Journal of ELECTRONIC MATERIALS, Vol. 40, No. 9, 2011
DOI: 10.1007/s11664-011-1700-3
© 2011 TMS

Reaction of Liquid Sn-Ag-Cu-Ce Solders with Solid Copper

J. CHRIAŠTEL'OVÁ,[1] L. RÍZEKOVÁ TRNKOVÁ,[1] K. POCISKOVÁ DIMOVÁ,[1] and M. OŽVOLD[1,2]

1.—Faculty of Materials Science and Technology, Slovak University of Technology, Paulínska 16, 917 24 Trnava, Slovak Republic. 2.—e-mail: milan.ozvold@stuba.sk

Small amounts of the rare-earth element Ce were added to the Sn-rich lead-free eutectic solders Sn-3.5Ag-0.7Cu, Sn-0.7Cu, and Sn-3.5Ag to improve their properties. The microstructures of the solders without Ce and with different amounts (0.1 wt.%, 0.2 wt.%, and 0.5 wt.%) of Ce were compared. The microstructure of the solders became finer with increasing Ce content. Deviation from this rule was observed for the Sn-Ag-Cu solder with 0.2 wt.% Ce, and for the Sn-0.7Cu eutectic alloy, which showed the finest microstructure without Ce. The melting temperatures of the solders were not affected. The morphology of intermetallic compounds (IMC) formed at the interface between the liquid solders and a Cu substrate at temperatures about 40°C above the melting point of the solder for dipping times from 2 s to 256 s was studied for the basic solder and for solder with 0.5 wt.% Ce addition. The morphology of the Cu_6Sn_5 IMC layer developed at the interface between the solders and the substrate exhibited the typical scallop-type shape without significant difference between solders with and without Ce for the shortest dipping time. Addition of Ce decreased the thickness of the Cu_6Sn_5 IMC layer only at the Cu/Sn-Ag-Cu solder interface for the 2-s dipping. A different morphology of the IMC layer was observed for the 256-s dipping time: The layers were less continuous and exhibited a broken relief. Massive scallops were not observed. For longer dipping times, Cu_3Sn IMC layers located near the Cu substrate were also observed.

Key words: Lead-free solders, Sn-Ag-Cu alloys, rare earth Ce, intermetallics, microstructure

INTRODUCTION

In the recent decade, introduction of certain legislation [e.g., waste from electrical and electronic equipment (WEEE) and the restriction of the use of certain hazardous substances (RoHS)] has driven research into lead-free solders to find a replacement for Sn-Pb solder. Of all the lead-free alloys investigated, Sn-Ag-Cu alloy has been proposed as the most promising substitute for Sn-Pb solders, because of its relatively good soldering performance, excellent creep resistance, and thermal fatigue reliability, as well as its compatibility with current components. However, there are still some shortcomings that need to be overcome, e.g., its somewhat higher melting temperature, hot tearing due to coarse proeutectic Sn dendrites, large Ag_3Sn plates that induce strain localization, and excess growth of interfacial compounds.[1,2]

It has been confirmed that adding a tiny amount of rare-earth (RE) elements may greatly enhance the properties of solder alloys. The wettability and tensile properties of Sn-3.5Ag solder alloy were improved by addition of 0.25% to 0.5% of the RE elements La and Ce,[3] while further addition of RE elements up to 1.0 wt.% reduced this beneficial influence. According to Ref. 2, the optimum Ce content ranges from 0.05 wt.% to 0.1 wt.%. The wettability and tensile strength of Sn-Ag-Cu solder can be remarkably improved by adding Ce at only about 0.03 wt.%[4] (probably the lowest published value of RE content in this regard). Li et al.[5] and Law et al.[6] found that the best RE content was

(Received December 1, 2010; accepted June 7, 2011; published online June 23, 2011)

Table I. Chemical composition of the solders investigated

Sn-3.5Ag	Sn-0.7Cu	Sn-3.5Ag-0.7Cu
96.48Sn-3.42Ag-0.1Ce	99.22Sn-0.68Cu-0.1Ce	95.83Sn-3.39Ag-0.68Cu-0.1Ce
96.47Sn-3.34-Ag-0.2Ce	99.13Sn-0.67Cu-0.2Ce	95.86Sn-3.28Ag-0.66Cu-0.2Ce
96.41-Sn-3.09Ag-0.5Ce	98.91Sn-0.59Cu-0.5Ce	95.95Sn-2.96Ag-0.59Cu-0.5Ce

