Diamond-Reinforced Metal Matrix Bulk Materials Fabricated by a Low-Pressure Cold-Spray Process

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Fully densified diamond-reinforced aluminum (denoted as Al-D) matrix bulk materials were successfully fabricated using a low-pressure cold-spray process. Two different temperatures of the processing gas were used in order to deposit the Al-D composite powders, and the thermophysical properties of the Al-D bulk materials were investigated. The interfaces between the matrix and reinforcement were observed by scanning electron microscopy in order to understanding of the relationship between the thermophysical properties and microstructure. The thermophysical properties of the Al-D bulk materials were better than those of pure Al processed under the same conditions. We believe that this cold-spray process can be successfully applied for fabricating Al-D bulk materials. [doi:10.2320/matertrans.M2014145]

(Rceived April 21, 2014; Accepted October 14, 2014; Published November 21, 2014)

Keywords: diamond, aluminum, Vickers hardness, cold-spray process, thermophysical properties

1. Introduction

Rapid improvements in electronic devices have been realized, but even better performance is required in many industries in order to realize a better digital experience. Higher-performance devices are being developed in order to minimize the device size and maximize device reliability and lifetime.1,2) Heat control is a critical issue because heat can directly affect the performance and lifetime of the device or part.3)

Copper and aluminum are widely used as heat-sink materials in electronic parts. The thermal conductivity of Cu (400 W/(m K)) is higher than that of Al (230 W/(m K)), and the densities of Cu and Al are 8900 kg/m³ and 2700 kg/m³, respectively. Some composites and alloys based on Cu and Al are being used as high-performance heat-sink materials and have shown good performance.4-6) However, the need for materials that can rapidly release heat from the devices with no detrimental side effects on device performance and that also facilitate facile mass production still persists. Diamonds possess a high thermal conductivity (~2200 W/(m K)) and a low coefficient of thermal expansion (CTE) ([1.0–2.3] × 10⁻⁶°C), and they are thermally stable.7,8) Many researchers have therefore focused their attention on diamond-reinforced materials in order to realize next-generation super-heat-sink materials that can be fabricated through casting and sintering processes.9,10)

Cold spraying is a relatively new process, and considerable research and development is needed to fully understand and control the process. In a low-pressure cold-spray process, the powder particles are sent through a high-velocity gas jet and collide with the substrate.11) This process is suitable for spray depositing temperature-sensitive materials such as nanoparticles and oxygen-sensitive materials such as Al.11)

Typical pressures in low-pressure cold spraying are less than 1 MPa, and the process is considerably simpler and more accessible than high-pressure cold spraying.11,12) Moreover, the number of structural defects is expected to be low because the applied pressure is low.11)

In this study, we fabricated Al-D bulk materials using a low-pressure cold-spray process, and the microstructure and thermophysical properties of the Al-D bulk obtained are discussed. However, the main purpose of this study is to investigate the possibility of producing Al-D bulk composite material by a low-pressure cold-spray process.

2. Materials and Methods

A gas-atomized Al powder (purity 99.7%, average particle size 34 µm, Poudres Hermillon, France) was used as the matrix material. Single-crystal MBD6 diamonds (average size 35–45 µm) manufactured by Henan Hengxiang Diamond Abrasive Co. Ltd., China, were used. The Al-D mixture was prepared with a fixed diamond volume fraction of 10% using tubular mixing equipment and mixing for 24 h (Turbula Shaker/Mixer Model T2C, Willy A. Bachofen AG, Maschinenfabrik, Germany). The obtained Al-D powder mixtures were deposited using self-made cold-spray equipment with 0.6 MPa compressed air as the carrier gas, as shown in Fig. 1. A tungsten carbide circular exit nozzle with a diameter of 4.8 mm was used for the spraying. The powders were sprayed without pretreatment onto a pure Al 1050 substrate using air flowing under a low pressure of approximately 0.5–0.6 MPa and a spray distance of 30 mm (1–6 g/min deposition rate). Two spraying gas temperatures, 220°C and 290°C, were employed to compare the effect of temperature. Pure Al powder was also prepared under the same conditions for comparison.

The density of the cold-sprayed Al-D bulk materials was measured based on the Archimedes principle after removing the substrate by machining. The thermal diffusivity of
samples with a diameter and thickness of 6 mm and 2–4 mm, respectively, without the substrate (size effect ignored) was measured in the direction vertical to the particle-deposition direction at room temperature using the Laser-Flash method (LFA 457 MicroFlash®️, NETZSCH, Germany). A CO₂ laser with a power intensity of 50 W and a maximum pulse of 10 ms was used. The thermal conductivity (λ) was calculated using the following equation:13)

\[ \lambda = k \times \rho \times C_p \]  

where \( k \) is the thermal diffusivity of the composite material and \( \rho \) and \( C_p \) are the density and specific heat of the samples, respectively. The CTE of the samples was measured with a differential dilatometer (DIL 402 CD, NETZSCH, Germany) using a heating rate of 2°C/min and a heating range from room temperature to 250°C in an argon atmosphere. The sprayed pure Al and Al-D bulk materials were observed by scanning electron microscopy (SEM JSM-840A, JEOL Co. Ltd., Japan). The macro Vickers hardness of the composites were measured according to EN ISO 6507-1 with loads of 20 kg, applied for 15 s (220, GNEHM Härteprüfer AG and Paar MTH4 microhardness tester).

