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TiC AND Al-Ti-C SKELETONS PRODUCED BY COMBUSTION SYNTHESIS

A porous skeleton of TiC carbide was successfully fabricated by combustion synthesis ignited in a microwave field. The synthesizing temperature has been remarkably affected by the time of ball milling or positioning in a single mode microwave reactor. The combustion products were characterized by XRD and SEM investigations. To moderate the reaction and avoid the explosion mode, an aluminium powder was added to the mixture. The prepared TiC, Al-Ti-C skeletons were next infiltrated with an AlSi12 aluminium alloy by the squeeze casting method. The composite materials exhibited a relatively homogeneous microstructure with low porosity.

Keywords: TiC, Al-Ti-C, skeleton, combustion synthesis, microwave, composite

SZKIELETY TiC ORAZ Al-Ti-C OTRZYMYWANE W PROCESIE SYNTEZY SPALENIOWEJ

Porowate szkielety z węgla TiC zostały wytworzone poprzez syntezę spalenkową aktywowaną w polu mikrofalowym. Na temperaturę syntezy znacząco wpływa czas mechanicznego mieszania proszków wyjściowych oraz pozycja próbki w polu reaktora mikrofalowego. Produkty reakcji zostały zbadane w oparciu o analizę XRD oraz na mikroskopie skaningowym z sondą BSE. W celu wyhamowania dynamiki reakcji i uniknięcia eksplozyjnego przebiegu do mieszaniny wyjściowej dodawano proszek Al. Wytworzone kształtki TiC, Al-Ti-C nasączone stopem aluminium AlSi12 metodą prasowania w stanie ciekłym. Kompozyty charakteryzowały się dostatecznie jednorodną mikrostrukturą z nielicznymi porowatościami.

Słowa kluczowe: synteza spalenkowa, mikrofałe, szkielet, TiC, kompozyt

INTRODUCTION

Microwaves as a nonionizing electromagnetic radiation can be successfully used in the selective heating of metallic and ceramic materials [1-4]. As compared to conventional heating, the process proceeds in materials with a reverse thermal gradient, reducing microstructural coarsening or porosity of the sintered minerals [5]. Depending on the absorption mechanism, materials can be classified into dielectric and conductive loss types. Graphite is treated as a dielectric material and its absorption ability could be improved by mechanical milling [6]. In non-ferromagnetic metals (Ti, Al), microwave interaction is restricted to the surface only and relate to an eddy current induced by a microwave field (the magnetic component). In a typical single mode reactor, the energy transmitted from the magnetron through a transmission line is absorbed by material precisely positioned in the applicator for optimum coupling of microwave energy. The field components of electromagnetic radiation can be separated into the nodes of the electric and the magnetic field. Metallic particles, in contrast to graphite, are heated more efficiently in the node of the magnetic field [7, 8]. Microwaves penetrate the skin of metal to depth

δ , moreover their energy decreases to 37 % (1/e) of its surface value. For metals, δ ranges from 0.1 to 10 μm and is defined as [9-11]:

$$\delta = \frac{1}{\sqrt{\pi f \sigma \mu}} \quad (1)$$

where f is the microwave frequency, usually 2,4 GHz, μ is the magnetic permeability and σ is the specific conductivity. For fine metallic powders, the skin significantly affects heating of a particle core, especially since penetration depth increases with temperature [5].

In the presented investigations, microwave heating of particle skin was used for to ignite and support combustion synthesis. The produced TiC skeleton with a sufficiently open porosity was infiltrated with an aluminium alloy for reinforcing composite materials.

EXPERIMENTAL PROCEDURE

AlfaAesar -325 mesh Ti and C powders were milled for 4, 6 10 and 14 h. The processes were performed in a attritor containing hard steel balls of 11 mm in diame-

ter under an argon atmosphere. The ball to powder ratio (BPR) was 20:1; whereas the rotational speed 80 rpm. A specially designed single mode microwave reactor comprising a rectangular waveguide, a chamber with a quartz tube and ended with a tuner was built (see Fig. 1).

