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Effects of Co Addition on the Microstructure and Tensile Behavior of Sn-3.0Ag-0.5Cu Solder Alloy†

CHENG Fangjie*, NISHIKAWA Hiroshi** and TAKEMOTO Tadashi***

Abstract

The effects of Co addition on the microstructure and tensile behavior of Sn-3.0Ag-0.5Cu lead-free solder were explored. The addition of Co resulted in the formation of $CoSn_2$ intermetallic compounds (IMCs). The amount of Co has a notable effect on the morphology of $CoSn_2$ IMCs. The $CoSn_2$ phases presented needle shapes with 0.2mass% Co addition, however it presented block shapes with 0.5mass% Co addition. Similar to the SAC baseline, after high temperature aging, the microstructure of Co-containing solders became notably coarsened. During aging, the Cu_6Sn_5 IMCs tended to grow around the $CoSn_2$ phases. In the cast condition, the addition of small amounts of Co had little effect on the tensile strength of SAC-based solder alloys, although it notably suppressed the ductility. After aging, the Co-containing SAC solders showed two trends, one was the decrease of ultimate tensile strength, the other was the increase of ductility. Small additions of Co worsened the ductility of SAC-Co solder alloy, however the high temperature aging suppressed this negative effect.

KEY WORDS: (Lead-free solder), (Isothermal aging), (Minor element addition), (Microstructure), (Tensile behavior)

1. Introduction

Due to the environmental and health concerns associated with lead, the research activities to find suitable lead-free substitutes for the traditional PbSn in electronic assembly have been conducted within the past decade. There are several lead-free alloy systems, e.g., Sn-Ag, Sn-Cu, Sn-Ag-Cu, Sn-Bi etc., are proposed as candidates. In Japan, the hypoeutectic composition Sn-3.0Ag-0.5Cu (SAC) has been one of the industry standard lead-free solder. However, there are still some shortcomings with this ternary lead-free solder. For example, the formation of large primary Sn dendrites reduces the resistance to thermal-mechanical fatigue[1]. In addition, the excessive reaction between lead-free solders and substrate materials is also a problem for SAC solders [2,3]. In order to meet the different application requirements, solders with desirable properties are being extensively sought. Micro-alloying is an effective method to modify the microstructural and mechanical properties of SAC alloys. It has been reported that the addition of Co into Sn-Ag-Cu solder could produce great changes in the interfacial reaction between the solder and Cu substrate, as well as the refinement of the β-Sn phase[4,5]. Also, some researches indicates that the minor addition of Co could suppress the dissolution of iron-based materials in the molten solder[6]. To date, most of the experiments have focused on the growth of intermetallic compounds (IMCs) layers at the interface between the solder and substrate, less attention concerning the evolution of bulk solder. However, many of the solder joints are required to operate in higher temperature environments. In the present work, the effects of Co addition on the microstructure and tensile behavior of SAC bulk solder, before and after high temperature aging, have been explored.

2. Experimental procedures

The nominal ingot composition in the present work was Sn-3.0Ag-0.5Cu-0.2Co and Sn-3.0Ag-0.5Cu-0.5Co (mass%), hereafter abbreviated as SAC-0.2Co and SAC-0.5Co, respectively. The standard Sn-3.0Ag-0.5Cu (SAC) solder was used as a baseline. The alloys were re-melted at about 317°C for 1 h in a graphite crucible and then cast into rod-shape ingots. The cooling rate of the ingot was about 8°C/s, which was equivalent to practical soldering conditions.

An isothermal aging treatment was carried out in an oil bath at 150°C for 168 h and 504 h, respectively. The microstructures of the samples were examined with an optical microscope. An EPMA was used to identify the elemental distribution after the aging treatment. For the examination of the mechanical properties, tensile tests were carried out at room temperature under a strain rate

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of 1×10^{-3}/s using an INSTRON5500R type tensile test machine. The shape and size of tensile test specimens are according to JIS Z-6198-2.

