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Manufacturing of ceramic matrix composite using a hybrid process combining TiSi₂ active filler infiltration and preceramic impregnation and pyrolysis

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The manufacturing of silicon carbide reinforced ceramic matrix composites by a hybrid process is explored. Fibre preforms are infiltrated with TiSi₂ powders using the slurry method. Using TiSi₂ active filler leads to reduce the porosity by the subsequent formation of nitride phases after treatment under N₂ atmosphere at low temperatures ($\leq 1100^\circ\text{C}$). Taking into account the influence of the specific surface area of the powder on the nitridation rate, it is shown that it is possible to produce nitrides TiN and Si₃N₄ at 1100°C with an interesting volume expansion inside the composite. To complete the densification of the composite, a polymer impregnation and pyrolysis (PIP) process are performed with a liquid polymeric precursor. Characterizations of the composites show that mechanical properties are improved with the presence of the TiN and Si₃N₄ phases, and the number of PIP cycles.

Keywords: CMC; active filler; slurry impregnation; flexural strength; nitridation.

1. Introduction

In the preparation of Ceramic Matrix Composites (CMC), densification of fibre preforms can be performed via different routes, such as Chemical Vapour Infiltration (CVI), Polymer Impregnation and Pyrolysis (PIP), sol-gel route, Reactive Melt Infiltration (RMI) or Slurry Infiltration and Hot Processing (SI-HP) or using several other techniques^[1-6]. In order to be competitive on the civil aeronautics market, low cost CMC processing such as liquid phase

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routes including polymer impregnation/pyrolysis are particularly developed. Using complementary methods of densification such as slurry impregnation with filler powder and liquid polymer impregnation enables to obtain an effective process with a low price/performance ratio. Adding fillers to the polymer allows modulating certain properties of the final ceramic, such as mechanical behaviour, electrical or thermal properties. However, an inherent shrinkage is observed after pyrolysis of the polymer, even when inert powders are inserted in the matrix. The repetition of numerous impregnation and pyrolysis cycles is then necessary to obtain a dense material ^[7]. P. Greil suggested overcoming this problem with the addition of active fillers, which react during pyrolysis under reactive atmosphere to form oxides, carbides or nitrides leading to significant volume expansions ^[8-18]. These reactions occur with a volume expansion that can compensate for the polymer shrinkage. However, most active fillers react only at high temperatures ($T > 1400^{\circ}\text{C}$). This can be a major drawback if the fibres are damaged during the heating at high temperatures.

Titanium disilicide powder (TiSi_2 , density = 4.01 g/cm^3) is identified as an interesting active filler ^[19]. Under nitrogen atmosphere, the nitridation of TiSi_2 starts around 1000°C , and leads to the formation of TiN ($d = 5.43 \text{ g/cm}^3$) and Si_3N_4 ($d = 3.19 \text{ g/cm}^3$) with a 57 volume percent increase when the reaction is complete. It is well-known that the powder size can influence the reaction rate; therefore several studies were performed to prepare ceramic composites with a small size powder obtained by ball-milling ^[20-22]. To control the process, the nitridation of TiSi_2 must be well understood. In the first part of this paper, we explore the influence of temperature and time on the nitridation rate of micron and submicron TiSi_2 powders. The preparation of the composites and the mechanical behaviour (3-point bending tests) of CMC containing powders of TiSi_2 or TiSi_2 nitrided within their matrices are then presented.

2. Materials and experimental procedure

A high purity micrometer-sized TiSi_2 powder (C-54 stable phase, 99.95% in purity, $\sim 45 \mu\text{m}$, Neyco) is used during this work. A study of XRD patterns by Rietveld method (fullprof 2K^[23]) shows the presence of 8.6% wt of free silicon and of 91.4% wt of TiSi_2 phase. This raw powder is milled with a planetary ball mill (Retsch PM200). Nitridation of powder is performed in a thermogravimetric analyser (Setaram TAG24). Sections of nitrided TiSi_2 grains are prepared using ion polishing system (Cross Polisher JEOL Ltd). These sections are observed with a Scanning Electron Microscope (SEM) Quanta 400 FEG microscope whereas the chemical composition is analyzed by Energy Dispersive X-ray spectroscopy (EDX), operated at 5 kV (spatial resolution : around 2 nm in these conditions). Volumes are measured with a helium pycnometer (Micromeritics AccuPyc II 1340 - 1 cm³ model). Specific surface areas are determined by the BET method with an ASAP 2010 (Micromeritics); samples are degassed by heating at 220°C during 4 h immediately prior to measurements. The phases present in the samples are determined by X-Ray Diffraction (XRD), with a Bruker D8 Advance apparatus in Bragg-Brentano geometry, working with the Cu K α radiation. XRD patterns are recorded using a step size of 0.01° for the 2 θ range 10-90°, and a counting time of 0.3 s per step.

