Solar Powder Metallurgy: Preparation of TiC – TiB₂ Ceramic Foam

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Abstract. The solar powder metallurgy was used to prepare TiC–TiB₂ ceramic foams in 40kW horizontal solar furnace at Plataforma Solar de Almeria (PSA), Spain. The foams were prepared using self-propagating high-temperature synthesis from the green compacts of powder mixture of Ti + 15 vol.% B₄C. The foaming was performed under protective argon atmosphere at various heating rates. It was shown that it is possible to prepare successfully TiC–TiB₂ ceramic foams with porosity around 45%. The foaming temperature or ignition temperature was found to be around 1380 °C. The optimal heating rate for foam preparation was found to be 220°C/min. It was confirmed that 2 pieces of precursor will join successfully to create single foam. Further, graphite and alumina moulds were tested for possible preparation of 3D shapes. The EDS investigations confirmed the creation of TiB₂, TiC and complex TiBₓC₁₋ₓ phases.

1. Introduction

The TiC–TiB₂ composites can be characterized not only by high-melting points, high hardness, excellent wear resistance and good thermal stability, but also by superior properties such as enhanced fracture toughness and bending strength compared with constituent ceramic components [1]. For this reason they are very attractive for application as advanced structural materials in aircraft propulsion systems and space thermal protection systems.

However, the application of TiC–TiB₂ composites has been limited due to the fact that they have been difficult to process. Various methods, such as reactive sintering, reaction hot pressing, spark plasma synthesis, transient plastic phase processing, and self-propagating high-temperature synthesis (SHS) or termed combustion synthesis (CS) have been developed for the synthesis of TiC–TiB₂ ceramic composites with various porosity [1-4].

Recently authors used Solar Powder Metallurgy to study the preparation of fully dense titanium samples using solar furnace via pressure less sintering [5]. It was shown that significant advantage of solar furnace is simple handling and significant shortening of heating/cooling times. Therefore, the aim of the proposed work is to study experimentally a possibility to prepare TiC–TiB₂ ceramic composite foams with regard to determination of foaming temperature, dependence of final foam structure on heating rate, possibility to join various pieces of foamable precursor into the one piece of foam and finally to determine the proper mould material for TiC–TiB₂ foaming, which is necessary for preparation of complex 3D shapes.
2. Experimental

The Hydrogenated–dehydrogenated (HDH) Ti powder (purity 99.4%, supplied by Kimet Special Metal Precision Casting Co., Ltd., China) and B₄C powder (98% purity, normal grade, UK Abrasives, Inc., USA) were used for the investigations (see Figure 1). Ti powder is of typical angular shape while B₄C is of irregular shape. The powder size distributions were determined using Fritsch Analysette 22 laboratory equipment. Ti powder has \(d_{50} = 25 \mu m\) and \(d_{90} = 46 \mu m\). B₄C is standard boron carbide powder of powder size F600, i.e., 3 - 19 \(\mu m\).

The powders corresponding to the composition of Ti + 15 vol.% of B₄C were dry mixed in Turbula mixer for 30 minutes. Then the powder mixture was compacted by uniaxial pressing at 280 MPa, which was optimal pressure for used pressing die. The typical geometry of green compacts before sintering was: diameter of 15.2 mm and height of 4 mm. The compacts were weighted and finally the porosity was calculated using known geometry. The observed volumetric porosity was approximately 42% for all samples.

Figure 1. HDH titanium powder (left) and B₄C powder (right).

Figure 2. Left – interior of SF40 solar furnace during experiment: open shutter, vacuum/gas chamber mounted on table and concentrator; right – ceramic foam prepared in alumina tube.

