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A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 60 2015 Issue 2

DOI: 10.1515/amm-2015-0219

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PROCESSING AND PROPERTIES OF MAX PHASES – BASED MATERIALS USING SHS TECHNIQUE

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Authors present results of works on the interesting new group of advanced ceramics called MAX phases – Ti-based ternary carbides and nitrides. They have an original layered structure involved highly anisotropic properties laying between ceramics and metals, with high elastic modulus, low hardness, very high fracture toughness and high electrical and heat conductivity. Using Self-Propagating High-Temperature Synthesis (SHS) in the combustion regime it is possible to prepare MAX phases-rich powders that can be used as the precursors for preparation of dense MAX polycrystals by presureless sintering or hot-pressing. Different novel Ti-based phases with layered structures, namely: Ti_3AlC_2 and Ti_2AlC have been synthesized in a combustion regime. The possibility of controlling of combustion phenomena for obtaining near single-phase products is discussed in details as well as some of properties of the materials tested as structure and functional ceramics.

Keywords: MAX phases, SHS, Hot-pressing, Ti_2AlC, Ti_3AlC_2

Autorzy przedstawiają wyniki badań nad nową interesującą grupą zaawansowanych materiałów ceramicznych nazywanych fazami MAX – potrójnymi węglikami i azotkami tytanowymi. Posiadają one oryginalną strukturę warstwową, z której wynikają silnie anizotropowe właściwości (wysokie moduły sprężystości, niska twardość, bardzo wysoka odporność na kruche pękanie, dobre właściwości elektryczne i cieplne) umiejscawiające je pomiędzy ceramiką a metalami.

Dzięki zastosowaniu Samorozwijającej się Syntezy Wysokotemperaturowej SHS możliwe było otrzymywanie bogatych w fazy MAX proszków, mogących służyć jako prekursory w preparatyce gęstych polikryształów za pomocą spiekania pod ciśnieniem lub swobodnego. Przeprowadzone zostały syntezy dwóch materiałów warstwowych: Ti_3AlC_2 i Ti_2AlC. W artykule przedstawiono możliwości kontrolowania procesu spalania w celu uzyskania niemal jednofazowych produktów a także przedstawiono niektóre właściwości badanych materiałów pod kątem zastosowania jako materiały funkcjonalne i strukturalne.

1. Introduction

In the Ti-Al-C-N system, among many covalent materials, such as carbides or nitrides, exist a group of ternary and quaternary compounds, referred in literature as H-phases, Hägg-phases, Novotny-phases or thermodynamically stable nanolaminates and recently their most common name is MAX phases. They gain their name due to the $M_{n+1}AX_n$ stoichiometry, where M is an early transition metal, A is an element of A groups (mostly IIIA or IVA) and X is carbon and/or nitrogen. Heterodesmic structures of these phases are hexagonal, P63/mmc, specifically layered and involve at least two types of chemical bonds metallic, covalent or ionic. They consist of alternate near close-packed layers of M_6X octahedrons with strong covalent bonds and layers of A atoms located at the centre of trigonal prisms. The M_6X octahedral, similar to those forming respective binary carbides, are connected one to another by shared edges. Different type of MAX phases labelled 211, 312 or 413 (and even the higher order such as 514, 615, and 716) are recognized in the literature. These symbols are representing the stoichiometry of MAX phase materials, e.g. Ti_2AlC represents 211 type phase, Ti_3AlC_2 – 312 type and Ti_4AlN_3 – 413 type. The respective phases vary by the number of M layers separating the A-layers: in the 211's there are two in the 312's three M-layers and in the 413 there are four layers [1-5].

This uncommon heterodesmic layered structure of MAX phases gives as a result set of unique properties which locates them on the boundary between metals and ceramic filling the gap between these two types of materials. They combine some features characteristic for metals such as low hardness, good compressive strength, high fracture toughness, ductile behaviour, good electrical and thermal conductivity with high stiffness, moderately low thermal expansion coefficient and excellent thermal and chemical resistance typical for ceramics. The best recognized representative of MAX phase materials is Ti_3SiC_2.

