# INFLUENCE OF INDIUM ADDITION ON THE AgCu25Zn20Cd20 ALLOY MICROSTRUCTURE

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In our investigation of the AgCu25Zn20Cd20 alloy, cadmium was partly or fully replaced by indium due to its toxicity. The influence of this substitution on the fraction, morphology and the distribution of the identified phases has been examined, and the indium distribution in the single phases was established. Melting intervals of several alloys have been determined and their hardness in the cast or in heat-treated state was measured. By means of X-ray diffraction (XRD) phase analysis the intermetallic phase of $\delta$-CuIn has been already established in the alloy with 5 wt.% In. The hardness of the cast alloys was strongly increased and the technological procedures of their manufacture was reduced in the presence of that phase. With higher fraction of indium in the alloy the quantity of the ternary eutectic ($\alpha_{Ag}+\alpha_{Cu}+\beta$-AgCd) in the microstructure was decreasing, and the quantity of ternary mixed crystals $\alpha_{Ag}$ increased up to 60 vol.%, while the quantity of $\alpha_{Cu}$ remained fixed. By substitution of indium for cadmium, the melting point decrease to 586 °C and a smaller solidification interval in the alloy of AgCu25Cd15Zn20In5 have been observed.

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

# VLIV PŘÍSADY INDIA NA MIKROSTRUKTURU SLITINY AgCu25Zn20Cd20

Příspěvek obsahuje výsledky studia vlivu přísady india na mikrostrukturu slitiny (pájky) AgCu25Zn20Cd20. Indium nahrazuje v této slitině toxické kadmium. Byl studován vliv přísady india na morfologii, distribuci a podíl fází ve struktuře slitin a byla stanovena distribuce In v jednotlivých fázích slitiny. Dále byl stanoven teplotní interval tavení některých slitin a jejich tvrdost ve stavu po odlití a po tepelném zpracování. Byla aplikována metoda rentgenové difrakční analýzy, pomocou níž byla zjištěna ve slitině s 5 hm. % In přítomnost intermetalické fáze $\delta$-CuIn. Tato fáze zvyšuje tvrdost slitiny v litém stavu a omezuje její technologické zpracování. Vyšší podíl india ve slitině koresponduje s nižším podílem ternárního eutektika a s vyšším podílem krystalitů tuhého roztoku alfa, který se zvyšuje až na 60 obj. %. Nahrazením kadmia indiem se sníží teplota tavení slitiny na 586 °C a pozoruje se menší teplotní interval tuhnutí.

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## 1. Introduction

Ag-Cd-Cu-Zn alloys have wide industrial application. They are used in technology of soldering (gas, electroresistant, continuous) with or without protective atmosphere. Due to the high vapour pressure of cadmium and zinc their use in vacuum is not advisable.

Toxicity of cadmium oxides, which are formed during production of solders and their applications, requires substitution of other metals for it. By substitution of indium for cadmium, a decrease of melting point and unchanged hardness in AgCu25Zn20Cd20 alloy were expected.

## 2. Experimental

For investigation of the influence of indium substitution on the microstructure of the basic alloy of AgCu25Zn20Cd20, the alloys were made of the following two master alloys A: 39 wt.% Ag, 19.1 wt.% Cu, 21 wt.% Zn, and 20 wt.% Cd and B: 29.4 wt.% Ag, 28.3 wt.% Cu, 21.4 wt.% Zn, and 21.2 wt.% Cd. Silver of purity of 99.95 %, granulated electrolytic copper, zinc of p.a., and indium of 99.99 % were added to obtain the needed chemical composition.

Alloys were inserted in evacuated quartz tubes to 0.2 Pa and melted in a medium-frequency induction furnace. All alloys, whose compositions differed by more then 0.5 wt.%, were prepared again. Reguluses of the alloys were homogenized for 300 hours at 500 °C and then quenched in ice-cold water.

Microstructures of reguluses and homogenized alloys were examined by optical microscope. Due to the fine granular structure, the metallographic identification of all phases was uncertain, therefore the X-ray phase analysis was needed to complete our investigation. The hardness of the alloys was measured in both the cast and homogenized state. Liquidus and solidus temperatures were determined for some alloys.

