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Deposition Behavior of Copper Fine Particles onto Flat Substrate Surface in Cold Spraying

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Cold spray is a promising process to fabricate high-quality metallic coatings. However, it is necessary to improve some properties, especially the adhesive strength of the coating to the substrate to clarify deposition mechanism of the solid particles onto substrate surface. In this study, deposition behavior of the cold sprayed copper fine particles was observed precisely and the adhesive strength of the coating was evaluated. The deposition behavior of the sprayed individual copper particles on mirror polished stainless steel substrate was fundamentally investigated. The interface microstructure between sprayed particle and substrate revealed that an amorphous-like band region was recognized at interface during coating fabrication at high power conditions. For the deposition mechanism of the cold sprayed particles onto substrate surface, it was indicated that the deformation of the particles initially induce the destruction of its surface oxide and an appearance of the active fresh surface of the material may enhance the bonding between particles and substrate. On the other hand, in coating fabrication at high power condition, bonding between particle and substrate may be possibly formed via oxygen-rich amorphous-like layer at interface.

Keywords adhesion strength, cold spray, deposition efficiency, deposition mechanism, metal jet, nanoscratch testing

1. Introduction

Thermal spraying is a versatile technique to fabricate abradable and protective thick coatings for various applications, such as wear, erosion, oxidation, and corrosion-resistant coating. However, change in the chemical composition of the raw materials often occurs in thermal spray process due to the high heating rate or heating over the materials melting point. To overcome such problems, cold spraying has been developed in this decade. In cold spray process, the degradation of the materials can be effectively suppressed because the particles are sprayed in a solid state without melting. To control and improve cold spray process, adhesion mechanism of the particle to the substrate surface have to be verified. The adhesion mechanism of solid particles to the substrate may be affected by some factors, such as mechanical anchoring, elemental diffusion, as reported in previous studies (Ref 1-6). However, it is not completely understood yet.

To establish a controlling way for the cold spray process, adhesion mechanism of the particles to the substrate surface was examined in this study. The coating properties, such as deposition efficiency, adhesive strength, cross section microstructure at coating/substrate interface, were investigated. Therefore by this study, the adhesion mechanism of the cold sprayed particle was verified.

Moreover, to characterize collision behavior of the solid particles to the solid substrate, metal jetting behavior induced at interface between particle and substrate was precisely observed on an individual particle. The relationship between occurrence of metal jet and deposition efficiency of the particles was statistically analyzed. Through the relationship obtained, controlling method for the cold spray process was proposed.

2. Experimental

All the experiments were carried out by a self-designed cold spray system as shown schematically in Fig. 1. Laval-barrel type nozzle was used for the spraying. A nozzle with the barrel length of 300 mm was used for the investigation of the particle deposition mechanism. On the other hand, a special nozzle with barrel length of 100 mm was used to investigate the metal jetting behavior of the particles. The propellant gas was nitrogen and air was used for the powder feeding. Gas pressure was varied between 1.0 and 3.0 MPa, and gas was heated up to 673 K. In application of the cold spray to the electric fields, fundamental knowledge on the

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coating formation by using fine powder is sometimes required, especially for some kinds of devices. Therefore, the raw materials were water atomized spherical copper powders (SFR-Cu, Nippon Atomized Metal Powder Corporation, Noda, Chiba, Japan) with a mean diameter of 5 μm as shown in Fig. 2. Powder feed rate for the coating fabrication was kept at 15 g/min. The substrate material was stainless steel SUS304, which was sand blasted for the coating formation and mirror polished for the particle collection on its surface. Spraying distance was 20 mm and traverse speed of the torch was 20 mm/s for the coating formation. The shear adhesive strength of the coating was evaluated by the specimens with 1 mm thickness × 10 mm × 10 mm, which has a coating on its side surface with thickness of 700 μm. The testing method is shown schematically in Fig. 3. Shear strength was given as a value of the fracture load divided by the rectangular coating area. To know the deformation of the substrate by deposition of individual particle, sprayed particle was removed by a scratching. After the removal of each particle, trace of the particle was analyzed by atomic force microscopy (AFM, Nanoscope IIIa+D3100, Digital Instruments, Woodbury, New York). The focused ion beam (FIB, Quanta 200 3D, FEI Co., Hillsboro, Oregon) was used to prepare the sample for observation of the cross section microstructure of an individual particle. To observe the coating/substrate interface microstructure, transmission electron microscopy (TEM, JEM-2100F, JEOL) was used in the study.

