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Preparation of amorphous Si_3N_4–C plate by chemical vapour deposition

TOSHIO HIRAI, TAKASHI GOTO
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, 980, Japan

Chemical vapour deposition of a Si–N–C system has been studied by using $SiCl_4$, NH_3, H_2 and C_3H_8 as source gases at deposition temperatures (T_{dep}) of 1100 to 1600° C, and total gas pressures (P_{tot}) of 30 to 100 torr. To control the amount of carbon in these deposits the propane gas flow rate [$FR(C_3H_8)$] was varied from 0 to 200 $cm^3 min^{-1}$. Homogeneous plate-like amorphous deposits were successfully prepared at $T_{dep} = 1100$ to 1300° C, $P_{tot} = 30$ to 70 torr and $FR(C_3H_8) = 25$ to 100 $cm^3 min^{-1}$. The deposits were composed of amorphous silicon nitride and carbon and the carbon content increased up to 10 wt% with increasing $FR(C_3H_8)$. The surfaces of the deposits had a pebble-like structure.

1. Introduction

In view of their good thermal and mechanical properties and oxidation resistance, silicon nitride (Si_3N_4) and silicon carbide (SiC) are promising materials for high temperature gas turbine applications [1]. Recently, materials composed of Si, N and C have been extensively investigated for possible uses as new high temperature materials. Parr *et al.* [2] and Lange [3] prepared Si_3N_4–SiC composites using SiC powders by reaction-sintering and hot-pressing, respectively, to improve the mechanical properties of Si_3N_4 sintered bodies.

Nickl and Braunmühl [4] have studied chemical vapour deposition (CVD) of the Si–N–C system by using $SiCl_4$, CCl_4, H_2 and N_2 as source gases and obtained Si + SiC + Si_3N_4 deposits. However, they have not provided any information on the properties of these deposits. Jacobson [5] has obtained an amorphous Si_3N_4 powder containing 0.1 to 5 wt% of carbon by CVD using $SiCl_4$, NH_3, N_2 and CH_4. He has reported that this powder is useful in the preparation of fully dense SiAlON ceramics.

In a CVD study of the Si–N system, we succeeded in preparing massive amorphous and crystalline CVD-Si_3N_4 at high deposition speeds (maximum 1.2 mm h^{-1}) using $SiCl_4$, NH_3 and H_2 [6, 7], and investigated the properties of the CVD-Si_3N_4 [8–11]. Using the same apparatus and methods for preparing CVD-Si_3N_4, the CVD of a Si–N–C system was carried out by adding C_3H_8 gas to the source gases. This paper describes the effects of CVD variables (deposition temperature, total gas pressure and gas flow rate) on the deposition of the Si–N–C system.

2. Experimental procedure

2.1. Sample preparation

The experimental set-up is illustrated in Fig. 1. The graphite substrate (40 mm × 12 mm × 2 mm) was heated by transmitting an electric current. The deposition temperature, T_{dep}, was measured using a two-colour pyrometer. The total gas pressure, P_{tot}, was regulated in the range of 30 to 100 torr* by needle valves. $SiCl_4$ vapour (purity: 99.9%), NH_3 gas (99.9%), H_2 gas (99.9999%) and C_3H_8 gas (94.5%) were used as source gases. The $SiCl_4$ container was maintained at 20° C and the saturated vapour of $SiCl_4$ was carried with H_2 gas. The $SiCl_4$ vapour and NH_3 gas were separately introduced through a double tube nozzle into the CVD chamber to prevent premature vapour reaction [6]. In this present investigation, NH_3 gas and ($SiCl_4$ + C_3H_8 + H_2) gases were introduced through the

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*1 atm = 760 torr = 0.1013 MPa.

