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Ceramics International 39 (2013) 7499–7505

CERAMICS INTERNATIONAL

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Combustion joinining of carbon/carbon composites by a reactive mixture of titanium and mechanically activated nickel/aluminum powders

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Received 21 December 2012; received in revised form 27 February 2013; accepted 28 February 2013
Available online 14 March 2013

Abstract

Combustion joining of carbon/carbon (C/C) composites using a mixture of titanium and mechanically activated Ni/Al powders as a reactive medium is reported. A minimum preheating of the sample stack to 630 K is required to initiate the joining process. A robust crack- and pore-free joint layer ($\sim 75-100$ μm in thickness), which is composed of $NiAl_x$ and $TiC_y(O_z)$ phases, is produced. Tensile-strength testing of the joined C/C composites shows that the fracture does not occur along the joint layer.

Keywords: A. Milling; A. Joining; B. Composites; D. Carbide

1. Introduction

Carbon/carbon (C/C) composites, due to their low density, high strength-to-weight ratio, as well as high thermo;elastic stability at elevated temperatures, are attractive thermo-structural materials for a variety of applications. These key characteristics enable use of C/C composites for manufacturing of rocket nozzles, noses and leading edges of reentry vehicles, as well as gas turbine engine components [1,2]. In addition, the high thermal-shock and wear resistance that C/C composites possess make them suitable for aircraft brake disks, where temperatures during harsh landing conditions (i.e., rejected take-off) can be as high as 2000 K [3–5].

As the demand for such materials increases, development of techniques for joining C/C composites with various complex structures is drawing more attention. Specifically, rapid and energy-efficient techniques for joining C/C composites are of great interest for industries such as aircraft brake manufacturers. For example, one of the many possible applications is the refurbishment of carbon-brake disks by bonding a new piece to a used C/C core to produce a carbon-brake disk that meets special performance requirements. However, joining of refractory C/C composites is a challenging task. Mechanical or adhesive means could be used to join such materials but the applications are limited. For example, since carbon-brakes should be highly refractory components, C/C parts joined by traditional mechanical or adhesive joining methods would not hold up to harsh environments. Moreover, unlike metals, C/C composites do not lend themselves to welding, and even brazing can be difficult because many commonly used filler metals exhibit little or no wetting of carbon materials.

Few studies have reported joining of C/C composites. In general, the techniques that could be applied to join C/C composites include: reactive metal brazing [6], solid-state diffusion bonding [7,8] a combination of these approaches [9], as well as adhesive organic resin bonding [10] and hot-pressing [11]. As mentioned above, C/C composites joined via reactive metal brazing and adhesive bonding can be

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http://dx.doi.org/10.1016/j.ceramint.2013.02.099

utilized only at relatively low temperatures. The other techniques require relatively long-time (hours), high-temperature (up to 2000 K) sample treatment and application of high external bonding loads. Such conditions often lead to the decrease of the materials' properties. Hence, a method for joining of C/C composites which is rapid and energy-efficient and can produce a robust refractory joint without a significant change of the properties of the materials to be joined is still a challenging and demanding task.

Combustion joining (CJ) is an attractive method for joining of a variety of materials [12,13]. It was derived from self-propagating high temperature synthesis (SHS), or combustion synthesis (CS), which was initially developed for materials synthesis. CJ is drawing attention as an effective tool for joining of refractory substances [14–18]. Some characteristics of CJ include: (i) short (seconds) processing time; (ii) energy efficiency, since the chemical energy of the internal system is primarily used for the production of the material; (iii) simple technological equipment; (iv) the ability to produce joint layers with functionally graded properties. White et al. [15] reported joining of refractory C/C composites via a class of refractory materials (carbides, borides, etc.) by CJ. However, a short-term (~30 s) but high-temperature (up to 2000 K) preheating of the joint stack was required in order to initiate the chemical reaction in the joint layer, which affected the composite properties.