3. Results and Discussion

The gas-atomized pure Al particles had irregular shapes with a broad particle-size distribution, whereas the MBD6s showed various angular shapes, as can be seen in Figs. 2(a) and (b), respectively. Overall, the MBDs were well dispersed among the pure Al particles after tubular mixing, without the need for an added process control agent (Figs. 2(c) and (d)). It is to be noted that this simple tubular mixing is sufficient to produce Al-D mixtures without serious agglomeration.

Figure 3 shows the Al-D bulk materials deposited onto the Al 1050 substrate by the cold-spray process. The pure Al and the Al-D specimens showed similar thicknesses (around 9 mm) when cold sprayed at 220°C (Figs. 3(a)–(d)). The deposition thickness of the Al-D sample cold sprayed at 290°C (around 3.5 mm) was less than that of the Al-D sample cold sprayed at 220°C (Figs. 3(c)–(f)). The bulk materials of pure Al deposited at 220°C and Al-D deposited at 290°C showed porosities of approximately 4% and 2%, respectively.

It is very difficult to keep the fixed volume fraction of 10% diamond in the deposited bulk due to difficulty of cold
spraying of hard diamond particles and density difference of the Al and D powders. Because of this reason, the D fraction will be changed after cold splay. Thus, it should be handled carefully in case of the mixture of soft and hard powders under the cold spray process. The highest density value was therefore achieved from the Al-D bulk material deposited at 290°C. Despite achieving close to full density, the thickness of the Al-D bulk material deposited at 290°C sample was the lowest. It is estimated that the thickness of Al-D could be controlled by controlling the experiment temperature parameters. The fly-off rates (nondeposition rate) of the powder particles are somewhat higher in the case of a high-temperature process as a result of the low viscosity and large fluidic flow when the powder particles are sprayed onto the Al substrate. Furthermore, it is very difficult to measure the actual deposition temperature of the powder particles during processing. However, based on our observations, the deposition temperature can be assumed to be around 200°C and/or 270°C, which are lower than the temperature of air gas.

Thermal measurement samples were prepared by machining from the deposited bulk materials. The thermal diffusivity of Al-D cold sprayed at 220°C was slightly higher than that of pure Al. The Al-D cold sprayed at 290°C showed an almost 50% increase in thermal diffusivity as compared to Al-D cold sprayed at 220°C, as indicated in Table 1. It is estimated that the processing temperature is one of the key factors affecting thermal diffusivity and the thickness of the Al-D bulk materials fabricated using the cold-spray method. The thermal conductivity of the bulk samples was calculated with theoretical $C_p$ values based on the eq. (1). The highest value was achieved for Al-D cold sprayed at 290°C, and this value is almost 50% higher than that of Al-D cold sprayed at 220°C, as indicated in Table 1. In case of Al-D cold sprayed

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (kg/m³)</th>
<th>Relative density (%)</th>
<th>Thermal diffusivity (mm²/s)</th>
<th>$C_p$ (J·g⁻¹·k⁻¹)</th>
<th>Thermal conductivity (W/mK)</th>
<th>CTE</th>
<th>Vickers Hardness (HV10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al Bulk@220°C</td>
<td>2700</td>
<td>96.0</td>
<td>37.9</td>
<td>0.9</td>
<td>91.8</td>
<td>24.1</td>
<td>30</td>
</tr>
<tr>
<td>Al-Diamond Bulk@220°C</td>
<td>2780</td>
<td>95.6</td>
<td>40.4</td>
<td>0.82</td>
<td>92.7</td>
<td>19.8</td>
<td>59</td>
</tr>
<tr>
<td>Al-Diamond Bulk@290°C</td>
<td>2780</td>
<td>98.1</td>
<td>60.2</td>
<td>0.82</td>
<td>142.2</td>
<td>17.4</td>
<td>91</td>
</tr>
</tbody>
</table>
at 220°C, the thermal conductivity was only 1% higher than that of the pure Al bulk. Further, the thermal conductivity of the Al-D bulk material cold sprayed at 290°C was lower than that of the pure Al sample fabricated by a conventional casting process (230 W/(m K)).\textsuperscript{14} Even though we achieved lower porosity (~2%). In general, thermal performance is directly related to the interfacial properties. If the reinforcing material is not strongly connected with the matrix material, heat transfer between the matrix material and the reinforcement remains inefficient, even if the porosity of the sample is very low. We observed grain boundaries in the pure Al bulk and many pores, as shown in Figs. 4(a)–(c). The observed pores may act as barriers to continuous heat transfer through the Al-D interfaces when the materials were exposed to a high temperature. In general, Al is easy to oxidize in air at room temperature synthesizing Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{15} However, we could not avoid this problem after mixing of the Al-D powders and during cold spraying because the synthesis was carried out in open air, leading to oxidation of Al. An inert or reducing atmosphere during synthesis should therefore offer better thermal properties.

