High-temperature mechanical properties of preceramic paper-derived $Ti_3Al(Si)C_2$ composites obtained by spark plasma sintering

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Abstract. In the present work, the flexural strength of $Ti_3Al(Si)C_2$-based composites was investigated at 25, 800 and 1000 °C using small punch technique. The composites were spark plasma sintered at 1150 °C and 50 MPa from preceramic paper with $Ti_3Al(Si)C_2$ powder filler. Sintered composites represent a multi-phase system with secondary TiC and Al_2O_3 phases and have more than 900 MPa of flexural strength at room temperature. It was revealed that at 800 °C the flexural strength of composites decreases to 690 MPa. At 1000 °C, the flexural strength of composites further decreased to 620 MPa, however, an anomalous displacement of punch was detected during the fracture test attributed to the $Ti_3Al(Si)C_2$ brittle-to-plastic transition of the fracture mechanism.

1. Introduction

MAX-phases are nanolaminated structures with the general formula $M_{n+1}AX_n$, where n varies from 1 to 3, M is a transition metal, A is an element of the IIIA-IVA subgroup, X is carbon or nitrogen. They represent a unique class of materials that combines the properties of ceramics and metals such as high temperature and corrosion resistance, good thermal and electrical conductivity, thermal shock resistance, good machinability, etc. [1, 2]. Due to their excellent properties, MAX-phases are good candidates to be used as high-temperature materials in aerospace and other industries. Al-based MAX-phases are the most promising candidates because of their superior high-temperature corrosion resistance [3], and especially Ti_3AlC_2 due to its good mechanical properties and lightweight [4]. Additionally, it was showed earlier that a particular substitution of Al by Si in A-layers of Ti_3AlC_2 MAX-phase can improve the flexural strength by ~20% [5]. However, MAX-phases are susceptible to brittle-to-plastic transition at elevated temperatures which accompanied by degradation of mechanical properties. Two main mechanisms are responsible for brittle-to-plastic transition: grain boundary sliding suggested by Barsoum et al. [6] and activation of additional slip planes [7]. Strengthening the MAX-phase based materials by secondary phases, solid solutions, fibers [8], etc. should decrease the influence of brittle-to-plastic transition of MAX-phases on the mechanical properties of composites. In work [9] was shown that using spark plasma sintering (SPS) and preceramic paper filled with $Ti_3Al(Si)C_2$ powder it possible to obtain the nearly dense composites strengthened by secondary phases and solid solution in A-layers of MAX-phase. Using a preceramic paper as a feedstock for sintering MAX-phase-based composites allows to easily control physical and chemical properties of composites by manipulating powder fillers or by the preceramic paper itself. At present time there is no data on the mechanical

behavior of paper-derived MAX-phase-based composites at elevated temperatures. This work is aimed to fill this gap by performing high-temperature mechanical tests on preceramic paper-derived $Ti_3Al(Si)C_2$-based composites.

2. Materials and methods

Preceramic paper with the following composition: 87 wt% of $Ti_3Al_{0.75}Si_{0.25}C_2$ powder, 7.3 wt% of cellulose fibers, 3 wt% of Al_2O_3 powder was obtain on a laboratory dynamic hand-sheet former D7 (Sumet Systems GmbH, Germany). The technique of preceramic paper manufacturing is clearly described in [10]. The $Ti_3Al(Si)C_2$-based composite samples with the diameter of 20 mm were obtained by spark plasma sintering (SPS) using SPS 10-4 (Advanced Technology, USA) apparatus. Composites were sintered at the temperature of 1150 °C and pressure of 50 MPa. The phase composition was analyzed by X-ray diffraction analysis (XRD) using XRD 7000S (Shimadzu, Japan) diffractometer equipped with OneSight high-speed 1280-channel detector. Diffraction data were refined by the Rietveld method in FULLPROF software. Mechanical tests were performed at 25, 800 and 1000 °C on LFM-125 (Walter&Bai AG, Switzerland) tensile testing machine. For the mechanical tests, the fabricated composites were cut into samples with a diameter of 7.9 mm and a thickness of 1 mm. Flexural strength was measured using a small punch technique where round-shaped samples were placed on the support ring, and the load was applied to the center of samples by small punch [11]. The fracture surface was analyzed using scanning electron microscope (SEM) (TESCAN Vega 3, Czech Republic).

3. Results and discussion

Figure 1 presents the diffraction pattern of the initial preceramic paper and composite sintered at 1150 °C and 50 MPa. It can be seen that sintered composites represent a multiphase material system with secondary TiC and Al_2O_3 phases. The phase composition of sintered composites was as follows: 82.5 vol% of $Ti_3Al(Si)C_2$, 12.5 vol% of TiC and 5.0 vol% of Al_2O_3.

