THERMAL PROPERTIES OF SINTERED DIAMOND WITH SMALL AMOUNTS OF METAL

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Thermal resistance properties of sintered diamonds with 1 to 5 vol% Co, Ni or super invar alloy were investigated at 1100–1300°C in a vacuum of 1–1.8 × 10⁻⁷ Pa. The thermal resistance of these sintered diamonds was strongly dependent on the amount and kind of metal species. Sintered diamonds with small amounts of super invar alloy had superior resistance against both graphitization and cracking. The temperature dependence of the thermal conductivity of sintered diamond with 1.3 vol% Co was measured up to 110°C. Thermal conductivity slightly increased with increasing temperature.

1. Introduction

Most sintered diamonds available commercially have superior mechanical properties such as hardness, wear resistance, transverse rupture strength, etc., but the electrical resistivity of the sintered mass has a very low value, similar to that of metal. The low electrical resistivity is due to a continuous network of large amounts of metallic Co phase which is used as a sintering aid. The large amounts of metallic phases such as Co in sintered diamonds deteriorate their physical properties at high temperatures because of graphitization and chipping or micro-cracking, caused by the catalytic action of the metal and by differences in the thermal expansion coefficients of diamond and additive metals.

It is very interesting to investigate the physical properties of the sintered diamonds with small amounts of metals. In this context, we have already reported the synthesis of sintered diamond with 1 to 5 vol% Co or Ni and their improved physical properties such as electrical resistivity, hardness, etc. Also, these sintered diamonds are expected to have improved thermal properties compared to sintered diamonds with large amounts of metals.

In this paper, the effects of metal content and metal species on the thermal resistance properties of sintered diamonds with 1 to 5 vol% Co, Ni or super invar alloy and the temperature dependence of the thermal conductivity of diamond with 1.3 vol% Co are described.

2. Experimental procedures

Diamond sintering

Commercially available synthetic diamond powders (General Electric Co. Ltd., 2–4 and 20–40 μm), ultrafine Co and Ni powders (Vacuum Metallurgical Co. Ltd., 30 nm) and plates of Co (purity; 99.9%), Ni (purity; 99.9%) and super invar alloy (Ni 31%, Co 4–6%, Mn 0.3–0.4%, C 0.07%, remainder Fe) were used as starting materials. Powder mixtures of diamond and metal were prepared by mechanical mixing and magnetron sputtering methods. Starting materials and sintering conditions are shown in Table 1. These starting materials were sintered at 7.7 GPa and 2000°C for 1 hr using a belt-type high pressure apparatus. The details of the starting material preparations and the physical properties such as microstructure, hardness and electrical resistivity of these sintered diamonds have been described in previous papers. 5–6

Thermal resistance property

Sintered diamonds obtained under the conditions of Table 1 were polished using a rotating cast iron scribe. The thermal resistance of polished sintered diamonds was investigated by heat treat-
Table 1. Starting materials and sintering conditions

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Starting materials</th>
<th>Additive</th>
<th>Sintering conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diamond</td>
<td></td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>DN-5</td>
<td>2-4 µm</td>
<td>5 vol%Ni Mecha.</td>
<td></td>
</tr>
<tr>
<td>DNSpu.</td>
<td>2-4 µm</td>
<td>1 vol%Ni Sput.</td>
<td></td>
</tr>
<tr>
<td>DC-5</td>
<td>2-4 µm</td>
<td>5 vol%Co Mecha.</td>
<td></td>
</tr>
<tr>
<td>DCoSpu.</td>
<td>2-4 µm</td>
<td>1.5 vol%Co Sput.</td>
<td></td>
</tr>
<tr>
<td>DCoSpu. C&amp;F</td>
<td>2-4 µm</td>
<td>1.3 vol%Co Sput.</td>
<td></td>
</tr>
<tr>
<td>DlnSpu.</td>
<td>2-4 µm</td>
<td>1.2 vol%Invar Sput.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>2000</td>
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<td></td>
<td></td>
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<td>2000</td>
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<td></td>
<td></td>
<td></td>
<td>2000</td>
</tr>
</tbody>
</table>

Mecha.: Mechanical mixing, Sput.: Magnetron sputtering.
Invar: super invar (Ni 31%, Co 4-6%, Mn 0.3-0.4%, C 0.07%, Remainder Fe).
DCoSpu C&F: 2-4 µm, 2 gr+20-40 µm, 1 gr.

mment at 1100–1300°C for 30 min in a vacuum of 1 to 1.8×10⁻³ Pa. X-ray diffraction patterns were taken before and after the heat treatment to investigate graphitization. Also, after the heat treatment the surfaces were observed by an optical microscope and SEM with an energy dispersive X-ray analyser to check micro-cracking, cracking and precipitates from inside the sample.

