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Cold Spraying of Mixed Sn-Al Powders onto Carbon Fibre Reinforced Polymers

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Abstract

Pure metal coatings have successfully been cold sprayed on to Carbon Fibre Reinforced Polymers (CFRPs) in previous studies at McGill University. As a means to improve coating conductivity for lightning-strike protection (LSP) purposes, coatings with mixed metal powders were sprayed. There is also the possibility of improving the deposition efficiency (DE) since single component tin coatings previously had a maximum DE of only 20%. The studied coatings were based on a mix of tin and aluminum powders, the latter being a metal commonly used in the aerospace industry for its lightweight properties. The different coatings were characterized and compared to results on pure tin coatings and on mixed Sn-Cu and Sn-Zn coatings. The deposition efficiency (DE) was measured for different conditions and compared to those of previous studies. Mixing tin and aluminum powders is discussed and various mechanisms related to cold spraying mixed powders on CFRPs are explored.

Introduction

CFRPs are appreciated in the aeronautic industry for their better strength-to-weight ratios than typically used aluminum alloys (e.g. the 2000 and 7000 series) [1]. On the downside, they are poor electrical conductors – approximately 1000 times less conductive than their aluminum counterparts [2] – which makes them prone to damage due to lightning strikes that aircraft endure once per year on average [3]. In this context, metallization of composite materials (e.g. CFRPs) has received increasing interest [1, 2, 4-6]. This would allow the usage of polymer composites in an industry where the demand is foreseen to double over the next 20 years [7] all while fulfilling physical and mechanical requirements.

Metallizing CFRPs can be achieved through a series of approaches, with cold-spray appearing as a legitimate alternative: it belongs to the thermal spray technologies, but using relatively low temperatures when compared to other techniques, thus limiting the risk of oxidation of the metallic particles and the heat damage of the substrate [4]. Trials have been performed and mixed results have been obtained, issues generally being related to erosion of the soft substrate due to the higher hardness of most metallic powders [2, 8, 9]. Nonetheless, some researchers have encountered success in depositing tin particles on polymeric substrates [2, 10, 11].

To improve the DE of metals on metal substrates, ceramic components (e.g. silica) have been mixed with the metal powder [12]. Che et al. [13] furthered this research for CFRP substrates by mixing two metal powders (tin with copper and tin with zinc) which lead to a higher DE of the tin. A secondary outcome was a slight improvement of the electrical conductivity of the coating with 10% of either secondary component (SC) – increasing percentages of copper did not necessarily lead to higher electrical conductivities though.

In this work, mixed aluminum-tin powder was cold-sprayed on CFRPs. The choice of aluminum is similar to that of copper and zinc [13] with both the DE and electrical conductivity expected to improve. Tin-aluminum mixed powder with a 90:10 weight ratio was cold sprayed onto a CFRP substrate at various process conditions with a low-pressure cold spray system. Microanalysis of the coatings was performed and the deposition mechanism of the mixed powders on CFRP is discussed. The DE was also measured at each condition and a discussion on the improvement of the DE by mixing powders is proposed, with several mechanisms being considered based on previous studies [2, 13].

Experimental Methods

The feedstock materials used in this work are listed in Table 1. The particle sizes of the feedstock powders were measured with a laser scattering particle size analyzer (LA-920, HORIBA, Japan). The tin powder was relatively spherical and had a broad monomodal and non-symmetrical distribution, whereas the aluminum powder, which was also spherical, had a more continuous size distribution with a higher average particle size. The hardness of the aluminum powder was greater than that of the tin powder. Both powders were of commercial purity. The SEM images of the single component powders were presented by Che et al. [2]. The powders were mixed at National Research Council Canada, Boucherville in a metallic can without additional media (e.g. milling balls) with a double movement powder mixer for 1h. No significant morphological changes or hardening were noticed in the mixed powder when

