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DEVELOPMENT OF Al-Ti-C POROUS STRUCTURES FOR REINFORCING ALUMINUM MATRIX COMPOSITES

Open-porous preforms from Al-Ti-C compounds were successfully ignited and synthesized by combustion synthesis in a microwave field. The reaction course and the temperature were remarkably affected by the preparation method and molar ratio of the substrates, as well as the position of the green sample in the microwave field generated by a single mode microwave reactor. The manufactured structures were characterized by SEM investigations. The addition of aluminum powder to the mixture moderates the reaction and temperature variations, allowing the course of synthesis in explosive mode to be avoided. Among the reported developed materials the following can be distinguished: Ti-Al intermetallics, titanium carbides and MAX phases belonging to the Ti-Al-C system. The prepared and selected Al-Ti-C preforms were subsequently infiltrated with an AlSi12 aluminum alloy by the squeeze casting method. The composite materials exhibit a relatively homogeneous microstructure with low residual porosity and a good reinforcement/matrix interface.

Keywords: Al-Ti-C, preform, SHS synthesis, microwave, metal matrix composite, MAX phase

OPRACOWANIE POROWATYCH STRUKTUR Al-Ti-C DO UMACNIANIA KOMPOZYTÓW Z OSNOWĄ ALUMINIOWĄ

Otwarte porowate preformy ze związków Al-Ti-C z powodzeniem zapalono i zsyntetyzowano poprzez syntezę spaleniową w polu mikrofalowym. Znaczący wpływ na przebieg i temperaturę reakcji miał sposób przygotowania i stosunek molowy substratów oraz położenie próbki w polu mikrofalowym generowanym przez jednomodowy reaktor mikrofalowy. Wytworzone struktury scharakteryzowano za pomocą badań SEM. Dodatek proszku aluminium do mieszaniny łagodzi przebieg reakcji i zmiany temperatury, pozwalając uniknąć przebiegu syntezy w trybie wybuchowym. Spośród wytworzonych materiałów można wyróżnić następujące: fazy międzymetaliczne Ti-Al, węgliki tytanu i fazy typu MAX należące do układu Ti-Al-C. Przygotowane i wyselekcjonowane preformy Al-Ti-C następnie infiltrowano stopem aluminium AlSi12 metodą prasowania ze stanu ciekłego. Materiały kompozytowe wykazują stosunkowo jednorodną mikrostrukturę o niskiej porowatości resztkowej i dobrej granicy faz umocnienie/osnowa.

Słowa kluczowe: Al-Ti-C, preforma, synteza SHS, mikrofale, kompozyt metaliczny, faza MAX

INTRODUCTION

Microwave-activated SHS (self-propagating high-temperature synthesis), which was defined in [1] as MACS, enables the production of porous structures for the reinforcement of composite materials. Microwave heating improves the process and affects the structure and degree of transformation of the initial mixture of substrates. The benefits of using microwaves or plasma have already been confirmed many times [2, 3]. The microwave radiation falling on the heated material induces an internal electromagnetic field. Depending on the absorption mechanism, the materials can be classified as dielectric-loss materials or heated by conduction losses and the conversion of electrical energy into heat according to the Joule-Lenz law. In terms of the ability to absorb microwaves, graphite can be treated as a dielectric material, and the degree of absorption can be effectively improved by mechanical milling [4]. In non-ferromagnetic metals (Ti, Al), the interaction of microwaves is limited only to the surface and is related to the eddy currents induced by the microwave field (magnetic component). Relating the penetration depth to the Ti particle size, an appropriate r/δ ratio of 3.4 was obtained. On the other hand, taking into account the difficulties in determining the value of the dielectric and magnetic loss factor and the complexity of the heating process, experimental verification is necessary. Usually, a mixture with metallic powders is more efficiently heated in a field with a higher concentration of the magnetic component H_x [5, 6] when surface currents are induced. However, in some cases, with a given particle size and electrical conductivity, energy absorption may be greater in areas with a high intensity of the electrical component E_y [6]. This issue has not yet been thoroughly investigated, and when heating multi-component materials, both mechanisms can occur simultaneously.

