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Effects of crystallinity of starting carbons on diamond formation in presence of nickel under high pressure and high temperature condition

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The processes of graphitization and diamond formation of several carbons in the presence of nickel were investigated under 8 GPa at temperatures up to 1800° C. Diamond was formed easily from graphitized pitch coke which had a well-developed graphitic structure and in less amount from glassy carbon preheated at about 3000° C which was partly graphitized. On the other hand, pitch coke and glassy carbon, preheated at about 2000° C and not graphitized, did not transform to diamond but remained graphitized even in the diamond stable region. Diamond from graphitized pitch coke and glassy carbon preheated at about 3000° C grew to form by direct bonding.

1. Introduction

Diamond is usually synthesized from crystallized graphite in the presence of transition metals and their alloys (especially, iron, cobalt and nickel) as solvent-catalyst [1, 2]. The mechanisms of diamond formation is thought to be the precipitation of diamond from supersaturated solutions of metals with carbon in the diamond stable region as shown in Fig. 1. In addition to diamond, elemental carbon forms in various states from amorphous material to well-crystallized graphite. The crystallinity of parent carbons may influence the transformations to diamond. However, there are few published reports in this area. This paper examines further this aspect of diamond formation.

Wentorf [3] investigated diamond formation from different carbons and carbonaceous compounds in the pressure range 9.5 to 15 GPa and in the temperature range 1200 to 3000 K. Amounts and properties of formed diamond are strongly dependent upon the starting materials. Kasatochkin *et al.* [4] reported rates of diamond formation from various starting carbons in the presence of solvent-catalyst metal at pressures up to 8 GPa and temperatures up to 1700° C. Well-crystallized graphite immediately converted to diamond, while the partially graphitized carbon required an incubation period before being transformed to diamond. These authors also proposed that the amounts of diamond formed from graphitizable carbon exceeded those from non-graphitizable carbons. Recently, the behaviour of non-graphitizable glassy carbon under high pressure and high temperature conditions without additions of metals was reported by Hirano *et al.* [5]. The results indicated that even in the diamond stable region up to 10 GPa, glassy carbon was first metastably graphitized and then transformed to diamond.

In this work, nickel was employed as a typical solvent-catalyst for the diamond formation through the formation of the simple eutectic system with carbon. The process of the diamond formation in the nickel–graphite system may be simpler than with other metals which form stoichiometric carbides. The driving force for diamond formation should be the solubility difference between the stable diamond and the metastable graphite in a nickel solution. If amorphous carbon could be used as a parent material, then the degree of supersaturation would be expected to increase as compared with well-crystallized graphite, which accelerates diamond formation. In order to investigate the

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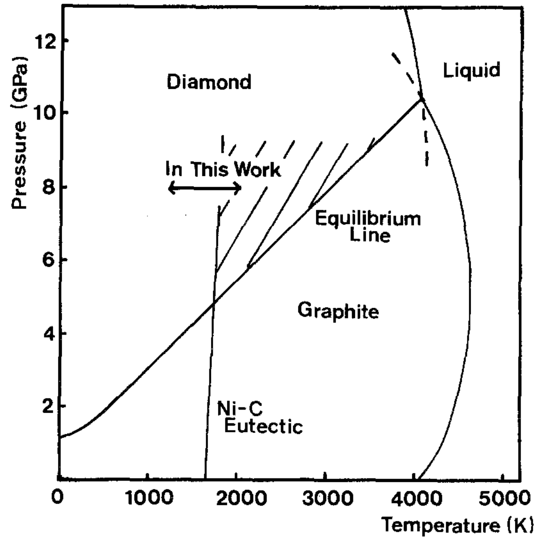

Figure 1 Simplified carbon phase diagram with nickel-carbon eutectic and experimental conditions in this work.

