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Cold spray of mixed metal powders on carbon fibre reinforced polymers

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Abstract: Metallization of polymers and polymer composites has attracted interest recently. Cold spray is an emerging coating method, but direct cold spray of metals on carbon fibre reinforced polymer (CFRP) is difficult. Previous results show that tin coatings can be cold sprayed on CFRP, but the deposition efficiency is relatively low. In this work, copper and zinc powders were mixed with tin to investigate the effect of mixing on deposition efficiency of the coating. The mixed metal powders were cold sprayed on CFRP with a low-pressure system at various conditions. Results show that the addition of copper and zinc led to much higher deposition efficiencies compared to the pure tin coating. Based on the results, the deposition mechanism of the mixed metal powders on CFRP is discussed, the effect of mixing powders on deposition efficiency is analyzed and several mechanisms are proposed accordingly.

3610 University St, Rm 2400

Montreal H3A 0C5, Canada

June 25, 2017

Dear Editor,

We would like to submit our manuscript entitled "Cold Spray of Mixed Metal Powders on Carbon Fibre Reinforced Polymers" for consideration by Surface and Coating Technology.

This manuscript describes original work and is not under consideration by any other journal. All authors approved the manuscript and this submission.

In this manuscript, we studied cold spray of various mixed metal powders onto CFRP and the results show that the addition of a second component into tin powder may largely increase the deposition efficiency. This manuscript is a good supplement to our previous work of cold spray of single-component powders onto CFRP (<u>https://doi.org/10.1016/j.surfcoat.2017.01.083</u>). The results in this manuscript are likely to be of great interest to the researchers and engineers in the area of cold spray as well as metallization of CFRP.

Please address all correspondence concerning this manuscript to me at <u>hanqing.che@mail.mcgill.ca</u>.

Thank you!

Sincerely,

Hanqing Che

List of changes and replies to the reviewer's comments

Reviewer #1:

1. It was found in this work that a number of factors may affect the deposition behavior of mixed powders, e.g. the density, hardness, morphology, etc., as discussed in Section 4.5. However, it is uncertain, at the current stage, that which factor may play the most important role. In fact, it is indeed possible that different factors may have different importance in different mixed binary systems. This article attempted to point out those factors that may play a role, while we agree that future work is indeed needed to determine the importance of those factors in different mixed systems.

2. As suggested by the reviewer, the experimental method and results of conductivity measurement of the coatings were added into Sections 2 and 3 (new sub-sections 2.3 and 3.4, and new Figs. 7 and 8 added), highlighted in light blue. The effect of post-spray annealing on conductivity was also assessed. These added contents are also enclosed at the end of this letter.

On the other hand, since the current work focused on DE, the as-sprayed coating thicknesses vary significantly. For adhesion test, it has been proved that coating thickness affects the adhesion strength, so it is necessary to spray coatings with similar thickness so that reasonable comparison can be made with regard to the bonding strength. Nevertheless, we agree that the effect of mixing powders on adhesion strength is important, so this has been added into Section 5 as a comment on future work: "Last but not least, it is needed to examine the effect of mixing powders on the coating/substrate adhesion strength".

3. The following has been added to the last paragraph in Section 1: "The deposition efficiency was measured at each condition and the electrical conductivity of the composite coatings was evaluated."

4. The previous Figs. 7 and 8 are now numbered Figs. 9, and 10, respectively.

Added subsections and figures:

2.3. Electrical conductivity measurements

The electrical conductivity measurements were performed at École Polytechnique de Montréal by using the four-point resistivity/conductivity measurement method [25]. Before the measurements, the as-sprayed top surfaces were slightly ground with 1200# grit sandpaper to remove the loose particles and obtain flat surfaces. For each sample, the measurements were taken at three different locations, and the average was taken. The pure tin coating cold sprayed at 300°C and 60 psi in the previous work [12] was also measured for comparison.

To examine the effect of post-spray annealing on the electrical conductivity, several small sections of various Sn-Cu coatings cold spayed at 300°C and 60 psi were annealed at 200°C in a box furnace for three durations, 1 h, 7 h, and 12 h. The top surfaces of the coatings were slightly ground with 1200# grit sandpaper to remove the superficial oxide layer before conductivity measurements. After the measurements, the samples were cross-sectioned, prepared as per metallographic samples and characterized with a Hitachi SU 3500 SEM.

3.4. Electrical conductivity and influence of annealing

The measured conductivities for various coatings cold sprayed at 300°C and 60 psi are presented in Fig 7a. All the measurements on one sample are within 7%. The conductivity of bulk tin is included in Fig 7a as a benchmark. It can be seen that the cold sprayed tin coating is approximately 49% as conductive as bulk tin, indicating the bonding in the cold-sprayed state is not as conductive as the "100%" metallic bonding in the bulk material. The 10Zn coating exhibits a higher conductivity than the pure tin coating. For the Sn-Cu coatings, the conductivity of the 10Cu coating is comparable to the cold sprayed tin coating, although the mixed coating is not fully dense. In contrast, the 30Cu and 50Cu coatings exhibit much lower conductivity, despite the fact that copper is several times more conductive than tin. In general, the addition of the more conductive copper into tin did not increase the overall conductivity, but led to a decrease instead, and the rule of mixtures is obviously not applicable for predicting the electrical conductivity of the mixed coatings. The decrease may be caused by the porosity and the increasing number of Cu/Sn interfaces in the coating, which may both behave as the barriers for electrons. However, the conductivity of the 30Cu coating is lower than that of 50Cu, probably due to the near-surface defects in the 30Cu coating (Fig. 5b). The conductivities of the 30Cu and 50Cu coatings cold sprayed at 350°C and 60 psi (not shown) are lower than their respective counterparts at 300°C.

Fig 7b shows the comparison of conductivity before and after annealing in various Sn-Cu coatings cold sprayed at 300°C and 60 psi. All the measurements on one sample are within 7%. For all three compositions, the annealing treatment rendered more conductive coatings, regardless of the annealing time. The conductivity in all three coatings first increased significantly (62% in 10Cu, 367% in 30Cu and 220% in 50Cu) after annealing for 1 h, followed by a slight decrease with longer durations. The increase can mainly be attributed to the

annihilation of the defects in the coating and sintering. In general, a higher copper content tends to lead to a larger increase in conductivity after annealing. The 10Cu coating annealed for 1 h possesses the highest conductivity, which corresponds to 80% as conductive as bulk tin. For all the Sn-Cu coatings annealed under the same condition, the higher the copper content, the lower the conductivity. Similar to the as-sprayed state, the addition of the more conductive copper did not improve the overall conductivity of the mixture coating, indicating the Cu-Sn boundaries are not beneficial to electron flux.

