

# The Control of Reagents in the ICVI Process

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## ABSTRACT

The purpose of this work was to study the influence of the concentration and the proportion of reactant gases on the depositing efficiency and C/SiC (CVI) composite properties in the ICVI procedure, and the influence of the length-to-diameter ratio of the cavity on the deposition was also investigated. A novel, simple in-line controller for reactant gases was introduced. The results were analyzed by XRD and SEM and composite mechanical tests. The results showed that the simple in-line controller can control the MTS vapor flow and the H<sub>2</sub>/MTS ratio. A pure SiC matrix is formed at a H<sub>2</sub>/MTS molar ratio of about 3, a matrix with a large amount of free carbon is formed at H<sub>2</sub>/MTS molar ratio less than 1, while no free silicon is found in the depositing matrix at H<sub>2</sub>/MTS molar ratio of more than 10 (about 15). The depositing rate increases and the depth decreases with increased use of MTS. The deposition in a cavity of a length-to-diameter ratio above 5 is faster and more uniform.

## INTRODUCTION

Continuous-fiber ceramic matrix composites (CFCCs) have potential applications in high-temperature thermal structures of aerospace vehicles and propulsion systems, since they offer high strength and toughness properties along with low density [1]. CVI-SiC matrix composites, offering many advantages, such as high strength and toughness and improvement in resistance to oxidation with respect to the C/C composites and other ceramics, have been successfully applied in liquid propellant booster engines [2,3]. Ceramic fibers (such as Nicalon fibers) lose strength at

temperatures higher than 1200°C because of crystallization, which leads to a decrease in the mechanical properties of the fibers and reinforced composites. Thus the carbon fibers are the best candidate material for the ceramic matrix composites due to their ability to maintain strength at elevated temperatures. The common fabrication processes for 3D C/SiC composites are chemical vapor infiltration (ICVI) [3] and polymer precursor conversion (PPC). The extensive interest in the CVI process arises for several reasons. First, the C/SiC composites fabricated by the CVI process have attractive mechanical properties, particularly enhanced fracture toughness. Second, low stresses and temperatures are utilized in the CVI process, which minimizes damage to fibers. A third advantage of the CVI process is that pre-coating of the fibrous perform which might be required to tailor fiber/matrix bonding can be performed as an initial step in the CVI process using different reagents but the same CVD equipment. Of all the CVI processes, only the isothermal CVI (ICVI) has been industrialized to fabricate successfully composite components, as it permits fabrication of any irregular shape and any thick component. The common reagent system used for SiC deposition is CH<sub>3</sub>SiCl<sub>3</sub> (MTS)-H<sub>2</sub>, where the stoichiometric ratio, Si:C=1, is suitable for SiC deposition and the hydrogen is used as a carrier for MTS which is liquid at room temperature. The reaction of the SiC matrix for CVI is:



The key ICVI process variables are temperature, pressure, H<sub>2</sub>/MTS molar ratio, and concentration. The reagent concentration and the H<sub>2</sub>/MTS molar ratio influence the properties of the matrix and composites heavily. The purpose of this work was to study the

influence of the concentration and the properties of reagent on the depositing efficiency and the properties of the matrix and the composites in the ICVI process, and to introduce a novel, simple in-line controller for reactant gases.

