INFLUENCE OF INDIUM AND TIN ON THE AgCu25Zn20Cd20 ALLOY MICROSTRUCTURE

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In our investigation of the AgCu25Zn20Cd20 alloy, cadmium was partly or fully replaced by indium and tin due to its toxicity. The influence of this substitution on the fraction, morphology and distribution of the identified phases has been examined. Beside α_{Ag} and α_{Cu} the intermetallic phases of β-AgCd(Zn), β-CuSn and δ-CuIn have been established after annealing of the alloys at 500 °C for 300 hours by X-ray phase analysis. The presence of the β-CuSn phase shows the influence of indium on the stability of that phase at lower temperatures. By microanalysis the distribution of metals in the present phases has been qualitatively determined. The influence of indium and tin on the liquidus and solidus temperatures is similar to that of the substitution of cadmium only by indium. Measured hardness of the cast alloys shows the favourable influence of the common substitution with indium and tin in comparison with substitution with one metal only.

Key words: soldering, silver solders, intermetallic compounds, phase diagrams, precious metals, indium, tin

VLIV INDIA A CÍNU NA MIKROSTRUKTURU SLITINY AgCu25Zn20Cd20

Při výzkumu slitiny AgCu25Zn20Cd20 bylo toxické kadmium jednak částečně, jednak úplně nahrazené indiem a cínem. Byl studován vliv této substituce na podíl, morfologii a distribuci identifikovaných fází ve slitině. Po žíhání slitin při teplotě 500 °C po dobu 300 hodin byly ve struktuře kromě fází α_{Ag} and α_{Cu} stanoveny též intermetalické fáze β-AgCd(Zn), β-CuSn a δ-CuIn. Identifikace těchto fází proběhla metodou rentgenové difrakční analýzy. Přítomnost fáze β-CuSn ukazuje vliv india na stabilitu této fáze za nízkých teplot. Distribuce kovových prvků v přítomných fázích byla kvalitativně určena mikroanalýzou. Vliv india a cínu na teploty likvidu a solidu je podobný jako v případě, kdy je kadmium ve slitině substituováno pouze indiem. Tvrdost slitin změřená v litém stavu ukazuje příznivý vliv společné substituce kadmia indiem a cínem ve srovnání s jeho substitucí pouze jedním z obou kovů.

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1. Introduction

For the soldering of steel, ceramics, copper, nickel and its alloys the solders of the Ag-Cu-Zn-Cd system are used. Due to the cadmium toxicity the investigation of the metal substitutes in the solders requires to preserve the low melting point, good wettability and working properties of alloys. For the AgCu25Zn20Cd20 alloy the influence of the cadmium substitution with the combination of indium and tin has been examined on the fraction, morphology and distribution of phases in the microstructure. The weight ratio of the added indium and tin was 1:1. After annealing for 300 hours at 500 °C the present phases in the alloys have been identified by the X-ray analysis. The melting intervals and the hardness in the cast and heat-treated state have been determined for some alloys.

2. Experimental

For investigation of the influence of substitution of cadmium with indium and tin on the microstructure and the properties of AgCu25Zn20Cd20 alloy two master alloys (**A** and **B**) of the following compositions [wt.%] were used: **A**: 39 % Ag, 19.1 % Cu, 21 % Zn and 20 % Cd; and **B**: 29.4 % Ag, 28.3 % Cu, 21.4 % Zn and 21.2 % Cd. Silver of purity of 99.95 wt.%, electrolytic copper, zinc of p.a., indium of 99.99 % and technical tin were added to obtain the needed composition. Alloys were remelted in the evacuated quartz tubes in an induction furnace. The rough-cast alloys were homogenized for 300 hours at 500 °C and then quenched in ice-cold water.

Microstructures of as-cast and homogenized alloys were examined by optical microscope. Powder samples for X-ray analysis have been prepared by the heat-treated alloys. The preparation of the samples and the investigation conditions have been described in our previous publications [1, 2].