0.1 wt.%. In particular, addition of 0.1 wt.% RE to Sn-3.5Ag-0.7Cu solder improved its wetting behavior, and the intermetallic compounds (IMC) layer formed between the solder and a Cu substrate was inhibited during thermal aging. Study of wettability[7] showed that addition of 0.1% RE to Sn-3.5Ag-0.7Cu can significantly improve the wetting angle. RE addition of up to 0.5 wt.% to Sn-Ag alloy resulted in a decrease in the values of the contact angle; a minimum contact angle was observed with 0.5 wt.%. The wetting angle of Sn-0.7Cu solder is also improved with addition of 0.5% RE elements. Dudek et al.[8] found that addition of La (up to 0.5 wt.%) to Sn-Ag-Cu solder alloys refines the microstructure by decreasing the length and spacing of the Sn dendrites and decreases the thickness of the Cu_6Sn_5 intermetallic layer at the Cu/solder interface. According to Zhou et al.,[9] there are considerable improvements in mechanical properties with 0.05% and 0.1% addition, but addition of 0.4% La is disadvantageous. From this brief review, one can see that no agreed value of RE concentration has been determined. Dudek et al.[8] pointed out that discrepancies in microstructures and mechanical properties have also been reported in the literature. The variability in microstructures can likely be attributed to the wide variety of processing parameters and procedures applied. Thorough study of the properties of RE-containing solder alloys is therefore needed.

In this paper, we present the development of Sn-Ag, Sn-Cu, and Sn-Ag-Cu solder alloys with addition of Ce and study of the effect of Ce on the melting behavior, microstructure, and IMC layer formation at the interface of the liquid solders with a Cu substrate. To eliminate the possible effect of variation in the processing parameters, the comparative study was performed under constant experimental conditions.

EXPERIMENTAL PROCEDURES

The solders used for the experiments were prepared in two steps from the metals Sn, Ag, and Cu with purity of 99.99%, and Ce of 99.9% purity. In the first step, Sn-Ag-Cu, Sn-Cu, and Sn-Ag alloys with eutectic composition were prepared. Precisely weighed starting materials were melted and mixed in a furnace. In the second step, Ce with higher concentration of 2 wt.% to 5 wt.% was melted into pure tin (melted in a vacuum at 500°C for 5 h[10]) and added to the solder alloys. The final compositions of the studied solders are listed in Table I. Dissolution of Ce in the precursors was verified using energy-dispersive x-ray analysis (EDX).[11] The melting behavior, being one of the most important characteristics of solder, was determined by differential scanning calorimetry (DSC). The microstructure of the solders and interfaces was observed by optical microscopy and scanning electron microscopy (SEM). EDX analysis was used to determine the Sn/Ag/Cu elemental composition of selected areas.

The formation of IMC layers on the Cu substrate was analyzed using solders without and with 0.5 wt.% Ce. Ground and polished Cu plates with dimensions of $20\ mm \times 10\ mm \times 1\ mm$ were ultrasonically cleaned, etched in 10 vol.% HCl solution to remove the oxide film, and rinsed with ethanol. Prior to soldering, the Cu plates were preheated on a hot plate, and a small amount of flux (solution of resin in ethanol) was applied. We hope that the preheating also aids elimination of possible residual flux. After flux application, the specimens were dipped into liquid solder held at temperature of 40°C above the solder melting point. Dipping times of 2 s, 4 s, 16 s, and 256 s were used. Samples for microstructural analysis were prepared by a usual metallographic procedure, being polished and etched with 5% HNO_3 + 2% HCl + methanol solution for etching time of 2 s to 5 s.

