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A Plasma Spray Process for the Manufacture of Long-Fiber Reinforced Ti-6Al-4V Composite Monotapes

T. Valente and C. Bartuli

A fabrication method for titanium matrix composite monotapes reinforced by long SiC fibers is described. The plasma spray technique, carried out in an inert atmosphere, was used to deposit the metal matrix onto previously arranged continuous fibers.

Major benefits are due to a controlled operating environment (the entire process is performed in a neutral gas atmosphere) and to the high solidification rate of the melted material. The formation of deleterious brittle reaction products between the fiber and matrix is therefore limited. Plasma spraying, normally used as a coating technique, was modified to produce a long composite monotape. This required a suitable arrangement of the fiber, placed onto a cylindrical substrate, and the identification of suitable operating conditions, as described in the present work. The results of characterization tests performed on the tape, with special reference to the quality of the fiber/matrix interface, are summarized. Results of preliminary diffusion bonding experiments carried out by means of a hot pressing system are also reported.

1. Introduction

METAL matrix composites (MMCs) with different reinforcements, such as whiskers, long fibers, or particulates, are taking on a primary role in the field of advanced materials[1-4] due to their properties of lightness and stiffness, which are guaranteed by the coupling of a ceramic reinforcement with a metallic matrix. Some problems still remain for most of these materials, limiting their production and their application. Among these, control of adhesion between the matrix and the reinforcement, together with the high production costs, represent the main obstacles to the widespread use of MMCs. It should be pointed out that interfacial properties control the efficient transfer of stress from the matrix to the ceramic fiber, allowing the combination in the composite of extreme lightness with good mechanical behavior. To this end, the fabrication method used plays a primary role.

The plasma spray process is widely used as a coating technique,[5-8] but it can also be used in the manufacturing process of titanium alloy matrices reinforced with long silicon carbide (SiC) fibers, as demonstrated on a laboratory scale in the present article and as reported, for other matrix materials, in previous studies.[9-16]

In this article, the operating conditions of the plasma spraying process are described together with the physicochemical and mechanical characterization of the products, with special reference to the fiber/matrix interface.

Key Words: hot pressing, metal matrix composites, SiC fibers, spray forming, Ti-6Al-4V monotape

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2. Plasma Spraying Manufacture of Composite Monotapes

The plasma spray manufacturing process of composite monotapes basically consists of the deposition of successive layers to form a compact metallic matrix on previously arranged ceramic long fibers that are wound on a substrate. The substrate, as well as the automatic system used for its movement, together with the torch used for the spraying process, are placed into a pressure-controlled chamber during the entire operation.

In terms of the quality of the fiber/matrix interface, plasma spraying in an inert atmosphere limits the damage caused by impurities or inclusions in the deposited material. The oxygen concentration in the atmosphere can be carefully controlled from the moment of the melting of the matrix-forming material until its complete solidification on the substrate. Consequently, embrittlement and loss of adhesion between fiber and matrix due to partial oxidation of the metal are prevented. Finally, the short liquid metal/ceramic contact times ($\cong$ 100 ms)[13] limit undesirable reactions between the metal matrix and the ceramic fiber.

3. Materials and Methods

3.1 *Materials*

Two types of powder, produced by Plasma Technik as a special lot, were sprayed, consisting of pure titanium and Ti-6Al-4V alloy, both with a particle size distribution of 36 to 83 μm. Pure titanium was used to carry out preliminary optimization work on the process parameters.

The SiC/C fibers (SCS-6) were fabricated by Avco-Textron Specialty Materials by chemical vapor deposition of β-SiC onto a graphite core. They were chosen because of their suitability for