Here we report an improved combustion-based technique for bonding of C/C composites by utilizing a CJ approach with a reactive mixture of titanium and mechanically activated Ni/Al powders. Incorporation of mechanically activated powders allowed initiation of the stack joining reaction after only preheating up to 630 K. The influence of the CJ parameters, including temperature, applied pressure and durations on the quality of the joint layer was investigated. The microstructure, phase and elemental composition of the joint layer were also studied. Finally, tensile-strength testing of joined C/C composites was performed.

2. Material and methods

2.1. Mechanical activation

The mechanical activation (MA) of Ni+Al mixture is described in detail elsewhere [19]. Short-term (15 min) high-energy ball milling (HEBM) of an equiatomic Ni+Al powder mixture (15 g of Ni+Al mixture per batch) was carried out using a PM100 (Retsch, Germany) planetary ball mill with a 250 mL stainless steel jar and 2 mm diameter stainless-steel balls as the milling medium in an inert atmosphere (argon). The ball-to-mixture ratio was 2:1. The rotational speed of the mill was 650 rpm. X-ray diffraction (XRD) analysis was performed to determine the phase composition of the initial Ni+Al mixture and after 15 min of MA. Results suggested that no new phases (NiAl, $NiAl_x$ solid-solution, etc.) were formed after 15 min ball milling of Ni+Al powder mixture under the investigated conditions. It was shown [20] that such a mechanical activation treatment allows one to significantly decrease the self-ignition temperature of Ni/Al reactive mixture.

2.2. Materials preparation

Cylindrical C/C samples (10 mm in diameter × 12.5 mm in length) were fabricated from a commercial C/C aircraft brake disk (Honeywell Aerospace, South Bend, IN) with a density of 1.67 ± 0.04 g/cm^3 and a total open porosity of ~15%. A thin disk (0.3 g, 10 mm in dia. × 2 mm in height), cold-pressed from the powder medium, was placed in between the two C/C composite pieces to be joined. The disk was composed of 0.1 g of pure Ti powder (−325 mesh, Alfa Aesar) and 0.2 g of mechanically activated Ni/Al composite with a molar ratio of 1:1 (initial Ni and Al powders, −325 mesh, Alfa Aesar).

2.3. Joining method

A detailed description of the joining device and the experimental conditions is published elsewhere [21]. The stack (C/C–(Ti+Ni/Al+Ti)–C/C) to be joined was placed between two cooper electrodes in a specially designed press-die, which was connected to a DC power supply. The electrodes are part of a pneumatic system, which applies a uniaxial load to the sample. All operational parameters such as pressure (P), applied current (I), and others were defined by a programmable logic controller (PLC). As DC current passed through the stack, it was preheated due to the electrical resistance of the material. The experimental parameters used were initial load, $P_i = 4$ MPa; final load, $P_f = 20-40$ MPa; delay time between ignition and final load application, $\Delta t = 5$ msec; applied current, $I = 300-400$ A; joining duration, $t = 5$ s.

A high-speed infrared thermal imaging system (SC6000; FLIR Systems, Boston, MA) was used to monitor the temperature–time evolution of the process. Thermal images and videos were captured in frame sizes ranging from 64 × 8 to 640 × 512 over several different temperature ranges using commercial software (FLIR ThermaCAM Researcher).

2.4. Materials characterization

Cross-sections of joined C/C composites were prepared and microstructures, as well as elemental and phase compositions of the joint layers were examined with a scanning electron microscope (LEO series EVO 50), which was equipped with an Oxford Instrument EDS analyzer. X-ray diffraction was also performed (Scintag, X1 Advanced Diffraction System, Scintag Inc., USA). Joined C/C samples were machined to the desired configuration and tensile-strength tests ($T_0 = 300$ K) were performed with a universal testing machine (Enduratec ELF 3000, Bose

Corporation, MA) at a rate of 1 mm/min and a load up to 500 N, to evaluate the mechanical properties of the joined materials. The microstructure and compositions of the fracture surfaces were also studied by SEM and EDS.

