Wettability and Interface Reaction of Sn-Cr powder alloy on Poly-crystalline Diamond (PCD)

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Abstract. In this work, the isothermal wetting of the Sn–Cr powder alloy containing 1.0, 2.0 and 4.0 wt.% Cr on Poly-crystalline diamond (PCD) substrates was investigated using a sessile drop method. The addition of active Cr significantly improved the wettability of Sn-Cr alloy at a temperature above 700 °C, and a minimum contact angle less than 20° was observed between Sn-2wt%Cr alloy and PCD substrate. The interfacial reaction between Sn-2Cr and PCD were strongly dependent on wetting temperature. A thick and continuous layer of chromium carbide was formed as wetting temperature increased from 700 to 750 °C, which consequently enhanced the wettability of Sn-Cr alloy on PCD substrate.

1. Introduction
Due to its ultra-high hardness, synthetic diamond has been used as cutting abrasives of machining tools for decades [1-3]. Recently, synthetic diamond also attains increasing applications in modern electronic devices because of its superior optical and thermos-mechanical properties. For the aforementioned application, synthetic diamond is often bonded to itself or metallic substrates to provide mechanical, electrical, and thermal connections. Among existing connection techniques, brazing using Ni-Cr, Cu-Sn, and Ag-Cu filler alloys containing active elements of Ti, Cr, or V is considered as a promising one [4-7]. Previous studies have shown that the addition of these carbide-formers is an effective means to improve wettability of filler alloy on diamond, as well as other carbonous materials [13-15]. However, most filler alloys used for diamond brazing have a melting point above 880 °C [8-10]. As a result, most existing studies have focused on the wettability of filler alloys on graphite at relatively high temperatures (above 900 °C) [16-19]. Little information is available about the wettability and interface reaction of synthetic diamond at a relatively low temperature, which is the key factor for optimizing the brazing temperature. Consequently, synthetic diamond is still brazed at temperatures well above its graphitization temperature (approximately 700 °C in vacuum), which not only induces undesirable thermal damages of brazed diamond, but also make the fabrication of diamond devices challenging [11-12]. Therefore, understanding the wettability of synthetic diamond and diamond-based materials at relatively low temperatures is of fundamental importance for the development of diamond brazing technique, and hence the fabrication of modern diamond devices.

In this work, the isothermal wetting behaviour of Sn-Cr alloys on poly-crystalline diamond (PCD) was in-situ investigated at 650, 700 and 750 °C. Microstructural observation and compositional
analysis of solidified wetting samples were executed using scanning electron microscopes. It was revealed the interfacial chromium carbides formed during wetting experiment at 650 °C. Wetting temperature strongly affected interface formation of chromium carbides, and hence the wettability of Sn-Cr alloy on PCD substrate that increasing wetting temperature to 750 °C resulted in a minimum contact angle less than 20°.

2. Experiment Details
The Co-W-sintered poly-crystalline diamond (PCD, Huanghe Whirlwind Co., Ltd., Zhengzhou, China) with an average diamond grain size of 5μm in a dimension of 10 mm×10 mm×0.7 mm were used as substrate. The Sn-xCr (in wt.%, x=1,2,4) powder alloys were prepared by mixing Sn (99.99 wt.%, ~50μm) and Cr (99.7 wt.%, ~20μm, ) metal powders (Changsha Tianjiu Co., Ltd., Hunnan , China) in a ball milling machine for 4 hours. The mixed powders were cold pressed under a pressure of 400 MPa into a cylindrical compact in a diameter of 3 mm. Prior to wetting experiment, both PCD substrates and Sn-Cr compacts were cleaned in an ultrasonic alcohol bath. After cleaning, Sn-Cr compacts were horizontally placed in the middle of the PCD substrates, as shown in Fig.1. Then, the assembled samples were engaged into a quartz tube, which was heated in an electrical resistance tube furnace.