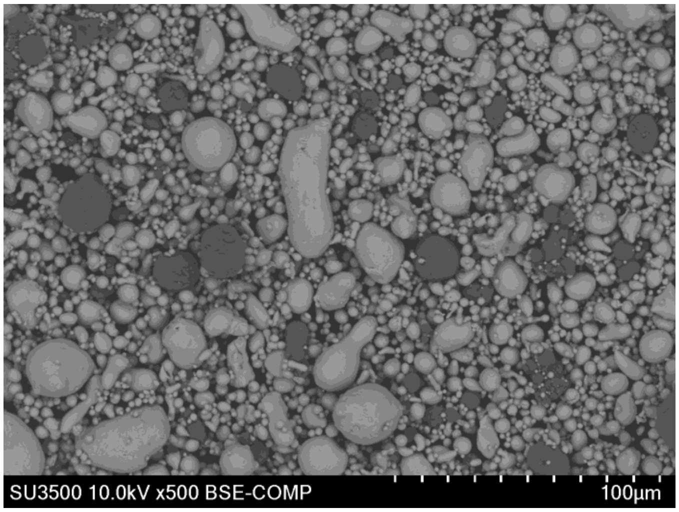

Figure 1: BSE-COMP image of the mixed Sn-10Al powder: Al presents the darker contrast

Table 1: Properties of the feedstock powders used in this work

Powder	Morphology	Supplier	D_{avg}	Hardness
Al	Spherical	Valimet	25 µm	27 HV
Sn	Relatively Spherical	Centerline, SST	17 µm	11 HV

Table 2: Principal cold spray parameters

Powder	Carrier Gas Temperature °C	Gas Pressure psi
Sn-10Al	280, 300	60, 80, 100

compared with the starting powders. The BSE image of the mixed powder is presented in Fig.1.

The CFRPs used in this work were provided by Bombardier Aerospace (Montreal, Canada). The CFRP material consists of a thermosetting epoxy matrix with continuous carbon fibre reinforcements. The CFRP-panels were made of four plies of 5276-1/G30-500 epoxy carbon prepreg ($[0/90]_{2s}$). Sheet sections of dimensions 7 x 7 cm were used as substrates during the cold spray campaigns. Sample preparation before cold spraying was limited to simply degreasing the samples with acetone: when cold spraying on a metal substrate, the substrate is usually grit blasted to improve metallurgical bonding, but this would result in erosion with a CFRP substrate.

The cold spray campaigns were carried out at the McGill-NRC cold spray facility at National Research Council Canada in Boucherville. The cold spraying was performed at low-pressure with a commercially available CenterLine SST system (Supersonic Spray Technologies, CenterLine Windsor Limited, Canada). This choice enabled the use of the so-called "downstream injection" mode, where the particles were injected in the main gas stream after the throat of the nozzle. The risk of clogging the nozzle when using metals with low fusion points, such as tin, was thus limited. The primary cold spray parameters are listed in Table 2. These parameters were chosen based on previously successful cold-spray campaigns with tin [2]. The carrier gas was nitrogen, the stand-off distance was 18 mm and the gun travel speed was 25 mm/s. The powder feeder rate was set to 1 revolution per minute (RPM), which gave a measured feeding rate of 11 g/min. Only one pass was sprayed for each set of conditions, with a step size of 1 mm. Note that previous spraying of single component aluminum on CFRPs generated no deposition because of erosion, whereas pure tin generated a coating with a maximum DE of 20% [2]. After the cold spray process, the samples were prepared as metallographic samples and characterized with a Hitachi SU3500 SEM.

Results

Figure 2 shows the DE of the mixed powder Sn-10Al at 280°C and 300°C as a function of the gas pressure. For comparison purposes, the DE results of pure tin for identical conditions are also included in this figure (DE at 80 psi and 100 psi at 280°C were not measured) [2]. For all conditions, deposition was achieved. The retention rates of aluminum in the mixture coating were measured at the cross-section and at the top surface for each coating at 60 psi and 100 psi. These were determined through area analysis at the polished coating cross-sections and through EDX mapping for the top surfaces. The deposition efficiency for each pure element in the coating is also calculated through the proportionality that exists between the overall DE and the weight fractions measured for each component at the cross-sections. The results are listed in Table 3. The retention rate of aluminum at the top surface is much lower than the retention rate at the cross-section. Furthermore, the retention rates in the coating (cross-section measurements) are also very low as compared to the initial proportion of aluminum in the powder mix, except at 280°C and 100 psi where they are close to the initial 10% input of Al in the mixed powder. Overall, the DE of aluminum in the coating remains low (under 40% of the initial Al input). The cross-sectional micrographs of the mixed powder coatings cold sprayed at various conditions are presented in Fig.3; the tin has the brighter contrast. All the coatings were relatively dense with

