JOURNAL OF MATERIALS SCIENCE 31 (1996) 6073–6076

Measurements of elastic and anelastic properties of reaction-formed silicon carbide ceramics

A. WOLFENDEN, K.A. OLIVER
Mechanical Engineering Department, Texas A and M University, College Station, TX 77843, USA
M. SINGH
NYMA, Inc., Lewis Research Center Group, Cleveland, OH 44135, USA

The piezoelectric ultrasonic composite oscillator technique (PUCOT) was used to measure dynamic Young's modulus, damping, strain amplitude, and the strain-amplitude dependence of damping on three reaction-formed silicon carbide (RFSC) specimens. The data were compared with results found on NC 203 SiC. The temperatures used to conduct the tests ranged from 595 –1049 °C, and this information complemented data collected earlier. The main results are as follows: the modulus for RFSC specimens decreases with increasing temperature over a range of approximately 350–260 GPa from room temperature to 1049 °C, the modulus for NC203 ranges from 450–415 GPa over the same temperature range, and damping of RFSCs is independent of strain amplitude and has little temperature dependence.

1. Introduction

As technology advances, there becomes a greater need for improved higher quality materials. The materials industry has greater demands for high-temperature materials that can be used for applications such as advanced propulsion systems, energy conversion devices, and high-temperature structures. Reaction forming is a low-cost and affordable manufacturing process for the fabrication of high-performance ceramics and ceramic matrix composite materials [1–5]. By using the reaction-forming technique over existing methods such as hot isostatic pressing and sintering, lower processing temperatures, shorter processing times, and complex shape fabrication capabilities are possible. This new material must have a low silicon content, high strength and toughness, high thermal conductivity, and good oxidation resistance, and compare favourably with the current commercially produced SiC by Norton Co. (NC203) [6].

In this ongoing experiment, the piezoelectric ultrasonic composite oscillator technique (PUCOT) was used to measure dynamic Young's modulus, damping, strain amplitude, and the strain-amplitude dependence of damping on three reaction-formed silicon carbide (RFSC) specimens. The data are compared with those for NC203 and extend the earlier results to higher temperatures [7].

2. Experimental procedure

The materials used in this experiment were fabricated by a reaction-forming process at NASA Lewis Research Center in Cleveland, OH, and processing details are given elsewhere [1–5]. The porous carbon preforms were made of high char resin, a liquid pore-forming agent, and a catalyst. This mixture was then heated at a slow rate to form the microporous carbon matrix. These carbon preforms were infiltrated with silicon and Si–Mo alloys at the infiltration temperatures (1450 –1500 °C) for different periods of time.

Examples of the microstructure of RFCSs are shown in Figs 1 and 2. RFSC 2 was made from a carbon preform infiltrated with pure silicon. To reduce the amount of free silicon left in the final product, RFSC 3 and 4 were made from a silicon–molybdenum melt with 1.7 and 3.2 at% Mo, respectively. During the infiltration process, silicon was consumed by reaction with carbon and $MoSi_2$ precipitated as a second phase. The presence of $MoSi_2$ in the RFSC material has a number of advantages. The precipitate formed uses silicon that would otherwise be free and available to weaken the material. Also, a silicon–molybdenum alloy infiltration decreases exothermic reaction temperatures [2, 5]. The amount of $MoSi_2$ that forms depends on the alloy composition [5]. Table I shows the theoretically calculated volume fractions of reinforcing phases in each specimen.