The MAX phases may find many potential applications depending on the features they possess. Thanks to the their mechanical properties they can be used e.g. as a part of ceramic based armours based on functionally graded materials (FGM) for armoured personal carriers, patrol vehicles, helicopters or

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even main battle tanks. They can also be used as a matrix in ceramic-based composites reinforced by covalent phases [5, 6]. They are known for their excellent electric conductivity and their metal like resistivity drops linear with decreasing temperature (in fact Ti_3SiC_2 and Ti_3AlC_2 conducts better than titanium metal) [7-10]. They are known to be good thermal conductors therefore they can be used as a heating elements (e.g. Ti_2AlC, Ti_3SiC_2) [11]. They have also high temperature stability and even at high temperatures they do not melt but decomposed into regular carbides or nitrides enriched with A element liquids [7-10]. They are also known for their high thermal shock resistance. Potential applications of these materials are wide and varies from mentioned above lightweight armours, protective layers, high temperature oxidation resistant elements, heating elements, cladding materials for nuclear applications and many others [7-10]. Probably the best know application is Ti_3SiC_2 elements manufactured by Sandvik Materials Technology under MAXthal brand [9].

The MAX phases materials can be manufactured by numerous methods including hot pressing (HP), hot-isostatic pressing (HIP), pressureless sintering (PS), slip casting or thin film techniques [8]. The main disadvantage of these methods is the fact that they are time and cost consuming thus they are not efficient. The solution for this problem may be Self-propagating High-temperature Synthesis (SHS).

The Self-propagating High-temperature Synthesis (SHS) is a method applied for obtaining over 1000 materials such as carbides, borides, nitrides, oxides, intermetallic compounds and composites. This technique is basing on utilization of exothermal effect of chemical synthesis. The second of the conditions necessary to carry out the synthesis is to provide adiabatic conditions in the reacting system. This synthesis can proceed in a powder bed of solid substrates or as filtration combustion where at least one of the substrates is in gaseous state. An external source of heat has to be used to initiate the process and then the self-sustaining reaction front is propagating through the bed of substrates until all of them are consumed. This process could be initiated by the local ignition or by the thermal explosion. The final form of the synthesized material may depends on kind of precursors used for synthesis and the technique applied [12].

The main purpose of this work was to obtain dense, single phase or near single phase ternary MAX phase materials during hot-pressing of SHS derived Ti_2AlC and Ti_3AlC_2 active precursors powders with lowest possible content of TiC impurities which affect properties of the sintered material, decreasing its pseudo-plastic behaviour. The possibility of obtaining powders with high content of Ti_3AlC_2 by SHS synthesis was proved by authors in their previous work, where use of excess intermetallic material, namely TiAl and Ti_3Al together with elemental titanium powder and carbon resulted with high quality active sintering precursors [13, 14]. Also other authors are confirming possibilities of synthesis of powders or bulk material characterised with high purity of the MAX phase. In the paper by X.H. Wang and Y.C. Zhou a vast part concerning the state of art of latest Ti_2AlC and Ti_3AlC_2 synthesis method can be found [8]. Possibility of using intermetallic materials in the MAX phases in Ti-Al-C system SHS synthesis were proved in paper of Lopacinski et.al [15]. The possibility of Ti_3AlC_2 synthesis with use of elemental powders during synthesis was reported by A.G. Zhou et.al and mixture of both MAX phases (Ti_3AlC_2 and Ti_2AlC) was obtained as a result [16]. The thermal explosion as an ignition system during the SHS process was applied by Y. Khoptiar and I. Gotman [17]. Also works by Liu et.al provides information about SHS synthesis of Ti_3AlC_2 [18].