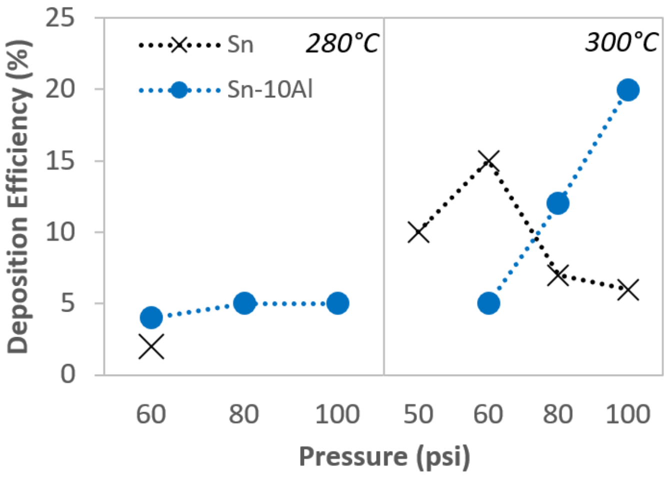

Figure 2: Deposition efficiency of Sn-10Al mixed powder at 280°C and 300°C, compared with pure Sn powder

Table 3: Retention rates of aluminum measured at the cross-sections and top surfaces and calculated deposition efficiencies for aluminum and tin in the coating

Temperature (°C)	**Pressure** (psi)	**Volume fraction of Al** (%) Cross-section	Top surface	**Weight fraction of Al** (%) Cross-section	Top surface	**Deposition Efficiency** (%) Overall	Al	Sn
280	60	2.9	0.5	1.1	0.2	4	1	5
280	100	21.6	1.6	9.3	0.6	5	4	5
300	60	1.6	0.8	0.6	0.3	5	~0	5
300	100	3.4	0.8	1.3	0.3	20	3	22

small defects mainly localized around the aluminum particles. (Note that 10%wt Al is equivalent to 23%vol Al.) Small numbers of Al particles are noticeable in the coating which exemplifies the low retention rates of Al.

At 280°C and 60 psi, Fig. 2 shows that the DE for the mixed powder is higher than the DE of pure tin. When the gas pressure was increased at 280°C, the DE of the mixed powder barely increased. On the other hand, the retention rates of Table 3 indicate an exceptionally sharp increase of the aluminum in the tin coating between 60 psi and 100 psi (9% as compared to around 1% for the other conditions). When observing the cross-sectional micrographs of the coating at 280°C, more aluminum particles are visible in the coating at 100 psi (Fig.3b) than at 60 psi (Fig.3a), thus confirming the evolution of the Al retention rate. There does not seem to be an obvious relation between Al retention and overall DE.

At 300°C and 60 psi, the DE of pure tin is higher than the DE of Sn-10Al, as seen on Fig. 2. With increasing pressure, the DE of the mixed powder increases almost linearly while the DE of pure tin decreases sharply between 60 psi and 80 psi than decreases slowly between 80 psi and 100 psi. For these higher pressures, it can also be seen that the DE for the mixed powder is higher than the DE for pure tin. Very low retention rates of Al at 300°C were obtained (around 1%) (Table 3) and

