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MICROWAVE ASSISTED SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF Ti_3SiC_2 MAX PHASE

A method was developed to manufacture Ti_3SiC_2 MAX phase preforms characterized by open porosity. Samples compacted from elemental powders of Ti, SiC and C with the molar ratio of 3:1.2:1 were heated and synthesized in a microwave field under atmospheric pressure. As this particular composition of elements exhibits rather low reactivity, it was necessary to apply the "coupled" mode of the SHS method. The initiated synthesis first proceeded with the formation of Si-Ti intermetallic and TiC precipitates, whose highly exothermic reactions resulted in a significant increase in temperature to ca. 1800°C. Next, these phases were almost completely transformed into a plate-like Ti_3SiC_2 MAX phase forming the porous structure of the samples. Although the majority of the synthesized material consisted of Ti_3SiC_2, some inclusions such as $TiSi_2$, TiC and SiC were also found and identified in the material by the means of scanning electron microscopy and XRD analysis. The manufactured preforms can be used for components working in extreme conditions (heat exchangers, catalyst substrates, filters) or as a reinforcement for composite materials.

Keywords: MAX phases, SHS synthesis, microwave, porous microstructure

WSPOMAGANA MIKROFALAMI SAMOROZPRZESTRZENIAJĄCA SIĘ WYSOKOTEMPERATUROWA SYNTEZA FAZY Ti_3SiC_2 TYPU MAX

Opracowano metodę wytwarzania preform fazy Ti_3SiC_2 typu MAX o porowatości otwartej. Sprasowane z proszków elementarnych Ti, SiC i C w stosunku molowym 3:1.2:1 próbki ogrzewano i syntetyzowano w polu mikrofalowym pod ciśnieniem atmosferycznym. Ponieważ ta szczególna kompozycja pierwiastków wykazuje relatywnie niską reaktywność, konieczne było zastosowanie "sprzężonego" trybu metody SHS. Po inicjacji syntezy jako pierwsze wytworzone zostają fazy: Si-Ti i TiC, pomiędzy którymi zachodzą wysoce egzotermiczne reakcje powodujące gwałtowny wzrost temperatury do ok. 1800°C. Następnie fazy te są niemal całkowicie przekształcane w płytkowe wydzielenia fazy Ti_3SiC_2 typu MAX, formując jednocześnie porowatą strukturę kształtek. Pomimo faktu, iż w przeważającej część otrzymany materiał stanowiło Ti_3SiC_2, znaleziono w nim również niewielkie ilości wtrąceń, które za pomocą skaningowej mikroskopii elektronowej (SEM) oraz analizy składu chemicznego metodą dyfrakcji rentgenowskiej (XRD) zidentyfikowano jako $TiSi_2$, TiC i SiC. Wytworzone preformy mogą znaleźć zastosowanie w budowie elementów pracujących w ekstremalnych warunkach (wymienniki ciepła, katalizatory, filtry) lub jako wzmocnienia materiałów kompozytowych.

Słowa kluczowe: fazy MAX, synteza SHS, mikrofale, porowata mikrostruktura

INTRODUCTION

Ternary carbides or nitrides, defined by the general formula $M_{n+1}AX_n$ and commonly called MAX phases, combine the best features of metals and ceramics in a unique way. The symbol M belongs to the group of early transition metals, A is an element such as Al, Ga, In, Ge, Sn, Pb, Si, and X stands for carbon or nitrogen. They are also called machinable ceramics with a molecular structure of layered three-component systems [1].

Titanium-silicon carbide (Ti_3SiC_2) is one of the most frequently described MAX phases type with a 312 structure. It was correctly identified for the first time by Jeitschko and Nowotny in 1967 [2]. It was described earlier by Bruckle, who however, described it as Ti_2SiC [3]. Its hexagonal crystalline structure, with the space group $P6_3/mmc$ and crystal lattice parameters a = 3.06 A, c = 17.66 A, is composed of Si atoms separated from each other by three Ti layers that accumulate C atoms around each other [4]. MAX phases remarkably merge the best features of metals and ceramics, being electrically and thermally conductive, readily machinable and highly resistant to extreme conditions

(wear, oxidation, corrosion, chemical environments). Moreover, they possess a low coefficient of thermal expansion and good mechanical properties, even at elevated temperatures. MAX phases can be used, among others, as liquid metal or hot gas filters, vibration damping materials, oxidation resistant coatings, biomedical materials for the production of biocompatible implants, engine components, heat exchangers, catalysts or electrodes [5-9].