RESULTS AND DISCUSSION

DSC measurements were conducted in an inert gas atmosphere. The calorimeter (PerkinElmer) was calibrated prior to testing using a standard high-purity tin sample. Samples (20 mg to 40 mg) of the solders were placed into an aluminum pan. An empty aluminium pan was used as a reference. The heating/cooling rate was 10°C min^{-1} or 2°C min^{-1}. The melting points of alloys were evaluated from DSC heating curves for the second of three runs. The melting points of the alloys with addition of 0.5 wt.% Ce were almost the same as those for the samples without Ce, being 227°C and 227.2°C for Sn-0.7Cu and Sn-0.7Cu-0.5Ce, respectively, and 221.3°C for Sn-3.5Ag and 217°C for Sn-3.5Ag-0.7Cu with and without Ce.

Figure 1 shows the microstructures of the solders with different Ce contents. The first column shows the microstructures of a near-eutectic Sn-Ag-Cu solder. As expected, the microstructure consists of Sn dendrites, eutectic, and IMC. The dendrites are formed from β-Sn solid solution containing a small

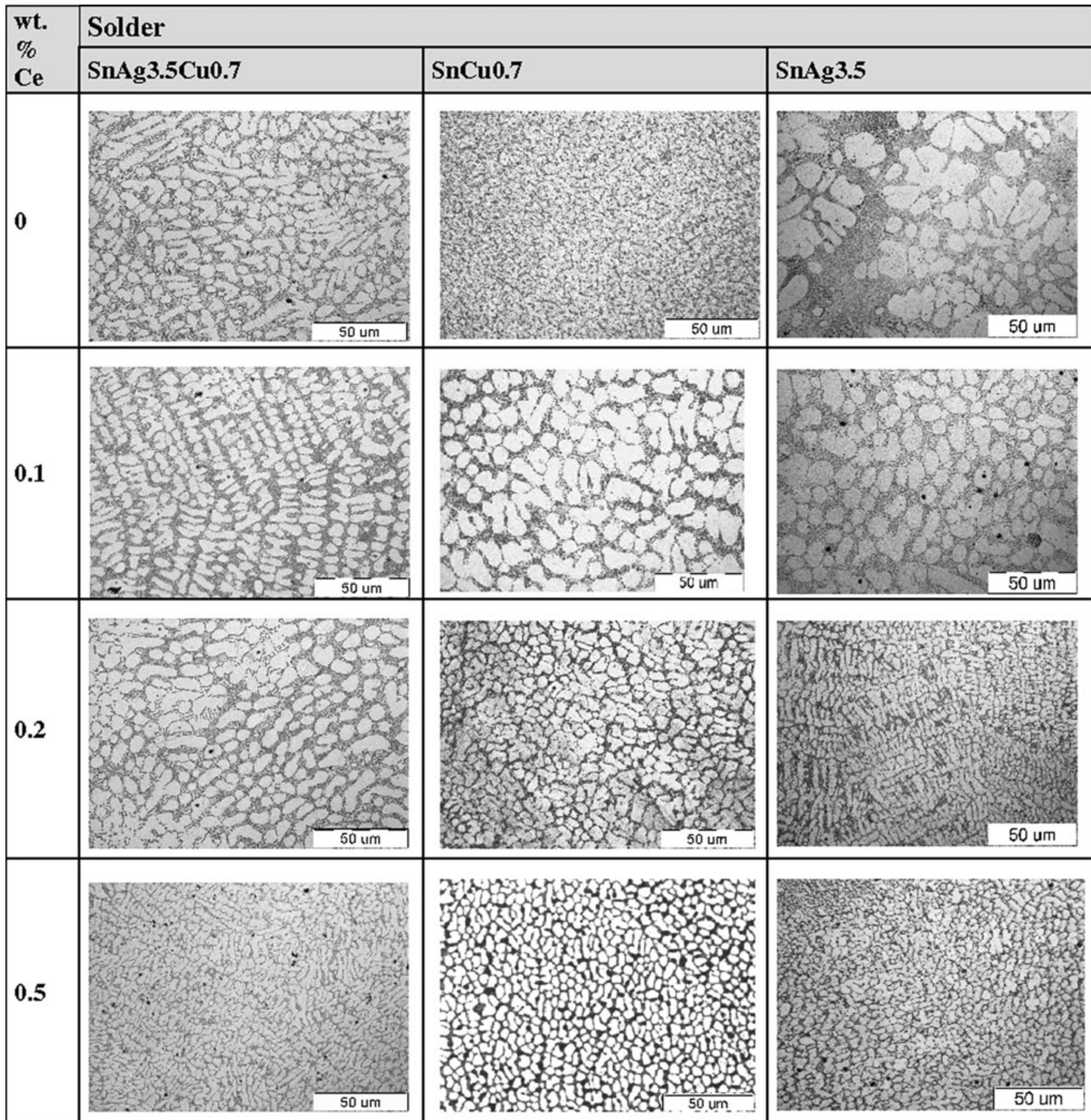

Fig. 1. Microstructures of solders with different Ce contents.

amount of Ag and Cu. The microstructures of the Sn-Ag-Cu eutectic solders with addition of 0.1 wt.% or 0.2 wt.% Ce are similar to those of the solder without Ce. However, evident differences are observed with addition of 0.5 wt.% Ce; the microstructure is finer and the β-Sn grains are smaller.

Microstructures of the Sn-Cu-based solders are shown in the second column of Fig. 1. The microstructure of the Sn-0.7Cu eutectic solder is markedly changed with the addition of only 0.1 wt.% Ce, showing coarser grains. However, thereafter, the microstructure of the Sn-Cu-Ce solders became finer with increasing content of Ce, and its distribution became more homogeneous. This effect was most apparent for the Sn-Ag-based solders. The sizes of the β-Sn grains were reduced with 0.1 wt.% Ce addition, and the regions with segregated Ag_3Sn intermetallics became narrower.

The solder reacts with the Cu substrate during soldering (dipping the Cu substrate into the molten