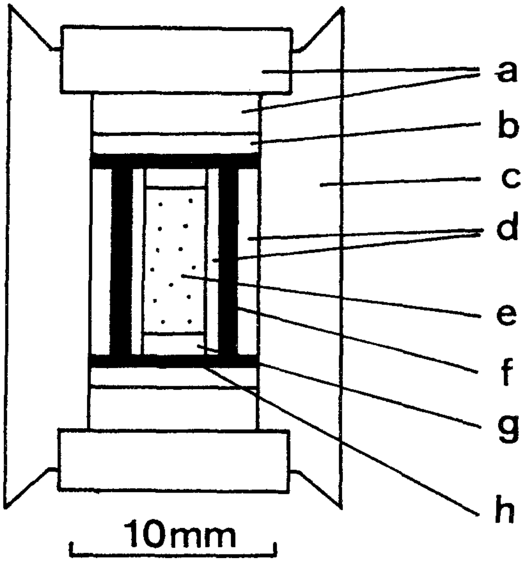

Figure 2 High pressure cell arrangement (a) WC disc; (b) SKH-9 disc; (c) pyrophyllite holder; (d) fired pyrophyllite sleeve; (e) sample; (f) GC heater; (g) fired pyrophyllite chip; (h) graphite plate.

effects of crystallinity (degree of graphitization) of starting carbons on diamond formation, graphite, graphitizable pitch coke and non-graphitizable glassy carbon were heat-treated with nickel under high pressure and high temperature. The behaviour of each carbon with respect to diamond formation was examined.

2. Experimental details

Table I shows the lattice constant $c_{0_{002}}$, the crystallite size $L_{c_{002}}$, degree of graphitization P and the fraction of the graphitic component from (002) X-ray diffraction profiles of the four parent carbons. The graphitized pitch coke (GPC) was prepared by heating the pitch coke at 2800° C. The graphitizable pitch coke (PC) was prepared by carbonization of coal-tar pitch at about 1500° C. Glassy carbons were preheated at about 2000° C (GC-20) and 3000° C (GC-30). The glassy carbon GC-20 had only the non-graphitic and non-graphitizable component, while the glassy carbon GC-30 has both the non-graphitic and non-graphitizable as well as the graphitic component.

Conversions were carried out in a girdle-type high-pressure cylinder [5] up to pressures of 8 GPa, temperatures of 1800° C and 30 min duration. The powder mixture was heated by alternating electric current passing through the glassy carbon heater (Fig. 2). Pressures were calibrated at room temperature by the pressure induced polymorphic transition of reference metals (bismuth, thallium and barium) followed by changes in electrical resistivity [6]. Temperatures were determined from the melting points of silver and gold under pressure and required applied electric powers. The pressure effect on the melting points were taken from data of Cohen *et al.* [7]. Reported pressures and temperatures may be in error by about 5%.

The mixture of 80 wt% starting carbon and 20 wt% nickel (about 95 at% carbon and 5 at% nickel) in the pressure cell first compressed to the required pressure, the entire girdle-type pressure cylinder immersed into flowing cold

TABLE I Crystallinities of parent carbons

	$c_{0_{002}}$ (pm)		$L_{c_{002}}$ (nm)		P		Fraction of G (%)
	NG	G	NG	G	NG	G	
GPC		672.2		91		0.92	100
PC	688.6		4.1		0		0
GC-30	683.4	672.8	5.4	38	0.27	0.88	19
GC-20	692.7		2.6		0		0

NG: Non-graphitic component; G: graphitic component.

water and then the electric power was applied to heat the mixture to the desired temperature. After heat treatment, the sample was quenched to room temperature under pressure and decompressed.

