

Influencing factors for diamond formation from several starting carbons

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The possible influencing factors for diamond formation which prevent non-graphitic carbons from transforming to diamond in the presence of nickel as solvent-catalyst were pursued. The relative amount of nickel to carbon did not affect the behaviour of each starting carbon on diamond formation. The existence of a graphitic structure in the starting carbon was not the major prerequisite for diamond formation. Adsorbed gases on the starting carbon and atmospheric gases in the high pressure cell were found to be the most important influencing factors for diamond formation. Hydrogen and chemical species containing hydrogen atoms were the most harmful.

1. Introduction

Diamond is usually synthesized from artificial graphite in presence of a 3d-transition metal as a solvent-catalyst under static pressure [1]. Diamond formation is thought to proceed by the dissolution of metastable graphite into the molten metal and the precipitation of stable diamond from super-saturated solution in the diamond stable region. It is well known that elementary carbon exists in various forms from amorphous to highly crystallized graphite except diamond. The starting carbons must influence diamond formation, but there are a few reports which mention this point.

Kasatochkin *et al.* [2] reported the rate of diamond formation from various parent carbons in the presence of a solvent-catalyst. They suggested that the well crystallized graphite directly transformed to diamond, while amorphous carbon needed an incubation time for the transition to diamond, in which amorphous carbon was graphitized intermediately. On the other hand, Gankevich *et al.* [3] studied diamond formation from cokes and vitreous carbon preheated at various temperatures in the presence of a solvent-catalyst. Their results indicated that the crystallinity of the starting carbon was very important for diamond formation but graphite formed from amorphous carbon under high pressure did not transform to diamond

so readily. Tsuzuki *et al.* [4] investigated the behaviour of several starting carbons in the presence of nickel as a solvent-catalyst under high pressure and showed that amorphous carbons were only graphitized under conditions where graphite transformed to diamond. From the carbon contents of the nickel solid solution of carbon formed (Ni_xC), they suggested that amorphous carbons have higher solubilities into molten nickel than well-crystallized graphite in correspondence with the difference of their free energies. The simple diamond formation mechanism of the dissolution of graphite and the precipitation of diamond in molten nickel solid solution could not explain these experimental results. There must be important factors other than the solubility of carbon for the supersaturation.

In this work, nickel was used as the typical solvent-catalyst for the diamond formation. Graphitized pitch coke (GPC), pitch coke (PC) and glassy carbons preheated at about 3000°C (GC-30) and 2000°C (GC-20) were employed as starting carbons. In order to elucidate the factors influencing diamond formation other than the solubility of carbon, a series of experiments to investigate the following were carried out; the relative concentration of nickel, the mixture systems of GPC and other carbons, the seeding of diamond and the gases adsorbed on carbon.

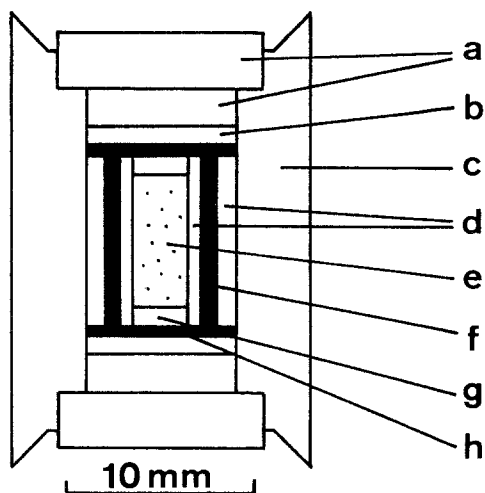


Figure 1 High pressure cell arrangement for girdle-type high pressure apparatus. a is the WC disc, b is the SKH-9 disc, c is the pyrophyllite holder, d is the fired pyrophyllite sleeve, e is the sample, f is the GC heater, g is the fired pyrophyllite chip and h is the graphite plate.