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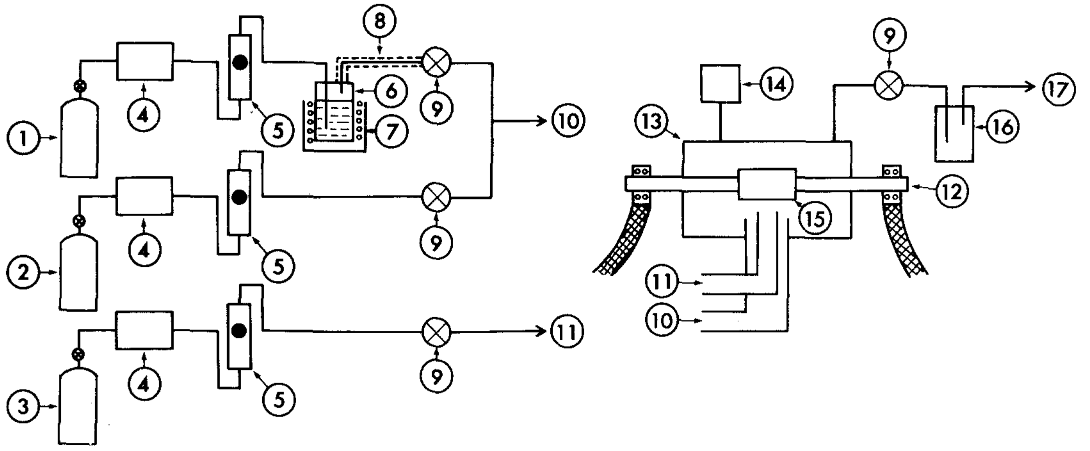

Figure 1 Schematical diagram of deposition apparatus. (1) H_2 gas; (2) C_3H_8 gas; (3) NH_3 gas; (4) gas purifier; (5) flow meter; (6) $SiCl_4$ reservoir; (7) constant temperature bath; (8) ribbon heater; (9) pressure regulator; (10) $SiCl_4 + H_2 + C_3H_8$ gas inlet; (11) NH_3 gas inlet; (12) copper electrode; (13) reaction chamber; (14) manometer; (15) graphite heater (substrate); (16) cold trap; (17) rotary pump.

inner and outer tubes, respectively. The gas flow rate was measured by a flow meter. In reference to previous work [6, 12, 13], the flow rates of H_2 and NH_3 gases [$FR(H_2)$ and $FR(NH_3)$] were respectively fixed at 700 and 60 cm^3 min^{-1}. The flow rate of propane gas [$FR(C_3H_8)$] was controlled in the range of 0 to 200 cm^3 min^{-1}. The deposition conditions are summarized in Table I.

2.2. Microstructure and chemical composition

The as-deposited surfaces and the fracture surfaces were coated with gold (5 to 10 nm in thickness) and observed by means of scanning electron microscopy (SEM) (Hitachi-Akashi: MSM-4). The polished surfaces of the deposits were examined by electron spectroscopy for chemical analysis (ESCA) (AEI-Kokusai Denki: AEI-ES200). The structures of various parts of plate-like deposits were examined by an X-ray diffractometer (Ni filtered K_α, JEOL: DX-GO-S). The content of carbon was determined by chemical analysis, and the contents of Si and N were examined by electron probe microanalysis (EPMA) (Shimazu: EMX-SM) using amorphous CVD-Si_3N_4 as a standard sample.

TABLE I

Deposition conditions	
Deposition temperature, T_{dep} (° C)	1100 to 1600
Total gas pressure, P_{tot} (torr)	30 to 100
Gas flow rate, FR(cm^3 min^{-1})	
$FR(H_2)$	700
$FR(SiCl_4)$	170
$FR(NH_3)$	60
$FR(C_3H_8)$	0 to 200
Deposition time, t(h)	0.5 to 8

3. Results

3.1. Preparation of Si–N–C deposits

Figs 2 to 5 show the characteristics of Si–N–C deposits obtained under various CVD conditions.

At T_{dep} = 1100 and 1200° C, as indicated by X in Fig. 2, the deposition temperature became uncontrollable above P_{tot} = 80 torr due to the formation of by-product powders in the vapour phase. Homogeneous plate-like amorphous deposits were also obtained at P_{tot} = 30 to 70 torr and

