Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 39 (2013) 8861–8864

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Diffusion coefficient of carbon in Fe–Ni alloy during synthesis of diamond under high temperature and high pressure

I-Chiao Lin, Chung-Jung Lin, Wei-Hsing Tuan*

Department of Materials Science & Engineering, National Taiwan University, Taipei 10617, Taiwan

Received 12 November 2012; received in revised form 3 April 2013; accepted 22 April 2013
Available online 30 April 2013

Abstract

Synthetic diamond particles were prepared under high temperature and high pressure using arrayed seeds. A dense Fe–Ni alloy shell covered each diamond seed during synthesis; the growth of diamond particles was controlled by the diffusion of carbon through the metallic shell. The diffusion coefficient of carbon through Fe–Ni melt at 1600 K and 5.5 GPa is about 5×10^{-6} cm^2/s, with an activation energy for diffusion of 336 kJ/mol.

Keywords: D. Carbon; Diamond synthesis; High pressure; High temperature; Diffusion coefficient

1. Introduction

Diamond is the hardest substance found in nature; its thermal conductivity as well as electron mobility is good. Synthetic diamonds are therefore used widely in abrasives, cutting and polishing tools, and heat sinks. As early as 1953, Sweden scientists synthesized the first man-made diamond [1–4]. The synthesis of diamond has subsequently attracted a lot of attention. Nowadays, diamonds can be synthesized using high pressure high temperature synthesis (HTHP), chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques. The CVD and PVD methods produce only diamond (or diamond-like carbon) films; however, the HTHP method is capable of mass-producing diamond particles. The technique is well accepted in industry.

According to the phase diagram, graphite can transform to diamond at very high temperature and pressure. The addition of some metals can reduce the synthesis temperature and pressure. These metals are thus sometimes termed as metallic catalysts for the HTHP process [4]. The commonly used metallic catalysts are group VIII metals, such as Fe, Co, Ni and their alloys. The use of other metals (Al, Nb, Mn, Cr, etc.) and non-metals (magnesium carbonate, barium carbide, hydroxides, carbonates and phosphorous [3–7]) has also been reported. However, the transition metals are more popular, because the yield from these metals using the HTHP process is higher [4].

During the heating stage of the HTHP process, the metal catalyst is melted to form a shell covering each diamond nucleus. The carbon from the graphite then diffuses through the metallic melt to deposit itself onto the surface of the diamond nucleus, and the diamond particle grows. The slowest step in the growth of diamond is the diffusion of carbon through the metallic melt [5,8]. The synthesis of diamond particles is thus a diffusion-controlled process.

Many studies had been conducted to determine the diffusion coefficient of carbon in molten Fe under 1 atm. Nevertheless, the diffusion coefficient of carbon in metallic melts under high pressure is seldom reported, perhaps because high temperature and high pressure are involved. The high-pressure diffusivity is lower than 1-atm diffusivity [9]. Only a few studies had been conducted to investigate the diffusion coefficient of carbon in metals under high pressures [5,10,11]. Table 1 summarize these reported data. The diffusion coefficient of carbon in Fe–Ni melt under high pressure has not been reported before.

In the study of Strong and Hanneman [5], the growth of one diamond seed on Ni melt was investigated. The growth rate of (111) face of the seed was used to estimate the diffusion coefficient. Sibanda et al. had used a diffusion couple to

---

*Corresponding author. Tel.: +886 2 33663899; fax: +886 2 23659800.
E-mail address: tuan@ntu.edu.tw (W.-H. Tuan).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.04.078

Table 1
Reported values of diffusion coefficient of carbon in transition metals under high temperature and high pressure.

Metals	Condition		Diffusion coefficient (cm^2/s)	References
	Pressure (GPa)	Temperature (K)		
Ni	5.4	1690	2×10^{-5}	[5]
Ni	5.8	1840	4×10^{-5}	[5]
Fe–Co	4.2	1563	1×10^{-6}	[10]
Fe–Co	4.2	1603	1×10^{-6}	[10]
Fe	5.7	1688	4×10^{-5}	[11]
Fe–Ni	5.5	1623	8×10^{-6}	This study
Fe–Ni	5.5	1573	1×10^{-6}	This study

determine the diffusion coefficient of carbon through Fe–Co alloy [10]. No diamond was formed under the conditions they used. Strong and Chrenko had explored the processing conditions to form large diamond gem [11]. The diffusion coefficient was estimated from the growth of a few diamond particles. In the present study, many diamond seeds were used for each batch.