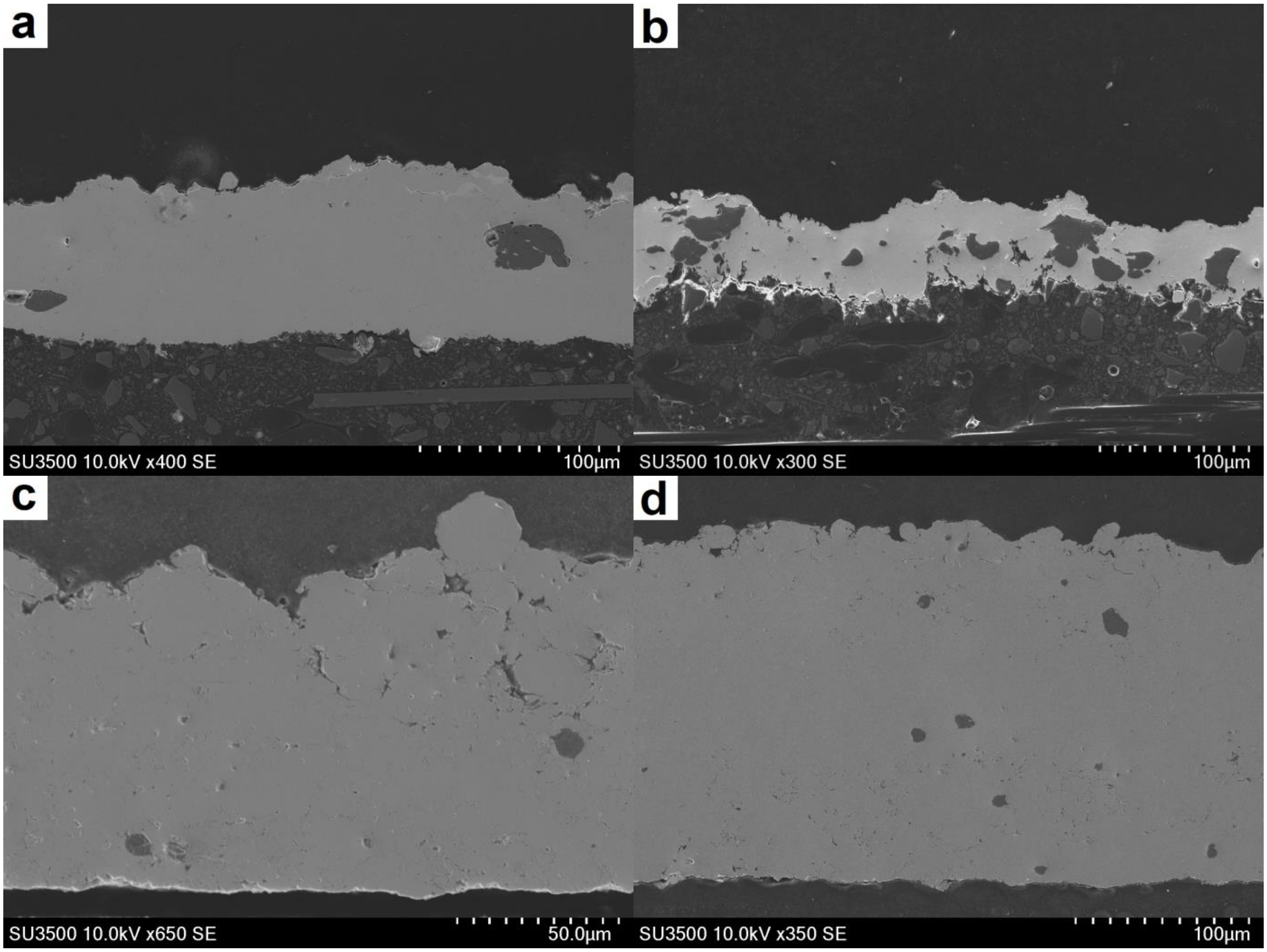

Figure 3: SEM images of the cross-sectional microstructures for the Sn-10Al coatings: (a) 280°C and 60 psi, (b) 280°C and 100 psi, (c) 300°C and 60 psi, (d) 300°C and 100 psi.

the increase of DE of the composite feedstock powder that was observed with the increase of pressure at 300°C is mainly related to an increase of the DE of tin. Again, this seems to indicate that there is no relation between the retention rate of Al and the overall DE of the coating, yet opposite trends for a pure tin coating and a "near-pure" tin coating are clearly identified. When observing the cross-sectional microstructures at 300°C (Fig.3c, Fig.3d), a similar coating as the one obtained at 280°C and 60 psi is visible, with few Al particles present.

