



matrix composites, and chemical processing environments for steel matrix composites. These systems deserve exploration, again with emphasis on fundamentals, rather than the development of this or that specific composite.

These windows of opportunity in research are ones which, in large part, call for partnerships between different laboratories and researchers. For instance, a capability for controlled processing of these materials is needed for the generation of samples and microstructures that can be used in the exploration of microstructure-property relations. Unlike unreinforced alloys, in which the microstructure can be varied using conventional and well-established deformation and heat-treatment processes, the processing

of MMCs requires specialized equipment and know-how. The establishment of a European centre of excellence in MMC research, able to cover the entire spectrum from processing to performance, and providing a hub for such a coordinated effort, would be highly opportune.

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6.6. Ceramic Matrix Composites

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6.6.1. Introduction

Ceramic matrix composites (CMCs) have been developed to overcome the intrinsic brittleness and lack of reliability of monolithic ceramics, with a view to introduce ceramics in structural parts used in severe environments, such as rocket and jet engines, gas turbines for power plants, heat shields for space vehicles, fusion reactor first wall, aircraft brakes, heat treatment furnaces, etc. It is generally admitted that the use of CMCs in advanced engines will allow an increase of the temperature at which the engine can be operated and eventually the elimination of the cooling fluids, both resulting in an increase of yield. Further, the use of light CMCs in place of heavy superalloys is expected to yield significant weight saving. Although CMCs are promising thermostructural materials, their applications are still limited by the lack of suitable reinforcements, processing difficulties, sound material data bases, lifetime and cost.

6.6.2. Ceramic Matrix Composite Spectrum

A given ceramic matrix can be reinforced with either *discontinuous* reinforcements, such as particles, whiskers or chopped fibres, or with *continuous* fibres. In the first case,

the enhancement of the mechanical properties, in terms of failure strength and toughness, is relatively limited but it can be significant enough for specific applications, a well known example being the use of ceramics reinforced with short fibres in the field of the cutting tools ($\text{SiC}_w/\text{Si}_3\text{N}_4$ composites). Among the discontinuous reinforcements, whiskers are by far the most attractive in terms of mechanical properties. Unfortunately, their use raises important health problems both during processing and in service. Conversely, continuous reinforcements, such as fibre yarns, are much more efficient, from a mechanical standpoint, but they are more expensive and more difficult to use in a ceramic matrix in terms of material design and processing.

There is a wide spectrum of CMCs depending on the chemical composition of the matrix and reinforcement. *Non-oxide* CMCs are by far those which have been the most studied. Such a choice could appear surprising since the atmosphere in service is often oxidizing. That choice could be explained as follows. The most performant fibres, in terms of stiffness, failure strength, refractoriness and density are non-oxide fibres, i.e. carbon and silicon carbide fibres. Further, carbon fibres are extensively used in volume production of polymer-matrix composites. As a result, they are much cheaper than all the other fibres (glass fibres excepted). Second, in order to avoid compatibility

problems, which are crucial at high temperatures, non-oxide fibres are preferably embedded in non-oxide matrices. Hence, the first non-oxide CMCs have been *carbon/carbon* (C/C) composites. They have been initially designed and produced for use in rocket engines and re-entry heat shields, i.e. under extremely severe service conditions but short lifetimes. In a second step, *C/SiC* and *SiC/SiC* composites were developed in order to increase the oxidation resistance of the materials and hence their lifetimes in oxidizing atmospheres. Silicon nitride was also used as matrix although it is less stable at high temperatures than silicon carbide.

Oxide-CMCs would obviously be the best choice, from a thermodynamic standpoint, for long term applications in oxidizing atmospheres. Unfortunately, oxide fibres, although they are refractory, tend to undergo grain growth at high temperatures, (which results in a fibre strength degradation) and exhibit a poor creep resistance. Further, they display much higher densities than say carbon fibres (4 g/cm³ for alumina versus 2 for carbon). Attempts have been made to improve the high temperature properties of oxide fibres with limited success. Despite these disadvantages, $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ and derived CMCs have been, and are still, extensively studied.

6.6.3. State of the Art in CMC Processing

CMCs can be produced according to either *gas phase* routes or *liquid phase* routes, each of them having advantages and drawbacks.

