In situ TiC–Fe–Al2O3–TiAl/Ti3Al composite coating processing using centrifugal assisted combustion synthesis

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1. Introduction

Self-propagating high-temperature synthesis (SHS) leads to the in situ production of composites with reactive initial substances through an exothermic chemical reaction [1]. The heat generated by the reaction ignites and sustains a propagation combustion wave through the reactants as the anticipated product is created [2]. SHS is characterized as a high-temperature process that makes it an alternative, more economical method for ceramic industries compared to conventional ceramic processing. SHS is a feasible technique for the preparation of advanced ceramics, catalysts and nanomaterials [3].

The centrifugal SHS process of Fe2O3 and Al is a spontaneous reaction propagation and simultaneous rapid synthesis under the effect of centrifugal acceleration. The reaction occurs in the inner surface of the centrifugal tube where the Al melts and Fe2O3 reduces in the initial stage [4]. The self-sustained exothermic reaction propagates through a pre-mixed powder in the form of a high-temperature reaction wave with rapid heating rate and short reaction time. This is followed by phase separation and solidification of the Al2O3 and Fe products [5]. Finally, the product of the centrifugal SHS reaction between Fe2O3 and Al is a metal–ceramic Al2O3–Fe composite [6]. The post-processing of the ceramic-layered tubes may pose some disadvantages for the ceramic layer. Various local reinforcement components such as titanium carbide composites can assist in this regard.

Titanium carbide (TiC) has many desirable properties, among which are high hardness, low density, high melting temperature, high modulus, great corrosion resistance and excellent wetting properties to Fe [7,8]. The application of TiC particulate has been noted in wear resistant parts, thermal fatigue, erosion-resistant materials, and high performance tooling. The most frequently reported TiC–Fe composite is fabricated either by ex situ methods like powder metallurgy or in situ in the medium of Fe [9,10]. TiC is thermodynamically stable in steels, and thus provides fine reinforcement for wear resistant applications [11].

The TiC resulting from the reaction between Ti and C starting powders is characterized by high hardness, good wettability, low density, and chemical stability with the Fe-based matrix. In situ functionally-graded materials (FGM) consisting of ceramic and intermetallic components is appropriate for a number of post-processing applications, such as piping branches and orifice nubs of...
thick ceramic-coated pipes. It will enhance the inner-most layer of the ceramic surface that undergoes mechanically damages and crack propagation while transporting fluids or material. This would prevent the ceramic surface of the pipe from eroding, corroding or cracking excessively.

Ferro-TiC is a superwear cermet with good erosion resistance, machinability and hardenable properties [12,13]. TiC–Fe cermet has low sputtering or brazing capabilities under atmospheric conditions with large surfaces [14]. Therefore, ex situ TiC–Fe is not economical when used as an insert in the case of ceramic-lined pipes. A number of papers have been published on the synthesis of TiC-reinforced Fe-based composites [15–17] using different starting materials under normal gravity conditions and with powder metallurgy technique. The advantage of powder metallurgy is that the product’s surface quality and precision are excellent; however, production cost is high, while product shape and size are restricted. For these reasons, several works on the liquid-based means have been published in the past decade [18].

Gowtam et al. studied Fe–TiC steel FGM using SHS reaction followed by centrifugal casting [19] (Fe2O3, MnO2, and TiO2 powders in the presence of C, in situ TiC-reinforced steel composites [20], cast-sintering [21], as well as spark plasma sintering [22] and chemical vapor deposition [23]. In another study conducted by Huang et al., TiC–TiB2 ceramics were prepared via combustion synthesis under a high gravity field [24]. Recently, Shi et al. reported a processing and abrasive wear study of Fe–Al2O3–TiC composite by pressure-less Ti-activated reactive melt infiltration [25]. The production of in situ TiC–Fe–Al2O3 composite system under centrifugal force utilized the heat generated by the highly exothermic thermite reaction of Fe2O3 and Al, whereby the reaction of Ti and C can be achieved at a rapid heating rates and short reaction times. The adiabatic combustion temperatures of the SHS Fe2O3 + Al and Ti + C reactions can reach 3622 °C and 3290 °C, respectively [19], much higher than the melting point of Al and Fe2O3 [26]. The advantage of this process is that once ignited, no further externally applied energy is required to complete the reaction [27]. Al2O3–Ti–TiAl/Ti3Al processing using SHS is reported elsewhere but not under centrifugal processing conditions [28,29]. So far, to the best of the authors’ knowledge, no report has been put forth describing the production of an in situ TiC–Fe–Al2O3–TiAl/Ti3Al composite system under centrifugal force using Fe2O3, Al, Ti, and C as starting materials. In this paper, the locally reinforced functionally graded coating, and the intermetallic layers of the composite product before and after immersion into a humid environment are investigated.