Pore size, pore volume, and carbon particle size of the carbon preform all effect final properties of the RFSC. The infiltration rate used also plays an important role in determining properties of the material. Pore volume can be used to prevent what is known as choking-off. If the infiltrant is unable to pass through to all areas of the porous preform, there will be excess carbon because the silicon will react too quickly to

0022–2461

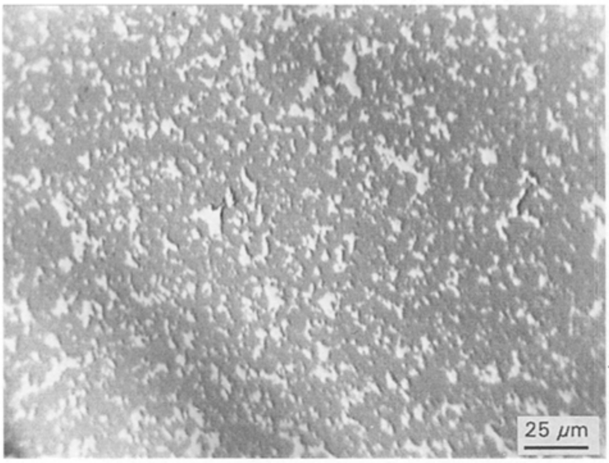

Figure 1 Microstructure of reaction-formed silicon carbide (RFSC 2) material (white areas are silicon and grey areas are silicon carbide).

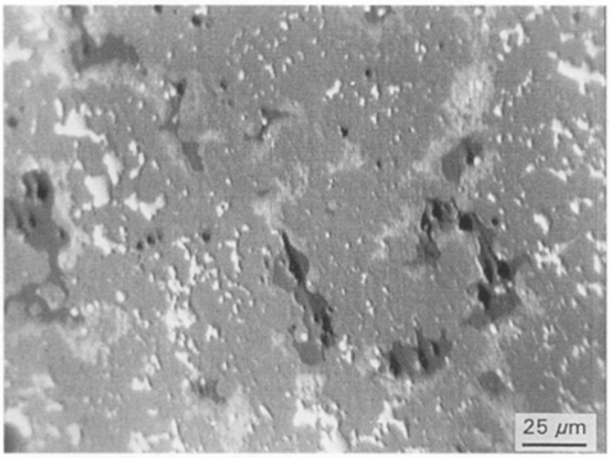

Figure 2 Microstructure of reaction-formed silicon carbide (RFSC 3) material (white areas are silicon and molybdenum disilicide and grey areas are silicon carbide).

form SiC. An increase in infiltration rate will allow the melt to react throughout the specimen and not block off flow of free silicon to the inner carbon preform. This is also dependent on the density of carbon in the preforms. Through experimentation and modelling, the best infiltration rate can be found to allow the silicon to react with the carbon without choking-off pores.

Use of the PUCOT requires that the density of the material be known. The density of each specimen was found by the Archimedes technique.

The PUCOT uses resonating crystals to measure the data of interest. Two α-quartz crystals of the same frequency, in this case 120 kHz, were glued together with Loctite glue and attached to a jig. The drive crystal and gauge crystal were both connected electrically to the closed-loop crystal driver. The resonant frequency of the two crystals was measured with this equipment. For tests operating at high temperature, a fused quartz spacer rod must be attached to the quartz crystals and tuned to the resonant frequency. This tuning designated the test temperature used for experiments done with this particular tuned rod. The rod and crystals were attached together with Loctite. To glue a specimen at the other end of a tuned rod, special cement, Sauereisen D-29, was used to withstand high temperatures. From the density and estimated Young's modulus of the specimen, test temperature, and expansion coefficient, the required length of the specimen was determined. After cutting the material to the appropriate length, it was attached to the quartz rod and crystals and lowered into the furnace at room temperature to prevent thermal shock. When the appropriate temperature was reached, measurements of the drive crystal voltage, the gauge crystal voltage, and the resonant period of the system were recorded and entered into a computer program. Other details of the PUCOT are given elsewhere [9 –12].

For metallographic work, representative samples of each specimen in the longitudinal and transverse directions were mounted in bakelite and polished. In this form, the microstructure of each sample could be viewed with an optical microscope.

