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Behavior of Porosity and Copper Oxidation in W/Cu Composite Produced by Plasma Spray

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A spherical tungsten (W)/copper (Cu) composite powder was plasma-sprayed onto a boron-nitride-coated graphite substrate to produce heat sink material for the electronic packaging by atmospheric plasma spray using different input powers. At the surface of the deposited layer, Cu became oxidized to cuprite (Cu_2O). The degree of oxidation at the surface layer did not vary significantly with input power. Very little Cu_2O was detected at the inner layers after grinding off the 70 µm from the surface. The input powers had a strong effect on the porosity in the deposit layers. The porosity in the deposit layers at 25 kW was very small, about 3 vol%. The microstructures of W/Cu composite were discussed.

Keywords cuprite, oxidation, plasma spray, porosity, spherical tungsten/copper composite powder

1. Introduction

Tungsten (W)/copper (Cu) composite has been used for heat dissipation materials in microelectronic devices, diverter plates as plasma facing components in thermonuclear fusion reactors, and warhead materials in the military field.[1] It is suited to these applications because it has (a) a low coefficient of thermal expansion ($\sim 6 \times 10^{-6}$ /K) as an electronics substrate, similar to that of gallium arsenide, (b) a fairly high thermal conductivity (160 W/mK for W) and very high melting temperature (3410 °C for W), (c) a high energy threshold of hydrogen sputtering, (d) a low vapor pressure, and (e) ductility and high strength.

The manufacturing methods[2,3] for metal matrix composites include powder metallurgy, co-spray, squeeze casting, compocasting, liquid pressure forming, pressureless infiltration, solid-state diffusion bonding. W/Cu composites have usually been fabricated by the infiltration of a desired tungsten shape (skeleton) with liquid Cu to achieve full densification. However, the composite needs several subsequent processing steps (compaction, sintering, and infiltration) that require considerable energy and high cost.[4,5] Compared with this infiltration, a plasma spraying process that directly sprays powders onto substrates has major advantages for the formation of thin or thick layers in some industrial applications.[6-8] Plasma spray coating has a strong mechanical bonding and a high deposition rate, can form functionally gradient materials, and can cover a large area.[9] R.G. Castro et al.[10] and Yoshiyasu Itoh et al.[11] reported that atmospheric plasma spraying of tungsten and copper powders causes surface oxidation. They did experiments injecting W and Cu powders separately in the low-pressure plasma spray (LPPS) jet to decrease the oxidation and porosity. But compared with our atmospheric plasma spray, LPPS is limited in the surface area due to the chamber. In addition, LPPS did not significantly decrease the porosity in the coatings. They did not evaluate the oxidation between the surface and inner layer of the LPPS coatings.

In the present work, we used a spherical W/Cu composite powder as a powder raw material. The purposes of this research are to decrease the porosity, to characterize the oxidation between the surface and inner layer, and to control the chemical composition uniformly in the coatings, using atmospheric plasma spray.

Table 1 Plasma Spraying Parameters

Classification	Condition
Power	25, 30, 35 kW
Primary gas flow rate	Argon-75psi, 70.8 l/min
Secondary gas flow rate	Hydrogen-50psi, 1.98, 3.54, 6.66 l/min
Carrier gas	Argon-100psi, 14.16 l/min
Spray distance	100 mm
Powder feeding rate	25 g/min
Traverse rate	30 mm/s

2. Experimental Procedures

The starting powder (spherical shape produced by spray-drying process, 72W-28Cu vol%, −325 mesh) was dried in an oven at 100 °C for 24 h in air to protect against powder clogging in the powder feed hose and oxidation from surface moisture during plasma spray. The dried powder was introduced into the plasma spray gun (9 MB) by argon carrier gas after the substrate was preheated to a stabilized temperature (230 °C at 25 kW, 335 °C at 30 kW, and 350 °C at 35 kW, respectively). The plasma spray parameters are listed in Table 1. The graphite substrate (100 × 80 × 20 mm), which contains a Cu tube (diameter: 12 mm) inside with an inserted thermocouple, was specially designed to control the substrate temperature.

