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COMPOSITES THEORY AND PRACTICE

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THERMAL PROPERTIES OF Al ALLOY MATRIX COMPOSITES REINFORCED WITH MAX TYPE PHASES

A method was developed for manufacturing Al-Si alloy matrix composites reinforced with MAX phases by squeeze casting pressure infiltration of porous preforms. MAX phases in the Ti-Al-C system were synthesized using self-propagating high-temperature synthesis (SHS) in the microwave assisted mode in order to obtain spatial structures with open porosity consisting of a mixture of Ti_2AlC and Ti_3AlC_2. The manufactured composite together with a reference sample of sole matrix material were subjected to the testing of thermal properties such as: thermal conductivity, thermal diffusivity and thermal expansion in the temperature range of 50÷500°C, which corresponds to the expected working temperatures of the material. The specific heat and mass change during heating were also established by means of thermogravimetric analysis. The obtained thermal conductivity coefficients for the Al-Si+Ti-Al-C composite were higher than for the sole MAX phases and equaled 27÷29 W/m·K. The thermal expansion values for the composite material were reduced two-fold in comparison with the matrix.

Keywords: **MAX phases, SHS synthesis, microwave, porous structure, squeeze casting, thermal conductivity, thermal expansion**

WŁAŚCIWOŚCI CIEPLNE KOMPOZYTÓW NA OSNOWIE STOPU Al UMACNIANYCH FAZAMI TYPU MAX

Opracowano metodę wytwarzania kompozytów na osnowie stopu Al-Si wzmocnionego fazami typu MAX metodą infiltracji ciśnieniowej porowatych preform. Fazy typu MAX syntezowano metodą samorozprzestrzeniającej się syntezy wysokotemperaturowej (SHS), wspomaganej mikrofalami w układzie Ti-Al-C, w celu uzyskania przestrzennych struktur o porowatości otwartej z mieszaniny faz Ti_2AlC i Ti_3AlC_2. Wytworzone materiały kompozytowe wraz z próbką referencyjną w postaci materiału osnowy poddano badaniom właściwości cieplnych, tj. przewodności cieplnej, dyfuzyjności cieplnej oraz rozszerzalności cieplnej w zakresie temperatur 50÷500°C, który przyjęto jako spodziewany zakres temperatur pracy wytworzonych materiałów. Wyznaczono również wartości ciepła właściwego oraz, za pomocą analizy termograwimetrycznej, zmiany masy w stosunku do zmiany temperatury. Uzyskane współczynniki przewodności cieplnej dla materiału kompozytowego Al-Si+Ti-Al-C były wyższe niż dla samych faz typu MAX i wynosiły 27÷29 W/m·K. Zmierzone wartości współczynnika rozszerzalności cieplnej dla materiału kompozytowego były dwukrotnie niższe w odniesieniu do materiału osnowy.

Słowa kluczowe: fazy MAX, synteza SHS, mikrofale, porowata struktura, infiltracja ciśnieniowa, przewodność cieplna, rozszerzalność cieplna

INTRODUCTION

MAX type phases, also called machinable ceramics, is a group of carbides and nitrides described by the general formula $M_{n+1}AX_n$, which are characterized by a layered ternary molecular structure [1-3]. Their crystalline arrangement is composed of M-X layers interconnected with the A element. Chemical bonding between the particular layers is mainly metallic, while between the M and X elements it is covalent. MAX phases remarkably merge the best features of metals and ceramics. Two titanium aluminum carbides Ti_2AlC and Ti_3AlC_2 are of the most extensively elaborated MAX phases as they are the most lightweight and oxidation resistant [4]. Both of them are good thermal conductors with a low coefficient of thermal expansion, which together with their superior wear properties, can make these MAX phases and their composites excellent candidates for applications as structural materials for elements working at elevated temperatures: high-temperature bushings, brake discs or heat exchangers. The thermal conductivity of MAX phases at room temperature (RT) falls within the range of 12÷60 W/m·K, while their thermal expansion coefficient equals approximately $6 \div 10 \cdot 10^{-6}$ K^{-1} [5]. One might notice the fact that MAX type phases are good thermal conductors