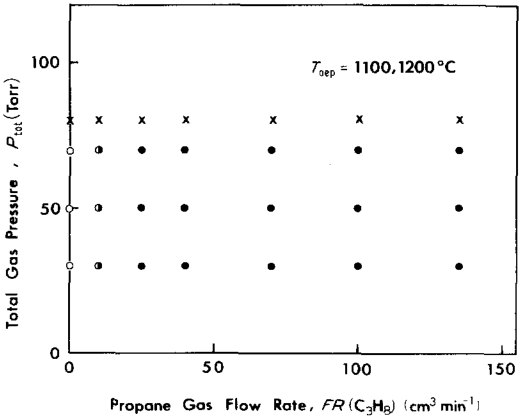

Figure 2 Effect of the propane gas flow rate [$FR(C_3H_8)$] and the total gas pressure (P_{tot}) on the deposits prepared at T_{dep} = 1100 and 1200° C. ○: amorphous Si_3N_4, ◐: amorphous Si_3N_4 + amorphous deposit, ●: homogeneous amorphous deposit, X: uncontrollable conditions.

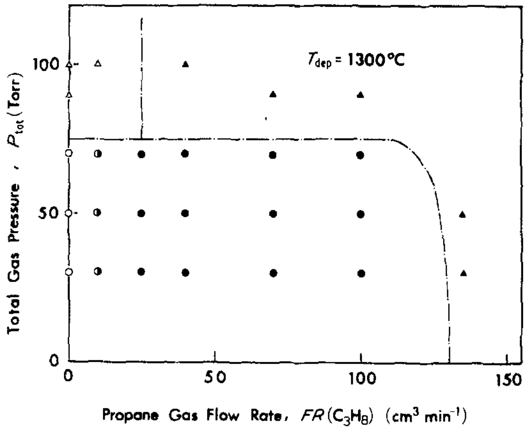

Figure 3 Effect of the propane gas flow rate [$FR(C_3H_8)$] and the total gas pressure (P_{tot}) on the deposits prepared at T_{dep} = 1300° C. ○: amorphous Si_3N_4, ◑: amorphous Si_3N_4 + amorphous deposit, ●: homogeneous amorphous deposit, △: amorphous deposit + α-Si_3N_4, ▲: amorphous deposit + pyrolytic carbon.

$FR(C_3H_8) = 25$ to $135\,cm^3\,min^{-1}$. The colours of these deposits were, respectively, white, white plus black, and black at $FR(C_3H_8) = 0$, 10 and $25\,cm^3\,min^{-1}$ or above, respectively.

At T_{dep} = 1300° C, as shown in Fig. 3, homogeneous amorphous deposits were obtained at P_{tot} = 30 to 70 torr and in the range of $FR(C_3H_8)$ = 25 to $100\,cm^3\,min^{-1}$, and the colours of the deposits were similar to those prepared at T_{dep} = 1100 and 1200° C. Pyrolytic carbon or α-Si_3N_4 was co-deposited heterogeneously with the amorphous deposits in the regions indicated by ▲ and △ in Fig. 3.

At T_{dep} = 1400° C, as shown in Fig. 4, the characteristics of the deposits formed were also dependent on P_{tot} and $FR(C_3H_8)$. For example, at P_{tot} = 30 torr, amorphous deposits and α-Si_3N_4 were heterogeneously co-deposited at $FR(C_3H_8)$ = 0 to $40\,cm^3\,min^{-1}$, whereas amorphous deposits and pyrolytic carbon were heterogeneously co-deposited at $FR(C_3H_8) = 135\,cm^3\,min^{-1}$.

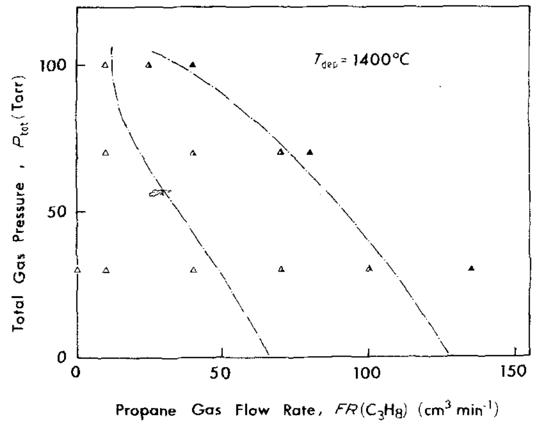

Figure 4 Effect of the propane gas flow rate [$FR(C_3H_8)$] and the total gas pressure (P_{tot}) on the deposits prepared at T_{dep} = 1400° C. △: amorphous deposit + α-Si_3N_4, ◭: amorphous deposit + α-Si_3N_4 + pyrolytic carbon, ▲: amorphous deposit + pyrolytic carbon.