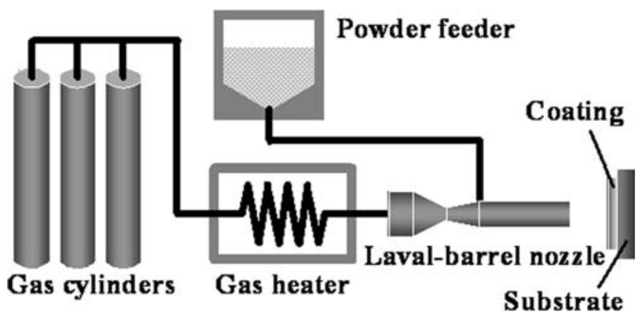

Fig. 1 Schematic of cold spray system

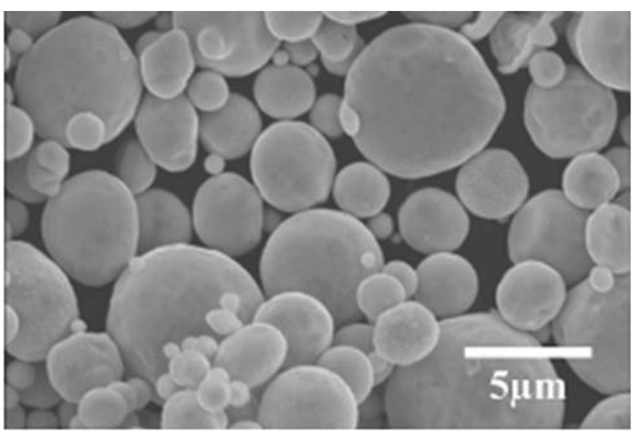

Fig. 2 Morphology of Cu powder used

3. Results and Discussion

3.1 Particle Adhesion Mechanism

First, to clarify the effect of gas pressure on the particles deposition, the relationship between particles deposition efficiency and gas pressure with gas temperature of 673 K was investigated as shown in Fig. 4. It is clear that the deposition efficiency increases with increasing the gas pressure. As it is pointed out that the deposition efficiency generally increases with the particles velocity, it can be estimated in this experiment that the particles velocity increases with the gas pressure. Moreover, shear adhesive strength of the coating was investigated to clarify the effect of gas pressure on the adhesive property. The shear adhesive strength of the coating obtained with gas