The BSE images showing the cross-sectional microstructures of the annealed Sn-Cu coatings are shown in Fig. 8. For the 10Cu coating, annealing for 1 h did not significantly alter the microstructure, as shown in Fig. 8a, although it still shows some signs of diffusion since there exists a grey layer between the bright tin matrix and the dark copper particles. After 7 h annealing, Fig. 8b shows that significant diffusion took place, as the grey layer grew larger and the copper particle shrank. The grey phase is the Cu₆Sn₅ intermetallic phase, according to the EDX analysis (38.6 wt. % Cu). Between the copper core and the Cu₆Sn₅ intermetallics, there is a thin and dark grey layer of Cu₃Sn intermetallics (60.5 wt. % Cu), which is indicated by the black arrow in Fig. 8b. The emergence of the Cu₆Sn₅ and Cu₃Sn intermetallics agrees with the equilibrium phase diagram [26]. When annealing for 12 h, the copper cores continued shrinking and totally disappeared at many places while the Cu₆Sn₅ and Cu₃Sn intermetallics kept growing, only few smaller copper cores left in the coating, as shown in Fig. 8c. The two intermetallic phases, Cu_6Sn_5 and Cu_3Sn , are much less conductive than copper [27]: Cu_3Sn is 15% as conductive as copper and Cu_6Sn_5 is 8% as conductive as copper and only 58% as conductive as tin. Hence, for prolonged annealing duration, more of the less conductive Cu₆Sn₅ intermetallics

formed, decreasing the conductivity. After 7 h, the amount of the Cu_6Sn_5 did not increase much, so that the conductivity remains almost unchanged in 10Cu from 7 h to 12 h in Fig. 8.

As for different copper contents, the cross-sectional microstructures of the 10Cu, 30Cu and 50Cu coatings after annealing at 200°C for 7 h are shown in Figs. 8 d, e and f, respectively. It can be seen that the amount of Cu_6Sn_5 after 7 h annealing increases with the increasing copper content. For the 10Cu coating, it can be seen in Fig. 8d that the Cu_6Sn_5 phase is distributed as islands in the coating, and tin is still the matrix; for the 30Cu coating shown in Fig. 8e, the Cu_6Sn_5 phase accounts for more than half of the coating in volume, whereas the residual copper cores and tin account for the rest; in the 50Cu coating, the less conductive Cu_6Sn_5 intermetallics further grew and formed a continuous network, whereas the original tin matrix largely shrank and became isolated, as shown by the bright area in Fig. 8f. In general, the coating with a higher Cu content (up to 50 wt. %) has a larger amount of the less conductive Cu_6Sn_5 intermetallics after annealing (at 200°C up to 12 h).



Fig. 7. Electrical conductivity measurements for (a) various coatings cold sprayed at 300°C, 60 psi and (b) various Sn-Cu coatings before and after annealing at 200°C for different durations.



Fig. 8. BSE SEM images showing the cross-sectional microstructures of various Sn-Cu coatings cold sprayed at 300°C and 60 psi after annealing at 200°C: (a) 10Cu 1h, (b) 10Cu 7h, (c) 10Cu 12h, (d) 10Cu 7h at low mag, (e) 30Cu 7h, and (f) 50Cu 7h.

Highlights

- Metallic coatings were directly cold sprayed on CFRP.
- It is found that mixing metal powders can largely increase the deposition efficiency of the component powders.
- The deposition mechanism of the mixed metal powders on CFRP is discussed, and a few mechanisms for the improvement in deposition efficiency are proposed.

Cold spray of mixed metal powders on carbon fibre reinforced polymers

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Abstract

Metallization of polymers and polymer composites has attracted interest recently. Cold spray is an emerging coating method, but direct cold spray of metals on carbon fibre reinforced polymer (CFRP) is difficult. Previous results show that tin coatings can be cold sprayed on CFRP, but the deposition efficiency is relatively low. In this work, copper and zinc powders were mixed with tin to investigate the effect of mixing on deposition efficiency of the coating. The mixed metal powders were cold sprayed on CFRP with a low-pressure system at various conditions. Results show that the addition of copper and zinc led to much higher deposition efficiencies compared to the pure tin coating. Based on the results, the deposition mechanism of the mixed metal powders on CFRP is discussed, the effect of mixing powders on deposition efficiency is analyzed and several mechanisms are proposed accordingly.

Keywords: Cold spray; Mixed metal powders; Carbon fibre reinforced polymer; Metallization of polymers

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1. Introduction

Metallization of polymers and polymer composites, e.g. carbon fibre reinforced polymer (CFRP), has attracted substantial interest recently [1-5]. Among a variety of approaches, cold spray is an emerging coating method and a number of explorations have been reported [4, 6-11]. Direct cold spray of metal powders on various polymeric substrates is usually difficult and erosion of the substrates has been reported, by a number of researchers, to be the key obstacle [6, 7, 9]. Nevertheless, few successful deposition results have been reported when spraying tin onto the polymeric substrates [4, 9, 12]. This may be attributed to the low critical velocity as well as the low melting point of tin [12]. However, since the deposition efficiency (DE) of pure tin on CFRP is relatively low [12], further endeavors are required to improve the deposition efficiency and make the process more economically favorable.

In conventional cold spray, the feedstock powder is usually single-component powder [13]. In the past few years, cold spray of mixed powders has been investigated. In general, mixed powders are used for two main reasons, to improve the cold sprayability of the powder and to fabricate intermetallic or composite coatings. For the former, it has been found that mixing powders can improve the cold sprayability (i.e. increase DE, decrease porosity, etc.) of the component powders as well as the coating/substrate adhesion. This is usually accomplished by adding a ceramic component into a metal powder (e.g. adding alumina into aluminum) [14-17], but Yue et al. [18] have found that mixing two metal powders can also result in similar results. On the other hand, cold spray of mixed powders has also been used to fabricate composite coatings (e.g. Al/SiC) [19, 20] and intermetallics, especially those that may otherwise experience severe oxidation or decomposition when spraying with other high-temperature thermal spray techniques [21-24].

