



# **Silicon Carbide Nanotube Oxidation at High Temperatures**

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# Abstract

**Silicon Carbide Nanotubes (SiCNTs) have high mechanical strength and also have many potential functional applications. In this study, SiCNTs were investigated for use in strengthening high temperature silicate and oxide materials for high performance ceramic nanocomposites and environmental barrier coating bond coats. The high temperature oxidation behavior of the nanotubes was of particular interest.**

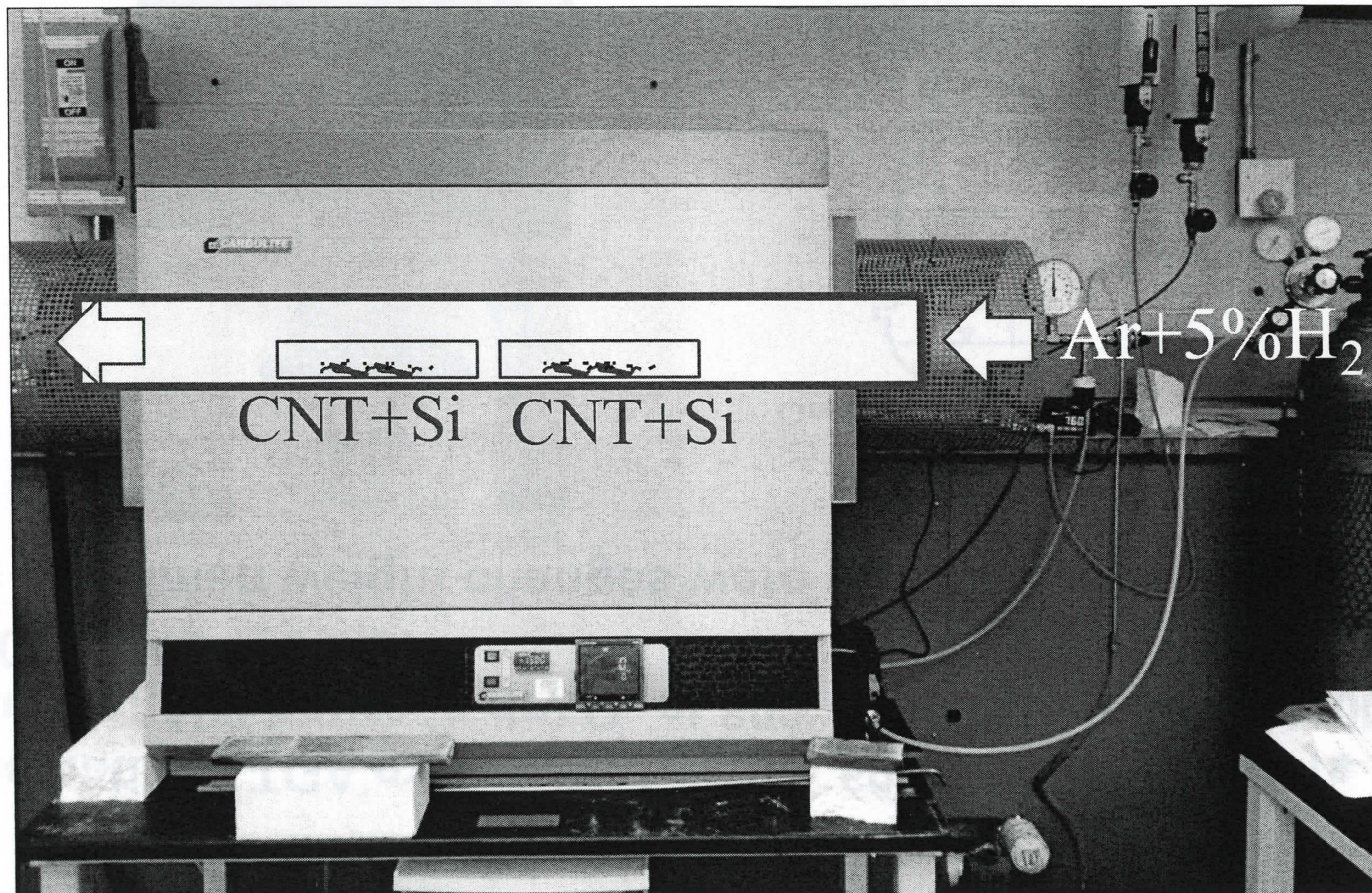
**The SiCNTs were synthesized by a direct reactive conversion process of multiwall carbon nanotubes and silicon at high temperature. Thermogravimetric analysis (TGA) was used to study the oxidation kinetics of SiCNTs at temperatures ranging from 800°C to 1300°C. The specific oxidation mechanisms were also investigated.**