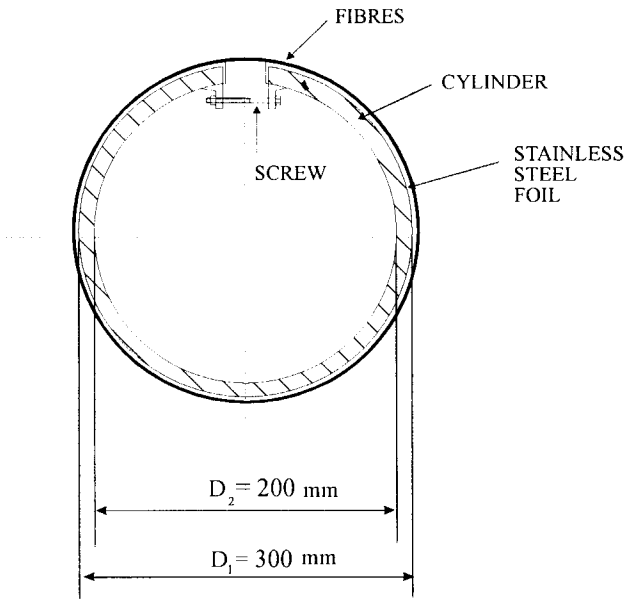

Fig. 1 Schematic top view of the cylindrical substrate, stainless steel foil, and the fiber. The fiber tensioning system is also illustrated

Table 1 Primary spraying parameters

Pressure in the deposition chamber	500-800 mbar
Plasma torch	F4VP-PT
Plasma gases	ArH_2; ArN_2
Current intensity	700 A
Powder feed	5 g/min
No. of torch passes	32

titanium and titanium alloy matrices. The carbon core had a diameter of 34 μm; the total fiber diameter was 140 μm. The outer layer of the SiC fiber consisted of a carbon-rich coating, about 3 μm thick, whose composition varied with the distance from the surface of the fiber. The maximum carbon content was detected on the surface, whereas the highest silicon percent was measured at a distance of about 1 μm from the surface.[17] The outer layer was designed both to protect the fiber from strength degradation and to enhance the mechanical properties of the composite material.

3.2 *Fiber Arrangement*

The substrate onto which the titanium matrix was deposited consisted of a silicon carbide continuous fiber, spiral wound onto a cylinder-shaped rolled steel sheet, with an outer diameter of 30 cm and a thickness of 5 mm. To avoid adhesion between the cylindrical support and the composite, a mirror-polished stainless steel foil, 0.5 mm thick, was interposed between the fibers and the substrate. Once the matrix was deposited onto one side of the fiber array, the tape was detached from the substrate, turned over, rewound around the cylinder, and prepared for the second step of the spraying process. Winding of the continuous fiber onto the support was performed by rotating the cylinder at a constant rate on a lathe, while applying constant tension to the fiber being wound. The winding step between each fiber was 300 to 500 μm.

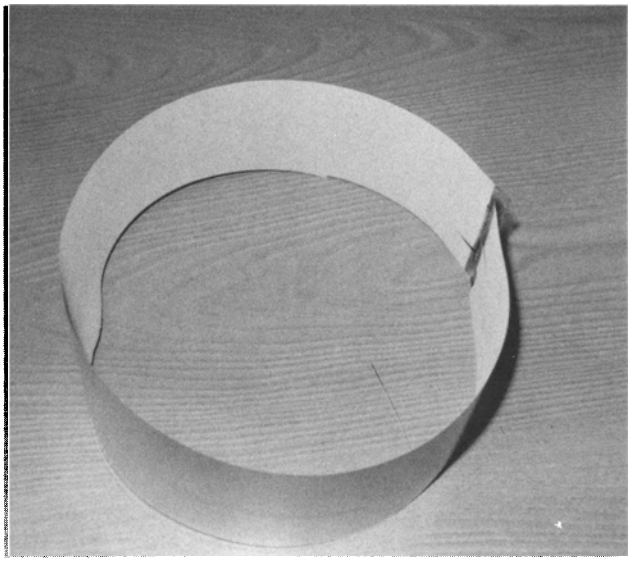

Fig. 2 Plasma-sprayed composite monotape

One of the main problems during the preparation of the substrate is to provide sufficient tension to the fibers wound around the cylinder during handling and loading of the cylinder into the deposition chamber and during the spraying process, without risk of damage or breakage to the fiber during the winding stage on the lathe. With this aim, the ends of the cylindrical-rolled sheet were kept close together by means of two groups of screws (á schematic of the top view of the cylinder is given in Fig. 1). Once the fibers were wound around the substrate, the diameter of the cylinder was increased by loosening the screws, and the fibers were fixed in their original position.