One of the most interesting groups of materials existing in the elaborated system is known as MAX type phases. The term is derived from their general formula M_n+1AX_n, (M – early transition metal, A – an element from group A (e.g. Al, Ga, In , Ge, Sn, Pb, Si), X – carbon or nitrogen, n = 1-3) [7]. In spite of their chemical composition and molecular structure, MAX phases can be described as layered ternary carbides or nitrides, but in terms of their properties, they are determined as machinable ceramics [8, 9]. They are characterized by the most beneficial features of metals and ceramics, i.e. high thermal and electrical conductivities, good thermal stability, resistance to oxidation and corrosion. Moreover, MAX phases offer favorable mechanical properties such as tensile and compressive strengths, Young's modulus, hardness and wear resistance, ensuring good machinability at the same time. Both the MAX phases occurring stably in the evaluated system, Ti_2AlC and Ti_3AlC_2, are the most oxidation resistant and the lightest ones. When SHS is applied for manufacturing MAX phases, it promotes the formation of porosity in the material. As a result, spatial open-porous preforms can be obtained and used for additional metal infiltration processes in order to fabricate a composite material. Some of the most challenging aspects of the mentioned infiltration are connected with residual porosity or an unsatisfactory level of pore saturation. Recently published research results on aluminum matrix composites reinforced with Ti-Al-C MAX phases focus on hot pressing (HP) [10] or spark plasma sintering (SPS) [11]. The long reaction time required for both of these techniques leads to the in-situ formation of multiple Ti-Al inclusions (e.g. Al_3Ti, Al_4C_3), deteriorating the quality of the composite. Moreover, in the case of Ti_3AlC_2-Al composites manufactured by SPS, the authors indicate that residual porosity and poor bonding at the matrix-reinforcement interface occur in the material [11]. Another interesting method recently employed for the manufacturing of such metal matrix composites (MMCs) was ultrasonic agitation casting [12], but being a variant of the stir casting method, it is exposed to several difficulties such as density segregation and the tendency of the reinforcement to gather in agglomerates.

In the performed research, microwaves heated the graphite powder volumetrically and metal particles on their outer layer in order to initiate and maintain combustion synthesis. Multiple trials with various selected molar ratios of the substrates in green samples were conducted. Among others, also MAX phase preforms were successfully synthesized. Due to the open porosity, preforms with interconnected voids enabled the subsequent production of dense composite materials reinforced with them. The produced Al-Ti-C compound preforms with appropriate porosity were then saturated with liquid aluminum alloy by means of the squeeze casting pressure infiltration method, thus strengthening the composite casting.

EXPERIMENTAL METHODS AND APPROACH

The synthesis of porous structures may require activation of the powders by mixing in a ball mill. The Ti and C powders (AlfaAesar – 325 mesh) were milled for 4, 6, 10 and 14 h in an attritor containing hard steel balls 11 mm in diameter under argon atmosphere. The ball to powder ratio (BPR) was 20:1, whereas the rotational speed equaled 80 rpm. For the purpose of MAX phase synthesis, the same Ti and C powders were only mixed with aluminum (99.9% Al, AlfaAesar – 325 mesh), maintaining the molar ratio of Ti:Al:C as 2:1:1.

Measured portions of the mixtures were pressed (460 MPa) to produce cylindrical samples. A specially designed single-mode microwave reactor including a chamber with a quartz tube in a rectangular waveguide ended with a tuner was utilized [13]. The compacts were synthesized in different areas of the microwave field with the required magnetron power (400-600 W) for ignition. The temperature was measured with a Raytek pyrometer and the 0.6 mm diameter spot of the measuring beam was directed at the center of the specimen side wall.

The produced preforms were infiltrated by squeeze casting with the EN AC-44200 (10.5-13.5% Si; 0.4% Fe; 0.35% Mn; 0.1% Zn; 0.15% Ti) casting alloy at the temperature of 720-740°C. Firstly the preforms were preheated to 550°C, and shortly before pouring the alloy, they were placed in the die. Almost immediately a pressure of 100 MPa was applied and held for 30-60 s to ensure complete saturation.

Investigations of the structures were performed with a light microscope and a Hitachi S-3400N scanning electron microscope equipped with an EDS microanalyzer SwiftED3000.

RESULTS AND DISCUSSION

Microstructure, XRD and EDS analyses

To control the kinetics of the process as well as the structure and properties of the porous preforms, alloying elements were introduced. One of the most common elements is aluminum, which, when melted, usually initiates the reaction and forms intermetallic compounds. Therefore, attempts to produce preforms with the Al:Ti:C elements in a different stoichiometric ratio were made.