can be explained by their good electric conductivity, as on the basis of the Wiedemann-Franz law thermal electron conductivity is directly proportional to electric conductivity. Nevertheless, the overall thermal conductivity of the material is both influenced by phonon and electron thermal conductivity [6]. In these terms, MAX phases can be divided into two groups: 1) materials containing Al or S, in which the thermal conductivity is mainly defined by high phonon thermal conductivity, 2) the rest in which phonon thermal conductivity can be neglected [7]. The RT thermal electron conductivities of Ti_2AlC and Ti_3AlC_2 phases are respectively 20÷20.5 W/m·K, 21 W/m·K, while their phonon thermal conductivities are 12.5÷26 W/m·K and 19 W/m·K. The above mentioned values create the theoretical overall thermal conductivities of 33÷46 W/m·K for Ti_2AlC and 40 W/m·K for Ti_3AlC_2 [1]. Different experimental values for Ti_2AlC were reported by Barsoum et al. as 23 W/m·K, which is far lower than calculated [8]. Moreover, in the review paper by Wang it was stated that the thermal conductivity coefficient for Ti_3AlC_2 equals 27.5÷40 W/m·K [9]. Son et al. determined the thermal expansion coefficient (TEC) for Ti_3AlC_2 in the temperature range of 0÷1000°C as $8.2\div11.6\cdot10^{-6}$ K^{-1} [10]. Commercial Ti_2AlC powders were tested in vacuum for temperatures from 25 to 1000°C with the heating rate of 3°C/min and resulted in TECs of $8\div10\cdot10^{-6}$ K^{-1} [11]. Wang presented similar studies on Ti_2AlC and Ti_3AlC_2 obtaining the following values: $8.2\div9.62\cdot10^{-6}$ K^{-1} and $9.0\div9.2\cdot10^{-6}$ K^{-1}, respectively [9]. Together with thermal conductivity and expansion, thermal stability at elevated temperatures has also been one of the main concerns of researchers to date. The thermal stability of Ti_2AlC was elaborated by Adamaki et al. The Ti_2AlC MAX phase was heated to 1200°C and subsequently rapidly cooled at the cooling rate of 90°C/s while continuously compressed with a pressure of 50÷150 MPa. Neither visible changes in the microstructure, nor deterioration of the mechanical properties was observed [12]. At higher temperatures MAX type phases do not melt congruently, but they are decomposed via a peritectic reaction into A rich liquid phases and binary carbides or nitrides $M_{n+1}X_n$ [5].

Among the most commonly reported methods of manufacturing 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. Despite the fact, that SHS is one of the most efficient fabrication methods, it is strictly connected with the creation of porosities in the material. Therefore, the necessity for additional infiltration occurs in order to obtain a dense and consistent composite material [13-17].

In the present study open-porous MAX phase skeletons are manufactured by the means of microwave assisted self-propagating high-temperature synthesis (MASHS). Preforms belonging to the Ti-Al-C system were taken under consideration: a mixture of Ti_2AlC and Ti_3AlC_2. Squeeze casting infiltration with the Al-Si lightweight casting alloy is hereby proposed as an alternative to the conventional techniques used for producing MAX phase based composites, which ensures the most precise filling of open porosities of the reinforcement. The manufactured composites together with a reference sample of sole matrix material were subjected to the testing of thermal properties such as: thermal conductivity, thermal diffusivity and thermal expansion in the temperature range of 50÷500°C, which corresponds to the expected working temperatures of the material. Specific heat and mass change during heating were also established. In combination with the remarkable tribological properties described in a previous work [18], the presented results show that the manufactured MAX phase based composite materials are promising candidates for wear- and high-temperature-resistant applications.