Thermal conductivity

The thermal conductivity of sintered diamond was measured by the comparative method described by Burgemeister¹⁷,²⁸ using commercially available apparatus (Rigaku Co. Ltd., J-300). A sample with the cross-section 2×2 mm² was clamped between gold probes. The surfaces of the sample and probes were blackened with a thin layer of black paint. Part of the radiation from a circle (0.035 mm in diameter) on the surface was focussed by a mirror objective on the indium antimonide cell of a Barnes RM-2A microscope. A heat flow was set up in vacuum conditions of 1–10 Pa and the corresponding temperature gradient was measured using the indium antimonide temperature detector. The ratio of the thermal conductivities is inversely proportional to the ratio of the temperature gradient of the gold probes and the unknown sample. The thermal conductivity of the gold probe is known, and thus the unknown thermal conductivity of the sample can be calculated.

3. Results and discussion

Sintered diamonds with 1 to 5 vol% Co, Ni or super invar alloy were synthesized under the conditions of 7.7 GPa and 2000°C for 1 hr. The sintered diamonds obtained were ground using a diamond wheel. No graphite was detected in these sintered diamonds by X-ray diffraction, and their Vickers hardness and electrical resistivity at room temperature were above 80 GPa and above 10⁸ Ω-cm, respectively.⁴,⁹ The average grain size of all sintered diamonds except DCoSpu C&F was about 4 µm, which is similar to that of the starting materials, as shown in Fig. 1(A). From SEM observation, the microstructure of DCoSpu C&F was composed of fine (about 4 µm) and coarse (above 20 µm) grains, as shown in Fig. 1(B).

As described above, sintered diamonds with small amounts of metal, which had high hardness and high electrical resistivity, were used for the study of thermal resistance and thermal conductivity measurements.

Thermal resistance

Thermal resistance of these sintered diamonds was investigated by heat treatment at 1100°C for 30 min in a vacuum of 1–1.8×10⁻³ Pa. From X-ray diffraction of the samples after heat treatment, no graphite was detected in the samples with Co or super invar alloy additive, but a small amount of
graphite was clearly observed in the samples with Ni additive. The amount of graphite increased qualitatively with increasing Ni additive. From these results, it is considered that the sintered diamonds with Ni additive are easily graphitized compared with those with Co or super invar alloy additives.

The surfaces of sintered diamonds after heat treatment were observed by an optical microscope and SEM with an energy dispersive X-ray analyser. Many cracks were observed in sample DC-5, but only two cracks were observed in samples DcoSpu and DcoSpu C&F. Many micro-cracks were observed in sample DN-5. In contrast, no cracks were observed in either sample DNSpu and DInSpu.

It is clearly seen from the surface observation that cracking induced by heat treatment increased markedly with increase in additive metal content. Also, it was found that cracking induced by the heat treatment was strongly dependent on the kind of metal species present. This may be due to the difference of the thermal expansion coefficients of additive metal. The thermal expansion coefficients of Ni and super invar alloy are smaller than that of Co. Therefore, sintered diamonds with Co additive were easily cracked compared to those with Ni and super invar alloy additives.

More detailed observation of the surfaces was made by SEM. Many tiny precipitates with spherical shapes were observed in all of the examined samples. Figs. 2(A) and (B) show back-scattered electron images of DCoSpu and DInSpu, respectively. Many tiny precipitates can be clearly seen in these figures. Energy dispersive X-ray analysis confirmed that these precipitates were composed of metal or metal-rich phases.

From the results of X-ray diffraction and surface observation, the thermal resistance of the sintered diamonds after heat treatment is summarized in Table 2. It is clearly seen from this table that
sintered diamond with super invar alloy was superior in resistance against both graphitization and cracking compared to sintered diamonds with Co or Ni additives.