Powder samples for X-ray analysis were prepared by heat treated and stress--free annealed alloys. X-ray investigations were carried out by the Guinnier method using monochromatic X-rays with the wave length of $\lambda = 154.178$ pm. Crystallographic planes were graphically indicated from monograms of tetragonal crystal systems. The basic cells parameters of the phases were calculated using known formulas, and the single-phase fractions were determined on the base of visual intensity estimation of blackening reflexes of line systems.

## 3. Results and discussion

In our standard solder of AgCu20Zn20Cd20 (Fig. 1) 5 wt.% of silver was substituted with copper. In the microstructure the fraction of copper mixed crystals was increased (dark dendrites), but fraction of the ternary eutectic ($\alpha_{\mathrm{Ag}} + \alpha_{\mathrm{Cu}} +$

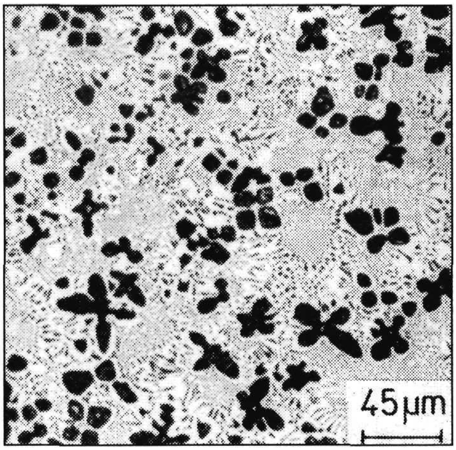


Fig. 1. AgCu20Zn20Cd20 alloy.

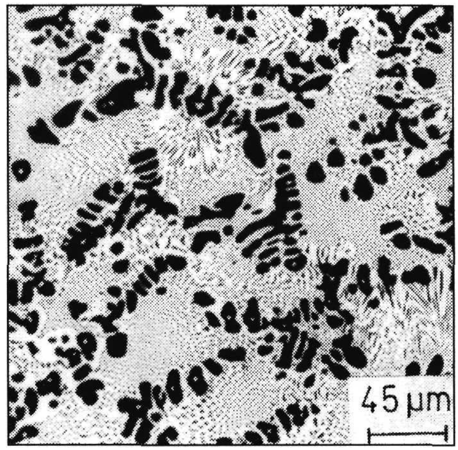


Fig. 2. AgCu25Zn20Cd20 alloy.

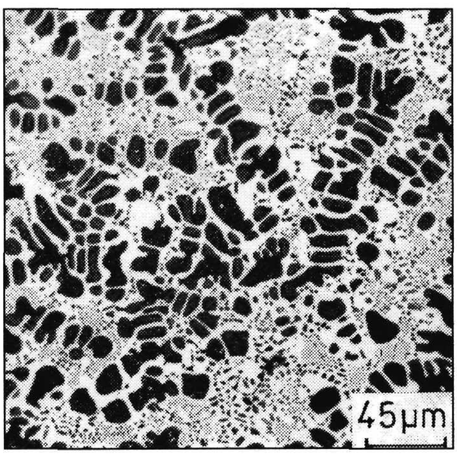


Fig. 3. AgCu25Zn20Cd15In5 alloy.

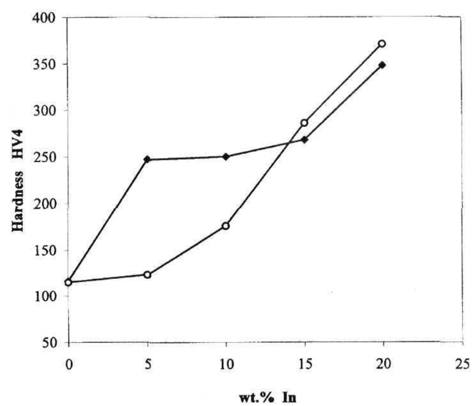


Fig. 4. Hardness of the AgCu25Zn20Cd-(In)20. ♦ as cast, o annealed.