3.3 *Operating Conditions*

A vacuum plasma spray (VPS) deposition system from Plasma Technik, A.G. (Wholen, CH) was used for all plasma spray operations. Before starting the spraying process, the deposition chamber was evacuated to 0.1 mbar to reduce impurities in the working atmosphere. After the cleaning step, the pressure was increased to 500 to 800 mbar by bleeding an inert gas (Ar) into the chamber. The substrate was then plasma sprayed. The torch (Plasma Technik, F4VP PT) was automatically controlled from outside the chamber, and its alternating movement was perpendicular to the cylinder axis. Local overheating of the substrate was thus avoided, and the total amount of material deposited onto the fibers could be more precisely dosed. Further control of substrate temperature was achieved by directing an inert gas jet in front of or behind the substrate.

Table 1 lists the main spraying parameters for manufacturing the composite monotape. The final product of the spraying process was approximately 1 m long and 30 cm wide, with long fibers arranged parallel to the maximum length.

4. Results

The monotape fabricated with the described process is shown in Fig. 2. A scanning electron micrograph (SEM) of a

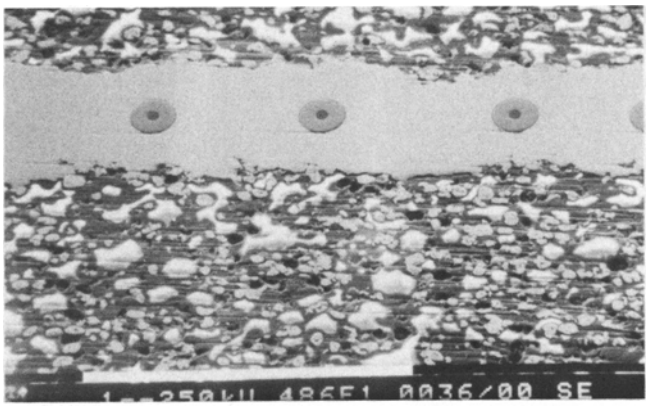

Fig. 3 Cross section of a composite monotape (SEM micrograph)