Another observation concerns the microstructure of the coating around the aluminum particles, as seen in Fig.4. In Fig.4a, an aluminum particle at the top of the coating at 280°C and 60 psi is shown in detail. The black arrows point out thin layers of tin on the "shoulders" of the aluminum particle. The aluminum and tin are contiguous on the bottom of the particle. A white arrow indicates a tin particle beside the thin layer of tin: this could be a particle that was bonded to the aluminum particle but has broken off by some shearing action leaving a thin layer of tin. This seems to indicate a strong bonding of the tin with the aluminum. Around the particle, planar defects and voids can be observed, indicating loose bonding of the aluminum in the coating: mechanical interlocking is what seems to maintain the Al particles in the coating. These defects can be better seen in the micrograph of an aluminum particle in the coating at 300°C and 100 psi (Fig.4b). Similar microstructures around the aluminum seem observable – defects, contiguous interfaces – regardless the cold-spray process parameters.

SEM images of the top-surface Al particles in the different coatings are presented in Fig.5. At 300°C and 100 psi, small satellites of tin appear, as shown in Fig.5c and Fig.5d. These satellites are below 1µm in size and can be understood as a splashing phenomenon associated with liquid metal as described by Che et al. [2], the temperature of the gas stream being superior to the melting point of tin (232°C), the outer surface of the impinging tin particles begins to melt in the gas stream. Upon impact with relatively high temperatures and pressures (thus velocities), it would be consistent to have splashing of this melted tin, which could give these satellites. These satellites were not as noticeable with the other cold-spray process parameters (Fig.5a, Fig.5b). This could be explained by lower carrier gas temperature and pressures that diminish the partial fusion process of the tin (lower temperature effect) and the splashing phenomenon (lower velocity effect).

Discussion

The previous results demonstrated an increase of the overall DE of the mixed metal powders on CFRPs as compared to the DE of pure components [2]. When studying each separate component in the mixed-powder coating, it is also noticed that the DE is higher than when depositing a single component (except for tin at 300°C and 60 psi). A previous study demonstrated similar conclusions with zinc and copper [13] and several mechanisms explaining the effect of mixing powders were proposed, yet they do not necessarily apply in the same ways to aluminum. In this section, the notable differences and similarities between the previous results will be discussed and the various mechanisms that could explain the improvement of the DE with the mixed powders are explored.

Another noteworthy difference that arises between the current study and the previous study [13] is the evolution trend of DE as seen in Fig.6. At 300°C, the increase of the gas pressure brought a decrease of the DE for pure tin and for the mixed powders Sn-10Cu and Sn-10Zn (the DE of Sn-10Cu was not measured at 100 psi), whereas in this study, an increase of the pressure with Sn-10Al has led to an opposite trend. More surprisingly, with 10%Al, the coating is almost pure tin as seen in Table 3, yet the behavior of this tin is opposite from the behavior of pure tin. Che et al. [13] considered the deposition of tin with pressure as a bell-shaped curve, dominated on one side by an increasing deposition due to higher velocities and on the other side by a decreasing deposition due to erosion. A combination of the physical properties of the powder and of the cold-spray operating conditions could affect the maximum DE of tin but also the pressure for which this maximum is achieved. When considering the results obtained between this study and previous studies [2, 13] at 300°C, the observable