Among the most commonly reported methods of Ti_3SiC_2 MAX phase manufacturing, both in powder or bulk shape, the following examples can be distinguished [10, 11]: hot pressing (HP), reactive hot pressing (RHP), hot isostatic pressing (HIP), self-propagating high-temperature synthesis (SHS), in situ and spark plasma sintering (SPS). SHS is one of the most efficient fabrication methods, usually strictly connected with the formation of porosities in the material, which is highly beneficial to create spatial open-porous preforms. Microwave assisted self-propagating SHS is a variation of conventional SHS, in which the source of heat is microwave radiation [12-14]. In contrast to conventional heating methods, microwave heating allows heating of the sample material from the inside, in a fast and effective manner. Depending on the location of the sample in the reactor chamber, the maximum electric or magnetic components of the microwave radiation are focused on the sample. The advantages of microwave heating include: the possibility of selective heating of the sample from the inside, a high degree of automation and that it is an efficient process that does not require large amounts energy.

In the presented study porous MAX phase skeletons were successfully manufactured by the means of microwave assisted self-propagating high-temperature synthesis (MASHS). Ti_3SiC_2 open-porous MAX phase preforms were prepared and characterized by means of scanning electron microscopy and XRD analysis.

EXPERIMENTAL METHODS AND APPROACH

Commercial powders of Ti (99.5% Ti, –325 mesh size, Alfa Aesar), SiC (99.9% SiC, –325 mesh size, Alfa Aesar) and graphite (99.5% C, –325 mesh size, SGL Carbon Ltd graphite) were used as the starting materials to fabricate Ti_3SiC_2. To prepare a stoichiometric reactant mixture, the following Ti:SiC:C molar ratio was used: 3:1.2:1. The above composition was employed to manufacture the MAX phase material by the coupled microwave assisted self-propagating high--temperature synthesis (MASHS) method. The amounts of Ti, SiC, and C powders were firstly weighed with the accuracy to 0.001 g and mixed in a ball mill with ZrO_2 balls for 10 minutes. Subsequently, the powders were uniaxially cold-pressed in a hydraulic press into samples in the shape of pellets with a 22 mm diameter under the pressure of 930 MPa for 60 seconds. Afterwards, the prepared samples were subjected to MASHS, which was conducted in a microwave reactor [15]. The magnetron power was adjusted to the range of 300÷400 W. The green samples were additionally isolated with Saffil fibre. As the Ti-SiC-C composition is not reactive enough to start the synthesis by itself, it was necessary to apply SHS in its "coupled" mode. Thus a second pellet was prepared from a Ti-Al-C system, elaborated by the authors in previous studies [16, 17]. The Ti-SiC-C compact was placed on the Ti-Al-C one and during SHS of the first pellet, the second one was ignited. The ignition temperature for the Ti-Al-C system equaled ~670°C, when the melting point of Al was attained, and the exothermic combustion reaction of this sample triggered initiation of the synthesis in the Ti-SiC-C system. The whole reaction took place in an inert Ar atmosphere. The temperature was measured by a Raytek Marathon MM pyrometer with a measuring spot diameter of 0.6 mm. For the produced preforms structure observation and XRD phase identification were performed with a Hitachi 3000 TM scanning microscope and a Bruker AXS D8 Advance diffractometer.

RESULTS AND DISCUSSION

MASHS

Figure 1 shows exemplary temperature dependencies in the function of time during MASHS in the analyzed system - Ti-Si-C, and in the Ti-Al-C one for the purpose of comparison. The synthesis of Ti_3SiC_2 requires a significantly higher energy input than the one for the Ti-Al-C system (containing highly reactive Al), especially when SiC is used as the source of Si because of the low reactivity of the substrates. Therefore, the necessity to apply the coupled mode of SHS occurs. Coupled SHS was elaborated and extensively studied by Merzhanov et al. [18, 19].