Specimens before and after treatment were analysed by X-ray powder diffraction and scanning electron microscope. Specimens treated are of two types of diffraction profile of the (0 0 2) X-ray diffraction line of carbon. One was symmetrical following correction of diffraction intensities for Lorentz-polarization, atomic scattering and absorption factors. The other profile was composed of non-graphitic and graphitic component, i.e. the so-called composite profile. The composite profiles were resolved into two components by a method proposed by Noda *et al.* [8]. The amount of the graphitic component was calculated from the ratio of the area of the graphitic component to that of the non-graphitic component. Some specimens were highly graphitized and showed the (0 0 4) diffraction line. The amount of diamond was determined from the relative intensities of diamond (1 1 1) diffraction line to the graphite (0 0 2) diffraction line, using an established calibration curve. In all experiments, the use of nickel gave only nickel solid solutions of carbon Ni$_x$C. The lattice constant of Ni$_x$C was measured by the X-ray diffraction line using silicon as the internal standard.

3. Results

3.1. Behaviour of graphitized pitch coke (GPC)

Graphitized pitch coke had only the graphitic component before treatment. The mixture sample of 80 wt% GPC and 20 wt% nickel was treated at 8 GPa and temperatures up to 1700° C. Fig. 3 shows the changes of the relative amounts of the carbon phases in the specimen heated at various temperatures for 10 min. Diamond formation began at 1400° C, amounts increasing with heat treatment temperature and reaching to 95 wt% of the carbon phases at 1700° C. On the other hand, the crystallinity of the graphitic component in the specimen decreased from the initial L_c of 91 m, to 40 nm at 1700° C with increasing treatment temperature and diamond formation.

The diamond formed on raising the temperatures to 1700° C. About 5 min was required before reaching 1700° C and about 60 wt% of diamond had been formed just before the temperature reached 1700° C. Diamond formation was equilibrated for 5 to 10 min and amounts of diamond were unchanged even by heat treatment for 30 min at 1700° C.

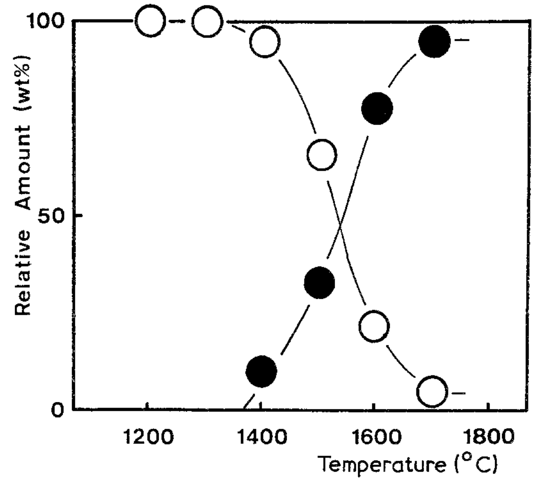

Figure 3 Changes in relative amounts of carbon phases formed by the mixture of 80 wt% GPC-20 wt% nickel at 8 GPa for 10 min: graphitic component (○); diamond (●).

3.2. Behaviour of pitch coke (PC)

The pitch coke was graphitizable and had only the non-graphitic component before treatment. The mixture of 80 wt% PC and 20 wt% nickel was treated at 8 GPa and temperatures up to 1700° C. Fig. 4 shows the changes of the relative amounts of the carbon phases in the specimen heated at various temperatures for 10 min. Only the non-graphitic component was found at around

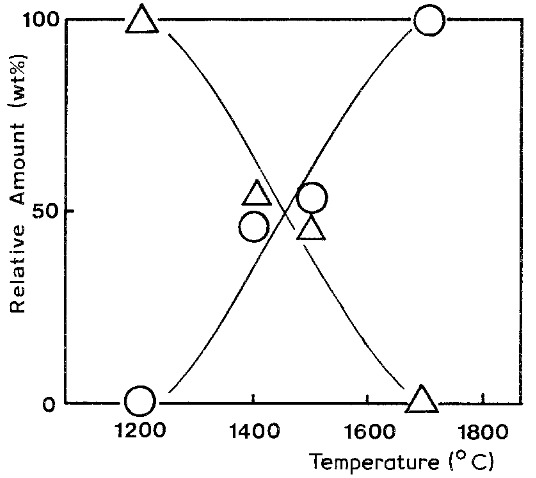

Figure 4 Changes in relative amounts of carbon phases formed by the mixture of 80 wt% PC-20 wt% nickel at 8 GPa for 10 min: non-graphitic component (Δ); graphitic component (○).