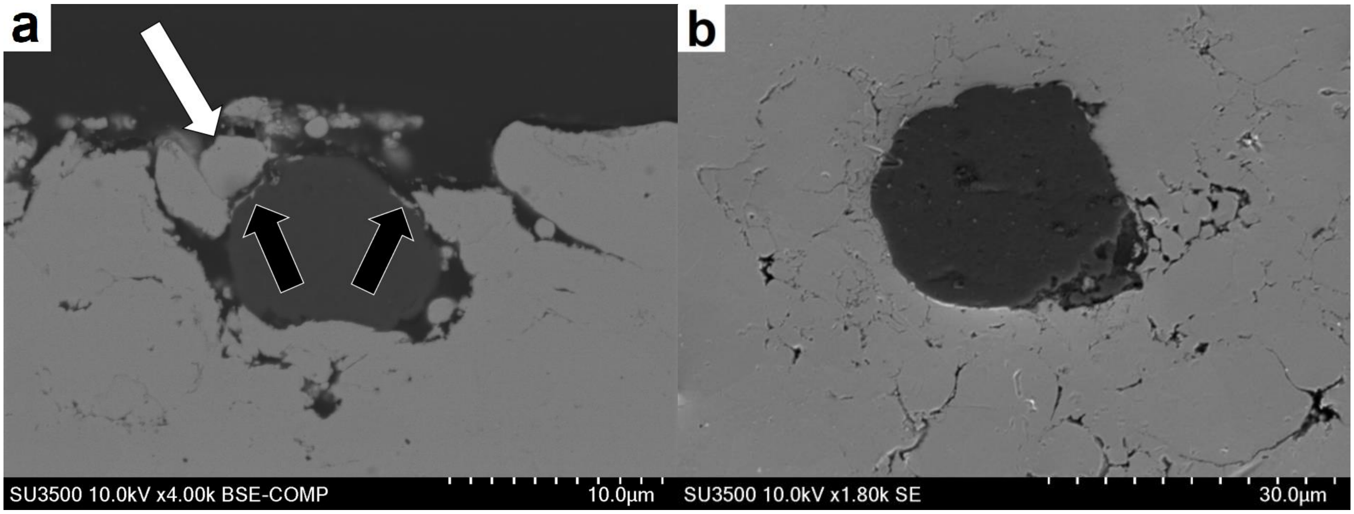

Figure 4: SEM images of Al particles in the cross-sectional microstructures for the Sn-10Al coatings: (a) 280°C and 60 psi, (b) 300°C and 100 psi.

