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# Effects of copper-based alloy on the synthesis of single-crystal diamond

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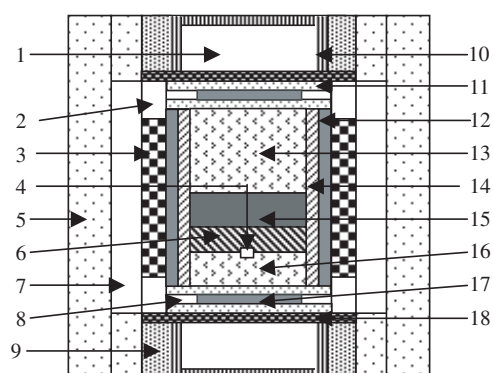
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## Abstract

The catalytic effects of copper-based alloys in diamond growth have been investigated. A single crystal of diamond has been obtained by the temperature gradient method (TGM), using Cu–Mn–Co and Cu–Co alloys as catalysts. It was found that the melted Cu–Mn–Co and Cu–Co alloys show low viscosity. The eutectic temperatures of these two alloys with graphite were between 1130 and 1150 °C, and the temperature of the transition to diamond was over 1300 °C at 5.5 GPa. High-quality diamond could not be obtained in Cu–Co alloy by the TGM. Our results suggest that adding Cu to a catalyst cannot decrease the reaction temperature for diamond growth.

## 1. Introduction

Conventional catalysts for diamond crystal growth usually include nickel, cobalt and iron, doped with Al, Ti, Zr, Mn, Cr etc [1, 2]. Synthetic diamond obtained using catalyst alloys usually requires temperatures over 1200 °C and pressures of 5–6 GPa. Catalyst alloys that can decrease the reaction temperature and pressure for diamond growth have been focuses of research interest. Cu is a metal with a low melting point and a low abundance in the Earth, so we anticipated that using a Cu-based catalyst could decrease the reaction temperature and pressure for diamond growth. Using pure Cu as a catalyst, it has been shown that the reaction pressure and temperature were 6.7 GPa, 1700 °C and 6.0 GPa, 1400–1500 °C, by the film growth (FG) method [3] and the TGM [4] respectively. The diamond growth rate achieved by using a pure Cu catalyst is much lower than that achieved using the catalyst conventionally used: commercially available synthetic diamond, with poor crystal quality [4]. Therefore, pure Cu is not a good catalyst for diamond growth. This work investigates the catalytic effects of Cu–Mn–Co and Cu–Co alloys in growing high-purity diamond single crystals.



**Figure 1.** The sample set-up for the synthesis of diamond. 1, 2, 5, 8, 9: pyrophyllite; 7, 13, 16: dolomite; 3: NaCl sleeve; 10: hardened steel ring; 17: subheater; 11: Mo electrode; 12: graphite heater; 15: carbon source; 6: solvent; 4: seed diamond; 14: insulator tube; 18: metal plate.

## 2. Experimental details

A cubic anvil high-pressure apparatus was used in our experiments [5]; it has a newly developed pressure/temperature control system. This eliminates temperature and pressure fluctuation. We assembled the samples in the high-pressure, high-temperature chamber as shown in figure 1 [6]. We used Cu, Mn and Co powders, 5  $\mu\text{m}$  in particle size, for making the catalyst, in the ratio 50:40:5. We re-shaped the catalyst into a  $\varnothing 6.5 \text{ mm} \times 2 \text{ mm}$  circular disc at 580 MPa before use.

We used Cu and Co foils in composing the Cu–Co alloy. Their thicknesses were 0.3 and 0.4 mm respectively. These foils were layered alternately in the reaction chamber, which made the Co:Cu weight ratio 57:43. Typical high-purity graphite (boron: <1 ppm) was used as the carbon source. The {100} faces of small synthetic diamond crystals were used as the growth faces for the diamond crystal. The {100} face is towards the surface of the catalyst. Because diamond crystal begins to grow 40 min after the catalyst enters the liquid state, we may expect the component to be homogeneous before the diamond crystal growth occurs. The diamond crystal growth experiment was carried out for 2–25 h at 5.5 GPa and 1350 °C. In the synthesis experiment, a graphite tube was used as a heater; a  $\text{SiO}_2$  glass tube was used as an insulator, placed inside the heater to prevent the melted metal from polluting the heater, because the polluted graphite would transform into diamond under the diamond growth conditions. The temperature differences were adjusted by using subheaters with different thicknesses. The temperature gradient was 20–25 °C  $\text{mm}^{-1}$ . The diamond obtained and residual carbon were observed by optical microscopy.