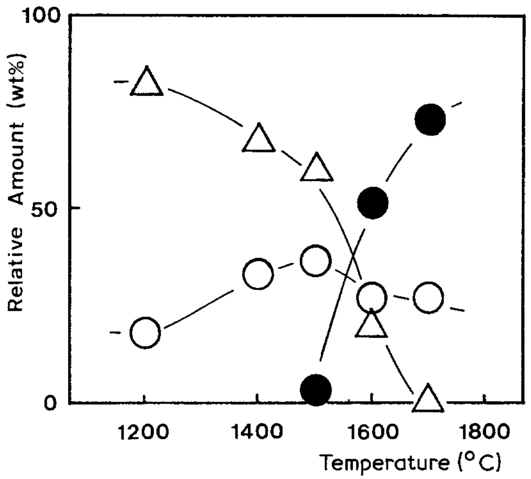

Figure 5 Changes in the relative amounts of carbon phases formed by the mixture of 80 wt % GC-30-20 wt % nickel at 8 GPa for 10 min: non-graphitic component (△); graphitic component (○); diamond (●).

1200° C and graphitization took place at 1400° C even in the diamond stable region. The amount of the graphitic component increased with increasing treatment temperature. At 1700° C, diamond formation could not be observed. With increasing amounts of graphitic component, the crystallinity of graphitic component increased to c_0 of 672 pm and L_c of 27 nm at 1700° C.

Graphitization proceeded during heating to 1700° C but non-graphitic carbon remained on reaching 1700° C. The amount and the crystallinity of graphitic component increased with heat treatment time and equilibrated in 10 min, with no diamond formation.

3.3. Behaviour of glassy carbon (GC-30)

Glassy carbon (GC-30) has both non-graphitic and graphitic components before treatment. Fig. 5 shows changes in the relative amounts of the carbon phases in the specimen heated at various temperature for 10 min. The amounts of these two components at 1200° C did not change from initial values. The metastable graphitic component increased with increasing heat treatment temperature, followed by diamond formation at 1500° C. The amount of diamond increased to 70 wt% at 1700° C and the coexistent graphitic component had c_0 of 672 pm and L_c of 30 nm.

Graphitization and diamond formation occurred simultaneously during heat treatment to 1700° C. About 40 wt% of diamond was formed and the non-graphitic component in addition to the graphitic existed before the treatment temperature reached 1700° C. The amount of diamond formed was equilibrated at about 70 wt% for 2 to 5 min and unchanged with prolonged treatment for longer times at 1700° C.

3.4. Behaviour of glassy carbon (GC-20)

Glassy carbon (GC-20) has only the non-graphitic component before treatment. Fig. 6 shows the changes of relative amounts of the carbon phases at various temperatures for 10 min. Diamond form did not take place even at 1800° C, graphitization of glassy carbon only being observed by heat treatment above 1200° C. The graphitic component formed at 1800° C had c_0 of 672 pm and L_c of 50 nm.

The amount and crystallinity of the graphitic component increased with the treatment time at 1700° C and equilibrated for 10 min. Diamond formation could not be detected by treatments even for 30 min at 1700° C.

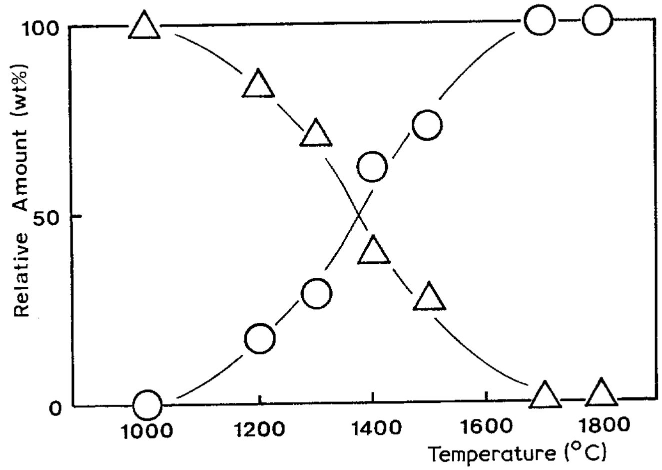

Figure 6 Changes in relative amounts of carbon phases formed by the mixture of 80 wt % GC-20-20 wt % nickel at 8 GPa for 10 min: non-graphitic component (△); graphitic component (○).