Authors presents the result on optimization of SHS and HP processes in order to obtain large, dense samples of MAX-phase Ti_3AlC_2 material with extremely interesting performance both mechanical and functional.

2. Experimental

Following the experience gained during previous synthesis of ternary materials such as Ti_2AlN, Ti_2AlC and Ti_3AlC_2 intermetallic materials in the Ti-Al system, metallic titanium powder and graphite powder as a source of carbon were selected to be used as precursors for SHS synthesis of Ti_3AlC_2 powders [13, 14, 19-23].

The intermetallic powders in the Ti-Al system were synthesized by SHS method with thermal explosion ignition system. This decision was made due to the relatively low availability of fine commercial intermetallic powders in the Ti-Al system. TiAl powder was selected to be synthesized by SHS method [13, 19]. Commercially available titanium powder and metallic aluminium powder were used for the synthesis. The mixtures for SHS reaction were set in stoichiometric proportions according to equation:

$$Ti + Al \rightarrow TiAl \tag{1}$$

Mixtures of powders were initially homogenized in a ball-mill for 24 hours. After that the homogenized mixture was placed in a graphite crucible which was heated in a graphite furnace until thermal explosion in the whole volume of powder occurred and the SHS reaction was initiated. Obtained products were mechanically disintegrated and crushed in a roll crusher to the grain size ca. 1 mm. Then they were ground to the grain size ca. 10 μm for 4 hours in the rotary-vibratory mill in dry isopropanol, using WC balls as a grinding medium. After this process obtained powders were dried and used as substrates for synthesis of ternary MAX phase materials. Other powders used during synthesis of Ti_2AlC and Ti_3AlC_2 were commercially available aluminium powder (grain size below 6.4 μm, +99% pure), graphite powder used as a source of carbon (Merck no. 1.04206.9050, 99.8% pure, grain size 99.5% <50μm), titanium powder (AEE TI-109, 99.7% pure, ~100 mesh).

Basing on results obtained during researches on optimization of substrate stoichiometry in SHS process initiated by local ignition, two reactions were selected for obtaining of Ti_2AlC and Ti_3AlC_2 powders respectively [13, 14].

$$1.2TiAl + Ti + C \rightarrow Ti_2AlC \tag{2}$$

$$1.1TiAl + 2Ti + 2C \rightarrow Ti_3AlC_2 \tag{3}$$

In the previous researches smaller, 25g samples were examined, while in these researches upscaling process up to 125-200g took place, and its effect on phase composition of powders was observed. These substrates were homogenized in the ball-mill for 24 hours. Next the homogenized powder

mixtures were placed in the SHS chamber and ignited by the local ignition system. The time of ignition was 60 second. After the synthesis process obtained products were ground in dry isopropanol for 4 hours using rotary-vibratory mills and WC grinding balls. The XRD analysis method was applied to determine phase composition of the fine powder products. The data for quantitative and qualitative phase analysis were acquired from ICCD [24]. Quantities of the respective phases were calculated according to the Rietveld analysis [25]. The measurements were made within an accuracy of ±0.5 wt.%.

In the next step of the experimental procedure the SHS derived Ti_2AlC and Ti_3AlC_2 precursor powders were placed in a 2 inch diameter graphite die and subjected to the hot-pressing process. Ti_2AlC powder was hot-pressed at 1100°C, the annealing time was 1 hour and the maximum pressure applied was 25MPa. In the case of Ti_3AlC_2 powder the same sintering conditions were applied except for the maximum temperature which was 1300°C. After hot-pressing and removing the graphite foil from the surfaces of the samples, obtained dense pellets were investigated by XRD method in order to determine phase composition of the samples. The apparent density of the samples was determined by the hydrostatic weighing method.