3. Results and discussion

3.1. Temperature–time history of the joining process

Fig. 1a shows a schematic illustration of the C/C joining configuration. The reactive medium stack (Ti+Ni/Al+Ti) is placed between two C/C composites. Once triggered, the heat release and high temperature of the Ni/Al reaction facilitate the interaction between the Ti and the C/C composites, forming a TiC phase and simultaneously bonding the C/C composites. After the joining process, it is expected that a *functionally graded* joint layer (i.e., C/C–TiC–NiAl–TiC–C/C) will be produced. Fig. 1b shows a set of infrared images of the temperature–time history of the joining process. Four different stages can be outlined: Joule preheating of the sample stack (A); reaction initiation in the joint layer (B); continued heating owing to the Ni/Al chemical reaction (C); cooling stage (D). A typical CJ temperature–time profile of C/C composites acquired from the area of the joint layer by the high-speed infrared thermal imaging system over the 750 − 1650 K temperature range is shown in Fig. 1c. It shows that there are two peaks in the temperature–time curve. The first peak can be attributed to the initiation and combustion of the mechanically activated Ni/Al composite powder. This reaction is triggered at a low temperature (< 750 K) and leads to a temperature increase up to ~1500 K. The second peak is

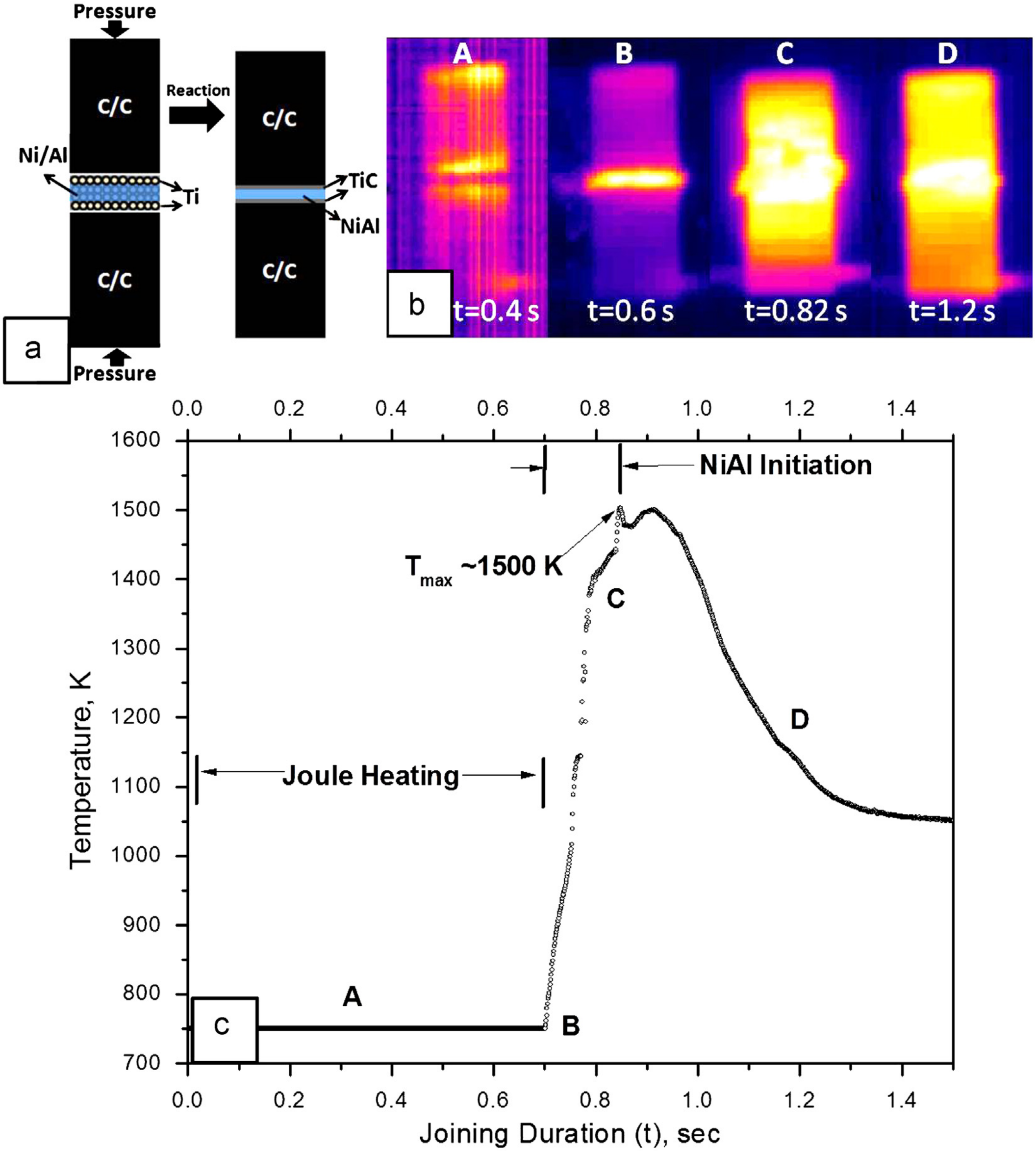

Fig. 1. Schematic illustration of the C/C joining configuration (a), snapshots of thermal images (b) and a typical temperature–time profile of the C/C joining process (c) (A, Joule preheating of the sample stack; B, reaction initiation in the joint layer; C, stack preheating owing to chemical reaction; D, cooling stage).

related to the subsequent interaction of Ti powder and C/C composite, leading to formation of a TiC_y phase in the vicinity of the joining region.

To determine the ignition temperature of Ni/Al MA composite powder, an additional experiment was carried out and the obtained temperature was ~630 K. The joining process was completed in 5 s, followed by sample cooling and cleaning of the squeezed melt from the surface before further characterization. It is crucial to note that the whole stack was preheated only to ~630 K, followed by a higher temperature increase due to the chemical reaction in the reactive mixture. This temperature provides the conditions for joining, which takes place only in the vicinity of the joint layer.