In *gas phase routes*, i.e. the so-called chemical vapor infiltration (CVI) processes, the reinforcements (usually as a multidirectional preform) is densified by the matrix deposited from a gaseous precursor, e.g. an hydrocarbon for carbon or a mixture of methyltrichlorosilane and hydrogen for silicon carbide. It is now well established that a fibre coating, referred to as the interphase, has to be deposited on the fibre prior to the infiltration of the matrix in order to control the fibre-matrix (FM) bonding and the mechanical behavior of the composite. Pyrocarbon (PyC), boron nitride or (PyC-SiC)_n and (BN-PyC)_n multilayers, with an overall thickness ranging from about 0.1 µm to about 1 µm, displaying a layered crystal structure (PyC, BN) or a layered microstructure (multilayers), are the most common interphase materials in non-oxide CMCs. The main role of the interphase is to deflect the microcracks which form in the matrix under loading and hence to protect the fibre from notch effect (mechanical fuse function).

There are several versions of the CVI-process. The most commonly studied and used version is isothermal/isobaric CVI (or I-CVI). It is a relatively slow process since mass transfer in the preform is mainly by diffusion and it yields some residual porosity and density gradient. Conversely, I-CVI is a clean and flexible process (it can be used to densify simultaneously a large number of preforms, eventually of different shapes). For these reasons, it is the preferred process at the plant level. It is well suited to the fabrication of relatively thin parts.

In order to increase the densification rate and hence to reduce the processing times, temperature or/and pressure gradients can be applied to the preform. In temperature gradient CVI (TG-CVI), or forced CVI (F-CVI), the processing time can be reduced by one order of magnitude with respect to I-CVI. A similar processing time lowering has also been reported for the film-boiling (or calefaction) process, in which the heated fibre preform is directly immersed in a liquid matrix precursor.

Finally, pressure pulsed-CVI (P-CVI) has been recently presented as a way to engineer, at the micrometre (or even nanometre) scale, either the interphase or the matrix. Based on this technique, multilayered *self-healing* interphases and matrices (combining crack arrester layers and glass former layers) have been designed and produced, through a proper selection of chemical composition of the layers. An example of such highly tailored composites is shown in Fig. 6.10.



Fig. 6.10. Example of multilayered self-healing matrix ceramic matrix composite produced by P-CVI. The matrix comprises crack arrester layers and glass-forming layers.



In the *liquid phase routes*, the fibres first coated with an interphase (e.g. by I-CVI) are embedded in a liquid precursor of the matrix. In the *reactive melt infiltration* (RMI) processes, a fibre preform is impregnated by capillary forces with a liquid which reacts either with a solid phase used to consolidate the fibre preform (SiC-Si matrices formed through liquid silicon infiltration of a carbon-consolidated preform) or with the atmosphere (Al_2O_3 -Al matrices formed through liquid aluminium infiltration and chemical reaction with an oxidizing atmosphere). Among other advantages, the RMI-processes are fast and can be applied to thick preforms. They also yield materials of low residual porosities and high thermal conductivities.

In the *polymer impregnation and pyrolysis* (PIP) processes, the fibres are embedded in a polymeric precursor of the matrix, such as a thermosetting resin or a pitch for carbon or a polycarbosilane for SiC, and the green composite is then pyrolyzed. Such processes are relatively flexible since the composition of the precursor can be tailored. Conversely, a shrinking of the matrix occurs during the pyrolysis step owing to the evolution of gaseous species. As a result, several PIP-sequences have to be applied in order to achieve a low enough residual porosity, which is time and labour consuming. Shrinkage can be limited by loading the liquid precursor with suitable fine powder, i.e. by using a slurry. Finally, the residual porosity can also significantly be reduced through a hot pressing step, an alternative that supposes that the matrix displays enough plasticity not to damage the fibres. This liquid impregnation/hot pressing technique is well suited to the fabrication of glass-ceramic matrix composites.

6.6.4. Expected Breakthroughs and Future Visions

The future of CMCs is directly depending on progress that would be achieved in the availability of higher performance constituents (fibres, interphases and tailored matrices) as well as in processing cost reduction.

As far as the *reinforcements* are concerned, two main breakthroughs are expected: (i) the availability of a *low cost* non-oxide fibre that could be used up to about 1500°C and (ii) the development of a refractory oxide fibre resistant to grain growth and creep. Oxygen-free quasi-stoichiometric SiC fibres display much better high temperature properties than their Si-C-O counterparts fabricated from polycarbosilane according to the Yajima's route. However, they are too costly (with respect to carbon fibres and CMC volume production) and their failure strain is too low. Amorphous Si-B-C-N fibres, presented as creep resistant at high

temperature, are still at a development stage. Although alumina-based binary oxide fibres, e.g. mullite/alumina or alumina/YAG fibres, represent a significant progress in terms of creep resistance with respect to pure α -alumina fibres, further improvement is still necessary to match the high temperature properties of non-oxide fibres. Finally, nanotubes, with their outstanding mechanical properties, may raise problems similar to those previously encountered with whiskers.

