

Thermal Diffusivity, Specific Heat and Thermal Conductivity of Chemically Vapor-Deposited Si_3N_4

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There has been increasing interest in high temperature structural materials which can withstand the severe conditions of temperature, pressure and atmosphere in applications such as gas turbines. Silicon nitride (Si_3N_4) seems to be satisfactory in most applications as a high temperature structural material because of its superior oxidation and thermal shock resistance, and high hardness and mechanical strength.¹

From a practical standpoint, the thermal properties (thermal diffusivity, specific heat and thermal conductivity) of Si_3N_4 are of extreme importance for its high temperature applications. The thermal properties of hot-pressed Si_3N_4 (HP- Si_3N_4) and reaction-sintered Si_3N_4 (RS- Si_3N_4) have been investigated by many workers.²⁻¹⁸ Nevertheless, information on chemically vapor-deposited Si_3N_4 (pyrolytic Si_3N_4) is not available in the literature. The present paper describes the thermal properties of Py- Si_3N_4 (crystalline, amorphous and a mixture of both) measured by a laser flash method¹⁹ in the range 20°–1300°C. Based on present data, the relations between the thermal properties and structures of Py- Si_3N_4 are also discussed.

Experimental

Specimens

The Py- Si_3N_4 was deposited onto a directly heated graphite substrate by chemical vapor deposition of the system $\text{SiCl}_4\text{-NH}_3\text{-H}_2$. The apparatus and procedure were described in Ref. 20. The structure of Py- Si_3N_4 is crystalline or amorphous, depending on the deposition temperature (T_{dep}) and the total pressure (P_{tot}). The deposition conditions, structures and densities of the specimens used in measuring the thermal properties are shown in Fig. 1 and Table I. For the measurements, the as-deposited Py- Si_3N_4 was machined to a disk 5 mm in diameter and 0.5–1.2 mm thick.

Measurements

Thermal diffusivity and specific heat were measured via a laser flash method using a thermal constant analyzer.* The apparatus is shown schematically in Fig. 2. The source of the energy pulse was a ruby laser with a wavelength of 6943 Å. The incident direction of the laser beam was parallel to the growth direction of Py- Si_3N_4 . The apparatus was equipped with Nichrome (20°–900°C, 10^{-3} torr) and tungsten (500°–2200°C, 10^{-6} torr) furnaces. The measurements were made during heating and cooling at a rate of 5°C min⁻¹. For monitoring the temperature response of the back surface of the specimen, an InSb or PbS ir detector or a Chromel-Alumel thermocouple was used selectively (Table II). If the specific heat is to be measured via a laser flash method, the absorption coefficient of laser energy for the specimens should be known, but there is no information about Py- Si_3N_4 . Therefore, the following techniques were adopted: 1) for measurements at 20°–900°C, vitreous carbon† (≈0.4 mm thick) with the known value of specific heat was attached to the front surface of the specimen with silver paste.‡ This tech-

Thermal properties of crystalline and amorphous pyrolytic Si_3N_4 prepared from the system $\text{SiCl}_4\text{-NH}_3\text{-H}_2$ via chemical vapor deposition were measured in the range 20°–1300°C by a laser flash method. In this range, the thermal diffusivity and conductivity of crystalline Py- Si_3N_4 are higher than those for amorphous Py- Si_3N_4 . The specific heat of Py- Si_3N_4 is independent of structure. The structure of the amorphous Py- Si_3N_4 is discussed in terms of the temperature dependence of the thermal diffusivity.

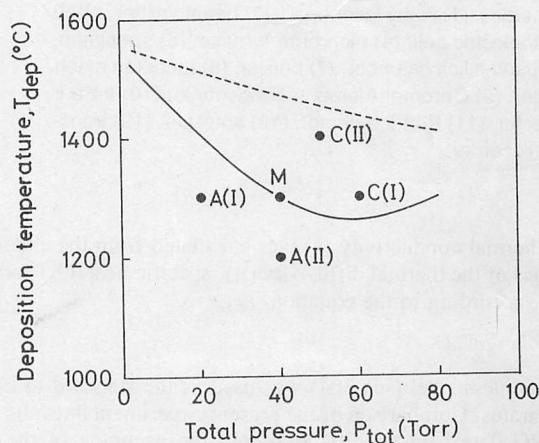


Fig. 1. Conditions for preparation of Py- Si_3N_4 specimens. Thermal properties were measured for Py- Si_3N_4 prepared under conditions marked with filled circles (see Table I for specimen characteristics).

nique yielded precise values for the specific heat.²¹ 2) For measurements at 800°–1300°C, technique 1) cannot be used because of the impracticality of silver paste at these temperatures. For this reason, the measurements were performed on the specimen without the use of vitreous carbon, and the measured values of specific heat were corrected using a method proposed by Mitsuhashi and Takahashi.²²

When InSb and PbS ir detectors were used, the front surface of the specimen was coated with colloidal carbon§ because of the transparency of Py- Si_3N_4 to the laser beam. The maximum temperature in the present measurements was set at 1300°C, in consideration of the crystallization of the amorphous Py- Si_3N_4 .²³

Table I. Characteristics of Py- Si_3N_4 Specimens

Specimen	Structure	Preferred orientation	Density (g cm ⁻³)*
C(I)	Crystalline [†]	(110), (210) and (222)	3.18
C(II)	Crystalline [†]	(222)	3.18
M	Mixture [‡]		2.85
A(I)	Amorphous		2.84
A(II)	Amorphous		2.60

*Theoretical density of $\alpha\text{-Si}_3\text{N}_4$ is 3.18 g cm⁻³.