**EXPERIMENTAL**

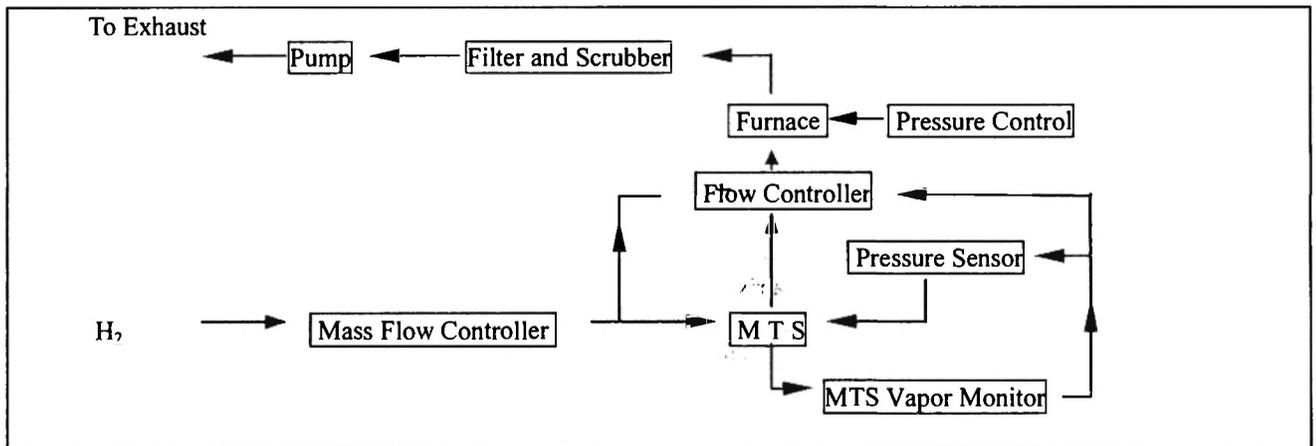
The properties of the carbon fibers used in this work are listed in Table 1. The in-line control CVI system consists of three basic subsystems: reactant supply, reactor (furnace containing the fibrous perform or substrate), and effluent gas-handling equipment (Figure 1). The gas-handling equipment consists of control and monitor, which can control the reagent concentration and the H<sub>2</sub>/MTS molar ratio. The SiC matrix is

deposited from a CH<sub>3</sub>SiCl<sub>3</sub> (MTS)-H<sub>2</sub> precursor under a reduced pressure of 3 kPa.

**Table 1**  
Properties of the carbon fibers (3K, PAN-base) in this work

Fiber diameter (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Fracture elongation %
6.7	3290	225	1.49

The MTS vapor flow was 10 to 50g/h and the hydrogen flow was regulated according to the desired H<sub>2</sub>/MTS ratio. H<sub>2</sub>/MTS molar ratio (α) was defined as follows:



**Fig. 1:** Schematic diagram system for the CVI process

$$\alpha = \Delta N_1 / \Delta N_2 \tag{2}$$

$\Delta N_1$  is the consumption of hydrogen (mole/h), and  $\Delta N_2$  that of MTS (mol/h)

$$\Delta N_1 = C_o \cdot P \cdot Q / (R \cdot T) \tag{3}$$

$$\Delta N_2 = \Delta W / M_n \tag{4}$$

P is the pressure of hydrogen flow (MPa), Q is the hydrogen flow in the flow-meter (l/h), C<sub>o</sub> is the coefficient of the real hydrogen flow to the flow-meter, C<sub>o</sub> = 3.8; R is the gas constant, R = 0.0082 l • MPa •

K<sup>-1</sup> • mole<sup>-1</sup>, T is the ambient temperature (K), ΔW is the consumption of MTS (g/h), M<sub>n</sub> is the molecular weight of MTS, M<sub>n</sub> = 149.48 g/mole. Thus Eq. (2) becomes

$$\alpha = 23 Q / \Delta W \tag{5}$$

$$Q = 0.0433 \Delta W \cdot \alpha \tag{6}$$

The hydrogen flow was calculated according to Eq. (6). In order to analyze the deposition microstructure, the SiC matrix was deposited on the polished surface of a graphite substrate (40mm × 40mm × 6mm) and then

peeled off and analyzed by x-ray diffraction (XRD) and scanning electron microscopy (SEM). In the fabrication of the composites, the carbon fibers were first braided into 3D fibrous preforms through a four-step braiding technique with a fiber volume content of about 50%. Then the fibrous preforms were coated with pyrolytic carbon as an interphase from the cracking of C<sub>3</sub>H<sub>6</sub>-N<sub>2</sub> precursor at about 900°C and whose mean thickness was about 0.3 μm. In the third step, The SiC matrix was deposited within the pores of the fibrous preform. The matrix distribution in the porous preform was also characterized through metallograph analysis. A three-point bend test was performed using a 16mm span for testing the shear strength of the composites and a 50mm span for testing flexural strength at a crosshead speed of 0.5mm/min at room temperature. The span-to-depth ratio was about 5 for shear specimens and about 17 for flexural specimens. The fracture toughness (K<sub>IC</sub>) of composites was examined by the single edge notch beam (SENB) method using a 40mm span and a 0.2mm notch width and a 3mm notch depth at a crosshead speed of 0.2mm/min.

