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Analytical stability study of the densification front in carbon- or ceramic-matrix composites processing by TG-CVI

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Abstract

Thermal-gradient chemical vapor infiltration (TG-CVI) is a group of alternatives to classical CVI, involving a strong thermal gradient. It allows one to fabricate, e.g. carbon-matrix or ceramic-matrix composite materials starting from a fibrous preform and a gaseous precursor, the cracking of which results in a solid deposit constituting the composite matrix. The main interest of these processes short fabrication time; however, their control is difficult. Past modelling works [Vignoles, G.L., Goyhénèche, J.-M., Sébastian, P., Puiggali, J.-R., Lines, J.-F., Lachaud, J., Delhaès, P., Trinquecoste, M., 2006. The film-boiling densification process for *C C* composite fabrication: from local scale to overall optimization. Chemical Engineering Science 61, 5336–5353; Nadeau, N., Vignoles, G.L., Brauner, C.-M., 2006. Analytical and numerical study of the densification of carbon/carbon composites by a film-boiling chemical vapor infiltration process. Chemical Engineering Science 61, 7509–7527] have shown that process control and optimization are possible and are based on the notion of densification front. In this paper, a 2D transverse stability study is presented for this front. A condition for stability is worked out; the influence of processing parameters is discussed. It appears that in usual processing cases, the stability criterion is fulfilled, but that it could be violated if some careless process up-scaling is performed.

Keywords: Composites; Materials processing; Modelling; Porous media; Process stability

1. Introduction

Chemical vapor infiltration (CVI) is one of the main routes for the processing of carbon and ceramic matrices in thermostructural composites (Naslain and Langlais, 1990; Besmann et al., 1991). Its principle rests on the heterogeneous deposition reaction of a gaseous precursor inside the preform, a porous medium constituted by fiber felts or woven fabrics which are intended to reinforce the future material. The first implementations of CVI—still in use today—were carried out in isothermal conditions. It has been shown experimentally and theoretically (Middleman, 1989; Chung et al., 1991; Fédou et al., 1993; Sotirchos, 1991) that isothermal CVI (I-CVI) involves the competition between gas diffusion and reaction. A straightforward Thiele modulus analysis implies then that moderate temperature and low pressure are adequate conditions to avoid premature pore plugging and thus to preserve the material quality, in terms of matrix deposition homogeneity (Reuge and Vignoles, 2005). The drawback of such conditions is that the chemical kinetics are dramatically slow, turning I-CVI a very lengthy and expensive process.

A variety of CVI modifications have then been designed in order to overcome this limitation. We refer the interested reader to the exhaustive review of Golecki (1997) for a discussion of all modifications. Most of them rely on the use of a thermal gradient, because this can help controlling the chemical reaction and make it happen at the right place first—that is, at the center of the preform, or at its borders which lie farthest from the impinging gas flux (Gupte and Tsamopoulos, 1989; Melkote and Jensen, 1990).

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The forced CVI (F-CVI) process was initially based on the intent of accelerating chemical deposition by forcing the gases through the pores with a pressure drop (Besmann et al., 1991; Vaidyaraman et al., 1995; Besmann and McLaughlin, 1994; Starr et al., 1991), but it has been rapidly found out that the superposition of a thermal gradient would enhance the quality and processing time. Golecki et al. (1994) have implemented a “rapid densification” process based on isobaric conditions and the creation of a “hot side” and “cold side” on the preforms. Impeding the gas entrance by the hot side helps in densifying the pore bottom at first and the pore mouth at last, as wanted. In practice, one uses a central inductor or resistor around which the preforms are settled. Thermal-gradient isobaric CVI (TG-CVI) has also been considered with in situ heat production, like microwave heating (MW-CVI) (Gupta and Evans, 1991; Morell et al., 1992; Devlin et al., 1992) or radio-frequency induction heating (RF-CVI) (Devlin et al., 1996; Midha and Economou, 1997; Leutard et al., 2002), with the idea of creating a hot deposition zone directly at the preform center. Houdayer et al. (1984) have implemented a “film-boiling” process, also called Kalamazoo, which consists in having the preform, heated as in the preceding processes, merged into boiling precursor. This helps one to maintain its surface temperature at a constant, well-known value, and ensure a very strong thermal gradient (Bruneton et al., 1997). All these CVI modifications have the advantage of allowing one to work with higher pressures, higher temperatures, and consequently higher rates and lower processing times.