†Alpha Si_3N_4 , ‡ $\alpha\text{-Si}_3\text{N}_4$ and amorphous Si_3N_4 .

*TC-3000-UVH, Sinku Riko Co., Yokohama, Japan.
†Glassy carbon GC-20, Tokai Carbon Co., Tokyo, Japan.

‡Silver paste P-382, Tokuriki Honten Co., Tokyo, Japan.
§Hitasol AF-2, Hitachi Powdered Metals, Co., Tokyo, Japan.

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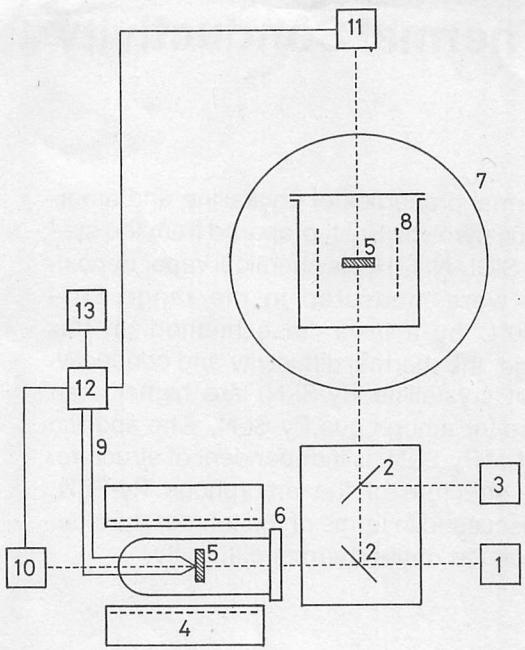


Fig. 2. Diagram of apparatus for measuring thermal properties. (1) Ruby laser head, (2) beam splitter, (3) Si photoelectric cell, (4) nichrome furnace, (5) specimen, (6) fused-silica chamber, (7) bell jar, (8) tungsten mesh heater, (9) Chromel-Alumel thermocouple, (10) InSb ir detector, (11) PbS ir detector, (12) amplifier, (13) transient recorder.

Thermal conductivity (k) was calculated from the experimental values of the thermal diffusivity (α), specific heat (C_p) and density (D), according to the equation

$$k = \alpha C_p D \quad (1)$$

Stainless steel (sus 304) was used as the standard to check the apparatus. Comparison of the present experimental results with the TPRC data²⁴ on sus 304 indicated the accuracy of the thermal diffusivity and the specific heat to be within 3 and 5%, respectively.

Results and Discussion

Thermal Diffusivity

The α values for Py-Si₃N₄ depend markedly on structure, as shown in Fig. 3. At 20°C, α for crystalline Py-Si₃N₄, specimen C(I), is ≈ 25 times greater than that for amorphous Py-Si₃N₄, specimen A(II). The α of specimen C(I) decreased abruptly with increasing temperature from 0.257 cm² s⁻¹ at 20°C to 0.046 cm² s⁻¹ at 1300°C. As shown in Fig. 4, the temperature dependence of α for HP-Si₃N₄, RS-Si₃N₄ and Sialon is not remarkable compared with that of specimen C(I), except for those reported in Refs. 13 and 17. Similar behavior can be observed in a comparison between CVD-SiC²⁵ and HP-SiC.¹⁸ The α values for RS-Si₃N₄ (Ref. 13) in Fig. 4 are considerably higher because of a continuous metal phase of "free silicon." In this case, the temperature dependence may reflect that of silicon.²⁶

In crystalline dielectric ceramics, heat is transferred mainly by lattice vibration, and thermal resistance results from phonon-

Table II. Detectors Used for Monitoring the Transient Temperature Response of Specimens

Measurement	Temp. range	
	20°–900°C	800°–1300°C
Thermal diffusivity	InSb*	PbS*
Specific heat	CA†	PbS*

*Infrared detector; †Chromel-Alumel thermocouple.