3. Results and discussion

Indium and tin were partly or entirely substituted for cadmium in the basic alloy of AgCu25Zn20Cd20. In our previous investigations, in which indium [1] or tin [2] only were substituted for cadmium, an effect on the melting point depression and the strong increase of the hardness of alloy were observed. The investigations showed the technological need for the substitution of cadmium up to 5 wt.% by indium. After the total substitution of cadmium with tin, the essential melting point depression has been established by the strong increase of the alloy hardness, so that such technology of the soldiers is not suitable for the AgCu25Zn20Cd20 alloy manufacture. 5 wt.% of cadmium has been substituted together by indium and tin to determine the both influences on the properties of the AgCu25Zn20Cd20 alloy. The microstructure of the AgCu25Zn20Cd15In2.5Sn2.5 alloy (Fig. 1) is composed by the primary precipitated mixed crystals of copper (α_{Cu}), bright phase of α_{Ag} and

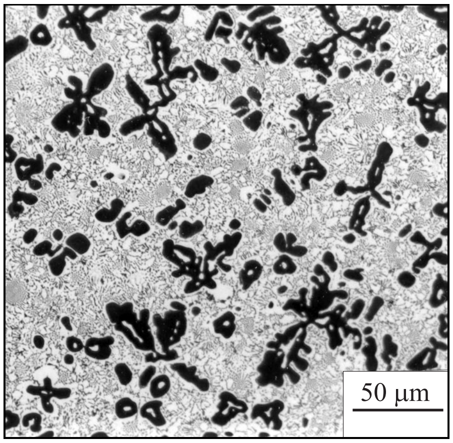

Fig. 1. AgCu25Zn20Cd15In2.5Sn2.5 alloy as cast.

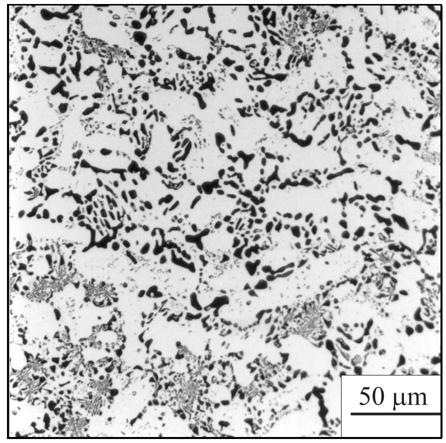

Fig. 2. AgCu25Zn20Cd15In2.5Sn2.5 alloy annealed.

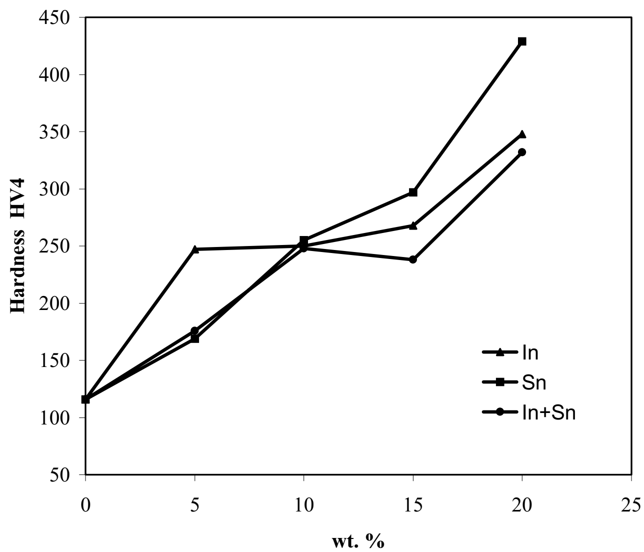

Fig. 3. Hardness of the cast AgCu25Zn20Cd(In,Sn)20 alloys.

70 vol.% of eutectic $[\alpha_{Cu} + \alpha_{Ag} + \beta\text{-AgCd(Zn)}]$. After the heat treatment at 500 °C the copper mixed crystals (dark grains) coagulated, the fraction of α_{Ag} increased and that of the eutectic decreased (Fig. 2), but its fraction in the microstructure is larger than in the alloys where cadmium was substituted only with indium or tin.

