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Manufacturing of Al Alloy Matrix Composite Materials Reinforced with MAX Phases

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Abstract

A method for manufacturing of Al-Si alloy (EN AC-44200) matrix composite materials reinforced with MAX type phases in Ti-Al-C systems was developed. The MAX phases were synthesized using the Self-propagating High-Temperature Synthesis (SHS) method in its microwave assisted mode to allow Ti_2AlC and Ti_3AlC_2 to be created in the form of spatial structures with open porosity. Obtained structures were subjected to the squeeze casting infiltration in order to create a composite material. Microstructures of the produced materials were observed by the means of optical and SEM microscopies. The applied infiltration process allows forming of homogeneous materials with a negligible residual porosity. The obtained composite materials possess no visible defects or discontinuities in the structure, which could fundamentally deteriorate their performance and mechanical properties. The produced composites, together with the reference sample of a sole matrix material, were subjected to mechanical properties tests: nanohardness or hardness (HV) and instrumental modulus of longitudinal elasticity (EIT).

Keywords: MAX phases, SHS synthesis, Microwave, Porous structure, Squeeze casting

1. Introduction

The MAX type phases, whose name originates from the 90s, are a relatively new group of material consisting of triple carbides or nitrides defined by the general formula $M_{n+1}AX_n$, where M is an early transition metal, A is an element from group A (including Al, Ga, In, Ge, Sn, Pb, Si), and X is carbon or nitrogen [1]. MAX phases, also called the “machinable ceramics”, have the molecular structure of ternary three-component systems [2-3]. Their crystal structure is composed of layers of M-X elements arranged alternately with the layers of the element A. The bonds between the layers are metallic, while between the elements M and X they are covalent. The MAX type phases uniquely combine the advantages of metals and ceramics. They exhibit high thermal and electrical conductivity, good machinability, high resistance to temperature changes, oxidation and corrosion. They possess high strength properties, also retained at elevated temperatures. Vickers hardness of the MAX type phases is in the range of 2-8 GPa. They are therefore harder than most metals, but less hard than ceramics. All these features ensure that the MAX type phases have a special place among the materials used in the construction of machines. Currently, approximately 70 phases of the MAX type are known. They can be readily synthesized in solid or porous form and applied in the form of thin coatings [4-5].

Titanium-aluminum carbides Ti_2AlC and Ti_3AlC_2 are the lightest and the most resistant to oxidation ones among the MAX type phases [6]. The density of Ti2AlC is 4.11 g/cm^3, and its thermal and electrical conductivities equal respectively 23-46 W/m·K and 4.42x10^6 S/m [7]. The coefficient of thermal expansion of this material is 8.2x10^{-1} °C^{-1}, while its Young's modulus can be up to 277 GPa [8]. Ti_2AlC was firstly obtained by a team of researchers Jeitschko and Nowotny in the form of a thin film by Chemical Vapor Deposition (CVD) in 1967. Ti_3AlC_2 is one of the most frequently studied examples of MAX phases with the 312 structure. It was primarily identified by Pietzka and Schuster in 1994. It is characterized by high thermal and electrical conductivity, easy workability and high impact resistance - just like metals. It also possesses low density (4.2 g/cm^3), high Young's modulus, high strength at elevated temperatures, low coefficient of thermal expansion, and excellent resistance to oxidation and acids. As the only example of MAX phases, it shows increased plasticity at elevated temperatures [9]. There are many methods used for obtaining of Ti_2AlC and Ti_3AlC_2, among others: Reactive Hot Pressing (RHP), Hot Isostatic Pressing (HIP), Spark Plasma Sintering (SPS), Pulse Discharge Sintering (PDS) and Self-propagating High-temperature Synthesis (SHS) [10]. In nearly all of the previously described studies, TiC and Ti_2AlC [11] are also created during the synthesis of Ti_3AlC_2.

Among the most commonly reported methods of manufacturing of MAX phase based composites the following can be distinguished: Hot Pressing (HP), Reactive Hot Pressing (RHP), Hot Isostatic Pressing (HIP), Self-propagating High-temperature Synthesis (SHS), in situ, Spark Plasma Sintering (SPS) and pressure or pressureless infiltration. Nevertheless, the techniques used so far to infiltrate porous preforms of the MAX type phases, which also require a lot of time and energy, do not provide a sufficient degree of filling of open porosities. This problem can be solved by the proposed Squeeze Casting method [12-16].