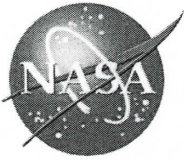


## Experimental: SiCNT Nanotube and Nanotube Coating Processing

- SiCNTs were synthesized in the furnace in a  $\text{Ar}+\text{H}_2$  reducing environment. Carbon nanotube and Si powders were mixed and heat treated in two process cycles for 4 hours each at  $1400^\circ\text{C}$ .

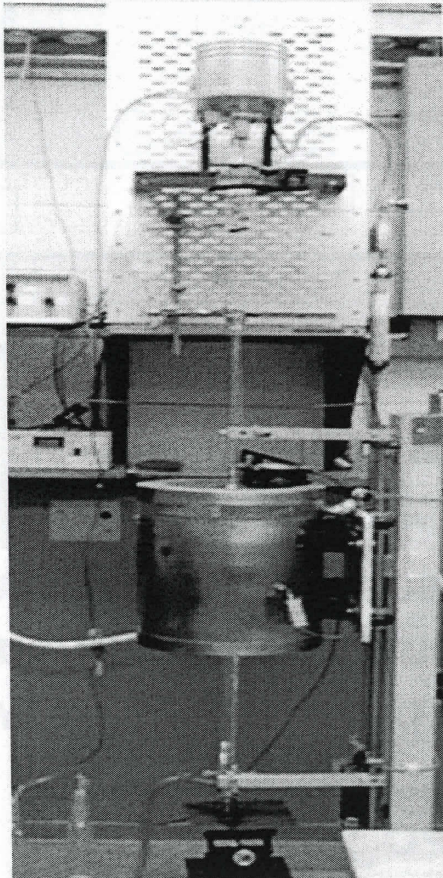




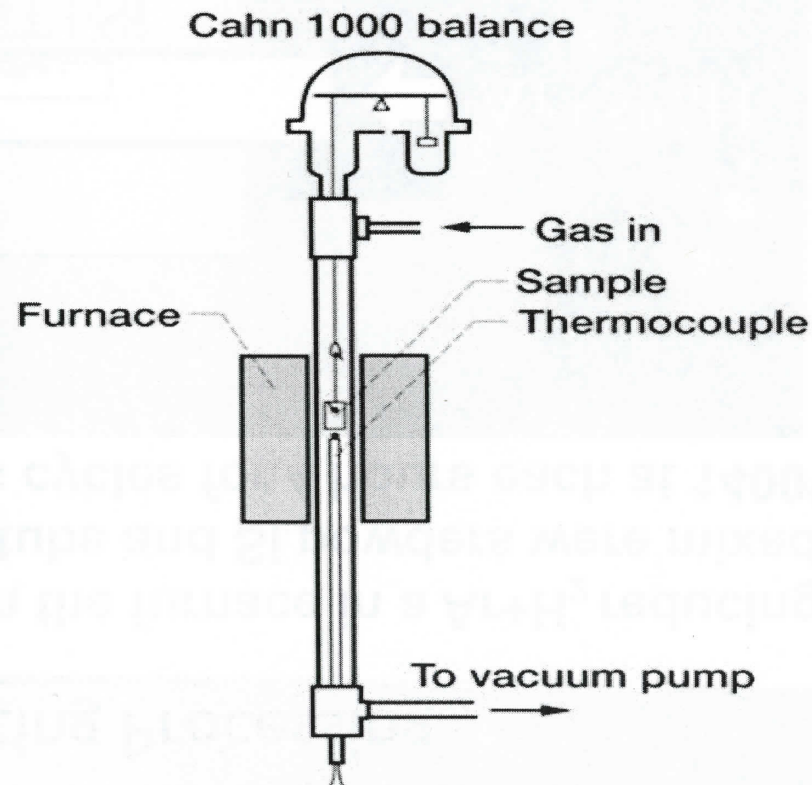


## Experimental: Thermogravimetric Analysis

- Schematic of TGA experiment setup. 60-100 mg of SiCNTs were tested for 100 hours in dry  $O_2$  at 800°C, 900°C, 1000°C, 1100°C, 1200°C, and 1300°C.
- The Specimen weight changes were recorded vs. time.



TGA







- Previous work<sup>1,2,3</sup> predicted that formation of SiO<sub>2</sub> on the nanotube surface follows a parabolic rate law:

$$\left(\frac{\Delta w}{A}\right)^2 = K_p t + C \quad (1)$$

$\Delta w$  = change in weight

$A$  = initial surface area = 134500cm<sup>2</sup>/g

$K_p$  = parabolic rate constant

$t$  = time

$C$  = constant

- The rate constant ( $K_p$ ) are related to temperature by the Arrhenius equation:

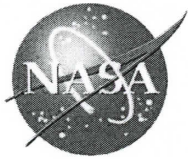
$$K_p = A \exp(-Q/RT) \quad (2)$$

$Q$  = activation energy

$R$  = gas constant

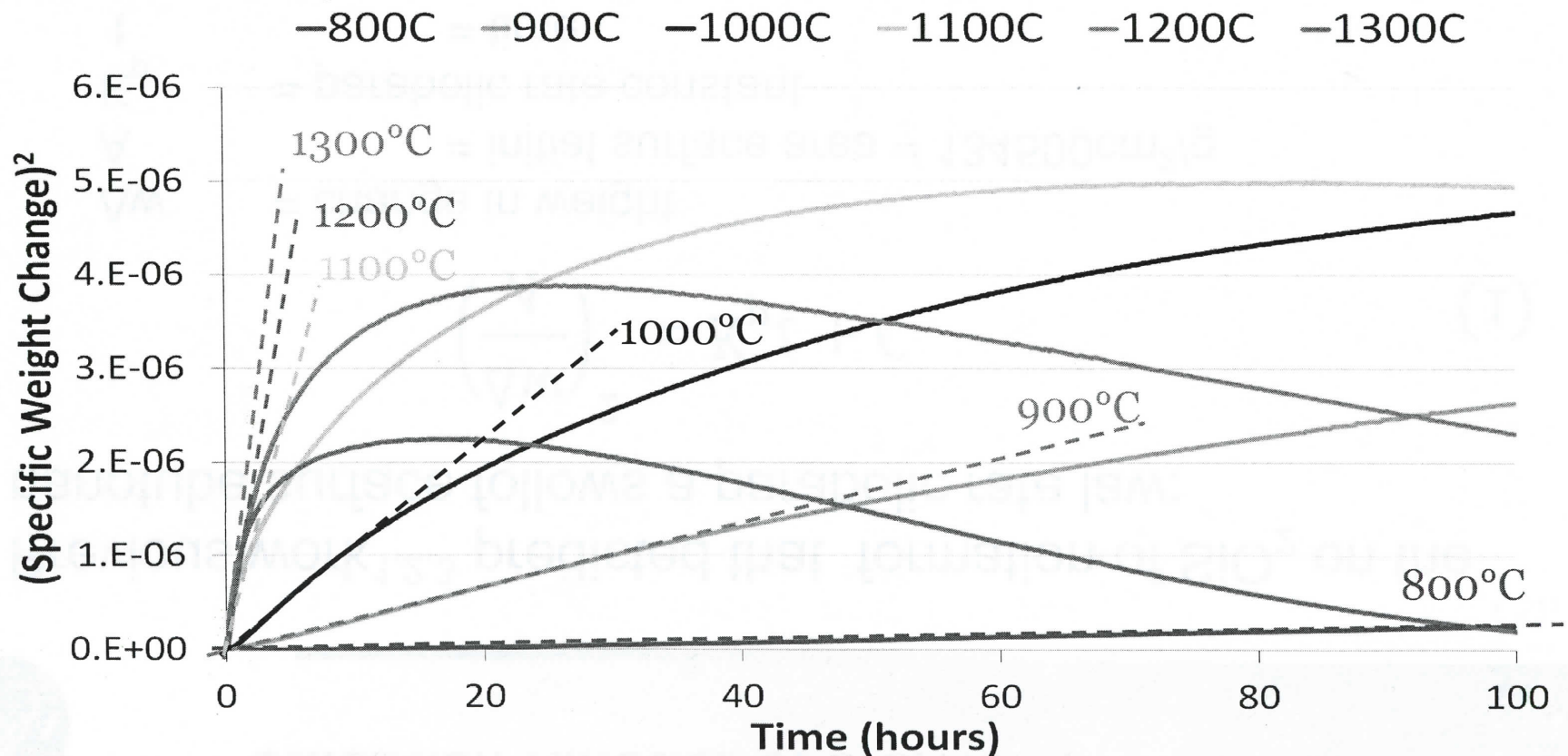
$T$  = temperature



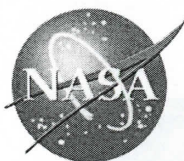


## Specific Weight Gain vs. Time for SiCNTs

- (Specific weight change)<sup>2</sup> vs. time is plotted for each temperature. The oxidation behavior appears pseudo-parabolic at 800°C up to 1200°C for the fiber-like SiCNTs, and  $K_p$  was calculated using equation 1. For 1000°C to 1300°C, initial shrinking fiber surface area causes the reaction to slow down over time. Only the initial, parabolic portion of each curve was used to calculate  $K_p$ .