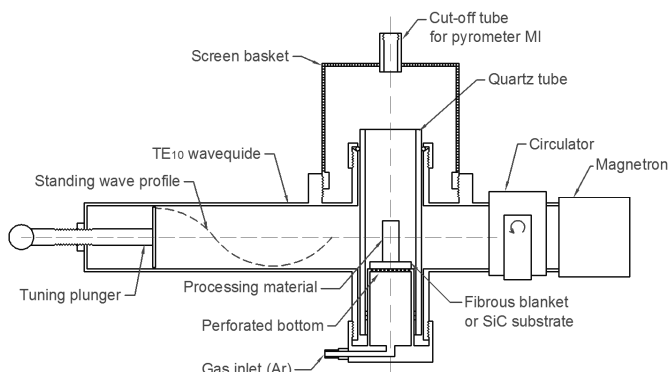


Fig. 1. Diagram of single mode microwave reactor with circulator to protect 2.45 GHz magnetron

Rys. 1. Schemat reaktora mikrofalowego wraz z cyrkulatorem do ochrony magnetronu o częstotliwości 2,45 GHz

The temperature was measured with a Raytek pyrometer and 0.6 mm dia. spot of measuring beam was directed at the centre of the specimen side wall. The produced skeletons were infiltrated with an AlSi12 aluminium alloy (Table 1) by the direct squeeze casting method. Samples preheated to ca. 500°C were placed in the die, poured with molten metal and almost immediately 100 MPa was applied. Structures investigations were performed with an optical microscope and a Hitachi S-3400N scanning microscope equipped with an EDS microanalyser. Phase identification was carried out using a Rigaku Ultima IV X-ray diffractometer.

TABLE 1. Chemical composition of EN AC 44200 aluminium alloy

TABELA 1. Skład chemiczny stopu aluminium EN AC 44200

Alloy	Si	Fe	Mn	Zn	Ti	Al
44200	10.5÷13.5%	0.4%	0.35%	0.1%	0.15%	balance

EXPERIMENTAL RESULTS

The penetration depth for Ti determined from equation (1) is 6.4 μm and with the selected 44 μm Ti particle size, provide a proper r/δ ratio. On the other hand test assumptions based on the complex behavior of the magnetic and dielectric loss factors can lead to ambiguous results and should be verified by experiment. Metallic powder is heated more efficiently in the node of the H_x magnetic field (Fig. 2b) when the internal electric field is induced. However, in some cases, e.g. depending on the size of the particle and level of electrical conductivity, the power absorbed by the sample could be higher in the electric field E_y [8].

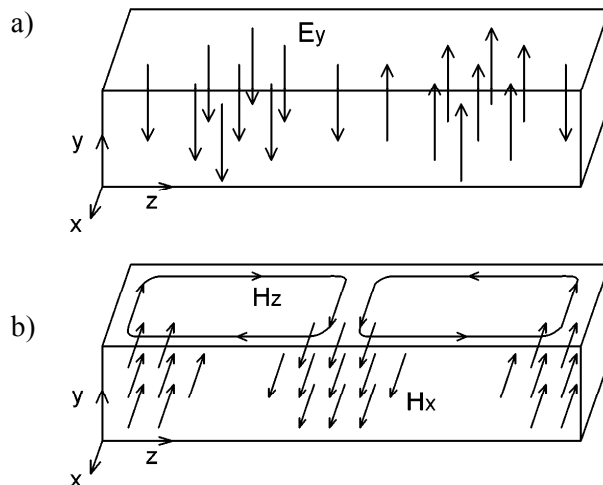


Fig. 2. Electric E field (a) and magnetic H field (b) distribution patterns for TE₁₀ mode waveguide

Rys. 2. Rozmieszczenie składowych elektrycznych E (a) oraz magnetycznych H (b) pola w falowodzie TE₁₀

The ignition of a disc sample pressed under 480 MPa, prepared from powder milled for less than 6 h was impossible. Likewise, when the magnetron was supplied with 300 W of power, a reaction can not start. Using high level microwave energy (600 W) led to an explosive reaction and blowing up of the sample (milled 14 h). Depending on the process parameters, synthesis begins immediately, when the power was turned on (see Fig. 3, A curve), or with an overheating period preceding ignition (curve D) when the specimens were positioned in the electric field node E_y (see Fig. 2). Heating a 10 h milled mixture or with a lower microwave power, slightly reduces the synthesis temperature from 2300 to 2200°C as well as the initial preheating period (15÷30 s) before synthesis occurred (B, C curve). At these process parameters, the reaction proceeded calmly and the TiC skeleton was not destroyed.