The synthesis of diamond involves nucleation and growth processes. Previous studies have indicated that both size variation and shape uniformity are improved through the use of arrayed seeds [12]. More importantly, the nucleation process can be suppressed by using arrayed seeds; only the growth process takes place during diamond synthesis. In the present study, diamond particles were synthesized using arrayed seeds. Since the growth is controlled by the diffusion of carbon through the metallic catalyst at high temperature and high pressure, the diffusion coefficient of carbon through the transition metal melt can be determined.

2. Experimental method

Graphite powder (Morgan Carbon, USA) was used as the carbon source; the graphitization was 95%. Mixtures of Fe powder (BASF Co., Germany) and Ni powder (Inco Co., Canada) were used as the metallic catalysts. The starting weight ratio of the graphite, Fe and Ni powders was 0.30, 0.49 and 0.21, respectively. The powders were first mixed in a high-speed mixer (SM-30, Jaw Chuang Co., Taiwan); the mixture was then die-pressed to a disc with a diameter of 40.8 mm and a thickness of 0.86 mm. Diamond seeds with average size of 70 μm were used. To facilitate the placement of diamond seeds, a steel plate with arrayed holes was used. The seed was inserted into each hole first. The steel plate was then put on the top of graphite–Fe–Ni powder compact to allow the position of seeds. The diamond seeds were arrayed with separation of 0.8 mm in both x- and y-directions. There were 1993 diamond seeds in each powder compact. Several powder compacts were stacked into the reaction chamber. The distance between the seeds in z-direction was about 0.8 mm.

The high pressure and high temperature experiments were carried out using a six-sided anvil-type apparatus. The reaction chamber was side-heated by a Ni–Cr heating tube and insulated with a pyrophyllite (aluminum silicate hydrate, $Al_2Si_4O_{10}(OH)_2$) outside cylinder. Temperature measurements in the reaction chamber were carried out using Ni–Cr_2/Ni–Si thermocouples. Pressure calibration at ambient temperature was conducted using the phase transformation points of Ti, Tl and Ba. The stacked powder disks were pre-heated at 1423 K in vacuum (10^{-4} Torr). After the heat treatment, the disks were encapsulated using a metallic Fe container. The maximum pressure reached 5.5 GPa during the synthesis. The synthesis temperature was either 1573 K or 1623 K, and the time at synthesis temperature varied from 0 to 1560 s.

Both sand blasting and chemical etching were used to remove the metal shell from diamond particles after synthesis. Sand blasting is a quick technique to remove a large amount of Fe–Ni alloy. However, some metal shell remained on the surface of the diamond particles. The synthetic particles were then immersed in sulfuric acid to remove the metallic film from the surface. A scanning electron microscope (SEM, JSM5600, JEOL Co., Japan) was employed to observe the morphology of the diamond particles. The size classification was conducted using sieves. The shape index of the crystals was determined according to the diamond PDA999 standard (Element Six, Ireland) with a shape classification machine (IST, Diashape Co., Switzerland).

3. Results and discussion

In the present study, the starting graphite powder was 126 g in weight; diamonds of around 20–22 g (100–110 carats) were collected after each synthesis run. With the synthesis carried out at $T=1573$ K and $P=5.5$ GPa or at $T=1623$ K and $P=5.5$ GPa for 660–2500 s, the size of diamond particles ranged from 230 to 460 μm. Over 60% of diamond particles fell into a shape index range from 1 to 3. Fig. 1 shows the morphology of the diamond particles. The particles exhibit hexoctahedral shape and sharp edges. The figure demonstrates that the quality of the diamond particles is high.

