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ON THE PHASE EQUILIBRIA IN THE SYSTEM Ag-Sn-Zn

RÓWNOWAGI MIĘDZYFAZOWE W UKŁADZIE Ag-Sn-Zn

The phase equillibria in the system Ag-Sn-Zn have been studied using scanning electron microscope, X-ray and microharness measurements, differential scanning calorimetry and optical microscopy. 27 alloys have been prepared and annealed for 3 months at 380°C. All ternary phases are based on the binary ones. The microhardness values of the γ phase are the highest in the system Ag-Sn-Zn. The ternary β phase (formed on the base of the binary AgZnβ phase) contains up to ≈ 13 at.% Sn, while the γ and ε phases – up to ≈ 0.2 at.% Sn only. The solubility of Zn in the Ag-Sn-based intermetallic ε (Ag_3Sn) and ζ (Ag_4Sn) phases is also significant. An isothermal section of the phase diagram at 380°C has been constructed.

Równowagi międzyfazowe w układzie Ag-Sn-Zn zbadano przy pomocy skanningowej mikroskopii elektronowej (SEM), dyfrakcji rentgenowskie (XRD), pomiarów mikrotwardości, kalorymetrii skanningowej (DSC) oraz mikroskopii optycznej. Przygotowano 27 stopów, które wyżarzano następnie w 380°C przez 3 miesiące. Wszystkie rozpatrywane fazy trójskładnikowe wywodzą się z faz podwójnych. Najwyższą twardość w układzie stwierdzono dla fazy γ. Faza potrójna β (powstała na bazie fazy podwójnej β-AgZn) zawiera aż do ~ 13 at.%Sn, podczas gdy fazy: γ i ε zawierają tylko do ~ 0.2 at.%Sn. Rozpuszczalność cynku w fazach międzymetalicznych układu Ag-Sn: ε-Ag_3Sn i ζ-Ag_4Sn jest również znaczna. Na podstawie badań własnych skonstruowano przekrój izotermiczny układu potrójnego w 380°C.

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1. Introduction

The thermodynamic [1-7], structural [8-10] and other specific properties [11] of the system Ag-Sn-Zn have been subject of intensive studies. The reason for this interest is that these alloys are suitable for use as lead-free solder.

In this work the phase equilibria in the system Ag-Sn-Zn and at 380°C have been studied using X-ray, scanning electron microscope (electron microprobe), microhardness measurements, differential scanning calorimetry (DSC) and optical microscopy.

2. Experimental

The alloys (Table 1) have been prepared from pure components (at least 99.99%, production of Aldrich) sealed under vacuum 1.10^{-6} torr in quartz tubes. The tubes have been gradually heated up to 1000°C (e.g. above the melting point of Ag), annealed for 24h, thereafter the temperature has been gradually lowered to 380°C. After 3 month annealin at the latter temperature the alloys have been quenched in water.

The phase composition of the specimens quenched from 380°C has been investigated using X-rays diffraction (Fe K_α radiation). Literature data [12, 13] about the pertinent binary and ternary AgSnZn phases have been used. Optical microscopy studies have been performed on the polished specimens etched with 3% HNO_3 (alcohol solution) to reveal the phase boundaries.

We performed DSC studies of two specimens, sealed in evacuated quartz ampoules cut out of alloys No 26 and No 27 (see Table 1) using a Setaram 121 microcalorimeter.

Three consecutive heating/cooling cycles have been performed with heating rate 2 deg.min^{-1} and cooling rate 10 deg.min^{-1}. The highest temperatures were 250, 710 and 500°C, for the first, second and third run, respectively. The microscopic observations show that this alloy was melted at the working temperature (380°).

Two identical endothermic peaks have been found at each run – Fig. 1. We suggest that the first peak (198°C) could be associated with the reaction U_9: $\varepsilon + L \leftrightarrow (Sn) + (Zn)$. The second peak in Fig. 1 (at $\approx$ 213°C) is, probably, due to the reaction U_8: $L + \gamma \leftrightarrow \varepsilon + (Sn)$.

Two consecutive heating/cooling cycles have been carried out on the specimen cut of alloy No 27 (mass 0.4061 g) containing β' phase (rose-violet coloured particles, characteristic for the ordered β' phase, have been observed in the specimen). This observation agrees with the microprobe analyses results where crystals corresponding to the β (or ζ) area of homogeneity have been found. It seems that the X-ray analyses confirm these observations, but there are identification difficulties due to the possible overlapping of the reflexes of some of phases with those of Sn and Zn. This alloy has not been entirely melted at the temperature of 380°C.

The maximal temperatures of the both runs are 500°C. Six peaks have been observed for the first run, and four peaks for the second run. The first reproducible peak ($\approx$ 216°C,

TABLE

Chemical and equilibrium phase composition of the specimens. Column 1 – the consecutive number; columns 2, 3, 4 (X_{Ag}, X_{Sn}, X_{Zn} respectively) – initial mole fraction of the constituents; 5 – the retained equilibrium phases at 380°C; columns 6, 7, 8 – the chemical composition of the solid equilibrium phases as shown in the column 9.