The substrates were coated with boron nitride (BN) to protect against the formation of tungsten carbides at the interfaces between the substrates and sprayed layers. Tap water was flowed through the copper tube to stabilize the temperature at the substrate during plasma spraying. The BN-coated substrate plates were coated with the W/Cu composite by a plasma spray gun controlled by a computer program, which moves the gun in *x* and

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y directions. The deposit layers were separated from the graphite substrates and the cross section and inner surface layer were examined by image analysis. The thickness of the sprayed coating layer was about 1 mm. A JEOL 8600 scanning electron microscope (SEM) and Nikon Epiphot 200 optical microscope were used to characterize the microstructures, porosity, and the volume fraction of W and Cu in the deposits. Phases at the sectioned surfaces and inner layers were identified by a Rigaku x-ray diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm) at 36 kV and 26 mA. The Lasertec (Model: VL2000, Japan) (Korea Institute of Machinery and Materials, Changwon, Korea) was used to measure the surface roughness of the sprayed layers.

2.1 Preparation of Spherical Tungsten/Copper Composite Powder

There is an insolubility and large density difference between W (density: 19.3 g/cm^3) and Cu (density: 8.96 g/cm^3). To achieve homogeneous W distribution in the plasma sprayed layers, it is necessary to use a spherically agglomerated W/Cu composite powder. Thus the spray-drying process, which utilizes well-dispersed materials to be agglomerated and organic binder, was applied. Polyvinyl alcohol of 0.5 wt.% in distilled water as a binder was added. W powder (<1 μm, purity 99.9%) and Cu powder (<45 μm, purity 99.9%) were mixed in a proper ratio (72W-28Cu vol.%) and ball milled in the steel container with cemented tungsten carbide balls (diameter: 8 mm) at a ball-to-powder weight ratio of 1:1 for 20 h Centrifugal atomization was used with nitrogen as a drying gas at the temperature of 200 °C and rotating disc speed of 10 000 rpm. The collected powder was investigated by the Coulter LS-130 particle size analyzer and SEM.

3. Results and Discussion

3.1 Powder Characterization

It is very difficult to plasma spray small particles (<1 μm) because they stick to each other and cause clogging in the powder feed hose. Therefore, spherically agglomerated W/Cu composite powder was synthesized. The particle size distribution of the W/Cu composite is inhomogeneous as shown in Fig. 1. Most particles are below 25 μm diameter. The spray-dried granules