In this work, mixed metal powders were cold sprayed on CFRPs. The reasons for studying mixed powders are as follows. First, it is desired to improve the DE of tin on CFRP by mixing tin with other metal powders. Moreover, given the cold-sprayed coating in this work is primarily for lightning strike protection [12], mixing tin with a more conductive metal (e.g. copper, zinc) may potentially increase the overall conductivity of the coating (conductivity results are not reported in this article). Various Sn-Zn and Sn-Cu mixed powders were cold sprayed onto CFRP at various conditions with a low-pressure cold spray system. The deposition efficiency was measured at each condition and the electrical conductivity of the composite coatings was evaluated. The deposition mechanism of the mixed powders on CFRP is discussed. The effect of mixing powders on the deposition efficiency of the feedstock powder is analyzed, and several mechanisms are proposed accordingly.

2. Experimental methods

2.1. Starting materials and mixing of powders

The starting single-component materials used in this work were commercial-purity tin (CenterLine, basically spherical), copper (CenterLine, dendritic morphology), and zinc (CenterLine, irregular shaped) powders, with average particle sizes of 17, 30, and 40 μm, respectively (measured by a Horiba LA-920 laser scattering particle size distribution analyzer). The scanning electron microscope (SEM) images of the single-component powders are shown in Figs. 1 a to c. Four different compositions of mixed powders were prepared for cold spray, namely, Sn-10 wt. % Zn (10Zn), Sn-10 wt. % Cu (10Cu), Sn-30 wt. % Cu (30Cu), and Sn-50 wt. % Cu (50Cu). The powders were mixed in a metallic can (no additional media, e.g., mixing balls) with a double-movement powder mixer for one hour at National Research Council Canada, Boucherville. The SEM images of the mixed powders are shown in Figs. 1 d to f. For 10Zn, as

shown in the backscattered electron (BSE) image in Fig. 1d, the two materials did not show significant contrast, but the zinc particles are slightly larger and more irregularly shaped than the majority of tin particles. No obvious morphological change or hardening (based on the indentation test results, not shown) were found in the mixed powders when compared with the starting powders. The 50Cu powder (not shown) showed similar results as 10Cu (Fig. 1e) and 30Cu (Fig. 1f), with no significant changes in particle morphology or hardness being found.

The substrates used in this work were CFRP panels provided by Bombardier Aerospace (Montreal, Canada). The CFRP materials consist of a thermosetting epoxy matrix and continuous carbon fibre reinforcements. Each panel is made of four plies of Cycom 5276-1/G30-500 epoxy carbon prepreg ($[0/90]_{2s}$). For the cold spray experiments, sheet sections of dimensions 7 x 7 cm were used as the substrates. Prior to the cold spray experiments, these sections were degreased with acetone. No other surface preparation methods were adopted, unlike metal substrates, which are often grit blasted before cold spray (the CFRP substrates would be eroded during grit blasting).

2.2. Cold spray

Cold spray experiments were carried out at the McGill-NRC cold spray facility at National Research Council Canada, Boucherville. Considering the previously successful results with the single-component tin powder [12], a commercially available CenterLine SST system was used to perform the low-pressure spray. Nitrogen was selected as the carrier gas, and the above-mentioned four mixed powders were sprayed at various conditions, which are listed in Table 1. Only one layer (one pass) was sprayed at all conditions. The powder feeder was set at 1 revolution per minute (RPM), and the actual feeding rate was measured for each powder before the spray, which is also shown in Table 1. It can be seen that the feed rate varied from 10 to 13 g/min, which probably depends on the feedstock composition, although there is some inherent

variation in feed rate for any given setting. In the previous work on cold spray of pure tin [12], the nozzle quickly clogged at 325°C; whereas for 30Cu and 50Cu powders in this work, the nozzle did not clog up to a gas temperature of 350°C, probably because the copper particles served as "nozzle sweepers" to clear the nozzle. Temperatures above 350°C were not used in this work. It should be noted that previous cold spray of single-component copper powders at the conditions listed in Table 1 did not generate any deposition [12]; cold spray of single-component zinc was not performed. Deposition efficiency, which is the weight change of the substrate divided by the overall weight of powder sprayed during the time that the gun is actually over the sample, was measured during cold spray. After the cold spray experiments, the samples were prepared as per metallographic samples and then characterized with a Hitachi SU3500 SEM.

2.3. Electrical conductivity measurements

The electrical conductivity measurements were performed at École Polytechnique de Montréal by using the four-point resistivity/conductivity measurement method [25]. Before the measurements, the as-sprayed top surfaces were slightly ground with 1200# grit sandpaper to remove the loose particles and obtain flat surfaces. For each sample, the measurements were taken at three different locations, and the average was taken. The pure tin coating cold sprayed at 300°C and 60 psi in the previous work [12] was also measured for comparison.

To examine the effect of post-spray annealing on the electrical conductivity, several small sections of various Sn-Cu coatings cold spayed at 300°C and 60 psi were annealed at 200°C in a box furnace for three durations, 1 h, 7 h, and 12 h. The top surfaces of the coatings were slightly ground with 1200# grit sandpaper to remove the superficial oxide layer before conductivity measurements. After the measurements, the samples were cross-sectioned, prepared as per metallographic samples and characterized with a Hitachi SU 3500 SEM.

3. Results

3.1. Deposition efficiency

The deposition efficiency results of 10Zn powder at 280°C and 300°C as a function of gas pressure are shown in Fig. 2. Also shown in the plot, for comparison purpose, are the DE results of single-component tin at corresponding conditions (DE at 80 and 100 psi at 280°C were not measured) [12]. At all conditions, deposition was achieved and the DEs at 300°C were much higher than those of pure tin. In particular, the DE of the mixed powder was more than six times as large as that of pure tin at 300°C and 80 psi. It can also be seen clearly that at both gas temperatures, the DE of the 10Zn powder decreased with increasing gas pressure, following similar trend as the single-component tin powder at 300°C. However, 10Zn showed a slight decrease in DE from 60 psi to 80 psi but a large one from 80 psi to 100 psi, whereas pure tin showed a large decrease from 60 psi to 80 psi and a slight one from 80 psi to 100 psi.

