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COMPOSITES THEORY AND PRACTICE

Anna Koniuszewska*, Krzysztof Naplocha

Wrocław University of Technology, Faculty of Mechanical Engineering, Chair of Foundry, Plastics and Automation, ul. Łukasiewicza 5, 50-371, Wrocław, Poland
**Corresponding author. E-mail: anna.koniuszewska@pwr.edu.pl*

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MICROWAVE ASSISTED SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF Ti_2AlC MAX PHASE

A novel manufacturing method of Ti_2AlC MAX phases with TiC carbides was elaborated. Compacted from elemental powders, the samples were heated and synthesized in a microwave field under atmospheric pressure. Microwave radiation selectively heats the reactant particles, though additional SiC support was required. Graphite can be classified as a good absorber whereas in Al, Ti metallic particle electric eddy currents are induced only on the surface. Microwaves heat material from the inside to the outside and usually concentrate on the interface between materials with a different dielectric loss factor. Therefore, it is possible to induce and conduct the reaction, on the microscale, at metal-ceramic or even metal-metal contact points. Energy was transferred from the magnetron through the waveguide and after a few seconds synthesis began and spread to the entire volume of the cylindrical sample. The initiated SHS synthesis first proceeded with the formation of Al-Ti intermetallic and TiC precipitates whose highly exothermic reactions resulted in a significant increase in temperature to ca. 1600°C. Next, these phases are almost completely transformed into plate-like Ti-Al-C MAX phases forming a porous structure of the samples. Such materials can be ideal for components working in extreme conditions (heat exchangers, catalyst substrates, filters) or for composite reinforcing.

Keywords: **MAX phases, SHS synthesis, microwave, porous structure**

WSPOMAGANA MIKROFALAMI SAMOROZPRZESTRZENIAJĄCA SIĘ WYSOKOTEMPERATUROWA SYNTEZA FAZY Ti_2AlC TYPU MAX

Opracowano metodę wytwarzania MAX faz typu Ti_2AlC zawierającej wtrącenia węglików TiC. W celu zainicjowania syntezy wypraskę z proszków nagrzewano w polu mikrofalowym pod ciśnieniem atmosferycznym. Promieniowanie mikrofalowe selektywnie nagrzewa proszki substratów, jednakże zastosowano dodatkowo podkładkę wykonaną z SiC, która pełniła rolę absorbera. Grafit jest uważany za materiał dobrze pochłaniający energię mikrofalową, natomiast na powierzchni drobnych cząstek metalicznych Al, Ti są indukowane prądy elektryczne, co przy określonej oporności skutkuje wzrostem temperatury. Mikrofale nagrzewają materiał od wewnątrz i często koncentrują się na styku pomiędzy materiałami o różnym współczynniku strat dielektrycznych. W związku z tym możliwe jest indukowanie i kontrolowanie reakcji na styku cząstek metal-ceramika czy nawet metal-metal. Energia mikrofalowa była przenoszona z magnetronu, za pomocą falowodu, do komory procesowej, aby po kilku sekundach uruchomić syntezę SHS, która rozprzestrzeniała się w całej objętości cylindrycznej próbki. Po zainicjowaniu reakcji powstawały związki międzymetaliczne typu Ti-Al oraz węgliki TiC, co wydzielało znaczne ilości ciepła, powodując wzrost temperatury do ok. 1600°C. Następnie, związki te prawie całkowicie przekształcają się w płytkowe Ti-Al-C MAX fazy, które w makroskali tworzą porowatą strukturę próbki. Materiały takie mogą być wykorzystane na elementy pracujące w ekstremalnych warunkach (wymienniki ciepła, katalizatory, filtry) lub jako umocnienie materiałów kompozytowych.