The position in the microwave field was selected experimentally. A special ceramic-metallic insert was

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used to observe the heating (reddening) manner in the microwave module. Then the cylindrical samples were placed in the chamber and the time of ignition was examined. The location of the sample in the area of intense influence of the magnetic component was the most favorable. More details were presented in [14, 15].

The time of high-energy milling affected removal of the oxide layer and the creation of direct contact between the substrates. It was found that longer grinding, 10-14 hours, enabled ignition; nonetheless, the pressing force applied for compacting was also important.

The maximum synthesis temperature for all the conducted preliminary tests did not exceed 1500°C, and with the increase in Ti content, the kinetics of the process grew, determined by the dT/dt parameter. The temperature curve of the Al36Ti29C35 samples (the numbers correspond to the mole percentages) in the heating section pauses at about 635°C, which proves local melting of the Al powder (Fig. 1a, point A). At the temperature of approx. 900°C, the temperature pause may indicate allotropic transformation βTi → αTi (Fig. 1a and 1b, point B). In turn, the temporary slowdown in the temperature drop in the range 1100-1150°C, observed in the Al36Ti29C35 and Al20Ti40C40 samples, may be related to the formation of the $AlTi_3$ compound from the αTi solid solution (Fig. 1a and 1b, point C).

Typically, after melting, disrupting the oxide layer and enhancing diffusion, the liquid aluminum triggers synthesis, which can take place by means of intermediate steps. In the investigated system, it was assumed that the main phase of the reaction would occur between Ti and C. The resulting carbides would harden the matrix and at the same time form a saturable preform. With a smaller, 20% content of Al in the Ti-C mixture, the resulting structure contained spherical grains embedded in the matrix, creating large pores with relatively smooth walls. Such material had high strength and elasticity, but in most cases the porosity was closed.

Next, studies were continued for the composition of constituents enabling the fabrication of MAX phases within the system. Combustion synthesis was initiated when the melting point of Al was reached and then the propagation front went through the whole volume of the sample, leading the liquid-state reaction between the Ti-Al intermetallics and in-situ synthesized TiC. Finally, in region D (approx. 1600°C) MAX phase compounds (Ti_2AlC and Ti_3AlC_2) were produced. Area E corresponds to the reaction between the excess unreacted Ti and C forming TiC, which is the most common inclusion in MAX type phases containing Ti and C.

The Al36Ti29C35 samples with a more balanced proportion of Al and Ti contained evenly distributed lamellar precipitates in the matrix (Fig. 2). The results of EDS analysis for this material are presented in Figure 3. The porous walls are lined with plates protruding from the matrix, which provide an excellent place for mechanical connection with any infiltrating alloy. Unfortunately, in some cases the finer porosities were closed and unevenly distributed. The applied parameters of infiltration, with a higher metal temperature and extended metal saturation time, allowed the residual porosity to be reduced to 5-9%.