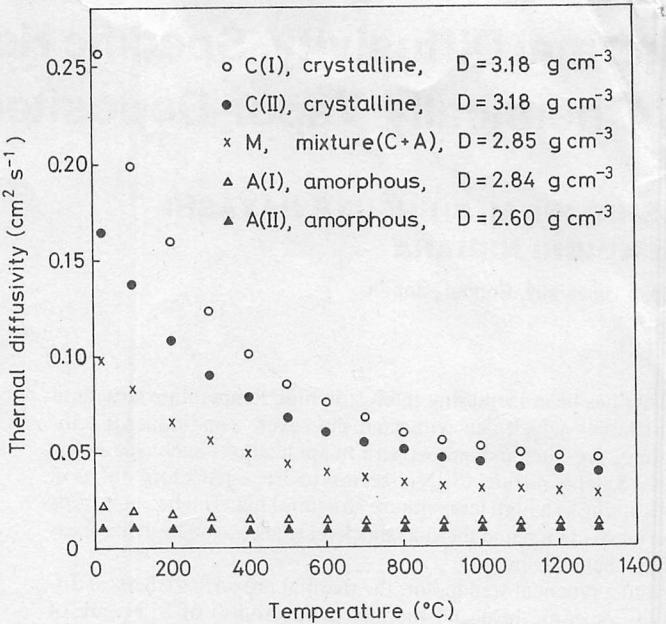


Fig. 3. Thermal diffusivity of Py-Si₃N₄.

phonon and phonon-imperfection (impurities, defects and microstructure) interactions. Thermal resistance for the former interaction depends strongly on temperature, but it is not so for the latter.²⁷ Both HP-Si₃N₄ and Sialon contain additives, and pores are involved in RS-Si₃N₄. Under such a situation, the phonon-imperfection interaction is thought to occur. This reaction indicates that the temperature dependence of the thermal diffusivity is relatively weak. On the other hand, since the crystalline Py-Si₃N₄ is highly pure and pore free,^{20,28,29} the phonon-phonon interaction behavior is predominant. The HP-Si₃N₄ which Kuriyama et al.¹⁷ prepared from a mixture of highly pure Si₃N₄ (99.9%) and 5 wt% MgO powders has high α values, as shown in Fig. 4. They explained that a formation of MgSiN₂ instead of MgSiO₃ and/or Mg₂SiO₄ at grain boundaries increases α , but they did not discuss the temperature dependence of α .

The α values of specimen A(II), which are almost independent of temperature, are 0.0095 ± 0.0008 cm² s⁻¹ in the range 20°–1300°C. As reported for vitreous carbon³⁰ and fused silica,³¹ α for amor-

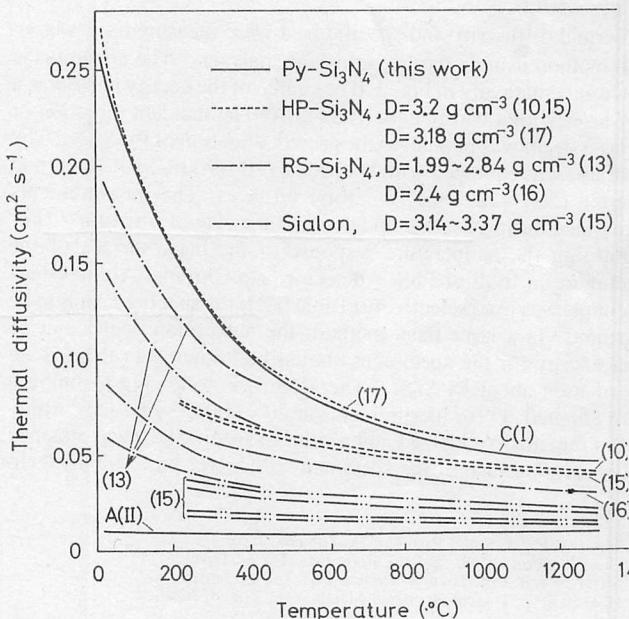


Fig. 4. Comparison of thermal diffusivity of Py-Si₃N₄ with data for HP-Si₃N₄, RS-Si₃N₄ and Sialon from references indicated.

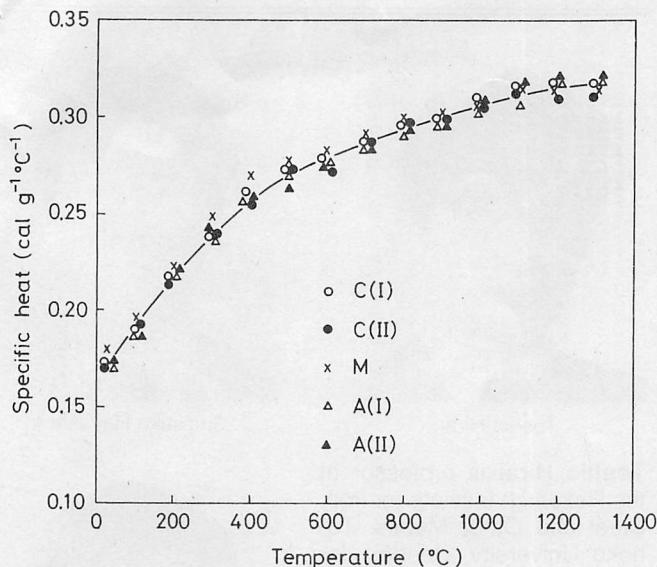


Fig. 5. Specific heat of Py-Si₃N₄.

phous dielectric ceramics generally does not vary greatly with increasing temperature. For amorphous materials, the mean free path for phonons gives information about the amorphous structures. Since α is related to the sound velocity (v) and the phonon mean free path (λ), α can be written

$$\alpha = 1/3v\lambda \quad (2)$$

The temperature dependence of v is not remarkable³²; v for the longitudinal wave in specimen A(II) is 9.2×10^5 cm s⁻¹ at 15 MHz.³³ Substitution of this value into Eq. (2) leads to a λ value of ≈ 3 Å, which is of the order of the dimensions of the Si₃N₄ tetrahedron.³⁴

As described in a previous paper,³⁵ specimen A(II) contains heterogeneous parts (dark spots ≈ 1 μm in diameter). Since the detailed structure of the dark spots is unknown, its effect on the thermal properties is not discussed in the present paper.