N	X_{Ag}	X_{Sn}	X_{Zn}	Equilibrium phases at 380°C	X_{Ag}	X_{Sn}	X_{Zn}	Solid equilibrium phases
1	2	3	4	5	6	7	8	9
1	0.2318	0.1691	0.5991	$\varepsilon+L$	0.266	0.002	0.732	ε
2	0.2296	0.152	0.6184	$\varepsilon+L$	0.227	0.002	0.771	ε
3	0.2921	0.1444	0.5635	$\varepsilon+L+\gamma$	0.293	0.004	0.703	ε
4	0.2289	0.2033	0.5678	$\varepsilon+L$	0.267	0.005	0.728	ε
5	0.1428	0.1916	0.6656	$\varepsilon+L$	0.177	0.001	0.822	ε
6	0.2974	0.2059	0.4967	$\gamma+L$	0.345	0.003	0.652	γ
7	0.2818	0.1464	0.5718	$\varepsilon+L+\gamma$	0.335	0.002	0.663	ε
8	0.3871	0.2346	0.3783	$\zeta+L$	0.528	0.074	0.398	ζ
9	0.5184	0.2414	0.2415	$\zeta+L$	0.577	0.127	0.296	ζ
10	0.619	0.1587	0.2223	$\zeta+Ag_3Sn_xZn_{1-x}$	0.628 0.711	0.133 0.228	0.239 0.061	ζ $Ag_3Sn_xZn_{1-x}$
11	0.6377	0.0976	0.2647	$\alpha+\zeta$	0.650 0.692	0.096 0.030	0.254 0.278	ζ α
12	0.7188	0.1003	0.1809	$\alpha+\zeta+\varepsilon'$	0.719	0.101	0.180	α
13	0.6818	0.2548	0.0634	$Ag_3Sn_xZN_{1-x}+L$	0.718	0.220	0.062	$Ag_3Sn_xZn_{1-x}$
14	0.8037	0.1069	0.0894	$\varepsilon'+\alpha$	0.846	0.072	0.082	α
15	0.2612	0.0534	0.6854	$\varepsilon+L$	0.273	0.002	0.725	ε
16	0.2114	0.0491	0.7395	$\varepsilon+L$	0.240	0.003	0.757	ε
17	0.3197	0.0526	0.6277	$\gamma+\varepsilon+L$	0.366 n.*	0.005 n.*	0.629 n.*	γ ε
18	0.3409	0.1008	0.5583	$\gamma+L$	0.341	0.101	0.558	γ
19	0.4004	0.0483	0.5513	$\gamma+L$	0.432	0.010	0.558	γ
20	0.6015	0.0482	0.3503	$\alpha+\zeta$	0.600 0.643	0.030 0.084	0.370 0.273	α ζ
21	0.4255	0.2012	0.3733	$\zeta+L$	0.628	0.154	0.218	ζ
22	0.7511	0.1513	0.0976	ε'	0.751	0.152	0.097	ε'
23	0.4007	0.0995	0.4998	$\gamma+L$	0.460	0.020	0.520	γ
24	0.4507	0.1487	0.4006	$\zeta+L$	0.525	0.067	0.408	ζ
25	0.5433	0.1497	0.3070	$\zeta+L$	0.570	0.105	0.325	ζ
26	0.0521	0.8036	0.1443	liquid at 380°C	0.311	0.002	0.687	ε^{**}
27	0.1512	0.8003	0.0485	$\zeta+L$	0.488	0.077	0.435	ζ^{***}