3. Results and discussion

3.1 Microstructures

In the cast condition, the microstructure of SAC bulk solder consists of dendritic β-Sn primary phase and Sn-Ag-Cu ternary interdendritic eutectic network, as shown in **Fig. 1(a)**. It will be seen that the size of β-Sn dendrite is very large, meanwhile, the Sn-Ag-Cu ternary eutectic is superfine.

After the addition of 0.2mass%Co into the SAC, some needle-like intermetallic compounds appeared, as shown in **Fig. 1(b)**. The quantitative analysis by EPMA indicated that these IMCs are $CoSn_2$ with a small amount of Cu. These $CoSn_2$ particles are mainly located in the interdendritic eutectic network. **Fig. 1(c)** showed the typical microstructure of SAC-0.5Co alloy in the as-cast condition. Addition of 0.5mass% Co resulted in the formation of many block-shape IMCs inside the eutectic network, which was also of the $CoSn_2$ type.

Generally, the microstructure of lead-free solders is metastable. In elevated temperature environments,

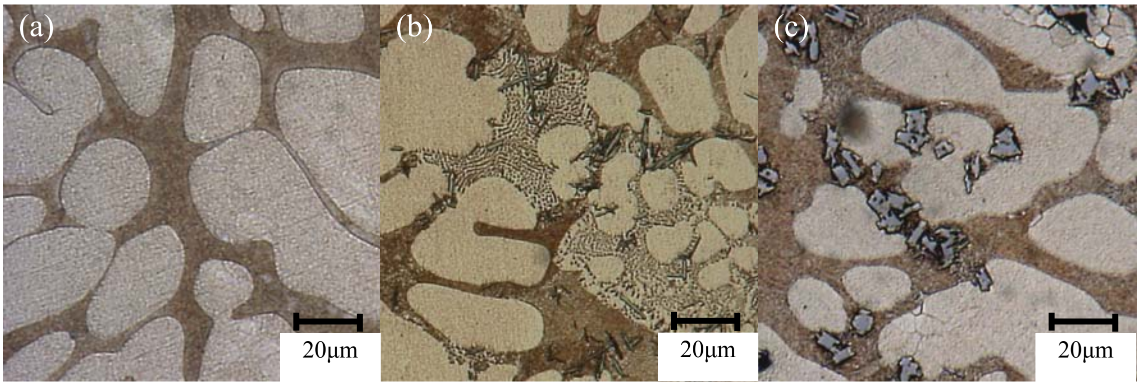

Fig. 1 Photomicrographs of (a) SAC, (b) SAC-0.2Co and (c) SAC-0.5Co solder alloys in the as-cast condition.

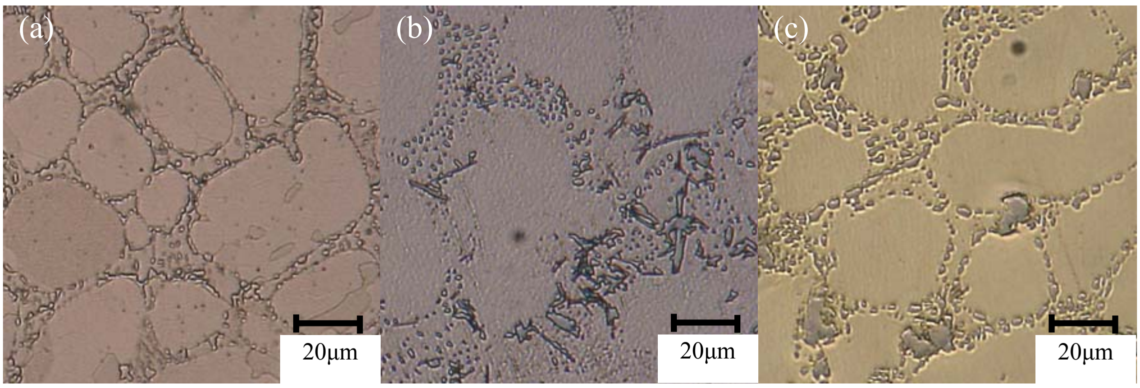

Fig. 2 Photomicrographs of (a) SAC, (b) SAC-0.2Co and (c) SAC-0.5Co solder alloys after aging at 150°C for 168h.