Specific Heat

Figure 5 shows the temperature dependence of the specific heat (C_p) of Py-Si₃N₄. The C_p of crystalline Py-Si₃N₄ is in accord with that of amorphous Py-Si₃N₄ within experimental error. Similar phenomena have been observed for natural graphite and vitreous carbon³⁰ and for quartz and fused silica.³⁶ Accordingly, the values

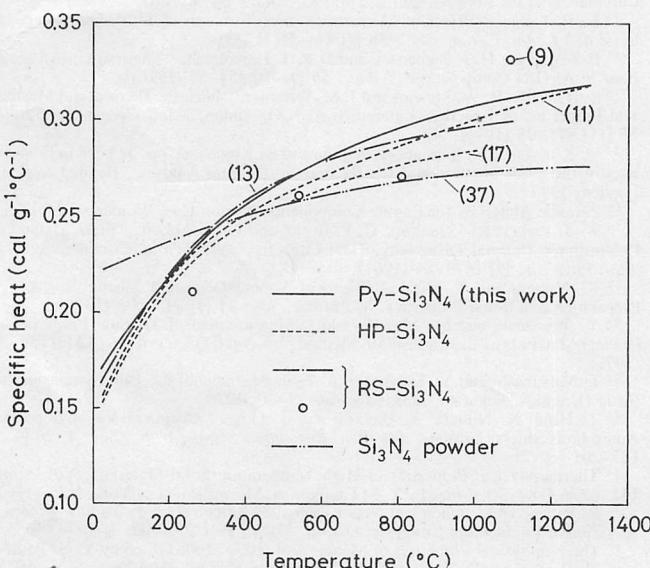


Fig. 6. Comparison of specific heat of Py-Si₃N₄ with data for HP-Si₃N₄, RS-Si₃N₄ and Si₃N₄ powder from references indicated.

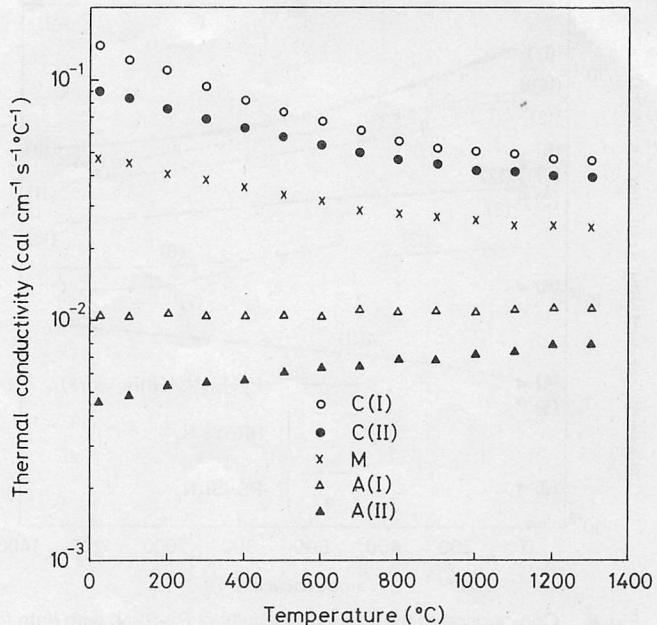


Fig. 7. Thermal conductivity of Py-Si₃N₄.

indicated by a solid line in Fig. 5 are taken as the C_p of Py-Si₃N₄. The C_p of Py-Si₃N₄ increases monotonically with increasing temperature from 0.171 cal g⁻¹ °C⁻¹ at 20°C to 0.319 cal g⁻¹ °C⁻¹ at 1300°C. No anomalies of the C_p are observed in any of the specimens.

Figure 6 shows the C_p of Py-Si₃N₄ along with the data for several kinds of Si₃N₄. The C_p of Py-Si₃N₄ is close to the values measured by other investigators,^{9,11,13,17} but is significantly different from the value estimated from the enthalpy of formation of Si₃N₄ by Pehlke and Elliott.³⁷

Thermal Conductivity

Figure 7 shows the thermal conductivity (k) of Py-Si₃N₄, which is obtained from Figs. 3 and 5, using Eq. (1). The k of specimen C(I) decreases with increasing temperature from 0.140 cal cm⁻¹ s⁻¹ °C⁻¹ at 20°C to 0.0467 cal cm⁻¹ s⁻¹ °C⁻¹ at 1300°C. Specimen C(II) also exhibited a negative temperature dependence of k . For a pyrolytic carbon with preferred orientations, the thermal conductivity parallel to the deposition surface is ≈ 60 times as high as that perpendicular to the deposition surface.³⁸ For HP-Si₃N₄, the observed anisotropy of k is thought to be related to the formation of elongated grains.¹⁴ The k of specimen C(II) is 36% lower than that of specimen C(I) at 20°C and 15% lower at 1300°C, yet both specimens are α -Si₃N₄ having a density of 3.18 g cm⁻³ and a grain size of ≈ 10 μm.^{28,29} Therefore, the difference in the k between specimens C(I) and C(II) likely results from different preferred orientations, as shown in Table I.