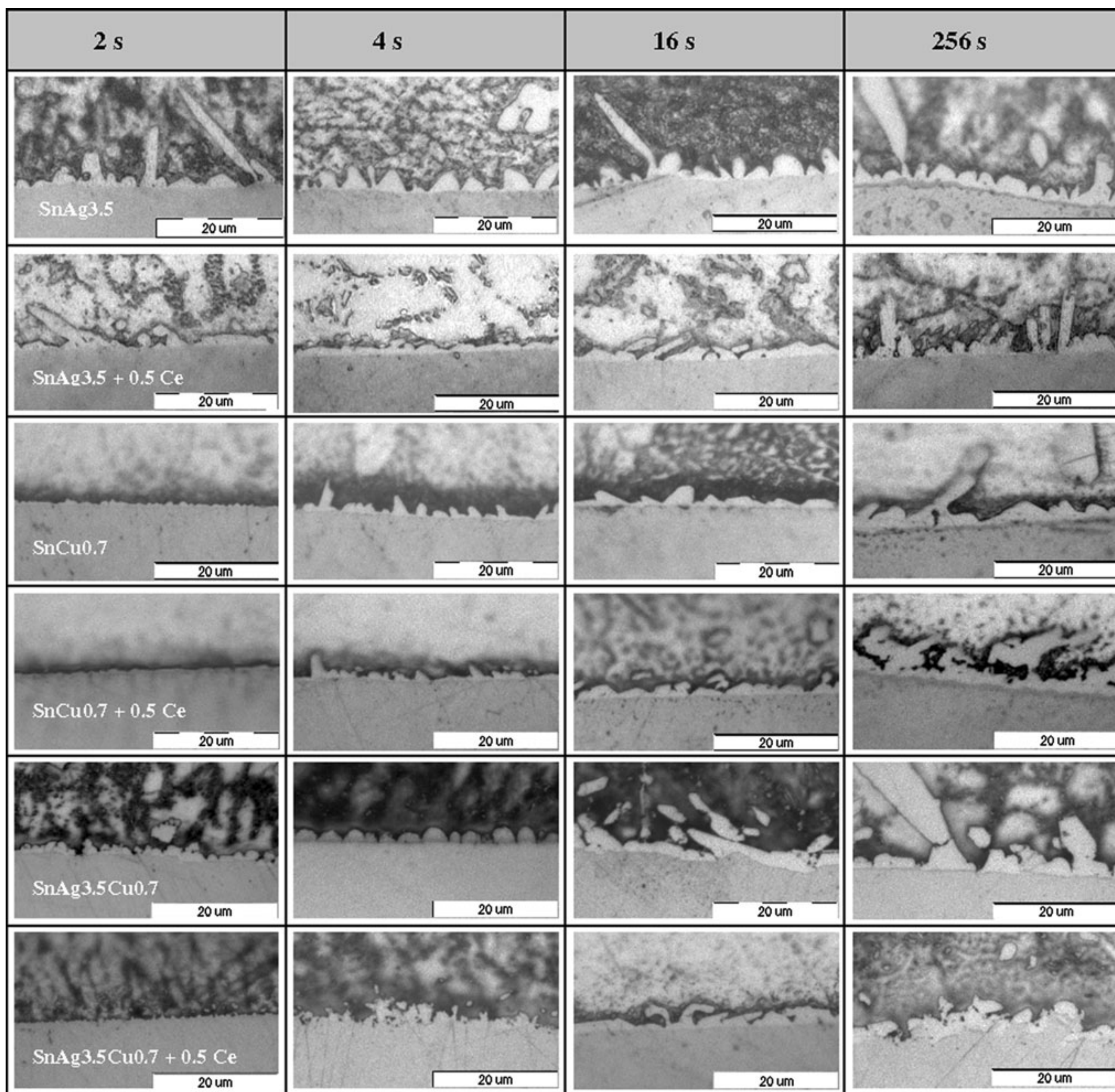

Fig. 2. Microstructure of the solder/Cu substrate interface for different soldering times.

solder) and forms an IMC layer at the joint interface. This IMC layer is required to achieve a good metallurgical joint. However, excessive growth of the IMC layer may have a negative impact on the soldered joint. The samples of the soldered Cu plates were cross-sectioned to observe and compare the pattern of the IMC layers. Microstructures of the interfaces are shown in Fig. 2. The morphology of the Cu_6Sn_5 IMC layer that developed at the interface between the solder and the substrate reveals a typical scallop-type shape. The IMC layer thickness increased with increasing soldering time. The scallops join together and grow with increasing time, and small parts of the IMC are separated from the Cu_6Sn_5 layer.

In the case of the Sn-Ag-based solder, we can observe a continuous IMC layer already after 2 s of soldering, with thickness of about 3 μm and scallops of Cu_6Sn_5 phase with size up to 15 μm. This was not observed with the Cu-containing solders, for which the IMC layer after 2 s of soldering was thinner. A uniform Cu_3Sn layer was also observed for samples prepared with Sn-0.7Cu, Sn-0.7Cu-0.5Ce, and Sn-3.5Ag solders for time of 256 s.

The Sn-3.5Ag-0.7Cu and Sn-3.5Ag-0.7Cu-0.5Ce samples for time of 256 s revealed differences in the morphology of the IMC layer created with the Ce-containing solder. The layer is not continuous and shows a cracked relief. This effect was already

observed for soldering time of 4 s. Long needles of Cu_6Sn_5 intermetallics were not observed. A similar effect of Ce can be seen in the images of the interface between the Cu substrate and the Sn-0.7Cu-0.5Ce solder.