Table 1. Results of X-ray and thermal analysis for AgCu25Zn20Cd(In, Sn)20 alloys

Ag	Cu	Zn	Cd	In	Sn	Phase composition [vol.%]		Lattice parameters [nm] *a*	*c*	*c/a*	Temperature [°C] Liq.	Sol.
35	25	20	20	–	–	68	α_{Ag}	0.41492				
						25	α_{Cu}	0.36967			624	600
						7	β-AgCd(Zn)	0.33021				
35	25	20	15	2.5	2.5	65	α_{Ag}	0.41384				
						20	α_{Cu}	0.36947				
						10	β-AgCd(Zn)	0.32320			590	578
						trace	β-CuSn	0.31080				
						trace	δ-CuIn					
35	25	20	10	5	5	45	α_{Ag}	0.41427				
						15	α_{Cu}	0.36503				
						20	β-AgCd(Zn)	0.32658				
						5	β-CuSn	0.30113				
						15	δ-CuIn	0.94204	0.94561	1.01		
35	25	20	5	7.5	7.5	25	α_{Ag}	0.41322				
						20	α_{Cu}	0.36487				
						25	β-AgCd(Zn)	0.32670				
						10	β-CuSn	0.30373				
						20	δ-CuIn	0.94021	0.93299	0.99		
35	25	20	0	10	10	15	α_{Ag}	0.41237				
						20	α_{Cu}	0.36421				
						20	β-AgZn(In)	0.32494			571	534
						15	β-CuSn	0.30935				
						30	δ-CuIn	0.92690	0.93692	1.01		

Beside lines of the phases of α_{Ag}, α_{Cu} and β-AgCd(Zn) on the X-radiograph of the AgCu25Zn20Cd15In2.5Sn2.5 alloy, the line systems of the intermetallic phases of β-CuSn and δ-CuIn appeared (Table 1). The hardness of the alloy in the cast state was 176 HV4, which was a little higher than for the substitution with tin, but substantially lower than for the alloy where only indium was substituted for cadmium. Common addition of indium and tin affected the hardness decrease in

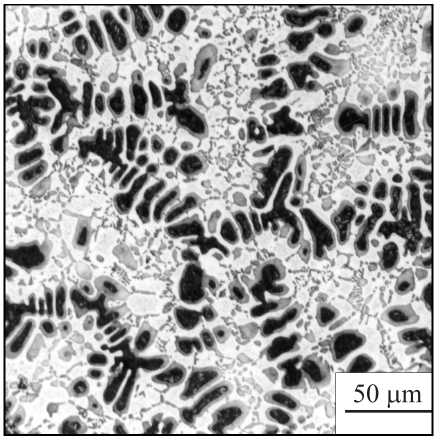

Fig. 4. AgCu25Zn20Cd10In5Sn5 alloy as cast.

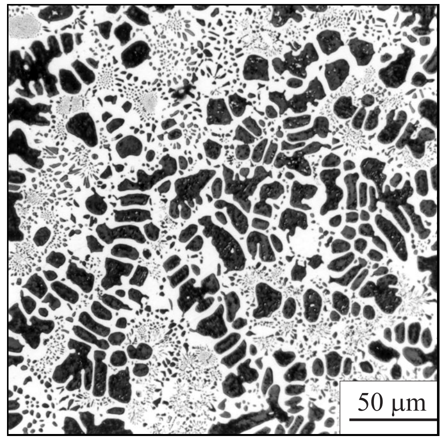

Fig. 5. AgCu25Zn20Cd15In5 alloy as cast.

the cast state in comparison with alloys, where only one metal was substituted for cadmium (Fig. 3). After the heat treatment the hardness of the alloy was 143 HV4, which was essentially lower compared to the alloy where the substitution with pure tin [2] was done.

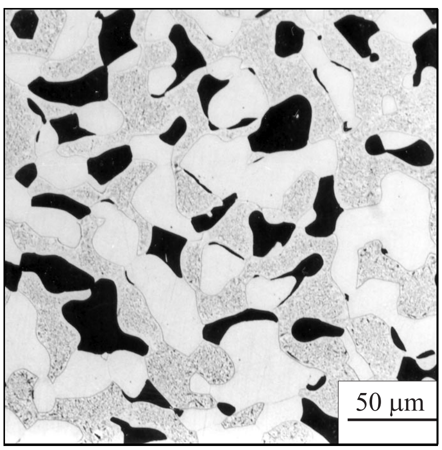

Fig. 6. AgCu25Zn20Cd10In5Sn5 alloy annealed.