2. Experimental procedure

2.1. Materials and methods

A centrifugal thermite (CT) machine was utilized to facilitate rapid centrifugal acceleration as well as temperature increase during the experiment. A bilayer graphite–steel compacted mold was fixed inside the CT reaction chamber. A high performance infrared thermometer, Raytek MM1MH5F3L, recorded the experimental real-time temperature data. The detailed procedure of using the centrifugal machine for thermite processing in metallic pipes is explained in recently published literature [4].

The starting materials, namely Al (<75 μm, 99% purity, Sigma Aldrich) and Fe2O3 (<5 μm, 97% purity, Sigma Aldrich) powders were dried for eight hours and mixed in a Retsch PM 200 Planetary Ball Mill for 4 h at 30-min intervals. The amount of 128 g of green powder stoichiometric mixture was prepared according to the following reaction equation: Fe2O3 + 2Al → Al2O3 + 2Fe, ΔH = −768.75 kJ mol⁻¹ [30]. Titanium (Sigma Aldrich, −100 mesh, 99.7% purity) and carbon (Sigma Aldrich, −1000 mesh, 99.9% purity) elemental powders were dried for 7 h at 125 °C, following which they were mixed according to the reaction equation: Ti + C → TiC, ΔH = −183 kJ mol⁻¹. A 75 mm long carbon steel pipe with inner and outer diameters of 69 mm and 75 mm, respectively, served as a bulk holder for graphite. The dried Ti + C green powder was compressed into a pellet and then inserted into the graphite mold’s pre-defined location (Fig. 1).

The thermite mixture was fed into the tube. Then increased the rotation speed was to 280-g acceleration, and followed by igniting an electric arc with a graphite electrode. The onset of thermite reaction was trailed by a titanium and carbon reaction, which occurred in response to the heat generated by the thermite (first) reaction. The released temperature was recorded by the infrared pyrometer.

2.2. Environmental conditions

A cross-section of the composite was prepared with a low-speed diamond cutter before being polished and cleaned in an ultrasonic acetone bath. The product was not etched. Subsequently, the sample was released and exposed to the air in a room under environmental conditions (high humidity, up to 80%).

2.3. Characterization

The as-sintered specimen was ground and analyzed using field emission scanning microscopy (FESEM), energy dispersive X-ray analysis (EDAX), X-ray diffraction pattern (XRD) and microhardness. The Rietveld method [31] was employed as part of quantitative phase analysis following XRD to calculate the phase contents in the specimen. In the Rietveld method, crystal structure and peak profile parameters are refined in several stages. The HighScore Plus 3.0e processed the Rietveld refinement stage calculations. A Mitutoyo SJ 201 profilometer measured the smoothness of the product’s inner-most surface. The instrument was calibrated to avoid reading errors. After calibration, the samples were measured for smoothness at three different locations in each region.