The thickness of the Cu_6Sn_5 IMC layer at the Cu/Sn-3.5Ag-0.7Cu solder interface is thinner after the addition of Ce for 2-s soldering (Fig. 2). As quoted in the "Introduction," many authors in the literature have emphasized this inhibition of the IMC layer, although no quantification of it has been published so far. We believe that this effect is neither striking nor unambiguous. Owing to the short time, the result can be seriously influenced by the processing procedure. This inhibition was not observed, however, after the 4-s dipping. During soldering, the alloy is in a liquid state, so that the small amount of RE, we believe, may barely influence the growth of the thin IMC layer. Dudek et al.[8] explain the lower intermetallic thickness of Cu_6Sn_5 for Sn-Ag-Cu alloy containing La as being caused by heterogeneous nucleation of Sn due to the presence of $LaSn_3$, so that Sn dendrites solidify more quickly. Thus, the solder remains in the liquid state for a shorter time, meaning less time for reaction with the Cu substrate and thus lower intermetallic thickness. Among the solders investigated in this work, the greatest changes in undercooling after adding Ce were revealed for the Sn-Cu alloy. As shown by our DSC measurements (Fig. 3), the change in the undercooling temperature is approximately 20°C, but no evident effect of IMC thinning was observed. Solder solidification probably begins at the solder/IMC interface and is not controlled by bulk solder solidification. The refinement of the solder microstructure will influence the growth of thicker layers and long scallops, compared with the dimension of the grain size of the refined solder. This is well observed for solders containing Ce (Fig. 2) for the time of 256 s; the layers are discontinuous and long scallops are cracked. A different situation will occur during aging when the solder is in a solid state.