The wetting experiments were carried out using the sessile drop method under a vacuum of $2 \times 10^{-3}$ Pa. The isothermal wetting experiments were performed at 650, 700 and 750 °C for 60 minutes. The wetting and spreading behaviours of melt Sn-Cr alloy was photographed by a camera, and the recorded images were used to extract the contact angle using a drop shape analysis software. After wetting experiments, selected samples were mounted in epoxy resin and polished perpendicularly to PCD substrates using methods for metallographic sample preparation. To explore the surface morphologies of interfacial reaction products, some of samples were etched in 20%HNO₃ solution to remove remained Sn-Cr alloys. A Phenom ProX scanning electron microscope (SEM) installed with an energy dispersive spectrometer (EDS) were used for microstructure observation and compositional analysis.

3. Results and discussion

3.1. Wettability Sn-Cr alloy on PCD
Figure 2 (a) shows the projective images of Sn-xCr filler alloys after being isothermally heated at 650, 700, and 750°C for 60 minutes. As indicated in Fig. 2(a), pure Sn shows poor wettability on PCD with the final contact angle of 127°, 118° and 119° at 650, 700 and 750°C, respectively, which is due to Sn does not wet PCD in the range of temperature used in this study. For these Sn-Cr alloys, the minimum contact angle after wetting test at 650 °C was 101°, which demonstrates Sn-Cr alloys remains a non-wetting behaviour on the PCD at 650°C. However, as the temperature increased to 700 °C, the contact angle of Sn-Cr alloys significantly reduced to less than 90°, with the minimum contact angle of 44° measured for Sn-2Cr alloy. As temperature further increased to 750 °C, the contact angles of all Sn-Cr alloys reduced to less than 30°, with the minimum contact angle of 9° for Sn-2Cr alloy. In Fig.2 (b), the final contact angles between Sn-xCr alloys and PCD isothermal heating for 60 minutes at variable temperatures are summarized. It can be clearly seen that the contact angles of all Cr-containing Sn-xCr
alloys were reduced in comparison to that of pure Sn. At each wetting temperature, the minimum contact angle is always observed for Sn-2Cr alloy. Therefore, it can be concluded that, both temperature and Cr contents strongly affect the wettability of Sn-xCr filler on PCD substrate at temperatures ranged from 650 °C to 750 °C. In addition, the PCD can be well wet at 750 °C, which is significantly lower than the brazing temperature using Ni-Cr-P or Ni-Cr-B-Si alloys.

Figure 2. (a) In-situ photographs of Sn and Sn-xCr alloys/PCD system after isothermal wetting tests at different temperatures, (b) summarized the final contact angle of Sn-xCr on PCD.

Figure 3. Isothermal wetting curves of Sn-xCr on PCD at different temperatures for 60 minutes.

Figure 3 shows the spreading kinetics of Sn-Cr alloy during isothermal heating at variable wetting temperatures. At 650 °C, sluggish spreading kinetics can be observed for all Sn-Cr filler alloys as the contact angles decreased slowly with heating time; and the final contact angle remained to be more than 90° after dwell time of 60 minutes. On the other hand, when the isothermal temperature increased to 750 °C, the contact angles rapidly decreased with time, and the fastest spreading was observed for Sn-2Cr alloy whose contact angle became less than 90° within 20 minutes. Hence, the spreading kinetic of Sn-Cr alloy were also dependent on the wetting temperature and Cr contents. However, as shown in both Fig.2 and 3, compared to that of pure Sn, the contact angles of Sn-Cr alloy was reduced by the addition of Cr elements at alloy wetting temperatures. This suggests that, the active element of Cr could react with PCD at temperature as low as 650 °C, which correspondingly modifies the balance at wetting triangle zone and result in a contact angles smaller than that of pure Sn. Thus, an appropriate temperature to braze PCD using Sn-Cr alloy could lie in 650 to 750 °C.

3.2. Interfacial microstructure between Sn-Cr and PCD

To reveal the mechanism of Cr-induced wetting of Sn-xCr alloys on PCD, the interfacial microstructure of wetting test samples was observed. Fig. 4(a) shows the cross-sectional images of Sn-2Cr after cooling to room temperature from 700 °C. Fig. 4(b) is enlarged from Fig. 4(a). It shows the triple junctions of the Sn-2Cr /PCD couples after wetting at 700 °C for 60min. As shown in Fig. 4(b), the solidified droplets mainly consist of gray phase and white phase. Also, two primary phases were identified by EDS spot analysis as a gray Cr phase and white β-Sn phase doped with W element. The gray Cr phase probably due to the precipitation of active chromium which dissolved into the liquid Sn
during the insulation stage during the cooling process [18]. The appearance of the W element in β-Sn phase was attributed to the diffusion of W from the PCD to the Sn-xCr alloy.