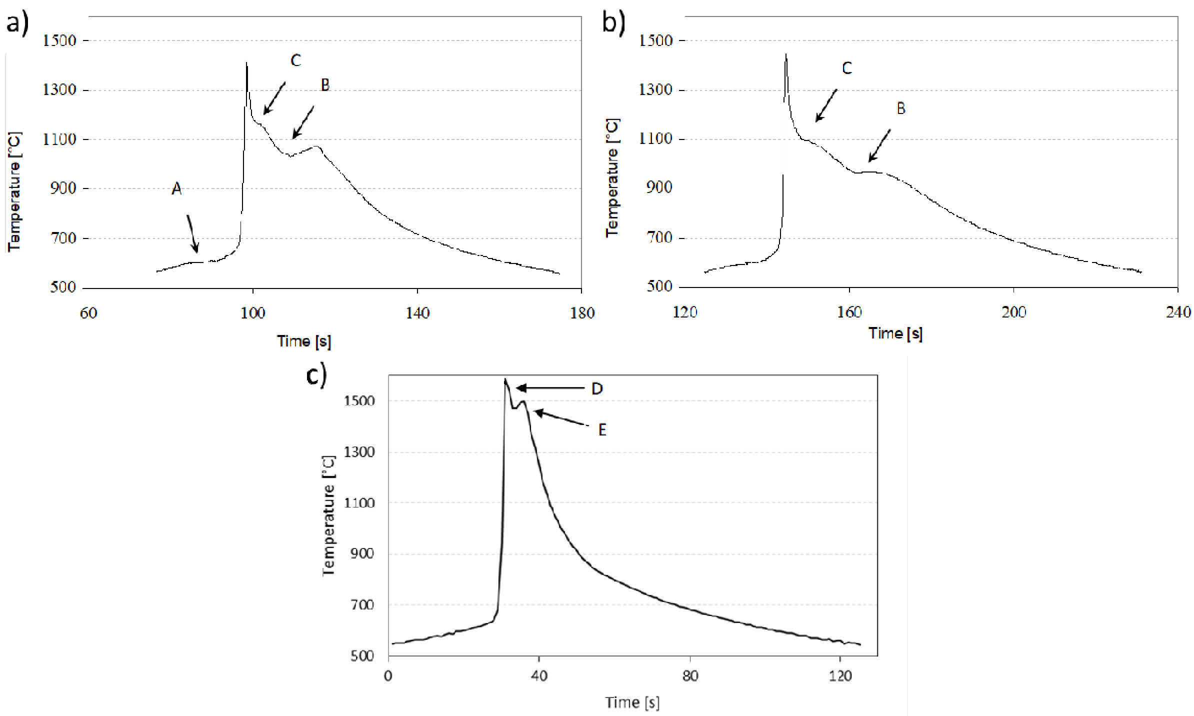

Fig. 1. Temperature profiles for synthesis of preforms: a) Al36Ti29C35, b) Al20Ti40C40, c) Ti-Al-C MAX phases
Rys. 1. Profile temperatur w trakcie syntezy preform: a) Al36Ti29C35, b) Al20Ti40C40, c) Ti-Al-C MAX phases

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Hence, in the next part of the research, more graphite was used to produce the compacts, and the content of the elements can be described by the formula Al36Ti12C52. The analysis of the homogeneity, porosity distribution, and the degree of saturation with the liquid alloy showed relatively regular scattering of pores of similar size (Fig. 4). Unfortunately, most of them, especially the smallest ones, were closed. The solid material had clear cuboidal inclusions that often accumulated around the pores. X-ray microanalysis showed that the matrix is formed by a solid solution of Al (Ti), in which there are small precipitates with a composition that can be described by the formula Ti53Al35C12. Overall, however, the structure was sufficiently homogeneous but possible infiltration, due to the partially closed porosities, may not produce satisfactory results.

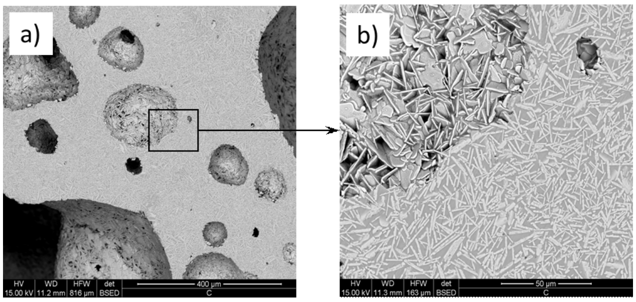
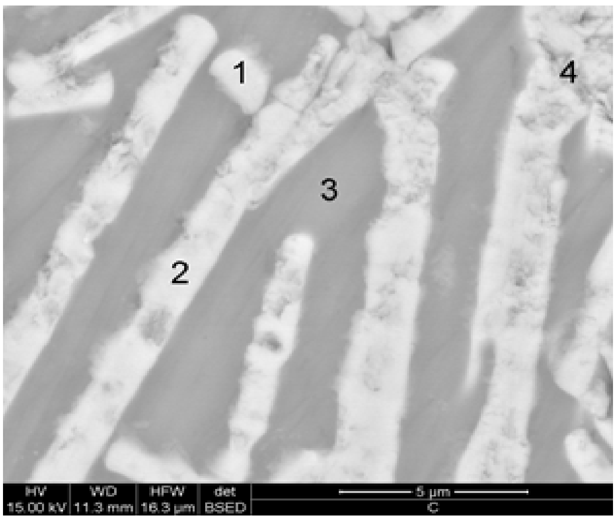


Fig. 2. Microstructure of Al36Ti29C35 specimen (a) with view of pore walls extended by plates protruding from Al3Ti matrix (b)

Rys. 2. Mikrostruktura próbki Al36Ti29C35 (a) z widokiem ścian porowatości z płytkami wystającymi z osnowy Al3Ti (b)



Element	Point [% at.]			
	1 (platelet)	2 (platelet)	3	4
C	6.62	6.97	-	5.86
Al	37.98	32.58	73.76	20.25
Ti	55.40	60.45	26.24	59.27
O	-	-	-	14.62