+ β-AgCd/Zn) was decreased to 70 vol.% (Fig. 2). The AgCd phase was not detected by optical microscope, but its presence was confirmed with X-ray phase analysis (Table 1) [1]. Intermetallic phase of β-AgCd(Zn) results from ternary systems of Ag-Cd-Zn [2, 3], in which both phases of β-AgCd [4] and β-AgZn [4] form a region of complete solubility with changing parameter of basic cell from 0.3156 nm,

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

| Alloys composition in weight % | | | | | Phase composition [vol. %] | Lattice parameters a [Å] | | Temperature Liquidus | Solidus |
|---|---|---|---|---|---|---|---|---|---|
| Ag | Cu | Zn | Cd | In | | Å | c/a | [°C] | |
| | | | | | 68 $\alpha_{Ag}$ | 4.14915 | | | |
| 35 | 25 | 20 | 20 | 0 | 25 $\alpha_{Cu}$ | 3.69669 | | 624 | 600 |
| | | | | | 7 $\beta$-AgCd(Zn) | 3.30211 | | | |
| | | | | | 55 $\alpha_{Ag}$ | 4.14314 | | | |
| | | | | | 25 $\alpha_{Cu}$ | 3.69583 | | | |
| 35 | 25 | 20 | 15 | 5 | 15 $\beta$-AgCd(Zn) | 3.27053 | | 586 | 568 |
| | | | | | Trace $\delta$-CuIn | | | | |
| | | | | | 50 $\alpha_{Ag}$ | 4.14915 | | | |
| | | | | | 18 $\alpha_{Cu}$ | 3.69555 | | | |
| 35 | 25 | 20 | 10 | 10 | 25 $\beta$-AgCd(Zn) | 3.27957 | | | |
| | | | | | 7 $\delta$-CuIn | 9.56089 | 1.02 | | |
| | | | | | 50 $\alpha_{Ag}$ | 4.14314 | | | |
| | | | | | 10 $\alpha_{Cu}$ | 3.67431 | | | |
| 35 | 25 | 20 | 5 | 15 | 25 $\beta$-AgCd(Zn) | 3.27541 | | | |
| | | | | | 15 $\delta$-CuIn | 9.55149 | 1.02 | | |
| | | | | | 60 $\alpha_{Ag}$ | 4.14154 | | | |
| | | | | | 20 $\alpha_{Cu}$ | 3.69469 | | | |
| 35 | 25 | 20 | 0 | 20 | 15 $\beta$-AgZn(In) | 3.26729 | | 584 | 555 |
| | | | | | 5 $\delta$-CuIn | 9.53845 | 1.01 | | |

for pure $\beta$-AgZn phase, to 0.333 nm, for $\beta$-AgCd phase (from the binary Ag-Cd system).

In our test basic alloy of AgCu25Zn20Cd20, cadmium was partly or completely substituted for indium. Due to its high solubility in silver and low melting point, lower melting points and a stable hardness in the cast- and thermal-processed states have been expected.

The substitution of cadmium up to 5 wt.% by indium did not essentially affect the morphology of microstructure, the quantity of mixed crystals of $\alpha_{Ag}$ and $\alpha_{Cu}$ was increased, but 35 vol.% of ternary eutectic ($\alpha_{Ag}$ + $\alpha_{Cu}$ + $\beta$-AgCd) was still present (Fig. 3). Measured hardness of AgCu25Zn20Cd15In5 alloy in the cast state was 246 HV4. This increase of hardness is the result of indium solubility in the silver mixed crystals and the presence of $\beta$-$Cu_3In$ intermetallic phase. After annealing at 500 °C the $Cu_3In$ phase was eutectically decomposed into two phases of $\alpha_{Cu}$ and $\delta$-CuIn, and the hardness decreased to 123 HV4 (Fig. 4). From measured basic cell parameters of the $\delta$-CuIn phase the constant axial ratio of $c/a = 1.02$ was evident, what shows the stable stoichiometric composition of the intermetallic phase and low solubility of other metals in that phase.

With further indium addition the quantity of eutectic phase ($\alpha_{Ag}$ + $\alpha_{Cu}$ + $\beta$-AgCd) in alloys decreased and was only 10 vol.% (Fig. 5). In the newly-formed alloy of AgCu25Zn20Cd10In10, the amount of $\alpha_{Ag}$ increased, while that of $\alpha_{Cu}$ remained fixed. By microanalysis of alloys the dissolution of indium in the silver mixed crystals as well as its presence in heterogeneous structure of the eutectic phase was confirmed (Fig. 6). In the alloy of AgCu25Zn20Cd5In15 the quantity of the copper mixed crystals decreased to 15 vol.% and a new eutectic space ($\alpha_{Ag}$ + $\alpha_{Cu}$ + $\delta$-CuIn + $\beta$-AgCd) appeared (Fig. 7). From X-ray and metallographic analysis of investigated alloys the presence of large number of eutectic spaces was concluded, what was confirmed by Petzow et al. [5, 6, 7] for the basic Ag-Cu-Zn-Cd system.