In the presented paper a method for manufacturing of Al-Si alloy matrix composite materials by squeeze casting pressure infiltration of porous MAX phase preforms was developed. MAX phases were synthesized in Ti-Al-C system using the Self-propagating High-temperature Synthesis in the Microwave Assisted mode (MASHS). Obtained spatial structures contained interconnected open porosity consisting of a mixture of Ti_2AlC and Ti_3AlC_2. Due to the use of microwave radiation for the MASHS synthesis of the MAX type phases in the form of preforms, their production process is much shorter, cheaper and more energy-efficient than the conventional methods of powder metallurgy. Prepared samples were subsequently subjected to squeeze casting pressure infiltration with Al-Si alloy (EN AC-44200). Residual porosity only takes up to several percent of the volume of materials produced, so it can be concluded that the degree of saturation achieved during infiltration is almost complete. The produced materials were tested for mechanical properties in order to determine the nanohardness or hardness (HV) and the instrumental modulus of longitudinal elasticity (EIT).

2. Experimental methods

Commercial powders of Ti (99.5 % Ti, -325), Al (99.9 % Al, -325, Alfa Aesar) and graphite (99.5 % C, -325SGL Carbon Ltd graphite) were used as starting materials with molar ratios 2:1:1 to prepare stoichiometric reactant composition to fabricate Ti_2AlC and Ti_3AlC_2. Prepared mixture of powders was used to produce the above mentioned MAX phases by the Microwave Assisted Self-propagating High-temperature Synthesis (MASHS). Ti, Al, C substrate amounts were firstly weighed with the accuracy of 0.001 g and mixed with ZrO_2 balls for 10 minutes. Subsequently they were cold-pressed in a hydraulic press into samples in the shape of pellets with 22 mm diameter under a pressure of 930 MPa for 10 seconds. Afterwards prepared samples were subjected to MASHS, which was conducted in the microwave reactor [17]. Temperature was detected by pyrometer Raytek Marathon MM with the measuring spot dia. of 0.6 mm. The ignition temperature for the Ti-Al-C system equaled ~ 670°C, when the melting point of Al was attained, while the combustion temperature exceeded 1600°C according to the reaction scheme described in the previous work [18]. Whole reaction took place in the inert Ar atmosphere. Prepared samples were further used as the reinforcement for composite materials based on MAX phases. Porous preforms were infiltrated with the use of squeeze casting method with the Al-Si alloy (EN AC44200). The die (80 mm in diameter) containing preforms was heated to 200-300°C. Metal melt in temperature of 720-740°C was pressurized to fill up the die under pressure of 90 MPa. For the produced composites the structures and phase identification were performed with a scanning microscope Hitachi S-3400N and Chemical Analyzer SwiftED3000. The produced materials were tested for mechanical properties to determine the nanohardness or hardness (HV) and the instrumental modulus of longitudinal elasticity (EIT). The research was carried out using the Oliver & Pharr method by the means of the Anton Paar NHT nanoindenter. Indentation parameters were gathered in Table 1.

Table 1.
Indentation parameters.

Parameter	Value
Acquisition rate	10 [Hz]
Loading type	Linear
Maximum load	50 [mN]
Loading rate	100 [mN/min]
Unloading rate	100 [mN/min]
Indenter type	Berkovich
Indenter material	Diamond

3. Results and discussion

3.1. Synthesis

For the first time the Self-propagating High-temperature Synthesis (SHS) was applied for the manufacturing of MAX phases in 2002 [3] for mixed Ti:Al:C (2:1:1 – molar ratio). It was observed that during the SHS reaction a plastic flow of the material occurs, which resulted in a significant deformation of the sample. The reaction scheme, in this and other works, is identical. The reaction is initiated at the melting temperature of aluminum (660 °C) and then proceeds by itself in a two-step process. In the first stage, Ti (melting point of Ti is 1660 °C) reacts with liquid Al to form an intermetallic phase. In the second stage of the synthesis, graphite diffuses into Ti favoring the formation of TiC. Next, most of TiC is dissolved in the Al-Ti liquid phase. At such a high temperature, the part of Al may evaporate and therefore during the cooling the Ti and C excess will react leading to the formation of TiC. Ti_2AlC and Ti_3AlC_2 precipitate during the cooling process from the Ti-Al-C liquid phase within the peritectic reaction [19-20]. To enable the Ti_3AlC_2 phase to be formed, it is necessary to exceed the temperature of 1300 °C. During the transformation, the sample in which the Ti-Al liquid phase is present undergoes a severe deformation consisting of axial elongation in the direction of the propagation of the reaction front and reduction of the diameter associated with the surface tension of the Ti-Al phase. The scheme for the production of MAX phases in the Ti-Al-C system is shown in Figure 1.