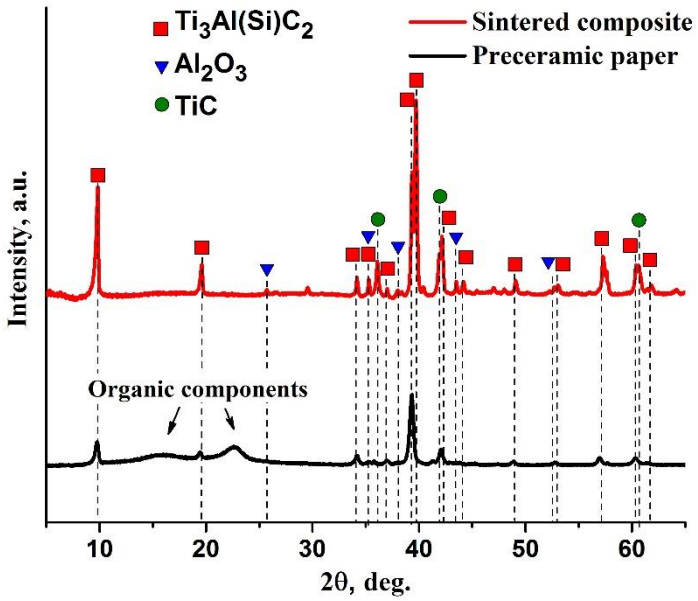

Figure 1. Diffraction patterns of preceramic paper and $Ti_3Al(Si)C_2$-based composite sintered at 1150 °C and 50 MPa.

The presence of secondary phases is contributed to the partial thermal decomposition of $Ti_3Al(Si)C_2$ during the sintering process. Commonly decomposition process of Ti-Al-C system MAX-phases occurs at temperatures about 1400 °C [12]. The lower temperature of the MAX-phase decomposition can be

attributed to peculiarities of the SPS process. During the SPS process, high-temperature sparks can be formed between particles of $Ti_3Al(Si)C_2$ powder [13], which can rise the local temperature above the sintering temperature. Additionally, the formation of TiC phase can be related to the presence of additional carbon from the decomposition of organic components (Figure 1).

It was found that the sintered composites exhibited a brittle fracture and flexural strength of 940 and 690 MPa at 25 °C and 800 °C, respectively (Figure 2). Hence, at 800 °C there was a decrease of flexural strength by 26%. It is also evident from the fracture diagram that at 800 °C the slope of the curve changed, indicating a change in the elastic properties of the composite.

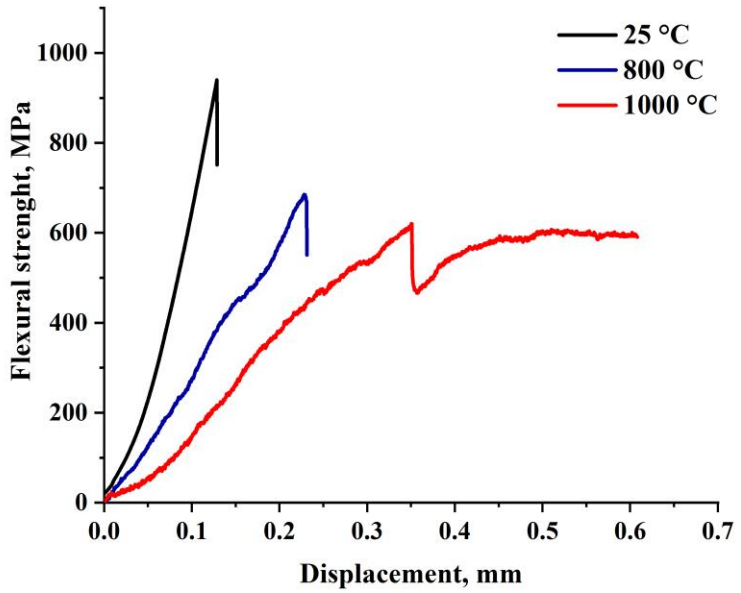

Figure 2. Fracture diagram for $Ti_3Al(Si)C_2$-based composites tested at 25, 800 and 1000 °C.

At 1000 °C, a change in fracture mechanism from brittle to plastic occurred. At a displacement of about 0.35 mm multiple cracks were initiated, accompanied by a decrease in the applied force; at constant force, cracks begin to propagate. For the composite tested at 1000 °C, the value of flexural strength at the time of crack initiation – 620 MPa (35 % decrease) – was measured.

