Effects of Cu Feedstock on Intermetallic Compound Formation in Cold Sprayed Cu-Sn Coatings

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Abstract

Cu-Sn composite coatings were deposited using various Cu feedstock powders with different sizes and shapes, and the formation of intermetallic compounds (IMCs) in the coatings was investigated. IMC formation by post-annealing of composite coatings could be affected. In addition, when Cu-Sn composite particles were employed, not only the Cu-Sn composites but also Cu-Sn IMCs (Cu6Sn5 and Cu3Sn) were observed at the interfaces between Cu and Sn particles in the as-sprayed state. In the case of the annealed Cu-Sn coatings, the Cu6Sn5 formed in the as-coated coatings was transformed into the Cu3Sn phase, and the embedded Sn particles were fully changed into the Cu3Sn phase. However, the intermetallic compound formation of Cu3Sn was different, depending on the shape and size of the Cu feedstock. Therefore, the deposition of Cu-Sn composite coatings using different Cu particles could have an influence on the formation of IMCs.

Keywords

Cold Spray; Cu-Sn; Composites; Intermetallic; Coatings

Introduction

In the thermal spray process, metallic and ceramic powders are melted by jets emitting hot gas with very high temperatures, after which coatings are formed through the solidification of the melted powders on the substrates. In the cold spray process, however, metallic powders are injected into a de Laval-type nozzle where they are accelerated to high velocities by a supersonic gas stream. When the metallic powders are impinged onto the substrate, their kinetic energy enables the production of coatings with severe deformation. Because the particles are deformed by collision with the substrate, ductile metallic powders must be chosen for the feedstock materials. Also, ceramic powders are unsuitable for feedstock materials in the cold spray process owing to the brittleness. However, in the case of metal (Al)/metal composites coated by the cold spray process, it is very easy to obtain high quality composite coatings because of the deformation behavior. In addition, intermetallic compounds (IMCs) in the coatings are easily obtained by post-annealing, as reported by many researchers. Wang et al. reported the characteristics and influence of heat treatment in Al/Fe composite coatings. Novoselova et al. reported the morphology, porosity, and hardness of Al/Ti composite coatings. Lee et al. investigated the formation of IMCs by post-annealing on cold sprayed Al/Ni and Al/Ti composites. In another case, intermetallic formation was realized by the interaction between the cold sprayed coatings and the substrates. H. Lee et al. reported the Al/Ni interface interaction for intermetallic compound formation produced by cold spraying and post-annealing. H. Bu et al. and K. Spencer et al. investigated the post treatments of Al coating/Mg substrate couples by cold spraying. In the case of Cu/metal composite coatings, few reports were available concerning Cu composite coatings by means of the cold spray process and their IMC formation by means of post-annealing. In this study, Cu-Sn composite coatings were deposited by cold spray on Al substrates, using various types of Cu powders, and annealing studies were carried out to transform the composite coatings into intermetallic compounds. Further, the properties of as-coated and annealed coatings were investigated. The results of these Cu-Sn coatings in the course of the cold spray will be applied in lead-free solders for flip chip connections and the anode electrodes for secondary batteries (Li ion batteries).

Experimental

A home-installed cold spray system was used in this work. The particles were accelerated through a converging–diverging de Laval-type nozzle with a throat diameter of 1 mm (inlet diameter, 7 mm). Pure air, instead of the usual helium and nitrogen, has been
used as both accelerating gas and powder feeding gas. The pressure before entering the gas heater was fixed at 2 MPa and the temperature of the gas passing through the nozzle ranged from 200 to 450°C which was measured in the nozzle beside the feedstock feed entrance. The distance between the nozzle and the substrate was 20 mm. The substrate and nozzle were stationary during deposition, and therefore, the deposit was formed in a mountain-like shape. The particle sizes and shapes of as-purchased Sn and Cu were confirmed by scanning electron microscopy (SEM). The Cu-Sn composites were coated onto Al substrates without sand-blasting. The deposition efficiency of the Sn feedstock was higher than that of the Cu feedstock. To produce Cu matrix coatings, a Cu-Sn composite must contain an overwhelming point of Sn even though the gas temperature was 300°C. The coated samples were annealed at 300°C under N2 atmosphere for 6 hours. The annealing heating rate was 5°C/min and followed by furnace cooling. The structures of the Cu-Sn composite and annealed coatings were analyzed by X-ray powder diffractometry (XRD, Rigaku), and the microstructures and compositions of the coatings were measured by field emission-scanning electron microscopy (FESEM) with energy dispersive spectroscopy (EDS, Philips, XL 30 ESEM-FEG) and optical microscopy (OM).