### Control of the H<sub>2</sub>/MTS ratio

Hydrogen was used as the MTS carrier, and its bubble number in MTS controls MTS vapor flow. So the hydrogen flow change would lead to a flow change in MTS vapor, which makes control of the desired H<sub>2</sub>/MTS ratio impossible. In this study, the pressure in the MTS supply can be tailored, which could change the MTS vapor evaporation rate and the MTS vapor flow. It is well known that supply pressure and temperature influence liquid evaporation. The lower the saturation pressure (P<sub>s</sub>), the higher the evaporation rate. The MTS vapor for SiC deposition consists of the vapor carried by hydrogen and the evaporation vapor. Therefore the MTS vapor flow increases with decrease of the supply pressure at the same temperature. P<sub>s</sub> was reduced pressure and can be expressed by the degree of vacuum.

It is noted that the saturation pressure (P<sub>s</sub>) of MTS is 18.6kPa at room temperature (293K) and 1atm (0.1MPa) at the boiling point (339K), thus the P<sub>s</sub> of MTS can be calculated according to the Clapeyron Equation

$$\lg \frac{P_1}{P_2} = \frac{H_0}{2.303 R} \frac{T_2 - T_1}{T_1 T_2} \tag{7}$$

## RESULTS AND DISCUSSION

### Calculation of hydrogen flow

For a given MTS vapor flow and H<sub>2</sub>/MTS ratio, the result of calculation of hydrogen flow was illustrated in Figure 2 according to Eq. (6).

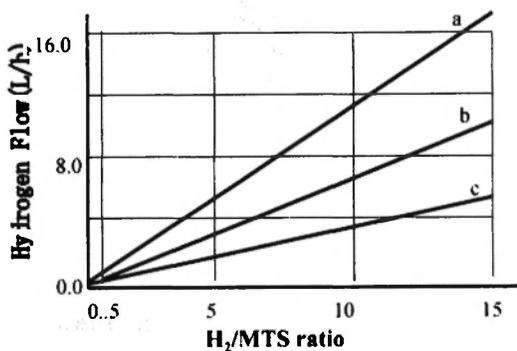
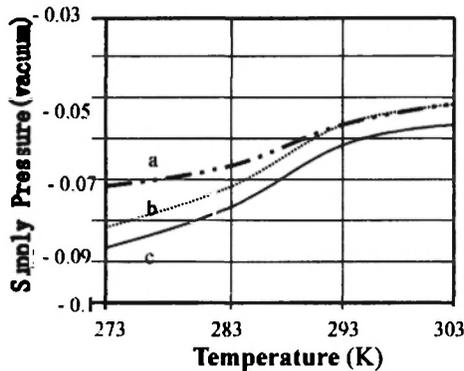


Fig. 2: Relation between MTS vapor flow and H<sub>2</sub>/MTS ratio: (a) ΔW = 10 g/h; (b) ΔW = 20 g/h; (c) ΔW = 30 g/h