Figure 4. (a) Cross-sectional images of Sn-2Cr/PCD after wetting test at 700 ºC for 60min; (b) wetting front microstructure of Sn-2Cr/PCD.

Figure 5. Wetting interfacial microstructure of Sn-2Cr/PCD for 60min. (a) 650 ºC, (b) 700 ºC, (c) 750 ºC, (d) the corresponding element X-ray lines at 750 ºC.

In addition, the cross-sectional microstructures of interface of Sn-2Cr/PCD are displayed in Fig.5. As shown in Fig.5 (a-c), there is a dark gray reaction layer at the interface between Sn-2Cr and PCD. The EDS analysis demonstrated that there is a enrichment of Cr and C element in the reaction layer. The result indicated a chromium carbides layer was formed at the interface of Sn-2Cr/PCD, which may be responsible for the increased wettability of alloy on PCD. In Fig.5 (a), the reaction layer is discontinuous and small when the wetting temperature was 650 ºC. It is obvious that the reaction layer was getting thicker and becoming continuous with the increasing of wetting temperature, as shown in Fig.5 (b-c). The results correspond to the results of wetting performance at different temperature in the previous section.

Figure 6. Top-view microstructure at the exposed interface after removal of the solidified Sn-2Cr drop.

Fig. 6 shows the surface morphologies of interfacial reaction products formed on PCD surface at wetting temperatures 750 ºC (note that the interfaces were examined after the Sn-2Cr alloy was removed by deeply etching in 20%HNO₃). It can be clearly seen that the continuous plate-like reaction product A and the separated block-shaped reaction product B were at the surface of the PCD. However, cracks were observed in the continuous plate-like
reaction product A. We believe that the thermal stress generated during the cooling was responsible for the cracks.

![Schematic diagram of wetting evolution of Sn-Cr alloy on PCD substrate.](image)

According to the cross-sectional phase information mentioned above and the wetting behavior described in Section 3.1, the wetting mechanism of Sn-Cr alloy on PCD substrate can be further discussed. Fig. 7 shows the schematic illustration of wettability process of Sn-Cr alloy on PCD substrate. As illustrated in Fig. 7(a), prior to heating, the solid Cr was evenly distributed in the metal bulk in vacuum. When the temperature was higher than the melting point of Sn-Cr alloy, the metal bulk began to become liquid filler and the solid Cr was dissolved into liquid filler and the contact angle was obviously greater than 90°, as shown in Fig 7(b). As the temperature increased to the corresponding wetting temperature, the dissolved Cr was gradually transported to the interface and C and W were transported to liquid filler and the contact angle was slightly decrease, as shown in Fig 7(c). After that, the Cr began react with PCD in the interface zone and a discontinuous Cr-C reaction layer was formed, leading to the decrease of contact angle, as demonstrated in Fig 7(d). Finally, in Fig. 7(e), the continuous reaction layer was formed in the interface zone and the Sn-Cr alloy droplet excellently spread on PCD substrate.

4. Conclusions

In this study, the wetting behavior and interfacial microstructure of Sn-Cr alloys with different Cr concentrations on the surface of PCD at different isothermal temperature were investigated. The following conclusions can be drawn:

1. There is a non-wetting behavior of Sn-xCr alloy on the PCD surface at 650 °C, and the active Cr in the brazing alloy significantly improves its wettability at least at a wetting temperature above 700 °C. The best wettability of Sn-Cr alloy on PCD substrate could be achieved for the content of 2wt.%Cr.

2. A Cr-C reaction layer was formed at the interface of Sn-2Cr/PCD, which was responsible for the wetting of the alloy on PCD substrate. The reaction layer is discontinuous and small when the wetting temperature was 650 °C, and a thicker and continuous Cr-C reaction layer was obtained at a higher isothermal temperature.

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