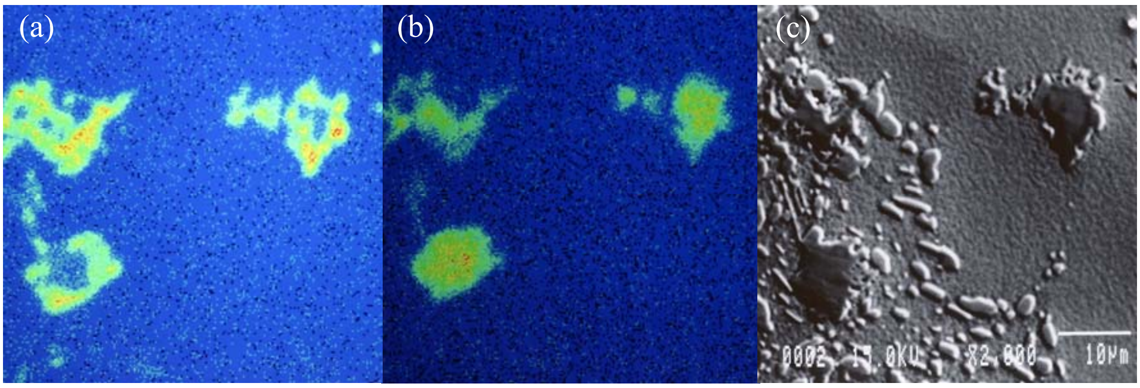

Fig. 3 The distribution of (a) Cu, (b) Co, and (c) SEM image in SAC-0.5Co solder alloy after aging at 150°C for 168h.

microstructural degradation, i.e. coarsening, will occur. **Figure 2** shows the microstructure evolution results of the three tested solder alloys after isothermal aging for 168h at 150°C. It is clear that substantial microstructural coarsening has occurred.

For the SAC solder, block shape Cu_6Sn_5 and granular Ag_3Sn precipitate particles have been formed inside the eutectic network. Some of the precipitate particles grow through the edge of the β-Sn phase. During aging, the change of β-Sn phases is very slight, and its outline is still clear and complete, as shown in Fig. 2(a).

After isothermal aging, the microstructure of SAC-0.2Co solder became coarsened, too, which is similar to SAC alloy, as shown in Fig. 2(b). The superfine eutectic network has been transformed into block or granular shape particles. Meanwhile, the $CoSn_2$ IMCs became thicker and smoother after aging. The element mapping results by EPMA indicated that some of the particles (mainly Cu_6Sn_5) have been grown near the $CoSn_2$ phases, which was responsible for the morphology change of $CoSn_2$ IMCs, as shown in **Fig. 3**. In fact, most of the Co has been concentrated into the $CoSn_2$ precipitates during the solidification process, so the Co_2Sn phase cannot grow significantly during the subsequent aging process. The microstructural evolution of SAC-0.5Co is similar to the SAC-0.2Co. For the same reason, after aging, the block-like $CoSn_2$ became larger and smoother, as shown in Fig. 2(c).

Extending the aging time from 168h to 504h, caused the growth rate of Cu_6Sn_5 and Ag_3Sn particles to slow down sharply for all three tested alloys, as well as the coarsening process. L. Snugovsky *et al.*[7] pointed out, that for the Sn-Ag-Cu alloys, approximately 40at.% of the copper in the solder is presented in the form of larger particles of Cu_6Sn_5 after the 100h aging treatment at 150°C. This value only increased to about 55at.% after 1000h aging. The reduction of Cu and Ag amounts in the eutectic network is the dominant factor for the decrease in the coarsening process.