3.2. *Microstructures and EDS analysis*

Fig. 2a shows typical back-scattered electron (BS) SEM images of a joined C/C sample cross-section in the vicinity of the joint layer. First, it can be seen at lower magnification that a crack-free joined layer ~75–100 μm in thickness was produced by the CJ method. Second, it was observed that part of the resulting interlayer infiltrated ~100 μm into the porous skeleton of the C/C composites. Third, compression during the reaction forced the molten reactive medium to bond with the C/C composites, yielding simultaneous formation of a dense, pore- and crack-free interlayer. Closer inspection of the joint layer (Fig. 2b) indicates that it consists of two characteristics regions: a light region (denoted as α) in the middle of the joined layer and an intermediate region (denoted as β) between the α region and the C/C matrix. A high-magnification image (Fig. 2c) shows a detailed structure of the β region, which is composed of three different phases.

EDS analysis along the joined sample was performed to evaluate the elemental compositions of these regions and results are summarized in Table 1. As shown in Fig. 2b and Table 1, points 1 and 2 are primarily composed of C phase. The β region (points 3, 4) consists of Ni, Al, Ti, C, and some oxygen while the α region (points 5 and 6) shows mostly Ni and Al phases. As shown above in the typical SEM images, three phases can be seen in the β region. A more detailed EDS analysis in the β region (point 7) reveals that the primary phase in β region is a Ti-rich phase and it contains a greater amount of C and O compared to other regions. However, point 8 in the β region shows that it is an O-rich phase (>30 wt.%). Note that additional EDS data obtained in other similar intermediate regions verified that the Ti was accumulated in the intermediate (β) regions (e.g., 35–45 wt.%). Elemental carbon was detected in the intermediate layer (β region), suggesting formation of a TiC phase after CJ.