After each run, the metal shell solidifies during cooling. The synthetic diamonds were arrayed at the original sites of the seeds. Each particle was covered with its metallic shell. The dense metallic surface layer was washed away using acid. Diamond particles with hexahedral or octahedral shapes were obtained. Fig. 2 shows the typical morphology of synthetic diamond particles covered with a metallic layer. Part of the

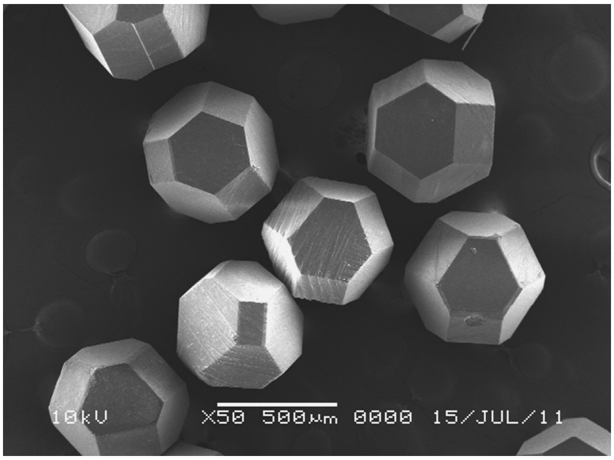

Fig. 1. Morphology of the diamond particles after synthesis at $T=1573$ K and $P=5.5$ GPa for 2560 s.

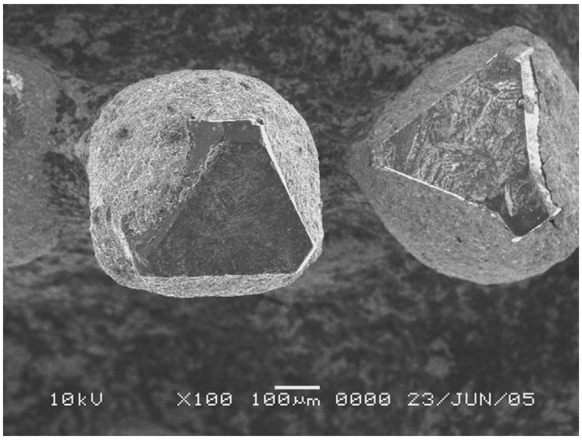

Fig. 2. Diamond particles covered with Fe–Ni alloy after synthesis. Part of the metallic shell was removed by sand blasting. The synthesis conditions were $T=1573$ K, $P=5.5$ GPa and $t=2560$ s.

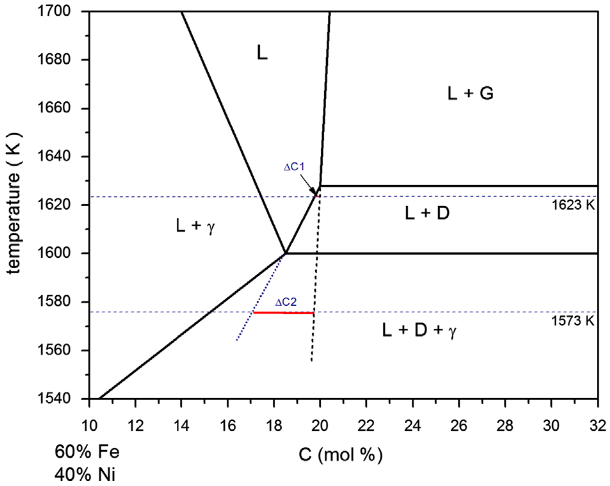

Fig. 3. Part of Fe–Ni–C phase diagram [7]. $\Delta C1$ and $\Delta C2$ are the solubility differences between L/(L+D) and L/(L+G) at 1623 K and 1573 K, respectively.

metallic layer was removed by sand blasting; the polyhedral shape with sharp edges can be observed. The average thickness of the metallic shell is around 40 μm.

Fig. 3 shows a part of the phase diagram for the Fe–Ni–C system at a pressure of 5.2 GPa [8]. In the present study, synthesis temperatures were 1573 K and 1623 K. From the figure, the over-saturation of carbon (ΔC) in Fe–Ni melt at 1573 K and 1623 K can be estimated as 2 mol% and 0.1 mol %, respectively. A relationship for the diffusion of carbon in metallic melt has been proposed by Strong and Hanneman [5]. They suggested that the growth of diamond is a diffusion process. The weight increase (Δw) of a diamond seed can be expressed as

$$\Delta w = K\frac{t}{\delta} \tag{1}$$

In the above equation, Δw is the weight increase from the seed diamond, t the growth time, δ the film thickness and K the reaction constant. Since the growth is controlled by the diffusion of carbon across the molten layer between the seed diamond and the graphite source, Fick's first law can be applied as

$$J = D\,\nabla C \tag{2}$$

In the above equation, J is the diffusive flux, D the diffusion coefficient, and ∇C the concentration gradient. Combining Eqs. (1) and (2), the following relationship is obtained:

$$\frac{\Delta w}{A} = D\frac{\Delta C}{\delta}t \tag{3}$$

where ΔC is the difference in solubility limits at the L/L+D (diamond) and L/L+G (graphite) boundaries and A the effective area during growth. Since D is a concentration-independent value over a small concentration gradient ΔC, the diffusion coefficient of carbon through the metallic melt can be calculated.