Słowa kluczowe: **fazy MAX, synteza SHS, mikrofale, porowata struktura**

INTRODUCTION

The general formula of MAX phases can be presented as $M_{n+1}AXn$ (MAX) where $n = 1, 2, 3$, M stands for an early transition metal, A is an IIIA or IVA element and X is either carbon or nitrogen [1]. Al containing a MAX phase can only have Ti, V, Cr, Nb or Ta as its M elements. Intermetallic MAX phases are called 'machinable ceramics', because they merge some of the best features of metals and ceramics. They are electrically and thermally conductive, readily machinable, plastic at elevated temperatures, relatively soft, damage tolerant and insensitive to thermal shock like metals. On the other hand, they are lightweight, creep, fatigue, corrosion and oxidation resistant, they show high mechanical strength at high temperatures and have a high elastic modulus and high fracture toughness just like ceramics. Regarding their molecular structure these materials are also hugely anisotropic, and they have a nanolaminate structure. Among the 70 different MAX phases discovered, Ti_2AlC is the most lightweight one. Its density is 4.11 g/cm^3. Ti_2AlC has good thermal (46 W/mK) and electrical (2,78 $\mu\Omega^{-1}m^{-1}$) conductivity, which indicates its possible applications such as high temperature electrodes, heating elements and gas burner nozzles. At room temperature, Ti_2AlC porous materials exhibit extremely high energy absorption during cyclic deformation [2, 3].

Many of the previous works on MAX phases have focused on producing fully dense materials [4-6] but they are an excellent candidate for porous materials as well. Due to their unique characteristics, they are ideal for high performance applications as lightweight components that work in extreme conditions i.e. heat exchangers, catalyst substrates, impact-resistant structures, solar volumetric collectors, diesel particle filters, rotating electrical contacts and bearings, nozzles and tools for die pressing [7, 8].

Two kinds of methods are usually used for producing ternary carbides: reactive sintering with proper starting reactants including hot pressure (HP) sintering, hot isostatic pressure (HIP) sintering and spark plasma sintering (SPS) and the other is combustion synthesis (SHS synthesis) including: the use of elemental powders as raw materials or the aluminothermic process. In SHS we can find a couple of disadvantages such as a high amount of residual phases (even 30% of volume), especially TiC, whose formation is usually difficult to avoid [9, 10].

As can be noticed, the main method of producing such materials is sintering which is time, cost and energy consuming. As an alternative method used for ceramics production which consumes much less energy, there is self-propagating high-temperature synthesis (SHS). The SHS synthesis of Ti-Al-C systems leads to the formation of Ti_2AlC and Ti_3AlC_2. The maximum temperature of the SHS synthesis of MAX phases is typically 1350÷1500°C [11-13]. In Poland, research on SHS synthesis used for obtaining MAX phases was reported by scientists from Cracow [4-6]. Lis and Pampuch performed one of the first successful studies on fabricating bulk MAX phases (in the 1990s). In addition, Godlewska reported conducting research in the field of the conventional combustion synthesis of Mg2Si [14].

In comparison with regular SHS processes, Microwave Assisted SHS (MASHS) is able to heat samples both selectively or volumetrically, according to the substrates electric and magnetic properties, especially whether they absorb or deflect microwaves.

EXPERIMENTAL METHODS AND APPROACH

For this research, commercial powders of Ti (99.5% Ti, −325), Al (99.9% Al, −325 mesh provided by Alfa Aesar) and graphite (99.5% C, −325SGL Carbon Ltd graphite) as starting materials were used with the molar ratio 2:1:1 to prepare a stoichiometric reactant mixture and fabricate Ti_2AlC by Microwave Assisted Self-propagating High-temperature Synthesis. Regarding the selected powders composition, the starting Ti, Al, C amounts were firstly carefully weighed with the accuracy to 0.001 g. Subsequently, those powders were mixed with ceramic balls for 10 minutes. Afterwards, the powders were uniaxially cold-pressed in a hydraulic press into samples in the shape of pellets 23 mm in diameter under a pressure of 800 MPa for 10 seconds. The weight of each pellet was 4 g. The SHS process took place in a microwave reactor. The scheme of the test stand is shown in Figure 1. The temperature was detected by a Raytek Marathon MM pyrometer with the measuring spot dia. 0.6 mm. Structure and phase identification were performed with a scanning microscope, Hitachi S-3400N and Chemical Analyzer, SwiftED3000.