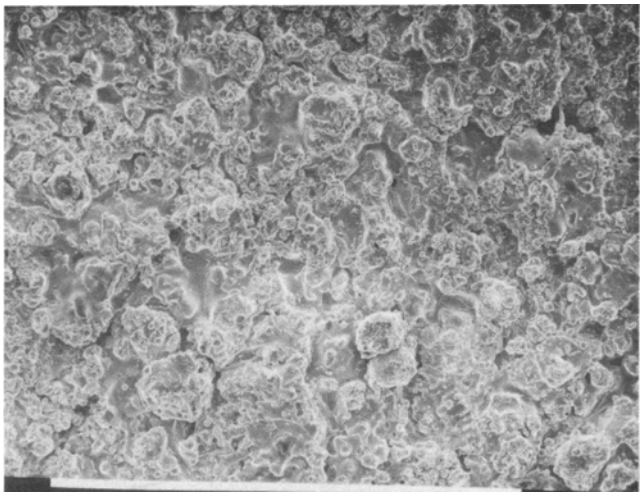

Fig. 4 SEM micrograph of plasma-sprayed Ti-6Al-4V matrix after chemical etching

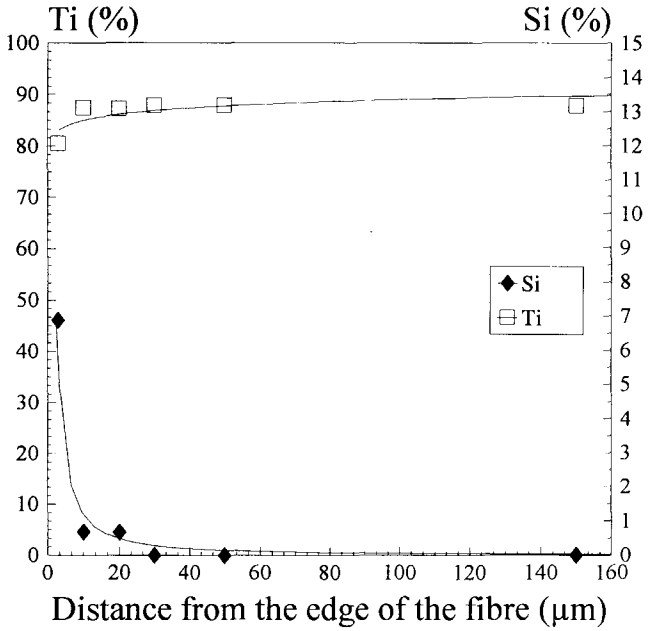

Fig. 5 Semiquantitative evaluation (EDS) of the atomic percentage of silicon and titanium as a function of the distance from the edge of the fiber

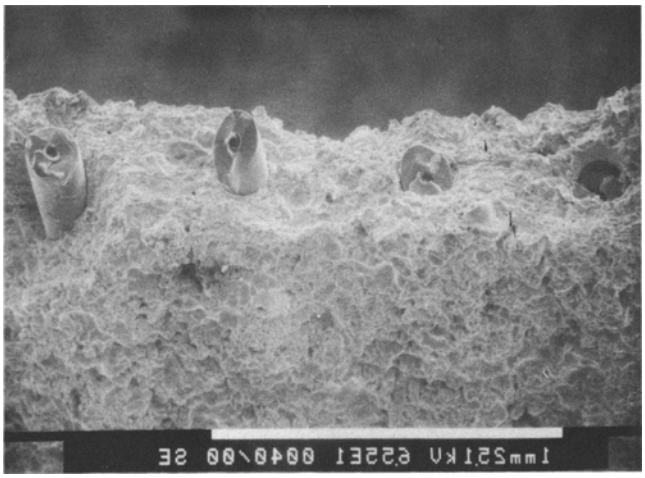

Fig. 6 Fracture surface of the composite monotape after ASTM D3552-77 tensile testing. Detail of the fiber/matrix interface (SEM micrograph)

cross section of the tape, perpendicular to the fiber axis, is illustrated in Fig. 3. The matrix porosity is lower than 1%, as evaluated by optical means. Microhardness tests were performed on a cross section of the coating; a load of 300 g was applied for a total time of 10 s. An average Vickers microhardness number (HV) of 507 was measured on a total of ten tests, with a standard deviation of 105 HV.

A small amount of oxidation products was formed on the monotape surface, resulting in blue-colored parts. Most probably, the atmosphere in the chamber was not sufficiently clean, thus causing titanium oxidation due to the high affinity of this metal for oxygen.

Another general observation concerns the embrittlement of the monotape due to the use of H_2 as the plasma gas.[18] Monotapes fabricated by using Ar/H_2 as plasma gases exhibited manufacturing problems when they were removed from the stainless steel substrate so that they could be sprayed on the other side. The bending radius that could be achieved before any crack formation occurred was too low to permit fabrication of good quality monotapes. Therefore, the plasma spray process had to be carried out by using Ar/N_2 as plasma gases. The ductility of the Ti-6Al-4V monotape could also be improved by means of post-heat treatments.

4.1 *Scanning Electron Microscopy and Elemental Analysis*

Scanning electron microscopy was carried out to obtain information concerning the microstructure of the sprayed matrix and the quality of the fiber/matrix interface. A Philips 505 electron microscope was operated at 25 kV, and both secondary and backscattered electrons were detected. The sprayed matrix exhibited a uniformly distributed porosity of about 1%. This feature can be considered independent of the presence of the SiC

