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Influence of oxide chemistry of feedstock on cold sprayed Cu coatings

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ABSTRACT

Pure Cu powders were coated on an Al substrate by cold spray. The characteristics of the coating properties and deposition efficiency were influenced by not only the processing parameters but also the chemistry of the feedstock. The coating pressure and temperature were fixed at 2.4 MPa and 480 °C, respectively. Vacuum annealed powder yielded about 60% of deposition efficiency (DE) and mid-50 Hv hardness. However, after 2 weeks of air exposure at room temperature, DE dropped to about 40%, but the hardness increased to 70 Hv. Furthermore, these properties turned out to be reversibly cycled by simple vacuum annealing and air exposure (aging). From XPS and oxygen determinator data, the cyclic behavior of the coating properties correlated well with the quantity of higher oxidation state in the feedstock. In contrast to previous work, it was found that the surface oxide of the raw materials could not be reduced to insignificant levels by collision among particles during flight in the jet stream of gas. As a consequence, the oxide content determined the amount of re-bounding particles which did not accumulate but rather tamped the surface of the coating, and this in turn affected DE and hardness. Therefore, maintenance of a good and desirable chemistry of feedstock is crucial in cold spray practice.

1. Introduction

Cold and thermal spray methods are representative and conventional coating processes that are often employed for producing thick metal films. These processes are used to secure upgraded mechanical, thermal, and electrical properties. In the cold spray process, the particles are propelled toward collision with the substrate by supersonic gas flow. The kinetic impact energy of the particles generates two distinctive features: firstly, mechanical/chemical bonding between the particles and substrate as well as among the particles stacked on the substrate. Secondly, severe plastic deformation (flattening) of the particles results in a highly work hardened state. In thick film coating of readily oxidized metals, cold spray has advantages over thermal spray, because in the latter the particles are completely or partially melted by a plasma, arc or flame. In addition to that, film qualities such as density and adhesion are known to be much better in many metals and alloys. Cu thick films have been gathering great attention these days in batteries, LED packaging, etc. Owing to the superior nature of the cold spray process described above, Cu coatings with high conductivity and adhesion and minimal oxidation are produced [1–4]. However, depending on the particular coating system and research group, there have been many distinctive and varied results reported for cold sprayed Cu. This is because the characteristics of the coating depend highly on the properties of the raw powder such as particle size, shape, and oxygen content [5–7] and also coating conditions including gas temperature, pressure, type, nozzle geometry, and substrate type [8–12]. Meanwhile, the role of initial chemistry of raw Cu powders has been relatively ignored. Basically, it can be assumed that Cu metal powder contains brittle oxides particularly concentrated at the surface. The quantity of oxide depends on powder preparation technique, size, shape, and storage history. Due to the lack of deformability of the oxide, critical coating characteristics such as

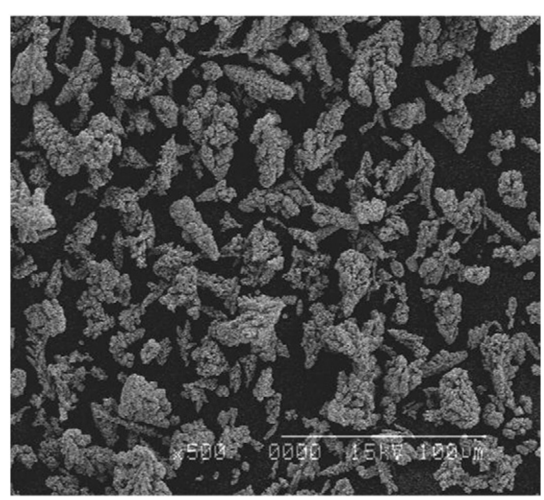

Fig. 1. SEM image of as-received Cu powder.

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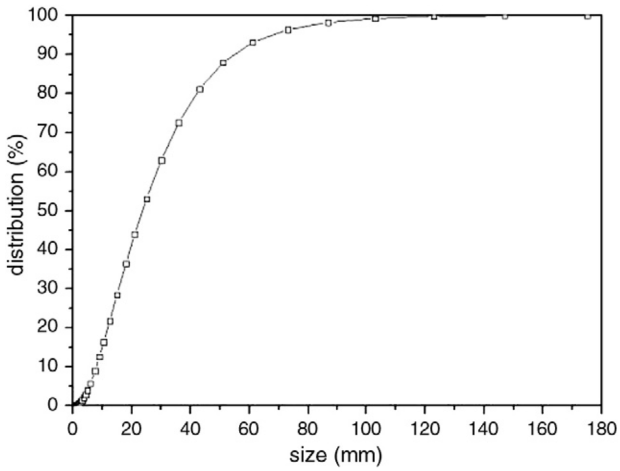

Fig. 2. Particle size distribution of Cu powder.

deposition efficiency and densification of the coating can be noticeably affected [13,18–21]. In this study, the effects of chemistry of the raw Cu powder were investigated in terms of deposition efficiency and mechanical properties.

2. Experimental procedure

A home-made cold spray system was used in this work. The powders were accelerated through a De Laval type nozzle (throat diameter, 1 mm; output diameter, 7 mm; length of spray nozzle, 100 mm).