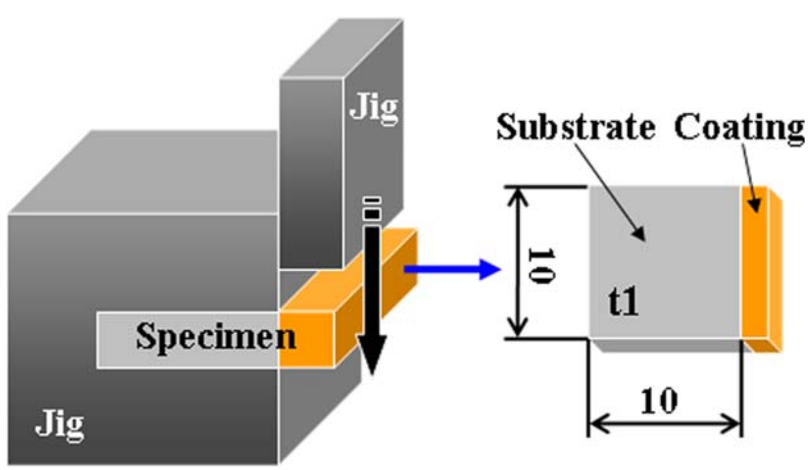

Fig. 3 Schematic of shear adhesive strength test for coating

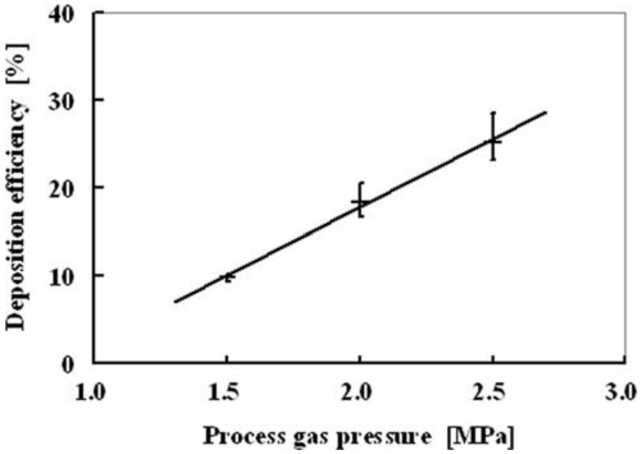

Fig. 4 Dependence of deposition efficiency of coating on gas pressure (Gas temperature, 673 K)

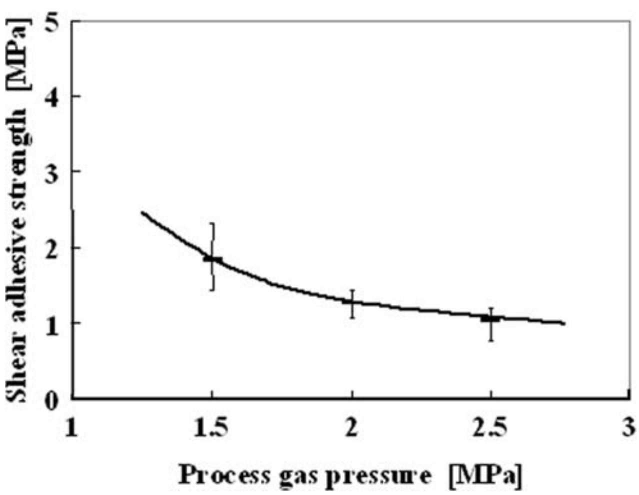

Fig. 5 Dependence of shear adhesive strength of coating on gas pressure (Gas temperature, 673 K)

temperature of 673 K is shown in Fig. 5. It indicates that the coating adhesive strength has relatively low value. This may be attributed to the scattering in the adhesive strength of each particle. As particles with weak adhesive strength are involved inevitably in the coating, those may work as a kind of defect on the mechanical strength of the coating. It is also clear in the figure that the adhesive strength of the coating decreases gradually with increasing the gas pressure. Increase of particles velocity with the gas pressure may cause the residual stress in the coating as a degradation factor. Hereby, the most possible reason may be attributed to the compressive stress induced in the spray process. In fact, spallation of the coating was observed in the worst case.

To clarify the deposition mechanism of the particle on the substrate surface, both trace of the particle on the substrate surface and cross section microstructure of the particle were observed precisely. AFM image on the substrate surface after removing the deposited individual particle is shown in Fig. 6. Color bar in the figure indicates the relative depth from the original surface level. The figure shows that the most deformed part of the substrate under the splat is almost <100 nm. Compare to the particle size, 5 μm, the substrate surface was not remarkably deformed by the collision of the particles. Cross section microstructure of the deposited particles on the substrate surface is shown in Fig. 7. It reveals that no remarkable deformation of the substrate can be observed in the materials combination. These results indicate that the contribution possibility of so-called anchoring effect on the adhesion mechanism of the cold sprayed particle to