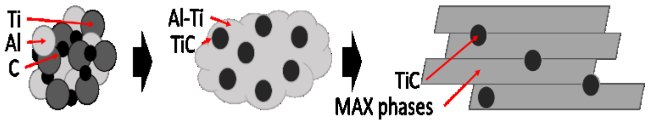


Fig. 1. Scheme of MAX type phases forming in Ti-Al-C system

3.2. Microstructures

Figure 2 shows the SEM microstructure of the resulting MAX phases. In the Ti-Al-C system, the samples, due to their considerable deformation during synthesis, form uneven porosities with a large dimension distribution. However, these are open porosities that are suitable for the infiltration process. The synthesized MAX type phases have a characteristic plate like nanolaminate structure. Due to the chaotic arrangement of the platelets packages, it is not possible to distinguish a directed texture of the material, which allows us to assume that the material will have rather isotropic mechanical properties [21]. The Ti_2AlC platelets have a length of 10-30 µm, while finer grains (5-10 µm) represent Ti_3AlC_2. Figure 3 shows exemplary results of EDS analysis for MAX type phases (1.35 - 36.636%, Al - 14.120%, C - 50.244%).

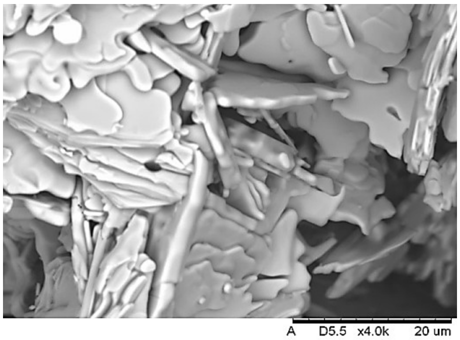
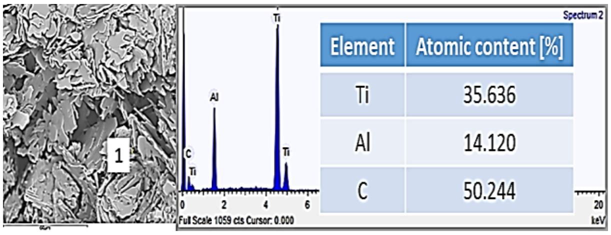


Fig. 2. Porous product of the SHS synthesis in the Ti-Al-C system: microstructure of MAX phases (Ti_2AlC and Ti_3AlC_2)



Element	Atomic content [%]
Ti	35.636
Al	14.120
C	50.244

Fig. 3. Exemplary EDS analysis results for MAX type phases in Ti-Al-C system

The manufactured material possesses also the undesirable inclusions of titanium carbide (TiC), as the formation of Ti_3AlC_2 and Ti_2AlC is also accompanied by the creation of TiC [22]. As it results from the literature analysis, researchers have so far failed to avoid this effect. TiC occurs in the material in the form of fine, spherical crystals with a diameter of ~1-2 µm. These carbides tend to accumulate within the inner parts of the porosities.

3.3. Squeeze Casting Infiltration

Microstructure of composite material produced after pressure infiltration with Al-Si alloy preforms in the Ti-Al-C system observed in optical microscopy is presented in the figure 4. The volumetric ratio of matrix to reinforcement was maintained at about 50:50. Manufactured materials contain only up to several percent of the residual porosity in the overall and therefore it can be stated that the achieved degree of saturation after infiltration is almost complete. This process is so effective that it allows the matrix material fill not only the interior of the porosities, but also the spaces between the MAX phases platelets. During the infiltration, there were no additional unwanted reactions between the matrix material and the preform observed. Al and Si elements coexist in the area of the matrix, while Ti, Al and C are distributed evenly in the reinforcement phase. Figure 5 presents the results of EDS analysis for the composite material (1 – matrix, 2 – reinforcement).