3.2 Tensile behaviors

The effects of Co addition on the tensile behavior of SAC-Co solder alloys are shown in **Fig. 4**. It will be seen that the addition of Co, in the as-cast condition, has a small effect on the tensile strengthen, but it clearly reduces the elongation. The higher the amount of Co addition, the lower the elongation.

For all the tested alloys in the present work, the tensile behavior changed notably after the high temperature aging process. Firstly, the ultimate tensile strength (UTS) tended to decrease after aging. With aging, the UTS degraded rapidly within the first 168h, and then it decreased hardly at all when extending the aging time to 504h. This tendency was consistent with the microstructural coarsening process discussed earlier. Secondly, the elongation of the SAC-Co alloys tended to increase with the aging time, however, the SAC baseline maintained a high elongation value irrespective of the aging time.

3.3 Fracture surface analysis

Figures 5(a)-(d) showed the fracture surface of SAC-0.2Co and SAC solders after a tensile test, in the as-cast condition and after high temperature aging respectively. In the as-cast condition, the fracture surface of SAC-0.2Co showed typical brittle fracture, as shown in Fig. 5(a). Thin plate-like $CoSn_2$ precipitates, which showed needle shapes in the two-dimensional metallograph, were detected in the fracture surfaces. In contrast, the fracture surface of the SAC baseline showed typical plastic fracture with many smooth dimples, as illustrated in Fig. 5(b). It indicated that, in the as-cast condition, the existence of the thin sheet-like $CoSn_2$ precipitates was responsible for the decrease of ductility for the Co-containing SAC solders.

After long term isothermal aging, the fracture surface of SAC baseline hardly changed and still showed a ductile fracture pattern, as shown in Fig. 5(d). However, the fracture pattern of SAC-0.2Co changed obviously. It was hard to find plate-like $CoSn_2$ IMCs in the fracture surface, which showed a similar fracture pattern to the SAC baseline solder, as shown in Fig. 5(c). It can be

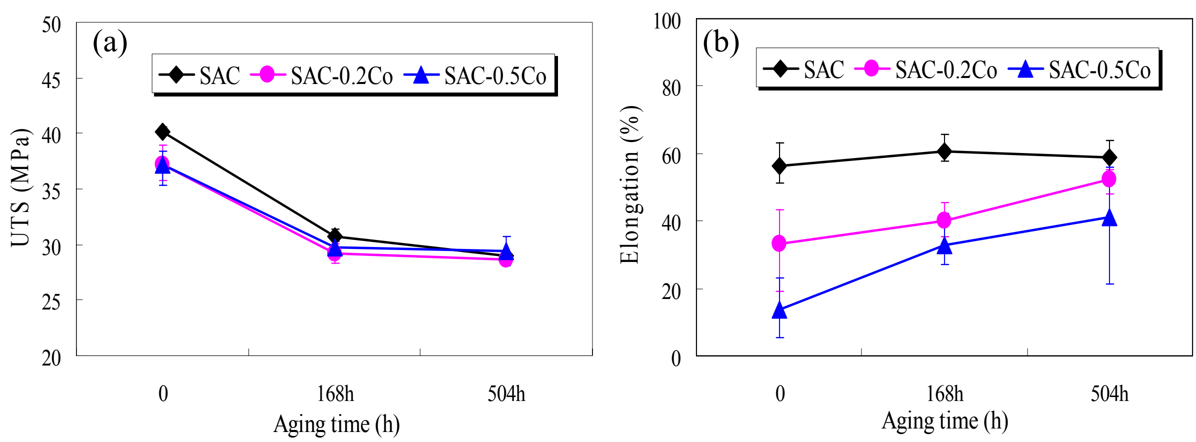

Fig. 4 The tensile behavior of SAC-Co solder alloys and the SAC baseline (a) UTS and (b) Elongation.

