CHANGES IN ELECTRICAL CONDUCTIVITY OF THE Ag-In-Sn-Cu ALLOYS AS INFLUENCE OF DIFFERENT TEMPERATURE REGIMES

Abstract

Among ecological solders the SIAC (silver-indium-tin-copper) alloys seemed to be the promising because of their properties. In this paper the results of Ag-In-Sn-Cu electrical conductivity measurements are performed as well as polynomial regression of the same. These results are obtained for different temperature regimes and conditions.

Keywords: Ag-In-Sn-Cu alloys, electrical conductivity, polynomial regression

INTRODUCTION

The currently used lead-based solders are under way to be replaced by lead-free alloys due to the environmental and health concerns. In that purpose, various physical, chemical and mechanical properties of the candidate alloy, as well as the economic aspect have been considered. A significant part of work is to find a substitute for common Pb-Sn solder alloy, which has become complex and widely discussed [1-12]. The proper alloy must have the certain characteristics to satisfy:

- Availability
- No Toxicity
- Melting temperature range
- Wettability
- Other process conditions

The solder chosen for a particular use should have a low enough melting temperature that the melted solder does not damage any temperature-sensitive components that are to be joined. However, the melting temperature should also be high enough that the joint formed will not be affected by the operating temperature of the device or by subsequent soldering operations. In modern electronic applications, the temperature sensitivity of microelectronic components requires the use of solders at relatively low temperatures. In comparison, solders for joining and sealing pipes in plumbing operations are generally applied at much higher working temperatures because the components are not as temperature sensitive.

Solders with small pasty ranges are also important in certain "step-soldering" operations where components are added to a device sequentially. These operations are also dependent upon solders with specific melting temperatures. In step soldering, the first components are joined using a relatively
high melting temperature solder. When later components are joined, a lower melting temperature solder is used so that the earlier-soldered joints are not affected by the soldering operation. Further components may then be added using solder with an even lower melting temperature. The availability of solders with different melting points is critical to such step-soldering processes. It is also important, if several soldering steps are to be performed, for the melting ranges of the solders to be small.

The question about melting temperature is one of the most difficult problems in the lead-free soldering transition, but not the only one. Ecological solder alloys must satisfy more requests in order to completely replace the standard solder alloys. Because of specific properties, there is not drop-in replacement yet.

However, the most promising ecological solder alloys, such as Sn-Ag or Sn-Ag-Cu have higher melting temperatures than conventional tin-lead solder. Because of that, in practice the temperature during electronic assembling must be raised by 30-40°C which reduces reliability and functionality of electronic components. Low processing temperature is desirable for preventing damage of electronic devices during soldering. An attractive solution for melting temperature decrease is the addition of indium [9], so the indium based multicomponent solder alloys might have the appropriate characteristics.

Some of the alloys based on indium such as In-Sn, are mainly used in the process of cold soldering. The only faults of these alloys are high price of cost, but ductility, good lubricate and fatigue resistance are the qualities necessary for a good solders. Likewise, the alloys which possess some application in practise are Sn-In-Ag and Sn-In-Cu alloys.

Considering two suitable systems Sn-Ag-Cu and Sn-In-Ag and their properties as potential replacement for standard solder alloys, they can be combined for multicomponent alloy based on tin and indium, with the addition of silver and copper which might have better properties. In that case, there is the SIAC alloy (Sn-In-Ag-Cu). When indium is added to the ternary Sn-Ag-Cu alloys, it reacts with tin, silver and copper, and these reactions play an important role in defining microstructure and determining mechanical properties of the alloy.

A large number of researchers around the world as a part of international projects (e.g. COST531 [10]) work on establishing the thermodynamic, mechanical and structural properties of lead-free solders. Their results are reflected in the created databases that contain information about the melting point, density, viscosity, electrical and microstructural properties and phase diagram, starting from the binary and multicomponent alloys. In this way, for a certain type of process and specific requirements the optimum composition of the elements can be predicted, and the optimum alloy that could replace lead solder.

To contribute to the knowledge of ecological solder systems based on tin and indium, the results of the Ag-In-Sn-In-Cu system investigation are presented in this paper.

EXPERIMENTAL PART

Electrical conductivity of all prepared samples was measured at the room temperature using the standard apparatus SIGMAT-EST 2.069 (Foerster) eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals based on complex impedance of the measuring probe with diameter of 8 mm.

The Ag-In-Sn-Cu alloys with molar ratio In:Ag:Cu=7:2:1 and within the mole fraction of 0.5 to 0.95 for Sn were experimentally investigated. All samples were prepared from Ag, Cu, In and Sn of 99.99% purity. The chosen samples were investigated in two series A and B with the same compositions and various thermal conditions. The samples from A group, having masses approximately 2 g, were prepared by the induction melting under argon atmosphere, and the procedure
was repeated several times to improve homogeneity, while the B samples were melted in electrical furnace up to 873K in argon atmosphere, annealed at 473K one hour, and slowly cooled with the furnace to the room temperature. In both cases, the mass loss of samples was less than 1%.

Prepared samples were investigated by the standard apparatus in order to obtain the electrical conductivity for all samples.

RESULTS AND DISCUSSION

Twenty tin rich alloys with compositions along cross section with molar ratio In:Ag:Cu=7:2:1 have been experimentally investigated. Ten compositions were chosen from wide concentration area in Ag-In-Sn-Cu system, due to the previous investigations [1-12].