Fig. 2d shows further microstructure and corresponding EDS mapping analyses of the joined C/C composites. The obtained mapping results indicate that Ti is located primarily in the intermediate layers while Ni and Al phases are uniformly distributed in the joined layer. Such an elemental distribution can be explained by a three-step joining mechanism: (1) at an early stage the mechanically activated Ni/Al composite powders are rapidly initiated by direct heating of the C/C sample stack, forming NiAl solid solutions; (2) melting of the Ti powder (~1900 K) due to the chemical reaction of Ni/Al and the continued Joule heating of C/C sample; a minor part of the molten Ti diffuses into the NiAl solid solutions (α region) while the majority of the mobile Ti stays active in the high

Table 1
The point EDS analysis of joined C/C composites in Fig. 2b and c.

Spectrum	C	O	Al	Ti	Ni	Total
1	99.55	0	0.45	0	0	100
2	98.9	0	0	0	1.1	100
3	**30.06**	**0**	**3.81**	**42.23**	**23.89**	**100**
4	**25.8**	**9.78**	**12.78**	**3.97**	**47.66**	**100**
5	0	0	**25.73**	1.85	**72.44**	100
6	0	0.34	**26.21**	1.73	**71.72**	100
7	9.48	**12.01**	14.5	**40.56**	23.45	100
8	0.2	**32.1**	21.05	**10.58**	36.07	100

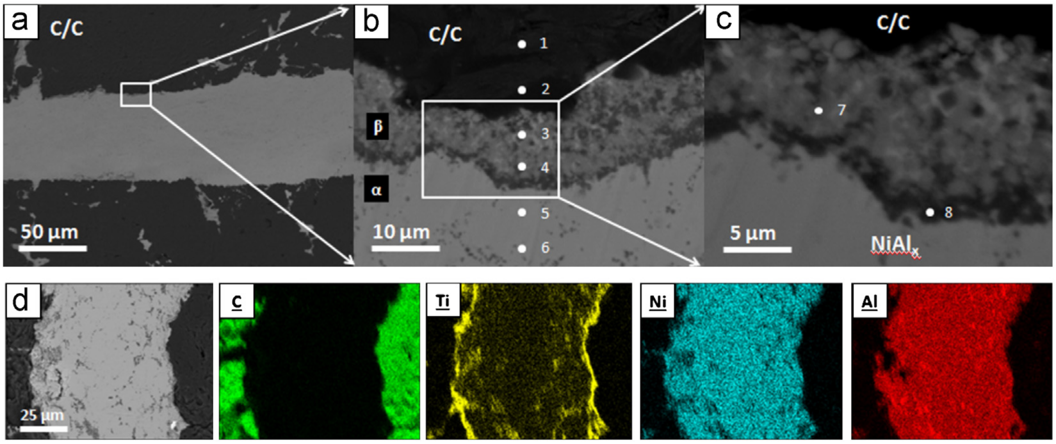

Fig. 2. Typical cross-sectional microstructural images of joined C/C composites (a–c) and associated EDS mapping analysis and elemental maps (d); close-up images (b, c) showing distinctive joined layers. Points (1–6) represent where EDS analyses were performed.

temperature environment and is squeezed into the boundary of the intermediate layer and the C/C matrix (β region); (3) the molten Ti reacts with the C/C composite and forms a TiC_y phase (β region).

Additional work was performed to investigate the phase compositions of the joined C/C sample. The joined sample was machined and polished in order to reveal the joint layer. XRD analysis was performed in the vicinity of the joint layer to identify possible phases, and the corresponding pattern is shown in Fig. 3. As expected, three phases can be seen in Fig. 3, namely, C, TiC and NiAl. The results prove that there is formation of TiC and NiAl phases in the joint layer after the joining process.