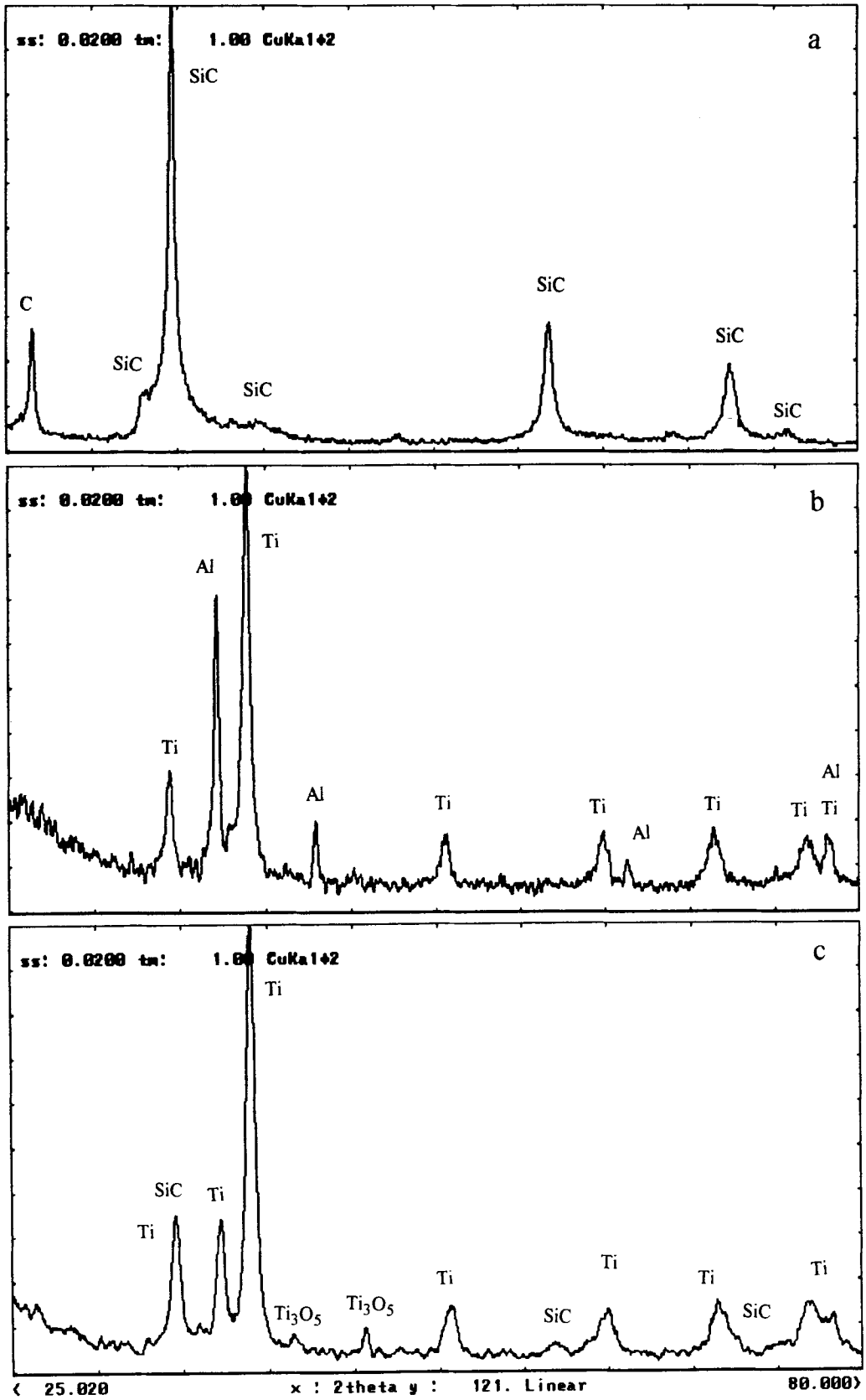

Fig. 7 X-ray diffraction patterns (a) As-received fiber (b) As-sprayed matrix (c) As-sprayed composite

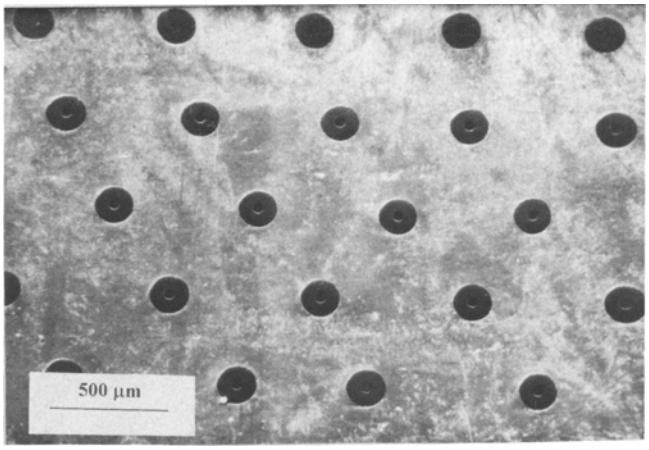

Fig. 8 Cross section of the hot pressed composite sample (SEM micrograph)