The compositions for both series A and B were the same and are given in Table 1.

| Table 1 | The compositions of Ag-In-Sn-Cu samples |
|---------|----------------------------------------|
| Alloy   | Sn  | In  | Ag  | Cu  |
| A1,B1   | 0.5 | 0.35| 0.1 | 0.05|
| A2,B2   | 0.55| 0.315| 0.09| 0.045|
| A3,B3   | 0.6 | 0.28| 0.08| 0.04|
| A4,B4   | 0.65| 0.245| 0.07| 0.035|
| A5,B5   | 0.7 | 0.21| 0.06| 0.03|
| A6,B6   | 0.75| 0.175| 0.05| 0.025|
| A7,B7   | 0.8 | 0.14| 0.04| 0.02|
| A8,B8   | 0.85| 0.105| 0.03| 0.015|
| A9,B9   | 0.9 | 0.07| 0.02| 0.01|
| A10,B10 | 0.95| 0.035| 0.01| 0.005|

Electrical conductivity of all twenty samples was measured in three series and than the average values were calculated in order to obtain the dependence from composition. The results of measured values for Ag-In-Sn-Cu alloys are given in Tables 2 and 3.

| Table 2 | Electrical conductivity measured values for the Ag-In-Sn-Cu alloys – A |
|---------|---------------------------------------------------------------|
| Alloy   | Electrical conductivity MS/m | I    | II   | III  | Average |
| A1      | 7,933 | 8,030 | 7,946| 7,970|
| A2      | 8,451 | 8,515| 8,378| 8,448|
| A3      | 3,120 | 3,179| 3,074| 3,124|
| A4      | 4,806 | 5,004| 4,756| 4,855|
| A5      | 4,808 | 5,107| 4,872| 4,929|
| A6      | 8,668 | 8,794| 8,806| 8,756|
| A7      | 6,299 | 6,563| 6,437| 6,433|
| A8      | 8,562 | 8,555| 8,570| 8,562|
| A9      | 8,690 | 8,833| 8,673| 8,732|
| A10     | 5,555 | 5,709| 5,575| 5,613|
Table 3 Electrical conductivity measured values for the Ag-In-Sn-Cu alloys – B

| Alloy | Electrical conductivity (MS/m) |   |   |   |   |
|-------|--------------------------------|---|---|---|---|
|       | I    | II  | III | Average |
| B1    | 2.544 | 2.603 | 2.602 | 2.583 |
| B2    | 2.867 | 2.720 | 2.657 | 2.748 |
| B3    | 1.552 | 1.650 | 1.623 | 1.608 |
| B4    | 1.590 | 1.645 | 1.648 | 1.628 |
| B5    | 3.138 | 3.215 | 3.161 | 3.171 |
| B6    | 1.726 | 1.848 | 1.552 | 1.709 |
| B7    | 2.802 | 2.815 | 2.703 | 2.773 |
| B8    | 3.283 | 3.169 | 3.361 | 3.271 |
| B9    | 1.655 | 1.800 | 1.604 | 1.686 |
| B10   | 1.300 | 1.613 | 1.591 | 1.501 |

All measured electrical conductivity values for A and B series showed many deviations. Rapidly changes which are observed are influenced by various intermetallic compounds in microstructure [12], so there could not be precisely defined increasing or decreasing curve as it was in the Ag-In-Sn or Cu-In-Sn alloys [7].

The differences in obtained measured values for A and B samples were obviously consequences of various thermal conditions. All alloys were not exposed to the same temperature regime. In contribution to this, there were differences in the structure and micro-hardness too [12].

Figure 1 $\sigma$ (MS/m) = $f$ (XSn) for Ag-In-Sn-Cu alloys – A
In order to decrease the number of future experiments in the field of the best substitute for common Pb-Sn solder alloy, the regression model was applied. Polynomial regression was used to get an equation or dependence of electrical conductivity vs. composition with the following expression:

$$Y = A_0 + A_1 X + A_2 X^2 + A_3 X^3 + \ldots + A_n X^n + R$$

where R is error which is normally distributed.

The results of electrical conductivity polynomial regression model are equations based on dependency of tin content in the alloy. These functions are shown in Figures 1 and 2. Therefore, equation (2) is for Ag-In-Sn-Cu alloys - A, and (3) is for Ag-In-Sn-Cu alloys - B. Both of expressions are polynomial of fourth order.

$$\sigma(MS/m) = -1210.58275 X^4 + 2907.51671 X^3 - 2420.34324 X^2 + 794.10808 X - 71.17413$$  

(2)

$$\sigma(MS/m) = -138.36823 X^4 + 235.40618 X^3 - 74.94735 X^2 - 46.37578 X + 23.89535$$  

(3)

**CONCLUSIONS**

The results of electrical conductivity measurement and polynomial regression model of chosen alloys from the Ag-In-Sn-Cu system were presented in this paper, enabling better understanding of these types of alloys. The application of this type of regression model is in calculation of electrical conductivity for these alloys in any point, so the number of necessary experiments could be decreased. Also, the
influence of thermal regime on obtained electrical conductivities was pointed out through results for two series of alloys.

As a potential candidate for ecological solder alloy, Ag-In-Sn-Cu alloys need to be well investigated, so the findings from this paper enable expansion of the existing database for this type of alloys.

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