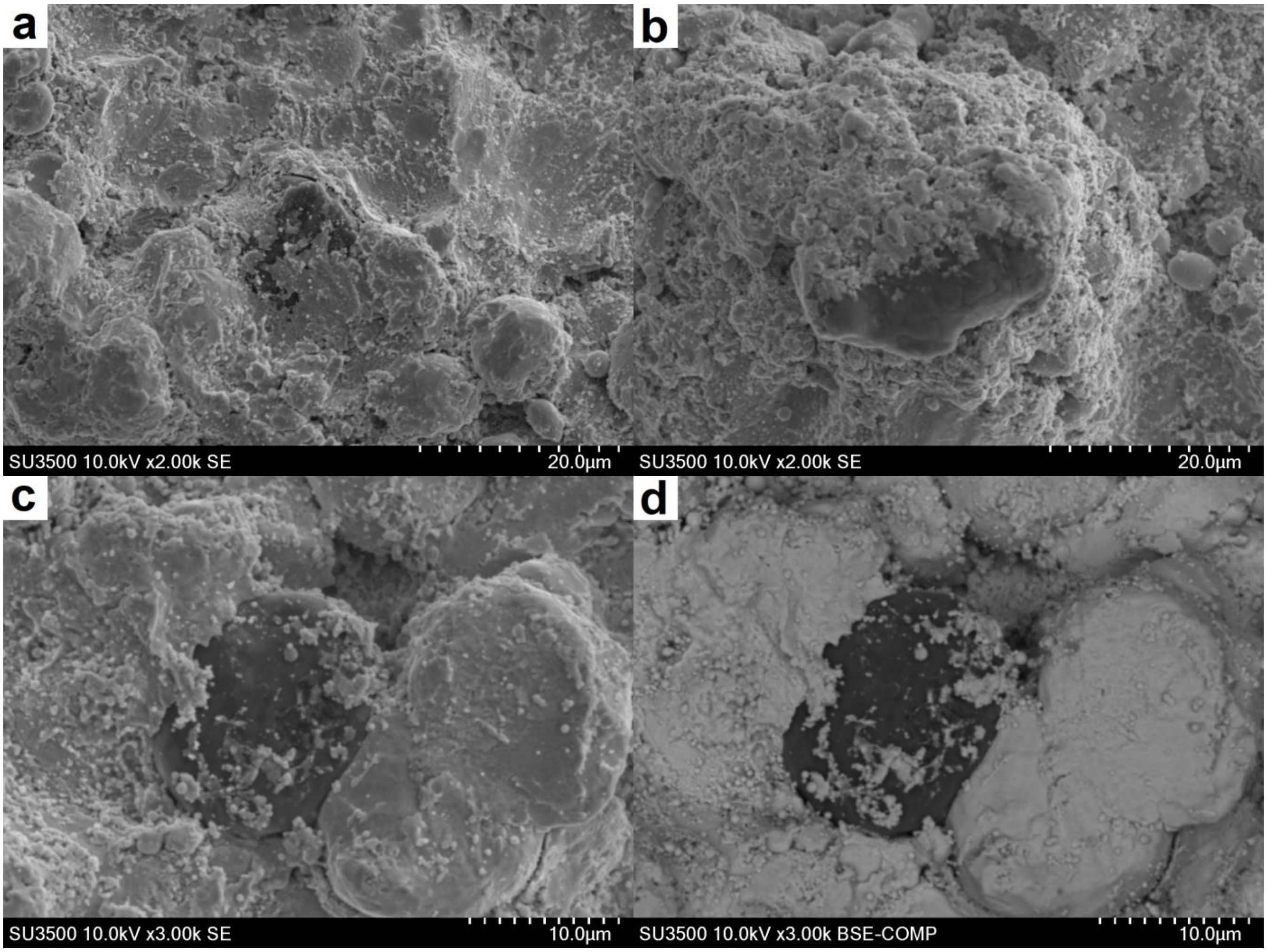

Figure 5: SEM images of Al particles at the top surface of the Sn-10Al coatings: (a) SE image at 280°C and 60 psi, (b) SE image at 280°C and 100 psi, (c, d) SE and BSE-COMP images at 300°C and 100 psi

trends and relative DEs could simply be a result of changing the secondary component (SC) in the mixed powder. In this case, 10%Zn and 10%Cu would have an effect of increasing the DE of the tin. The maximum for these SC is obtained for a pressure under 60 psi, just like the maximum DE of single component tin which is obtained for 60 psi, therefore zinc and copper would not affect the ideal spraying pressure. On the other hand, 10%Al would bring about a shift of the curve, and the ideal pressure would then be over 100 psi.

Che et al. [13] considered the potential factors that could influence the deposition behavior of tin. Some factors may apply for the mixed Sn-10Al powder. *Tamping of the tin by the SC is supposed to be a main DE improvement mechanism, as is commonly acknowledged when adding ceramic powders to metallic powders to reduce porosity and increase the DE [14]. Powder hardness was then considered as a potential key parameter in the deposition process. When analyzing the results, copper was described as having the most success in increasing the DE of tin for its greater hardness (55 HV, compared to 33 HV for zinc and 11HV for tin) [13]. And yet, the aluminum powder used in this work had a hardness of 27 HV – therefore similar to that of the zinc used in the previous study – yet the DE of tin with 10%Zn was higher in all considered conditions than with 10%Al, as shown in Fig.6. Note should be taken that the differences could arise from the different particle sizes (40µm for the zinc and 27µm for the aluminum). *Furthermore, in the previous study [13], the powders used had similar densities (8.96 $g.cm^{-3}$ for copper,

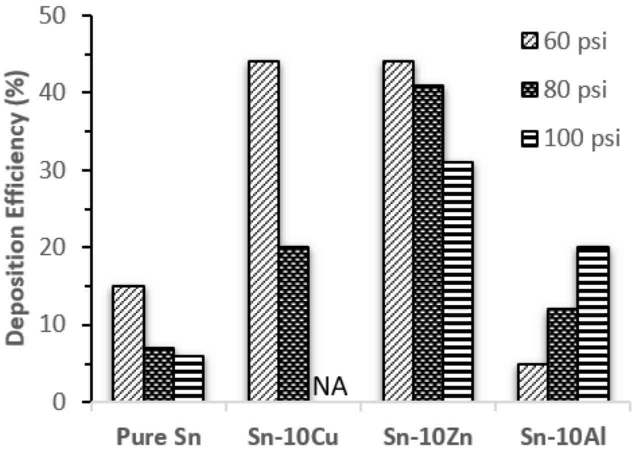

Figure 6: Deposition efficiency of Sn-10Al mixed powder at 300°C, compared with data from pure Sn powder, Sn-10Cu and Sn-10Zn [2, 13]