Composites are fabricated from 2D fibre preforms (~ 2 mm thickness) made of woven Nicalon fibres (Nippon Carbon Co.) and they are covered by PyC interphase. These SiC-based fibres are unstable at high temperatures because of the silicon oxycarbide phase they contain, which decomposes beyond 1150 °C; the manufacturing of CMC is therefore limited to this maximum temperature when using these fibres.

To prepare the CMC, the fibre preforms are first consolidated by one PIP cycle with a phenyl-containing polysiloxane (resin 1 – Table 1), then impregnated with a slurry containing the TiSi_2 powder.

The active filler powders are mechanically mixed with ethanol in order to obtain slurry. The addition of poly-ethylene imine (PEI) enabled to stabilize the colloidal suspension. A

concentration of 15% V of active filler powder could be obtained with an optimum concentration of 2.5 mg of PEI per square meter of powder. The fibre preforms are immersed in a beaker of suspension and the impregnation is performed under vacuum for one hour. The samples are then removed from the suspension, and the solvent is evaporated by heating at 100°C under vacuum for one hour. The composites impregnated with the active filler are then nitrified under a flow of nitrogen gas at a ramping rate of 10°C/min up to 1100°C, and maintained at this temperature for 5 h. It is important to notice that the nitridation is performed before impregnation of polymer. **To suppress the contact with oxygen during pyrolysis an oxygen scavenger is used.** Treatments are carried out in a furnace using alumina crucibles. A methyl-polysiloxane (resin 2 – Table 1) requiring no solvent is chosen as preceramic polymer to perform the final PIP process. Impregnation is carried out in a beaker under vacuum during one hour. The samples are cured by a thermal treatment of 1 h at 60°C under vacuum and pyrolysis is achieved by heat **treatment** up to 1000°C. The mechanical behaviour of CMC samples is explored using bending test. The ultimate flexural strength (σ_R) is calculated according to the equation (1):

$$\sigma_R = 3 F L / 2 w t^2 \quad (1)$$

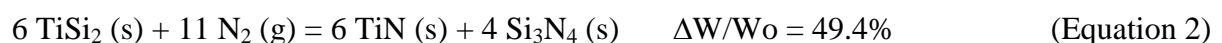
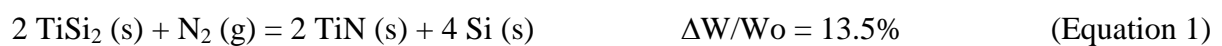
where F is the maximal applied force, L the support span (50 mm), w the width (~ 10 mm) and t the thickness (~ 2 mm) of the specimen. We used a universal testing machine (Instron 5860) at a cross-head speed of 0.5 mm/min at room temperature.

3. Results and discussion

3.1. Nitridation process

3.1.a. Commercial TiSi₂ powder

According to the Ti-Si-N phase diagram ^[24-27], the nitridation of TiSi₂ is described by equations 1 and 2 depending whether it is partial or complete.



In order to study the phenomenon of nitridation as a function of temperature, a non-isothermal nitridation of as received TiSi₂ powder ($d_{50} \sim 10 \mu\text{m}$ – Table 2) is first performed. The sample

is heated from 20 to 1300°C at a low rate of 1°C/min in pure flowing nitrogen gas. The weight gain and its derivative are plotted as a function of the temperature in Figure 1. From those measurements, it appears that no significant weight gain is obtained until the temperature reaches 900°C. In Figure 1, it is possible to observe two phenomena on the curve of thermogravimetric analysis. The first began at 1130°C until 1250°C. It is attributed to the transformation of TiSi_2 into free silicon and TiN according the Equation 1 (partial nitridation), into the surface and inside the grains. The mass gain corresponds to around 14 % that is expected ^[22]. The second phenomenon corresponds to the transformation of free silicon on Si_3N_4 according the Equation 2 (complete nitridation) as it is described by Cordoba et al. ^[28]. Our studies are oriented on CMC prepared with Nicalon fibre for aeronautic applications. These SiC based fibres are unstable at high temperature ($>1150^\circ\text{C}$). The manufacturing of CMC is therefore limited to temperature of 1100°C.