2. Experimental procedure

The high pressure and temperature treatments were accomplished with a girdle-type high pressure apparatus at pressures of 7 and 8 GPa and temperatures of 1700°C in the diamond stable region. Fig. 1 shows the high pressure cell arrangement in which the sample was heated by an alternating electric current passed through the glassy carbon heater. The pressure was calibrated at room temperature by the pressure-induced phase transition of Bi, Tl and Ba [5]. The temperature was determined from the relation of the melting points of Ag, Au and Ni under high pressure to the applied electric power; the pressure effect of Ag, Au and Ni were calibrated [6, 7]. The sample in the pressure cell was compressed to the desired pressure and then electric power was applied to heat the sample to 1700°C. After heat treatment, the sample was quenched to room temperature under high pressure and then decompressed.

Four starting carbons were used in this work. Graphitized pitch coke (GPC) had only a well-developed graphitic structure and readily transformed to diamond up to 95 wt% of carbon in presence of 20 wt% nickel at 8 GPa and 1700°C. Pitch coke (PC) consisted of a non-graphitic and graphitizable component. The glassy carbon treated at about 3000°C (GC-30) had both graphitic and non-graphitic components and partially converted to diamond up to 75 wt% of carbon

under the same conditions as the GPC. The glassy carbon treated at about 2000°C (GC-20) contained a non-graphitic and non-graphitizable components. Both PC and GC-20 were graphitized and did not form diamond in the presence of 20 wt% nickel at 8 GPa and 1700°C.

The present work was carried out in order to discover why diamond does not form from amorphous carbon even in the presence of 20 wt% nickel at up to 8 GPa and 1700°C in the diamond stable region, and also to discover the effects of the relative amount of nickel to carbon, the mixture of other starting carbons and GPC, the addition of diamond seed crystals, the pre-treatment of starting carbon under reduced pressure, other additives, and the treatment of GPC in various gases, on diamond formation. The amount of diamond formed by high pressure and temperature treatment was determined from the relative intensity of diamond 111 X-ray diffraction to that of graphite 002 X-ray diffraction, using an established calibration curve.

3. Results and discussion

3.1. Effect of the relative amount of nickel to carbon on diamond formation

In previous work [4], a powder mixture sample of 80 wt% carbon and 20 wt% nickel was used. In order to elucidate the effect of the relative amount of nickel to carbon on diamond formation, nickel foil of 0.1 mm thickness was placed on the centre of the carbon sample perpendicular to the compression axis, instead of mixing nickel powder, to increase the local concentration of nickel.

GPC transformed well to diamond in a wide region of the specimen where nickel diffused at 8 or 7 GPa and 1700°C for 10 min. A small quantity of diamond also formed from GC-30 in a narrower region under 8 GPa. GC-30 was mainly graphitized except that trace quantities of diamond formed only where nickel had diffused under 7 GPa. GC-20 was graphitized with the formation of a trace amount of diamond under 8 GPa but graphitized fully under 7 GPa. PC was graphitized only at 8 GPa and 1700°C.

In the case of GC-20, a trace amount of diamond formed when using nickel foil but the basic behaviour of diamond formation from each starting carbon was not influenced by the amount of nickel to carbon. These results indicate that the relative amount of carbon is not the key influencing factor for the diamond formation.

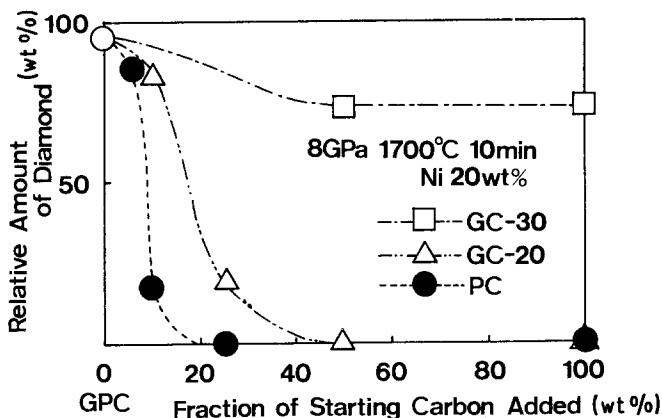


Figure 2 Changes of diamond yields with added amounts of each carbon to GPC in the presence of 20 wt % nickel at 8 GPa and 1700° C for 10 min.