7.265 g.cm^{-3} for tin and 7.14 g.cm^{-3} for zinc), whereas aluminum has a density of 2.70 g.cm^{-3}. If density is relatable to the tamping effect, this could also provide an explanation as to why the DE of tin with aluminum is smaller, but this would not explain why there could be a shift in the DE curve of tin as aluminum has lower density and so higher pressure would be required to have a similar tamping effect.

*Another notable comparison point is the retention rates of the SC and its morphology. The low retention rate of zinc in the previous study (maximum 3% [13]) is comparable to the low retention rate of aluminum in this work and opposed to the high retention rate of copper [13]: when considering their morphology, the zinc and aluminum particles were relatively spherical as opposed to the irregular copper particles. This comparison offers consistency to the idea that retention of the SC is based on mechanical constraint (trapping in the coating) and eventually could impact the retention of tin in the coating.

*As tamping by the SC is probably a main DE improvement mechanism, viewing the SC composition from other characteristics rather than weight fraction could be of interest: 10%wt in tin is 17%mol for both zinc and copper, but 33%mol for aluminum. 10%wt in tin is also equivalent to a volume fraction of 8%vol for copper, 10%vol zinc and 23%vol for aluminum. Therefore, there are twice as many or twice the volume of Al particles participating in the tamping effect of the coating than the other SC, but given the low density of aluminum the tamping could be considered as less effective, hence the differences with the mixed zinc-tin powder. A study from the perspective of a particle surface ratio would be appropriate, but implementing the particle size would necessarily be included and given the large particle size distributions for each powder, values could be quite inaccurate. A broader study of mixing powders would be valuable as to effectively locating the maximum DE for each SC and understanding how these parameters influence the DE and the ideal carrier gas pressure.

The retention of aluminum may also be supported by the microstructural data: even though the aluminum particles seem to induce a certain number of defects in the immediate surrounding tin, there seems to be evidence of strong bonding between the tin and the aluminum. This could possibly be explained by a wetting mechanism related to the presence of melting tin remnants in the form of submicron satellites at 300°C and 100 psi. Finding evidence of this bonding mechanism could confirm a major aspect of the cold spraying of mixed powders raised by Che et al. [13] that is the interactions between particles (Al on Al, Sn on Sn but also Al on Sn, Sn on Al). How the deposition will take place and how the subsequent layers will be formed in the coating is thus ultimately modified, with an evident dependence on the principal cold-spray parameters (carrier gas temperature and pressure) and thus, the particle velocity. Understanding the interactions between particles in the case of the CFRPs has proven to be quite difficult as erosion is undeniably a factor of complication, therefore studying the cold-spraying of mixed powders and their various interactions on well known-metals would be an enriching study to carry out.

Conclusion

Mixed Sn-Al powders were cold-sprayed at various conditions onto CFRPs with a CenterLine low-pressure cold spray system. The addition of aluminum led to better deposition efficiencies than with pure tin, yet the DE results were not as good as in previous studies with zinc and copper. Retention rates of aluminum were relatively low and the coatings were mainly composed of tin. Comparison with previous studies revealed that the DE of single component tin had a different trend than what was observed for the DE of Sn-10Al mixed powders and probable explanations were discussed. The microstructural data seems to reveal strong bonding between tin and aluminum, with the presence of melting remnants. Further studies are required to produce more data relating the powder properties and the cold spray parameters, as to confirm the presence of trends for the various powders and to achieve an optimization of the powder mixing process. Also, complimentary studies would be required to analyze the interactions between the secondary component and the tin particles.

Acknowledgment

The authors wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Green-SEAM strategic network and the McGill Engineering Doctoral Award (MEDA). The industrial partner, Bombardier Aerospace, is gratefully acknowledged. Mr. Frédéric Belval from National Research Council Canada, Boucherville, is acknowledged for his contribution to the cold spray experiments.

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