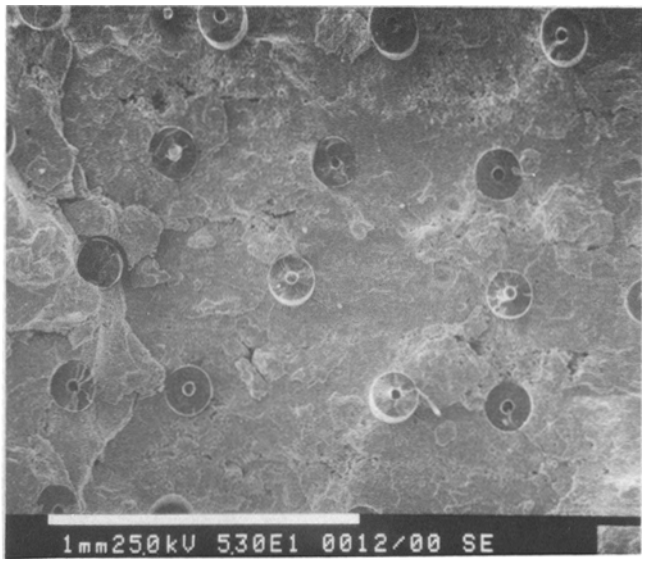

Fig. 9 Fracture surface of the hot pressed composite sample after tensile testing (SEM micrograph)

fiber (the fiber/matrix interface appeared continuous and free from macroporosity), but only dependent on the spraying conditions.

Metallographic samples were chemically etched with a solution of 40 ml of HNO_3 (65%), 10 ml of HF (40%), and 50 ml of distilled water at room temperature for 2 min to reveal microstructural details. The presence of some unmelted particles (Fig. 4) was observed. Further optimization of the plasma spray process could alter this microstructural feature and improve coating cohesion. Macroscopic delamination, or cracks originating from thermal stresses, are absent. As pointed out, no damage or degradation of the reinforcement was observed at the fiber/matrix interface. Results of a semiquantitative analysis of the distribution of the elements in the metal matrix, obtained by means of energy-dispersive spectroscopy (EDAX 9900 spectrometer), are shown in Fig. 5. In this diagram, the atomic percentage of titanium and silicon are plotted against the distance from the fiber edge. A certain amount of silicon (about 7% at the interface), coming from the silicon-rich layer of the fiber coating, was detected in the metal matrix. This could either suggest the existence of reaction products (such as titanium silicide), as reported in the literature,[19-24] or simply a silicon migration. No carbon was detected in the matrix, thus indicating an absence of titanium or mixed carbides.

The interface morphology indicated good wetting properties between the SiC fibers and the Ti-6Al-4V matrix. Good bonding at the interface is consistent with the fracture surface of samples that were subjected to tensile tests, because limited fiber pull-out was observed. Figure 6 shows the surface of the fiber exposed by the fracture; the outer layer of the fiber after the tensile test is still in contact with the matrix, thus confirming the possible existence of a certain chemical bond at the interface due to the presence of reaction products according to EDS results, even though the fiber surface was not damaged.

4.2 *X-Ray Diffraction Analyses*

X-ray diffraction analyses were performed by means of a Siemens D 500 diffractometer, using Ni filtered Cu Kα radiation, in the 2θ range of 5 to 80°, with a scanning step of 0.02° and a scanning step time of 1 s.

To verify the occurrence of noticeable reactions taking place between the different components of the metal matrix and the ceramic reinforcement during the spray process, X-ray diffraction analyses were carried out on three different samples: (1) as-received fibers, (2) as-sprayed matrix material, and (3) as-sprayed composite material.

