Behaviour of graphite-diamond conversion using Ni-Cu and Ni-Zn alloys as catalyst-solvent

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Diamond was synthesized using the catalyst-solvents of Ni-Cu and Ni-Zn alloys with relatively low melting temperature in order to decrease the conversion temperature. The lowest temperature limit for diamond synthesis was not changed with the addition of copper to nickel but decreased by 100° C with the addition of zinc. The temperature limits were found to coincide with the eutectic temperatures of the alloy-carbon systems, which indicates that diamond forms when the metal melts. The yield of diamond decreased with the addition of copper or zinc, but increased with increasing temperature or pressure. The result suggests that a catalytic effect of the metal should be considered. Crystals grown from the alloys did not show a different morphology from those grown in nickel, although the crystal size tended to be small, 0.2 to 0.4 mm across.

1. Introduction

Diamond is obtained from graphite directly at very high pressure and temperature above 13 GPa and 3000° C [1, 2]. However, if a proper metal is used as a catalyst, the conversion pressure and temperature decrease drastically to the range of 5.5 GPa and 1400° C [3, 4]. Therefore, it is still an interesting subject to seek effective catalysts which can transform graphite to diamond at lower temperature and pressure.

The catalysts that have been found to be most effective are mostly metals of Group VIII in the periodic table and their alloys. Because the metals and alloys can act as conversion catalysts when they become solvents of carbon above their melting points, they are called catalyst-solvents [5]. In this sense, alloys with low melting temperature are the most attractive among them. As a successful instance, diamond can be synthesized using Ni-Ge alloy as a catalyst-solvent below 1000° C [6]. Recently it was reported [7] that the region of diamond formation is shifted in the lower temperature and pressure direction (4.3 GPa and 1020° C) when copper with a low melting temperature is added to Ni-Fe alloy. This shift has been explained in terms of the decrease of melting temperature of the alloy. On the other hand, it has also been reported that the conversion temperature to diamond is not decreased with the addition of copper nickel [8-10].

In order to understand the relationship between the melting process of the alloy and diamond formation, diamond synthesis experiments were conducted using the Ni-Cu alloy. Furthermore, Ni-Zn alloy was also employed because zinc with its extremely low melting temperature is expected to influence the conversion temperature more distinctly than copper. The effects of copper and zinc on the yield and morphology were also investigated.

When a sample assembly was prepared, both the alloy and pure nickel were placed in two upper and lower isothermic positions in a higher-pressure cell to estimate the difference of conversion temperature precisely by observing the growth features of diamond from both regions.

2. Experimental procedure

2.1. Starting materials

Commericially available synthetic graphite was used as a carbon source. Nickel, copper and zinc of purity 99.5, 99.9 and 99.9999%, respectively, were used for the preparation of catalyst-solvents.

Ni-50 wt % Cu alloy was prepared in an arc-melting furnace. The composition of the alloy determined by electron probe microanalysis (EPMA) was 50.16 wt % Ni and 49.84 wt % Cu.

Ni-50 wt % Zn alloy was prepared using a diffusion method [11]. Weighed quantities of nickel powder and zinc grains were sealed in a double-walled quartz ampoule and reacted at 1100° C for 3 days and then annealed at 900° C for 2 weeks. The composition of the ingot obtained was homogeneous, with 50.2 wt % Ni and 49.8 wt % Zn according to EPMA.

2.2. Diamond synthesis

Synthesis experiments were carried out using a modified belt-type high-pressure apparatus with a bore

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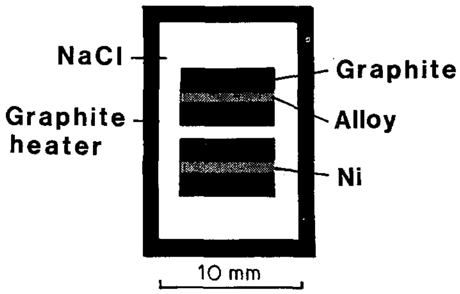


Figure 1 Sample assembly for diamond synthesis.

diameter of 25 mm [12]. The sample assembly inside a heater is shown in Fig. 1. Discs of metal and graphite were used with the sizes of 1 and 1.5 mm thickness, respectively, and 7 mm diameter. In all runs, a nickel disc was also assembled at an isothermal position with the Ni–Cu or Ni–Zn disc. The growth features from nickel were useful as an indicator of the temperature inside the heater.