3. Results and discussion

Once the reaction occurred under the influence of centrifugal acceleration, the molten Al2O3–Fe infiltrated the Ti + C pellet. The infrared pyrometer recorded the reaction temperature released up to 2925 °C. Centrifugal force pushed the molten material to the inner surface of the Ti + C pellet. The molten semi-products were forcibly trying to penetrate the porous Ti + C media, and it formed an in situ TiC–Fe–Al2O3 composite. This reaction lasted

![Fig. 1. Schematic diagram of a steel pipe and graphite crucible assembly (a) charged with the green mixture and mounted Ti + C pellet before reaction (left), (b) after reaction (right) while subjected to centrifugal force.](image-url)
only 2.5 s from ignition until Fe solidification, at which point it is assumed that reaction and infiltration is stopped. The thermite reaction products (Fe and Al₂O₃) deposited according to their densities [32] at the graphite mold’s innermost layer, and then diffused inside the TiC zone. The reactions created a porous TiC product. The product formed, i.e. TiC–Fe–Al₂O₃ composite, had a round, rough innermost layer surface, and was microscopically porous at the cross-section. The average roughness \( (R_a) \) value in Fig. 2, region 4 (specimen’s face) was about 3.12 \( \mu \)m. The rapid heating and super-cooling process of the material would have caused surface imperfections [33]. Increasing the amount of thermite mixture fed into tube does not improve the innermost surface quality significantly, since it is a rapid melting and cooling process. As for FESEM–EDAX analysis, an electron beam scanned along a pre-selected line across the sample, while X-rays detected discrete positions along the line. Line analysis of the X-ray energy spectrum in Fig. 2 provides plotting of the relative elemental concentration for each element versus position along the white line at the center of the figure.

In Fig. 2 layer (1), TiC-rich area, there was only a small amount of Al representing Al₂O₃ or Al intermetallic detected as well as a high amount of Fe which penetrated the TiC zone. The intermetallic compounds comprising Ti, Al and Fe were mostly located in zone (2). All the starting elements participated in the experiments, thus increasing the quality of joining properties to each other; however, Fe was most uniformly distributed along area (2). The product’s middle layer (2) and (3) contained the highest amount of Al. The carbon content was diffused in all the layers, although titanium was diffused inside the Al-rich layer (3). The elemental composition of layer (4) was rich in Fe. The very weak signal in layer (4) for C and Ti is noise. There are some imperfection deposition happened since the pellet was situated at the head of the pipe whereas the highest temperature gradient exists. The high temperature gradient can cause the molten iron at the surrounding area moving to the head and created an unexpected layer [33]. Therefore, the layer (4) mainly contains Fe.

A typical area of the product’s TiC zone is shown in Fig. 3 before (a) and after (b) being exposed to environment where different locations are highlighted based on EDAX elemental analysis. The pores of Ti–C zone area seemed to be filled by the molten composite due to high centrifugal acceleration that acts as an external force. At high gravity pressure the molten composite wet the ceramic surface and filled the pores [34]. There are extensive reports of molten metal capillary infiltrating a porous medium to form a ceramic-metal composite [35].

Fig. 3(b) shows a micrograph image of the sample that was exposed to environmental conditions and the corresponding EDAX elemental analysis of different locations at points 1 and 2, and zone 3 are provided in Table 1. Various compounds were identified in the sample including iron oxide, titanium oxide, and carbon-based compounds such as TiC and Fe₃C. According to the literature, corrosion begins at high interfacial energy and relatively weak bonding locations, such as grain boundaries [36].

A scaling issue was also encountered here that increased the surface area. This phenomenon is similar to corrosion problems are mostly the result of tuberculation [37]. The findings are comparable to those of Tao et al. regarding the flower-like anatase TiO₂ hierarchical spheres assembled by nanosheets synthesized by gly- cine via a hydrothermal approach [38]. Tao et al. claimed that the obtained TiO₂ sample demonstrated good photocatalytic activity of decomposing of methyl orange under sunlight [38]. The oxide layer in Fig. 3(b) is needle-like (flower-like) with sharp edges. This sort of surface changes are significant with respect to tribological behavior as they cause fretting corrosion damage in biomedical applications [39]. According to EDAX results, the corroded area consisted of FeO, Al₂O₃, TiO₂, and TiC components after three-day exposure to the environment. However, the SEM-EDAX analysis in Fig. 3(b) shows that points 1 and 2 contain very little oxygen (<1%), which might suggested very little or no corrosion occur at that point.