EXPERIMENTAL METHODS AND APPROACH

Ti (99.5% Ti, -325), Al (99.9% Al, -325, Alfa Aesar) and graphite (99.5% C, -325SGL Carbon Ltd graphite) commercial powders were used as the starting materials with molar ratios 2:1:1 to prepare a stoichiometric reactant mixture and fabricate Ti_2AlC and Ti_3AlC_2. The above composition was used to fabricate the above mentioned MAX phases by the coupled microwave assisted self-propagating high-temperature synthesis (MASHS). The Ti, Al, C powder amounts were firstly weighed with the accuracy to 0.001 g and milled with ZrO_2 balls for 10 minutes. Subsequently, the powders were uniaxially cold-pressed in a hydraulic press into samples in the shape of pellets with a 22 mm diameter under the pressure of 930 MPa for 10 seconds. Afterwards, the prepared samples were subjected to MASHS, which was conducted in a microwave reactor [19]. The temperature was detected by a Raytek Marathon MM pyrometer with the measuring spot diameter 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 a previous work [20]. The prepared samples were subsequently used as the reinforcement for composite materials based on MAX phases. Porous preforms were infiltrated by means of the squeeze casting method with the Al-Si alloy (EN AC44200). The die containing preforms were heated to 200÷300°C. The liquid alloy at the temperature of 720÷740°C was pressurized to fill up the die under pressure of 90 MPa. For the produced composites the microstructure and phase identification were performed with a scanning microscope Hitachi S-3400N and Chemical Analyzer SwiftED3000. The thermal properties (thermal diffusivity and thermal conductivity) were measured within the

temperature range 50÷500°C using a Laser Flash Analyser LFA457/Netzsch. The measurement principle is as follows. The front side of a parallel plane of a solid sample is heated by a short laser pulse (Nd-YAG). The induced heat propagates through the sample and causes a temperature increase on the rear surface. This temperature rise is measured versus time using an infrared detector. The thermal diffusivity (a) and, in most cases, the specific heat (c_p) can be ascertained using the measured signal. If the density (ρ) and the specific heat are known, the thermal conductivity (λ) is determined from the relation:

$$\lambda = c_p \cdot a \cdot \rho \quad (1)$$

where: λ - thermal conductivity in [W/mK], ρ - density in [g/cm^3], c_p - specific heat in [J/g K], a - thermal diffusivity in [mm^2/s].

The thermal expansion coefficient values were determined using a DIL 402 Netzsch dilatometer. Measurements of specific heat and weight loss (TG curves) were made on an STA 449 F1 Jupiter Netzsch device. All the measurements were carried out in a protective atmosphere of argon.

RESULTS AND DISCUSSION

In the Ti-Al-C system the SHS reaction is initiated at the temperature of ~670°C, corresponding to the melting point of aluminum. Then the reaction propagation front passes simultaneously through the entire volume of the sample. The synthesis starts after a few dozen seconds of microwave heating. During the solidification process MAX type phases are formed: Ti_2AlC and Ti_3AlC_2 and secondary phases, e.g. TiC. After the complete course of the synthesis, the samples are visibly deformed. As a result of the solid-liquid reaction, they undergo two types of deformation. Radial compression is due to the surface tension occurring in the Al-Ti liquid alloy, and axial elongation is consistent with the propagation direction of the synthesis front and parallel to the growth direction of the MAX type phase plates. The material synthesized in this way is highly porous. The obtained porosity is open and suitable for the pressure infiltration process. The microstructures of the produced material before after pressure infiltration of the preforms in the Ti-Al-C system with the Al-Si matrix alloy observed in scanning microscopy are shown in Figure 1. Residual porosity only takes up to several percent of the volume of the produced materials, hence it can be concluded that the degree of saturation achieved during infiltration is almost complete. This process is so effective that it allows the matrix material to be injected not only into the interior of the porosity, but also between the MAX phase platelets. During the infiltration, no additional undesirable reactions between the matrix material and the preform were observed. Within the composite material, no additional phases, oxidation products, mutual diffusion between the matrix and reinforcement or other adverse effects resulting from the squeeze casting infiltration were found.

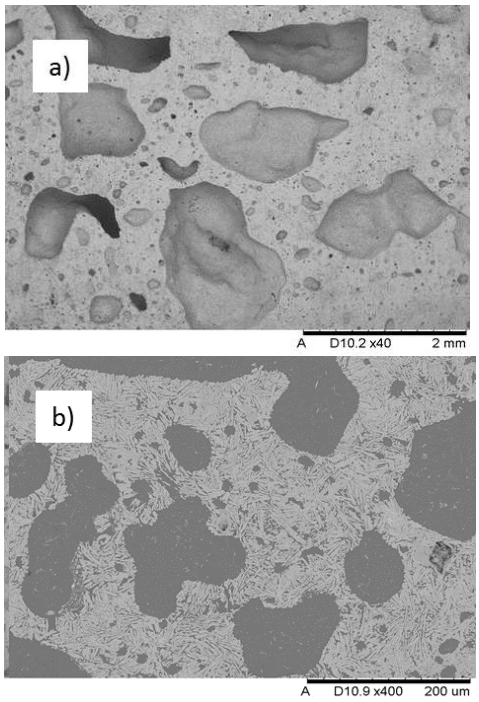

Fig. 1. SEM images of: a) Ti-Al-C MAX preform, b) Ti-Si-C MAX/Al-Si composite

Rys. 1. Mikrografie SEM: a) preforma fazy MAX w układzie Ti-Al-C MAX, b) materiał kompozytowy Ti-Al-C MAX/Al-Si