After the substitution of 10 wt.% Cd the fraction of α_{Ag} increased (Fig. 4) and α_{Cu} decreased in the microstructure of the AgCu25Zn20Cd10In5Sn5 alloy [1]. Microstructure of that alloy is very similar to the AgCu25Zn20-Cd15In5 [1] alloy (Fig. 5). Peritectically formed copper-indium β-phase (grey), which surrounds the dendrite branches of α_{Cu}, is well visible. That phase decomposed eutectoidly at 574 ℃ into α_{Cu} and δ-CuIn [3], which was confirmed by the XRD analysis. After the heat treatment the microstructure of the alloy was composed of 15 vol.% of α_{Cu}, 45 vol.% of bright phase of silver mixed crystals, and of the heterogeneous phase, in which the phases β-AgCd(Zn), β-CuSn and δ-CuIn were presented and identified by X-ray analysis (Table 1, Fig. 6). The phenomena of the intermetallic cubic

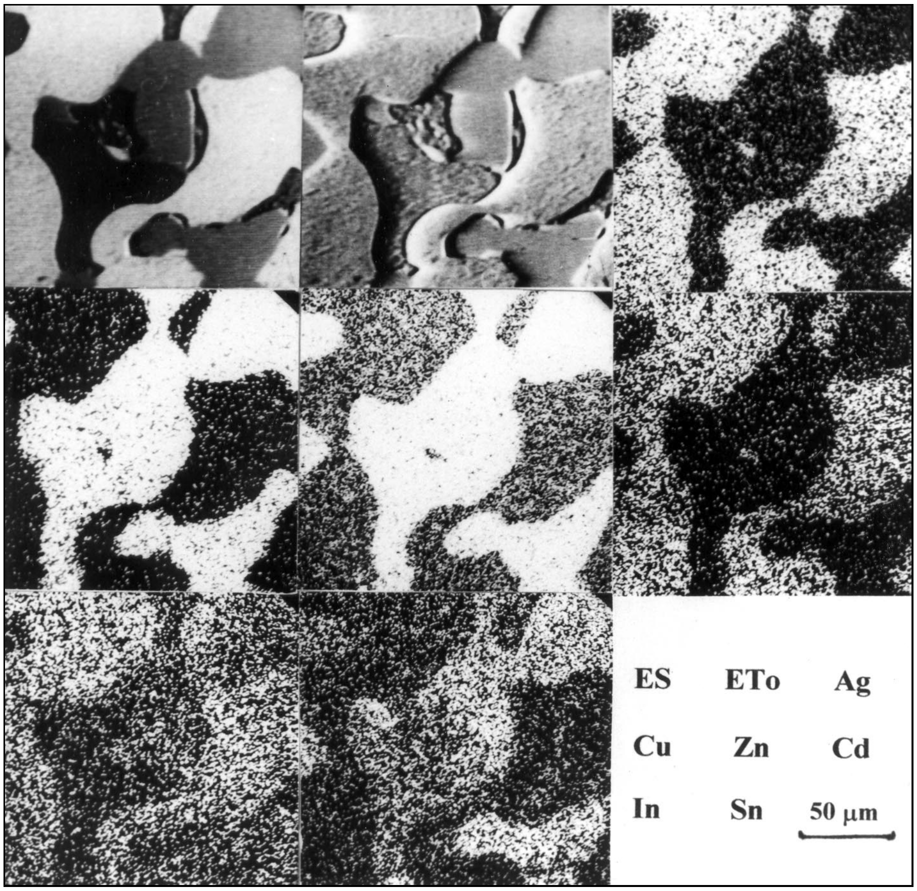

Fig. 7. The microanalysis distribution of Ag, Cu, Zn, Cd, In and Sn in the AgCu25Zn20-Cd10In5Sn5 (ES – distribution of secondary electrons, ETo – topography of the analysed area).

phase of β-CuSn at our annealing temperatures shows that indium and tin stabilize the Hume-Rothery phase, which has to be confirmed by the additional investigation. After the substitution of 10 wt.% cadmium by indium or tin, the fraction of eutectic phase decreases to 5–10 vol.%, while the eutectic fraction in the alloy of AgCu25Zn20Cd10In5Sn5 still represents 40 vol.%. The solubility of zinc and tin in the copper mixed crystals was confirmed by the microanalysis of that alloy (Fig. 7). Cadmium, indium and zinc were dissolved in α_{Ag} phase and the elements of copper, zinc, indium, and tin in the heterogeneous part of the microstructure.