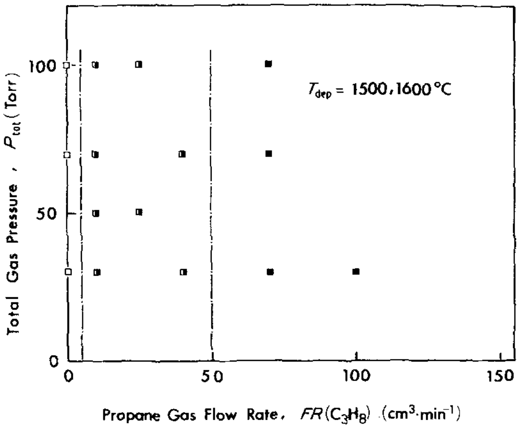

Figure 5 Effect of the propane gas flow rate [$FR(C_3H_8)$] and the total gass pressure (P_{tot}) on the deposits prepared at T_{dep} = 1500 and 1600° C. □: α-Si_3N_4, ◨: α-Si_3N_4 + β-SiC, ■: β-SiC + pyrolytic carbon.

At T_{dep} = 1500 and 1600° C, as shown in Fig. 5, α-Si_3N_4 was always obtained at $FR(C_3H_8) = 0\,cm^3\,min^{-1}$ regardless of P_{tot}. A heterogeneous mixture of α-Si_3N_4 and β-SiC was obtained at $FR(C_3H_8)$ = 10 to $40\,cm^3\,min^{-1}$, and β-SiC and pyrolytic carbon were heterogeneously co-deposited above $FR(C_3H_8) = 70\,cm^3\,min^{-1}$.

3.2. Morphology of deposits

A typical homogeneous amorphous deposit obtained in the present work is shown in Fig. 6b and compared with the amorphous CVD-Si_3N_4 (Fig. 6a). The colours of these deposits were respectively white and black. Fig. 7 shows the morphology of the deposits in Fig. 6, which were observed by SEM. Both surfaces indicated a pebble-like structure with a diameter of 0.1 to 0.3 mm. There appears to be no difference between the homogeneous amorphous deposit obtained in the present experiments and the amorphous CVD-Si_3N_4.

The density and deposition rate of the homogeneous amorphous deposits obtained here were respectively 2.80 to $3.00\,g\,cm^{-3}$ and 0.07 to $0.6\,mm\,h^{-1}$ depending on deposition conditions. Detailed results on the density and deposition rate will be reported in a forthcoming paper.

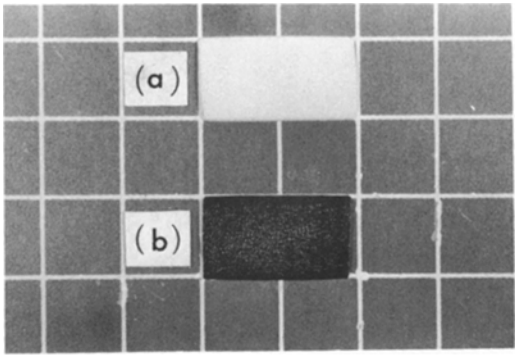

Figure 6 Surfaces of the amorphous Si_3N_4 and the homogeneous amorphous deposit prepared at $T_{dep} = 1300°C$, $P_{tot} = 30$ torr and (a) $FR(C_3H_8) = 0\ cm^3\ min^{-1}$ and (b) $FR(C_3H_8) = 100\ cm^3\ min^{-1}$. (1 division = 12.5 mm).

3.3. Carbon analysis

Fig. 8 indicates the distribution of Si, N and C in a cross-section of the homogeneous amorphous deposit prepared at $T_{dep} = 1300°C$, $P_{tot} = 30$ torr and $FR(C_3H_8) = 70\ cm^3\ min^{-1}$. EPMA revealed that Si, N and C were uniformly distributed in the deposit. Similar results were observed in all the deposits marked by ● in Figs 2 and 3. The Si to N atomic ratio determined by the EPMA was about 3/4. Thus, the homogeneous amorphous deposits containing carbon are abbreviated as Am.CVD-(Si_3N_4–C).