Unfortunately, when synthesis proceeds in low temperature conditions with a preheating period, incompletely processed powders were detected in the product (D curve). The XRD analysis of the mixture after milling revealed no reaction nor the presence of the starting powder (Fig. 4). Combusted specimens positioned in the node of H_x , prepared from 10 h ball milled particles comprised only of TiC carbide and their structures were relatively compacted and strong enough for infiltration.

When synthesis was performed with a longer overheating period, numerous close pores were observed in the carbide structure. After infiltration even under high pressure, porosities in the composite microstructure are created (Fig. 5b). Fortunately, the interface between TiC and the reinforcement were developed without porosities or chemical reaction products. The produced composite materials reveal good hardness (increase from 60 to 110 HB) and excellent wear properties.

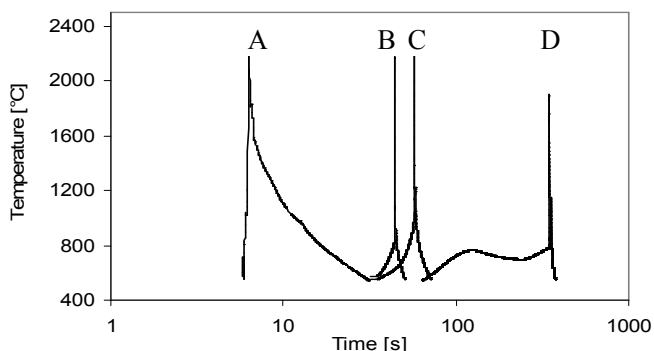


Fig. 3. Synthesis temperature profiles of ball milled Ti-C mixture heated with different microwave power and position. A - 14 h ball milled, 600W microwave power, located in node of H_x magnetic field, B - 10 h-600 W- H_x , C - 10 h-400 W- H_x , D - 14 h-600 W- E_y .

Rys. 3. Profile temperaturowe syntezy mieszaniny Ti-C grzanej przy różnym zasilaniu magnetronu oraz przy różnym ustawieniu próbek w polu reaktora. A - 14 godzin mechanicznie mieszany proszek, 600 W zasilanie, pozycja próbki w składowej magnetycznej H_x , B - 10 h-600 W- H_x , C - 10 h-400 W- H_x , D - 14 h-600 W- E_y .

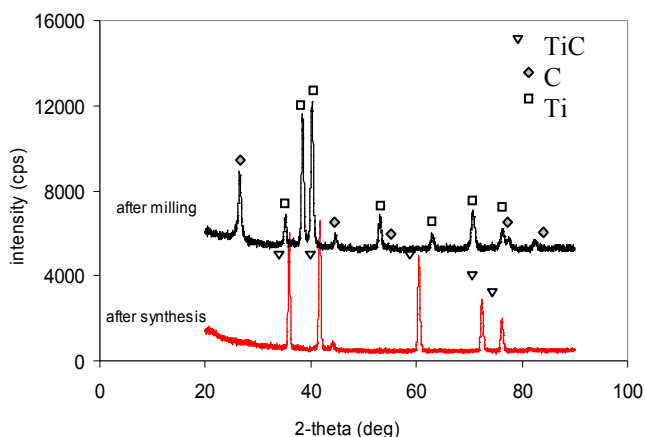


Fig. 4. XRD patterns of ball milled Ti and C particles mixture and TiC combustion product

Rys. 4. Analiza fazowa XRD mechanicznie mieszanych proszków Ti i C oraz produktu reakcji

Another way to moderate the process and produce an open porosity strong skeleton was an addition of Al to the powder mixture and synthesis of them in similar conditions. Using a 20 vol. % of Al facilitated ignition and led to a completely different structure (Fig. 6). Globular compacted grains formed large pores with a relatively smooth wall. The structure was characterized by high strength and open porosity.