The amorphous Py-Si₃N₄ exhibited a positive temperature dependence of k ; k for specimen A(II) increases significantly with increasing temperature from 0.0046 cal cm⁻¹ s⁻¹ °C⁻¹ at 20°C to 0.0079 cal cm⁻¹ s⁻¹ °C⁻¹ at 1300°C.

Figure 8 shows k for Py-Si₃N₄ (C(I) and A(II)), HP-Si₃N₄ and RS-Si₃N₄; k for specimen C(I) is the highest. The spread of the k data for HP- and RS-Si₃N₄ is thought to be related to the additive content and porosity of the specimens.

Thermal Decomposition, Oxidation and Crystallization

From an examination of the thermal decomposition of Si₃N₄,³⁹ the fraction decomposed is estimated to be $\approx 10^{-5}$ after the specimens are heated for 30 min at 1300°C. The present writers⁴⁰ reported that the oxidation weight gain of Py-Si₃N₄ was not detected (sensitivity: 0.5 μg) at 1300°C under an oxygen pressure of 760 torr. Thus, the thermal decomposition and oxidation of specimens are negligible in the present work. Repeating a heating-cooling cycle did not cause any variations in thermal diffusivity and specific heat. It was confirmed by X-ray diffraction that neither specimen A(I) nor A(II) crystallized up to 1300°C.

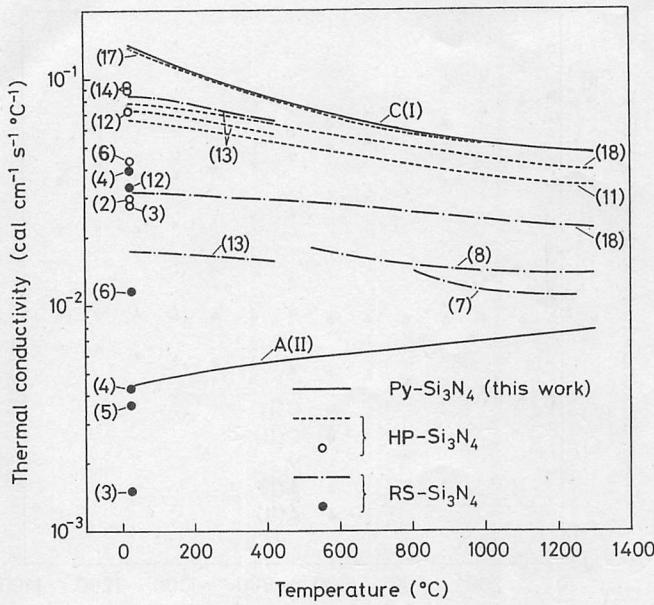


Fig. 8. Comparison of thermal conductivity of Py-Si₃N₄ with data for HP- and RS-Si₃N₄ from references indicated.

Conclusions

The thermal diffusivity of the crystalline Py-Si₃N₄ prepared at $T_{dep}=1300^{\circ}\text{C}$ and $P_{tot}=60$ torr decreased abruptly with increasing temperature from $0.257 \text{ cm}^2 \text{ s}^{-1}$ at 20°C to $0.046 \text{ cm}^2 \text{ s}^{-1}$ at 1300°C . The thermal diffusivity of the amorphous Py-Si₃N₄ prepared at $T_{dep}=1200^{\circ}\text{C}$ and $P_{tot}=40$ torr did not vary remarkably with increasing temperature in the range $20^{\circ}\text{--}1300^{\circ}\text{C}$ and was $0.0095 \pm 0.0008 \text{ cm}^2 \text{ s}^{-1}$. From the thermal diffusivity and the sound velocity ($9.2 \times 10^5 \text{ cm s}^{-1}$), the mean free path of phonons in the amorphous Py-Si₃N₄ was estimated to be $\approx 3 \text{ \AA}$, which is of the order of the dimensions of the Si₃N₄ tetrahedron.

The specific heat of Py-Si₃N₄ increased monotonically with increasing temperature from $0.171 \text{ cal g}^{-1} \text{ °C}^{-1}$ at 20°C to $0.319 \text{ cal g}^{-1} \text{ °C}^{-1}$ at 1300°C . No difference in the specific heat between crystalline and amorphous Py-Si₃N₄ was observed.

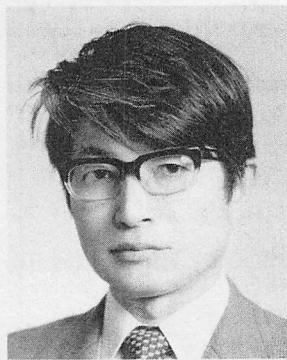
The crystalline Py-Si₃N₄ prepared at $T_{dep}=1300^{\circ}\text{C}$ and $P_{tot}=60$ torr exhibited a negative temperature dependence of the thermal conductivity (0.140 and $0.0467 \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$ at 20° and 1300°C , respectively), while the amorphous Py-Si₃N₄ prepared at $T_{dep}=1200^{\circ}\text{C}$ and $P_{tot}=40$ torr showed a positive temperature dependence (0.0046 and $0.0079 \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$ at 20° and 1300°C , respectively).