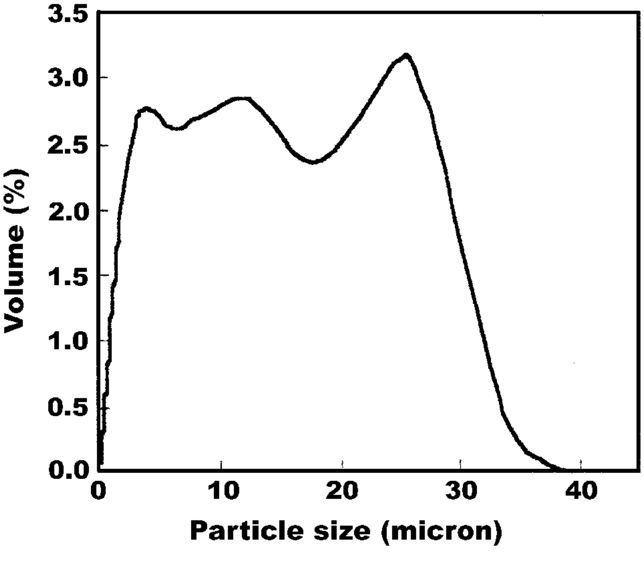

Fig. 1 Particle size distribution of powder

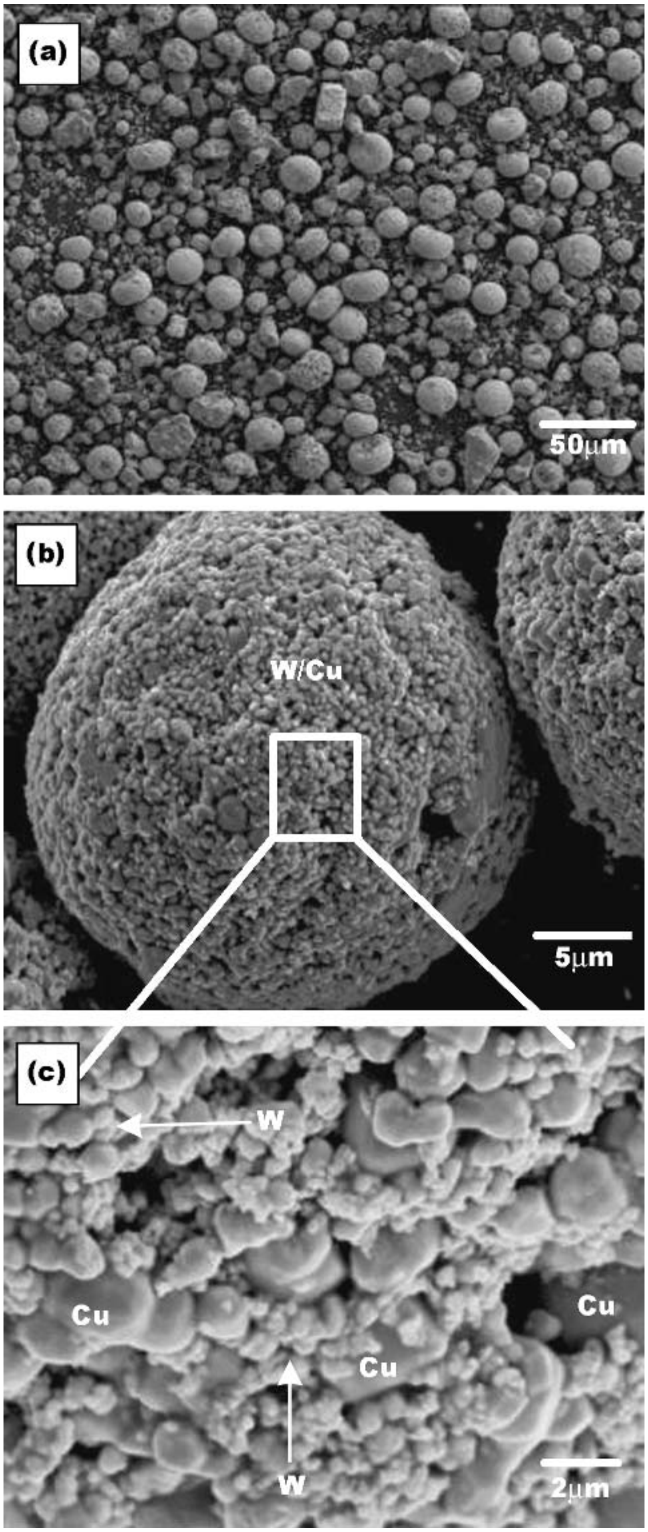

Fig. 2 SEM image of 72W-28Cu powder

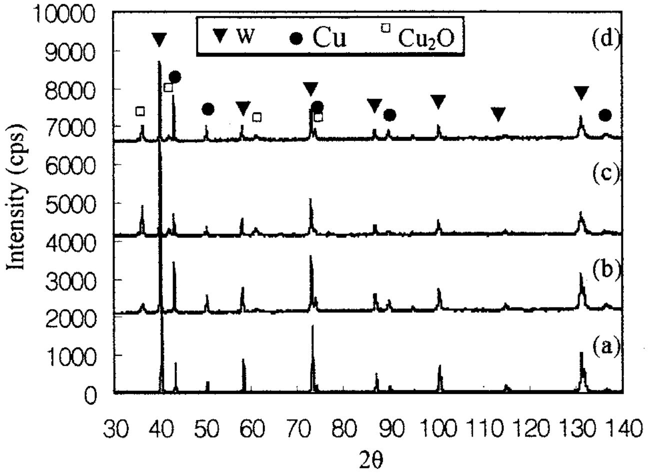

Fig. 3 X-ray diffraction patterns of **(a)** powder, **(b)** 25 kW, **(c)** 30 kW, and **(d)** 35 kW input powers

