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A COMPARATIVE STUDY OF THE FEASIBILITY OF CELLULAR MAX PHASE PREFORMS FORMATION BY MICROWAVE-ASSISTED SHS AND SPS TECHNIQUES

Two methods were evaluated in terms of manufacturing of MAX phase preforms characterized with open porosity: microwave-assisted self-propagating high-temperature synthesis (SHS) and spark plasma sintering (SPS). The main purpose of fabrication of such open-porous preforms is that they can be successfully applied as a reinforcement in metal matrix composite (MMC) materials. In order to simulate the most similar conditions to microwave-assisted SHS, the sintering time of SPS was significantly reduced and the pressure was maintained at a minimum value. The chosen approach allows these two methods to be compared in terms of structure homogeneity, complete reactive charge conversion and energy effectivity. Study was performed in Ti-Al-C system, in which the samples were compacted from elemental powders of Ti, Al, C in molar ratio of 2:1:1. Manufactured materials after syntheses were subjected to SEM, XRD and STEM analyses in order to investigate their microstructures and chemical compositions. As was concluded, only microwave-assisted SHS synthesis allows the creation of MAX phases in the studied system. SPS technique led only to the formation of intermetallic secondary phases. The fabrication of MAX phases' foams by microwave-assisted SHS presents some interesting advantages compared to conventional manufacturing methods. This work presents the characterization of foams obtained by microwave-assisted SHS comparing the results with materials produced by SPS. The analysis of SPS products for different sintering temperatures provided the better insight into the synthesis of MAX phases, supporting the established mechanism. Dissimilarities in the heating mechanisms that lead to the differing synthesis products were also discussed.

Keywords: MAX phases, SHS synthesis, microwave, SPS, porous preforms

1. Introduction

Among the group of MAX phases – ternary carbides or nitrides merging the best features of metals and ceramics – two complex carbides, Ti_2AlC and Ti_3AlC_2, can be distinguished as the lightest and the most oxidation resistant ones [1-3]. Ti_2AlC was first obtained by the team of researchers Jeitschko and Nowotny in the form of a thin film manufactured by chemical vapor deposition (CVD) in 1967 [4]. Subsequently, Ivchenko and Lesnaya produced this material by sintering a mixture of Al, Ti, C powders in an Ar protective atmosphere at 1500°C [5]. A group of researchers from Drexel University (USA) under the leadership of M. W. Barsoum contributed significantly to the development of these materials, as their studies showed that it is possible to produce Ti_2AlC by reactive hot pressing (RHP) and reactive hot isostatic pressing (RHIP) from a mixture of Ti, Al_4C_3, C at respectively 1600°C, 40 MPa, 4h and 1300°C, 40 MPa, 30 h [5]. Other researchers have used the in-situ method of hot pressing or spark plasma sintering (SPS). The main disatvantage of these methods is the necessity of long-term use of high-temperature furnaces with high energy consumption.

Ti_3AlC_2 is one of the most extensively studied examples of the MAX type phases with 312 structure. It was identified for the first time by a team of researchers Pietrzyk and Schuster in 1994. As the only one of MAX type phases it shows increased plasticity at elevated temperatures [6]. Ti_3AlC_2 can be obtained during SHS, inter alia, from the following powder mixtures: Ti/Al/C, Ti/Al_4C_3/TiC and Ti/Al/TiC. In most of the described studies, secondary phases of TiC and Ti_2AlC are also present in the product in addition to Ti_3AlC_2 [7]. Ti_3AlC_2 can be also successfully fabricated by SPS [8].

SPS method has been found suitable for compaction of powders through the simultaneous application of direct current pulses of high intensity and mechanical pressure. The electric current induces a temperature elevation within the sample by Joule's effect. The duration of a whole process belongs to the

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TABLE 1

SHS synthesis of MAX phases in Ti-Al-C system

Source	Powders composition	Reaction temperature (T_c) [°C]	MAX phase, vol. content %	Secondary phases
[10]	2Ti/Al/C	2100	Ti_2AlC	TiC, $TiAl_3$, TiAl, Ti_3Al
[11]	2Ti/Al/C	1000-1200	Ti_2AlC, 85%	TiC
[11]	1.5Ti/Al/0.5C/0.5TiC	1000-1200	Ti_2AlC, 90%	TiC
[11]	2Ti/0.25C/0.25Al_4C_3	1000-1200	Ti_2AlC	TiC
[12]	1.2TiAl/Ti/C	1100	Ti_2AlC, 95.4%	$TiAl_2$, 4.6%
[12]	1.1TiAl/2Ti/C	1300	Ti_3AlC_2, 73.8%	Ti_2AlC, 11.3%, TiC 14.9%
[13]	3Ti/Al/2C	1500	Ti_2AlC, Ti_3AlC_2	TiC
[14]	2Ti/Al/C	1600	Ti_2AlC	TiC

range of merely few minutes. This technique enables both faster heating and cooling rates and due to this both the sintering time and grain growth of the specimen are significantly reduced.