Results and Discussion

Fig. 1 shows SEM images of the as-purchased Cu and Sn powders used in these experiments. The smaller Cu powders were under 10 μm with spherical shape, while the larger Cu powders were under 44 μm with dendritic shape (Figs. 1(a) and 1(b)). The micro-sized Sn powders were sieved to ≤325 mesh (≤44 μm) with irregular shape (Fig. 1(c)). Fig. 2 shows XRD patterns of cold sprayed Cu-Sn composite coatings using Cu powders with different shapes and sizes. Peaks corresponding to a newly formed phase were present, suggesting significant chemical interactions among Cu/Sn particles during coating, regardless of the Cu particles’ properties. In particular, two types of Cu-Sn intermetallic compounds, Cu3Sn and Cu6Sn5, without the oxides (SnO, CuO), were observed. In addition, the Cu and Sn feedstock seemed to be neither molten nor semi-molten (Sn melting point: 232°C) because their flight/coating time was extremely short, so the temperature of the coatings did not reach the melting point of Sn even though the gas temperature was 450°C. Empirically, when the coatings were exposed to hot gas stream of 450°C for 10 seconds, the Sn feedstock were melted on the substrate. If the Sn was melted, the coatings would be destroyed (similar to the morphology of thermal sprayed coatings). While coating was made post-annealing, the Cu6Sn5 phase disappeared and only Cu3Sn peaks were observed after complete reaction of the embedded Sn. The Gibbs free energies of the Cu3Sn and Cu6Sn5 phases were negative values, and the Gibb’s free energy of the Cu3Sn phase was lower than that of the Cu6Sn5 phase. Fig. 3 shows the OM images of the as-coated Cu-Sn composite coatings by cold spray under different conditions. Similar to the cases of other composite coatings by cold spray, such as Al-metal and Al-ceramic coatings, the “embedded particles phenomena” of Sn particles were observed, accompanied by severe plastic deformation and possible inter-particle bonding between Cu and Sn in the Cu matrix. In spite of the type of the Cu powder and the gas temperature conditions, significant differences in morphology were not observed. Only the plastically deformed and embedded Sn particles (without melting) were found in the Cu matrix despite an increased gas temperature of 450°C. In addition, it is likely that the embedded soft Sn particles which had high strain energy could interact with the Cu matrix. However, the annealed Cu-Sn composite coatings seemed to differ with respect to Cu powder shape (Fig. 4). It was found that, in the as-coated state, the embedded Sn particles, including the intermetallic compounds (Cu3Sn/Cu6Sn5) reacted with the Cu matrix and grown in the Cu-Sn coatings by using the smaller Cu powders (10 μm). Therefore, the annealed intermetallic compounds (Cu3Sn) were coarser than the as-coated Sn/IMC particles (Sn/Cu3Sn/Cu6Sn5). Despite the changes in the gas temperature, these results seemed to be the same in all of the annealed Cu-Sn coatings obtained using the smaller Cu powders. It was assumed that the diffusion path of the embedded Sn particles could be provided by the defects resulting from the strain of the smaller Cu (10 μm)-Sn coating systems. In contrast, in the larger Cu (44 μm)-Sn coating systems, the coarsening effect of the embedded Sn particles by post-annealing was less significant than that of the embedded Sn particles in the smaller Cu (10 μm)-Sn coatings. From these results, it was considered that the diffusion route of Sn particles into the Cu matrix or the interaction between Sn and the Cu matrix was very different according to the type of Cu powder.
In order to clearly confirm the compositions and phases of the as-coated and annealed Cu-Sn coatings, coatings prepared under different conditions were measured by the backscattered electron imaging and EDS. Fig. 5 and Fig. 6 show the EDS and backscattered images of the as-coated Cu-Sn coatings, in which the intermetallic compounds were found at the interfaces between Cu and Sn, regardless of gas temperature. Most interestingly, the IMCs of Cu₆Sn₅/Cu₃Sn (confirmed by XRD (Fig. 2)) were formed by the diffusion of Cu particles that were impacted into the Sn particles. Compared to the XRD data, it was also confirmed that the mixed IMCs of Cu-Sn (Cu₆Sn₅/Cu₃Sn) were detected by EDS at the interfaces, and residues of Sn were also observed. Fig. 7 and Fig. 8 show the EDS and backscattered images of the annealed Cu-Sn coatings. The results of the images and EDS were in agreement with the OM and XRD data. To prove that the smaller Cu powders (10 μm) were more severely deformed than the larger Cu powders (44 μm) by the high velocity impact, pure Cu coatings were deposited using both the finer and the coarser powders under the same deposition conditions as the Cu-Sn composite coatings (Fig. 9). As mentioned above, more severe deformation occurred with the smaller Cu particles than that with the larger Cu particles during spraying. As a result of these phenomena, the pores in the Cu coating prepared from the larger Cu powders were easily identified by the lower extent of deformation. Therefore, it was concluded that the more severe deformation as a result of the high velocity of the Cu particles could supply the energy for the coarsening of the IMC (the faster diffusion).

