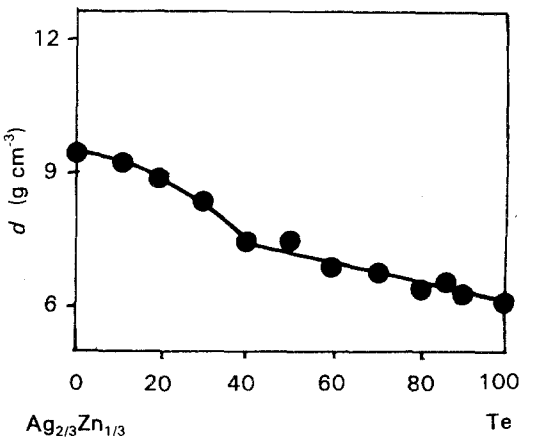

Figure 4 Density versus composition dependence of samples from the $Ag_{2/3}Zn_{1/3}$–Te system.

concentration range $0.05 \leqslant x \leqslant 0.95$, the diffractogram features the typical lines of the Ag_2Te and ZnTe phases [9, 10] whose intensity is greatest around a composition corresponding to $x = 0.4$. This is the intersection point of the Ag_2Te–ZnTe section with $Ag_{2/3}Zn_{1/3}$–Te (Fig. 1). In the concentration range $0.0 \leqslant x \leqslant 0.4$, the characteristic interplane reflections of Ag_2Te, ZnTe and the alloy $Ag_{2/3}Zn_{1/3}$ appear, and in the range $0.4 < x < 1.0$ the phases Ag_2Te, ZnTe and tellurium exist. This form of Strich-diagram suggests the presence of two three-phase regions in the system at room temperature: one in the range $0.0 < x < 0.4$, and the other in the range $0.4 < x < 1.0$. This conclusion is also confirmed by investigations of the microstructure of samples with similar compositions. Only the sample with composition $(Ag_{2/3}Zn_{1/3})_{0.6}Te_{0.4}$ is two-phase, while all the remaining samples are three-phase.

Owing to the small size of the phase fields, when measuring the microhardness of the various compositions of the system, polygons were drawn of the empirical distribution probability of microhardness. Their form indicated, to a first approximation, the number of phases in each sample. Fig. 3 shows graphically the relationship between microhardness and composition. The presence of three values of HV (for each composition in the concentration ranges $0.0 < x < 0.4$ and $0.4 < x < 1.0$) is indicative of the presence of three phases in the samples. The steep change in HV (dashed line) in the range $0.00 < x < 0.05$ shows that in these regions, restricted solid solutions were formed on the basis of an alloy with composition $Ag_{2/3}Zn_{1/3}$.

The density–composition relationship is shown in Fig. 4. At $x = 0.4$, $\rho = 7.4\ g\,cm^{-3}$. Practically, it is equal to the density of a sample with a composition corresponding to the equimolar ratio between Ag_2Te ($\rho = 8.5\ g\,cm^{-3}$) and ZnTe ($\rho = 6.34\ g\,cm^{-3}$).

DTA investigations failed to determine the temperatures of the various phase transitions in the $Ag_{2/3}Zn_{1/3}$–Te system, as well as the course of the liquidus curve. A different number of endothermal defects was observed on the derivatograms, whose values are given in Table I.

Two typical nonvariant equilibria (peritectic and eutectic) are observed in the system $(Ag_{2/3}Zn_{1/3})_{1-x}Te_x$ at temperatures $810 \pm 10\,^{\circ}C$ and $350 \pm 10\,^{\circ}C$, respectively. The compositions of the peritectic and eutectic points are at $x = 0.15$ and $x = 0.7$, respectively. The endothermal effect at $315 \pm 10\,^{\circ}C$ is most probably related to the peritectic decomposition of a phase with the most probable composition Ag_2ZnTe_2, which is stable at high temperatures (above $515\,^{\circ}C$). This phase melts congruently at $880 \pm 10\,^{\circ}C$. (The results from the high-temperature X-ray diffraction investigation of this phase will be published later.)

At $x = 0.4$ and $475 \pm 10\,^{\circ}C$, the following reaction takes place

$$Ag_2Te + ZnTe \rightleftharpoons \alpha + L \qquad (1)$$

where α is a solid solution on the basis of $Ag_{2/3}Zn_{1/3}$, and L is a melt.

The endoeffects at $120 \pm 10\,^{\circ}C$ are related to the phase transition α-$Ag_2Te \rightleftharpoons \beta$-$Ag_2Te$ [11].

TABLE I Phase transition temperatures in samples of the $Ag_{2/3}Zn_{1/3}$–Te system

Sample	Composition (% Te)	Endothermal effects (°C)					
		I	II	III	IV	V	VI
1	0	725	–	–	–	–	–
2	5	750	–	–	515	–	–
3	10	780	–	–	515	–	–
4	15	810	125	–	515	810	–
5	20	835	120	–	–	810	700
6	30	847	125	–	475, 515	810	780
7	40	880	125	–	475, 515	–	–
8	45	830	120	350	480, 515	–	685
9	50	800	120	355	515	–	–
10	60	720	125	355	515	–	–
11	70	360	–	–	–	–	–
12	80	390	–	360	–	–	–
13	85	395	120	–	–	–	–
14	90	425	115	–	–	–	–
15	95	445	115	345	–	–	–
16	100	455	–	–	–	–	–

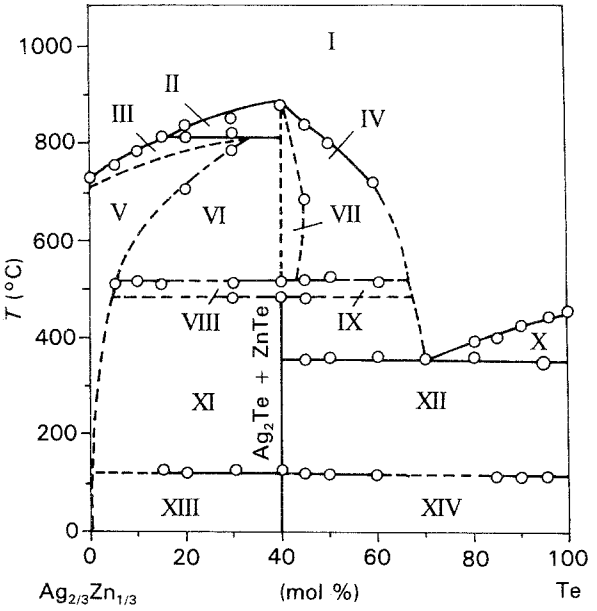

Figure 5 State diagram of the $Ag_{2/3}Zn_{1/3}$–Te system: (a) meld (a field I); (b) solid solution on the basis of Ag_2ZnTe_2(a field VII); (c) solid solution on the basis of $Ag_{2/3}Zn_{1/3}$ (a field V).

Finally, after summarizing the results from all investigations, the most probable phase image of the polythermal section $Ag_{2/3}Zn_{1/3}$–Te was built-up (Fig. 5). It has a complex form, with 14 phase fields with different numbers of phases in them. Four isotherms of non-variant equilibria are proved to exist. At high temperatures a phase with a composition Ag_2ZnTe_2 is assumed to be formed that melts congruently at 880 ± 10 °C.

Acknowledgement

The authors thank the Ministry of Science and Higher Education for financial support in carrying out the present investigation.

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Received 3 August 1992
and accepted 31 August 1993