Fig. 3. Chemical composition analysis of Al36Ti29C35 specimen

Rys. 3. Analiza składu chemicznego próbki Al36Ti29C35

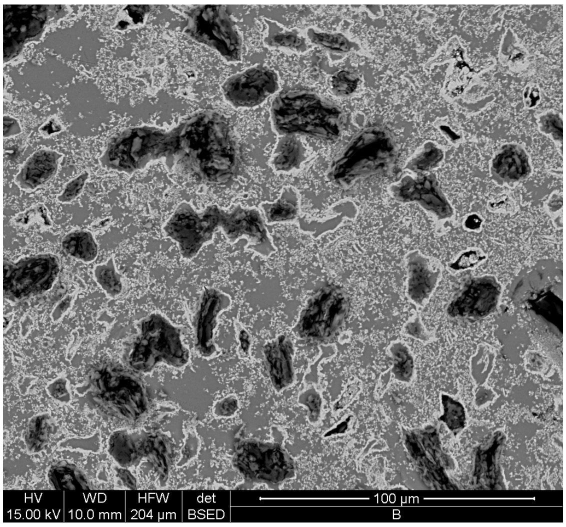


Fig. 4. Microstructure of Al36Ti12C52 specimen, non-homogeneous, mostly closed porosity distribution

Rys. 4. Mikrostruktura próbki Al36Ti12C52, niejednorodny, w większości zamknięty rozkład porowatości

Figure 5 presents the characteristic plate-like structure of the MAX phases (Fig. 5a) and their exemplary EDS test results (Fig. 5b), indicating the presence of Ti_3AlC_2. As stated in [16, 17], when the combustion temperature exceeds 1300°C, the formation of Ti_2AlC is followed by a reaction between Ti_2AlC and TiC, causing the creation of Ti_3AlC_2. After cooling, both of these MAX phases usually coexist in the material, together with some TiC impurities. The longer plates (10-30 μm) correspond to Ti_2AlC, while the smaller ones (5-10 μm) belong to Ti_3AlC_2. The overall porosity of the synthesized preform is shown in Figure 6a, revealing uneven pores with a wide range of sizes. Nevertheless, the created voids are open and interconnected and can be further subjected to the infiltration process. This is also enhanced by the fact that the MAX phase platelets are stacked together in lamellar nanolaminates, connected to each other at different angles, which makes the whole preform possible to be saturated with liquid metal. Such spatial arrangement of reinforcement ensures the isotropy of the mechanical properties [18].

The finally obtained Ti_2AlC-Ti_3AlC_2/Al composite material is presented in Figure 6b. Almost no residual porosity was observed after the squeeze casting infiltration, but it is assumed to take only up to several percent of the whole sample volume. The degree of filling of the preform by the matrix is evaluated as almost complete, as not only the larger pores were saturated, but aluminum was also pressed into narrow spacings between the MAX phase platelets. No additional layers (e.g. oxides or intermetallics) at the interface were found, which proves that no harmful reactions during infiltration or mutual diffusion of the constituents took place in the process. The coherent boundary separating the AlSi12 matrix and Ti_2AlC-Ti_3AlC_2 preform confirms good wettability.

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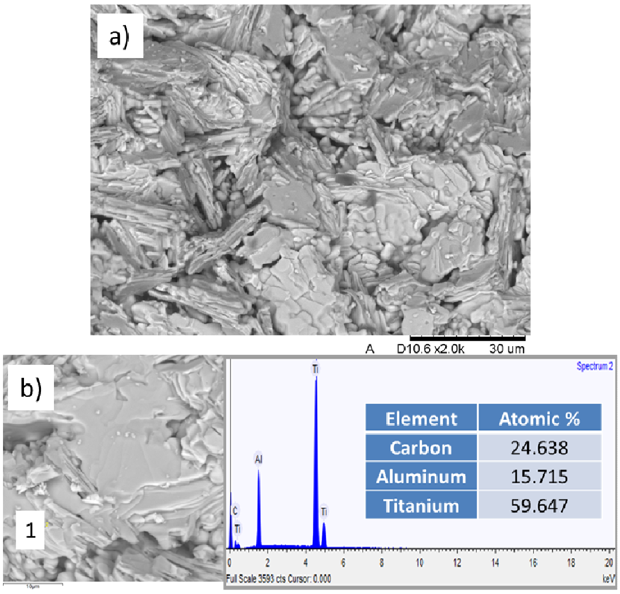