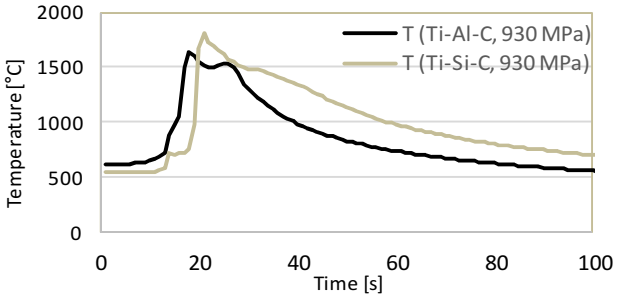

Fig. 1. Temperature-time dependencies of coupled SHS in Ti-Si-C systems (Ti-Al-C was added as reference)

Rys. 1. Zależność temperatury od czasu dla sprzężonej syntezy SHS w układzie Ti-Si-C (krzywa odpowiadająca Ti-Al-C dla porównania)

As Si tends to evaporate partially during SHS, the Si excess was taken into account by increasing the molar ratio of the initial mixture Ti:SiC:C to 3:1.2:1. The reason why SiC was chosen instead of free Si is be-

cause in previously reported studies it was found to promote the formation of high purity Ti_3SiC_2 [20]. Moreover, this particular composition was reported by Saeed et al. to maximize the Ti_3SiC_2 content in the material synthesized by SHS [7].

In the case of the coupled SHS technique, the temperature measurement is recorded from the surface of the Ti-Si-C sample, for which the maximum reaction temperature exceeds 1800°C. After the synthesis, samples of both systems can be taken and analyzed separately. The synthesis initiates shortly after the start of microwave heating. In the Ti-Al-C system the SHS reaction is initiated at a temperature of ~670°C, corresponding to the melting point of aluminum. Subsequently, the reaction propagation front passes simultaneously through the entire volume of the sample. Thus, the Ti-Al-C sample, in which the SHS reaction occurs earlier, creates an energy impact, which corresponds to the first peak visible on the curve for the Ti-Si-C system. The subsequent temperature drop may be responsible for the energy absorbed by the allotropy transformation of Ti. It is considered that if the SHS reaction temperature does not exceed 1330°C, which is the lowest Ti-Si eutectic point, then SHS is based on a solid-solid reaction [20]. In this case, due to the higher reached temperature, it was a diffusive solid-liquid reaction, but only with a small amount of liquid phase. In the case of a Ti/SiC/C composition, the reaction mechanism is initiated by the dissolution of SiC carbide in the Ti particles [20], resulting in Ti-Si intermetallic and free C. Simultaneously, C and Ti create TiC during a highly exothermic reaction of TiC formation, which allows the SHS synthesis to be self-sustaining. After the intermetallic Ti-Si phase is formed, it further reacts with TiC in order to fabricate Ti_3SiC_2. The presence of additional phases in the material during the synthesis of Ti_3SiC_2 may be additionally caused by its decomposition at elevated temperatures. In this case, during the solidification stage the MAX Ti_3SiC_2 is formed together with secondary phases: $TiSi_2$, TiC and SiC.

After the synthesis the reactant pellet was only slightly deformed, which can be explained by the solid-liquid reaction mechanism with a limited amount of liquid phase, described by Equations (1)-(3) and Figure 2.

$$SiC + Ti \rightarrow Ti - Si + C \quad (1)$$

$$Ti + C \rightarrow TiC \quad (2)$$

$$Ti - Si + TiC \rightarrow Ti_3SiC_2 \quad (3)$$

Microstructure and XRD analysis

Figure 3a presents the overall porosity of the obtained material. In this case, the porosities are much more uniform, regular and finer than in i.e. the Ti-Al-C system, which allows the authors to suppose that this material will be characterized by a good homogeneity of properties. The Ti_3SiC_2 phase consists of elongated plate-like grains 10÷20 μm in length and 1÷3 μm in thickness, which are connected together in the form of layered nanolaminates. In Figure 3b, on the surface of a sample fracture, the microstructure of the Ti_3SiC_2 MAX phase with characteristic round TiC inclusions is shown. The presence of hard carbides is expected to be beneficial for resistance to brittle fracture as it should block the propagation of cracks within the material [21]. The XRD analysis of the sample fracture indicated Ti_3SiC_2 as well as inclusions of: $TiSi_2$, TiC and SiC. The possible limitation of the amount of SiC in the substrate composition could help to eliminate the remaining SiC phase. In the synthesized material, unlike reported in other papers [10], no Ti_5Si_3 inclusions were found.

