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Joining of ceramic matrix composites to high temperature ceramics for thermal protection systems

C. Jiménez [a], K. Mergia [b,*], M. Lagos [a], P. Yialouris [b], I. Agote [a], V. Liedtke [c], S. Messoloras [b], Y. Panayiotatos [b], E. Padovano [d], C. Badini [d], C. Wilhelmi [e], J. Barcena [a]

[a] Tecnalia Research & Innovation, Industry and Transport Division, Mikeletegi Pasealekua, 2, Donostia-San Sebastian, Spain
[b] N.C.S.R "Demokritos", Institute of Nuclear and Radiological Science and Technology, Energy and Safety, Aghia Paraskevi, 15310 Athens, Greece
[c] Aerospace & Advanced Composites GmbH, Viktor-Kaplan-Straße 2, A-2700 Wiener Neustadt, Austria
[d] Politecnico di Torino, Department of Applied Science and Technology, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy
[e] Airbus Defence and Space GmbH, Dept. TCC 2/CTOIWMS, 81663 Munich, Germany

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ABSTRACT

The current work reports a novel approach for the integration of external protective SiC multilayers with ceramic matrix composite (C_f/SiC) with the view of application in aerospace heat protection systems. The integration method is based on diffusion brazing bonding. As a joining agent the MAX-Phase Ti_3SiC_2, produced by self-propagating high temperature synthesis, has been employed. The pressure applied during the joining process and its effect on the microstructure of the integrated structure is discussed. Microstructural analysis of the resulting joints is conducted using scanning electron microscopy coupled with energy dispersive spectroscopy and X-ray diffraction measurements. Analysis of the joints showed that the bonds are uniform, dense, with few crack vertical to the interface which are not detrimental for the performance of the joints. Ground re-entry tests showed that the joints survive 5 re-entry cycles at 1391 and 1794 °C without any detectable damage.

1. Introduction

One of the key technologies of today's aerospace applications refers to the effective protection of components subject to large heat loads like the heat shields of re-entry vehicles or the inner walls of combustion chambers. This issue is of great importance for future missions where considerably increased energy densities are expected.

Advanced ceramic matrix composite (CMC) materials based on SiC matrix reinforced with carbon fibers (C_f/SiC) are key materials for aerospace applications since they present superior mechanical properties and resistance against high temperatures and being at the same time lightweight and cost effective. For the application of these bulk ceramics in hostile environments appropriate coatings have to be developed that will prevent the oxidation of the carbon fibers. The current thermal protection systems are based on the use of ceramic matrix composite materials coated with SiC [1] or other carbide based materials. SiC exhibits excellent oxidation resistance at high temperatures, because the formed glassy silica films prevent oxygen diffusion very efficiently and thus serve as protection against further oxidation. However, the amorphous silica at temperatures above 1200 °C crystallizes to cristobalite causing surface cracking and also reacts with water or Na/K vapor, resulting in severe degradation of the silica film [2].

Alternatively to SiC coatings ultra high temperature SiC based multilayer ceramics can be employed in combination with CMCs in order to provide integrated systems with enhanced performance under the most severe re-entry conditions. The advantage in using multilayered ceramics stems from the capability of adjusting their architecture and chemical composition e.g., by incorporating ZrB_2 layers at the outer structure, and thus tuning the functionality of these protection layers to specific re-entry conditions i.e., the required service temperature and the oxidative environment these structures have to withstand. Therefore, advances in joining science and technology of CMC-ultra high temperature and oxidation resistant ceramics to SiC based multilayer ceramics are important in order to integrate these systems and realize the benefits of these advanced materials in aerospace applications.

A number of techniques for joining monolithic ceramic materials or CMCs to themselves have been developed such as solid state

* Corresponding author. Fax: +30 210 6545496.
E-mail address: kmergia@ipta.demokritos.gr (K. Mergia).

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sintering of the ceramics, diffusion bonding using various active fillers [3,4], transient eutectic-phase routes [4], glass–ceramic joining [5], metallic braze-based joining [6,7], SiC reaction forming [8], MAX-phase bonding [4,9], spark plasma sintering [10], integrated assembly method [11] or mechanical fastening [12]. However, to our knowledge no joining procedure for CMCs and SiC based multilayers systems has been reported so far.

The current work reports on a approach for the integration of external protective ceramic SiC based multilayers (SiC ML) with a thermostructural ceramic matrix composite (C_f/SiC). This structure is a part of a more complex system for a powerful thermal protection system under a reference mission (ESA's Advanced Re-entry Vehicle) [13]. The integration method of the two materials is based on the diffusion brazing bonding process. As a joining agent a filler metal based on a MAX-Phase Ti_3SiC_2, produced by self propagating high temperature synthesis, has been employed. Ti_3SiC_2 has good stability at elevated temperatures and it presents both metallic and ceramic properties and exhibits plastic behavior. It has a melting point higher than 3000 °C and a coefficient of thermal expansion (CTE) 9.12×10^{-6}/K between 25 and 1200 °C [14]. It has been used in the past for joining of SiC based ceramics for application in the temperature range 1200–1600 °C [9].

The process parameters of the joining method and their effect on the microstructure of the integrated structure are discussed. The structure and microstructure of the assembly has been investigated by optical microscopy, scanning electron microscopy with energy dispersive analysis and X-ray diffraction measurements. Results from thermal tests under re-entry conditions are presented and discussed with respect to the envisaged applications.