P<sub>1</sub> and P<sub>2</sub> are the saturation pressures at T<sub>1</sub> and T<sub>2</sub> respectively, H<sub>0</sub> is the heat content. The saturation pressure of MTS in the ambient temperature range is described in Table 2. The supply pressure at a given MTS vapor flow and hydrogen flow, that is MTS vapor flow and the H<sub>2</sub>/MTS ratio, are constant, as shown in Figure 3. Thus, the desired MTS vapor flow and H<sub>2</sub>/MTS ratio have been obtained. The XRD results of the deposition indicated that the deposition species are only influenced by the MTS vapor flow and the H<sub>2</sub>/MTS ratio and [[nothing with the MTS vapor flow and other process variables]] (such as temperature and pressure), which influence the deposition rate and uniformity (Fig. 4). A pure SiC matrix is formed at a H<sub>2</sub>/MTS molar ratio of about 3. Among the deposition SiC crystals, there is much more of SiC (111) (at 2<sup>θ</sup> = 35°) than SiC (220) at 2<sup>θ</sup> = 60° and SiC (311) (at 2<sup>θ</sup> = 70°). A deposition with a large amount of free carbon (C(002) at 2<sup>θ</sup> = 25°) is formed at a H<sub>2</sub>/MTS molar ratio of less than 1. This is in agreement with the previous

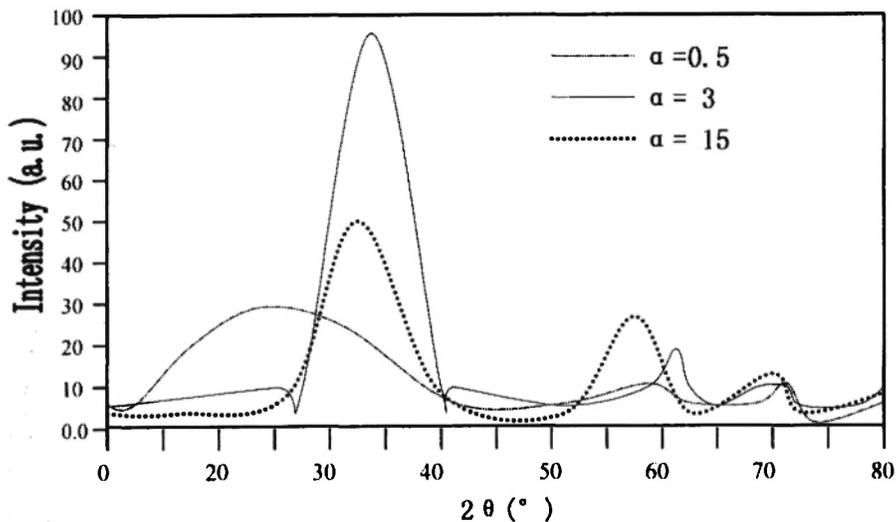
**Table 2**  
Saturation pressure of MTS in the ambient temperature range

Temperature (K)	273	278	283	288	293	298	303
Ps (degree of vacuum)	-0.094	-0.091	-0.089	-0.086	-0.083	-0.078	-0.073



**Fig. 3:** Supply pressure at a given MTS vapor flow and H<sub>2</sub>/MTS ratio of (a) ΔW = 10 g/h; (b) ΔW = 20 g/h; (c) ΔW = 30 g/h

and the H<sub>2</sub>/MTS ratio, which control the concentration of the reagent, strongly influence the depositing rate and depth. The depositing rate increases and the depth decreases with increasing MTS vapor flow and decreasing H<sub>2</sub>/MTS ratio, whereas a too low reagent concentration would lead to a very low depositing rate and would lengthen the depositing cycle. Therefore, at a low depositing temperature (about 1000°C), increasing the reagent concentration properly, with a MTS vapor flow of about 30 g/h, can give a relatively high rate and a deep and uniform deposition mean time (Fig. 5a), leading to improved performance composite and a shortened production cycle (within 60 hours), with