n.* – the composition has not been determined,

** – noneqilibrium composition due to the crystallisation at the cooling,

*** – the composition might be influenced by the crystallisation of the liquid.

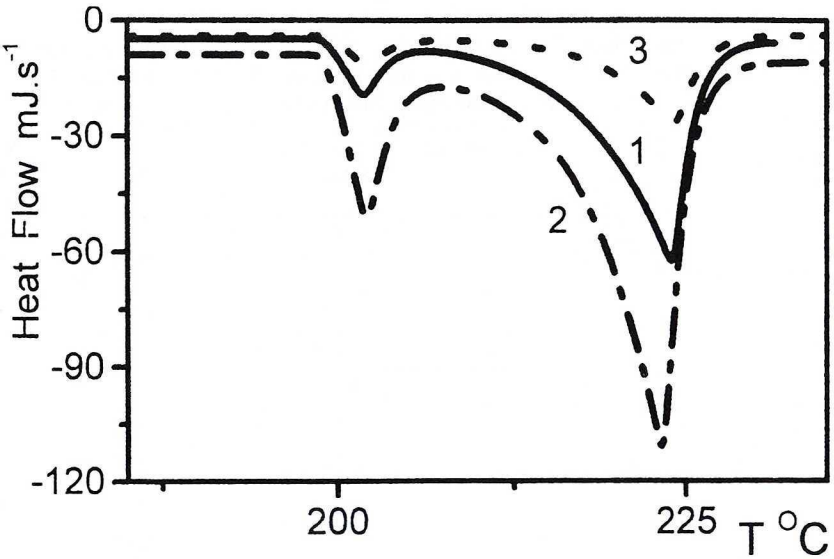

Fig. 1. DSC curves (heating rate 2 deg.min^{-1}) of the alloy No 26 in coordinates: Heat Flow (mJ.s^{-1}) vs. Temperature (°C). Curve 1 is for the first run, curve 2 – for the second one, and curve 3 for the third one. The heat flow values of the curves 2 and 3 have been divided by 0.5 and 2, respectively

second run) might correspond to the solidus (the eutectic temperature). Thus, at higher temperature the three phases existing for this composition at room temperature – Ag_3Sn, βSn and ζ (or β') have been partially or totally melted.

The microhardness is a specific property of each single phase. Thus this method is a sensible one for testing the mechanical properties and for phase identification. We studied the microhardness of the phases in specimens where relatively large single-phase areas exist.

We have found that the tin content is very small and constant in the ε phase (see Table) making possible to look for a dependence between the silver mole fraction (X_{ag}) and the microhardness (H). The statistical interpretation of 10 results lead to a linear dependence $H = (90 \pm 17) + (231 + 66).X_{Ag}$ MPa.

3. Conclusion

The authors' results are graphically represented in Fig. 2. No new phases have been discovered in the system.

Performing a thermodynamic investigation of the same system Ohtani et al. [7] have constructed and calculated two isothermal sections – at 190°C and at 420°C. Comparing the latter one with our results for 380°C one observes general agreement in the situation

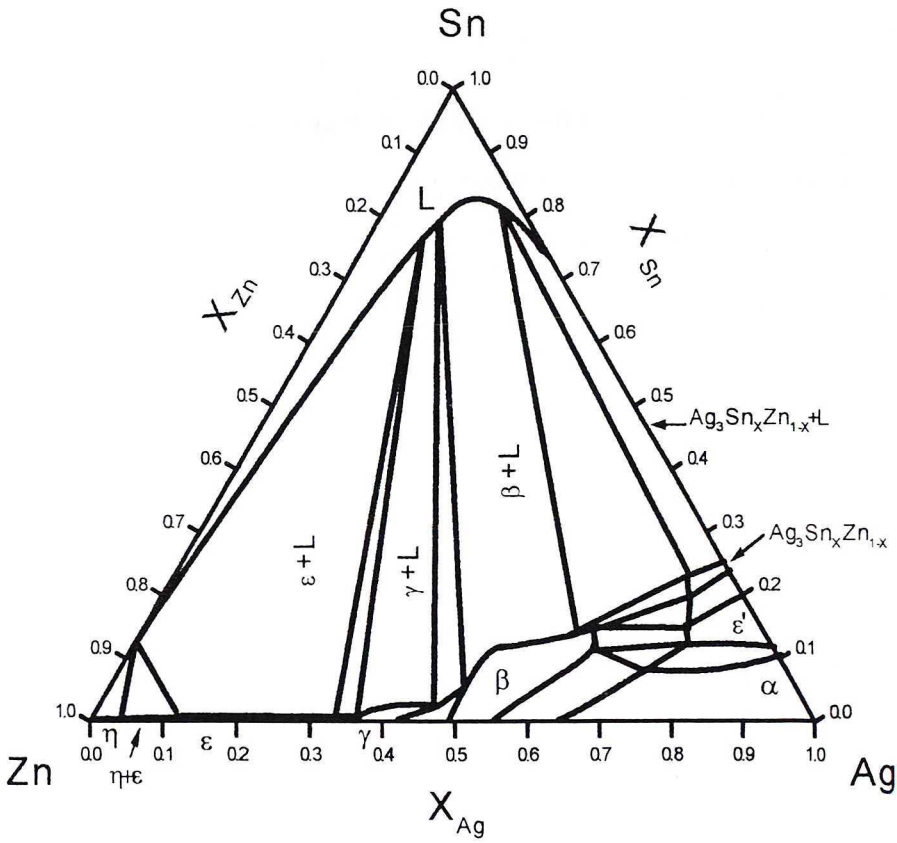

Fig. 2. The isothermal section of the ternary Ag-Sn-Zn diagram constructed at 653 K (380°C)

of the ternary fields $L+\varepsilon+\eta$, $L+\varepsilon+\gamma$, $L+\beta+\gamma$. Nevertheless we have obtained for the first time data about the zinc solubility in the binary Ag-Sn intermediate phase and of tin in the phases formed on the phases formed on the base of the binary AgZn phases.

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