3. Results and discussion

Figs 1 and 2 are typical microstructures of RFSCs. Fig. 1 is a longitudinal view of RFSC 2. The material is very uniform, with very little porosity. The white areas are silicon, the grey areas are SiC, and the few black spots are residual carbon. Fig. 2 represents RFSC 3 in the transverse direction. As in Fig. 1, the white areas are silicon, the dark grey areas are SiC, and the black spots are residual carbon. The light grey areas are a combination of $MoSi_2$ and residual molybdenum.

In general, the elastic properties of a material tend to decrease as temperature increases. Dynamic Young's modulus for SiC ceramic matrix materials is no exception. Table II lists the modulus found for temperatures ranging from room temperature to 1049 °C. As shown in Fig. 3, there is a linear relationship between modulus and temperature. Linear regression equations are listed in Table III. Commercially produced SiC ceramic matrix NC203 has the highest room-temperature modulus, but the modulus

TABLE I Volume fraction of reinforcing phases [8]

Specimen	Infiltrant	Vol. fraction SiC	Vol. fraction $MoSi_2$	Vol. fraction Si
NC203	–	1	–	–
RFSC 2	Si	0.857	0	0.143
RFSC 3	Si–1.7 at % Mo	0.857	0.033	0.110
RFSC 4	Si–3.2 at % Mo	0.854	0.062	0.081

TABLE II Measured values of Young's modulus for SiC matrix composites

Specimen	Infiltrant	Temperature (°C)	Modulus[a] (GPa)
NC203	–	20	(450)
		360	(434)
		514	(418)
		835	430
		1049	414
RFSC 2	Si	20	(344)
		350	(325)
		561	(320)
		835	327
		1049	326
RFSC 3	Si–1.7 at % Mo	20	(340)
		298	(276)
		455	(262)
		595	294
		835	324
		835	333
		949	318
RFSC 4	Si–3.2 at % Mo	20	(310)
		305	(302)
		595	286
		835	291
		949	261

[a] Parentheses denote measurements from [7].

TABLE III Linear regression equations for E (GPa) versus T (°C)

Specimen	Linear regression	Correlation coefficient R	Relative decrease (10^{-4} K^{-1})
NC203	$E = (-0.029\,13)\ T + 445$	0.82	−0.65
RFSC 2	$E = (-0.014\,26)\ T + 336$	0.63	−0.41
RFSC 3	$E = (-0.000\,41)\ T + 300$	0.18	0
RFSC 4	$E = (-0.042\,90)\ T + 313$	0.87	−1.38

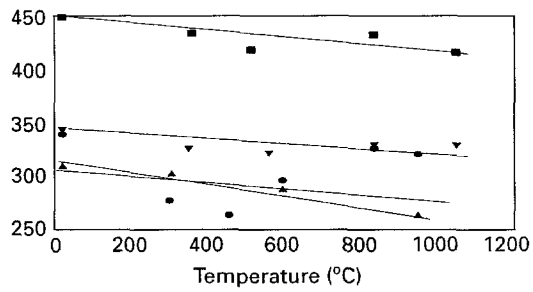

Figure 3 Dynamic Young's modulus versus temperature for SiC matrix composites. (■) NC203, (▼) RFSC 2, (●) RFSC 3 (▲) RFSC 4.

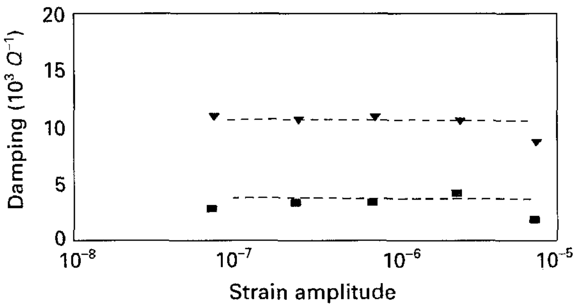

Figure 4 Damping versus strain amplitude for NC203 at (■) 835 and (▼) 1049 °C.