Results are illustrated and compared in Fig. 7. Peaks relative to silicon carbide and graphite are clearly evident in (a) and (c). Very intense peaks corresponding to titanium in (b) and (c) indicate that titanium is quantitatively predominant in the powdered sprayed samples. Peaks corresponding to aluminum are present; vanadium could not be detected, due to its very low content in the initial powders. Traces of Ti_3O_5 were also identified on the surface of titanium samples (b).

The presence of small amounts of fiber/matrix reaction products cannot be excluded *a priori*; however, no clear evidence can be found of their formation in the results mentioned.

4.3 *Diffusion Bonding*

Preliminary work was done on joining six monolayers by diffusion bonding using a hot press system. The process was performed in an inert atmosphere at a pressure of 85 MPa at 900 °C for 30 min. A polished cross section of the sample obtained is shown in Fig. 8.

Good general bonding was observed between the different monolayers after chemical etching of the sample, whereas the formation of reaction products at the fiber/matrix interface due to the exposure at high temperature was not detected after EDS or X-ray diffraction investigations.

The sample obtained was subjected to a tensile test (ASTM D3552-77), and an ultimate tensile strength (UTS) of 952 MPa was measured. No macroscopic delamination phenomena were observed (Fig. 9). The UTS value cannot be considered completely satisfactory if compared to values reported in the literature.[25-27] However, in the case of the present work, note that the volume fraction of fiber in the sample is low (V_f = 15%), and the

spray process and the hot pressing procedure were not fully optimized.

5. Conclusion

The plasma spray process in a controlled atmosphere was used to manufacture Ti-6Al-4V monotapes reinforced by continuous ceramic fiber. Fiber/matrix adhesion was satisfactory and sufficient to guarantee good mechanical properties of the final product. The deleterious formation of brittle compounds at the interface was limited, or totally avoided, by the precleaning process operated in the deposition chamber and by the high solidification rate of the sprayed droplets. Preliminary work on diffusion bonding of the monotape was carried out with satisfactory results, even though further improvements in the plasma spray process and the hot pressing procedure for the above-mentioned metal matrix composites are still necessary. The described results are considered very promising for further developments.