On the other hand, SHS, being a highly efficient method, is strictly connected with the formation of porosities in the material, what is beneficial for the creation of spatial open-porous preforms that can be further used as a reinforcement of composite materials [9]. Table 1 gathers the exemplary outcomes of previously reported studies on MAX phases SHS production.

Microwave-assisted SHS synthesis is a variation of conventional SHS, in which the source of heat is microwave radiation [15-20]. In contrast to conventional heating methods, microwaves allow the 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 a lot of energy. The disadvantage of this process is, however, the limitation of the possibility of its use, caused by the diversification of the dielectric features of the powder mixtures, especially in multi-component systems. This results in uneven heating, which may prevent the SHS reaction from initiating [21].

The presented paper evaluates the possibility of production of the open-porous MAX phases skeletons by two different techniques. Materials obtained by microwave-assisted SHS were compared to the ones produced by the means of more conventional technique: spark plasma sintering (SPS). SPS synthesis times were reduced in order to keep the process short and to decide whether it is possible to ignite the exothermic reaction within it. This approach allowed to compare these two methods in terms of structure homogeneity, complete reactive charge conversion and energy efficiency. Moreover, the results obtained via SPS for different sintering temperatures were used to support the reaction mechanism in Ti-Al-C system. As was also presented, thus prepared preforms can be readily applied as a reinforcement in composite materials manufactured by e.g. squeeze casting infiltration.

2. Materials and Methods

Commercial powders of Ti (99.5% Ti, -325, Alfa Aesar), Al (99.9% Al, -325, Alfa Aesar) and graphite (99.5% C, -325, SGL Carbon Ltd graphite) were used as starting materials for fabrication of Ti_2AlC and Ti_3AlC_2. To prepare stoichiometric reactant mixture the following Ti:Al:C molar ratio was used: 2:1:1. Above composition was used in green samples for the manufacturing of the MAX phase based materials by both the microwave-assisted SHS and the SPS techniques. Ti, Al, C powders amounts were firstly weighed with the accuracy to 0.001 g and mixed with ZrO_2 balls for 10 minutes. Subsequently powders were uniaxially cold-pressed in a hydraulic press into samples in the shape of pellets with 22 mm diameter under a pressure of 930 MPa.

Microwave-assisted SHS synthesis was conducted in the microwave reactor [21], for which other processing details were described elsewhere [22-24]. Whole reaction took place in the inert Ar atmosphere. Temperature was detected by pyrometer Raytek Marathon MM with the measuring spot dia. of 0.6 mm.

The prepared MAX skeletons prepared by microwave-assisted SHS were subsequently used for pressure infiltration – squeeze casting with an Al-Si eutectic alloy, AC 44200 (10-13.5% Si, 0.4% Fe, 0.05% Cu, 0.4% Mn, 0.1% Zn, 0.15% Ti, remainder Al). Molten metal at the temperature of 770°C was pressurized under the pressure of 90 MPa onto the ceramic preform for 1 min. Other experimental details for the manufacturing of composite materials with the use of squeeze casting infiltration were described in previous works of the Authors [23-24].

The consolidation by SPS was performed in a FCT spark plasma sintering furnace (model S8451). This equipment can supply a direct current of 10000 A of current under a maximum voltage of 10 V. The DC current was applied with a pulse time of 10 ms and a pause time of 5 ms. Cold pressed pellets of 22 mm diameter were introduced within the graphite die. The pressure applied during the process was 7 MPa and the maximum temperatures 700, 850, 1100 and 1250ºC. The holding time was 5 min in all cases.

XRD tests for preforms were conducted with a Bruker AXS D8 Advance diffractometer. The quantitative chemical composition analysis using the Rietveld method was performed in the Profex program. For the produced preforms the structures

were observed with a scanning microscope Hitachi 3000 TM. Composite materials with preforms after infiltration were also analysed in scanning (STEM) mode with the convergent beam with the use of Transmission Analytical Electron Microscopy using a JEOL 2100 Electron Microscope operated at 200 KV and equipped with JEOL JED-2300T EDS unit for the analytical measurements (JEOL, Japan).

3. Results and discussion

3.1. MAX phase synthesis via microwave-assisted SHS and SPS

SHS synthesis has been proven before to be able to be successfully applied for the creation of MAX phases in the studied system. The chosen composition of powders was previously used also by other researchers [25-26].