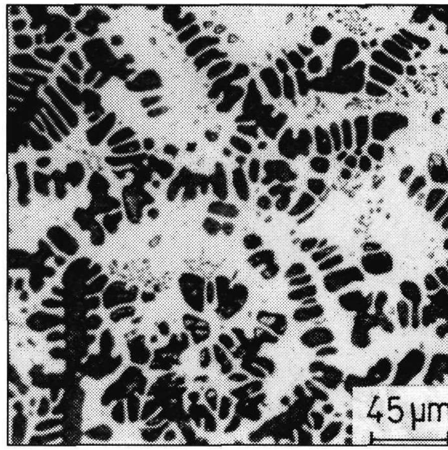

Fig. 5. AgCu25Zn20Cd10In10 alloy.

After total substitution of cadmium in the AgCu25Zn20In20 alloy (Fig. 8), its microstructure is composed of 10 vol.% of primary precipitated $\alpha_{Cu}$ mixed crystals (dark), 75 vol.% $\alpha_{Ag}$ mixed crystals (light) and 15 vol.% of heterogeneous quaternary eutectic phase. By comparison of both microstructures of AgCu25Zn20Cd20 and AgCu25Zn20In20, it was established that, due to addition of indium, quantity of $\alpha_{Ag}$ strongly increased, but the fraction of $\alpha_{Cu}$ primary mixed crystals and quaternary eutectic phase decreased. The amount of quaternary eutectic phase in the microstructure was lowered to 20 vol.%. It was established by our investigation that the hardness of alloys in the cast state strongly increased after substitution of indium for cadmium in AgCu25Zn20Cd20 alloy as a result of the formation of intermetallic phases of $\beta$-$Cu_3In$ and $\delta$-CuIn. With increasing quantity of indium in alloys the fraction of silver mixed crystals $\alpha_{Ag}$ was growing and $\alpha_{Cu}$ decreasing.

Thermal analysis of alloys shows that the temperature of liquidus decreased to 586 °C and that of solidus to 568 °C due to 5 wt.% of indium addition.