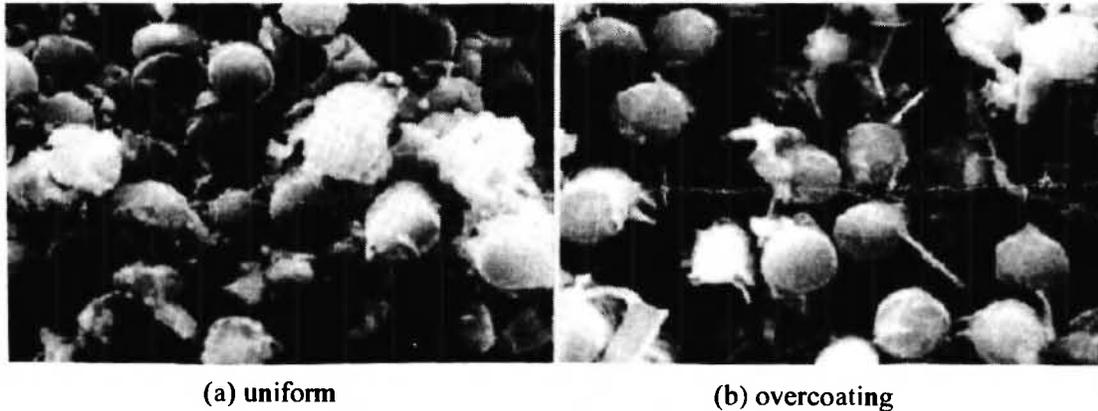


**Fig. 4:** X-ray diffractogram of the sample

study /4/, but no free silicon is found on deposition at a H<sub>2</sub>/MTS molar ratio of about 15; this is different from the study /5/ which showed free silicon on deposition at a H<sub>2</sub>/MTS ratio of more than 10.

The SEM analyses reveal that the MTS vapor flow

density exceeding 1.85 g/cm<sup>3</sup> and flexural strength and fracture toughness amounting to 465 MPa and 14.3 MPa • m<sup>1/2</sup>, respectively. Increasing the depositing temperature (>1200°C) or reagent concentration (MTS vapor flow > 40 g/h) would cause overcoating; the



**Fig. 5:** Morphology of the sample center

deposition is limited on the surface of the fibrous perform (Fig. 5b); after removal of the external coating, the composite density is merely  $1.45 \text{ g/cm}^3$ .

#### **Influence of the length-to-diameter ratio of the furnace cavity**

The studies showed that the length-to-diameter ratio of the furnace cavity affects the depositing rate and uniformity. The matrix deposited in a cavity of length-to-diameter ratio above 5 has a higher rate and uniformity than that of a length-to-diameter ratio below 3. The density of the specimens deposited in a cavity of a length-to-diameter ratio below 3 increases with the distance from the bottom of the cavity. Increasing the length-to-diameter ratio of the furnace cavity favors a decrease in the density difference with the distance from the bottom. This is because a furnace cavity with a high length-to-diameter ratio promotes fluent gas flow, entry of reactant gas and the gas products exhaust easily. Under optimum control conditions, the 3D C/SiC composites are formed within 60 hours, with a density exceeding  $1.85 \text{ g/cm}^3$ .

#### **CONCLUSIONS**

A novel, simple, in-line controller for reactant gases in the ICVI process is introduced, which can control reagent and the desired MTS vapor flow and  $\text{H}_2/\text{MTS}$  ratio. A pure SiC matrix is formed at a  $\text{H}_2/\text{MTS}$  molar ratio of about 3. A deposition with much free carbon is

formed at a  $\text{H}_2/\text{MTS}$  molar ratio of less than 1, and no free silicon is found on deposition at a  $\text{H}_2/\text{MTS}$  molar ratio of more than 10. The depositing rate increases and the depth decreases with increasing MTS vapor flow and decreasing  $\text{H}_2/\text{MTS}$  ratio. Increasing the reagent concentration properly to a MTS vapor flow of about  $30 \text{ g/h}$  at a low depositing temperature of about  $1000^\circ\text{C}$  can give a relatively high rate and a deep and uniform deposition mean time, leading to an improved performance composite and a shortened production cycle (within 60 hours), with density exceeding  $1.85 \text{ g/cm}^3$  and flexural strength and fracture toughness amounting to  $465 \text{ MPa}$  and  $14.3 \text{ MPa} \cdot \text{m}^{1/2}$ , respectively. The length-to-diameter ratio of the furnace cavity affects the depositing rate and uniformity. A high length-to-diameter ratio of the furnace cavity affects the depositing rate and uniformity. A high length-to-diameter ratio of a furnace cavity ( $>3$ ) is favourable in enhancing depositing rate and uniformity.

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