Sections of nitrided TiSi_2 grains are observed by SEM (Figure 2). EDX of TiSi_2 nitrided during 5 hours at 1100°C reveals the formation of TiN and Si when TiSi_2 reacts with nitrogen (Figure 2a). XRD patterns confirm the presence of TiN (JCPDS 38-1420) and Si (JCPDS 27-1402) phases, and the absence of Si_3N_4 . Only the 3 μm in diameter grains would completely react with nitrogen according to the equation 1. In the middle of the grain, the TiSi_2 phase is still present, with the expected stoichiometry. The process of nitridation explored at 1100°C during 5 hours is in good agreement both with the equation 1, and the data published previously ^[22], inducing a maximum weight gain of 13.5% ($\Delta W/W_0$) and a maximum volume gain of 36.9% ($\Delta V/V_0$).

Some thermodynamic studies in the Ti-Si-N ternary system indicate that TiSi_2 can be nitrided into TiN and Si_3N_4 at 1100°C. ^[25-27] This assertion is not confirmed by our first experiments, even after 8 hours of nitridation at 1100°C. In order to verify the existence of the Si_3N_4 phase, a TiSi_2 powder was nitrided at 1100°C during 50 h. The Figure 2b presents transverse sections of a TiSi_2 grain observed by SEM after such a treatment. EDX confirms the presence of the

TiN phase and demonstrates the formation of a slight quantity of the Si_3N_4 phase. XRD pattern confirms this assertion. The reaction kinetics of free silicon with nitrogen to form Si_3N_4 is very low.

It was decided to mill the starting powder with the intention to increase the specific area and to promote the reaction mechanism corresponding to the equation 2.

3.1.b. Influence of milling conditions on nitridation

A high-energy planetary milling with ethanol as solvent is performed in order to increase the efficiency of the nitridation reaction^[29]. Milling conditions and characteristics of sub-micron powders obtained are reported in Table 2.

Thermogravimetric analyses are performed on milled powders at 1100°C (Figure 3).

As expected, the nitridation of planetary milled powders begins clearly at a lower temperature of 650°C, with much steeper slopes during the heating stage. Furthermore, the weight gain exceeds 29.5 weight percent after 5 h at 1100°C. Such a high value implies the formation of Si_3N_4 .

After 5 h at 1100°C in N_2 , XRD patterns of all nitrated powders indicated the presence of TiN and Si (Figure 4). Only raw nitrated powders still exhibits peaks of TiSi_2 . The XRD pattern of the TiSi_2 powder nitrated after planetary milling included also small peaks corresponding to the $\beta\text{-Si}_3\text{N}_4$ phase.

3.2. Flexural strength of composites

Using infiltration of the milled TiSi_2 powder (25 ± 4 weight %), nitridation and PIP with the resin 2 (27 ± 5 weight % for the first impregnation), and different conditions of thermal treatments, various composites are produced and their mechanical properties are determined (Table 3). More particularly, the influence of (i) the presence of TiSi_2 powder, (ii) the

nitridation conditions and (iii) the repetition of the impregnation and pyrolysis cycles are studied. The flexural properties are obtained using 3-point bending tests. The strengths are distributed between 35 and 160 MPa with only one PIP cycle and reach 215 MPa with three PIP cycles. The same range of the higher flexural strength value is reported in literature for CMCs processed by liquid routes. Authors often choose to multiply PIP cycles ^[30-33], and sometimes introduce passive or active fillers ^[34-35]. As it was expected, the values of strengths depend particularly on the nature of the initial powder, the degree of advancement (progression) of in-situ reaction of nitridation and the number of PIP cycles. The last point can be explained regarding the final porosity of CMC measured as 15.5% for CMC2 and 7.3% for CMC5. Results are presented in more detail in the following paragraph.