Further increase of indium volume essentially did not affect the temperature

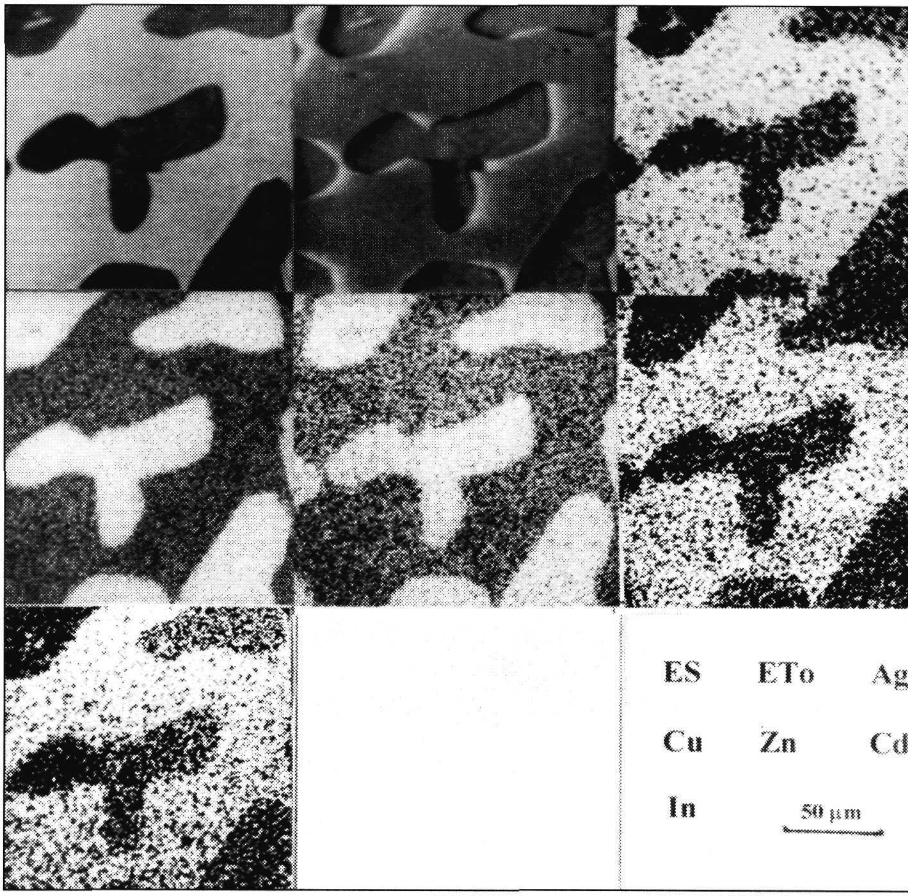


Fig. 6. The microanalysis distribution of Ag,Cu,Zn,Cd, and In in the AgCu25Zn20-Cd10In10 alloy (ES – distribution of secondary electrons, ETo – topography of the analyzed area).

change (Table 1). There was established only a little widening of the melting interval of AgCu25Zn20In20 alloy in comparison with the initial alloy.

## 4. Conclusions

By substitution of indium for cadmium in AgCu25Zn20Cd20 alloy the melting point decrease and stable hardness in the cast and thermal processed state have been expected. With increasing quantity of indium in alloys the volume fractions of eutectic and primary $\alpha_{Cu}$ mixed crystals was decreasing, but $\alpha_{Ag}$ increasing.

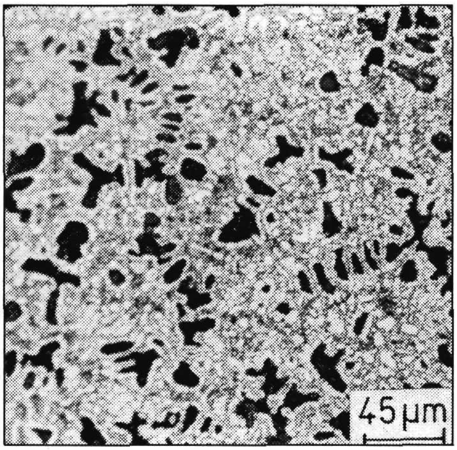


Fig. 7. AgCu25Zn20Cd5In15 alloy.

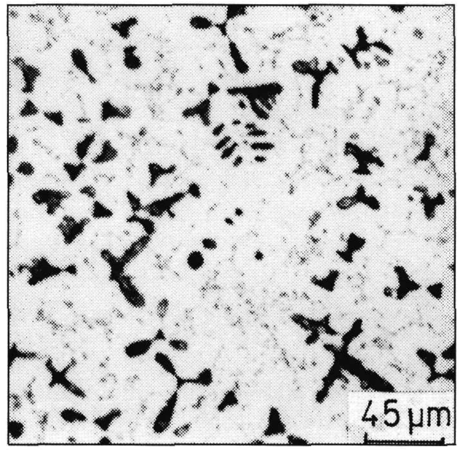


Fig. 8. AgCu25Zn20In20 alloy.

A new eutectic space of [$\alpha_{Ag}$ + $\alpha_{Cu}$ + $\delta$-CuIn + $\beta$-AgCd(Zn)] appeared, whose amount was less than 20 vol.% in the AgCu25Zn20In20 alloy. By X-rays analysis the intermetallic phase of $\alpha$-CuIn has been detected in AgCu25Zn20Cd15In5 alloy, which quantity increased up to 15 vol.% by substitution of 15 wt.% cadmium. The presence of intermetallic compounds of $\beta$-AgCd(Zn), $\beta$-$Cu_3In$ and $\delta$-CuIn, which affected the hardness of the alloys, has been established.

Our investigations confirmed practically logical substitution of cadmium in alloy of AgCu25Zn20Cd20 only up to 5 wt.%, since higher quantity of indium essentially did not affect the melting point of alloys due to the increasing quantities of intermetallic phases of $\beta$-$Cu_3In$ and $\delta$-CuIn and hardening of the silver mixed crystals. The technological procedures of manufacture of alloys are limited due to the brittleness of joints, since the dissolved indium increases their hardness.

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Received: 14.12.2000
Revised: 21.3.2001