Acknowledgments

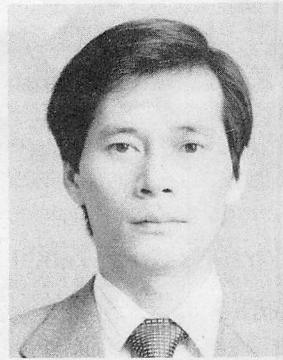
The authors wish to thank A. Kishi (Sinku Riko Co.) for suggestions on the apparatus and K. Endo for shaping the specimens.

References

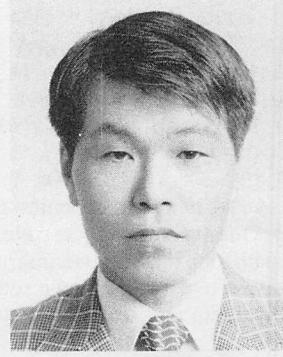
- D. J. Godfrey, "Use of Ceramics in High Temperature Engineering," *Met. Mater.*, **2** [10] 305-11 (1968).
- G. G. Deely, J. M. Herbert and N. C. Moore, "Dense Silicon Nitride," *Powder Metall.*, **8** [8] 145-51 (1961).
- E. Gleny and T. A. Taylor, "Mechanical Strength and Thermal Fatigue Characteristics of Silicon Nitride," *ibid.*, pp. 164-95.
- A. M. Sage and J. H. Histed, "Applications of Silicon Nitride," *ibid.*, pp. 196-212.
- P. Popper and S. N. Ruddlesden, "Preparation, Properties and Structure of Silicon Nitride," *Trans. Br. Ceram. Soc.*, **60** [9] 603-26 (1961).
- R. W. Powell and R. P. Tye; pp. 261-80 in *Special Ceramics 1962*. Edited by P. Popper. British Ceramic Research Assn., Stoke-on-Trent, 1963.
- M. E. Washburn, "Silicon Oxynitride Refractories," *Am. Ceram. Soc. Bull.*, **46** [7] 667-71 (1967).
- Thermophysical Properties of Matter, Vol. 2; pp. 662-63. Edited by Y. S. Touloukian, R. W. Powell, C. Y. Ho and P. G. Klemens. IFI/Plenum, New York, N.Y., 1970.
- Thermophysical Properties of Matter, Vol. 5; pp. 1087-89. Edited by Y. S. Touloukian and E. H. Buyco. IFI/Plenum, New York, N.Y., 1970.
- A. F. McLean, E. A. Fisher and R. J. Bratton, "Brittle Materials Design, High Temperature Gas Turbine," Tech. Rept. No. AMMRC CTR 72-19, September 1972.
- A. F. McLean, E. A. Fisher and R. J. Bratton, "Brittle Materials Design, High Temperature Gas Turbine," Tech. Rept. No. AMMRC CTR 73-9, March 1973 and Tech. Rept. No. AMMRC CTR 73-32, September 1973.
- M. L. Torti, R. A. Alliegro, D. W. Richerson, M. E. Washburn and G. Q. Weaver, "Thermal Conductivity of Py-Si₃N₄," *Am. Ceram. Soc. Bull.*, **57** [12] 667-71 (1978).
- W. George, "Thermal Property Measurements on Silicon Nitride and Silicon Carbide Ceramics Between 290 and 700 K," *ibid.*, pp. 147-67.
- F. F. Lange, "Effect of Microstructure on Strength of Si₃N₄-SiC Composite System," *J. Am. Ceram. Soc.*, **56** [9] 445-50 (1973).
- F. F. Lange, H. J. Siebeneck and D. P. H. Haselman, "Thermal Diffusivity of Four Si-Al-O-N Compositions," *ibid.*, **59** [9-10] 454-55 (1976).
- R. W. Wills, R. W. Stewart and J. M. Wimmer, "Intrinsic Thermal and Mechanical Properties of Reaction-Sintered Si₃Al₂N₆O₂ Sialon," *Am. Ceram. Soc. Bull.*, **55** [11] 975-78 (1976).
- M. Kuriyama, Y. Inomata, T. Kijima and K. Kuwabara; pp. 325-28 in Proceedings of the Fifth International Conference on Thermal Analysis. Heyden & Sons, London, 1977.
- Ceramic Materials for Engine Components. Norton Co., Worcester, Mass.
- W. J. Parker, R. J. Jenkins, C. P. Butler and G. L. Abbott, "Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity," *J. Appl. Phys.*, **32** [9] 1679-84 (1961).
- K. Niihara and T. Hirai, "Chemical Vapour-Deposited Silicon Nitride: I, Preparation and Some Properties," *J. Mater. Sci.*, **11** [4] 593-603 (1976).
- Y. Takahashi and M. Murabayashi, "Measurement of Thermal Properties of Nuclear Materials by the Laser Flash Method," *J. Nucl. Sci. Technol.*, **12** [3] 133-44 (1975).
- T. Mitsuhashi and Y. Takahashi; p. 71 in Abstracts of the 14th Symposium on Basic Ceramics, Fukuoka, Japan, January 29-30, 1976.
- T. Hirai, K. Niihara, S. Hayashi and T. Goto, "Chemical Vapor-Deposited Amorphous Silicon Nitride," *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **26** [4-5] 185-201 (1977).
- Thermophysical Properties of High Temperature Solid Materials, Vol. 3; pp. 161-62 and 189-90. Edited by Y. S. Touloukian. Macmillan, New York, N.Y., 1967.
- R. E. Engdahl, "Chemical Vapor Deposited Silicon Carbide Turbine Rotors," *Automotive Engineering Congress*, Detroit, Mich., Feb. 25-Mar. 1, 1974.
- Thermophysical Properties of Matter, Vol. 10; p. 160. Edited by Y. S. Touloukian, R. W. Powell, C. Y. Ho and M. C. Nicolau. Plenum, New York, N.Y., 1973.
- D. W. Lee and W. D. Kingery, "Radiation Energy Transfer and Thermal Conductivity of Ceramic Oxides," *J. Am. Ceram. Soc.*, **43** [11] 594-607 (1960).
- K. Niihara and T. Hirai, "Chemical Vapour-Deposited Silicon Nitride: II,