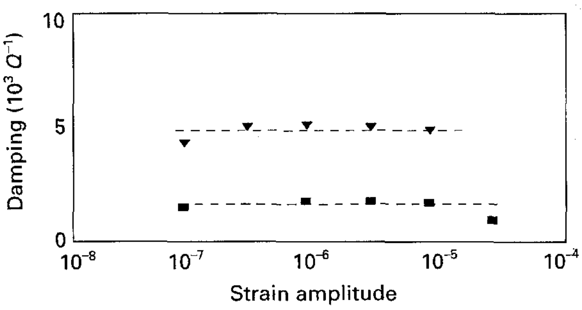

Figure 5 Damping versus strain amplitude for RFSC 2 at (■) 835 and (▼) 1049 °C.

for RFSC 3 decreases the least with respect to increasing temperatures. As can be seen in Fig. 3, the modulus found at 1049 °C for RFSC 3 is almost as high as that at room temperature. The result for this specimen does not follow the expected modulus trend as can be seen in Fig. 3. It was observed that the specimen (RFSC 3) was oxidizing at temperatures starting around 500 °C due to the presence of $MoSi_2$, therefore possibly causing an increase in the stiffness of the material. The modulus for the reaction-formed materials is lower than that for NC203, and the specimen with silicon infiltration has a higher modulus than those for the two with Si–Mo combinations. The correlation coefficients are listed in Table III. The values determine how sensitively the data follow the linear relationship between modulus and temperature. RFSC 3 has a low correlation coefficient, R, owing to the irregular effect of oxidation on the modulus.

The relative decrease of dynamic Young's modulus with increasing temperature is also included in Table III. This value was determined by normalizing the slope of the linear regression with respect to the modulus at room temperature. Small values for the relative decrease indicate that dynamic Young's modulus changes very little over the temperature range tested. The relative decrease of RFSC 4 is higher than the other values. The high molybdenum content (3.2 at %) in RFSC 4 will cause the value of relative decrease to increase towards values associated with metals. The typical range for metals is -4×10^{-4} to $-14 \times 10^{-4}\ K^{-1}$. In pure form, the relative decrease of silicon is $-0.55 \times 10^{-4}\ K^{-1}$, and molybdenum is $-1.3 \times 10^{-4}\ K^{-1}$ [13].

It can be seen in Figs 4–7 that damping is independent of strain amplitude for the test temperatures of 595, 835, 949 and 1049 °C. The slopes of the lines are very close to zero. The values found for damping can be affected by the amount of glue used to attach the specimen to the fused quartz spacer rod. Unfortunately, this will vary from experiment to experiment with the resulting scatter seen in Figs 4–7. There should be no significant strain-amplitude dependence of

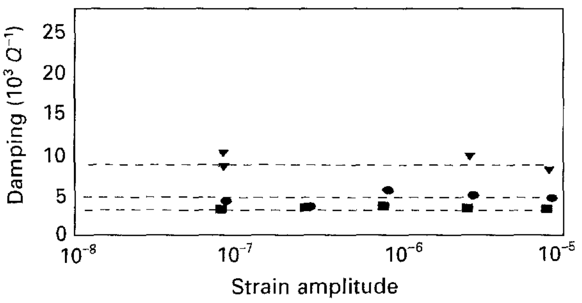

Figure 6 Damping versus strain amplitude for RFSC 3 at (●) 595, (■) 835, and (▼) 949 °C.

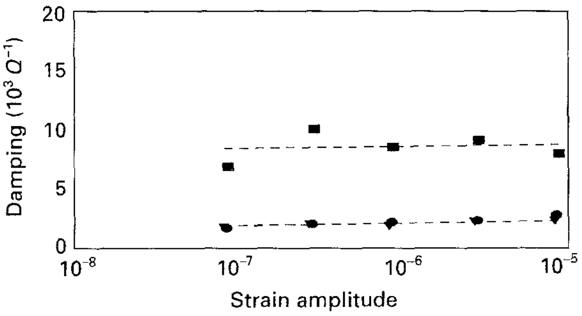

Figure 7 Damping versus strain amplitude for RFSC 4 at (●) 595, (▼) 835, and (■) 949 °C.