CONCLUSIONS

Small amounts of the RE element Ce were added to the eutectic alloys Sn-3.5Ag-0.7Cu, Sn-0.7Cu, and Sn-3.5Ag with the goal of improving their soldering properties. The microstructures of the alloys without and with different amounts (0.1 wt.%, 0.2 wt.%, and 0.5 wt.%) of Ce were compared. The Sn-0.7Cu alloy with eutectic composition showed the finest microstructure without Ce addition. The microstructure of the alloys became finer with increasing Ce content from 0.1 wt.% to 0.5 wt.%. Deviation from this rule was observed for the Sn-Ag-Cu solder with 0.2 wt.% Ce. DSC measurements showed no effect of 0.5 wt.% Ce addition on the melting point of the alloys.

The morphology of IMC formed at the interface between the liquid solder, held at temperature 40°C above its melting point, and a copper substrate for dipping times from 2 s to 256 s was studied and compared for solder with 0.5 wt.% Ce addition and without Ce. A Cu_6Sn_5 intermetallic layer was

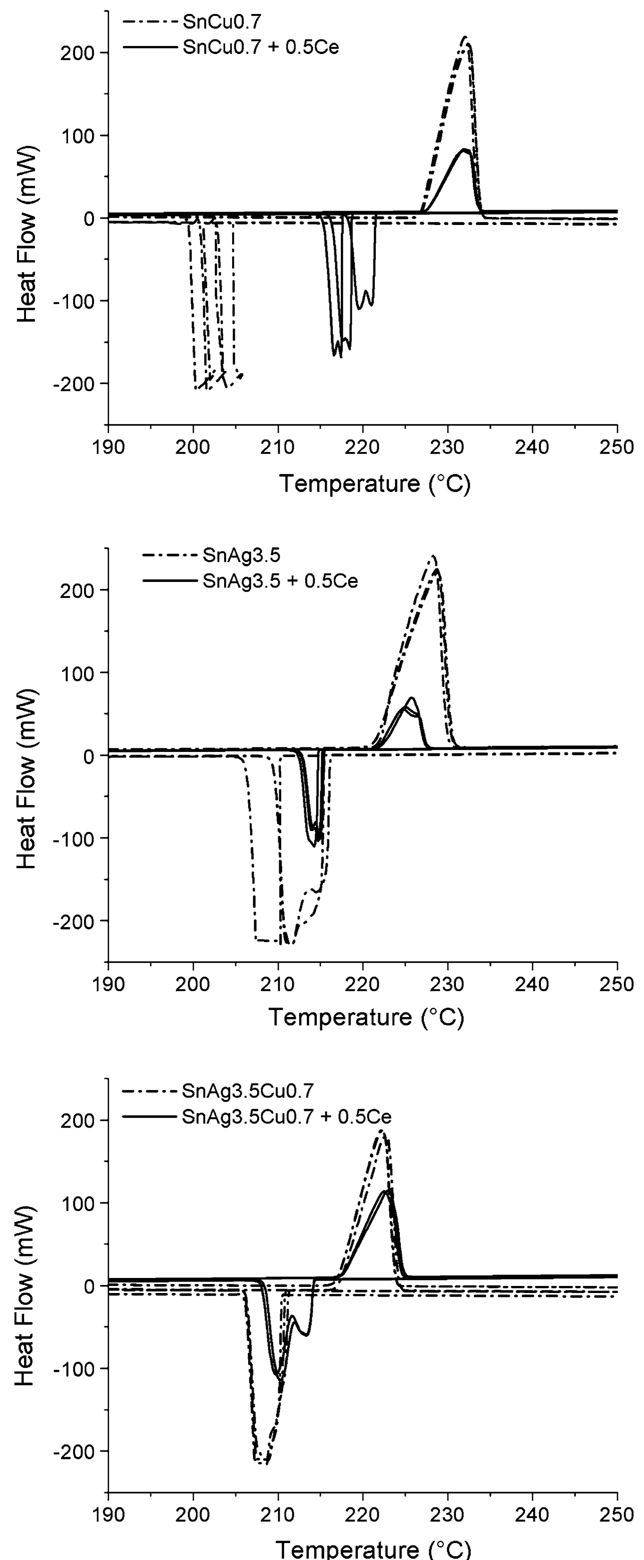

Fig. 3. DSC curves of the Sn-Ag-Cu-Ce solders.

formed at the interface between the solders and the substrate, revealing typical scallop-type morphology. The Cu_6Sn_5 IMC layer at the Cu/Sn-3.5Ag-0.7Cu solder interface was thinner after addition of Ce to the solder for 2-s soldering. However, this effect was no longer observed after 4-s dipping. We did not find any striking or unambiguous evidence that the growth of the Cu_6Sn_5 IMC layer was inhibited by addition of Ce for the short times of interest from the soldering point of view.

Different morphology of the IMC layer was observed for the solders containing 0.5 wt.