Fig. 5. Plate-like microstructure of Ti_2AlC-Ti_3AlC_2 preform (a), EDS test result for MAX phase platelet (b)

Rys. 5. Płytkowa mikrostruktura preformy Ti_2AlC-Ti_3AlC_2 (a), wyniki EDS dla płytki fazy typu MAX (b)

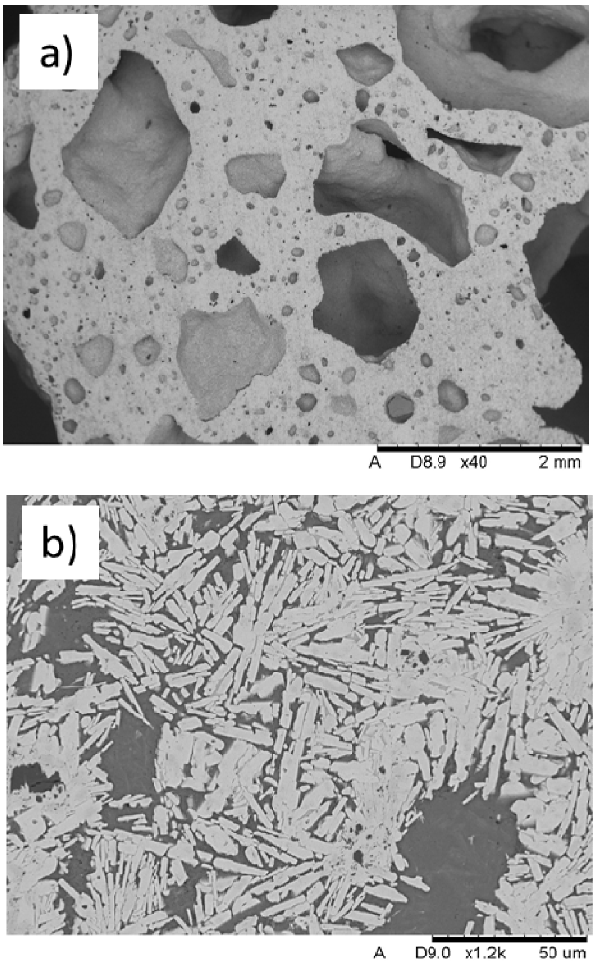

Fig. 6. Ti_2AlC-Ti_3AlC_2 preform: general view of open-porosity (a), after infiltration with AlSi12 alloy (b)

Rys. 6. Preforma Ti_2AlC-Ti_3AlC_2: widok ogólny porowatości otwartej (a), po infiltracji stopem AlSi12 (b)

CONCLUSIONS

A method of producing porous Al-Ti-C preforms that can be used for reinforcing composite materials by various Al-Ti intermetallics and ternary MAX phase carbides was developed. Based on the analysis of the synthesis process and the characteristics of the produced materials, the following conclusions can be drawn:

1. The synthesis of intermetallic preforms begins with the melting of Al particles and develops through several intermediate steps. The rapid course of the reaction and its low temperature can lead to the formation of closed microporosity and incomplete conversion.
2. A balanced proportion of elements in the starting mixture (36% Al + 29% Ti + 35% C) leads to the formation of a porous structure with walls lined with Ti60Al33C7 plates. They can enable good mechanical connection of the preform with the infiltrating alloy and thus a better stress transfer.
3. The reinforcing of composite materials with structures containing Al-Ti-C phases can be used in the production of machine parts exposed to intense wear. The presence of graphite can significantly improve the dry friction performance.
4. The molar ratio of Ti:Al:C equaling 2:1:1 ensures the formation of Ti-Al-C MAX phase preforms via microwave-assisted SHS. No additional steps such as ball milling, apart from weighing and mixing of the powders, are necessary. The manufactured structures are characterized by open porosity and a plate-like microstructure corresponding to the formation of Ti_2AlC and Ti_3AlC_2 platelets.
5. Pressure infiltration under conditions assuring prolonged maintenance of the metal in a liquid state, under high pressure, with a preform of sufficient strength, enables the impregnation of very fine pores and the production of a composite with a compact structure and a good interface between the reinforcement and the matrix. No additional undesired chemical reactions (e.g. oxidation, mutual diffusion, the in-situ formation of secondary products) were observed during the infiltration of Ti-Al-C MAX phases with the AlSi12 alloy, resulting in a well-saturated dense composite material.

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