The measured DE results of various Sn-Cu powders, in comparison to those of pure tin as benchmarks [12], are plotted in Fig. 3. It can be seen that, at most conditions, cold spray of the mixed powder resulted in a much higher DE than pure tin powder. Deposition efficiency of 10Cu at 280°C increased when the gas pressure was increased from 60 psi to 80 psi. At a gas temperature of 300°C, except for 50Cu at 60 psi, DE of all the mixed powders decreased with increasing gas pressure, following the same trend as pure tin at 300°C, a large decrease from 60 to 80 psi followed by a small one from 80 to 100 psi. In particular, DE of 50Cu at 300°C first increased from 60 psi to 80 psi, and then decreased from 80 psi to 100 psi; at 60 psi, DE of 50Cu was lower than that of pure tin. The DE curves for 30Cu and 50Cu as well as the pure tin tend to converge at 100 psi (data fall within 6% to 10%), although the data span much wider ranges at 60 psi (10% to 45%) and 80 psi (7% to 20%). At a higher gas temperature of 350°C, the DE results at 60 psi were much higher than those at 300°C (e.g. DE of 30Cu at 60 psi is 54% higher than

that at 300°C), then with increasing pressures, the DE curves for 30Cu and 50Cu followed the same trend as 30Cu and pure tin at 300°C. In general, the addition of copper into tin resulted in higher DE values than single-component tin, but the higher copper content in the mixed powder tended to lead to a lower DE (reduce the increment). Note that cold spray of single-component copper under the same conditions did not generate any deposition [12].

3.2. Microstructure

The SEM characterization results of the 10Zn coating cold sprayed at 300°C and 80 psi are shown in Fig 4. The light phase in the BSE images is tin and the dark particles are zinc. It can be seen from Fig. 4a that the coating is relatively thick and dense, but only few zinc particles can be observed. A zinc particle in the coating is shown in detail in Fig. 4b, in which the zinc particle is surrounded by many densely distributed, irregular-shaped small particles. Energy-dispersive xray (EDX) spectroscopy analysis indicates these particles are zinc, as shown by the EDX mapping of zinc in Fig. 4c. This microstructure is typical of the "dissolution-precipitation" phenomenon and can be an indication of tin melting in this work, and this will be discussed in Section 4.1. Figures 4 d and e show the secondary electron images of the top surface of the 10Zn coating. In general, zinc particles can barely be found at the top surface. A closer look of the top surface in Fig 4e reveals that there are a large number of small satellites attached to the particles at the top surface, and some traces of liquid, especially the frozen flowing liquid tracks as arrowed. This may indicate that tin (partially) melted during the process. A zinc particle at the coating surface is shown in Fig. 4f. This zinc particle is partially covered by a layer of tin, as shown by the EDX mapping. At the top surface of the tin layer, signs of liquid can also be observed.

For Sn-Cu coatings cold sprayed at 300°C and 60 psi, the cross-sectional microstructures are presented in Fig. 5. In the 10Cu coating, it shows in Fig. 5a that copper particles are basically

distributed homogeneously at the cross-sections. The coating is not fully dense and the pores basically distributed homogeneously across the cross-sections, with the amount and size of pores slightly larger near the top surface. The 30Cu coating is relatively dense, but there are a few lateral defects near the top surface, as shown in Fig. 5b. Copper particles are generally distributed homogeneously in the coating as well. A copper particle at the cross-section is shown in detail in Fig. 5c. The copper particle is tightly surrounded by tin, and a number of small particles, with diameters generally smaller than 0.5 µm, exist in the adjacent area of the copper particle. At the copper particle surface, especially the top surface (facing the succeeding layer), there are a number of "bulges", as arrowed. Energy-dispersive x-ray spectroscopy analysis of the small particles near copper as well as the bulges at the copper surface indicates these are Cu_5Sn_5 intermetallics [26]. Similar to Fig. 4b, this microstructure is typical of the "dissolutionprecipitation" phenomenon. The interface between the 30Cu coating and the CFRP substrate is shown in Fig. 5d, in which it can be seen that the Sn-Cu coating achieved good mechanical interlocking with the substrate, as numerous tin "protrusions" penetrating into the CFRP top surface. For the 50Cu coating, as shown in Fig. 5e, the porosity is relatively low (~1%), with most porosity existing in the top half of the coating and especially near the top surface. The dissolution of copper and precipitation of the Cu-Sn intermetallics are observed as well, as shown in Fig. 5f.

At a higher gas temperature of 350°C, the SEM images of the 30Cu coating are shown in Fig. 6. The coating is relatively dense, with a few pores and defects existing near the top surface and near the copper particles close to the coating/substrate interface, as shown in Fig. 6a. Copper particles are generally distributed homogeneously in the coating, but can be rarely seen near the top surface. At the top of the coating, a couple of irregularities (circled) can be observed. The copper particles in Fig. 6b also show a dissolution-precipitation microstructure, copper particles

being surrounded by numerous intermetallics precipitates in the adjacent tin matrix. The dissolution process of copper was well preserved during cooling, especially at the top of the copper particles. Due to the higher temperature, the intermetallic precipitates are relatively larger than those in Fig. 5c (the two images are not at the same magnifications). At the top surface, as shown in Fig. 6c, a number of large leaf-shaped clusters can be found, which correspond to the clusters observed in Fig. 6a. The reason for the formation of these clusters is unclear, but may be a combined effect of particle melting and bouncing. A higher-magnification image of the top surface is shown in Fig. 6d, showing signs of massive melting such that the originally smooth surface of the particles (Fig. 1) is totally transformed. The 50Cu coating sprayed at 350°C exhibits similar microstructural characteristics.

It should be noted that for all the composite coatings, regardless of the amount of the second component (SC), the SC particles can barely be found near/at the top surfaces or at the coating/substrate interfaces.

3.3. Retention of the SC materials

The weight fractions of the SC materials were measured by performing area analysis (and EDX mapping in case there were significant dissolution and diffusion of the SC materials) at the polished coating cross-sections, and EDX mapping at the top surfaces, and the results are listed in Table 2. It can be seen that for all mixed powders, the weight fraction of the SC materials measured at the top surfaces are much lower than those measured at the cross-section, implying that SC particles were unlikely to adhere to the surface alone without mechanical constraint. Hereafter, the weight fractions of SC only refer to those measured at the cross-sections. DE results for the individual components are also listed in Table 2, which were calculated by partitioning the overall DE based on the weight fraction of each component determined at the

cross-sections. Those calculated DE results are plotted in Fig. 7, along with the overall DE results of the mixed powders.

For 10Zn powders, it can be seen from Table 2 that the measured weight fractions of zinc are generally well below the as-mixed ratio, 10%, indicating poor retention of zinc. It shows in Fig 7 that at 300°C, DE of tin follows the same trend as the mixed powder while DE of zinc decreases linearly with increasing pressure, whereas at 280°C, DE of zinc slightly increases at higher pressure while DE of tin still follows the descending trend of the mixed powder.