2. Materials and methods

The C_f/SiC (SICARBON) ceramic composites were supplied by Airbus Defence and Space GmbH [15]. They consist of carbon fibers embedded in a silicon carbide matrix. The production process of this material is based on the polymer infiltration pyrolysis process (PIP). The infiltration of the carbon fibers with a pre-ceramic polymer-based and powder-filled slurry system is performed by liquid polymer infiltration (LPI) via filament winding. From the supplied material samples of 40×40 mm^2 were cut and used for all the experiments.

The SiC multilayers were fabricated by the tape casting technique followed by pressureless sintering [16]. The processing method involved several steps: SiC slurry preparation; tape casting; stacking, debinding and pressureless sintering. The SiC multilayers used in the current study consist of eleven dense SiC layers.

For the joining of the SiC to SICARBON, the ternary MAX compound $Ti_3Si_{1.5}C_2$ was used as a filler metal. The material was produced by self-propagating high temperature synthesis (SHS) in a reaction furnace and in argon atmosphere using titanium, silicon and carbon powders with atomic ratios 3Ti:1.5Si:2C. After the SHS process a foam was obtained and this foam was milled and sieved under 63 μm. The crystal structure of the filler was assessed by X-ray diffraction (XRD) measurements.

The joints were fabricated employing the diffusion brazing technique in a high vacuum hot press furnace at 1600 °C. The pressures used were 2.7, 7 and 25 MPa. For the joints fabricated at 2.7 and 7 MPa the pressure was applied at room temperature and kept constant during the thermal cycle. For the joint fabricated at 25 MPa at the beginning of the thermal cycle and up to 1400 °C a lower pressure of 15 MPa was applied up and for the rest of the thermal cycle during heating and cooling the pressure of 25 MPa was applied. A heating rate of 15 °C/min up to 1400 °C, followed by a heating rate of 10 °C/min up to 1600 °C and a slow cooling rate of 5 °C/min were applied.

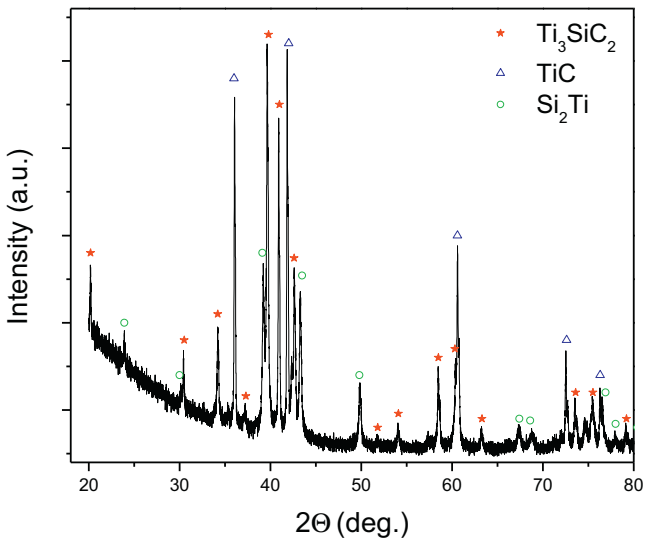

Fig. 1. XRD pattern of $Ti_3Si_{1.5}C_2$.

The XRD patterns were measured using a Bruker D8 diffractometer equipped with a Cu Kα radiation, a parallel beam stemming from a Göbel mirror and a Våntec position sensitive detector with 9° angular acceptance. The microstructure of the joints was examined using FEI Quanta Inspect scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS). For the EDS analysis, different accelerator voltages were used in the range between 12 and 20 kV and a standardless quantitative analysis was performed employing the ZAF correction approach.

Tests of the SiC-ML/CMC under re-entry conditions, i.e. temperature profiles under vacuum, were carried out at a ground re-entry test rig [17] at a maximum temperature of 1794 and 1391 °C for 5 cycles each. The tests were performed under vacuum and the thermal profiles used correspond to two control points of the ESA's Advanced Re-entry vehicle (ARV) [18].

3. Results and discussion

3.1. Filler composition and structure

The filler metal was produced by SHS. In the SHS process for the formation of Ti_3SiC_2, there is a competitive reaction between Ti and Si with C. The formation of TiC instead of Ti_3SiC_2 is thermodynamically favorable and TiC appears always as a secondary phase in the formation of Ti_3SiC_2. Thus, excess amount of Si was used in order to reduce the TiC content in the final material i.e., the initial atomic content was $Ti_3Si_{1.5}C_2$. The XRD pattern of the filler compound produced by SHS is depicted in Fig. 1. From the XRD pattern we observe that in addition to the $Ti_3Si_{1.5}C_2$ compound the minority phases TiC and $TiSi_2$ are present.

$Ti_3Si_{1.5}C_2$ crystallizes in the hexagonal $P6_3/mmc$ space group, TiC which crystallizes in the fcc cubic Fm-3m space group, and $TiSi_2$ in the orthorhombic face-centered Fddd space group. The formation of TiC as a secondary product during the combustion synthesis of the MAX phase Ti_3SiC_2 has been studied in different works [19,20]. From Rietveld analysis of the XRD spectra of the filler the % mole content of the phases present was determined as Ti_3SiC_2: 58% (77.4 wt%), TiC: 37% (19.2 wt%) and $TiSi_2$: 5% (3.4 wt%). Converting the mole content of these three phases to atomic ratios we find 3Ti:0.95Si:2.1C. Compared to the initial atomic ratios 3Ti:1.5Si:2C of the mixed powders, this shows loss of Si during the combustion synthesis.

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