Fig. 9 shows the effect of $FR(C_3H_8)$ on carbon content for Am.CVD-(Si_3N_4–C) prepared at $T_{dep} = 1100$ to $1300°C$. The carbon content increased with increasing $FR(C_3H_8)$, and it was minimally affected by T_{dep} and P_{tot} as shown in Figs 10 and 11.

3.4. Structure of carbon

Values of the lattice constant (c_0) of pyrolytic carbon in the heterogeneous deposits prepared at $T_{dep} = 1500$ and $1600°C$ were 0.689 and 0.690 nm. The carbon in Am.CVD-(Si_3N_4–C) showed no X-ray reflection, though an ESCA indicated a signal of a free carbon.

4. Discussion

4.1. Compounds of the Si–N–C system

Schutzenberger and Colson [14] and Weiss and Engelhardt [15] tried to prepare compounds of a Si–N–C system by heating a mixture of silica and carbon in a nitrogen stream, and detected Si_2C_2N and Si_3C_3N, respectively. At present, however, evidence shows that there are no compounds of the Si–N–C system [16, 17].

The deposits obtained in the present work were composed of amorphous Si_3N_4, carbon, α-Si_3N_4 and β-SiC as shown in Figs 2 to 5.

Rassaerts and Schmidt [18] proposed a phase diagram of a Si–N–C system at $P_{tot} = 760$ torr by using thermodynamic data on Si_3N_4, SiC and C_2N_2, as represented in Fig. 12. Lilov *et al.* [19] calculated the thermodynamic data for the Si–N–C system, and showed that Si_3N_4 could not exist at $P_{tot} = 4$ torr and above $1478°C$. The decomposition temperature of Si_3N_4 in the presence of carbon has been variously reported as mentioned above.

The present experimental conditions are indicated by the broken line in Fig. 12. The N_2 partial pressure in the reaction chamber might be considerably lowered by the consumption of NH_3 by the formation of large amounts of $Si(NH)_2$ and NH_4Cl powders [20]. Moreover, it was apparent

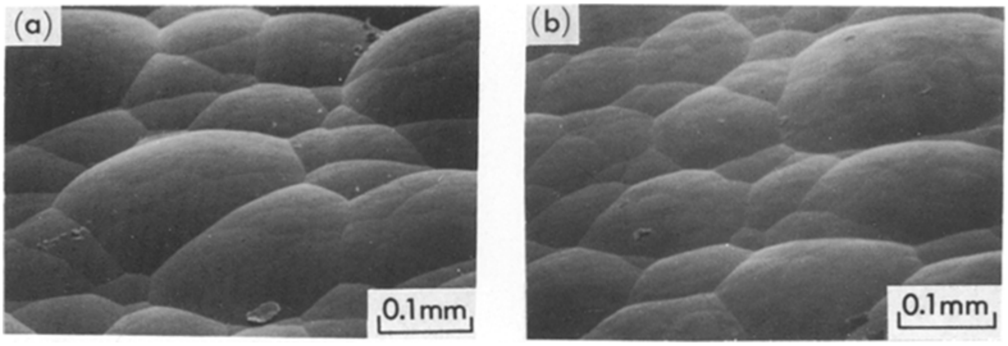

Figure 7 Scanning electron micrographs of the surfaces of the amorphous Si_3N_4 and the homogeneous amorphous deposit prepared at $T_{dep} = 1300°C$, $P_{tot} = 30$ torr and (a) $FR(C_3H_8) = 0\ cm^3\ min^{-1}$ and (b) $FR(C_3H_8) = 100\ cm^3\ min^{-1}$.