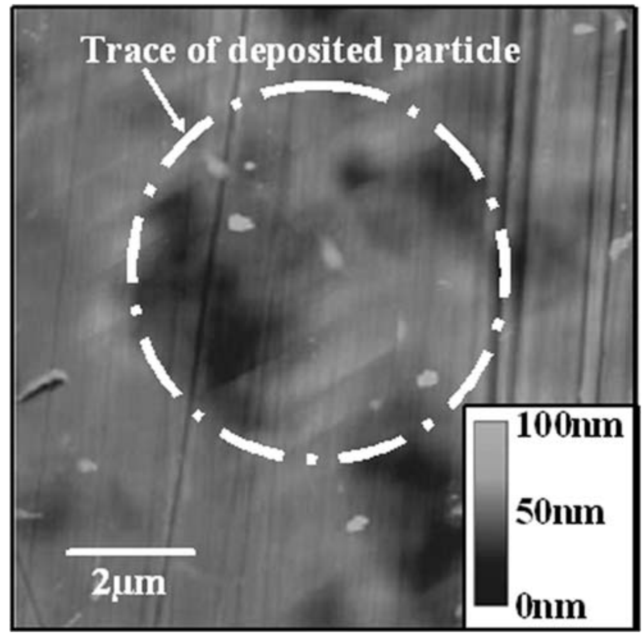

Fig. 6 AFM image of substrate surface after removing individual deposited particle (Gas pressure, 1.5 MPa; Gas temperature, 673 K)

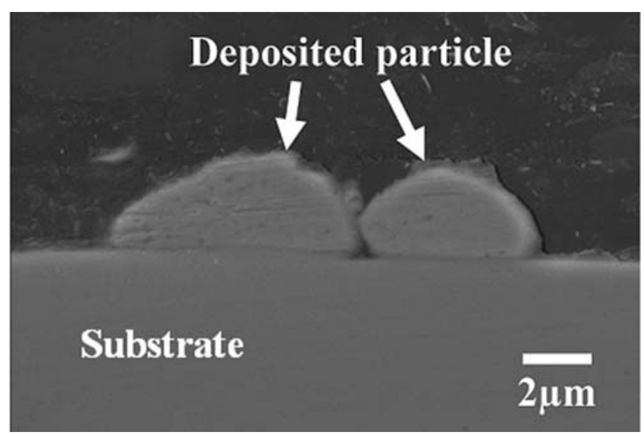

Fig. 7 SEM image of cross section microstructure of individual deposited particle (Gas pressure, 1.5 MPa; Gas temperature, 673 K)

the substrate surface may be quite low, and some other effects may participate. Moreover, Fig. 7 shows that the originally spherical particles adhere onto the substrate surface by deforming its shape. The deformation in the shape from spherical to some flattening shapes induces the increase of surface area, and this surface area increasing induces destruction of the oxide of the particle existed on its surface. The destruction of the surface oxide induces the appearance of fresh surface of the particles material, and bonding may be created by the fresh surface appeared at the interface. However, lower deformation of the substrate and particle may bring about the lower adhesive strength of the coating as shown in Fig. 5.

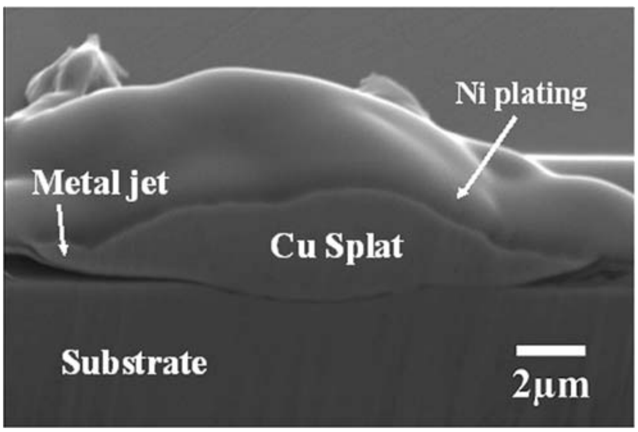

Fig. 8 Cross section microstructure of individual deposited particle

On the other hand, particle deposition with some deformation of the substrate was recognized in the particles with high power spraying conditions. Figure 8 shows the cross section microstructure of the particle which was sprayed under the conditions of working gas He with pressure 2.0 MPa, gas temperature 573 K, and Laval nozzle with length 100 mm. It is recognized from the figure that the collision center of the substrate deforms remarkably and metal jet along the interface between particle and the substrate is observed at the periphery of the flattened particle (Ref 7). In this case, mechanical interlocking mechanism may affect the deposition of the particles to the substrate. The higher adhesive strength is expected in this particle.