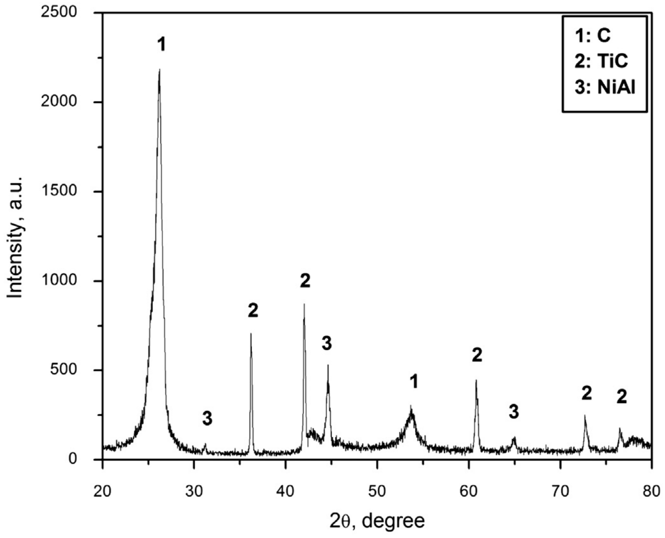

Fig. 3. Typical XRD analysis of joined layer.

3.3. Mechanical testing

Joined samples were machined to a configuration suitable for tensile-strength testing (see the insert in Fig. 4a) and three diameters (i.e., points $1-3$) were measured at the center of the joined sample for further stress–strain calculations. Fig. 4a shows a typical stress–strain (σ–ε) curve of a joined C/C sample and a schematic illustration of the joined and fractured samples (insert). As expected in brittle C/C materials, the rupture occurred without a pronounced strain difference ($\varepsilon \sim 0.04$) in the course of elongation. In this typical case, the obtained ultimate tensile strength of a joined C/C sample was ~5.8 MPa (Fig. 4a). More importantly, the rupture occurred at point 1, indicating that the joined layer (point 2) was stronger than the C/C matrix. Note that all data presented are results of statistical treatment of data from a set of 3 samples for the test group with a standard deviation of ± 0.5 MPa.

Again, the developed CJ technique provides a good joint and requires preheating of the C/C composite to a relatively low temperature (~630 K). As mentioned above, other techniques for C/C joining, which show relatively high mechanical properties for joined samples, are reported in the literature [6,11]. However, it is not appropriate to compare the results of the present work with literature data because the ″strength″ of the initial C/C composites used in these works are very different. It is important that, in our case, the sample failure occurs along the carbon matrix and not in the joined layer, indicating that the joined layer is mechanically stronger than the C/C composite.

In addition, based on the tensile strength the C/C composites possess after CJ, their potential applications can include nozzles of solid rocket motors, airplane wing edges or nuclear reactors [16,22]. These applications mainly