Figures 5 show the distribution of different constituents inside the composite CMC5. The homogeneity of impregnation in CMC5 can be observed Figure 5a. Consolidation residue is particularly localised within the bundle. The nitrided powder fills the inter-bundle macropores. This powder is consolidated by the PIP cycles. This SEM micrograph confirms the low porosity of the composite. Some cracks due to polymer shrinkage can also be observed.

Figures 6 exhibits typical load-displacement curves for all composites. The very first (slightly) non-linear part of the stress-displacement curves may be related to the progressive adjustment of the samples. This flexural behaviour is typical for a CMC. The first linear part of the curve shows an elastic behaviour of the material; it is followed by a cracking stage until the sample fails.

3.2.a Impact of TiSi₂ powder within the matrix and role of the nitridation on the mechanical properties

Figure 6 shows stress-displacement curves of the bending tests for composites obtained with 2D Nicalon fabric and with different matrix compositions : (i) submicron $\text{TiSi}_2 + \text{SiC}$ powders, nitrided during 5 h under N_2 at 1100°C (CMC1) ; (ii) submicron TiSi_2 powder nitrided during 5 h under N_2 at 1100°C (CMC2) ; (iii) same type of preparation but without nitridation (CMC3) ; and (iv) submicron TiSi_2 powder nitrided during only 1 h under N_2 at 1050°C (CMC4) ; one PIP cycle with resin 2 is performed in all cases. When SiC powder is introduced to replace part of the TiSi_2 in the first step of the composite process, the value of the ultimate flexural strength is lower while porosity volumes are the same inside the composites (CMC2). Characterization of composite obtained without nitridation (CMC3) or with less advanced nitridation (CMC4) shows the importance of the nitridation role on the cohesion of the composite probably due to the volume expansion and the improved bonding between powder grains. Even if TiSi_2 is only partially nitrided with a low amount of Si_3N_4 , the use of TiSi_2 nitridation improves significantly the flexural properties. The ultimate flexural strength of CMC5 corresponds to the higher value, and it is obtained when 3 PIP cycles are performed.

3.2.b. Impact of the completion of the nitridation reaction

In order to show the influence of the total nitridation of TiSi_2 powder on the mechanical properties of CMC, carbon fibres guipex preform (ex-PAN) were used instead of Nicalon ones because carbon fibres are stable under heat treatments; filled preforms can be treated up to 1300°C without degradation of carbon fibres. The same dimensions of samples are used to study the mechanical properties. CMC6 and CMC7 were fabricated in the same way than the others composites with only one PIP cycle and thermal treatment up to 1100°C and 1300°C respectively. Figure 7 shows the importance of completing the nitridation of the TiSi_2 according to mechanism corresponding to the Equation 2, leading to the presence of TiN and

Si_3N_4 . The completion of the nitridation reaction obtained after treatment up to 1300°C improves both the stiffness and the ultimate flexural strength of the composite CMC7 compared to CMC6.

Figure 8 shows the overall microstructure of a CMC with totally nitride TiSi_2 (CMC7). It can be observed that with nitridation at 1300°C , the grains fill the inter-bundle porosity efficiently.

These results show the influence of complete nitridation of TiSi_2 powder filled in a preform. It can be proposed that this step in the preparation of composites by a hybrid process is of major importance since that can improve the mechanical behavior of CMC.

Conclusion

A new hybrid process of CMC manufacturing involving a first step of infiltration and nitridation of TiSi_2 powders under nitrogen atmosphere was performed. First the influence of sized of active filler has been studied. The increase of the specific surface area of the TiSi_2 powder improves the nitridation kinetics and leads to facilitate the formation of Si_3N_4 at low temperature (1100°C). Secondly, relatively dense composites are produced by a process combining (i) the active filler impregnation, (ii) the in-situ nitridation process of this active filler, (iii) the impregnation and pyrolysis of a preceramic polymer. Choosing this liquid route and SiC Nicalon fibre preforms have enabled to develop a low-cost process performed at temperatures below 1100°C . The flexural strength of prepared composites depends on the composition of fillers. The better mechanical properties are obtained when the filler is all active. The presence of a larger proportion of Si_3N_4 in the matrix is associated with an increase of the ultimate flexural strength and of the Young's modulus as it was proved using C fibres reinforcement and at 1300°C as treatment temperature.

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