To clarify the microstructure, TEM observation on interface region between sprayed particle and substrate was conducted. In this case, substrate was composed of sputtered Ti and Cu both with 100 nm thickness. TEM image for interface region are shown in Fig. 9. Additionally, EDX analysis result on each position was shown in the figure. EDX analysis indicated the existence of oxygen at the interface between particle and sputtered Cu coating as shown in No. 5 in the figure. That is, preferential accumulation of oxygen was recognized at interface. Higher magnified TEM observation result near interface region is shown in Fig. 10. It indicates that the sprayed Cu particle contains sub grains with a few nanometers in size. This refinement may be induced due to the extremely high velocity collision and deformation of the particles onto the substrate surface (Ref 8, 9). Moreover, some amorphous-like layer was recognized at particle and substrate interface, which corresponds to the oxygen enrichment layer at interface as indicated in Fig. 9. Hereby, it is summarized

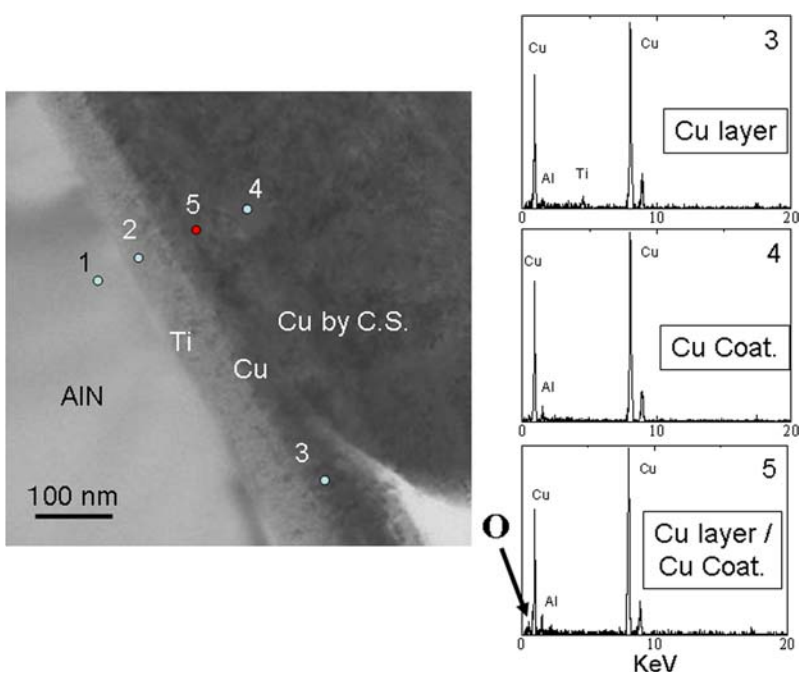

Fig. 9 TEM image at interface region and elemental analyses at each position (Gas pressure, 1.5 MPa; Gas temperature, 673 K)

that the deformation of the particles initially induces the destruction of its surface oxide and an appearance of the active fresh surface of the material may bring about the bonding between particles and substrate fundamentally. However, in the coating with high power condition, the substrate at the collision center deforms remarkably and metal jetting along the interface between particle and the substrate occurs at the periphery of the flattened particle. In this case, mechanical interlocking may affect the deposition and in some case, bonding between particle and substrate is possibly formed via oxygen-rich amorphous-like layer at interface.