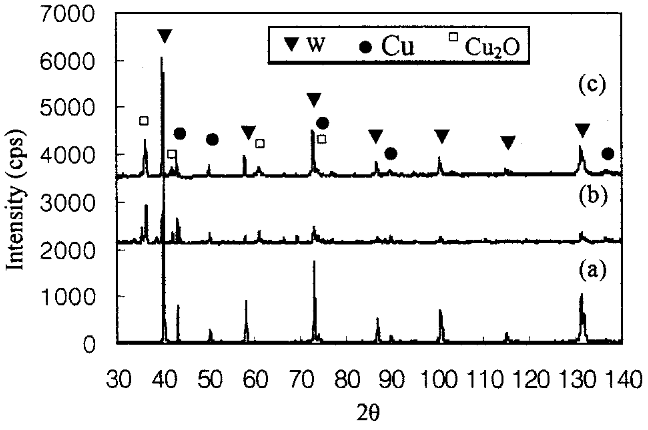

Fig. 4 X-ray diffraction patterns of **(a)** powder, **(b)** deposit layer from the powder, and **(c)** deposit layer from dried powder at 30 kW input power, respectively

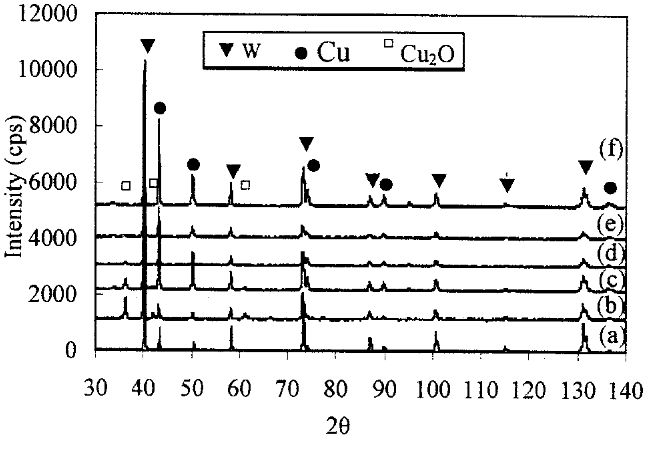

Fig. 5 X-ray diffraction patterns of **(a)** powder, **(b)** surface layer, and grinding surface **(c)** 20 μm, **(d)** 50 μm, **(e)** 140 μm, and **(f)** 200 μm off.

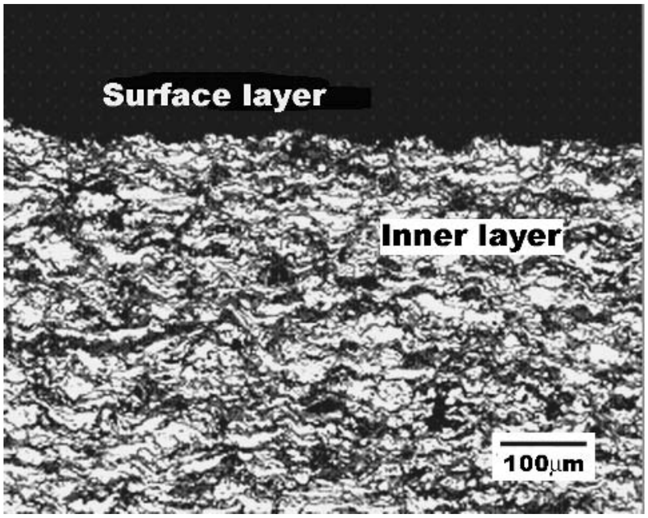

Fig. 6 Optical image of the cross section of deposit layer at 30 kW

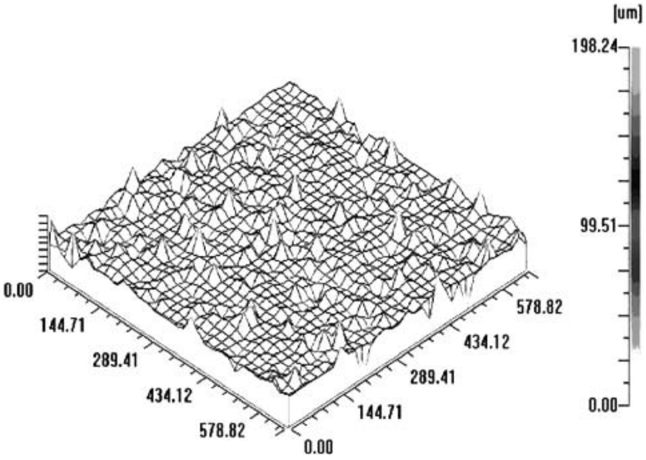

Fig. 7 Profile showing surface roughness

are spherical as shown in Fig. 2(a). Tungsten and copper particles are agglomerated in the large spherical particles in Fig. 2(b). At high-magnification tiny W particles (<1 μm) are bonded to each other with some large Cu particles, as shown in Fig. 2(c). It indicates that smaller W particles combined with larger Cu particles can be melted more easily than larger W particles in the plasma flame.