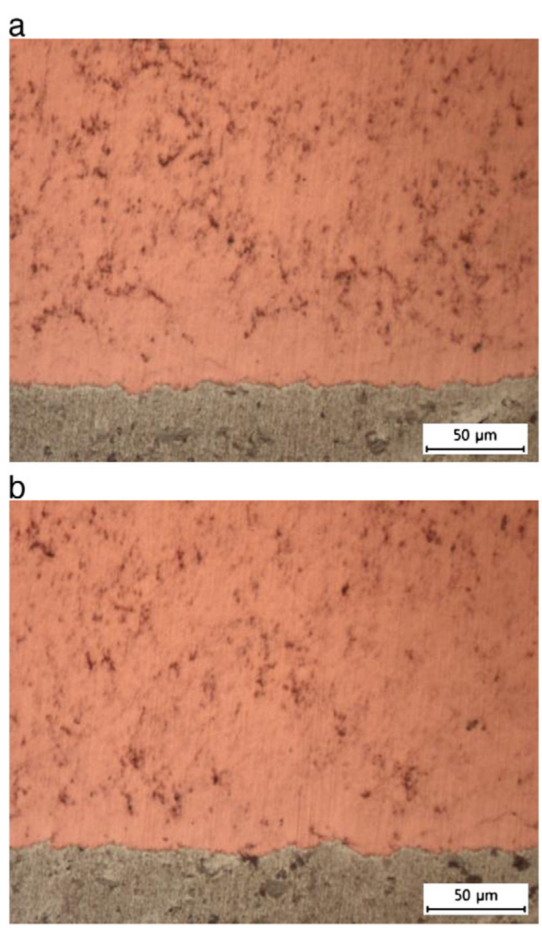

Fig. 3. OM images of Cu coatings with the different conditions of Cu powders. (a) Vacuum annealed (500×), and (b) aged (air exposed during 6 weeks) (500×).

Table 1
Chemical composition measured by XRF of as-received Cu powder.

	Chemical composition (wt.%)
Cu	Bal.
Si	0.0218
Fe	0.0108
Cr	0.0067
Ag	0.0324
Pb	0.0105

Pure Cu powders were sprayed onto the polished Al substrate without any prior sand blasting of the substrate. Compressed air was used as the accelerating gas. The input gas pressure and temperature were fixed at 2.4 MPa and 480 °C. The stand-off distance was 20 mm. Both the nozzle and substrate were stationary during spray. To change the feedstock chemistry, the powders were annealed in a vacuum furnace at 100 °C, 10^{-6} Torr for 6 h. To investigate the time transient chemistry, the vacuum annealed Cu powders were aged in air atmosphere from 1 to 6 weeks with/without vacuum keeping. The relative humidity and temperature were 30% and 25 °C, respectively. The particle size and morphology of the Cu powders were confirmed by scanning electron microscopy (S-2400 SEM, Hitachi, Japan). The morphology of the coatings was observed by optical microscopy (OM). Also, the particle size distribution was measured exactly by laser scattering particle size analysis (HELOS/RODOS, Sympatec GmbH, Germany). The chemical composition of the powders was examined by WD-XRF (ZSX Primus, RIGAKU, Japan). The coating efficiency was determined by weight measurement. 1 g of feedstock was prepared, and the weight of substrate was measured. After spraying, the weight of the coated substrate was measured. Then, the coating efficiency was determined by comparing the weight of feedstock and the difference in weight between initial substrate and coated sample. The hardness was measured using a Vickers hardness tester (HM-122, Akashi, Japan). The powder oxygen content was checked using an oxygen determinator (TC-600, LECO, USA) and the copper and Cu oxide feedstock were analyzed by X-ray photoelectron spectroscopy (SIGMA PROBE, ThermoVG, U.K.).

3. Results and discussion

Fig. 1 shows the SEM image of the as-received Cu powder used in these experiments. The Cu particle morphology was irregular (dendritic) and the particle size was under 50 μm. The Cu powder consisted of a wide distribution of particle sizes, with 90 vol.% less than 47.58 μm, 50 vol.% less than 23.64 μm, and 10 vol.% less than

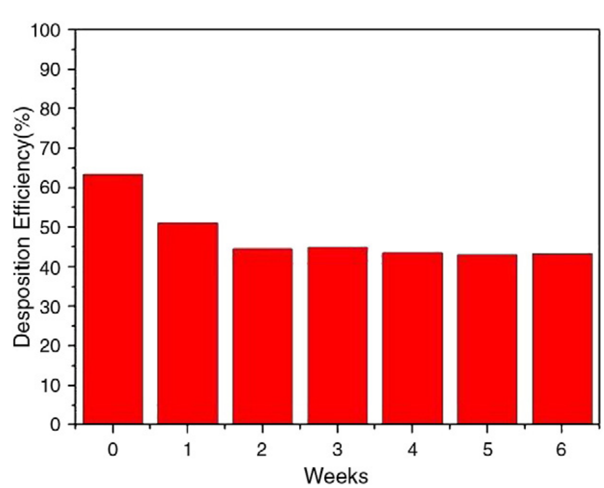

Fig. 4. Deposition efficiencies of Cu coatings using air exposed (aged) raw powder.