Figure 1a and 1b present respectively: the overall porosity of the obtained material [27] and its microstructure. Porosity gained by the means of this technique is open, interconnected, suitable for e.g. further infiltration process. Despite this fact, pores are uneven with wide range of dimensions. Moreover, the inner parts of the porosities tend to be partially covered with small, circular inclusions, identified as TiC crystals. Nevertheless, the MAX type phases exhibit typically platelike structure with platelets (5-20 μm in length, 1-5 μm in thickness) closely packed into the layered nanolaminates. Figure 2 presents the results of the XRD analysis for the microwave-assisted SHS synthesis. Quantitative Rietveld analysis allowed to estimate the content of particular phases – Ti_2AlC, Ti_3AlC_2 and TiC – within the final product, respectively as: 82.2%, 15.4% and 2.4%.

Figure 3 presents the STEM image of the composite material of Al-Si matrix reinforced with the manufactured preform. It reveals the uniform distribution of Ti, Al and C within the MAX phase platelets. Si crystallites of size up to 1-2 μm included in the

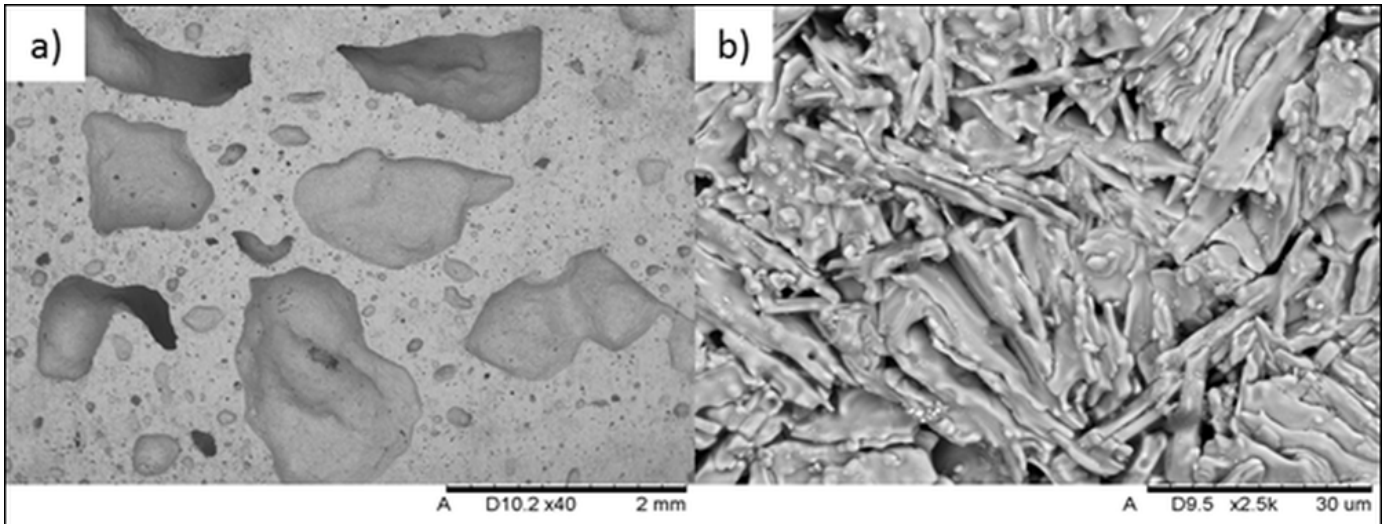

Fig. 1. Manufactured MAX phase preform: a) view of the overall open porosity [27], b) microstructure of MAX phase platelets

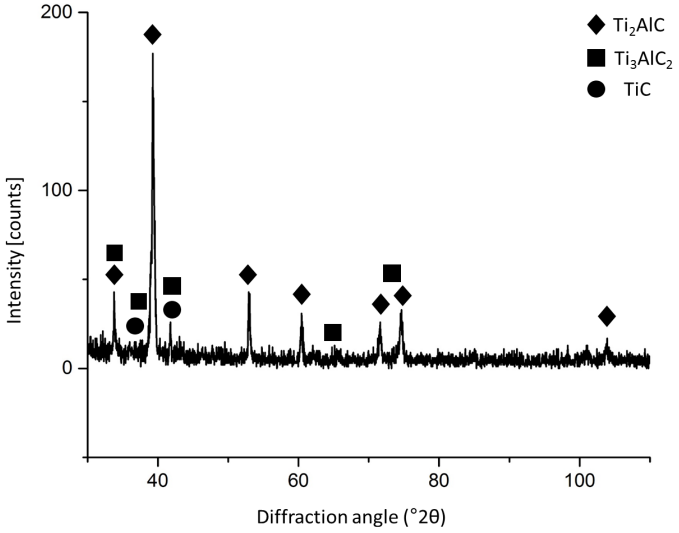

Fig. 2. XRD analysis of the MAX phase preform of Ti-Al-C system manufactured by microwave-assisted SHS

Al matrix were identified. As can be noticed, the squeeze casting infiltration is effective enough to ensure the precise filling of the preform's pores with the Al-Si alloy. Moreover, no undesirable interactions (i.e. mutual diffusion) between the phases of matrix and reinforcement were observed.