Recent modelling advances on the isobaric modifications of TG-CVI (Leutard et al., 2002; Lines et al., 2005; Vignoles et al., 2005, 2006; Nadeau et al., 2006) have emphasized the key role played by the densification front. Indeed, when this front exists, a quite complete infiltration may be performed in a single run, and in shorter processing times than in I-CVI. The existence of the front is subject to a criterion which translates the fact that diffusion has to be fast enough through the front itself (its width being dictated by the thermal gradient) to feed properly the deposition reaction inside it. The front characteristic quantities: width, velocity, and residual porosity left behind it, have been related to the experimental and preform parameters (Nadeau et al., 2006). One important issue has been left out so far: the stability of the front. This is the aim of the present contribution.

The first part of this paper will briefly recall the description of the TG-CVI processes and of the densification front. Balance equations will be written for heat, precursor gas and solid mass, at a local scale linked to the front itself, and at a larger scale. Then, an analytical stability study will be performed, leading to a dispersion relation. Finally, using this relation, the influence of process and material parameters on the front stability will be discussed.

2. CVI with thermal gradients

CVI processes involve the introduction of a precursor gas inside a porous preform. When temperature is high enough, this gas reacts with the preform: solid deposition then occurs and the pores are progressively plugged. When one part of the preform is maintained at a higher temperature, reaction occurs mainly there, because of the extreme sensitivity of reaction kinetics to temperature. All that has to be done is to feed the reaction zone by bringing gas from the raw, non-infiltrated side.

Mass and heat transport are the principal identified phenomena, together with deposition. Both take place in the porous medium:

- Mass transport (gas phase) is mainly due to a reactant gas concentration gradient. Except in the F-CVI modification, which involves high pressure gradients, the resulting flow is mostly diffusive.
- On the other hand, heat transport mainly occurs through the solid phase, by conduction. This is because thermal conductivity is much lower in the gas phase than in the solid phase.

During deposition, the porosity decreases until a percolation threshold is reached. Its value may be fairly low in “film-boiling” experiments. In a typical run with cylindrical symmetry and inner heating, the following steps occur (see Fig. 1):

1. The center of the preform is heated by contact with a carbon resistor or susceptor. Its outer boundary is in contact with cool precursor gas. It also loses heat by radiation, conduction, and possibly convection. In the film-boiling modification, the existence of a biphasic zone outside the preform guarantees that its outer side temperature is close to the precursor boiling point.
2. As soon as a sufficient temperature is attained, solid deposition will occur. The infiltration area, first located at the inner boundary, moves towards the exterior. As a consequence, the infiltrated part is not an obstacle for the mass flux, which settles from the outside to the inside, in order to counter-balance the precursor consumption in the front.
3. The infiltrated zone has a high thermal conductivity, as compared to the raw preform: consequently, the thermal gradient is pushed outside this zone and stays in the remaining raw preform zone.

3. Local front results

Some results derived in Nadeau et al. (2006) are recalled in order to introduce variables required for the stability study. After pore-scale averaging, the heterogeneous deposition rate obeys the following expression:

$$R = \sigma_v(\varepsilon) \cdot k(T) \cdot C, \tag{1}$$

where $k(T)$ is given by an Arrhenius law:

$$k(T) = k_0 \exp\left(-\frac{E_a}{\mathcal{R}T}\right). \tag{2}$$

From these relations it is seen that deposition depends on:

- The *accessible* gas/solid interface area $\sigma_v(\varepsilon)$, ε being the *open* porosity.
- The precursor gas concentration C.
- The temperature T through the chemical reaction constant.