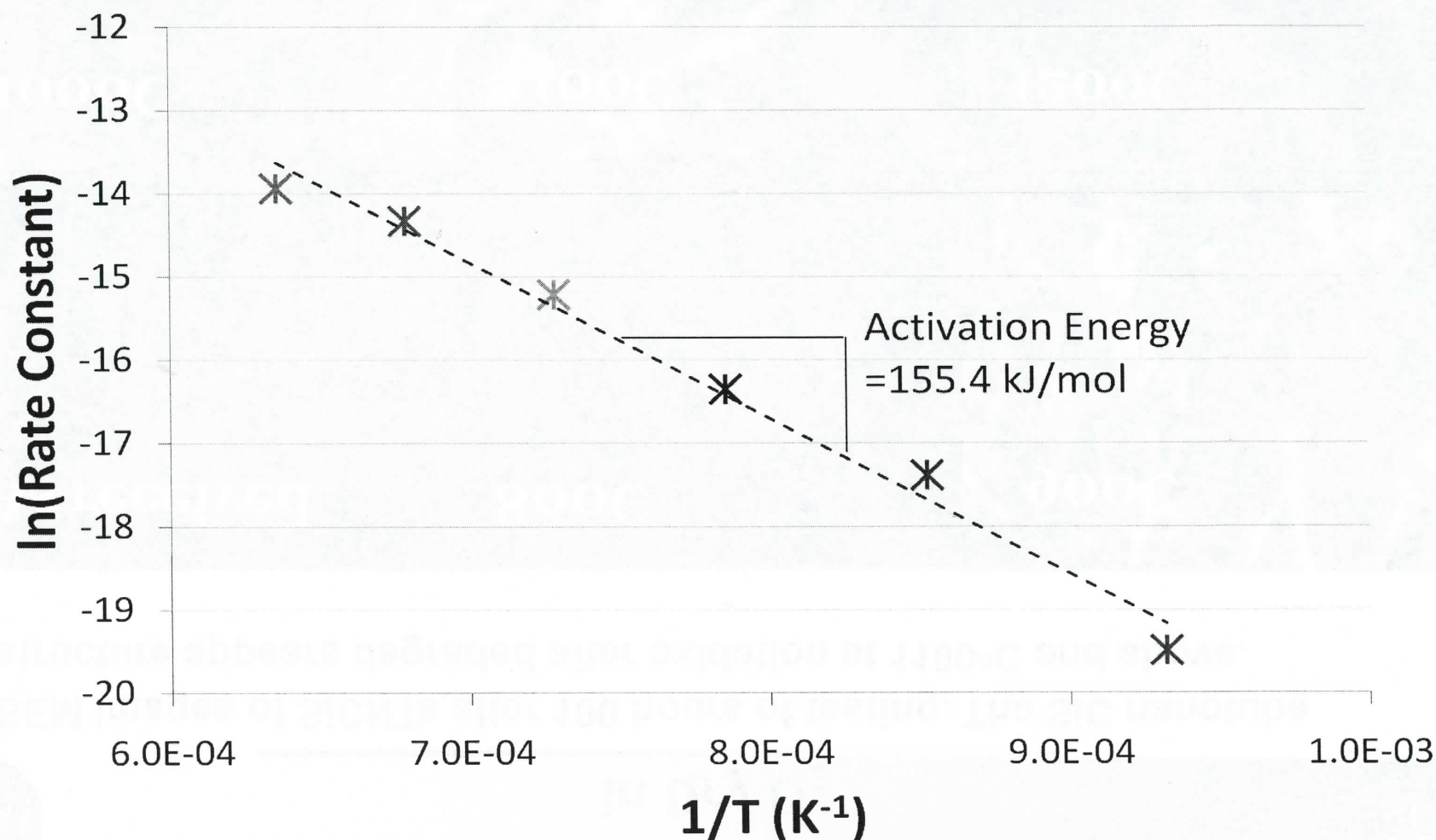




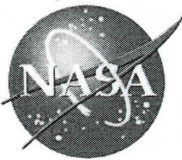


## SiCNT Oxidation Activation Energy Based on TGA Tests

- Equation 2 was used to calculate the activation energy ( $Q$ ) of 155 kJ/mol. The graph of  $K_p$  vs.  $1/T$  gives a straight line with little deviation, indicating that  $Q$  is valid for the 800°C – 1300°C temperature range.