As described above, no graphitization or cracking was observed by heat treatment of 1100°C in the sintered diamond with super invar alloy additive. It is very interesting to investigate the thermal resistance property of this sample at higher temperature conditions. DlnSpu heat-treated at 1100°C was treated again at 1200°C for 30 min in the vacuum and then treated at 1300°C for 30 min in the same atmosphere. X-ray diffraction patterns of the sample treated at 1200°C and that at 1300°C are shown in Figs. 3(B) and (C), respectively. From this figure, graphitization of the sintered diamond is not clearly observed up to 1200°C, but a small amount of graphite was confirmed in the sample treated at 1300°C. Also, DlnSpu without any heat treatment was treated at 1300°C for 30 min in the vacuum. The X-ray diffraction pattern of the sample was almost the same as that of Fig. 3(C). These results suggest that the graphitization rate of the sintered diamond with super invar alloy is fairly increased above 1300°C in the vacuum condition.

No cracking was observed on the surface of the sintered diamond after the heat treatment up to 1300°C in vacuum, as listed in Table 2. This shows that sintered diamond with small amounts of super invar alloy was superior against cracking. This may be due to a very low thermal expansion coefficient of super invar alloy compared with those of Co or Ni. These results suggest that super invar alloy is a desirable additive for the sintering of diamond to improve thermal resistance.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Heat treatment at 1100°C, 30 min</th>
<th>Heat treatment at 1300°C, 30 min</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Heat treatment at 1100°C, 30 min</td>
<td>Heat treatment at 1300°C, 30 min</td>
</tr>
<tr>
<td></td>
<td>Graphitization</td>
<td>Cracks</td>
</tr>
<tr>
<td>DN-5</td>
<td>small amount</td>
<td>many micro</td>
</tr>
<tr>
<td>DNSpu.</td>
<td>small amount</td>
<td>many micro</td>
</tr>
<tr>
<td>DC-5</td>
<td>no</td>
<td>many cracks</td>
</tr>
<tr>
<td>DCoSpu.</td>
<td>no</td>
<td>two cracks</td>
</tr>
<tr>
<td>C&amp;F</td>
<td>no</td>
<td>no cracks</td>
</tr>
<tr>
<td>DlnSpu.</td>
<td>no</td>
<td>no cracks</td>
</tr>
</tbody>
</table>

Fig. 3. X-ray diffraction patterns of sintered diamond, DlnSpu, after heat treatment in the vacuum. (A) 1100°C for 30 min. (B) 1100, 1200°C for 30 min. (C) 1100, 1200, 1300°C for 30 min.

Thermal conductivity

Samples of DCoSpu C&F for thermal conductivity measurement were shaped into 1.74×1.85×2.45 mm rectangular prisms having three parallel polished faces. Thermal conductivity of the sin-
tered diamond with this shape was measured by the method described in the experimental procedures. Figure 4 shows a typical temperature scan on the sample and probes. Temperature gradients and thermal conductivity are also shown in Fig. 4. The temperature gradients of sample and probes were calculated using cut-off data at 15% from the observed values. The cut-off points are shown in Fig. 4 as lines parallel to the temperature axis. The average thermal conductivity of the sample at 41.5–42.5°C was 3.46 ± 0.05 watt/cm·°K, as shown in Fig. 4. The average thermal conductivity was obtained from 5 thermal conductivity measurements.

The temperature dependence of the thermal conductivity of this sample is shown in Fig. 5. As shown in Fig. 5, the thermal conductivity slightly increased with increasing temperature. Usually, the thermal conductivity of single crystal diamond decreases with increasing temperature above room temperature. However, the temperature dependence of the thermal conductivity of polycrystalline cubic boron nitride has been reported by Sumiya et al. to be positive, as shown in Fig. 5; our experimental results on sintered diamond showed a similar temperature dependence. The reason is not clear as yet, but this phenomenon may be closely related to the grain size of sintered diamond as well as impurities and other defects.

4. Conclusion

Sintered diamonds with Ni additive are easily
graphitized compared with those with Co or super invar alloy additives by heat treatment of 1100°C for 30 min in a vacuum of 1 to 1.8×10⁻³ Pa.

Cracking of sintered diamonds by heat treatment increased markedly with increases of additive metal content. Also, cracking was strongly dependent on the kind of metal species. Sintered diamonds with Co additive were easily cracked compared to those with Ni or super invar alloy.

In the examined sintered diamonds, those with small amounts of super invar alloy had superior thermal properties in resistance against both graphitization and cracking.

The temperature dependence of the thermal conductivity of sintered diamond with 1.3 vol% Co was measured up to about 110°C. Thermal conductivity slightly increased with increasing temperature; the thermal conductivity of the sintered diamond at 42.5°C was 3.46±0.05 watt/cm·°K.

REFERENCES