Some mechanical properties of the hot-pressed MAX-phase samples such as Young modulus, shear modulus, Poisson ratio, Vickers hardness, fracture toughness and bending strength were investigated. In order to determine material constants (E, G and μ) the ultrasonic method was applied [26]. The surfaces of the samples were polished and the edges were prepared to obtain parallel faces ideal for ultrasonic tests. The velocities of transverse and longitudinal waves were measured in three directions and the values of material constants were calculated. The hardness of obtained materials was examined by Vickers indentation method with the 1kg load applied for 10 seconds using FV-700 Future Tech Corporation device. The bending strength was determined by three point bending method using Zwick/Roell BTC-FR2.5TS.D14 apparatus. The same device was applied for fracture toughness testing by Evans method. The beams for testing both fracture toughness and bending strength were cut with diamond saw from the hot pressed samples and then polished on Struers polishing machines with diamond disk with grades 220, 600 and 1200 respectively. Moreover, the notches were made on the beams prepared for Evans method testing.

Morphology of the obtained material was examined by Scanning Electron Microscopy using FEI NOVA NANO SEM 200 with EDS analyzer by EDAX.

3. Results and discussion

The X-ray diffraction analysis of intermetallic materials manufactured as a result of SHS synthesis with thermal explosion ignition system showed that obtained material consist mostly of the desired TiAl phase (76.5 wt.%) and other intermetallic phases such as Ti_3Al (14.2 wt.%), $TiAl_2$ (5.3 wt.%), $TiAl_3$ (2.9 wt.%) and others ($TiAlN_2$ or TiO 1.1 wt.%). The XRD results are presented on the Fig. 1.

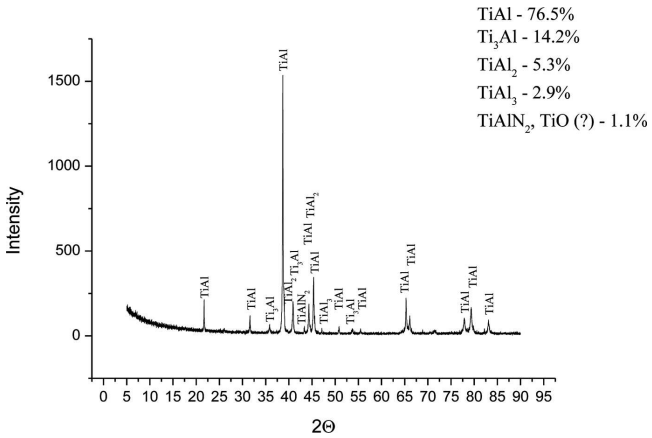

Fig. 1. XRD pattern of the TiAl powder obtained by SHS

The XRD phase analysis of SHS derived active precursors of MAX phases showed that in both powders the dominating phases are ternary MAX materials. In the case of 312 phase the obtained powder composition was: 73.8 wt.% of Ti_3AlC_2, 11.3 wt.% of Ti_2AlC, and 14.8 wt.% of TiC. Even better results were achieved in case of 211 phase powder which consist of dominating Ti_2AlC phase (95.4 wt%) and $TiAl_2$ phase (4.6 wt.%). These results also proved that upscaling process does not affect or even improve the phase composition of active sintering precursors of ternary phase materials in Ti-Al-C system [13, 14]. The XRD results are presented on Fig. 2 and Fig. 3 respectively.