In our experiments, diamond particles after synthesis for 660, 1080, 1320, 1560, 1800, 2100 and 2560 s at temperatures of 1573 K and 1623 K were collected. Depending on the synthesis conditions, the average size of these diamond particles varied from 230 to 460 μm; the effective surface area of synthetic diamond ranged from 45 cm^2 to 134 cm^2. The diffusion coefficients were thus 8.1×10^{-6} cm^2/s at 1623 K and 1.3×10^{-6} cm^2/s at 1573 K. Table 1 collects the values of diffusion coefficient for carbon through metallic melts from previous works [5,10–11]. The experimental conditions are also shown. The table shows that the diffusion coefficients varied from 1×10^{-6} cm^2/s to 4×10^{-5} cm^2/s as Group VIII metals, Fe, Co, Ni and their alloys, were used as catalysts.

The diffusion coefficient depends on the experimental conditions; the conditions used in this study and in the previous studies are shown in Fig. 4. The melting point of Fe–Ni–C alloy [13] and the transformation line from graphite to diamond are shown for comparison. The figure demonstrates that the synthesis of diamond took place above the melting point of Fe–Ni–C alloy. Diamond particles form only above the graphite–diamond transformation line (points in the area labeled "Diamond"). The experimental conditions reported by

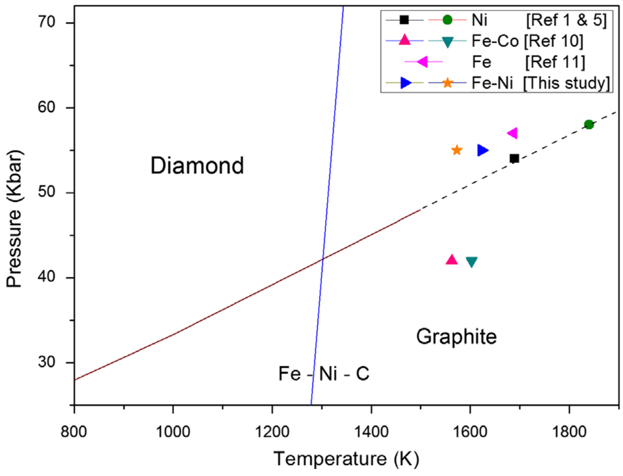

Fig. 4. *P–T* diagram for carbon [12]. The melting point of Fe–Ni–C alloy as a function of pressure is also shown for comparison.

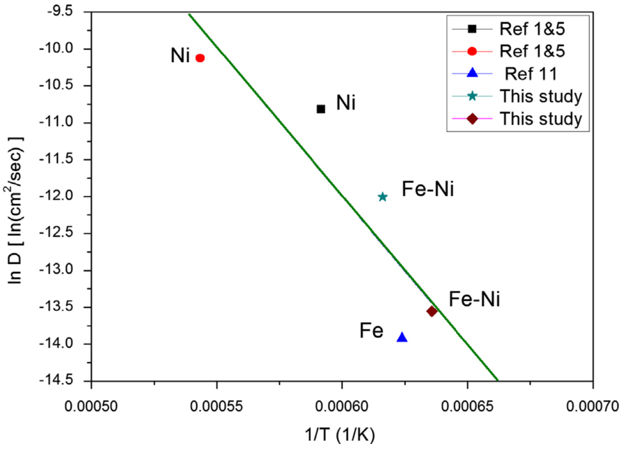

Fig. 5. Diffusion coefficient of carbon in transition metals as a function of temperature.