References

1. S.J. Harris, Cast Metal Matrix Composites, *Mater. Sci. Technol.*, Vol 4, 1988, p 231-239
2. M.G. Bader, Metal Matrix Composites Science and Technology, UNIDO, *Proc. Int. Workshop Composite Materials*, 28 Oct-8 Nov 1991, Trieste, Italy
3. J.G. Morley, *High Performance Fiber Composites*, Academic Press, London, 1987
4. P.R. Smith and F.H. Froes, Development in Titanium Matrix Composites, *JOM*, Vol 3, 1984, p 19-25
5. Functionally Effective Coating Using Plasma Spraying, *Sulzer Techn. Rev.*, Vol 3, 1986
6. S. Dallaire, Plasma Spray Forming of Coating and Parts, *CIM Bull.*, Vol 80 (No. 900), 1987, p 37-42
7. B.J. Gill and R.C. Tucker, Plasma Spray Coating Processes, *Mater. Sci. Technol.*, Vol 2, 1986, p 207-213
8. A.R. Nicoll, *Schriftenreihe Praxis Forum*, Plasma Technik A.G., 1990, p 152-160
9. T. Valente, R. Cigna, A. Conte, F. Pinna, A. Salito, and R. Turriziani, Fabrication of Aluminium Matrix Composites by Plasma Spraying and Secondary Techniques of Consolidation, *Proc. 2nd Plasma Technik Symp.*, Vol 4, S. Blum-Sandmeier, H. Eschnauer, P. Huber, and A.R. Nicoll, Ed., Hafliger Druck AG, Wettingen, CH, in press
10. C. Bartuli, F. Carassiti, R. Turriziani, and T. Valente, Manufacture and Characterization of Continuous SiC Fibre Reinforced Aluminum Composites by Low Pressure Plasma Spraying, *Composite Materials*, A.T. Di Benedetto, L. Nicolais, and R. Watanabe, Ed., Elsevier Science, Amsterdam, 1992, p 259-271
11. O. Betsalel, B. Shipigler, G. Gurevits, and O. Gafri, Manufacture of Fiber Reinforced Metal Matrix Monolayer Composites by Plasma Spraying, *Isr. J. Technol.*, Vol 24, 1988, p 425-432
12. H.D. Steffens, R. Kaczmarek, and U. Fischer, Fiber Reinforced Composites by Thermal Spraying, *Thermal Spray Technology: New Ideas and Processes*, D.L. Houck, Ed., ASM International, 1989, p 293-297
13. P.A. Dearnley and K.A. Roberts, Titanium Matrix Composites via Vacuum Plasma Spraying. 1. Optimizing Process Parameters, *Powd. Met. (U.K.)*, Vol 34, 1991, p 23-32
14. H.D. Steffens, H. Kern, R. Kaczmarek, U. Fischer, and J. Janczak, Mechanical Behaviour of Plasma Sprayed Fibre Reinforced Composites, *Proc. 2nd Plasma Technik Symp.*, Vol 3, S. Blum-Sandmeier, H. Eschnauer, P. Huber, and A.R. Nicoll, Ed., Hafliger Druck AG, Wettingen, CH, 1991
15. K.G. Kreider, R.D. Schile, E.M. Breinen, and M. Marciano, Technical Report AFML-TR-68-119, 1968
16. Metal Matrix Composites, *Emerging Technologies*, Vol 20, Technical Insights Inc., 1986
17. C. Bartuli, E. Bemporad, F. Carassiti, and T. Valente, Reazioni Interfacciali in Compositi Al/SiC Ottenuti Mediante Plasma Spray a Bassa Pressione, *I Compositi a Matrice Metallica: Fabbricazione, Proprietà e Applicazioni*, Milano, Italy, 1992, p 153-167 (in Italian)
18. W.R. Kerr, The Effect of Hydrogen as a Temporary Alloying Element on the Microstructure and Tensile Properties of Ti-6Al-4V, *Metall. Trans. A*, Vol 16, 1985, p 1077-1086
19. C. Jones, C.J. Kiely, and S.S. Wang, The Effect of Temperature on the Chemistry and Morphology of the Interphase in an SCS6/Ti-6Al-4V Metal Matrix Composite, *J. Mater. Res.*, Vol 5 (No. 7), 1990, p 1435-1442
20. W.J. Whateley and F.E. Warner, Kinetics of the Reaction Between SiC (SCS6) Filaments and Ti-6Al-4V Matrix, *J. Mater. Sci. Lett.*, Vol 4, 1985, p 173-175
21. A.J. Reeves, R. Taylor, and T.W. Clyne, The Effects of Interfacial Reaction on Thermal Properties of Titanium Reinforced with Particulate SiC, *Mater. Sci. Eng. A*, Vol 141, 1991, p 129-138
22. P. Martineau, R. Pailler, M. Lahaye, and R. Naslain, SiC Filament/Titanium Matrix Composites Regarded as Model Composites. Part 2. Fibre/Matrix Interaction at High Temperatures, *J. Mater. Sci.*, Vol 19, 1984, p 2749-2770
23. R.R. Kieschke and T.W. Clyne, Development of a Diffusion Barrier for SiC Monofilaments in Titanium, *Mater. Sci. Eng. A*, Vol 135, 1991, p 145-149
24. S.K. Choi, M. Chandrasekaran, and M.J. Brabers, Interaction between Titanium and SiC, *J. Mater. Sci.*, Vol 25, 1990, p 1957-1964
25. W.H. Kao and J.C. Dick, Development of SiC Reinforced Titanium Corrugated Structures, *J. Comp. Sci. Tech. Res.*, Vol 10 (No. 2), 1988, p 47-53
26. D.J. Chang and W.H. Kao, SiC Reinforced Titanium Corrugated Structures for High Temperature Applications, *SAMPE J.*, Vol 2, 1988, p 13-17
27. "Silicon Carbide Composites," Data Sheet, AVCO Specialty Materials Division, Lowell, MA