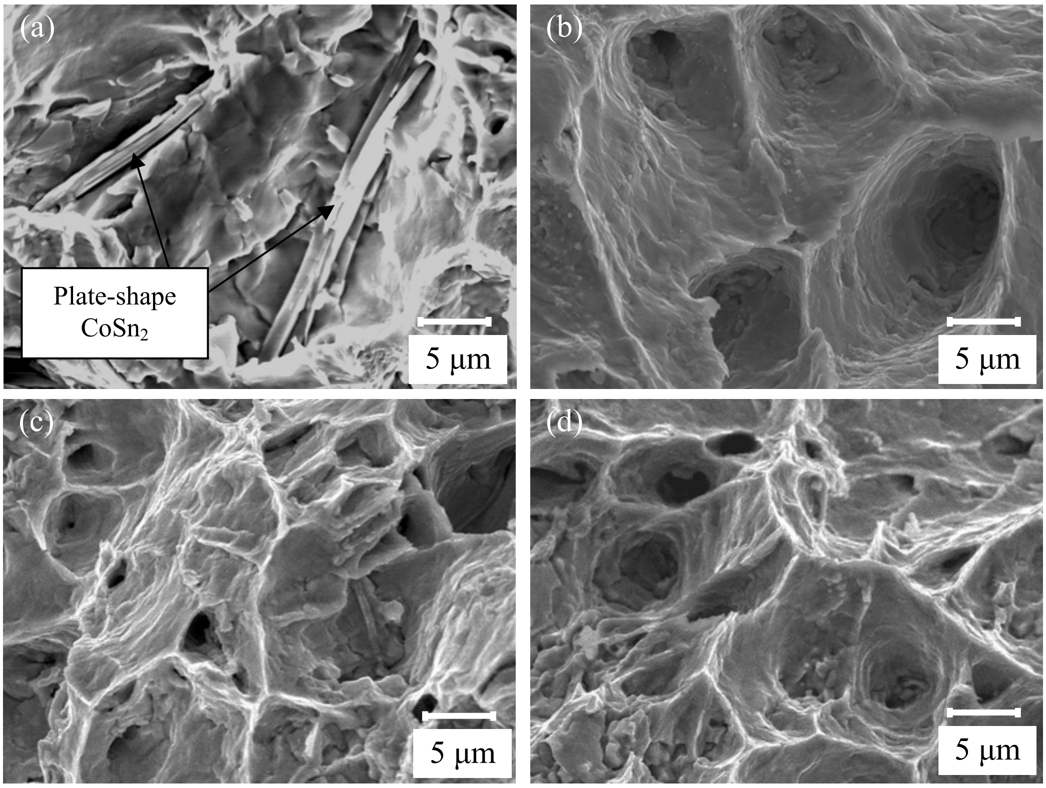

Fig. 5 SEM photographs of the fracture surface after tensile test of the
(a) SAC-0.2Co in the as-cast condition, (b) SAC in the as-cast condition,
(c) SAC-0.2Co aged for 504 h at 150°C, and (d) SAC aged for 504 h at 150°C.

conducted that the high temperature aging process changed the fracture mode of the SAC-Co solders.

4. Conclusions

The effects of the minor element Co on the microstructure and tensile behavior of SAC solder alloys were explored. The results summarized as following.

(1) The addition of Co to SAC solder induced the formation of $CoSn_2$ IMCs in the eutectic network. The amount of Co had a great effect on the morphology of $CoSn_2$ phase. In addition, the Co addition hardly affected the β-Sn phase.

(2) Similar to the SAC baseline, after high temperature aging, the microstructure of Co-containing solders became significantly coarsened. The Cu_6Sn_5 IMCs tended to grow around the $CoSn_2$ IMCs.

(3) In the as-cast condition, the presence of $CoSn_2$ IMCs reduced the ductility significantly. However, it hardly affected the tensile strengthen. After aging, the Co-containing SAC solders showed two trends, one was the decrease in ultimate tensile strength, the other was the increase in ductility. The small addition of Co reduced the ductility of the SAC-Co alloy, however the high temperature aging suppressed this negative effect.

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