The SPS cycles were performed using the cold pressed pellets and maintaining a very low pressure, trying to maximize the porosity. The SPS reaction was carried out for four different sintering temperatures: 700, 850, 1100 and 1250°C. However, in none of the cases considered, the formation of desirable MAX phases was found. The SPS synthesis in the Ti-Al-C system resulted only in intermediate phases such as intermetalics and binary carbides. For the highest one of the tested temperatures the product consisted of: $TiAl_2$, Ti_3Al, TiC and residual C (see Fig. 4).

It is supposed that extending the sintering process time or further raising the temperature could result in a continuous de-

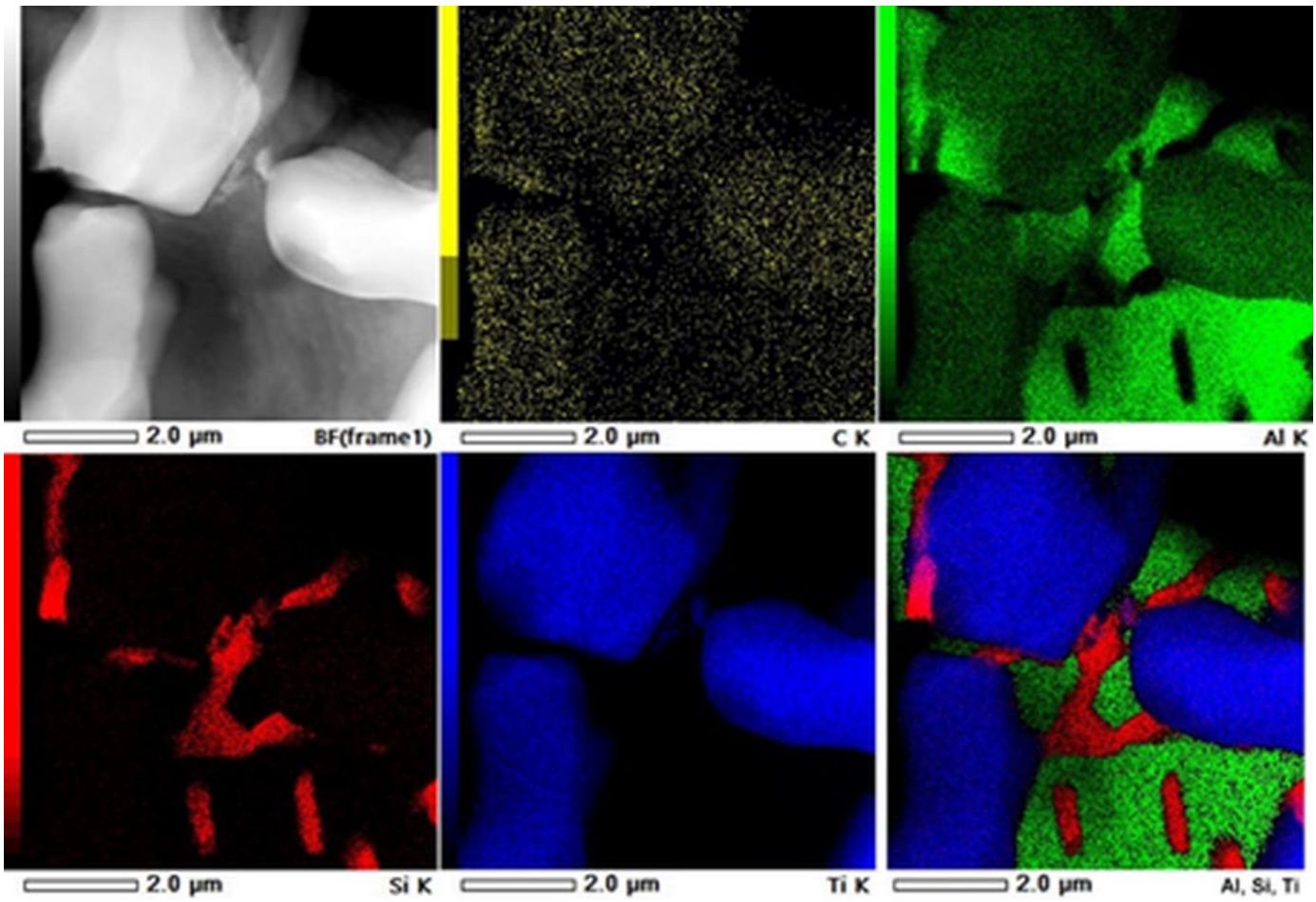

Fig. 3. STEM image at low-magnification and the corresponding EDS maps showing the distribution of the C, Al, Si and Ti elements on the analyzed area. The RGB image was obtained by overlapping of the Al, Si and Ti EDS maps