The thermal conductivity of MAX phases (λ) is usually higher than the one of binary MX or MA compounds. For the majority of MAX phases (except Ti_4AlN_3, Nb_2AlC and Ta_4AlC_3), their thermal conductivity is reduced to some extent together with an increase in temperature [1], which stands in agreement with the results of the performed tests. Table 1 presents the obtained results of thermal conductivity and thermal diffusivity for the obtained materials in the temperature range of 50÷500°C, while Figure 2 presents the change in thermal conductivity in the function of time. Together with increasing temperature, a slight reduction in thermal conductivity can be observed. In the case of th Al-Si+Ti-Al-C composite material, as well as for the matrix itself, a slight increase in thermal conductivity was observed for the highest of the tested temperatures, due to the approach to the melting temperature of Al and the accompanying increased mobility of the particles. Assuming the following values (23 W/m·K - Ti_2AlC, 27.5 W/m·K - Ti_3AlC_2) as correct for the MAX phases in the Ti-Al-C system, a slight improvement in the conductivity of the composite material was found (λ ~ 27÷29 W/m·K) in comparison with the reinforcement material. Al-containing MAX phases possess high Debye temperatures and therefore are decent phonon conductors [6]. Figure 3 shows the specific heat vs time curves for the tested materials. As one can notice, the specific heat increases together with the temperature, as was established in a previous study [7].

The measured change of mass from the thermogravimetric analysis (TGA) for the Al-Si matrix, the Al-Si+Ti-Al-C composite equaled respectively 0.35% and 0.17%.

TABLE 1. **Thermal conductivity and thermal diffusivity for obtained materials in temperature range 50÷500°C**
TABELA 1. **Przewodność cieplna i dyfuzyjność cieplna otrzymanych materiałów w zakresie 50÷500°C**

Temperature [°C]		Al-Si matrix		Al-Si+Ti-Al-C composite	
		Thermal diffusivity [$mm^2 \cdot s^{-1}$]	Thermal conductivity [$W \cdot m^{-1} \cdot K^{-1}$]	Thermal diffusivity [$mm^2 \cdot s^{-1}$]	Thermal conductivity [$W \cdot m^{-1} \cdot K^{-1}$]
50	Mean value	58.44	177.66	11.63	29.30
	Deviation	1.40	4.58	0.08	0.27
100	Mean value	54.48	163.86	10.92	28.27
	Deviation	0.69	2.26	0.07	0.23
200	Mean value	50.03	153.73	9.97	26.87
	Deviation	0.07	0.24	0.05	0.18
300	Mean value	46.49	144.38	9.43	26.41
	Deviation	0.32	1.04	0.01	0.03
400	Mean value	45.50	145.78	9.31	26.73
	Deviation	0.07	0.24	0.07	0.24
500	Mean value	43.49	170.61	9.08	27.33
	Deviation	0.19	0.61	0.04	0.15

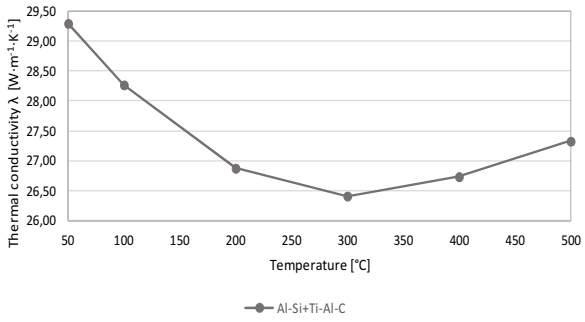

Fig. 2. Dependence of thermal conductivity λ [$W \cdot m^{-1} \cdot K^{-1}$] in function of time for tested Al-Si+Ti-Al-C composite material in temperature range 50÷500°C