![Fig. 2. Line profile analysis of a typical area of the TiC–Fe–Al₂O₃ specimen.](image)

![Fig. 3. FESEM micrograph of product cross-section (a) before; and (b) after exposure to the corrosive environment.](image)

<table>
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<tr>
<th>Table 1</th>
<th>EDAX elemental analysis of different areas/points.</th>
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<tr>
<td>Elements</td>
<td>C</td>
</tr>
<tr>
<td>Point 1</td>
<td>46.23</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.94</td>
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<tr>
<td>Area 3</td>
<td>11.79</td>
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X-ray diffraction pattern (XRD) of the whole specimen’s cross-section elaborates the existing phases in Fig. 4, and confirms the formation of a polycrystalline product with different TiC–Fe–Al2O3 composite phases. The compound’s intermetallic peaks of tetragonal titanium aluminide (TiAl, Ti3Al) were detected in the XRD pattern. The presence of intermetallic compounds enhances crystal properties in the form of ordered crystal structures [40].

The Ti and Al atoms occupy specific locations in the crystal structure rather than random locations as in the majority of solid solutions. Intermetallics have been shown to possess lower ductility properties, with environmental factors also playing a role in limiting ductility in intermetallics [36].

According to XRD and Rietveld refinement results, 28% of the product was composed of TiC (111), and (002) crystal direction with cubic structure. Hexagonal titanium (011), (010) crystal direction 28.2% and hexagonal carbon (002), (004) crystal direction 23.0% elements did not react with each other but took part in metallurgical alloying and joining.

2.5% of Al2.5Fe0.55Ti system (022) crystal direction is formed. The ternary iron [41] has a cubic structure, with a substantial capability of the developing intermetallic-based materials for high-temperature applications [42]. The Al–Fe–Ti alloy also has ferromagnetism properties [43]. The XRD pattern did not display a strong anatase peak, as this compound grew as a thin layer on the top surface layer of the composite. It was not readily detectable by normal XRD, but was perceived by FESEM. Corundum (Al2O3), wuestite (FeO), and Cohenite (Fe3C) were detected by XRD with 6.5%, 4.5%, and 2.2% quantity in the composite, respectively.

The relatively sharp peak (Ti, C) which represents the amount of unreacted titanium and crystallized carbon may seem to be high due to the XRD mechanism that scanned the whole area of the sample’s cross-section from the inner-most layer up to the...
outer-most layer. Starting from the outer-most layer of the sample, whereas the outer TiC pellet surface was not directly exposed to the heat. On the other hand, the reaction time was too short to propagate and transfer the generated heat inside the pellet, and besides, the intermetallic layers may have also prevented the rest of the specimen from reacting. The importance of the intermetallic layers is their support in providing a smooth transition of phases and compounds over the volume of the product.

The mechanical properties in terms of micro-hardness conforming to Fig. 3(b) was measured in zones 1 and 2. The hardness reading result are plotted in Fig. 5 versus the hardness of those in literature [44,45]. The maximum Vickers hardness value (2313 HV) was observed at a TiC-rich region, whereas the maximum hardness value of the less TiC-rich area was 1251 HV. Whereas the hardness variation is an indication of phase transition over the volume of the product [46].

Employing an in situ technique to produce net-shaped products of the reinforcing ceramic-alloy composite with substantial intermetallic constitutes will reduce post-processing cost and increase the service life of the manufactured parts significantly.

4. Conclusion

In the present study, the reaction temperature of the centrifugal thermite-assisted combustion synthesis between Al and Fe2O3 was observed to be above 2925 °C. According to FESEM–EDAX TiO2 were primarily formed after three days of exposure to a humid environment due to product surface corrosion however it was not detectable by XRD. In situ FGMs of TiC–Fe–Al2O3 were primarily formed after three days of exposure to a humid atmosphere. The importance of the intermetallic layers is their support in providing a smooth transition of phases and compounds over the specimen from reacting. The importance of the intermetallic layers is their support in providing a smooth transition of phases and compounds over the volume of the product [46].

Acknowledgements

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References