% Ce for time of 256 s. The layers were discontinuous and showed cracked relief. Massive scallops were not observed. For longer immersion times, Cu_3Sn IMC layers located near the Cu substrate were also observed. We believe that a tiny addition of RE may scarcely influence the growth of the thin IMC layers with dimensions smaller then the grain sizes of the refined solders during soldering, when the alloy is in a liquid state. For longer times, when the thickness of the IMC layers is greater then the crystalline sizes, the largest scallops are destroyed during solidification of the solder.

ACKNOWLEDGEMENTS

This contribution was prepared with the support of GA VEGA Ministry of Education of the Slovak Republic and the Slovak Academy of Science Projects No. 1/1000/09 and No. 1/0842/09.

REFERENCES

1. C.M.L. Wu, D.Q. Yu, C.M.T. Law, and L. Wang, *Mater. Sci. Eng. R* 44, 1 (2004).
2. X. Zhao, M. Zhao, X. Cui, T. Xu, and M. Tong, *Trans. Nonferr. Met. Soc. China* 17, 805 (2007).
3. L. Wang, D.Q. Yu, J. Zhao, and M.L. Huang, *Mater. Lett.* 56, 1039 (2002).
4. L. Zhang, S. Xue, L. Gao, Z. Sheng, G. Zeng, Y. Chen, and S. Yu, *J. Mater. Sci. Mater. Electron.* 21, 635 (2010).
5. B. Li, Y. Shi, Y. Lei, F. Guo, Z. Xia, and B. Zong, *J. Electron. Mater.* 34, 217 (2005).
6. C.M.T. Law, C.M.L. Wu, D.Q. Yu, L. Wang, and J.K.L. Lai, *J. Electron. Mater.* 35, 89 (2006).
7. L. Zhang, S.B. Xue, L.L. Gao, G. Zeng, Z. Sheng, Y. Chen, and S.L. Yu, *J. Mater. Sci. Mater. Electron.* 20, 685 (2009).
8. M.A. Dudek, R.S. Sidhu, N. Chawla, and M. Renavikar, *J. Electron. Mater.* 35, 2088 (2006).
9. Y.Ch. Zhou, Q.L. Pan, Y.B. He, W.J. Liang, W.B. Li, Y.Ch. Li, and C.G. Lu, *Trans. Nonferr. Met. Soc. China* 17, 1043 (2007).
10. D.Q. Yu, J. Zhao, and L. Wang, *J. Alloys. Compd.* 376, 170 (2004).
11. J. Chriašteľová, K. Pocisková Dimová, L. Rízeková Trnková, J. Lokaj, M. Turňa, and M. Ožvold, *METAL 2010: 19th International Conference on Metallurgy and Materials*, May 18th–20th 2010 Roznov pod Radhostem, Czech Republic. ISBN 978-80-87294-15-4.