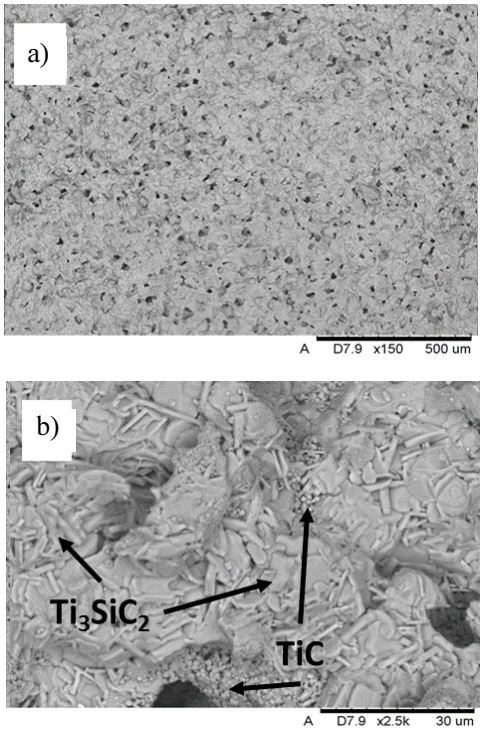

Fig. 3. Overall porosity of manufactured material after SHS (a), Ti_3SiC_2 microstructure with round TiC inclusions (b)

Rys. 3. Widok ogólnej porowatości materiału po syntezie SHS (a), mikrostruktura fazy Ti_3SiC_2 z kulistymi wtrąceniami TiC (b)

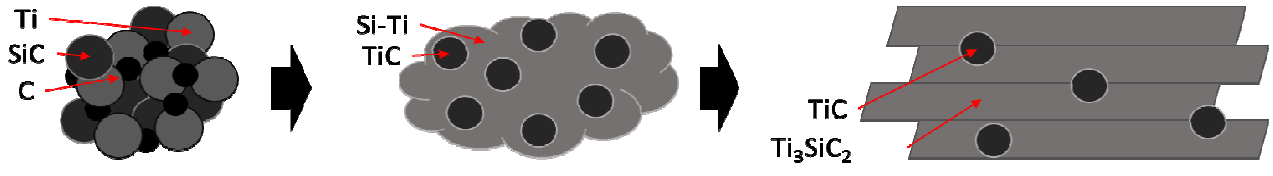

Fig. 2. Scheme of MAX phase formation in Ti-Si-C system

Rys. 2. Schemat powstawania faz typu MAX w układzie Ti-Si-C

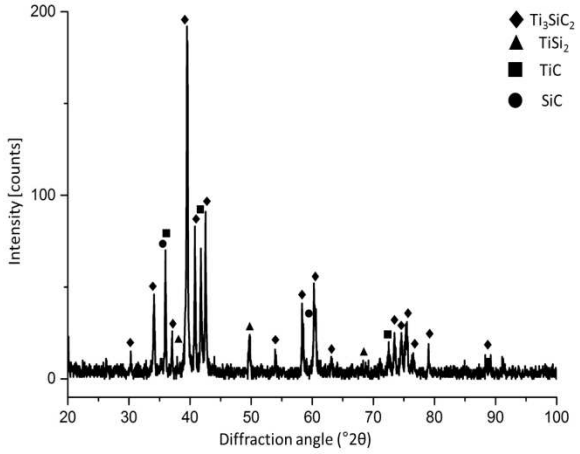

Fig. 4. XRD analysis of manufactured preform

Rys. 4. Analiza XRD wytworzonej preformy

CONCLUSIONS

Ti_3SiC_2 MAX phase preforms were successfully fabricated using the selected molar ratio of Ti:SiC:C as 3:1.2:1 in microwave assisted self-propagating high-temperature synthesis. The course of the synthesis started with a highly exothermic reaction of the formation of TiC carbide and an Si-Ti intermetallic phase. The synthesis temperature, at its maximum value, exceeded 1800°C. Subsequently, these intermediate phases were transformed into Ti_3SiC_2 MAX phase platelets. Although the obtained material exhibits rather high purity, it includes $TiSi_2$, TiC and SiC inclusions. MASHS allows MAX phase preforms with open porosity in the Ti-Si-C system to be obtained in a shorter and more energy-efficient process than conventionally used powder metallurgy methods.

Acknowledgements

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