Sibanda et al. [10] are also shown in the figure (points in the area labeled “Graphite”). Sibanda et al. measured the diffusion coefficient of carbon in ferrous metals at low pressure; the carbon remained in the graphite state after the measurement. The results from Sibanda et al. provide a basis for comparison. They confirm that the diamond particles form only when the pressure is above the graphite–diamond transformation line. The figure indicates that thermodynamic equilibrium is achieved under the temperature–pressure conditions used in the present study. Therefore, the diffusion coefficient of carbon through the metallic melt can be estimated.

The diffusion coefficients from Table 1 are shown in Fig. 5 as a function of temperature. Fe, Co, Ni and their alloys were used as the metallic catalysts for the synthesis of diamond particles, and their diffusion coefficients are close to a straight line with respect to temperature. Since these metals and alloys are similar in crystalline structure, the diffusion mechanisms should be very similar. By assuming that the diffusion mechanism is the same, the activation energy for the diffusion of carbon through the metallic melt can be calculated. From Fig. 5, the activation energy can be estimated as 336 kJ/mol.

4. Conclusions

The synthesis of diamond under high temperature and pressure is controlled by diffusion of carbon through the metallic melt. The diffusion coefficient of carbon is important for the control of the synthesis process. By using arrayed seeds, the growth process dominates the synthesis. A dense Fe–Ni alloy shell covers each diamond particle. The diamond particles grow as carbon diffuses through the metallic melt. The diffusivity is estimated by measuring the average size of diamond particles. The diffusion coefficients of carbon at temperatures of 1573 K and 1623 K at 5.5 GPa were 1×10^{-6} cm^2/s and 8×10^{-6} cm^2/s, respectively. These values match well with previous experiment results. As Fe, Co, Ni and their alloys were used as the catalysts, the activation energy for the diffusion process was 336 kJ/mol.

References

[1] D. Choudhary, J. Bellare, Manufacture of gem quality diamonds: a review, Ceramics International 26 (2000) 73–85.
[2] F.P. Bundy, H.T. Hall, H.M. Strong, R.H. Wentorf, Man-made diamond, Nature 176 (1955) 51–55.
[3] J. Sung, Graphite → diamond transition under high pressure: a kinetics approach, Journal of Materials Science 35 (2000) 6041–6054.
[4] C.M. Sung, M.F. Tai, Reactivities of transition metals with carbon: implications to the mechanism of diamond synthesis under high pressure, International Journal of Refractory Metals and Hard Materials 15 (1997) 237–256.
[5] H.M. Strong, R.E. Hanneman, Crystallization of diamond and graphite, Journal of Chemical Physics 46 (1967) 3668–3676.
[6] A.J. Irving, P.J. Wyllie, Subsolidus and melting relationships for calcite, magnesite and the join $CaCO_3$–$MgCO_3$ to 36 kb, Geochimica et Cosmochimica Acta 39 (1975) 35–53.
[7] V. Turkevich, T. Okada, W. Utsumi, A. Garan, Kinetics of diamond spontaneous crystallization from the melt of the Fe–Al–C system at 6.5 GPa, Diamond and Related Materials 11 (2002) 1769–1773.
[8] V.L. Solozhenko, V.Z. Turkevich, O.O. Kurakevych, W.A. Crichton, M. Mezouar, Kinetics of diamond crystallization from the melt of the Fe–Ni–C system, Journal of Physical Chemistry B 106 (2002) 6634–6637.
[9] M. Hillert, N. Lange, Diffusion of carbon in liquid iron, Journal of the Iron and Steel Institute 203 (1965) 273–274.
[10] M. Sibanda, R.H. Eric, A. Koursaris, Solid state diffusion of carbon in the Co-5% Fe–C system at high pressure: metallography and phase equilibrium, Journal of the South African Institute of Mining and Metallurgy 105 (2005) 465–472.
[11] H.M. Strong, R.M. Chrenko, Diamond growth rates and physical properties of laboratory-made diamond, Journal of Physical Chemistry 75 (1971) 1838–1843.
[12] Y.M. Chiang, D.P. Birnie, W.D. Kingery, Physical Ceramics: Principles for Ceramic Science and Engineering, first ed., Wiley, New Jersey 266–267.
[13] I.C. Lin, C.J. Lin, W.H. Tuan, Growth of diamond crystals in Fe–Ni metallic catalysis, Diamond and Related Materials 20 (2011) 42–47.