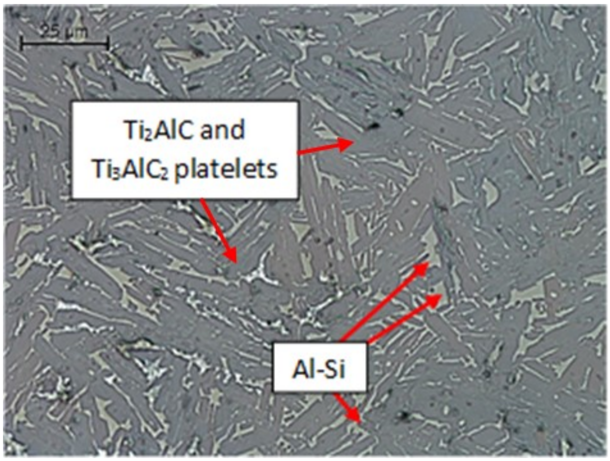
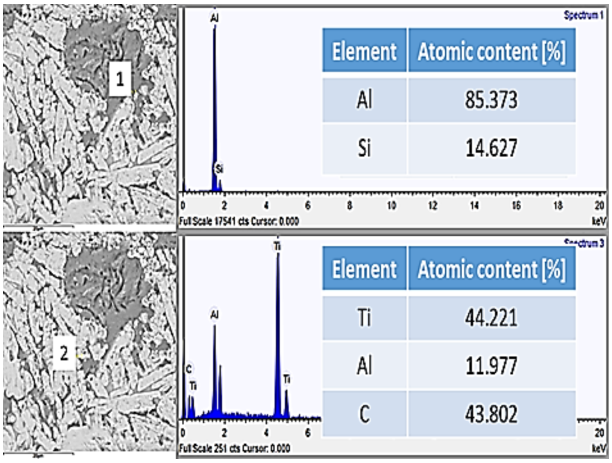


Fig. 4. Microstructure of the produced composite material of Al-Si alloy reinforced with MAX phases (Ti_2AlC and Ti_3AlC_2) - optical microscope



Element	Atomic content [%]
Al	85.373
Si	14.627

Element	Atomic content [%]
Ti	44.221
Al	11.977
C	43.802

Fig. 5. EDS analysis for the composite material (1 – matrix, 2 – reinforcement)

3.4. Mechanical properties

The produced materials were subjected for testing of mechanical properties in order to determine the nanohardness or hardness (HV) and the instrumental modulus of longitudinal elasticity (EIT). The research was carried out using the Oliver & Pharr method using the Anton Paar NHT nanoindenter. Obtained results for preform and for composite material in relation to the matrix parameters, are gathered in Table 2.

The MAX type phases are harder than metals and less hard than most of the ceramic materials. Due to the nanolaminate structure of the MAX phases, micro- or nano- hardness tests are carried out for them instead of the hardness test, because with a larger pressure area, the surrounding MAX type phases are getting stacked, which prevents reliable measurement. In addition, the hardness of the MAX phases drastically decreases together with the penetration of the indenter into the material. The measurement result depends to a large extent on its location. The hardness measured inside one of the MAX phase platelets will be significantly higher than the one measured for several grains [1].

Table 2.
Mechanical properties of the manufactured materials.

Property Material	Hardness (HV) [GPa]	Instrumental Young Modulus (EIT) [GPa]
EN AC-44200 matrix	1.6	29.0
Ti_2AlC/ Ti_3AlC_2 - preform	8.4	243.5
Ti_2AlC/ Ti_3AlC_2 - composite	5.8	118.3

The measured values of nano-hardness for preforms belong to the upper limit of the range previously presented by other researchers. In the case of composite material, the hardness values described in the literature usually do not exceed 2-4 GPa, while in the present work the results were up to 5.8 GPa, for composites based on EN AC-44200 alloy and Ti_2AlC/Ti_3AlC_2 reinforcement. The measured values of the Young's instrumental modulus are comparable to the literature data for the Ti_2AlC/Ti_3AlC_2 preform. For a composite material reinforced with Ti_2AlC and Ti_3AlC_2 MAX phases, an approx. 4-fold increase in hardness and instrumental Young's modulus was observed.

4. Conclusions

Pore-free, dense metal matrix composite materials reinforced with MAX type phases were successfully manufactured by the means of Microwave Assisted Self-propagating High-temperature Synthesis and subsequent Squeeze Casting Infiltration. The obtained composite materials possess a relatively homogeneous structure with no visible defects, discontinuities in the structure or non-infiltrated residual porosities, which could fundamentally deteriorate their performance and mechanical properties. Produced composite materials exhibit enhanced mechanical properties in comparison to the matrix, as their hardness and Young modulus were increased 4 times.

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