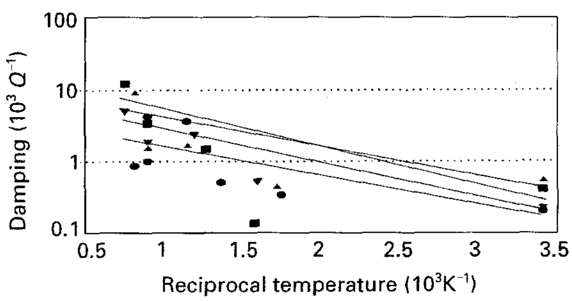

Figure 8 Damping versus reciprocal temperature for SiC matrix composites. (■) NC203, (▼) RFSC 2, (●) RFSC 3 (▲) RFSC 4.

damping in these materials because of the small number of dislocations generally associated with ceramics, and the inability of dislocations to move significant distances in the lattice at the test temperature used. Damping is expected to increase with increasing temperature and a dependence of this form is sought

$$Q^{-1} = Q^{-1}(0)\exp(-\Delta H/kT) \quad (1)$$

where $Q^{-1}(0)$ is a reference value of damping, ΔH is an effective activation energy and k is Boltzmann's constant. Despite the scatter in Fig. 8, all four materials show the expected dependence of damping (i.e. a negative slope). The corresponding values for ΔH are near 0.08 eV atom^{-1} and are essentially equal to the available thermal energy (kT) for atomic vibration at 1049 °C.

4. Conclusion

The dynamic Young's modulus for RFSC specimens decreases with increasing temperature over a range of approximately 350–260 GPa from room temperature to 1049 °C. The modulus for NC203 SiC ranges from 450–415 GPa over the same temperature span. Damping of RFSCs is independent of strain amplitude and has little temperature dependence.

Acknowledgements

The authors thank Scott Cronauer for metallographic assistance and Dr L.R. Cornwell and Dr H.R. Thornton for invaluable discussions.

References

1. M. SINGH and S. R. LEVINE, NASA TM 107001 (1995), Lewis Research Center, Cleveland, OH.
2. M. SINGH and D. R. BEHRENDT, NASA TM 105860 (1992), Lewis Research Center, Cleveland, OH.
3. *Idem, J. Mater. Res.* **9** (1994) 1701.
4. *Idem, Mater. Sci. Engng.* **A187** (1994) 183.
5. *Idem, ibid.* A (1994) Mater. Sci. Engng. **A194** (1995) 193.
6. M. SINGH, R. PAWLIK, J.A. SALEM, and D.R. BEHRENDT, "Advances in Ceramic Matrix Composites" (American Ceramic Society, OH, 1993) pp. 349–60.
7. A. WOLFENDEN, P.J. RYNN and M. SINGH, *J. Mater. Sci.,* **30** (1995) 5502.
8. D. R. BEHRENDT and M. SINGH, *J. Mater. Synth. Process.* **2**(2) (1994) 117.
9. J. T. HARTMAN Jr, K. H. KEENE, R. J. ARMSTRONG and A. WOLFENDEN, *J. Metals* April (1986) 33.
10. J. MARX, *Rev. Sci. Instrum.* **22** (1951) 503.
11. W. H. ROBINSON and A. EDGAR, IEEE Trans. Sonics Ultrasonics **SU-21** (1974) 98.
12. M. R. HARMOUCHE and A. WOLFENDEN, *J. Test. Eval.* **13** (1985) 424.
13. J. FRIEDEL, "Dislocations" (Pergamon Press, Reading, MA, 1964) pp. 454–7.

Received 14 June
and accepted 7 November 1995