Conclusions

It has been shown that the as-coated and annealed Cu-Sn composites were prepared under different coating conditions (such as the gas temperature and type of Cu powder) on Al substrates by cold spray. In our study of the as-coated Cu-Sn composites, regardless of the type of Cu particles, both raw materials displayed desirable mechanical energy capacities during the high-velocity impact collision coating and could accumulate enough potential energy to overcome the activation barrier of the course of compounding. Thus, from these results, intermetallic compounds of Cu-Sn in the as-coated state could be obtained at the interfaces between Cu and Sn by high velocity impact. In addition, a greater coarsening of the embedded Sn particles by post-annealing was found for the smaller Cu (10 μm)-Sn composite coatings, which may be due to the higher energy of the smaller Cu particles having the capability to overcome the compounding activation barrier by high velocity impact.

REFERENCES


Wang, HongTao, Li, ChangJiu, Yang, Guanjun, and Li, ChengXing. “Cold Spraying of Fe/Al Powder Mixture: Coating Characteristics and Influence of Heat Treatment


FIG. 1 SEM IMAGES OF THE AS-PURCHASED CU AND SN POWDERS USED IN THE EXPERIMENT:
Cu (10 μm), (b) Cu (44 μm), AND (c) Sn POWDERS (44 μm).

FIG. 2 XRD PATTERNS OF CU-SN COMPOSITE COATINGS:
(a) AS-COATED Cu (10 μm)-Sn, (b) AS-COATED Cu (44 μm)-Sn, (c) ANNEALED Cu (10 μm)-Sn, AND (d) ANNEALED Cu (44 μm)-Sn.
FIG. 3 POLISHED CROSS-SECTION IMAGES (OM) OF AS-COATED CU-SN COMPOSITE COATINGS WITH RESPECT TO TYPE OF CU POWDER AND GAS TEMPERATURE CONDITIONS:
(a) Cu (10 μm)-Sn, 200°C, (b) Cu (10 μm)-Sn, 350°C, (c) Cu (10 μm)-Sn, 450°C, (d) Cu (44 μm)-Sn, 200°C, (e) Cu (44 μm)-Sn, 350°C, AND (f) Cu (44 μm)-Sn, 450°C.

FIG. 4 POLISHED CROSS-SECTION IMAGES (OM) OF ANNEALED CU-SN COMPOSITE COATINGS WITH RESPECT TO TYPE OF CU POWDER AND GAS TEMPERATURE CONDITIONS:
(a) Cu (10 μm)-Sn, 200°C, (b) Cu (10 μm)-Sn, 350°C, (c) Cu (10 μm)-Sn, 450°C, (d) Cu (44 μm)-Sn, 200°C, (e) Cu (44 μm)-Sn, 350°C, AND (f) Cu (44 μm)-Sn, 450°C.
FIG. 5 THE BACKSCATTERED ELECTRON IMAGES OF AS-COATED Cu (10 μM)-Sn COMPOSITE COATINGS USING FESEM WITH EDS:
AT A GAS TEMPERATURE OF (a) 200ºC, (b) 300ºC, OR (c) 450ºC.

FIG. 6 THE BACKSCATTERED ELECTRON IMAGES OF AS-COATED Cu (44 μM)-Sn COMPOSITE COATINGS USING FESEM WITH EDS:
AT A GAS TEMPERATURE OF (a) 200ºC, (b) 300ºC, (c) 450ºC.

FIG. 7 THE BACKSCATTERED ELECTRON IMAGES OF ANNEALED Cu (10 μM)-Sn COMPOSITE COATINGS USING FESEM WITH EDS:
AT A GAS TEMPERATURE OF (a) 200ºC, (b) 300ºC, OR (c) 450ºC.
FIG. 8 THE BACKSCATTERED ELECTRON IMAGES OF ANNEALED CU (44 μM)-SN COMPOSITE COATINGS USING FESEM WITH EDS: AT A GAS TEMPERATURE OF (a) 200ºC, (b) 300ºC, OR (c) 450ºC.

FIG. 9 CROSS-SECTION IMAGES (SEM) OF PURE CU COATINGS USING DIFFERENT CU POWDERS: (a) 10 μm, (b) 44 μm.