3.5. Observation of carbons treated under high pressure and high temperature

Graphitized pitch coke (GPC) treated up to 1400° C at 8 GPa had the plate-like morphology of large layered structures of graphite. Diamond formed from GPC at 1700° C for 10 min is shown in Fig. 7a, and is intergrown by the direct bond formation with a grain size from 50 to 100 μm. The glassy carbon (GC-30) treated at 8 GPa changed its morphology from its irregular shape of grains at low temperature to layer structure at 1400° C because of an increased graphitic component. Fig. 7b shows diamond from GC-30 at 1700° C for 10 min, with the intergrown formation.

Both pitch coke and glassy carbon (GC-20) changed their morphologies to graphitic layer morphologies with increasing the heat treatment temperature. The specimens from PC and GC-20 treated at 1700° C for 10 min are shown in Fig. 7c and d, respectively.

4. Discussion

In the nickel–graphite system, the diamond formation mechanism is supposed to be the disolution-precipitation process in molten nickel. Nickel also has the catalytic effect on graphitization. From the well-crystallized graphite (GPC), diamond formed above the nickel–diamond eutectic temperature is known. The partially graphitized glassy carbon (GC-30) also transformed partly to diamond. On the other hand, the non-graphitic carbons of PC and GC-20 were only graphitized in the diamond stable region, and did not form diamond under same conditions of treatment of GPC and GC-30 carbons. Non-graphitizable glassy carbon (GC-20) was highly graphitized compared with the graphitizable PC. Under the conditions where diamond formation did not occur as for PC and GC-20, graphitization was considered to proceed by the disolution of non-graphitic carbon into the molten nickel followed by precipitation of metastable graphitic component instead of formation of stable diamond.

Carbons with poorer crystallinity as in non-graphitic carbon may have higher free energies than well-crystallized graphite, leading to higher solubilities in molten nickel. In order to evaluate