Figure 3a and b show SEM images of fracture surfaces for the sample tested at 25 °C. A well-distinguishable lamellar structure of $Ti_3Al(Si)C_2$ can be seen from SEM images. In addition, typical fracture mechanisms for layered materials – delamination, kink and pull-out of lamellar plates can be seen in the SEM images (Figure 3b and d). Delamination, kink and pull-out of lamellar plates occur during mechanical loading that enhances energy absorption by micro fracture, hindering the formation of macro cracks. It is complicated to analyze the fracture surfaces of composites tested at high temperature because of the oxides formation during testing. However, the fracture surface of composite tested at 800 °C exhibit a smoother morphology than those tested at 25 °C. It partially attributed to the presence of oxides and partially could be attributed to the local plastic flow of $Ti_3Al(Si)C_2$ MAX-phase. This effect is more pronounced in composite tested at 1000 °C (Figure 3e and f) where the fracture surface is rougher than at 25 and 800 °C. Figure 3e shows the side opposite the applied load and four radial cracks can be seen propagating from the center without total failure of the sample. The lamellar structure of $Ti_3Al(Si)C_2$ MAX-phase which is distinguishable at 25 °C and even at 800 °C was not observed at 1000 °C (Figure 3f). It probably attributed to the occurrence of $Ti_3Al(Si)C_2$ plastic flow and the surface oxidation.

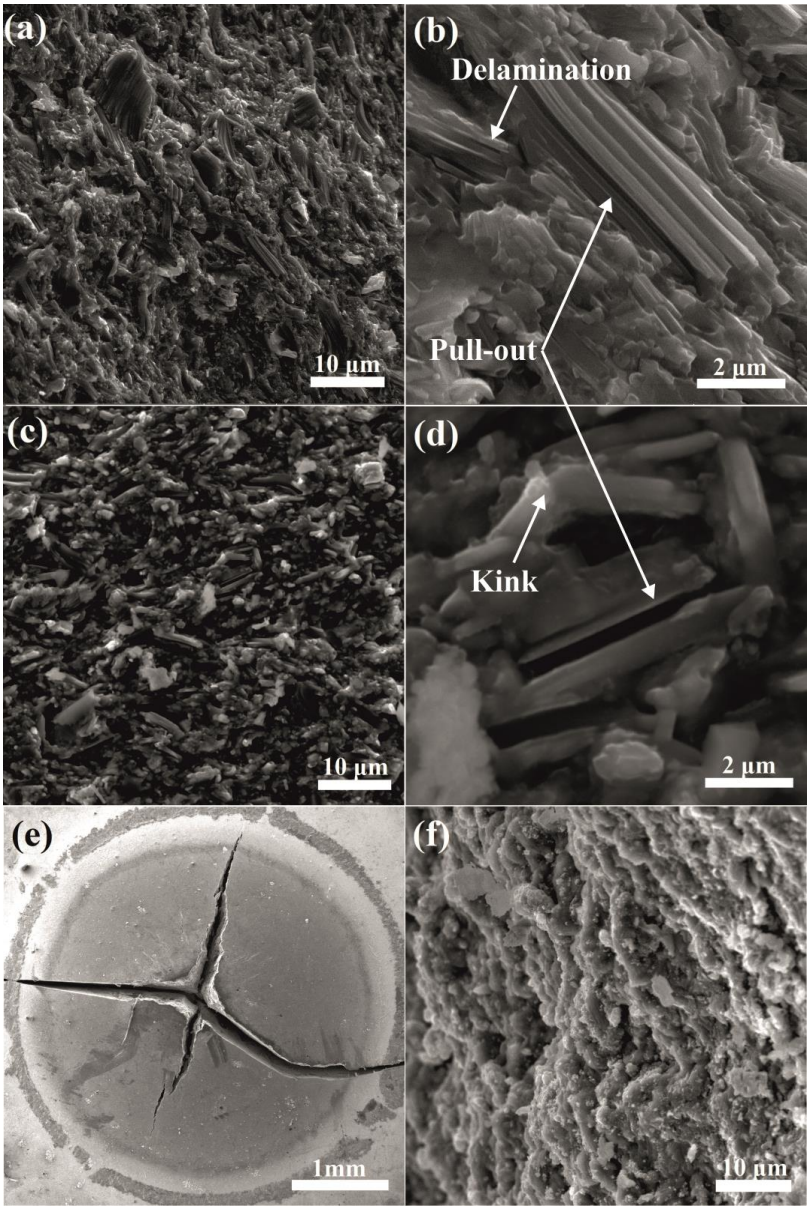

Figure 3. SEM images of fracture surfaces of $Ti_3Al(Si)C_2$-based composites tested at 25 °C (a, b), 800 °C (c, d) and 1000 °C (e, f)

4. Conclusion

The flexural strength of preceramic paper-derived $Ti_3Al(Si)C_2$-based composites was investigated at 25, 800 and 1000 °C by small punch technique. Obtained composites represent a multiphase system with secondary TiC and Al_2O_3 phases. The presence of secondary phases and solid solution are responsible for the flexural strength of 940 MPa at room temperature. The flexural strength of the composites decreased to 690 and 620 MPa with increasing testing temperature to 800 and 1000 °C, respectively. Additionally, brittle-to-plastic transition was observed at 1000 °C which leads to anomalous displacement of punch during high-temperature mechanical tests. Fracture surfaces of high-temperature tested composites show signs of plastic flow of $Ti_3Al(Si)C_2$ MAX-phase.

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