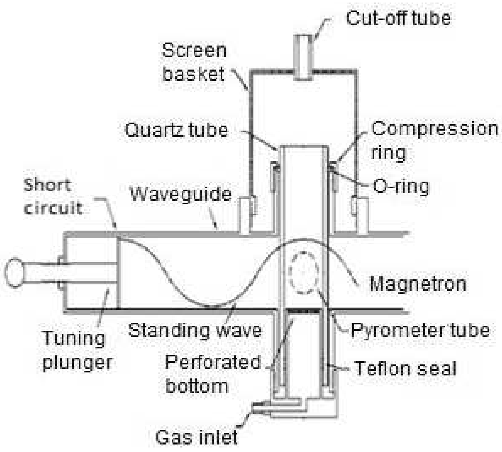

Fig. 1. Diagram of Microwave Assisted Self-propagating High-temperature Synthesis test stand [14]

Rys. 1. Schemat stanowiska badawczego do Samorozprzestrzeniającej się Wysokotemperaturowej Syntezy SHS Wspomaganej Mikrofalami [14]

RESULTS AND DISCUSSION

The sample was placed in the reactor chamber in the area of the greatest magnetic component influence of the generated microwaves [15]. The magnetron power was adjusted to the range of 200÷400 W. The specimen was placed on a Saffil pad, which is invisible for microwaves, and on a SiC pellet, whose role was to boost the reaction above the ignition temperature of the specimen substrates. The whole reaction took place in an inert argon atmosphere. The ignition temperature was reached and the synthesis started at ~670°C, when the melting point of Al was attained, as was reported in previous studies [11, 12]. The combustion temperature exceeded 1600°C and the reaction front went through the whole specimen. An exemplary temperature-time dependence is shown in Figure 2. It is additionally supported with the thermal-derivative analysis that points out the phase-changing points with peaks to facilitate interpretation of the curve. Thus, probably in area A the temperature fluctuation can correspond to the eutectic point between Ti_2AlCx and TiC determined in [16] at 1570°C. Moreover some residues of unreacted Ti particles (saturated with Al) can solidify. Then during cooling at about 1000°C (B area) a thermal effect was observed, which can be attributed to the transformation of sub-stoichiometric titanium carbide TiCx [17].

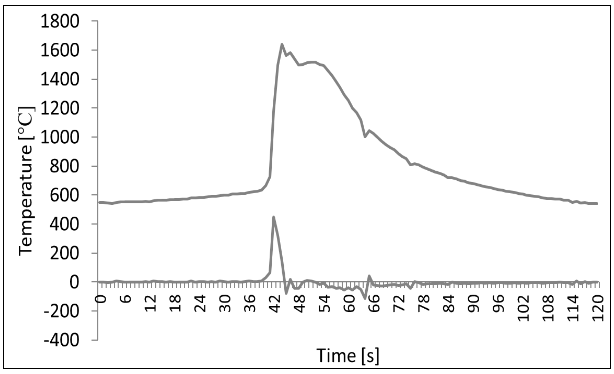

Fig. 2. SHS temperature-time dependence

Rys. 2. Zależność temperatura-czas dla syntezy SHS

After the synthesis, the reactant pellet was severely deformed, which can be explained by the reaction mechanism consisting of several self-sustaining reactions [18]. Ti_2AlC is supposed to be fabricated by a solid-liquid reaction. The firstly formed phases are Al-Ti melt, with Ti cores at the beginning, then TiC is formed at 900÷1200°C [15] together with an additional temperature increase. With the continuous increase in combustion temperature Ti is melted (~1660°C) [11]. Subsequently, most of the TiC dissolves into the liquid phase of Al-Ti and the reactant compact consists of an Al-Ti-C liquid phase. When the temperature decreases, Ti solidifies and forms TiC together with the residual C. During the cooling process, the Ti_2AlC MAX phase is precipitated from the solution of TiC and Al-Ti melt during the peritectic reaction according to the reaction's mechanism.

The final compact consists of Ti_2AlC and TiC inclusions. Compact deformation includes axial elongation and radial contraction. Radial contraction is believed to be caused by tension of the Al-Ti liquid phase. On the other hand, axial elongation is supposed to be caused by the flame propagation direction and the growth of Ti_2AlC grains in a terraced structure.