On the other hand, the copper retention in the mixed Sn-Cu coatings is much better than the Sn-Zn coatings. For all three compositions, it can be seen from Table 2 that the composite coatings generally retained the as-mixed percentage of each component at many conditions. Interestingly, the copper contents in the composite coatings at high-pressure conditions (80 and 100 psi) are significantly higher than the as-mixed ratio (e.g. 30Cu sprayed at 300°C and 100 psi contains 51 wt.% copper). Meanwhile, it can also be seen from Fig. 7 that at most conditions (except 10Cu at 280°C), DE results of copper were on the same level as or below the mixed powder at 60 psi, then they surpass the mixed powder at 80 psi and stay above those of tin and the mixed powder till 100 psi. The retention of SC will be further discussed in Section 4.3.

3.4. Electrical conductivity and influence of annealing

The measured conductivities for various coatings cold sprayed at 300°C and 60 psi are presented in Fig 7a. All the measurements on one sample are within 7%. The conductivity of bulk tin is included in Fig 7a as a benchmark. It can be seen that the cold sprayed tin coating is approximately 49% as conductive as bulk tin, indicating the bonding in the cold-sprayed state is not as conductive as the "100%" metallic bonding in the bulk material. The 10Zn coating exhibits a higher conductivity than the pure tin coating. For the Sn-Cu coatings, the conductivity of the 10Cu coating is comparable to the cold sprayed tin coating, although the mixed coating is not

fully dense. In contrast, the 30Cu and 50Cu coatings exhibit much lower conductivity, despite the fact that copper is several times more conductive than tin. In general, the addition of the more conductive copper into tin did not increase the overall conductivity, but led to a decrease instead, and the rule of mixtures is obviously not applicable for predicting the electrical conductivity of the mixed coatings. The decrease may be caused by the porosity and the increasing number of Cu/Sn interfaces in the coating, which may both behave as the barriers for electrons. However, the conductivity of the 30Cu coating is lower than that of 50Cu, probably due to the near-surface defects in the 30Cu coating (Fig. 5b). The conductivities of the 30Cu and 50Cu coatings cold sprayed at 350°C and 60 psi (not shown) are lower than their respective counterparts at 300°C.

Fig 7b shows the comparison of conductivity before and after annealing in various Sn-Cu coatings cold sprayed at 300°C and 60 psi. All the measurements on one sample are within 7%. For all three compositions, the annealing treatment rendered more conductive coatings, regardless of the annealing time. The conductivity in all three coatings first increased significantly (62% in 10Cu, 367% in 30Cu and 220% in 50Cu) after annealing for 1 h, followed by a slight decrease with longer durations. The increase can mainly be attributed to the annihilation of the defects in the coating and sintering. In general, a higher copper content tends to lead to a larger increase in conductivity after annealing. The 10Cu coating annealed for 1 h possesses the highest conductivity, which corresponds to 80% as conductive as bulk tin. For all the Sn-Cu coatings annealed under the same condition, the higher the copper content, the lower the conductivity. Similar to the as-sprayed state, the addition of the more conductive copper did not improve the overall conductivity of the mixture coating, indicating the Cu-Sn boundaries are not beneficial to electron flux.

The BSE images showing the cross-sectional microstructures of the annealed Sn-Cu coatings are shown in Fig. 8. For the 10Cu coating, annealing for 1 h did not significantly alter

the microstructure, as shown in Fig. 8a, although it still shows some signs of diffusion since there exists a grey layer between the bright tin matrix and the dark copper particles. After 7 h annealing, Fig. 8b shows that significant diffusion took place, as the grey layer grew larger and the copper particle shrank. The grey phase is the Cu₆Sn₅ intermetallic phase, according to the EDX analysis (38.6 wt. % Cu). Between the copper core and the Cu_6Sn_5 intermetallics, there is a thin and dark grey layer of Cu₃Sn intermetallics (60.5 wt. % Cu), which is indicated by the black arrow in Fig. 8b. The emergence of the Cu_6Sn_5 and Cu_3Sn intermetallics agrees with the equilibrium phase diagram [26]. When annealing for 12 h, the copper cores continued shrinking and totally disappeared at many places while the Cu₆Sn₅ and Cu₃Sn intermetallics kept growing, only few smaller copper cores left in the coating, as shown in Fig. 8c. The two intermetallic phases, Cu₆Sn₅ and Cu₃Sn, are much less conductive than copper [27]: Cu₃Sn is 15% as conductive as copper and Cu₆Sn₅ is 8% as conductive as copper and only 58% as conductive as tin. Hence, for prolonged annealing duration, more of the less conductive Cu₆Sn₅ intermetallics formed, decreasing the conductivity. After 7 h, the amount of the Cu_6Sn_5 did not increase much, so that the conductivity remains almost unchanged in 10Cu from 7 h to 12 h in Fig. 8.

As for different copper contents, the cross-sectional microstructures of the 10Cu, 30Cu and 50Cu coatings after annealing at 200°C for 7 h are shown in Figs. 8 d, e and f, respectively. It can be seen that the amount of Cu_6Sn_5 after 7 h annealing increases with the increasing copper content. For the 10Cu coating, it can be seen in Fig. 8d that the Cu_6Sn_5 phase is distributed as islands in the coating, and tin is still the matrix; for the 30Cu coating shown in Fig. 8e, the Cu_6Sn_5 phase accounts for more than half of the coating in volume, whereas the residual copper cores and tin account for the rest; in the 50Cu coating, the less conductive Cu_6Sn_5 intermetallics further grew and formed a continuous network, whereas the original tin matrix largely shrank and became isolated, as shown by the bright area in Fig. 8f. In general, the coating with a higher Cu

content (up to 50 wt. %) has a larger amount of the less conductive Cu_6Sn_5 intermetallics after annealing (at 200°C up to 12 h).

4. Discussion

As shown above, the addition of another metal powder into tin largely increased DE in most cases, even though, in the case of Cu, the single-component powder could not be successfully deposited under the same conditions. In this part, the dissolution-precipitation phenomena that have been observed are discussed, the deposition mechanism of the mixed metal powders is analyzed, and several mechanisms for the improvement in DE of the mixed powders are proposed. Moreover, the retention of SC materials is discussed, and the factors that influence the deposition behavior of mixed powders on CFRP are explored.