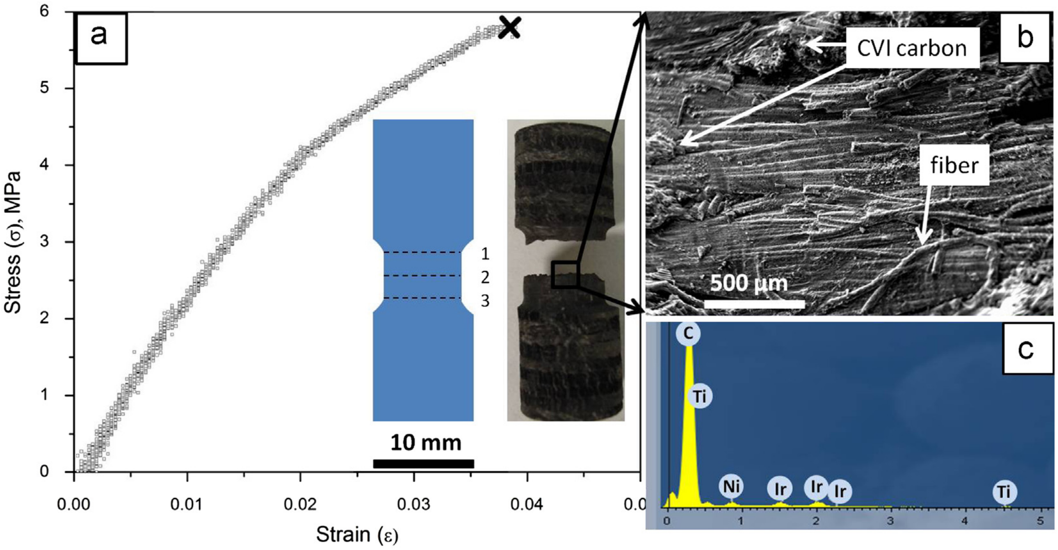

Fig. 4. Typical stress–strain curve of a joined C/C sample and schematic illustration of joined and fractured samples (a); SEM image of fractured surface (b) and its associated EDS area analysis (c).

require a consistent high temperature operating environment and do not subject materials to severe tensile stresses, which would be an ideal utilization for lower tensile-strength C/C composites. It is also believed that with further work to define more optimal joining parameters, the tensile strength of joined samples can be significantly increased.

An SEM micrograph of the fractured surface is shown in Fig. 4b. As can be seen in the micrograph, only carbon fibers and chemical vapor infiltrated (CVI) carbon (i.e., produced during C/C manufacturing) are observed on the fracture surface. There is no visible intermediate layer, $NiAl_x$ and $TiC_y(O_z)$, observed. The EDS area analysis (Fig. 4c) further suggests that the region shown in Fig. 4b is composed of carbon (primary phase), with a small amount (<4 wt.%) of elemental Ti, Ni and Ir (sputter-deposited during SEM sample preparation). The presence of such elements is mainly due to infiltration of the intermediate layer during CJ, as shown in Fig. 4a. These data confirm that the fracture occurs in the C/C matrix, and that the joint layer is mechanically stronger than the C/C composite material.

The present work focused primarily on validating the concept of *low temperature* joining of C/C composites with a reactive mixture of Ti powder and Ni/Al mechanically activated composites. The novelty of the technique is that use of a mechanically activated reactive medium enables joining of C/C composites by a rapid and energy-efficient CJ method by preheating the C/C stack to only 630 K, and produces a robust joint layer. Such a method could be further applied to joining refractory C/C composites with a variety of configurations, and has the potential for scaling up to join larger specimens.

4. Conclusions

The concept of combustion joining C/C composites using a mixture of titanium powder and mechanically activated Ni/Al composites as a reactive medium was validated. A minimum preheating of the sample stack to 630 K was required to initiate the joining process. Under current optimal experimental conditions, a robust crack- and pore-free joint layer ($\sim 75-100\ \mu m$ in thickness), which is composed of $NiAl_x$ and $TiC_y(O_z)$ phases, was produced at the interface. The XRD and EDS results also confirmed the obtained intermediate phases. Tensile-strength testing and associated SEM analysis on the C/C fractured surface revealed that the rupture takes place in the C/C matrix with an ultimate tensile strength of $\sim$5.8 MPa.

Acknowledgment

This work was supported by Grant # 14.A18.21.1944 of Russian Ministry of Science and Education and LLC "Summa Group". This work was partially supported by the Notre Dame Integrated Imaging Facility (NDIIF). The authors thank Prof. Ryan K. Roeder (University of Notre Dame) for fruitful discussion regarding tensile-strength testing, Mr. Travis L. Turnbull (University of Notre Dame) for testing measurement and Mr. Donald Gard (Physics machine shop, University of Notre Dame) for tensile-strength sample preparations.

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