The temperature was determined from the electric power input calibrated by a Pt – 6% Rh/Pt – 30% Rh thermocouple, ignoring the effect of pressure on e.m.f. The pressure was determined so that the growth region of diamond was consistent with the previous reports [13].

Each sample assembly was compressed to 5.4 to 6.1 GPa for Ni–Cu alloy and 5.8 GPa for Ni–Zn alloy. It was then heated to 1340 to 1450° C for Ni–Cu alloy and 1280 to 1470° C for Ni–Zn alloy and was held for 10 min.

2.3. Characterization of diamond

Unreacted graphite in the samples recovered from the high-pressure cell was dissolved in boiling mixed acid of H_2SO_4 and HNO_3, and grown diamonds were observed by an optical microscope and a scanning electron microscope. Textures of frozen metals were observed by a differential interference microscope after polishing and etching to decide whether the metal had been melted or not.

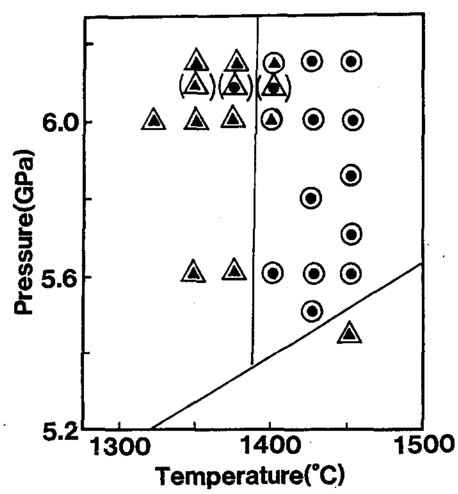


Figure 2 *P–T* region where diamond was formed in Ni–Cu alloy and nickel. (○) and (●) indicate that diamond was formed from Ni–Cu and nickel, respectively; (△) and (▲) indicate no formation from Ni–C and nickel, respectively. Results in parentheses were obtained when samples in Fig. 1 were configurated reversely to check the symmetry of the temperature gradient.

3. Results and discussion

3.1. Lowest limit of conversion temperature to diamond

A *P–T* region of diamond formation using Ni–Cu and nickel as catalyst-solvent is shown in Fig. 2. Diamond was formed in the same *P–T* region from both Ni–Cu and nickel except for two examples in which it was formed only in the Ni–Cu alloy. These two probably arise from a small temperature difference between the two positions which had been expected to be isothermic, because when the sample assembly was reversely configurated, diamond was formed only in nickel as shown in parentheses in Fig. 2. It is therefore concluded that the lowest limit of the conversion temperature to diamond in the case of Ni–Cu alloy is the same as in the case of pure nickel, and it was confirmed that the conversion temperature did not decrease with the addition of copper to nickel; it is suggested that copper does not play the same role in decreasing the conversion temperature in Ni–Cu alloy as in Ni–Fe–Cu alloy [7].

Table I compares the diamond formation temperature in the Ni–Zn alloy with that in pure nickel as a function of temperature. Diamond was formed above 1320° C in the Ni–Zn alloy whereas the lowest temperature was around 1420° C in the case of nickel. About 100° C a temperature difference in the lowest conversion temperature was found between Ni–Zn and pure nickel.