3.2. Effect of existence of graphite structure in starting carbon

GPC and GC-30 had a graphitic component which did transform to diamond, while PC and GC-20, composed only of non-graphitic component, were graphitized and did not give any diamond at 8 GPa and 1700° C. The existence of graphitic structure in the starting carbon might be of importance for diamond formation, thus, samples of GPC mixed with the other carbons were treated in the presence of 20 wt % nickel at 8 GPa and 1700° C for 10 min. Fig. 2 shows the changes of relative amounts of diamond formed from the mixture samples. In the GPC–GC-30 system, the amount of diamond decreased gradually from 95 to 75 wt % with an increase of the amount of GC-30 added to GPC. In the GPC–PC and GPC–GC-20 systems, the diamond yields decreased drastically with an increase of the amount of non-graphitic carbon and reached zero at 25 wt % PC and 50 wt % GC-20. GC-30, with only about 20 wt % graphitic component, transformed to diamond up to about 75 wt % at 8 GPa and 1700° C. Even if the main portion of the mixture is the graphitic component with a small amount of added non-graphitic component, no diamond was formed by the addition of non-graphitic component to 25 wt %. These results show that the existence of graphitic structure in the starting carbon is not the major condition for the diamond formation. The other factors associated with the addition of the non-graphitic component have to be examined.

3.3. Effect of seeding of diamond crystals

Non-graphitic carbon has a higher solubility in molten nickel than graphitic carbon [4]. When the degree of supersaturation is too high, the metastable phase can be crystallized first instead of the

stable phase due to the barrier of nucleation. This phenomenon is known as Ostwald's step rule [8]. Nucleation of diamond may control the diamond formation and be hindered by the large supersaturation. Diamond crystals, which were synthesized and separated from solvent–catalyst metal and residual graphite, were used as seed crystals. Samples of 76 wt % PC or GC-20, 4 wt % diamond and 20 wt % nickel were treated at 8 GPa and 1700° C for up to 30 min. In spite of the addition of diamond seed, no increase in the amount of diamond by this treatment was found. This fact indicates that the nucleation of diamond in this case may not be the key reason why diamond formation could not be observed from non-graphitic carbons, which have higher solubility in molten nickel than graphite.

3.4. Effects of adsorbed and atmospheric gases

Non-graphitic carbon has a different structure and surface activity from graphitic carbon and is thought to adsorb more gases than well-crystallized graphite. These gases can affect the diamond formation process. PC and GC-20 non-graphitic carbons were degassed at 2×10^{-5} torr and 1000° C for 3 h and quickly mixed with nickel and treated at 8 GPa and 1700° C for 10 min. The crystallinities of PC and GC-20 were not changed by the treatment in vacuum. A small amount of diamond formed from the GC-20 treated in vacuum. This fact shows that adsorbed gases prevent diamond formation from non-graphitic carbons.

In the atmosphere N_2 , O_2 , H_2O , organic species, CO , CO_2 etc. may be adsorbed on the carbon surface.

In order to determine the kind of gas influencing

TABLE I Effects of added compounds on diamond formation in the presence of nickel (75 wt % GPC, 20 wt % Ni, 5 wt % compound at 8 GPa and 1700° C for 10 min)

Compound	Diamond yield (%)
MgO	92
Mg(OH) ₂	0
MgCO ₃	90
CaO	96
Ca(OH) ₂	0
CaCO ₃	95
α-Al ₂ O ₃	90
Al(OH) ₃	0
SiO ₂ (α-quartz)	94
NiO	94
Ni(C ₅ H ₅) ₂	0
Fe ₃ O ₄	93
Fe ₂ O ₃	95
Fe ₂ (CO) ₉	88