3.2 Deposition Control by Metal Jetting Behavior of Particles

Metal jetting generally appeared with remarkable increase in the collision velocity of the cold sprayed particles (Ref 10). On the other hand, it has been pointed out that the deposition efficiency is enhanced with increasing the collision velocity. However, direct relationship between deposition efficiency and appearance of the metal jetting is not always revealed yet. To find way to control the deposition in cold spray process, metal jetting behavior of the particles was investigated fundamentally by using modified cold spray gun which has a special nozzle shape on its exit. Typical observation results of changing the metal jetting appearance with increase of gas pressure is shown in Fig. 11. It is clear that the metal jetting appears remarkably with increasing the gas pressure. To evaluate the metal jetting behavior quantitatively, a fraction of metal jet in deposited particles was measured in each process condition. The fraction of metal jet was defined as the ratio of the number of the particles with metal jet to the total number of the particles deposited on the substrate in measured area. The obtained result is shown in Fig. 12(a) which indicates that the fraction of metal jet increases transitionally with the gas pressure. This increasing tendency may be attributed to the increase of the particles velocity with increase of the gas pressure in the experiment. Under the same conditions, deposition efficiency of the coating was measured with increase of the gas pressure as shown in Fig. 12(b). It is recognized that the deposition efficiency of the coating increases also transitionally with increase the gas pressure. The results of Fig. 12(a) and (b) show that the changing tendency of the fraction of metal jet and the deposition efficiency correspond well with each other. This correspondence in both values may be attributed to the particles velocity which acts as an essential factor in the cold spray process. Therefore, the positive control and high efficiency coating formation are possible by setting the spray conditions in which the metal jetting preferentially recognized on the collision of an individual particle onto the substrate surface.

Finally, with using the modified nozzle, the effect of flattening behavior of the particle on the coating adhesive strength was investigated. The adhesive strength average of the coating was almost 6-7 MPa regardless of the gas

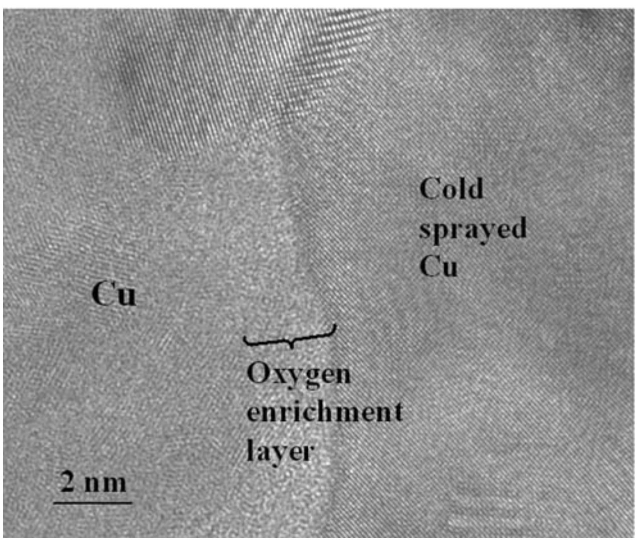

Fig. 10 Magnified cross section microstructure at interface region

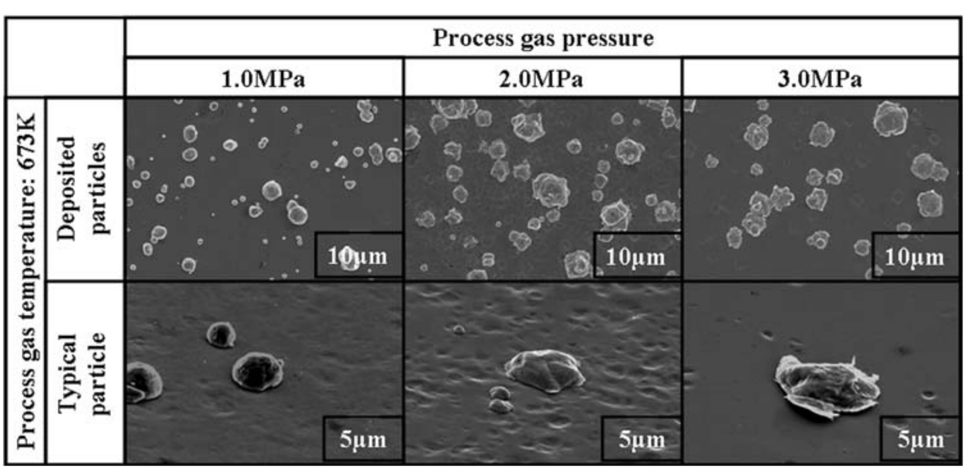

Fig. 11 Flattening behavior of typical deposited particle (Gas temperature, 673 K)