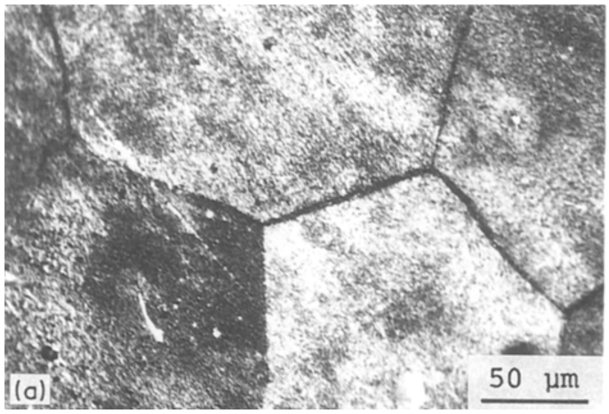
The melting point of nickel is 1455° C at ambient pressure. With the addition of 50% of copper or zinc, the melting temperature decreases by about 150 or 350° C, respectively. However, the above results indicate that copper does not play a role in decreasing the lowest temperature of diamond formation. In the case of Ni–Zn the temperature limit decreased by 100° C with the addition of zinc, but the amount of the fall is less than that expected from the decrease of the melting temperature.

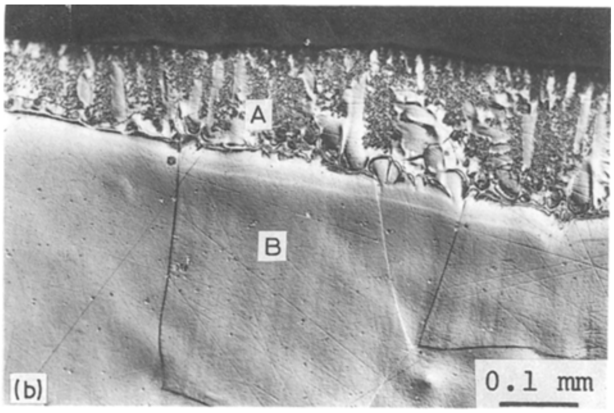
There may be two reasons why the conversion temperature is not decreased much even if copper or zinc is added to nickel: (i) diamond is formed when the alloy is melted, but the melting temperature does not decrease in the alloy–carbon system at high pressure, and (ii) diamond is not formed even if the alloy is melted. The former means that the metal plays the part of a solvent for diamond formation, whereas the latter means that the metal plays the part of a catalyst. To make clear the relationship between diamond formation and the melting process of the metal, the textures of frozen alloys are described in the following section.

TABLE I Result of synthesis experiments of diamond at 5.8 GPa using Ni–Zn and nickel as catalyst-solvent

	Temperature (° C)				
	1280	1320	1350	1420	1470
Ni–Zn	G*	D*	D	D	D
Nickel	G	G	G	D	D

*G = graphite, D = diamond.





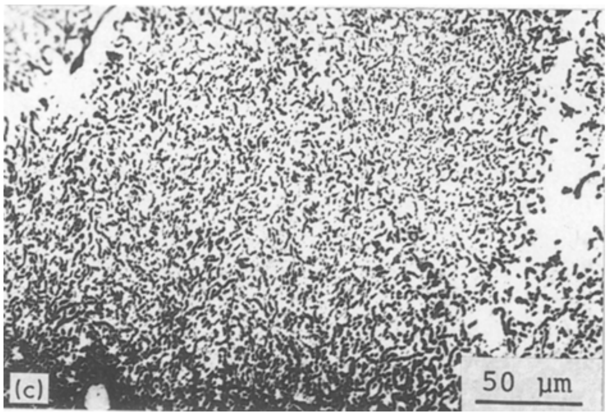


Figure 3 Textures of frozen Ni–Cu alloy recovered from diamond synthesis experiments at 5.6 GPa and at (a) 1375, (b) 1400 and (c) 1425° C. The textures appeared by etching in acid.

3.2. Textures of frozen alloys

Figs 3a, b and c show the textures of Ni–Cu alloys frozen from three different temperatures of 1375, 1400 and 1425° C, respectively, at 5.6 GPa in the diamond synthesis experiments. Fig. 3a shows recrystallized grains indicating that the alloy was not melted. No diamond was found on the metal disc. Fig. 3b consists of two regions. Region A shows eutectic texture, whereas region B shows recrystallized grains. Diamond crystals were found only in region A. The alloy was probably subjected to a temperature close to the eutectic temperature and the two regions are caused by the temperature gradient in the heater. The alloy frozen from 1425° C shows the eutectic texture as shown in Fig. 3c and diamonds were observed on the alloy. It is concluded from this result that the lowest limit of the conversion temperature coincides with the eutectic temperature of the alloy–carbon system, that is, diamond is formed above the temperature at which the metal is melted.