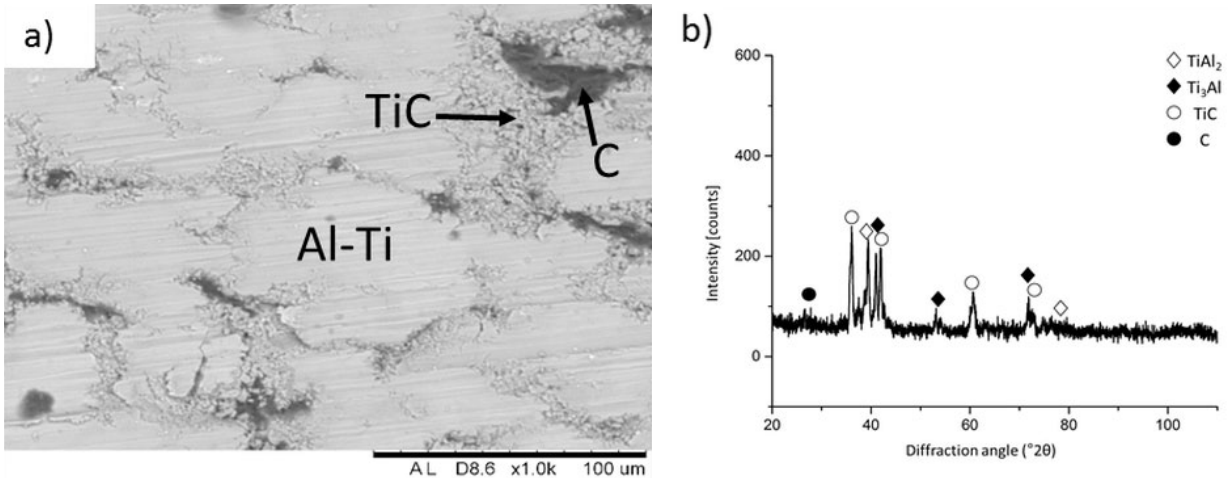

Fig. 4. SPS products for sintering temperature of 1250°C: a) microstructure, b) XRD analysis

velopment of the reaction between the titanium carbide and the Al-Ti intermetallic compounds, which in turn could lead to the formation of the MAX type phases. Nevertheless, the inability to get the initiation of an exothermic reaction within the tested short heating times and selected temperatures, places the SPS method as definitely less efficient and more energy consuming than the microwave-assisted SHS synthesis.

3.2. Formation mechanism of MAX phases

The MAX phase SHS synthesis in Ti-Al-C system, for which the exemplary temperature vs time dependences were presented in previous papers of the Authors [22-24], starts instantaneously when the melting point of Al is attained (660-670°C). Subsequently, two intermediate phases are being formed during

highly exothermic reactions: liquid Al-Ti phase and TiC carbides. These compounds react with each other to form Ti_2AlC and, followingly, Ti_3AlC_2. The maximum temperature observed during this synthesis exceeds 1600°C. It is predicted that if the combustion temperature in Ti-Al-C system exceeds 1300°C, then the mixture of these two MAX phases will be present in the final product, instead of the sole Ti_2AlC.

The results obtained from the SPS trials stay in agreement with the synthesis mechanism in Ti-Al-C system proposed in the Figure 5. Subsequent stages of this reaction were confirmed to consist of the formation of intermetallic Al-Ti phases and, afterwards, TiC carbide. Then these phases react with each other and form the desired MAX phases (see equations 1-2).

$$TiC + \textit{liquid}\ Al - Ti \rightarrow Ti_2AlC \quad (1)$$

$$TiC + Ti_2AlC \rightarrow Ti_3AlC_2 \quad (2)$$

In the case of the reaction at a maximum temperature of 700°C, unreacted substrates in the form of Ti, Al and C were present in the product and, as the reaction temperature exceeds the melting point of aluminum, also a small amount of intermetallic phase identified as Ti_3Al (see Fig. 6).

With the sintering temperature increasing to 850°C (see Fig. 7), the amount of intermetallic phases also escalates in the material, as Ti continues to merge with Al to form Ti_3Al and $TiAl_2$. In this case the product did not contain any unbound Al.