4.1. The observed dissolution-precipitation phenomena

The dissolution-precipitation phenomena were observed in various Sn-Zn and Sn-Cu coatings under different cold spray conditions. Namely, upon impact with the substrate, the SC particles become surrounded by liquid tin, and begin to dissolve into the enveloping tin melt; during cooling, small particles (Zn or Cu_6Sn_5) precipitate from the saturated Sn-SC melt (Figs 4b, 5c, 5f, and 6b). As well, the heterogeneous nucleation sites at the SC particle surface may also be frozen so the semi-spherical morphology is preserved (Figs. 5c, 5f, and 6b). It should be noted that the dissolution-precipitation microstructures cannot form by solid-state diffusion, for which the typical microstructure is diffusion rings or layers. Moreover, tin and zinc are thermodynamically immiscible [26], so the dissolution of zinc into tin in the solid state is impossible. Therefore, it confirms that melting of the tin particles occurred when cold spraying the tin-based mixed metal powders at 300°C and higher with the CenterLine system. The melting

of tin at gas temperatures of 300°C and higher with the same system has also been observed previously [12].

Thermodynamically, precipitations of zinc and Cu₆Sn₅ intermetallics particles from the Sn-Zn and Sn-Cu melts, respectively, during cooling are possible, according to the equilibrium phase diagrams [26]. However, cold spray is a non-equilibrium, highly dynamic process, during which the melting and cooling of the particles, if any, are rapid. Thus, it is important to examine the diffusivity of the SC atoms in liquid tin. Table 3 lists the pre-exponential of the Arrhenius equation, D_0 , the activation energy, Q, and the calculated diffusion coefficients, D, of the SC elements at 237°C, five degrees above the melting point of tin. Also included in Table 3 is the estimated time for an SC atom to diffuse 5 μ m in liquid tin, calculated based on the widely used estimation equation, $x \approx \sqrt{Dt}$ (*x* is the diffusing distance, and *t* the diffusing time) [28]. It can be seen that the diffusivities for both SC atoms are high in liquid tin, e.g. it takes less than 90 milliseconds for an atom to travel 5 micron meters in liquid tin. The high diffusivity provides enough time for the SC particles to dissolve into molten tin, and thus possibilities for zinc or Cu₆Sn₅ to precipitate during the highly dynamic cold spray process.

4.2. The mechanism of deposition of mixed powders

In paper [12], it is proposed that cold spray of metals on CFRP should be considered as a two-step process, the development of the first layer and the coating build-up. The deposition windows for each process are defined as $v_{int} < v < v_{ero,sub}$ and $v_{crit} < v < v_{ero}$, respectively, where v_{int} is the interlock triggering velocity, $v_{ero,sub}$ is the velocity leading to significant substrate erosion, v_{crit} is the critical velocity of the powder (on metallic substrates) and v_{ero} is the velocity leading to first layer erosion/removal. Similar to single-component powder, it is also necessary to differentiate the two processes when cold spraying the mixed metal powders onto CFRP. In this

work, no zinc or copper particles were found interlocked or in direct contact with the CFRP surface in all composite coatings, and the interface is Sn/CFRP in nature, so the development of the first layer proceeded by the same crack-filling mechanism as pure tin [12]. Namely, the particles impact the substrate and generate some micro-cracks in the surface of the CFRPs, then the molten/semi-molten tin particles fill in these cracks, interlocking with the substrate and forming the first layer. Therefore, the criterion for developing the first layer, $v_{int} < v < v_{ero,sub}$, is still applicable. It is understandable that the SC particles do not bond with CFRP, considering: 1) copper powder alone cannot be successfully deposited, and 2) both materials are much harder than tin thus more difficult to deform and fill the cracks under the low-pressure conditions.

As for the build-up of subsequent layers, there are four possible scenarios, namely, tin impacts on tin, SC impacts on tin, tin impacts on SC, and SC impacts on SC, as discussed below.

a) Tin impacts on tin

When a tin particle impacts on the previously deposited tin particles, the situation is similar to cold spray of pure tin, thus the criterion for pure tin, $v_{crit} < v < v_{ero}$, is applicable.

b) SC impacts on tin

When an SC particle impacts on the previously deposited tin particles, there are three possibilities, depending on the particle velocity. If the SC particle impacts on tin at low velocity, it is highly likely to bounce away, with at most some tamping effect, due to insufficient kinetic energy. When the velocity is too high ($v > v_{ero}$), the SC particle may erode the previously deposited tin layer. At medium velocities, the SC particle may adhere to the previously deposited tin most likely through mechanically interlocking at low-pressure conditions. It is also possible that, due to melting, the SC particle penetrates the molten/semi-molten tin, through which bonding may form by solidification (possibly metallurgical). However, the SC particles were

rarely observed at the top surfaces in this work, and the weight fractions of the SC materials at top surfaces were much lower than those measured at the cross-section. This indicates that the SC particles impact on the previously deposited tin particles at the conditions assessed in this work do not tend to generate bonding directly.

c) Tin impacts on SC

When a tin particle impacts on an SC particle, it is likely to bond to the SC particle surface at most conditions performed in this work. It is relatively easy for the molten/semi-molten tin to spread on and adhere to the SC particle. In particular, when a tin particle impacts an irregular-shaped copper particle, it may also fill in the spacing within the dendrite-shaped copper particles, making the retention of the tin particle easier.

More importantly, tin particles impacting on SC may help to retain the SC particles, which tend to bounce away upon impact. In this work, the SC particles were retained by trapping due to the subsequent flow of tin particles, as opposed to bonding. If there was no subsequent impact of tin particles, these SC particles would not be retained in the coating. The retained SC particle then has an opportunity to react with the molten tin. Indeed, as shown in Fig 5c, the copper particle was found dissolved into the surrounding tin.

d) SC impacts on SC

When an SC particle impacts on a previously deposited SC particle, due to the lack of kinetic energy, the particle velocity under the low-pressure condition cannot reach the critical velocity of SC (pure zinc powder was not cold sprayed in this work, and the critical velocity for zinc is reported to be 360-380 m/s [29]). Hence, the SC particle would bounce away, or at most tamp the previously deposited SC particle before bouncing away. The higher the content of SC in

the mixed powder, the more likely this scenario. This may help to explain the decreasing overall DE when cold spraying the mixed Sn-Cu powders with increasing copper content.

4.3. The retention of SC

The retention of SC in the composite coatings in this work varied for different mixed powders. In general, the SC contents in the Sn-Zn composite coatings were much lower than the as-mixed ratio, whereas in the Sn-Cu composite coatings the as-mixed ratio can be basically retained at many conditions and the copper contents are even higher than the as-mixed ratio at some conditions.

As mentioned above, the SC particles were first retained in the coating through mechanical constraint (trapping), instead of bonding. It is reasonable to believe that the morphology of the dendrite-shaped copper particles may play a role in retaining the copper particles, since retaining one arm of the dendrite-shaped copper particle can retain the whole particle. Whereas to retain a relatively spherical particle, such as zinc in this work, a large fraction of its surface has to be covered by tin, otherwise, the particle will escape, contributing to the low retention rate.