Figure 3 shows the overall open porosity of the achieved material. Figure 4 shows the microstructure of the Ti_2AlC MAX phase. It can be seen that the Ti_2AlC grains have a plate-like shape, typical for MAX phases, with many nanolaminates in each grain. The grains are distributed irregularly and closely packed into the porous structure. They have a typical size of 10÷20 μm. Exemplary Ti_2AlC grains with nanolaminates areas are indicated in Figure 4.

The line scan analysis presented in Figure 5 shows TiC carbide inclusions in the Ti_2AlC matrix. In the areas where the scan crosses the TiC grains, an explicit decrease in the amount of Al can be seen.

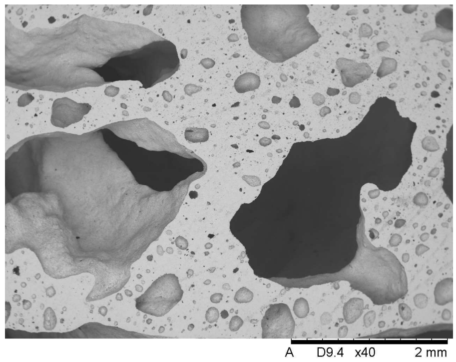

Fig. 3. Surface morphology of MAX phase material

Rys. 3. Morfologia powierzchni fazy typu MAX

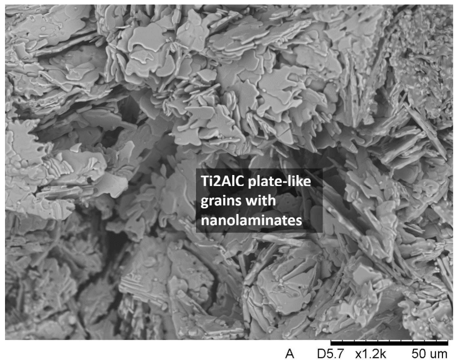

Fig. 4. Ti_2AlC microstructure - SEM observation

Rys. 4. Mikrostruktura Ti_2AlC - obserwacja SEM

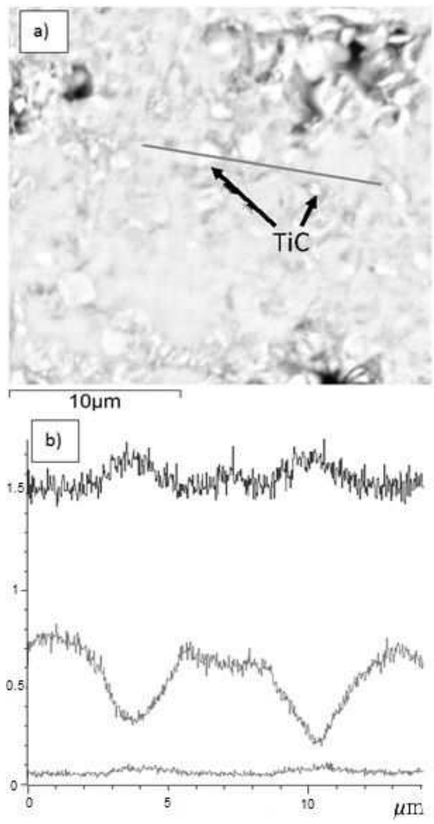

Fig. 5. Chemical analysis of obtained MAX phase material: a) micrograph with marked line scan, b) analysis of elements contents

Rys. 5. Analiza składu chemicznego otrzymanych MAX faz: a) mikrografia z zaznaczonym przebiegiem analizy liniowej, b) analiza zawartości pierwiastków

CONCLUSIONS

The Ti_2AlC MAX phase was successfully fabricated using the selected molar ratio of Ti:Al:C as 2:1:1 in Microwave Assisted Self-propagating High-temperature Synthesis. Sample compacts prepared from powders were subjected to microwave radiation which selectively preheats the substrates and supports the reaction. The synthesis started from highly exothermic reactions formed by the Al-Ti intermetallics and TiC carbides. The maximum temperature was about 1600°C. Next, these compounds were transformed into plate-like Ti_2AlC MAX phases. Although the obtained material exhibits a rather high purity, it still includes TiC crystals. The SHS process ensures a very short reaction time, and its microwave-assisted mode appears to be easily adjustable for MAX phases formation.

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