The foaming experiments were performed at the horizontal solar furnace SF40 in PSA, Almeria, Spain. SF40 is able to deliver up to 40 kW power at peak concentration ratios exceeding 7000 kW/m². This SF40 system consists of heliostat, shutter, parabolic concentrator and test table [6]. The test table is a mobile platform on which the chamber enabling sintering of specimens in vacuum/protective atmosphere is placed and three stepping motors control the table motions (see Figure 2). The prepared sample was placed on zirconium plate (400 x 400 x 3 mm). The specimen was placed inside of chamber under the focal spot. The chamber is evacuated through a Pfeiffer turbomolecular pump and gas system is connected to it. The sample was placed to be in optimal focusing distance with regard to solar spot size either free or inside graphite/alumina tubes. For these tests graphite tube with inner diameter of 18 mm and height of 30 mm was used. The used alumina tube has inner diameter of 14 mm and height of 30 mm. The size of solar spot was approximately 90 mm. Then the chamber was
evacuated (approximate value of the vacuum was around 8.10^{-1} Pa) and argon gas flow (400 l/hour under the pressure of 3 bars, technical purity argon 99.998% with maximal impurities of H_2 5 ppm mol/mol and of O_2 5 ppm mol/mol) was used during experiments.

Various heating rates were used during the experiments, the heating rate was controlled using shutter opening and was within the range of 90 – 1700 °C/min. Twenty experimental samples were foamed/sintered using SF40 solar furnace at temperatures between 1200 – 1600 °C for various dwell times between 5 to 30 minutes, most of them using heating rate of 220°C/min. The temperature was measured using pyrometer (emissivity 0.95) due to the reaction of titanium with thermocouples [5]. Remark: as the process is rapid it is not possible to use zirconium ceramic protection on thermocouples (see Figure 3). The main goal was to establish the optimal solar furnace parameters (shutter opening, temperature and time) necessary for good foaming of TiC-TiB_2 ceramic samples. The final porosity was determined from geometry and the weight of the samples in the case of sintering (not foamed). In the case of foamed samples that underwent foaming, the investigation of porosity was performed using X-ray micro tomography Phoenix Nanotom for non destructive analysis of the internal structure of materials.

After the experiments the samples were cut and samples for microstructure observations were prepared. Microstructure of samples was observed at PSA`s Materials Lab using Leica DMI 5000 Minverted digital microscope and at IMMS SAS using scanning electron microscope JEOL 7600F, equipped with Schottky thermal-emission cathode (thermal FEG - W-coated ZrO2) as well as Energy-dispersive X-ray energy (EDS) spectrometer from Oxford Instruments.

![Figure 3. Typical heating/cooling curve of the solar foaming of TiC – TiB_2, on the secondary y axis is plotted the shutter opening (dash curve): Solar foaming, heating rate 220°C/min, direct solar radiation 825 W/m^2.](image)

**3. Results and discussion**

The experimental works confirmed that when temperature of sample achieved certain foaming temperature self-propagating high-temperature synthesis took place and it was possible to create TiC–TiB_2 foams from Ti + 15 vol.% B_4C compacted precursor (see Figure 4). Further, it was shown that it is possible to prepare successfully TiC–TiB_2 ceramic foams with porosity around 45%. When the samples do not reached foaming temperature simple sintering took place with porosity varying according to sintering temperature and time.

Basically, the self-propagating high-temperature synthesis usually takes place during heating of mixtures of Ti with carbon, boron, TiC, TiN, B_4C and other additions when ignition temperature is reached [3]. In present work, at ignition temperature inside of investigated material titanium starts to react with boron carbide in a following way: 3Ti + B_4C \rightarrow TiC + 2TiB_2. This direct reaction is highly
exothermic ($\Delta H^0 = -686 \, \text{kJ/mol}$) and is connected with immediate increase of temperature measured by pyrometer as indicates sharp temperature increase in Figure 3. In all experimental runs the maximum observed foaming temperature was around 1750 °C. After that temperature was reached the immediate cooling of the sample was performed.

**Figure 4.** Typical results of different foaming conditions: left – sample foamed just below ignition temperature, heating rate 90°C/min, porosity 18%; right – sample foamed above ignition temperature, heating rate 220°C/min, porosity 44%.