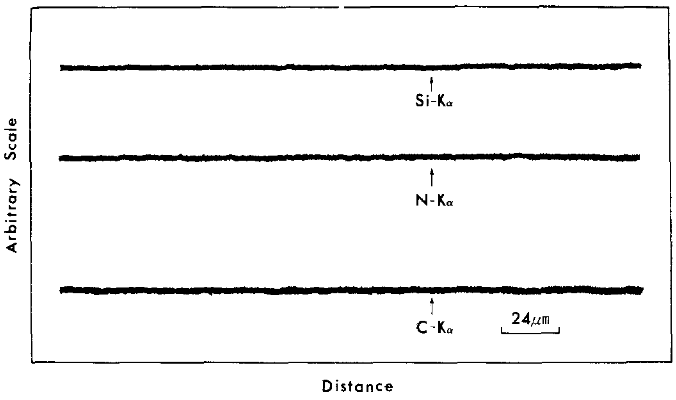

Figure 8 The results of an EPMA for Si, N and C content of cross-sectional surface of the homogeneous amorphous deposit prepared at $T_{dep} = 1300°$ C, $P_{tot} = 30$ torr and $FR(C_3H_8) = 70$ cm^3 min^{-1}.

that SiC was not formed below 1400° C. Thus, the present deposition conditions seem to be in the hatched area in Fig. 12.

4.2. CVD of a Si–N–C system

Nickl and Braunmühl [4] studied CVD of a Si–N–C system using $SiCl_4 + N_2 + H_2 + CCl_4$ gases at $T_{dep} = 1100$ to 1300° C and $P_{tot} = 715 \pm 15$ torr, and obtained a three-phase deposition mixture of Si, SiC and Si_3N_4. The structure of Si_3N_4 in the deposits was amorphous below $T_{dep} = 1200°$ C. At $T_{dep} = 1300°$ C, α-Si_3N_4 was also deposited.

In the present experiments, as shown in Figs 2 and 3, Am.CVD-(Si_3N_4–C) was formed without the formation of SiC at $T_{dep} = 1100$ to 1300° C and $P_{tot} = 30$ to 70 torr. Moreover, as shown in Fig. 5, Am.CVD-(Si_3N_4–C) was not obtained at $T_{dep} = 1500$ and 1600° C. In the present work, carbon was supposed to exist as a free carbon in Am.CVD-(Si_3N_4–C), although carbon exists as a combined carbon (SiC) in the results of Nickl and Braunmühl. This difference seems to be caused by the variation in the CVD conditions.

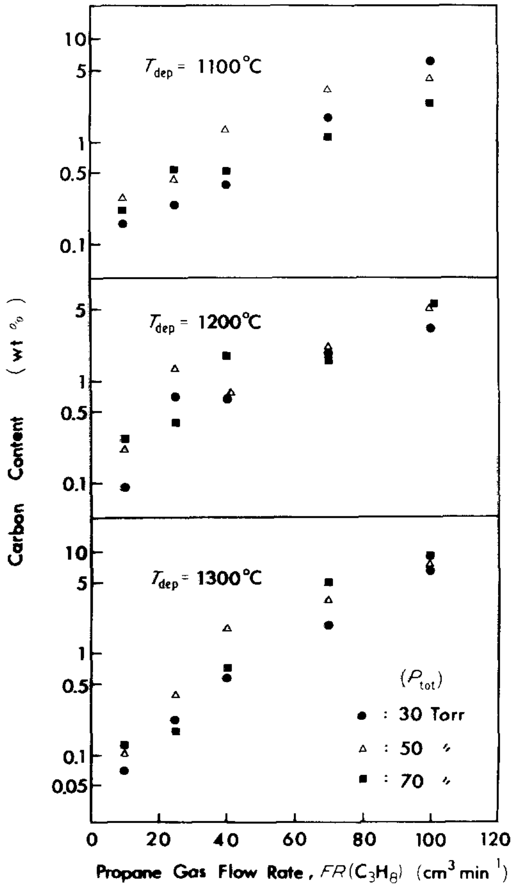

Figure 9 Effect of the propane gas flow rate [$FR(C_3H_8)$] on the carbon content of the homogeneous amorphous deposits prepared at $T_{dep} = 1100$ to 1300° C.

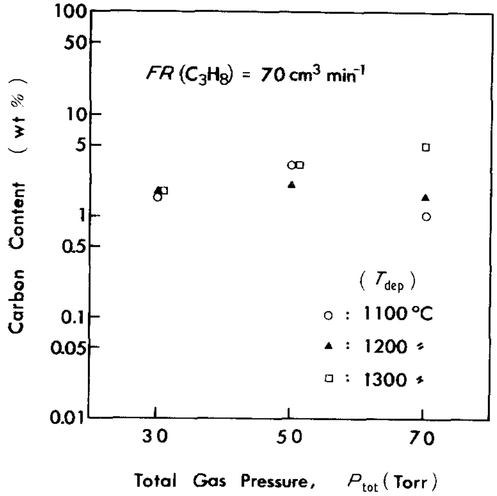

Figure 10 Effect of the total gass pressure (P_{tot}) on the carbon content of the homogeneous amorphous deposits prepared at $FR(C_3H_8) = 70$ cm^3 min^{-1}.