Rys. 2. Zależność przewodności cieplnej λ [$W \cdot m^{-1} \cdot K^{-1}$] od czasu dla badanych materiałów kompozytowych Al-Si+Ti-Al-C w zakresie 50÷500°C

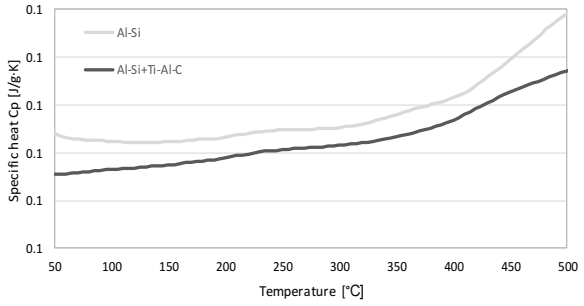

Fig. 3. Dependence of specific heat c_p [$J \cdot g^{-1} \cdot K^{-1}$] in function of time for tested materials in temperature 50÷500°C

Rys. 3. Zależność ciepła właściwego c_p [$J \cdot g^{-1} \cdot K^{-1}$] od czasu dla badanych materiałów kompozytowych Al-Si+Ti-Al-C w zakresie 50÷500°C

Figures 4 and 5 show the dependences of the relative elongation and thermal expansion coefficients in the function of the temperature. The measured values of thermal expansion confirm a more than two-fold improvement in the thermal dimensional stability of the produced composites compared to the matrix material. The temperature expansion of the composite material is comparable with that of the MAX type. In the case of the Al-Si + Ti-Al-C composite, the value of the expansion coefficient, analogous to the matrix material, shows a slow upward tendency to approx. 250°C and then decreases with a further temperature increase. The measured values correspond to the properties of the sole MAX phases, which usually belongs to the range of $5 \div 10 \cdot 10^{-6}$ K^{-1} [5].

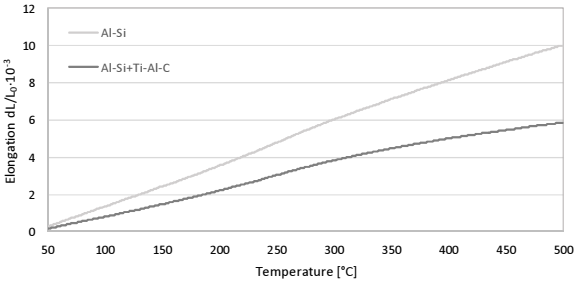

Fig. 5. Dependence of relative elongation in function of time for tested materials in temperature range 50÷500°C

Rys. 5. Zależność wydłużenia względnego od czasu dla badanych materiałów kompozytowych Al-Si+Ti-Al-C w zakresie 50÷500°C

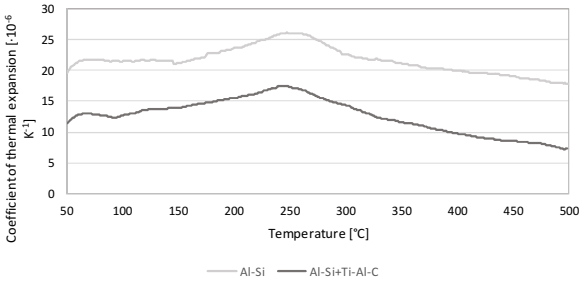

Fig. 6. Dependence of thermal expansion coefficient [K^{-1}] in function of time for tested materials in temperature range 50÷500°C

Rys. 6. Zależność współczynnika rozszerzalności cieplnej [K^{-1}] od czasu dla badanych materiałów kompozytowych Al-Si+Ti-Al-C w zakresie 50÷500°C

CONCLUSIONS

Pore-free, high-temperature resistant metal matrix composite materials reinforced with MAX phases were successfully manufactured by means of microwave assisted self-propagating high-temperature synthesis and subsequent squeeze casting infiltration. The obtained composite materials were characterized by a relatively homogeneous structure with no visible defects, discontinuities in the structure or non-infiltrated residual porosities, which could fundamentally deteriorate the thermal conductivity and stability at elevated temperature. The produced materials exhibit enhanced thermal conductivity and significantly increased thermal stability, as the thermal expansion coefficients for

them are two times lower than for the Al-Si matrix alloy. In combination with the remarkable tribological properties described previously, the presented study points to the manufactured MAX phase based composite materials as promising candidates for wear- and high-temperature-resistant applications.

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