Fewer pores (including etchant grooves) were found in Al-D cold sprayed at 290°C (Figs. 4(d)–(i)) after slight deep etching with 5% NaOH owing to the difficulty in observing the microstructure, which corresponds with the lower porosity result achieved by the Archimedes principle, as indicated in Table 1. Diamonds were observed on the polished surface of the Al-D bulk. The interface between the Al matrix and the diamond reinforcement exhibited good adhesion, as can be seen in Figs. 4(h) and (i). However, some regions (shown by the white arrows in Figs. 4(h) and (i)) were not well bonded owing to the presence of Al\textsubscript{2}O\textsubscript{3}. It is difficult to form a strong bond between Al\textsubscript{2}O\textsubscript{3} particles and metallic Al owing to strong ionic interatomic bonding.\textsuperscript{16} The poorly bonded regions and micropores were originally formed during the cold-spray process or they were created by the mechanical polishing step, as shown in Figs. 4(h) and (i) (white arrows and circles). Moreover, it is also possible that, if Al\textsubscript{2}O\textsubscript{3} exists at every boundary, it will hamper thermal transfer through the Al/Al and Al/D interfaces. The bond between Al and the diamonds is mechanical, and this mechanical bonding is not enough to allow proper thermal transfer through the interface. Also, these interface connections are easily removed, even during the mechanical polishing step. Because of the above reasons, we achieved lower thermal conductivity with a relatively high density.

The CTE of the obtained pure Al bulk (24.1 $\times 10^{-6}$\(^\circ\text{C}^{-1}\)) was slightly higher than the value reported in the literature (23.1 $\times 10^{-6}$\(^\circ\text{C}^{-1}\)).\textsuperscript{13,17} Lower CTE values of 19.8 $\times 10^{-6}$\(^\circ\text{C}^{-1}\) and 17.4 $\times 10^{-6}$\(^\circ\text{C}^{-1}\) were achieved in the case of Al-D bulk materials fabricated at 220°C and 290°C, respectively. These results imply that the mechanical interfaces in the samples could enhance the CTE; however, these CTE values of the Al-D bulk materials are still six times higher than the CTE of silicon chips (4.0 $\times 10^{-6}$\(^\circ\text{C}^{-1}\)).\textsuperscript{10} In general, it is difficult to avoid thermal stress at the interface between the chip and the heat sink and/or solder, leading to thermal deformation owing to the difference in the CTE values. Thus, the CTE values of the chip and heat sink materials should be close. Al\textsubscript{2}O\textsubscript{3} oxide also plays an important role in the thermal

Fig. 4 SEM micrographs of cold splayed (a)–(c) Al and (d)–(i) the Al-D bulk.
deformation because its CTE value of $8.0 \times 10^{-6} ^\circ\text{C}$ is relatively lower than that of metal. However, the relationship between the interface and thermal properties should be carefully investigated in order to realize a high thermal performance.

The Vickers hardness of the Al-D bulk sample cold sprayed at 290°C showed increases of almost 200% and 100% as compared to the pure Al and the Al-D sample cold sprayed at 220°C, respectively. These results indicate that the porosity of the samples was one of the influencing factors to the Vickers hardness. However, the Vickers hardness of the Al-D sample cold sprayed at 220°C was almost 100% higher than that of pure Al bulk, in spite of the similar porosity level (around 4%, as shown in Table 1). This enhancement was mainly the result of the addition of the diamond reinforcement.

4. Conclusion

Diamond-reinforced pure Al matrix bulk materials were successfully fabricated by a low-pressure cold-spray process. We achieved less porosity, around 2–4%, in the Al-MBD composite and the pure Al bulk materials. Despite the addition of diamond reinforcement, the thermal conductivity of the composite samples was less than that of pure Al samples owing to the presence of Al$_2$O$_3$ and the lack of proper interfacial linkages. The cold-sprayed Al-MBD bulk samples cold-sprayed at 290°C showed 200% and 300% higher Vickers hardness than the corresponding bulk samples of pure Al and Al-MBD cold-sprayed at 220°C. However, it is feasible to achieve further enhancement of the thermo-physical properties of the cold sprayed bulk materials through precise control of experimental parameters of the low-pressure cold-spray process.

Acknowledgements

This work was supported by the Pukyong National University Research Fund in 2013.

REFERENCES