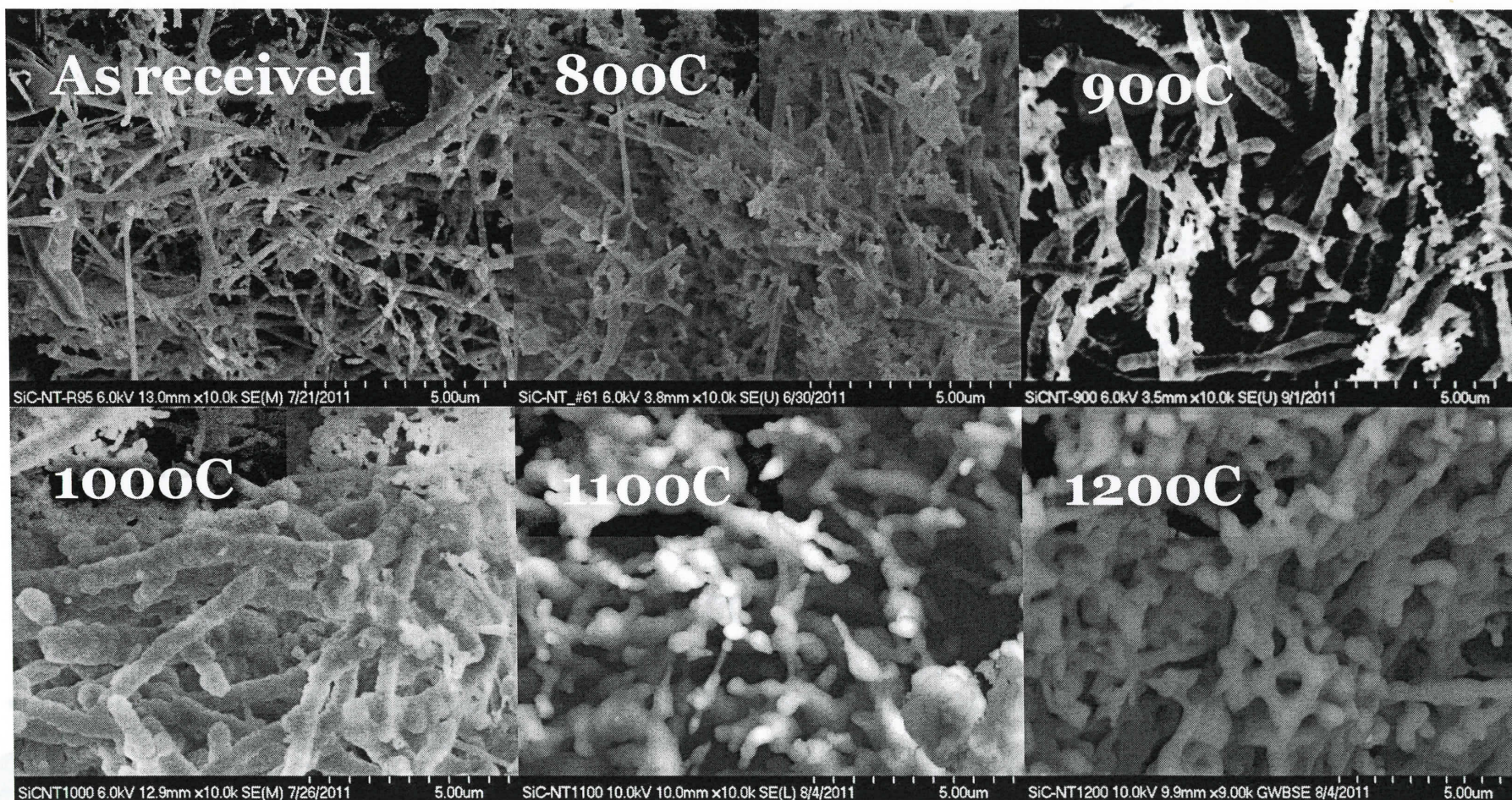




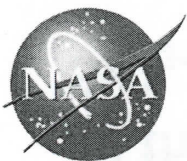


## SEM Observation of SiCNTs after 100 hr Oxidation in Dry O<sub>2</sub>

- SEM images of SiCNTs after 100 hours of testing. The SiC nanotube structure appears degraded after oxidation at 1100°C and above.