The above conclusion indicates that even if the

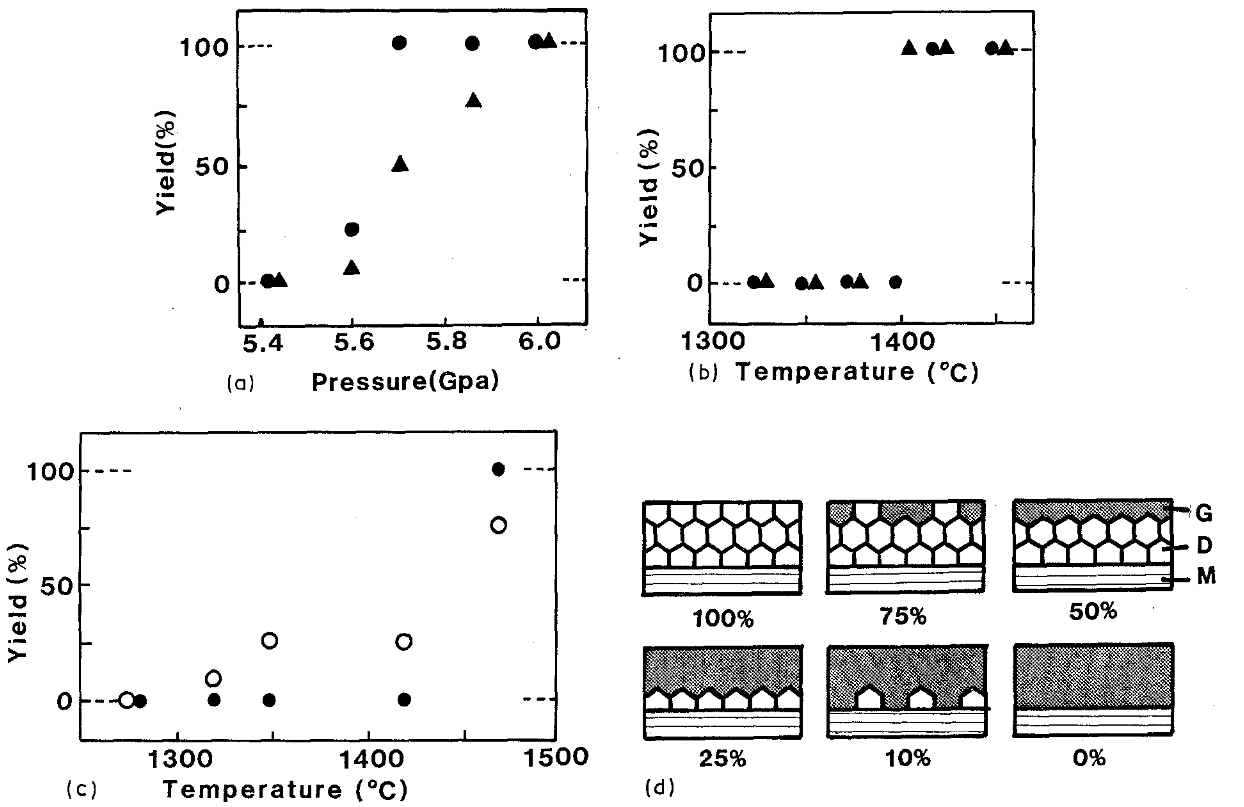


Figure 4 Yield of diamond grown from Ni–Cu alloy and nickel. (a) Variation with pressure: (●) nickel, (▲) Ni–Cu. (b) Variation with temperature: (●) nickel, (▲) Ni–Cu. (c) Yield of diamond grown from (●) nickel and (○) Ni–Zn alloy against temperature. The yield was roughly determined by observation of recovered samples using the schematic figure (d): G = graphite, D = diamond, M = metal.