In the microstructure of AgCu25Zn20Cd5In7.5Sn7.5 alloy is still more than 30 vol.% of the eutectic phase. After addition of 7.5 wt.% of tin and of the same quantity of indium, the β-CuSn phase appeared with a similar morphology like after the addition of 10 wt.% tin into the AgCu25Zn20Cd20 alloy [2]. The eutectic phase is also presented in the microstructure of the AgCu25Zn20In10Sn10 alloy after the complete substitution of cadmium (Fig. 8). With increasing fraction of substituted indium and tin for cadmium, the fraction of α_{Ag} phase in the microstructure decreased, the quantity of the α_{Cu} phase remained practically the same, while the fractions of the intermetallic phases increased (Table 1), what is reflected in higher hardness of the alloys. Cast alloys with the addition of 10 wt.% indium and tin have a similar hardness as the alloys, where only one metal was substituted for cadmium (Fig. 3). The hardness of alloys is lower at higher indium and tin content.

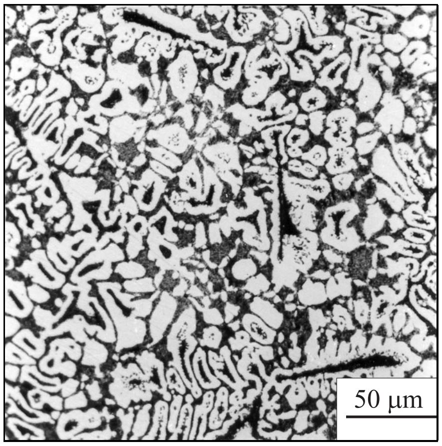

Fig. 8. AgCu25Zn20In10Sn10 alloy as cast.

By our investigation it was established that the influence on the melting interval is similar after the substitution of cadmium by indium and tin to that after the addition of indium only. After the substitution of 5 wt.% cadmium in the AgCu25Zn20Cd20 alloy the temperature of liquidus dropped to 590 ℃ and of solidus to 578 ℃. The melting interval of alloy increased after complete substitution of cadmium by indium and tin, therefore the casting properties of the alloy were improved.

4. Conclusions

By substitution of toxic cadmium with the combination of indium and tin in the cast AgCu25Zn20Cd20 alloy the decrease of hardness, the melting point depression and the increase of melting interval were expected in comparison with the addition of pure indium.

Both effects of indium and tin on the liquidus and solidus temperature are not strong and are almost equal at the substitution of 5 wt.% as for the AgCu25Zn20-In10Sn10 alloy with the temperature of liquidus of 571 ℃ and solidus of 534 ℃. At complete substitution of cadmium by indium and tin the melting point depression of the basic alloy of AgCu25ZnCd20 and the increase of the melting interval of the alloy have been observed in comparison with indium only.

The microstructure of the AgCu25Zn20Cd15In2.5Sn2.5 cast alloy is very similar to AgCu25Zn20Cd20 alloy. With increasing quantity of indium and tin in the alloys the fraction of the silver mixed crystals in the microstructure dropped, the fraction of α_{Cu} remained equal, while the content of the intermetallic phases of β-CuSn and δ-CuSn increased at decreasing quantity of the β-AgCd(Zn) phase. The phenomena of the β-CuSn intermetallic phase in the alloy, which was annealed at 500 ℃, indicates the influence of indium on the stability of that phase at lower temperatures, which has to be confirmed by the additional investigations. By microanalysis, the solubility of zinc and tin in the α_{Cu} phase was confirmed. Cadmium, zinc and indium were dissolved in α_{Ag} phase, and the metals of silver, copper, zinc, indium, and tin in the heterogeneous one, which was composed by β-AgCd(Zn), β-AgZn(In), β-CuSn, and δ-CuIn intermetallic phases. In the microstructures of the cast state the presence of the eutectic phase was established also at the complete substitution of cadmium.

It was found out by our investigations that after the substitution of cadmium by indium and tin in the AgCu25Zn20Cd20 alloy, the hardness of alloys decreased in comparison with the substitution of only indium [1] or tin [2].

Increasing fraction of the intermetallic phases in the microstructure increases the hardness of the alloys, which allows reasonable substitution of cadmium only up to 5 wt.%. Higher quantity fraction of the cadmium substitution increases the brittleness of alloys, what restricts the cold processing of these alloys and the quality of the solder joint.

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