3.2 X-Ray Diffraction Analysis

Heat sink composite materials generally require a proper composition, low porosity, low oxidation, and homogeneous microstructure to achieve the required thermal properties (especially to have a similar coefficient of thermal expansion and higher thermal conductivity relative to electronics substrates) and mechanical properties. Cuprite (Cu_2O) was found at the surface layer, as shown in Fig. 3. As input power was increased, the amounts of cuprite were not changed significantly. Tungsten oxides were not detected at the surface.

The formation of cuprite in the atmosphere is most likely the result of these reactions:

$$2Cu + H_2O = Cu_2O + H_2 \quad \text{(Eq 1)}$$

$$H_2O = 2H + O \quad \text{(Eq 2)}$$

If the powders contain enough moisture, the oxidation could occur more strongly during droplet solidification. To confirm the effect of the moisture in the powder, we plasma-sprayed the undried powder and dried powder. There were some differing peaks between two specimens, as shown in Fig. 4. However, the main peaks show W, Cu, and cuprite in the same way.

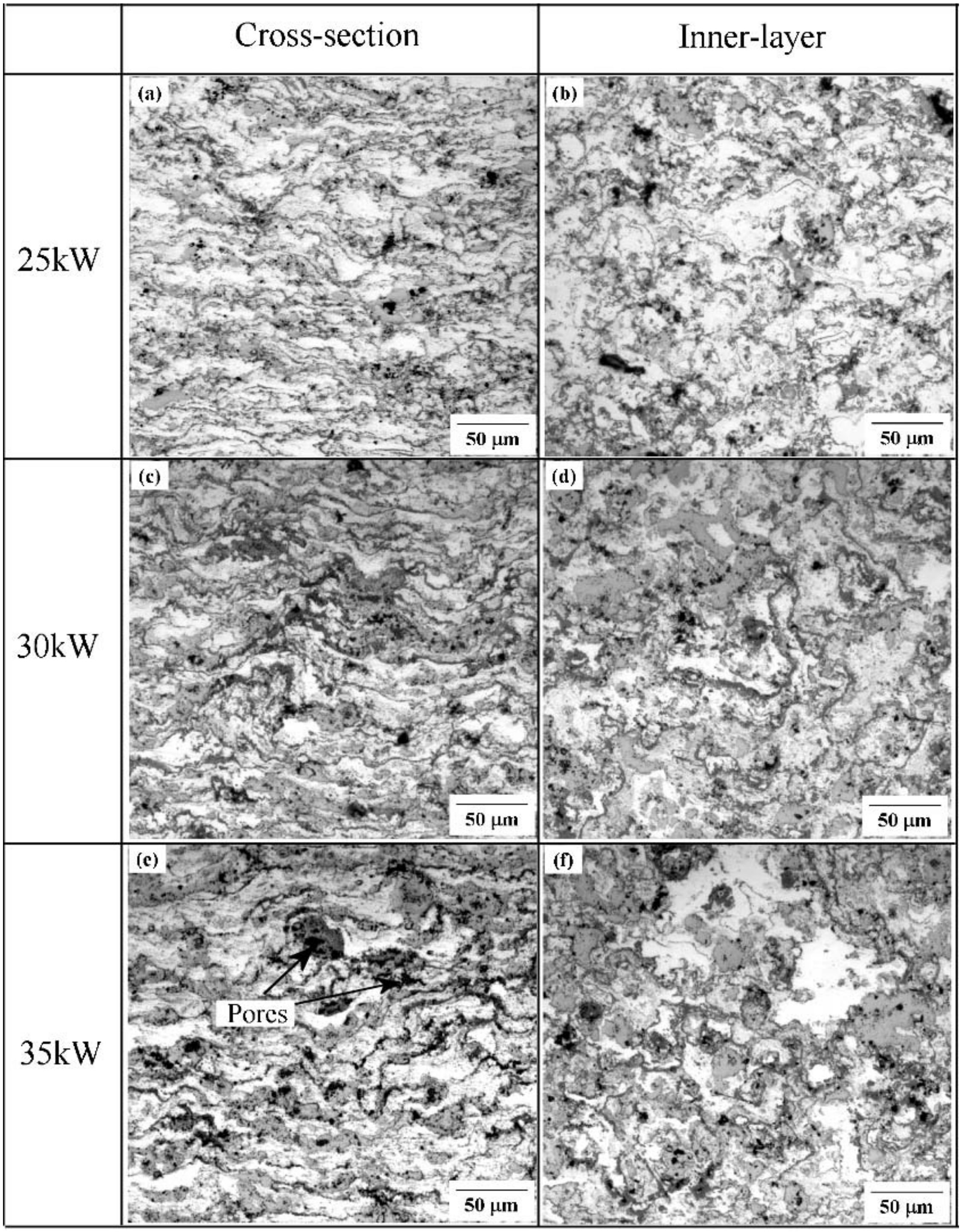

Fig. 8 Optical images of plasma spray deposits as function of input power after grinding the deposit surface 200 μm off

After 70 μm of surface layer was ground off, the cuprite was hardly seen at the inner layer as shown in Fig. 5.

Many researchers[10,11] have mentioned copper oxides in the coating, but they did not evaluate the oxidation between the surface and inner layer of coatings. We did measure the oxidation between them, and we found almost no oxidation at the inner layer. The reason for the absence of the cuprite at the inner layer is that there is not enough time for oxygen (O) to react with oncoming and overlapping molten particles during continuous plasma spraying with high temperature and rapid solidification of liquid droplets in the range of 10^5−10^6 K/s.[12] At the outer coating surface, however, there is enough time for O to react with Cu in air after plasma spraying. According to Jian Li et al.,[13] Cu was first oxidized to Cu_2O at 200 °C and then to CuO at 300 °C near the surface of the Cu during heat treatment in air. Furthermore, they investigated the oxidation kinetics of Cu thin film at temperature below 300 °C, finding that the oxidation of Cu thin film was time-dependent. In the present work, CuO was not observed at the surface layer. It seems that the rapid solidification reduced the temperature below 300 °C by cooling the deposit layer with compressive argon gas flow at the deposit surface from spray gun after finishing spraying for a few minutes.