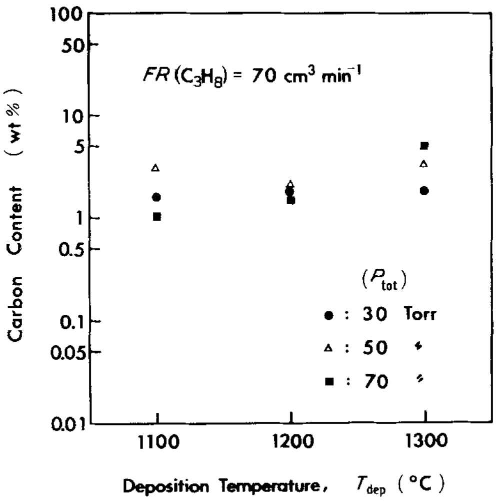

Figure 11 Effect of the deposition temperature (T_{dep}) on the carbon content of the homogeneous amorphous deposits prepared at $FR(C_3H_8) = 70\,cm^3\,min^{-1}$.

4.3. Crack formation in the deposits

Airey *et al.* [21] reported that the amount of cracks formed in the amorphous CVD-Si_3N_4 decreases with increasing T_{dep} and with decreasing deposition rate. They thought that the higher T_{dep} and the lower deposition rate, the more readily the stress relief occurs accompanied by the cluster rearrangement. In the present experiments many visible cracks were found in Am.CVD-(Si_3N_4–C) prepared at high P_{tot} and low T_{dep}. This is in good rearrangement. In the present experiments, many Kohler [22] reported that impurity particles cause crack formation in the amorphous CVD-Si_3N_4. The present experiments showed that crack formation was also remarkable in a high carbon Am.CVD-(Si_3N_4–C). It appears that carbon is present as a second phase in Am.CVD-(Si_3N_4–C).

On the other hand, as shown in Fig. 5, α-Si_3N_4 and β-SiC were heterogeneously co-deposited under the conditions of T_{dep} = 1500, 1600° C and $FR(C_3H_8) = 25$ to $40\,cm^3\,min^{-1}$. In these cases, cracks generated at the phase boundary of α-Si_3N_4 and β-SiC and extended to the α-Si_3N_4 phase. This crack formation was thought to be caused by the difference in the thermal expansion coefficients of Si_3N_4 and SiC. Almost no cracks were observed in the deposits composed of β-SiC and pyrolytic carbon.

4.4. Structure of carbon

As described in Section 3.4., the values of lattice constant, c_0, of the pyrolytic carbon were 0.689 and 0.690 nm. These values are in good agreement with the previously published data on pyrolytic carbon [23]. The structure of carbon in Am.CVD-(Si_3N_4–C) is not clear and further investigations using positron annihilation and neutron diffraction are presently being conducted.

5. Conclusions

(1) Homogeneous amorphous deposits [Am.CVD-(Si_3N_4–C)] were obtained at deposition temperatures (T_{dep}) of 1100 to 1300° C, total gas pressures (P_{tot}) of 30 to 70 torr and propane gas flow rates [$FR(C_3H_8)$] of 25 to $100\,cm^3\,min^{-1}$.