For Sn-Cu powders, it is interesting that at high-pressure conditions the copper contents in the composite coatings are higher than the as-mixed ratio, and the DE results of copper are higher than those of tin in the mixed powder or pure tin in the previous work [12], as shown in Table 2 and Fig. 9. This is true for all three Sn-Cu powders at temperatures of 300°C and 350°C, and pressures of 80 psi and 100 psi. The overturn from 60 psi to higher gas pressures signifies that the Sn/Cu and or Cu/Sn impacts are better than Sn/Sn impacts at high-pressure conditions. Note that for pure tin, DE at 300°C and 80 psi decreases as compared to 60 psi due to erosion [12], it is reasonable to believe that the tin on copper impacts alleviate the erosion problem. In particular,

the fact that the overall DE of 50Cu at 300°C and 80 psi is higher than that of 30Cu may be attributed to fewer Sn/Sn impacts in the 50Cu coating.

4.4. Effect of mixing powders on DE

The DE results for the mixed powders at most conditions are higher than those of pure tin. Traditionally, a common tool to predict the properties of a hybrid is the rule of mixture (ROM), which means DE of the mixed powder is given by the arithmetic average of DE of the components, weighted by their fraction. If compared with the predictions based on the ROM, the experimental results for all mixed powders are higher than the predictions (e.g. DE of 44% for 10Cu at 300°C and 60 psi compared to a ROM prediction of 14%). There are a number of possible improving mechanisms, which are discussed below.

i) Tamping

The tamping effect is a widely accepted mechanism when the addition of a harder component into the metal powders decrease the porosity and increases the overall DE [14]. Although the harder components in conventional cold spray are usually ceramics (e.g. alumina), the SC metals in this work were also much harder than tin. Besides the conventional tamping, the impact of the SC particles may also stop any loosely bonded particle from being dislodged, forcing it to adhere. It is, therefore, reasonable to believe that this effect can be achieved by the relatively harder SC particles.

ii) Lowering the melting point

It has been found in our previous work [12] that melting of tin contributed to the increase in DE with increasing gas temperature. For both binary systems examined in this work, the equilibrium phase diagrams [26] show that the existence of SC elements may lower the melting point of tin, and this is another possible mechanism of DE improvement.

For Sn-Zn powders, the equilibrium phase diagram [26] indicates that increasing zinc content can lower the melting point of tin, from 232°C for pure tin to 199°C (~13 wt.% Zn). Indeed, signs of higher degree of melting were observed in the Sn-Zn coatings (Figs 4 d and e), as compared with pure tin coatings cold sprayed at the same conditions [12]. For Sn-Cu system, less than 1 wt.% of copper in tin can decrease the melting point by 5 degrees [26]. Given the considerable difference in DE of pure tin at 290°C and 300°C [12], 5 degrees in the proximity of melting may play an important role in the deposition of Sn-Cu powders. Experimentally, melting of tin and dissolution of copper were observed in various Sn-Cu coatings.

Kinetically, it is unclear how fast the SC content may increase in pure tin during the highly dynamic cold spray process, but once tin melts, the SC particles can fast dissolve into the melt, indirectly prolonging the melting.

iii) Morphological effect

For Sn-Cu powders, the morphology of the dendrite-shaped copper particles may also play a role in the DE improvement. Not only that the dendritic copper particles are relatively easy to adhere to the previous layer, once anchored at the surface, they can also provide more asperities (tin fills into the gaps in the copper particles) and may behave as cushions, which will facilitate deposition and alleviate erosion, respectively.

4.5. Deposition behavior and influencing factors

Deposition behavior of single-component tin has been investigated in our previous work, as schematically shown by the solid curve in Fig. 10. One may consider the DE-velocity curve of tin [12] as a master curve, which basically consists of two regimes, the ascending part (deposition-dominant) in the low-velocity regime, and the descending part (erosion-dominant) in the high-velocity regime. The latter one is a complicated combination of multiple processes, including the deposition of particles, erosion of the substrate, and erosion of the previously deposited coating.

Since tin is the primary content, it may be assumed that the deposition behaviors of the tin-based mixed powders follow that of single-component tin (the particle velocities were not measured in this work, but it is reasonable to believe the DE-gas pressure curve would follow a similar trend). When comparing the results in this work to the master curve, it can be seen that most data fall into the erosion-dominant regime, showing a descending trend of DE with increasing gas pressure (including 10Zn at both 280 and 300°C, 10Cu at 300°C, 30Cu at 300 and 350 °C, and 50Cu at 350°C as well as at 80 to 100 psi at 300°C). On the other hand, some data points fall into the deposition-dominant regime and show an ascending trend, including 10Cu at 280°C, 50Cu at 60 to 80 psi at 300°C. It is, therefore, of interest to discuss a few factors that may affect the shape of the DE-pressure/velocity curve.

The effect of mixing powders depends not only on the SC characteristics of the powder, but also on the chemistry between the SC element and the primary element (e.g. phase diagram, etc.). In this section, only the powder characteristics are considered and their influence on the DE curve is discussed.

Hardness – Both SC materials in this work are harder than the primary tin powder, with copper being the hardest (five times as harder as tin). In general, adding a harder material resulted in a higher DE in most cases in this work, moving the DE curve upward (as arrow 1 in Fig. 10). This is mainly achieved by the tamping effect mentioned above. However, there is a limit to this

effect - when the SC is too hard it may also aggravate the erosion process. Further study is needed to determine this hardness limit (e.g. mixing tin with iron or harder SC).

The amount of SC – The effect of the amount of SC was assessed for the Sn-Cu system in this work; note that copper alone led to no deposition under the same conditions. The results suggest that, for SC that does not deposit, higher SC amount would push the DE curve downward in general (e.g. Cu-Sn at 350°C), or towards the bottom-right direction for the upswing in particular (e.g. 50Cu at 60 to 80 psi at 300°C showing retarded upswing), as arrow 2 in Fig. 10. This may be attributed to the increasing probability of SC on SC impact with increasing SC content.

Morphology – It seems that the addition of a dendrite-shaped powder may contribute to an increase in DE, according to the Sn-Cu results in this work. However, the fact that copper is harder than tin may also account for part of the increase. Further studies on mixing with spherical SC, or more SC morphologies, may help to better analyze the influence of SC morphology.

Density – The density of all the component powders are similar in this work, with copper being slightly denser. It is relatively difficult to draw conclusions based on the results in this work. However, some trial spray with Sn-Al powders (not included) indicates the addition of aluminum may have some detrimental effects. Further study on mixing tin with low-density materials (e.g. aluminum, titanium) is advised.