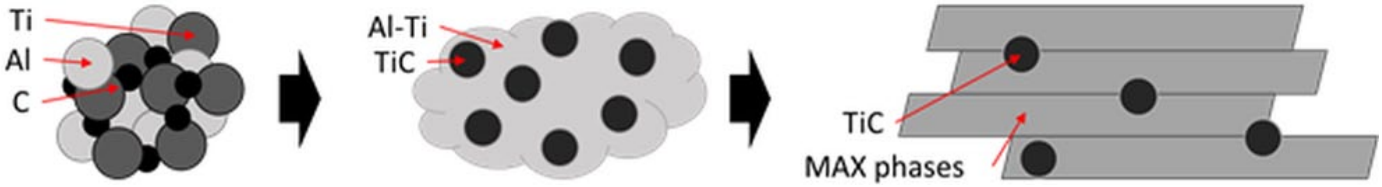

Fig. 5. Formation mechanism of MAX phases in Ti-Al-C system [28]

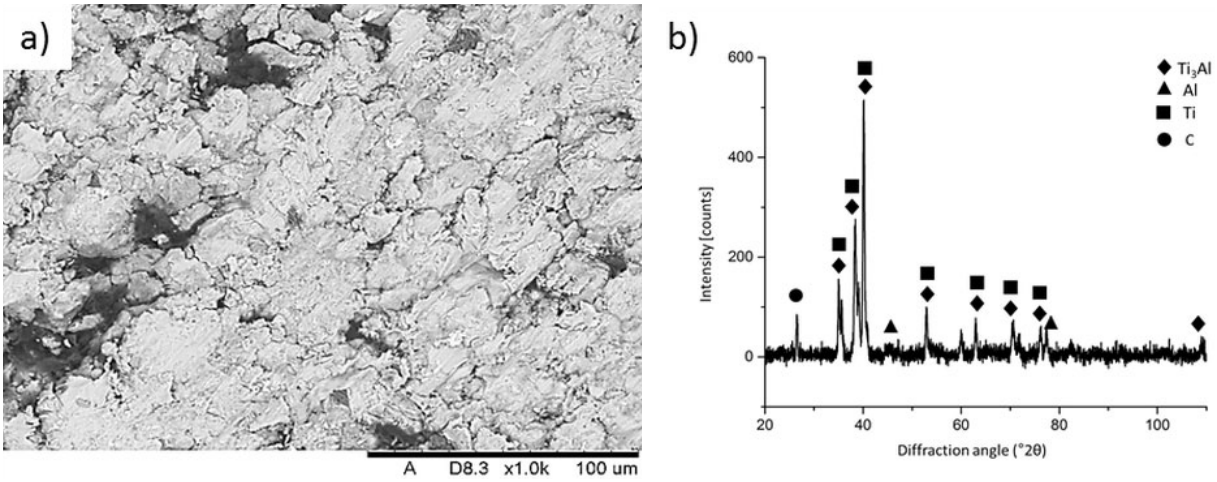

Fig. 6. SPS products for sintering temperature of 700°C: a) microstructure, b) XRD analysis

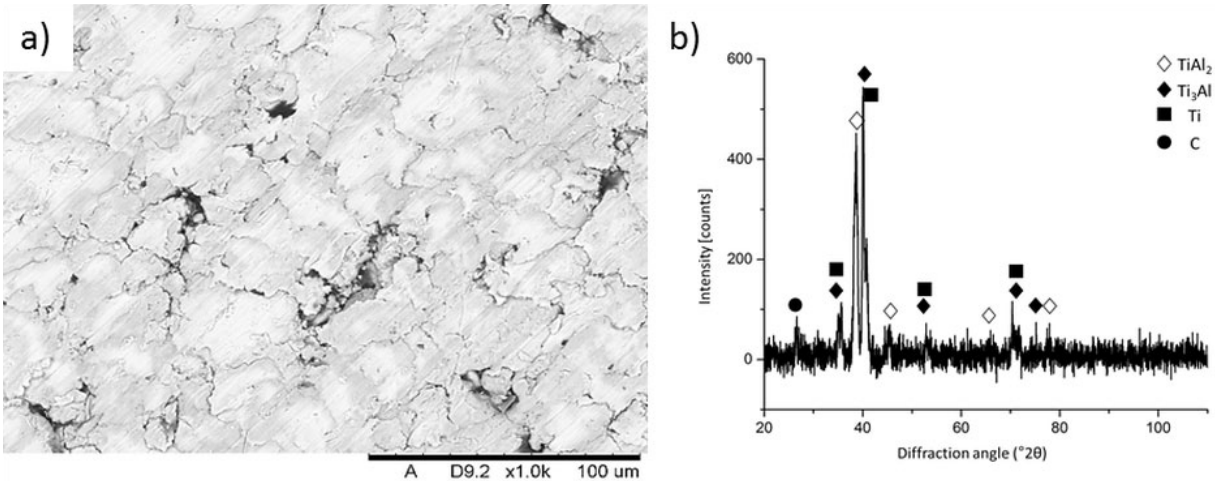

Fig. 7. SPS products for sintering temperature of 850°C: a) microstructure, b) XRD analysis