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- Density and Formation Mechanism," *J. Mater. Sci.*, **11** [4] 604–11 (1976).
²⁹ K. Niihara and T. Hirai, "Chemical Vapour-Deposited Silicon Nitride: III. Structural Features," *ibid.*, **12** [6] 1233–42 (1977).
³⁰ J. Yokoyama, M. Murabayashi, Y. Takahashi and T. Mukaibo, "Measurement of High-Temperature Thermal Properties of Glassy Carbon by Laser Flash Method," *Tanso*, **1971**, No. 65, pp. 44–47.
³¹ H. Kanamori, N. Fujii and H. Mizutani, "Thermal Diffusivity Measurement of Rock-Forming Minerals from 300 to 1100°C," *J. Geophys. Res.*, **73** [2] 595–605 (1968).
³² W. A. Fate, "High-Temperature Shear Modulus of Si_3N_4 and SiC ," *J. Am. Ceram. Soc.*, **57** [1] 49–50 (1974).
³³ T. Fukase; private communication.

- ³⁴ S. Wild, P. Grieveson and K. H. Jack; pp. 385–95 in *Special Ceramics 5*. Edited by P. Popper. British Ceramic Research Assn., Stoke-on-Trent, 1972.
³⁵ K. Niihara and T. Hirai, "Fractography of Chemical Vapour-Deposited Si_3N_4 "; to be published in the *Journal of Materials Science*.
³⁶ Pages 202–209 in Ref. 9.
³⁷ R. D. Pehlke and J. F. Elliott, "High-Temperature Thermodynamics of the Silicon, Nitrogen, Silicon-Nitride System," *Trans. AIME*, **215** [10] 781–85 (1959).
³⁸ Page 41 in Ref. 8.
³⁹ H. D. Batha and E. D. Whitney, "Kinetics and Mechanism of the Thermal Decomposition of Si_3N_4 ," *J. Am. Ceram. Soc.*, **56** [7] 365–69 (1973).
⁴⁰ T. Hirai, K. Niihara and T. Goto; p. 76 in Abstracts of the 1977 Spring Meeting of the Japan Institute of Metals, Tokyo, Japan, April 4–6, 1977. □

Ultrafine-Grain Tantalum Carbide by High Pressure Hot Pressing

(Continued from page 1125)

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Warren C. Yohe

effect of pressure in dramatically decreasing grain growth. This pressure effect on grain growth is similar to that found by Kudaka et al.² for micron-sized WC, although they did not measure the density of their samples, so it is not known whether their finest grain sizes coincide with high density values.

In previous experiments with submicron TaC, Leipold et al.¹⁰ achieved a minimum grain size of 2 μm with the conventional hot-pressing pressure of 0.04 GPa (0.4 kb) at 1800°C. Also, Sautereau et al.¹¹ sintered similar powder at 1300°–1600°C, achieving grain sizes of ≥2 μm. A comparison of grain growth data for 1600°C shows that Sautereau's sample grain size grew to 6 μm in 15 min (67 Å/s), Leipold's grew to 3 μm in 42 min (12 Å/s) and the authors' grew to 0.3 μm in 8 min (6 Å/s).

The pressure required to achieve zero grain growth simultaneously with maximum density appears to be between 1.5 and 3.0 GPa. At 1.5 GPa, the peak density sample (G-17) showed grain growth to 380 Å, whereas at 3.0 GPa the peak density sample (F-1) had a grain size of 220 Å, indicating no grain growth. Thus, it appears that achieving a 200-Å grain size at peak density would not be possible at the pressures used in conventional hot pressing.