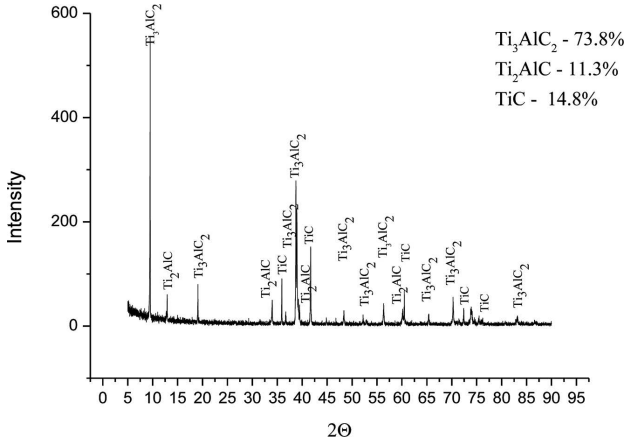

Fig. 2. XRD pattern of the Ti_3AlC_2 powder obtained by SHS

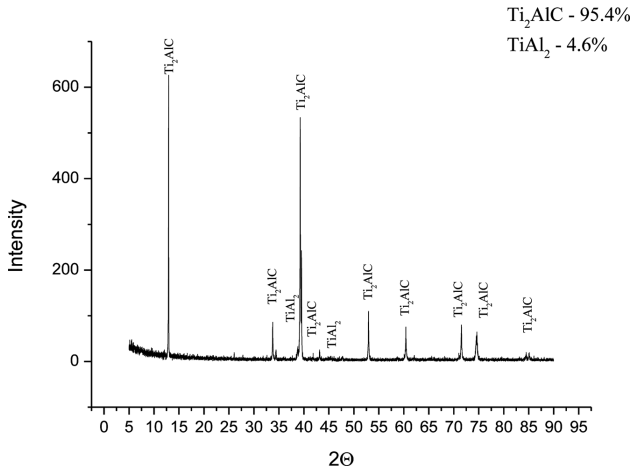

Fig. 3. XRD pattern of the Ti_2AlC powder obtained by SHS

TABLE 1

Products of SHS synthesis of Ti_3AlC_2 phase composition. The measurements were made within an accuracy of ±0.5 wt.%

Reaction No.	Weight of the sample [g]	Chemical reaction	Ti_3AlC_2 [wt.%]	Ti_2AlC [wt.%]	TiC [wt.%]	Al_4C_3 [wt.%]	$TiAl_2$ [wt.%]
2 [14]	25	1.2TiAl + Ti + C → Ti_2AlC	12.1	65.8	10.2	12.0	-
2	125	1.2TiAl + Ti + C → Ti_2AlC	-	95.4	-	-	4.6
Hot-pressed sample		1.2TiAl + Ti + C → Ti_2AlC	-	**98.7**	1.3	-	-
2 [13]	25	1.1 TiAl + 2Ti + 2C → Ti_3AlC_2	76.4	18.9	4.7	-	-
2	125	1.1 TiAl + 2Ti + 2C → Ti_3AlC_2	73.8	11.3	14.8	-	-
Hot-pressed sample	-	1.1 TiAl + 2Ti + 2C → Ti_3AlC_2	**90.3**	-	9.7	-	-