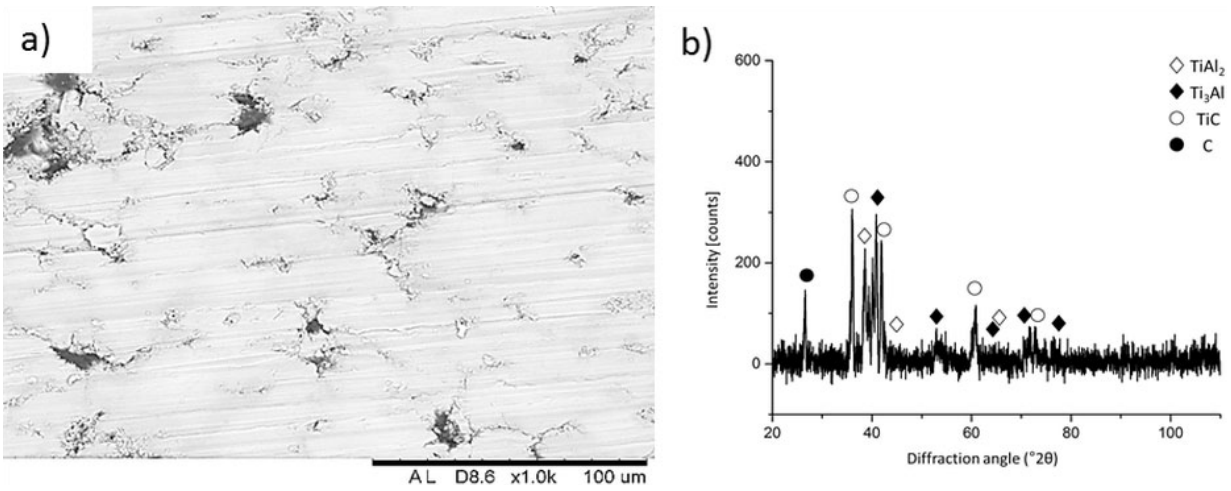

Fig. 8. SPS products for sintering temperature of 1100°C: a) microstructure, b) XRD analysis

In the next phase of the reaction, observed for a temperature of 1100°C (see Fig. 8), the unreacted Ti was combined with graphite in order to form TiC. For the last of the temperatures tested (1250°C), this trend was further continued (see Fig. 4), as Ti keeps diffusing to C even from Al-Ti phase, promoting the conversion of Ti_3Al into $TiAl_2$.

3.3. Comparison of heating mechanisms in SPS and microwave-assisted SHS techniques

SPS is usually used as a sintering technique for rapid consolidation of powders by the means of uniaxial force, pulsed direct electrical current (DC) under low atmospheric pressure. The maximum (peak) current $I_{\max}$ can be calculated by the equation (3), where I_{avg}, *period*, *on time* stand for, respectively, average current, time duration of periodic current pulse and the time when current is on [29].

$$I_{\max} = \sqrt{\frac{period}{on\,time}} I_{avg} \tag{3}$$

SPS is characterized by high heating rate, similarly as SHS, nevertheless it differs in terms of the heating mechanism. In SPS, Joule heating occurs when the passage of electric current goes through the particles of the sample (see Fig. 9a). The mechanism of the heating during SPS is a long debate within the SPS community [30]. It is clear the that the heating is different depending on the conductivity of the material. With non-conductive materials the current goes only across the graphite die but with conductive materials the current is distributed mainly across the material. The presence or not of sparks during SPS is other controversial issue but it could depend on the voltage used during the process [30]. In this paper a low voltage is used (<10 V) and sparks are less feasible [30]. In any case, if the sparks exist, no evidence of exothermic reaction was observed during processing.

On the contrary, in microwave-assisted SHS, micro current flows with electric discharge and arc which ignite the SHS reaction in many places. The heating is uniform in whole volume of the sample, as microwaves generate the inner electromagnetic field causing induced eddy current in each of the powders' particle (see Fig. 9b). Therefore in microwave-assisted SHS the energy impact is sufficient to ignite the self-sustaining exothermic synthesis, while in SPS the energy supplied is being scattered by partial local reactions inside the sample. According to Hill et al. [31] and Yoshikawa et al. [32] the simplified heating mechanism can be described with Maxwell equations (4-6), where:

$$\nabla \times E = -\frac{\partial B}{\partial t} \tag{4}$$

$$\nabla \times H = J + \frac{\partial D}{\partial t} \tag{5}$$

$$D = \varepsilon E,\ B = \mu H,\ J = \sigma E \tag{6}$$

where:

E – electric field,
H – magnetic field,
B – magnetic flux density,
J – eddy current,
D – electric displacement vector,
ε – dielectric permittivity,
μ – magnetic permeability,
σ – electric conductivity.