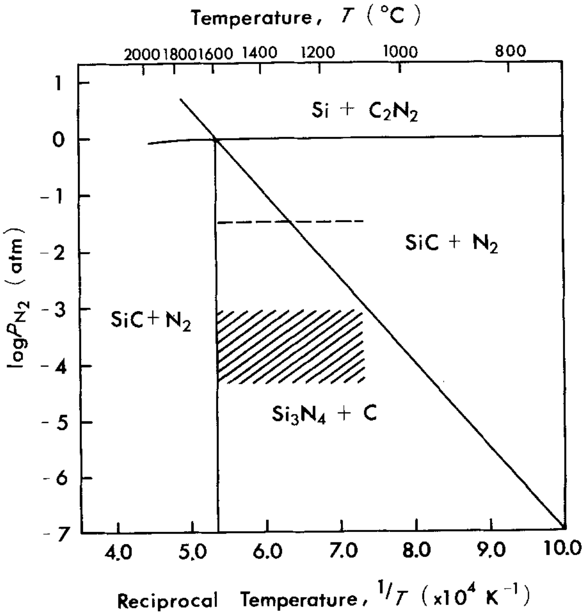

Figure 12 $\log P_{N_2}$–$1/T$ diagram of the Si–N–C system [18].

(2) Am.CVD-(Si_3N_4–C) was not obtained above $P_{tot} = 100$ torr and above $FR(C_3H_8) = 135\ cm^3\ min^{-1}$ at $T_{dep} = 1300°$ C. Above $T_{dep} = 1400°$ C, in all deposition conditions Am.CVD-(Si_3N_4–C) was not obtained.

(3) The surface of Am.CVD-(Si_3N_4–C) was black and showed a pebble-like structure.

(4) The carbon content in Am.CVD-(Si_3N_4–C) increased up to 10 wt% with increasing $FR(C_3H_8)$.

(5) The carbon in Am.CVD-(Si_3N_4–C) showed no X-ray diffraction peaks, but a signal indicating a free carbon was detected by ESCA.

(6) The Si to N ratio in Am.CVD-(Si_3N_4–C) was about 3/4.

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References

1. D. J. GODFREY, *Metals and Materials* **2** (1968) 305.
2. N. L. PARR, G. E. MARTIN and E. R. W. MAY in "Special Ceramics" edited by P. Popper (Academic Press, New York and London, 1960) p. 102.
3. F. F. LANGE, *J. Amer. Ceram. Soc.* **56** (1973) 445.
4. J. J. NICKL and C. BRAUNMÜHL, *J. Less-Common Metals* **37** (1974) 317.
5. H. W. JACOBSON, US Patent 4 036 653, July (1977).
6. K. NIIHARA and T. HIRAI, *J. Mater. Sci.* **11** (1976) 593.
7. *Idem, ibid.* **11** (1976) 604.
8. *Idem, ibid.* **12** (1977) 1233.
9. T. HIRAI, S. HAYASHI and K. NIIHARA, *Amer. Ceram. Soc. Bull.* **57** (1978) 1126.
10. T. HIRAI, K. NIIHARA and T. GOTO, *J. Amer. Ceram. Soc.* (1980).
11. T. HIRAI, M. SHIMADA and T. GOTO, *Yogyo-Kyokai-Shi* 88 (1980) 401.
12. T. HIRAI, K. NIIHARA and T. GOTO, *J. Mater. Sci.* **12** (1977) 631.
13. *Idem, J. Japan Inst. Metals* **41** (1977) 358.
14. P. SCHUTZENBERGER and A. COLSON, *Compt. Rend. Acad. Sci., Paris* **92** (1881) 1508.
15. L. WEISS and T. ENGELHARDT, *Z. Anorg. Allgem. Chem.* **65** (1910) 38.
16. M. M. BILLY and F. COLOMBEAU, *Compt. Rend. Acad. Sci., Paris* **264** (1967) 392.
17. E. GUGEL, P. ETTMAYER and A. SCHMIDT, *Ber. Dtsch. Keram. Ges.* **45** (1968) 359.
18. H. RASSAERTS and A. SCHMIDT, *Planseeber.* **14** (1966) 110.
19. S. K. LILOV, Yu. M. TAILOV, V. F. TSVETKOV and B. F. YUDIN, *J. Crystal Growth* **40** (1977) 59.
20. K. S. MAZDIYASNI and C. M. COOKE, *J. Amer. Ceram. Soc.* **56** (1973) 628.
21. A. C. AIREY, S. CLARKE and P. POPPER, *Proc. Brit. Ceram. Soc.* **22** (1973) 305.
22. W. A. KOHLER, *Met. Trans.* **1** (1970) 735.
23. T. HIRAI and S. YAJIMA, *J. Mater. Sci.* **2** (1967) 18.

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