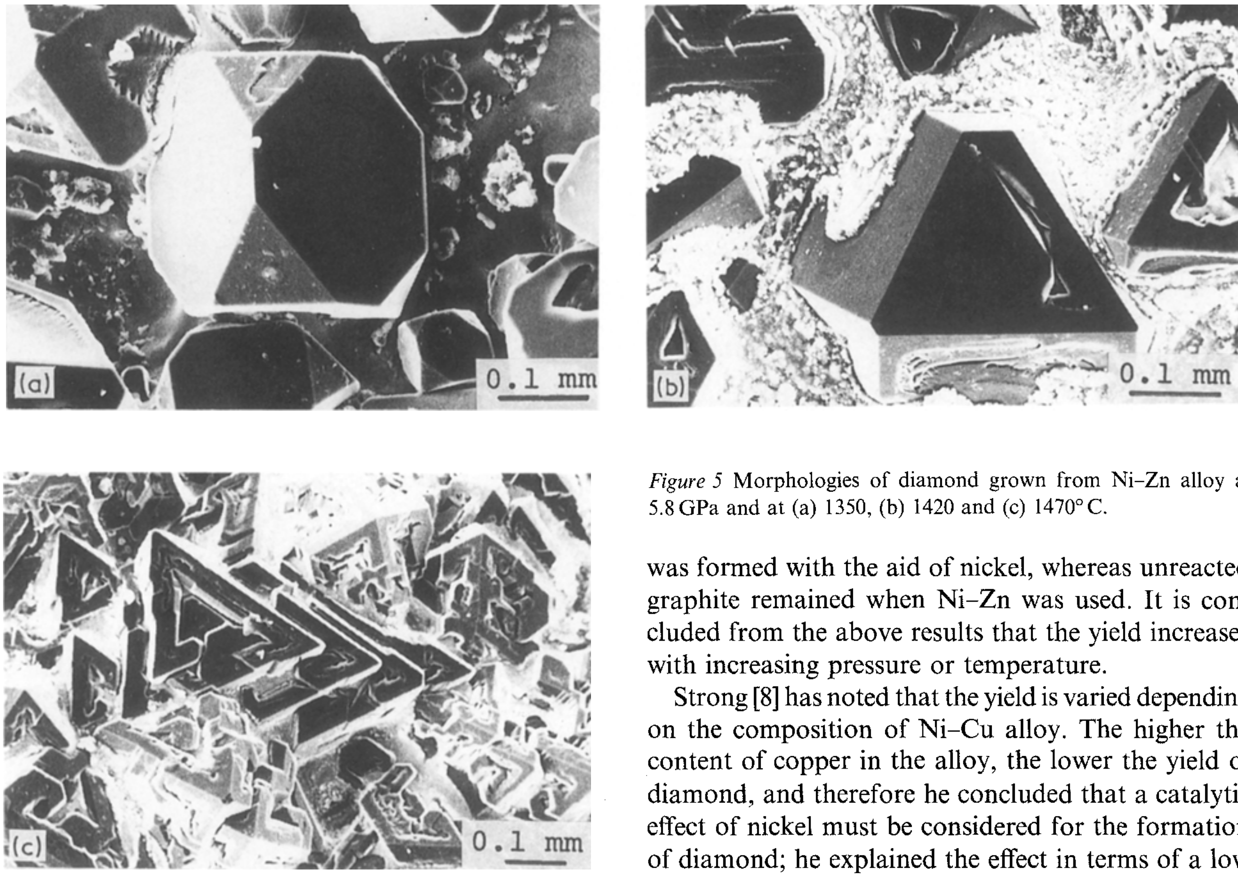


Figure 5 Morphologies of diamond grown from Ni-Zn alloy at 5.8 GPa and at (a) 1350, (b) 1420 and (c) 1470° C.

melting temperature of Ni–Cu alloy is decreased by the addition of copper, the eutectic temperature of the alloy–carbon system is not decreased. It is speculated that even if carbon is dissolved into the alloy, the melting temperature may only decrease slightly because the Ni–Cu alloy has a low solubility of carbon [8]. On the other hand, in the case of pure nickel the melting temperature decreases largely by dissolving carbon, because it has a high solubility of carbon. In the case of Ni–Zn alloy the lowest temperature of diamond formation also coincided with the eutectic temperature. The effect of zinc is also estimated to be the same as that of copper.