3.3 Microstructure

The microstructure in the cross section of deposit layer at the input power of 30 kW is seen in Fig. 6. Over the cross section the tungsten particle distribution in the deposit is homogeneous. The relatively smooth surface profile is presented in Fig. 7. The roughness of the surface Ra was 15.74 μm. Although several pores of about 5 μm are observed as shown in Fig. 8, the volume fraction of the porosity described in Fig. 9 is about 3-6 vol%, which is relatively small compared with the porosity of 14 vol% from Yoshiyasu Itoh et al.[11] They plasma sprayed W particles of 32.5 μm and Cu particles of 55 μm separately, while we used the agglomerated W/Cu composite particles consisting of tiny tungsten and copper particles. As input power was increased, the volume fraction of porosity and W content increased as shown in Fig. 9. At the input power of 25 kW only a small percentage of the injected W particles were melted, and many W particles remained solid due to insufficient energy to melt the tungsten particles. As a result, 42 vol% W was contained in this deposit from injecting 72W-28Cu vol% powder, while 50 vol% W was obtained in the deposit at 30 kW. Pores were found near the W-rich locations due to the immiscibility and large thermal expansion mismatch between the W and Cu (4.5 and 21.0 × 10^{-6} /K, respectively). During plasma spraying, Cu powders were completely melted but W powders were melted partially due to the high melting temperature of 3410 °C with the different particle size distribution, as shown in Fig. 1. In addition, either individual molten W droplet or partially melted W powders segregate due to insolubility between W and Cu, as shown in Fig. 10. Numerous, larger pores were found as shown in Fig. 8(e) and 8(f). To lower oxide content, and to achieve higher thermal conductivity and high velocity of particles in the plasma jet, the input power was increased by changing hydrogen flow rate to 6.6 l/min from 1.98 l/min, setting argon flow rate at 70.8 l/min as shown the experimental parameters in Table 1. It seems that especially the pores in and near the W grains are caused by rapid quenching and agglomeration of solid W particles. Compared with Fig. 8(a), more coarse W grains were exhibited in Fig. 8(e). The tungsten grains were grew to about 50 μm at 35 kW from