## 3. Results and discussion

### 3.1. Synthetic diamond obtained using Cu–Mn–Co as the catalyst

Figure 2 shows a section of the carbon heater transformed to diamond due to the leakage of melted solvent from the  $\text{SiO}_2$  insulator. To prevent the leakage of melted solvent at high temperature, we followed a two-step heating method. In this method, we first increase the temperature to 1000 °C, keep it there for 2 min, then increase it again to the required temperature. Our experimental results show that in the synthesis with catalysts based on Ni, Co and Fe, when the rate of temperature increase is less than 25 °C  $\text{min}^{-1}$ , the leakage of melted solvent will be eliminated. This rate is decreased to 5 °C  $\text{min}^{-1}$  when  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$



**Figure 2.** A section of the carbon heater transformed into diamond due to the leakage of melted solvent



**Figure 3.** A photograph of the carbon source after growing diamond using  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$  as the catalyst.

is used as the catalyst. This result suggests that melted Cu–Mn–Co alloys are low-viscosity alloys. Taking into account the phenomenon of the leakage of melted solvent and the two-step heating method, the eutectic temperatures of some metals and carbon can be speculated upon. In our experiment, the eutectic temperature of  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$  alloy and graphite was between 1130 and 1150 °C under 5.5 GPa. In addition, our experiments show that the temperature of the transition to diamond was 1300 °C for  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$  under 5.5 GPa. These experiments suggest that using  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$ , with its low melting point, as a catalyst could not decrease the temperature of the transition from carbon to diamond.

Figure 3 shows that when  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$  is used as the catalyst just a little of the carbon in the interface between the carbon source and the catalyst transforms into diamond; the rest of the carbon source remains as graphite when held under 5.5 GPa and at 1350 °C for 4 h. Under these synthesis conditions, the carbon source would usually transform into diamond in 10 min if one was using a good catalyst (a Fe–Co–Ni alloy). Therefore, the low transformation rate shows that the effect of  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5$  as a catalyst is very weak.

In addition, we also carried out an experiment on large-size single-crystal diamond growth using  $\text{Cu}_{55}\text{Mn}_{40}\text{Co}_5 + \text{Co}$  as the catalyst under 5.5 GPa and at 1300 °C. On increasing the Co content to 15% in the alloy, it is observed that the graphite used as the carbon source completely transforms into diamond, although a large-size single-crystal diamond is not obtained from the seed crystal. The results suggest that the catalytic effect of Cu–Mn–Co alloys is improved by increasing the Co content in the alloy.



**Figure 4.** A diamond crystal grown using  $\text{Cu}_{43}\text{Co}_{57}$  for 20 h.

### 3.2. Diamond synthesis using a Cu–Co catalyst

As mentioned in section 3.1, melted Cu–Mn–Co alloys have such properties as low melting point, low viscosity and high temperature of reaction for diamond growth. To observe the catalytic effects of Cu-based alloys further, a diamond growth experiment using  $\text{Co}_{57}\text{Cu}_{43}$  alloys as catalysts was carried out.

It is observed that  $\text{Co}_{57}\text{Cu}_{43}$  alloys have the same catalytic effect as Cu–Mn–Co alloys in our experiment. In the liquid state, leakage of  $\text{Co}_{57}\text{Cu}_{43}$  readily occurs, so the heating speed must be controlled at below the rate of  $5\text{ }^{\circ}\text{C min}^{-1}$ . The temperature of the transformation from graphite to diamond is  $1300\text{ }^{\circ}\text{C}$  under  $5.5\text{ GPa}$ ; the eutectic temperature of the alloys with graphite is also between  $1130$  and  $1150\text{ }^{\circ}\text{C}$ . That is to say, there are almost identical eutectic temperatures for graphite and the two types of catalyst.

Figure 4 shows a diamond crystal grown using  $\text{Cu}_{43}\text{Co}_{57}$  as the catalyst. The diamond crystal with (100) and (111) faces contains a lot of inclusions and spontaneous nuclei, and the surface of the crystal is not flat. Many experiments have been performed with a view to decreasing inclusions in diamond, restraining the formation of spontaneous nuclei and improving the quality of the crystal by changing the temperature gradient and the thickness of the catalyst layer. Unfortunately, the results are not encouraging. Therefore, we conclude that it is difficult to synthesize high-quality crystal using  $\text{Co}_{57}\text{Cu}_{43}$  alloys as catalysts.

## 4. Conclusions

The catalytic effects of Cu–Mn–Co and Cu–Co alloys on diamond growth have been investigated. It is found that the systems of graphite and Cu-based alloys have the same properties: low eutectic temperature, high reaction temperature for diamond growth and low viscosity. It is difficult to synthesize high-quality diamond crystal using Cu–Mn–Co and Co–Cu as catalysts. These results also suggest that the temperature of diamond growth cannot be reduced by adding Cu or other elements with low melting points to the catalyst.

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