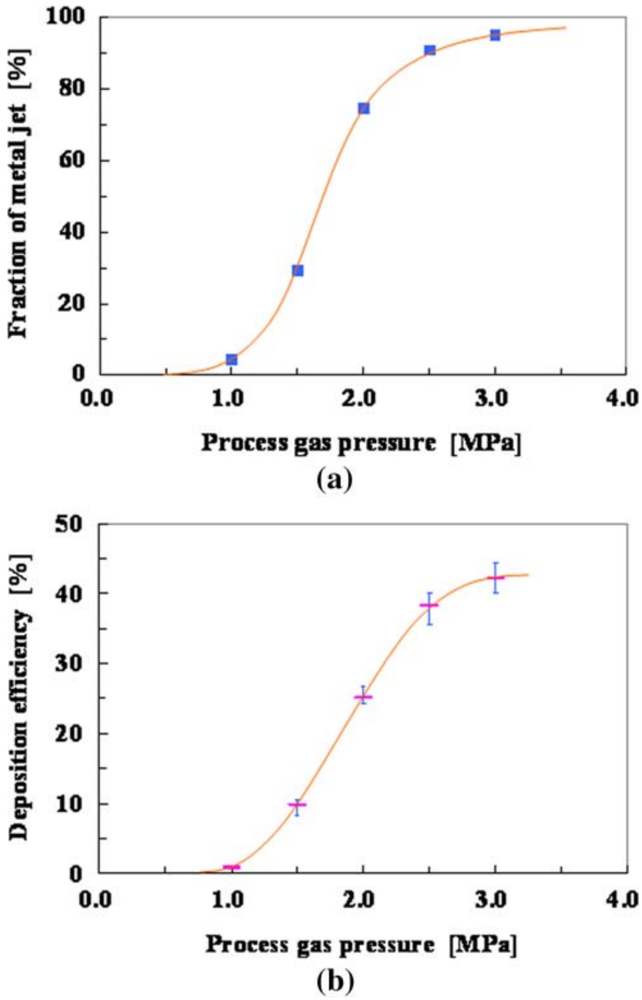

Fig. 12 Dependence of (a) fraction of metal jet in deposited particles, (b) deposition efficiency on gas pressure (Gas temperature, 673 K)

pressure. The result indicates that the flattening shape affect weakly to the adhesive strength of the coating. Some other factors, such as a residual stress, which may be induced in the spraying stage, may affect more on the adhesive property than the individual particles flattening behavior in the cold spraying process.

4. Summary

Deposition behavior of copper particles onto metal substrate surface by cold spray process was investigated precisely, and deposition mechanism was discussed from several viewpoints. Furthermore, to establish the deposition control in cold spray process, metal jetting behavior of the particles relating to some process factors was fundamentally investigated. The results obtained are summarized as follows:

(1) During coating fabrication at low power conditions, deformation of the particles initially induce the destruction of its surface oxide and an appearance of the active fresh surface of the material may induce the bonding between particles and substrate. On the other hand, during fabrication of the coating with high power conditions, the substrate at the collision center deformed remarkably and metal jetting along the interface between particle and substrate occurred at the periphery of the flattened particle. In this case, mechanical interlocking may affect the deposition and in sometimes bonding between particle and substrate is possibly formed via oxygen-rich amorphous-like layer at interface.

(2) The changing tendency of the fraction of metal jet and the deposition efficiency corresponded quite well with each other, which indicate that the evaluation result of the metal jetting behavior of an individual particle can be useful for estimating the deposition property of the cold spraying.

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