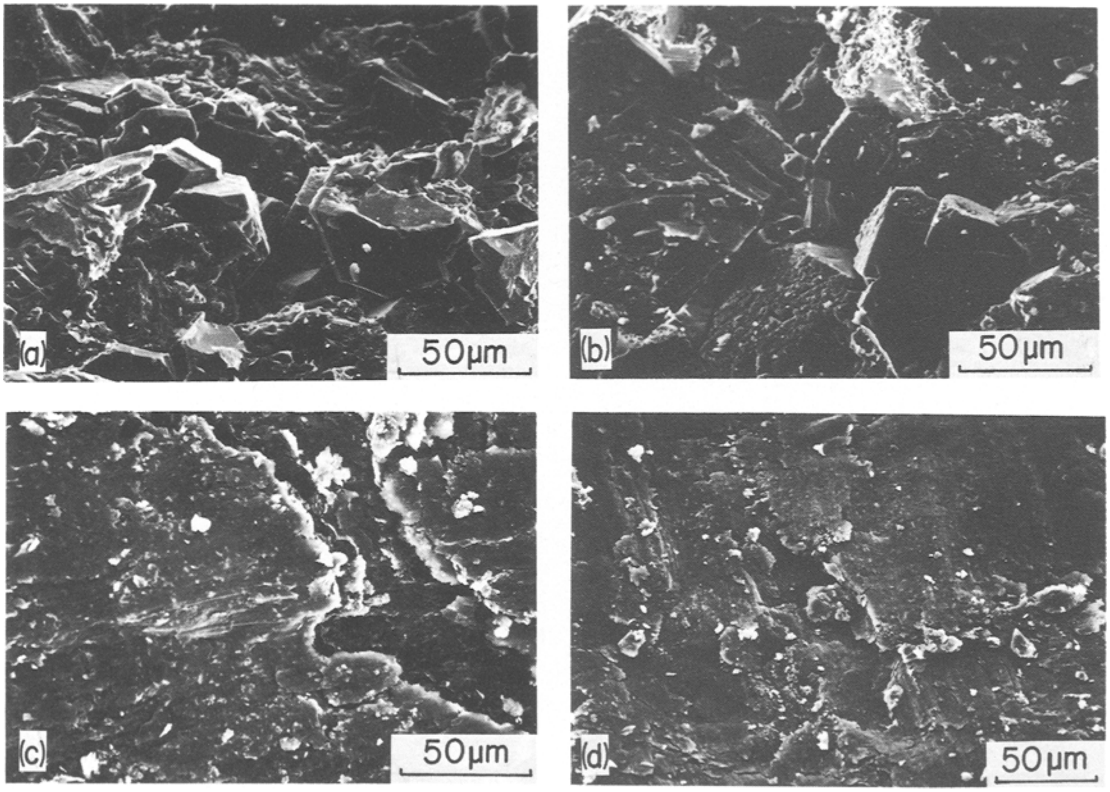

Figure 7 SEM photographs of samples of 80 wt% starting carbon–20 wt% nickel treated at 8 GPa and 700° C for 10 min: (a) graphitized pitch coke (GPC); (b) glassy carbon GC-30; (c) pitch coke (PC); (d) glassy carbon GC-20.

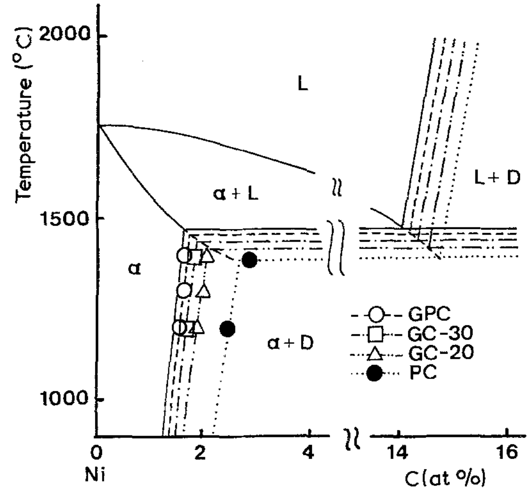

Figure 8 Presumed nickel-carbon phase diagram at 8 GPa together with measured solid solubilities of starting carbons into nickel.

this concept, the carbon contents of Ni_xC, which was formed in all experiment in this work in coexistence with diamond and/or carbons and interstitial solid solution of carbon, were determined from the lattice constants of Ni_xC (fcc) according to the equation proposed by Zwell *et al.* [9]. The molten nickel with carbon was difficult to quench at room temperature and hence carbon contents in quenched specimens above the eutectic point could not be determined accurately. Carbon contents were measured in the solid state region at lower temperatures. Fig. 8 shows the proposed phase diagram at 8 GPa determined by the measurement of the solid solubility of carbon in Ni_xC dependent on parent carbons. The outline of the phase diagram was deduced from that at 5.4 GPa reported by Strong and Hanneman [10]. Assuming that the solution state of carbon atoms in molten nickel was independent of the parent carbon, the solubilities of carbon in molten nickel above the eutectic point were deduced from solubilities in the solid state region by extending the phase diagram to a metastable region. Inspite of higher solubilities of PC and GC-20 than GPC, diamond could not form under these conditions. This implies that the solubility and the degree of graphitization of the parent carbon are the controlling factors for diamond formation but there exist other factors which eventually influence the diamond formation process.

The pre-treatment of parent carbon and the control of nucleation may affect diamond formation in presence of a solvent-catalyst.

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