diamond formation, firstly small amounts of H₂O or *n*-C₆H₁₄ in liquid at room temperature were added to the mixture of 80 wt % GPC and 20 wt % nickel from which diamond forms easily. No diamond was found in both cases. Secondly compounds, which are solid at room temperature but can produce gases at high pressure and temperature, were added to GPC. The samples of 75 wt % GPC, 20 wt % nickel and 5 wt % added compound were treated at 8 GPa and 1700° C for 10 min. Table I shows added compounds and the diamond yield. Stable oxides such as MgO, CaO, α-Al₂O₃ etc. did not affect the yield of diamond formed. The addition of hydroxides decreased the diamond yield to zero. In the case of carbonates of magnesium and calcium, which did not decompose under this condition, the diamond yield did not change. Transition metal oxides also did not affect the diamond formation. Organometallic compounds like nickelocene. Ni(C₅H₅)₂, which produces hydrogen on heating, reduced the diamond yield to zero. Iron nonacarbonyl, Fe₂(CO)₉, which decomposes to produce CO, had very little effect on the diamond formation.

The effects of intentionally adsorbed gas on GPC were also investigated. GPC was heat-treated at 300° C for 3 h and cooled down in flow of the given gas. Table II shows the intentionally adsorbed gases and the yield of diamond after the treatment at 8 GPa and 1700° C for 10 min. Hydrogen had the most remarkable inhibitory effect on diamond formation, whilst CH₄ and O₂ affected diamond formation slightly, while N₂ and CO₂ did not show any influence on the diamond formation. These results reveal that gases adsorbed on the

TABLE II Effects of adsorbed gases on graphitized pitch cokes on diamond formation in the presence of nickel (80 wt % GPC, 20 wt % Ni at 8 GPa and 1700° C for 10 min)

Gas	Diamond yield (wt %)
N ₂	95
O ₂	88
CO ₂	95
H ₂	76
CH ₄	89

starting carbon have the largest effects on diamond formation. H₂ and compounds evolving hydrogen atoms during treatment are the most harmful substances. It has been reported that natural diamond often includes various gaseous species such as H₂, CH₄, H₂O, O₂, CO₂ etc. [9–11]. The effects of gases might be a clue to elucidate details of diamond formation mechanism in the naturally occurring process and the synthesis by the solvent–catalyst method.

3.5. Function of Ni_xC solvent–catalyst formed under various conditions

Nickel reacts with each starting carbon to form a nickel solid solution of carbon (Ni_xC) at high pressure and temperature. Ni_xC formed from GPC, PC or GC-20 at 6 GPa and 1700° C was separated magnetically from residual carbon, mixed with GPC and then treated at 8 GPa and 1700° C for 10 min. Large amounts of diamond formed irrespective of the starting carbon from which the Ni_xC was synthesized. Ni_xC synthesized from GPC by the addition of H₂O or *n*-C₆H₁₄ also had the ability to form diamond. These results indicate that the activity of Ni_xC itself was not influenced by the starting carbon and the gases where Ni_xC had been synthesized.

Chemical species containing hydrogen atoms are harmful for diamond formation. There can be two possible mechanisms by which gaseous species influence diamond formation. One is that gaseous species accumulate on the carbon–molten nickel interface and prevent carbon from reacting with nickel. The other is that gaseous components dissolve in molten nickel and violate the catalytic ability of nickel to form diamond.

4. Conclusion

Graphitic carbon transforms to diamond, while non-graphitic carbon changes to metastable graphite even in the diamond stable region in the presence of nickel under high pressure and temperature

treatment [4]. Several possible influencing factors for the diamond formation other than solubility were studied by using four starting carbons and nickel.

The relative amount of nickel to carbon is not an influencing factor. The existence of graphitic structure in the starting carbon is not the major sufficient condition for diamond formation, neither is nucleation of diamond in the supersaturated nickel-carbon melt. The most important factor which is found in this work, is gases adsorbed on the starting carbons and atmospheric gases in the high pressure cell. Among these gases, H₂ and species containing hydrogen atoms are the most harmful for diamond formation. Ni_xC formed by the solidification of melt in atmospheres containing gaseous species still has a solvent-catalyst function in diamond formation. These results suggest that the starting carbon for diamond synthesis should be degassed before placement in the high pressure cell.

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