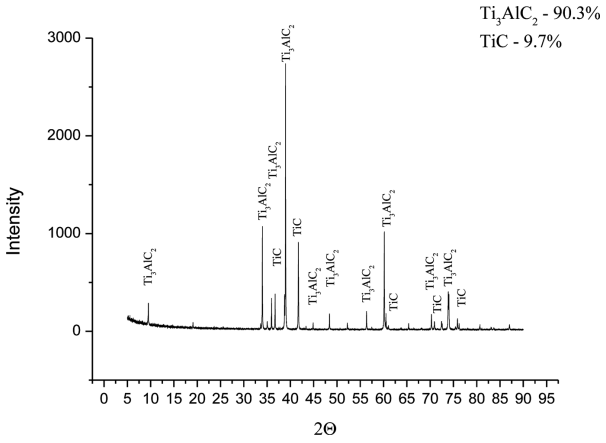

Fig. 4. XRD pattern of the Ti_3AlC_2 hot pressed at 1300°C for 1h

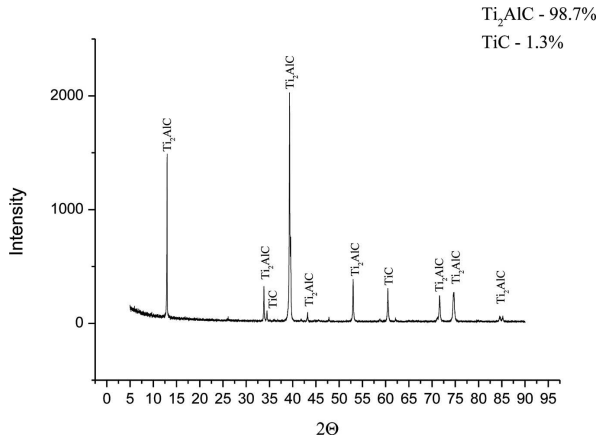

Fig. 5. XRD pattern of the Ti_2AlC hot pressed at 1100°C for 1h

The hot-pressing process showed that SHS derived active sintering precursors are very good powders to obtain dense polycrystalline MAX phases material. The amount of ternary phase was increased in both sintered powders and in the case of Ti_2AlC powder, hot-pressed material was almost single phase material (98.7 wt.% of Ti_2AlC) with low amount of TiC impurities (1.3 wt.%). The detailed information about phase composition of initial powders and sintered samples are presented in TABLE 1. The measurements were made within an accuracy of ±0.5 wt.%. The XRD analyses are presented on Fig. 4 and Fig. 5 respectively.

TABLE 2

Properties of hot-pressed Ti_2AlC and Ti_3AlC_2 materials

	Ti_2AlC	Ti_3AlC_2
Apparent density [g/cm^3]	2.96±0.02	4.20±0.03
Open porosity [%]	25.38±0.47	0.61±0.01
E [GPa] - diameter	75±1	323±3
E [GPa] - height	84±2	305±4
G [GPa] - diameter	32±1	136±1
G [GPa] - height	36±1	131±1
$\mu-$ diameter	0.182±0.07	0.186±0.03
$\mu-$ height	0.182±0.09	0.167±0.006
HV [GPa]	0.62±0.27	4.22±0.96
Bending strength [MPa]	79.9±16.9	526.5±42.1
K_{Ic} [MPa*m$^{1/2}$]	7.88±0.57	8.52±1.86

Mechanical properties of hot-pressed ternary materials are presented in TABLE 2. It is worth to notice that high porosity of Ti_2AlC sample may strongly affect its mechanical properties.

On Figure 6 example of the plate like structures of grains characteristic for MAX phases can be seen.

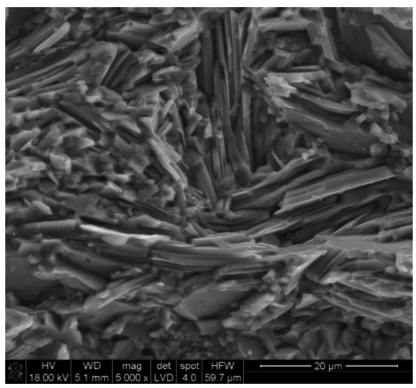

Fig. 6. SEM Morphology of Ti_3AlC_2 material

4. Conclusion

The experiments proved that SHS is a suitable method for obtaining active powder precursors for hot-pressing process in which single phase (Ti_2AlC) or near single phase (Ti_3AlC_2) materials were obtained. This method is not only possible but also effective and efficient.

The hot-pressing process promotes further chemical reaction towards formation of MAX phases eliminating impurities such as TiC, which strongly affects properties of material. However some optimal parameters of hot-pressing process must be still established to achieve full densification of Ti_2AlC materials. On the other hand the Ti_3AlC_2 manufactured in the HP process has very low porosity.

The morphology of obtained materials is characteristic for the MAX phases ternary material and consists of relatively large plate-like grains.

Mechanical properties of MAX phase materials were very good in the case of Ti_3AlC_2, and lower in the case of Ti_2AlC where high porosity strongly affected its properties.

Manufactured materials are very promising, but still some researches on optimization of sintering process of 211 material are necessary.

Acknowledgements

This work was supported by the National Science Centre under the grant no. 2472/B/T02/2011/40.

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Received: 20 February 2014.