On the other hand, in research presented by Rosa et al. [16] this approach can be further supplemented by the analysis of the impact of frequency of the applied microwaves on the ability of the material to convey the emitted energy. In their work the following power density distribution equation was introduced (7), where:

$$P_d(x,y,z) = \omega \varepsilon_0 \varepsilon''_{eff} E_l^2 + \omega \mu_0 \mu''_{eff} H_l^2 \tag{7}$$

where:

$P_d(x,y,z)$ – power dissipated by unit volume,
ω – $2\pi f$, where f stands for the frequency of the microwaves,

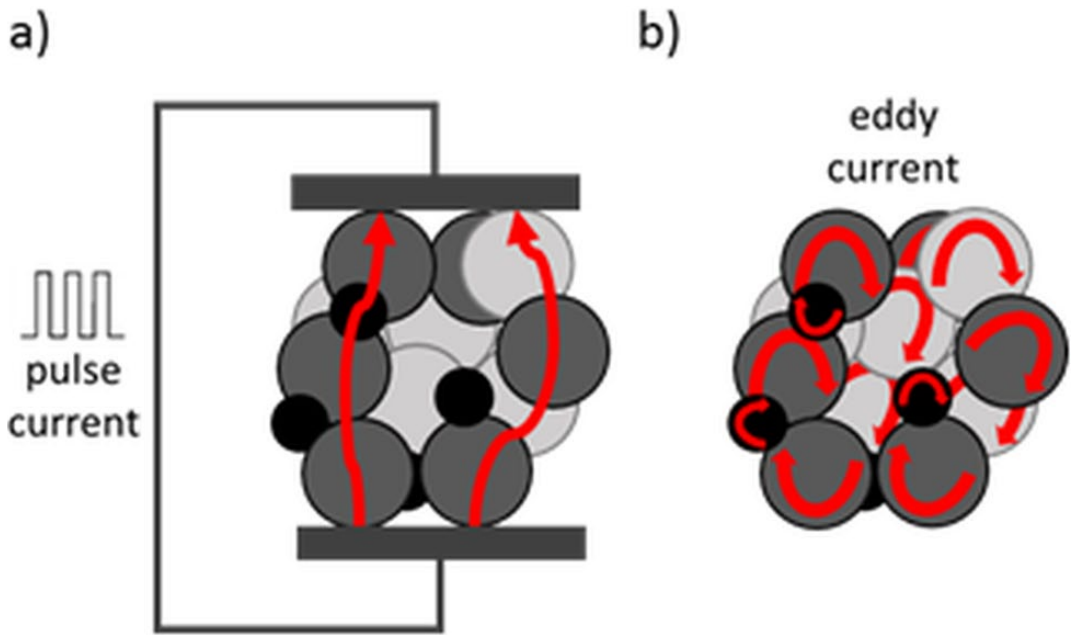

Fig. 9. Comparison of heating mechanisms: a) SPS, b) microwave-assisted SHS

ε_0, μ_0 – electric empty space permittivity and magnetic empty space permeability,

ε''_{eff}, μ''_{eff} – imaginary parts of the effective electric permittivity and magnetic permeability, depending strongly from eddy current,

E_l, H_l – local electric and magnetic fields.

The microwave power density distribution appears to be one of the most crucial parameters considering the heating mechanism. The application of microwaves can ensure a direct, instantaneous increase of the temperature uniformly throughout the whole volume of a sample.

4. Conclusions

Microwave-assisted SHS was found to be adequate for successful fabrication of cellular MAX phase preforms in Ti-Al-C system. This method allows the manufacturing of foam-like materials, while with SPS, even using reduced sintering time, low temperatures and low pressures, the products are rather dense. Moreover, the reaction observed in SPS was very limited, resulting with only secondary intermetallic phases instead of the intended product. Although the exothermic reaction was found impossible to be ignited by SPS, the outcomes of this study supported the synthesis mechanism proposed for Ti-Al-C system. The dissimilarities in the heating mechanisms are believed to be responsible for the differing products of both syntheses. In comparison to more conventional methods of powder metallurgy like e.g. SPS, microwave-assisted SHS synthesis, using the highly exothermic character of the MAX phase synthesis reaction, allows to shorten the duration of the manufacturing process while also reducing its energy consumption.

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