**Figure 5.** Microstructure of fractured foam and pore wall EDS point analyses of fractured cell wall of TiC – TiB$_2$ foam, solar foaming inside alumina tube at heating rate of 220°C/min: Spectra 1-3 - TiB$_2$, Spectrum 5 - TiC, Spectrum 4 - TiB$_x$C$_{1-x}$.

Various authors mention various ignition temperatures according to the used method of preparation: Bhaumik et al. are observed ignition temperature of 1977 °C [1]. In review work of Vallauri et al. [3] are mentioned various ignition temperatures in the range of 950°C - 1977°C according to the used technology, used materials mixtures and due to the production time and pressure. In the present work it was found that during solar foaming of the green compacts of powder mixture of Ti + 15 vol.% B$_4$C the foaming temperature or ignition temperature is around 1380 °C at optimal heating rate of 220°C/min. For higher hearing rates it is a little bit higher due to the heterogeneous temperature distribution within the sample with regard to pyrometer spot size. Inside foam pore walls EDS investigations confirmed the creation of TiB$_2$, TiC and complex TiB$_x$C$_{1-x}$ phases (Figure 5).

Most of foaming technologies of metals and ceramics require usually the optimization of foaming parameters [7]. It was shown, that during solar foaming of TiC–TiB$_2$ foam the most important parameter was heating rate of the sample. As indicates Figure 6 at low heating rates during foaming sample mostly undergoes exothermic reaction without any significant volume changes. At very high heating rates the foam not only underwent volume changes, but also certain collapse of foam is observed due to the overheating and inhomogeneous cooling during solidification. From the set of
investigated heating rates of 90, 170, 220, 260, 300 and 1700 °C/min the optimal heating rate was found to be around 220°C/min.

Figure 6. Effect of heating rate on solar foaming of TiC – TiB₂: left - heating rate 90°C/min; middle - heating rate 220°C/min; right - heating rate 300°C/min.

When it is necessary to foam complex 3D parts it is often required to use certain number of precursor pieces that will join during foaming into the single foam. Therefore this possibility for the investigated material was also tested. As proved in Figure 7 it is possible using solar foaming to create TiC–TiB₂ foam from more than one piece of precursor.

Figure 7. Joining of two precursor pieces during foaming in solar furnace: left – precursors before foaming; right – foam created from them at heating rate of 220°C/min.

Another important technological problem is a proper choice of the material for 3D moulds [8]. In this work alumina and graphite tubes were used to test the suitability of these materials for foaming of TiC–TiB₂ foam. The results are promising, but not fully satisfactory: Graphite is not suitable for due to high thermal conductivity leading to significant foam collapse during cooling process due to slower solidification (see Figure 8). On the contrary low thermally conductive alumina behaved much better. Unfortunately, the temperatures during exothermic reaction led to the reaction of foaming material with alumina. More experiments are needed in the next future. It is proposed to test zirconium or YSZ ceramic as a mould material, which will probably not react with the investigated composite mixture.

Figure 8. TiC – TiB₂ foams foamed at various moulds at heating rate 220°C/min: left – graphite mould with evident foam collapse; right - alumina mould with evident cracking of mould.
4. Conclusions
The experiments showed that it is possible to prepare TiC–TiB₂ ceramic foams with porosity around 45% using self-propagating high-temperature synthesis from the green compacts of Ti + 15 vol.% B₄C. The foaming temperature or ignition temperature is around 1380 °C and optimal heating rate is around 220°C/min. TiB₂, TiC and complex TiBₓC₁₋ₓ phases were observed using EDS investigations.

It was shown experimentally, that it is possible to create ceramic foam from more than one piece of precursor. Further experiments solved the problem with the proper moulding to obtain desired 3D shapes from TiC–TiB₂ ceramic foam: Graphite was not suitable due to high thermal conductivity leading to foam collapse during cooling. Low thermally conductive alumina was better, however reacted with foaming material. In the next future, it is proposed to test zirconium or YSZ ceramic as a mould material. The results are also promising for preparation of Ti based foams with certain amount of TiC–TiB₂ ceramic for biomedical applications [9].

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