The mapping of element distribution (Fig. 7) showed segregation of the Al and Ti, C elements where the Ti-C grains were embedded in a solid Al-Ti solution matrix. In some areas of the matrix where the solution was saturated with a Ti longitudinal, Al_3Ti compounds were formed. EDS microanalyses established rounded grains as a $Ti_{84}Al_{2}C_{14}$ compound. The produced skeletons can be subjected to infiltration though close micro pores and a wall thickness variation could be treated as structure defects.

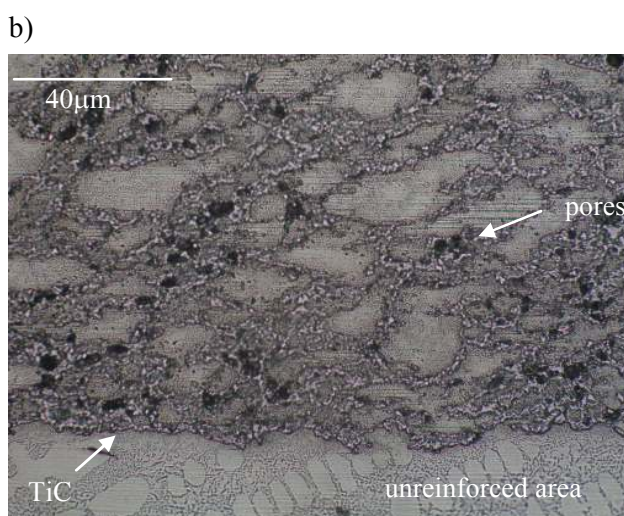
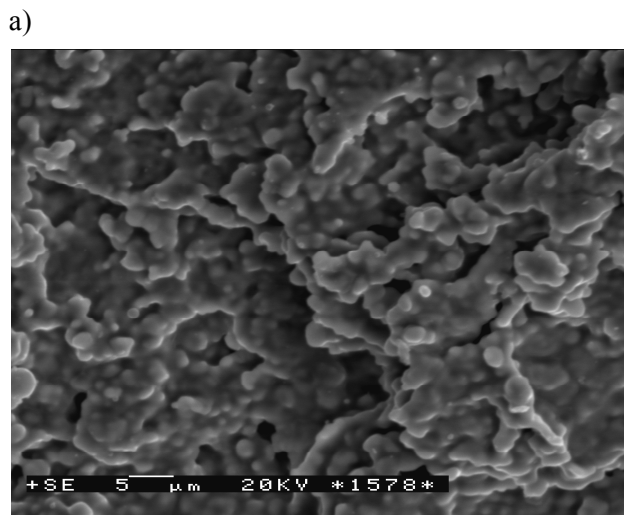


Fig. 5. Fracture of TiC skeleton (a) and siluminum based composite reinforced with it (b)

Rys. 5. Przełom szkieletu TiC (a) oraz umocnionego nim kompozytu na osnowie siluminu (b)