However, the possible presence of oxide phases suggested by the chemical analysis, density and micrographs requires that one consider that growth-inhibiting interactions between grain boundaries and oxide particles might contribute to grain growth inhibition in addition to the pressure effect. This case is not known quantitatively, however.

The attainment of a maximum Knoop hardness of 1800 kg/mm² at 2 kg load is an achievement when compared to previous results. One must be careful when comparing tests using different applied loads,

since significant elastic unloading occurs at light loads (<500 g) which results in an apparent increase in hardness with decreasing load. Readings at low loads can also be sensitive to surface work hardening from polishing. One-hundred-gram loads have been required for extremely small samples such as the single crystals which were 0.5–1 mm on a side. But higher loads give better results in larger samples when there are no problems with cracking at indentation corners, because the indentation is larger and, thus, more accurately measured. The hardness indentations did not produce cracks at 2 kg in our samples. For comparison, sample G-12 was retested under a 100-g load. The maximum hardness was 2300 kg/mm² instead of the 1700 kg/mm², measured at 2 kg. This is very much higher than previous results for a 100-g load, e.g. Rowcliffe et al.'s¹⁵ values on single crystals of $\text{TaC}_{0.99}$ of 1450–1650 kg/mm² and Santoro's¹⁶ value of 1600 kg/mm² measured on Ta filaments carburized to $\text{TaC}_{1.0}$ and 75-μm grain size.

Conclusions

The application of high pressure during hot pressing is an effective means of inhibiting grain growth, allowing a 200-Å grain size to be produced in TaC.

In the range 1.5–4.5 GPa, grain growth at a given temperature decreases with increasing pressure.

Oxidation of TaC powder with an ultrafine particle size poses a significant processing problem which resulted in a maximum attained density of 93% of that for pure, fully dense TaC. Vacuum degassing at 1000°C for 1 h is not sufficient to remove oxides.

A hardness of 1800 kg/mm² at a 2-kg load was attained in 200-Å TaC, which is higher than previously reported hardnesses on coarser TaC.

References

- C. K. Turner, Chemetal Corp.; private communication, 1974.
- K. Kudaka, H. Konno and T. Matoba, "High Pressure Sintering of WC Powders and WC-Co Powder Mixtures," *Nippon Kinzoku Gakkaishi*, **32** [2] 177–82 (1968); translated by Henry Butcher Translations, Altadena, Calif., 1970.
- D. Kalish and E. V. Clougherty, "High Pressure Hot-Pressing Refractory Materials," *Am. Ceram. Soc. Bull.*, **48** [5] 570, 572–78 (1969).
- A. J. Delai, R. M. Haag and T. Vasilos, "Synthesis of New Solid-State Materials by High Pressure Techniques," Tech. Rept. No. AFCRL-66-737, A. F. Cambridge Research Lab., 1966; pp. 24–25.
- G. E. Zima and J. F. Lakner, "High Pressure Consolidation of Submicron Tungsten," *Int. J. Powder Metall.*, **2** [3] 49–57 (1966).
- W. C. Yohe, "High Pressure Hot Pressing of Tantalum Carbide to Attain a Submicron Grain Size"; Ph.D. thesis, Cornell University, Ithaca, N.Y., 1977; pp. 52–67.
- C. E. Van Buren and H. H. Hirsch, "Hydrostatic Pressing of Powders"; pp. 403–41 in *Powder Metallurgy*. Edited by W. Leszynski. Wiley-Interscience, New York, 1961.
- W. B. Daniels and M. T. Jones, "Simple Apparatus for the Generation of Pressures Above 100,000 Atmospheres Simultaneously with Temperatures Above 3000°C," *Rev. Sci. Instrum.*, **32** [8] 885–88 (1961).
- Metals Handbook, 8th ed., Vol. 8; p. 42. Edited by T. Lyman. American Society for Metals, Metals Park, Ohio, 1973.
- M. H. Leipold and P. F. Becher, "Pressure-Densification in Tantalum Carbide," *Am. Ceram. Soc. Bull.*, **49** [7] 647–51 (1970).
- J. Sautereau and A. Mocellin, "Sintering Behavior of Ultrafine NbC and TaC Powders," *J. Mater. Sci.*, **9** [5] 761–71 (1974).
- J. L. Martin, P. Lacour-Gayet and P. Costa; pp. 113–35 in *Electron Microscopy and Structure of Materials*. Edited by G. Thomas et al. University of California Press, Berkeley, 1971.
- T. E. Davidson, J. C. Uy and A. P. Lee, "Tensile Fracture Characteristics of Metals Under Hydrostatic Pressures to 23 Kilobars," *Acta Metall.*, **14** [8] 937–47 (1966).
- Handbook of Chemistry and Physics, 45th ed.; p. B-228. Edited by R. C. Weast, S. M. Selby and C. D. Hodgman. Chemical Rubber Co., Cleveland, Ohio, 1964.
- D. J. Rowcliffe and W. J. Warren, "Structure and Properties of Tantalum Carbide Crystals," *J. Mater. Sci.*, **5** [4] 345–50 (1970).
- G. Santoro, "Variation of Some Properties of Tantalum Carbide with Carbon Content," *Trans. AIME*, **227** [12] 1361–69 (1963). □