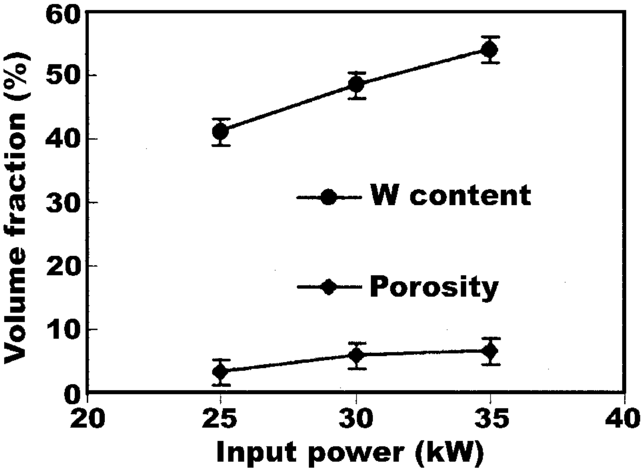

Fig. 9 Tungsten content and porosity as function of input power

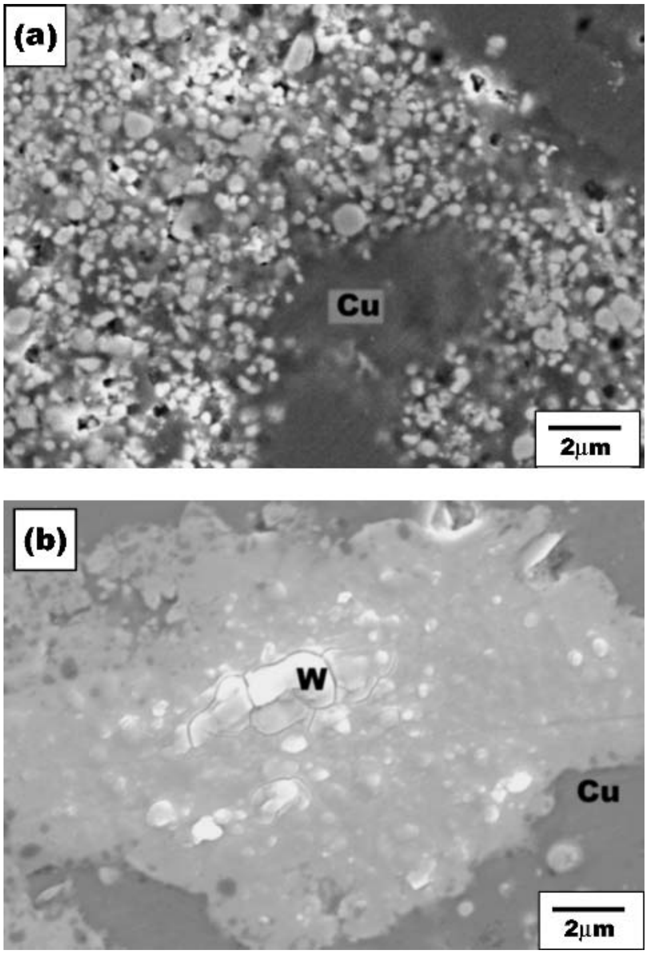

Fig. 10 SEM images of the inner layers from the different input powers: **(a)** 25 kW and **(b)** 35 kW

about 20 µm at 25 kW of input power. This explains why more W powder particles are melted at the input power of 35 kW than 25 kW as shown in Fig. 10(b). The prevalent pore sizes were about 5 µm at both 25 and 35 kW.

4. Conclusions

We found it feasible to apply atmospheric plasma spray for economically producing heat sink materials of tungsten/copper composites. The following conclusions can be derived from our work.

- A spherical W/Cu composite powder (−325 mesh) consists of agglomerated tiny W and Cu particles.
- W/Cu composite deposit layers with less porosity (about 3-6 vol%) and homogeneous compositions as well as uniform microstructures were developed using atmospheric plasma spray.
- Cuprite (Cu_2O) was formed at the outer surface layer, but almost no cuprite was detected at the inner layer after grinding the surface 70 µm off. Changing the input power did not affect the amount of oxidation significantly.
- Larger W grains were resulted as input power was increased. The prevalent pore size of the deposit layer was about 5 µm and most pores were found in and around the tungsten grains.
- The surface roughness of deposit layer (Ra) was 15.74 µm.

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