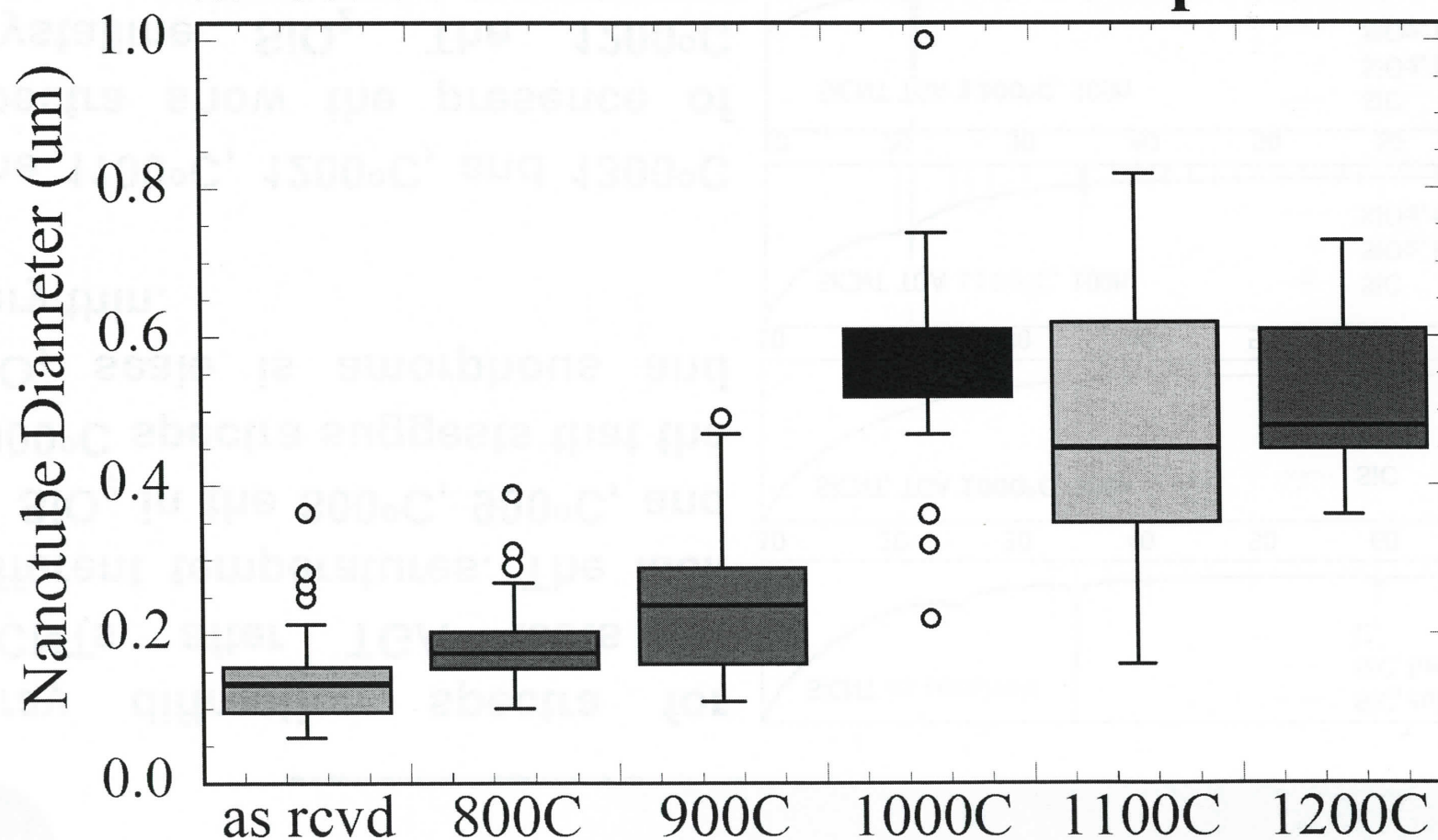




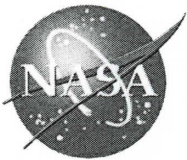
## SEM Observation of SiCNTs

- Box and whisker plot of nanotube diameters vs. TGA temperature. The SiCNTs grew in diameter during each test due to formation of a  $\text{SiO}_2$  scale.