The spectrum of suitable *interphase materials* that could be used in a realistic manner in CMCs remains extremely narrow. In non-oxide CMCs, there is presently no alternative to the carbon-based interphases. Boron nitride is obviously the only potential candidate. However, its sensitivity to moisture when poorly crystallized and its low bonding to SiC-based fibres are subjects of concern. Solving these two problems will be an interesting breakthrough. The search for new interphase materials, displaying a better oxidation resistance than carbon and boron nitride and which could be easily deposited *in situ* in multidirectional fibre preforms, should be strongly encouraged.

The recent discovery of the *self-healing multilayered matrices* (Fig. 6.10) has been an important breakthrough since it permits the use of non-oxide CMCs in oxidizing atmospheres. The concept should obviously be further developed in terms of material selection.

Finally, the processing cost of CMCs should be reduced (although the main contribution to the total cost of a given part is presently, e.g. in a SiC/SiC composite, that of the reinforcement, as previously mentioned). Gas phase route processes with a significant reduction of the overall densification time, liquid phase route processes with a limited number of PIP-sequences (through the use of appropriate precursors), both being compatible with CMC volume production, would obviously be significant breakthroughs.

6.6.5. Future Directions of Research

The interest of CMCs as thermostructural ceramics is now well established but their volume production at the plant level is still a challenge, which requires an important effort of research at the level of the European Union. Possible directions of research are:

- Development of *low cost ceramic fibres* (both non-oxide and oxide fibers) that could be used up to about 1500°C (the EU has presently no long term action that could be compared to what is done in Japan and U.S.).

- Development of *one or two* CMC(s), e.g. a SiC-based and an alumina-based composites, including that of an interphase material and a low cost processing technique, guided by one or two potential application(s).
- Development of sound *data bases* on CMCs and their constituents (including that of suitable standard tests and modelling).
- Development of the *durability* of CMCs, including that of suitable internal and external oxidation protection (for non-oxide CMCs), lifetime prediction, residual mechanical and thermal properties characterization and modelling.

6.7. Polymeric Composite Materials

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6.7.1. Introduction

Principal advantage of composite materials resides in the possibility of combining physical properties of the constituents to obtain new structural or functional properties. Composite materials appeared very early in human technology, the “structural” properties of straw were combined with a clay matrix to produce the first construction material and, more recently, steel reinforcement opened the way to the ferroconcrete that is the last century dominant material in civil engineering. As a matter of fact, the modern development of polymeric materials and high modulus fibres (carbon, aramidic) introduced a new generation of composites. The most relevant benefit has been the possibility of energetically convenient manufacturing associated with the low weight features. Due to the possibility of designing properties, composite materials have been widely used, in the recent past, when stiffness/weight, strength/weight, ability to tailor structural performances and thermal expansion, corrosion resistance and fatigue resistance are required. Polymeric composites were mainly developed for aerospace applications where the reduction of the weight was the principal objective, irrespective of the cost. The scientific efforts in this field were therefore focused to the comprehension and optimization of the structural performances of these materials. Structural composite materials have been also used in other fields such as automotive, naval transportation and civil engineering but the high cost still limits their applications. A continuous task has been making composite components economically attractive. The effort to produce economic attractive composite components has resulted in several innovative manufacturing techniques currently being used in the composite industry.

6.7.2. State of the Art

Nowadays, technology is devoted to the development of new materials able to satisfy specific requirements in terms of both structural and functional performances. The need of exploring new markets in the field of polymeric composites has recently driven the research in Europe towards the development of new products and technologies. In particular, activities on thermoplastic based composites and on composites based on natural occurring materials (environmentally friendly, biodegradable systems) have been of relevant interest in many European countries.

Since the beginning of the 90's years, U.S. and Japan have recognized the need of expanding composite applications. In the field of materials, Japan put more emphasis than U.S. on thermoplastic and high temperature resins. Moreover, due to the large extent of the textile industry in Japan, textile preforming is significantly more advanced than in U.S. and this could lead to the development of cost-efficient automated computer-controlled looms for complex textile shapes. In contrast to the U.S. approach of developing computational models to better understand manufacturing processes, Japanese manufacturing science appears to reside in experienced workers who develop understanding of the process over long period of time. However, Japanese process and product development methods are based on concurrent engineering methodology, which is based on the integration of product and process design.

Biomedical is another important field where composites are applied. Materials, able to simulate the complex structural properties of the natural tissues, which are composite in nature, have been developed but there are still few