3.3. Dependence of yield of diamond on temperature and pressure

The yield of diamond synthesized using Ni–Cu, Ni–Zn and pure nickel is plotted in Fig. 4 as a function of temperature and pressure. The yield was roughly estimated from observation of the growth features of diamond, as shown in Fig. 4d.

As seen in Fig. 4a, a lower yield was recorded in the case of Ni–Cu alloy than for pure nickel below 6 GPa, although no difference was found at 6 GPa. The yield increased more gradually with increasing pressure when Ni–Cu was used.

When the synthesis temperature was varied at a fixed pressure of 6 GPa, the yield rapidly increased around 1425° C when nickel and Ni–Cu were used (Fig. 4b). On the other hand, the yield gradually increased with increasing synthesis temperature from 1320° C when Ni–Zn was used (Fig. 4c). The yield was higher in the case of Ni–Zn than nickel up to 1420° C, but at 1470° C the yields were reversed; 100% of carbon was formed with the aid of nickel, whereas unreacted graphite remained when Ni–Zn was used. It is concluded from the above results that the yield increases with increasing pressure or temperature.

Strong [8] has noted that the yield is varied depending on the composition of Ni–Cu alloy. The higher the content of copper in the alloy, the lower the yield of diamond, and therefore he concluded that a catalytic effect of nickel must be considered for the formation of diamond; he explained the effect in terms of a low interfacial energy between nickel and diamond, which results in easy nucleation.

The present results indicate that the catalytic effect not only depends on the composition of the metal but also varies with temperature and pressure, and the dependence of the yield on the temperature and pressure is explained using the following formula for the nucleation rate, K, to form octahedral nuclei of diamond from graphite [14, 15]:

$$K = \frac{NkT}{h} \exp\left(-16 \frac{3^{1/2}\sigma^3 \rho_G^2}{(P - P_e)(\rho_D - \rho_G) \cdot kT}\right)$$

where σ is the interfacial energy; T, P and P_e are temperature, pressure and equilibrium pressure, respectively; ϱ_D, ϱ_G, N, k and h are the densities of diamond and graphite, Avogadro's number, Boltzmann's constant and Planck's constant, respectively. As seen in the formula, the nucleation rate changes as a function of interfacial energy, temperature and pressure. It indicates that even if the interfacial energy is high, it is possible that the nucleation rate increases if the temperature or pressure increases.

3.4. Morphology of the grown diamonds

The size of diamond grown from Ni–Cu and Ni–Zn alloys was about 0.2 to 0.4 mm, compared with 0.5 to 1 mm in the case of pure nickel. The morphological characteristics of the crystals were the same as those grown from conventional catalyst-solvents: namely, cubo-octahedrons were seen most commonly and $\{1\,1\,1\}$ faces tended to develop largely at high temperature when Ni–Cu was used. When Ni–Zn was used, the following morphological change $\{1\,0\,0\} > \{1\,1\,1\} \rightarrow \{1\,0\,0\} = \{1\,1\,1\} \rightarrow \{1\,1\,1\}$ was distinctly observed with increasing synthesis temperature (Fig. 5). A depression at the centre of the crystal surface was frequently observed, and crystals grown from Ni–Zn at high temperature showed a skeletal form with a large depression (Fig. 5c).

4. Conclusions

1. When copper was added to nickel catalyst-solvent, the conversion temperature did not decrease, whereas it decreased by 100° C with the addition of zinc to nickel. It is concluded that the lowest limit of the conversion temperature is determined by the eutectic temperature of the Ni–Cu (or Zn)–C system, which does not decrease much.

2. The yield of diamond decreased with the addition of copper or zinc, but increased with increasing temperature or pressure. This result suggests that a catalytic effect of the metal for diamond formation should be considered.

3. Crystals grown from the alloys did not show a different morphology from those grown from conventional metals, although the crystal size tended to be small, 0.2 to 0.4 mm across.

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