### Nanotube Diameter vs. TGA Temperature

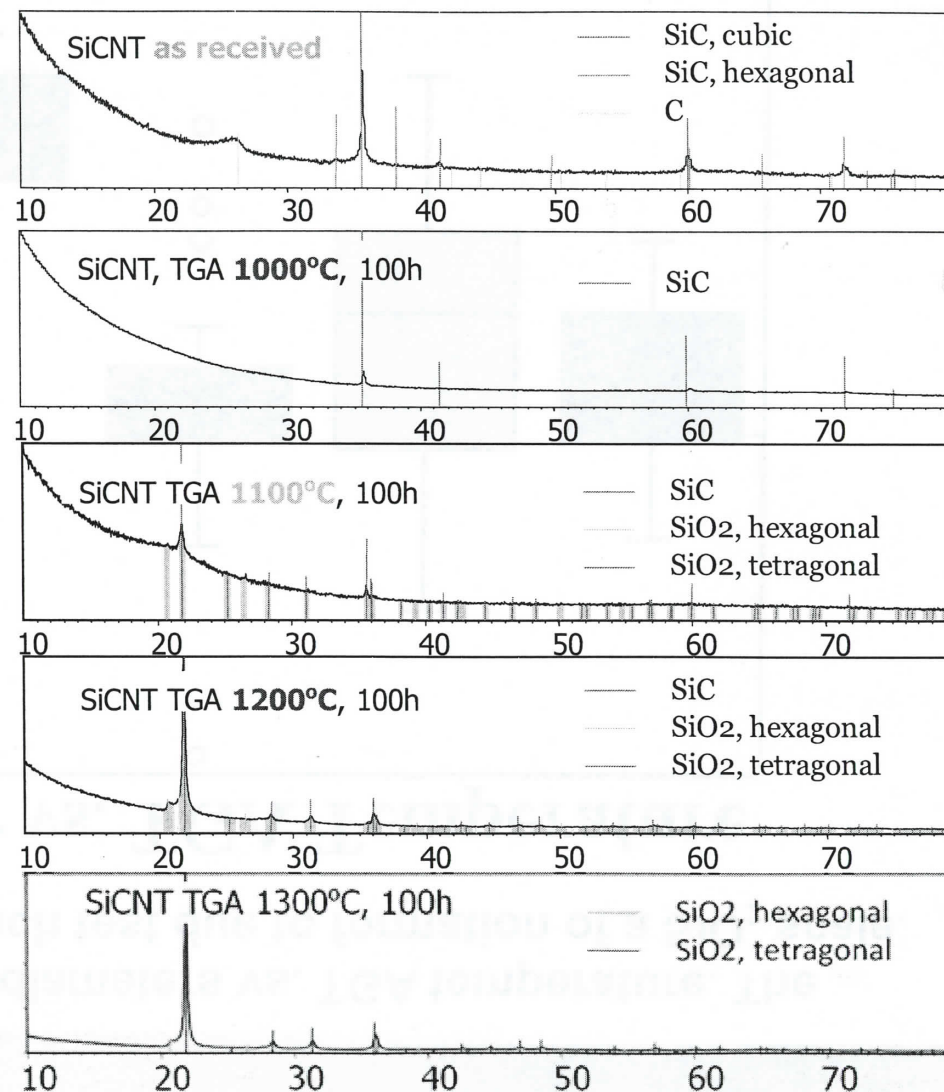


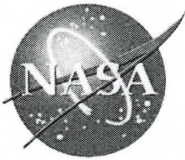




## X-Ray Diffraction Results of Oxidized SiCNT

- X-ray diffraction spectra for SiCNTs after TGA tests at different temperatures. The lack of  $\text{SiO}_2$  in the 800°C, 900°C, and 1000°C spectra suggests that the  $\text{SiO}_2$  scale is amorphous and very thin.
- The 1100°C, 1200°C, and 1300°C spectra show the presence of crystalline  $\text{SiO}_2$ . The 1200°C sample contains almost no SiC, and the 300°C spectrum does not contain SiC, suggesting that all the SiC has been converted to  $\text{SiO}_2$ .

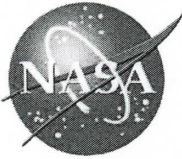




## Conclusions

- **SiCNTs exhibit pseudo-parabolic behavior when oxidized in pure O<sub>2</sub>, following fibrous SiC oxidation behavior.**
- **The activation energy was 155.4 kJ/mol based on TGA studies.**
- **SiCNTs retained their SiC core and nanotube structure for 100 hours in pure O<sub>2</sub> at 800°C-1000°C. Part of the SiC is retained at 1100°C, and almost no SiC remains for the SiCNTs at 1200°C and 1300°C after 100 hours of oxidation based on x-ray and TGA late stage weight loss results.**
- **The oxidation behavior suggests that the upper use temperature limit for SiCNTs may be 1200°C.**
- **Future work will investigate the effectiveness of a protective coating matrix such as Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in raising the upper use temperature for SiCNTs.**



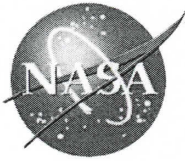


## References



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