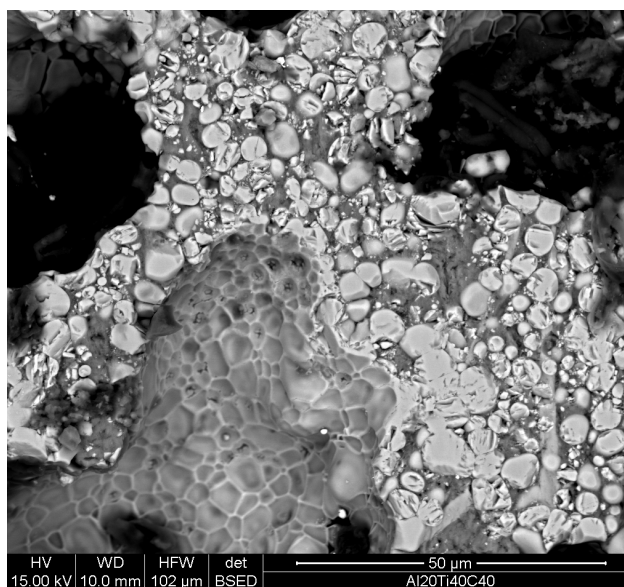


Fig. 6. Microstructure of $Al_2Ti_4C_4$ skeleton

Rys. 6. Mikrostruktura szkieletu $Al_2Ti_4C_4$

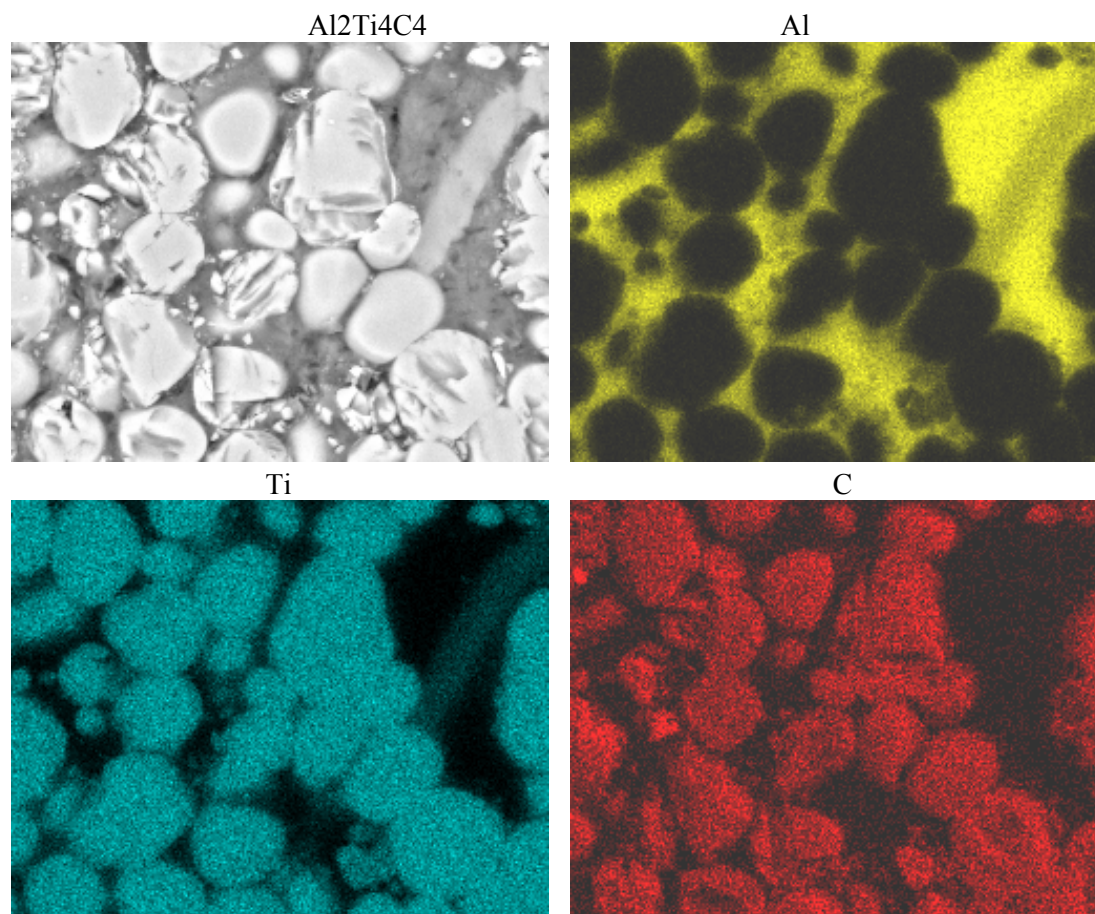


Fig. 7. Mapping of Al, Ti and C elements in $\text{Al}_2\text{Ti}_4\text{C}_4$ specimen
Rys. 7. Rozkład pierwiastków Al, Ti i C w próbce $\text{Al}_2\text{Ti}_4\text{C}_4$

CONCLUSIONS

The effect of milling time and microwave power on the synthesis course was investigated and controlled in order to moderate the reaction and produce a porous skeleton. XRD analysis of the mixture after milling confirmed no reaction nor the presence of the starting powder. Ignition of a disc sample prepared from powder milled less than 6 h was impossible. Similarly, when the magnetron was supplied with a 200–300 W power, a reaction cannot start. On the other hand, using high microwave energy (600 W) resulted in the explosive mode of combustion synthesis. Depending on the process parameters, synthesis can begin immediately, when the power was turned on, or with preheating period preceding ignition.

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