5. Conclusions and comments on future work

Mixed Sn-Zn and Sn-Cu powders with different compositions were cold sprayed onto CFRPs at various conditions using a CenterLine low-pressure cold spray system. It was found that the addition of a second metal powder can largely improve the deposition efficiency, even though the second component powder alone cannot generate any deposition onto the CFRPs. The copper contents in the composite coatings were similar to or higher than the as-mixed ratio, whereas the retention of zinc was much lower.

During cold spray of mixed powders, there are four possible impacting scenarios, namely, tin impacts on tin, SC impacts on tin, tin impacts on SC, and SC impacts on SC. When an SC particle impacts on tin or another SC particle, it tends to bounce away due to insufficient kinetic energy; whereas if a tin particle impacts on tin or an anchored SC particle, deposition of the tin particle can generally be achieved.

The possible causes of the improvement in DE include the tamping effect of the relatively harder SC particles, lowered melting point by the SC elements, and the morphology effect of the dendrite-shaped copper powder. The dissolution-precipitation phenomena were observed in various Sn-Zn and Sn-Cu coatings under different cold spray conditions, and they were enabled by the fast diffusion of zinc and copper in liquid tin.

This work is a first attempt to study the effect of mixing metal powders on their deposition on CFRP. For future work, it is recommended to mix tin with spherical copper and compare the deposition results with those in this work, so that the effect of powder morphology can be determined. It is also of interest to cold spray mixed tin-titanium powders to confirm the lowering melting point effect. In the tin-titanium system, the melting point increases dramatically with titanium content. It will then enable the analysis of how the changes in melting point will affect the cold sprayability. Moreover, mixing tin with low-density metal powders may enable a look into the effect of SC density on the deposition behavior of mixed powders. Last but not least, it is needed to examine the effect of mixing powders on the coating/substrate adhesion strength.

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Powder	Temperature	Gas pressure	Stand-off distance	Gun travel speed	Feeding rate
	°C	MPa (psi)	mm	$\text{mm}\cdot\text{s}^{-1}$	g·min ⁻¹
10Zn	280, 300				13
10Cu	280, 300	0.41, 0.55, 0.69 (60, 80, 100)	18	25	10
30Cu	300, 350		10		12
50Cu	300, 350				11

Table 1. Process parameters for the low-pressure cold spray of mixed powders.

Coating	Temperature	Pressure	Weight fraction of SC (%)		Deposition efficiency (%)		ncy (%)
	(°C)	(psi / MPa)	Cross-section	Top surface	Overall	SC	Sn
10Zn	280	80 / 0.55	1	_ *	24	2	26
		100 / 0.69	3	_	15	5	16
	300	60 / 0.41	3	-	44	13	47
		80 / 0.55	2	1	41	8	45
		100 / 0.69	1	_	31	3	34
10Cu	280	60 / 0.41	12	_	32	38	31
		80 / 0.55	10	_	39	39	39
	300	60 / 0.41	10	4	44	44	44
		80 / 0.55	11	3	20	22	20
30Cu	300	60 / 0.41	31	4	27	28	27
		80 / 0.55	45	-	15	23	12
		100 / 0.69	51	-	9	15	6
	350	60 / 0.41	29	4	40	39	41
		80 / 0.55	46	_	14	21	11
		100 / 0.69	42	_	11	15	9
50Cu	300	60 / 0.41	39	9	10	8	12
		80 / 0.55	61	_	19	23	15
		100 / 0.69	58	-	6	7	5
	350	60 / 0.41	30	5	24	14	34
		80 / 0.55	55	_	9	10	8
		100 /0.69	60	_	6	7	5

Table 2. The weight fraction of the SC materials and the calculated DE for each component.

* Not measured

Element	D_0	Q	<i>D</i> at 237°C	Time to diffuse 5 µm	
	cm ² /sec	cal/mol	cm ² /sec	sec	
Zn	6.2×10^{-4}	4880	5.03×10^{-6}	0.050	
Cu	1.8×10^{-4}	4200	2.85×10^{-6}	0.088	

Table 3. Diffusion data for zinc and copper in liquid tin (values of D_0 and Q taken from [30]).

Figure captions

Fig. 1. SEM images showing the single-component powders and mixed powders: (a) Sn, (b) Cu, (c) Zn, (d) 10Zn, (e) 10Cu, and (f) 30Cu.

Fig. 2. Deposition efficiency of 10Zn mixed powder at 280°C and 300°C, in comparison with pure Sn powder.

Fig. 3. Deposition efficiency of three Sn-Cu mixed powders at 280°C, 300°C, and 350°C, in comparison with pure Sn powder.

Fig. 4. SEM characterization of the cold sprayed 10Zn coatings: (a, b) cross-section at 300°C and 80 psi; (c) EDX mapping of Zn of the rectangle area in (b); (d to f) top surface at 300°C and 60 psi, the arrows in (e) are pointing at some frozen flowing liquid tracks and the inset in (f) is the EDX mapping of the rectangle area in (f).

Fig. 5. Cross-sectional SEM images showing the Sn-Cu coatings cold sprayed at 300°C and 60 psi: (a) 10Cu, (b to d) 30Cu, and (e, f) 50Cu; (c) shows a Cu particle in detail in the 30Cu coating, with the arrows pointing at the "bulges" at copper surface, (d) shows the 30Cu coating/substrate interface, (f) shows a Cu particle in detail in the 50Cu coating.

Fig. 6. SEM images of the 30Cu coating cold sprayed at 350°C and 60 psi: (a, b) cross-sectional images, and (c, d) top surface images; circled in (a) are irregularities at the top of the coating.

Fig. 7. Electrical conductivity measurements for (a) various coatings cold sprayed at 300°C, 60 psi and (b) various Sn-Cu coatings before and after annealing at 200°C for different durations.

Fig. 8. BSE SEM images showing the cross-sectional microstructures of various Sn-Cu coatings cold sprayed at 300°C and 60 psi after annealing at 200°C: (a) 10Cu 1h, (b) 10Cu 7h, (c) 10Cu 12h, (d) 10Cu 7h at low mag, (e) 30Cu 7h, and (f) 50Cu 7h.

Fig. 9. Plot of DE results of mixed powders (solid lines with markers) and each components (solid lines for Sn and dashed lines for SC) calculated based on weight fraction measurements.

Fig. 10. Schematic DE-pressure curves showing the possible effect of mixing powders.





















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