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COMPOSITES

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SYNTHESIS OF Ni_3Al COMPOSITES REINFORCED BY TiC, WC, ZrC, NbC, TaC - CARBIDE PARTICLES

Metal matrix composites (MMCs) dispersion hardened with particles are a product of modern and advanced technology. The functional properties of these materials depend on the type, size and volume fraction of the particles of the reinforcing phase, on the type of matrix, and on the method of fabrication. This study describes composite materials based on nickel aluminide Ni_3Al reinforced with ceramic particles of the carbides of metals such as W, Ti, Nb, Zr, and Ta, fabricated by the "in situ" SHSB method patented by the Faculty of Foundry Engineering, AGH University of Science and Technology. The most serious drawbacks of the commonly applied "ex situ" methods are microporosity, gravity segregation, and poor wettability of the particles by the liquid metal matrix. All these drawbacks can be avoided when the "in situ" method is applied. In this paper, the selected method was the "in situ" synthesis of the carbides of titanium, tungsten, zirconium, niobium and tantalum by a spontaneous exothermic reaction taking place in an Ni_3Al alloy melt. The selection of the intermetallic compound Ni_3Al as the composite matrix was dictated, among others, by its ability to become plastic, and by its high resistance to oxidation in a wide range of temperatures, combined with the high resistance to creep and tribological wear. The particles of TiC, WC, ZrC, NbC, and TaC were selected as the reinforcement of the composites. The techniques used in the investigation microstructures of the experimental materials included scanning microscopy and X-ray microanalysis.

Keywords: composite "in situ", intermetallic phase, SHSB Process, exothermic reaction, metal carbides of TiC, WC, ZrC, NbC, TaC

SYNTEZA KOMPOZYTÓW Ni_3Al UMACNIANYCH CZĄSTKAMI WĘGLIKÓW TiC, WC, ZrC, NbC ORAZ TaC

Kompozyty o osnowie metalowej (MMCs) umacniane dyspersyjnymi cząstkami są wytworem nowoczesnej technologii. Właściwości użytkowe tych materiałów zależą od typu, wielkości i udziału objętościowego cząstek fazy zbrojącej, od doboru osnowy oraz od metody ich wytwarzania. Prezentowana praca przedstawia opis materiałów kompozytowych na osnowie aluminidu niklu Ni_3Al, umacnianego cząstkami ceramicznymi węglików takich metali, jak W, Ti, Nb, Zr i Ta, wytworzonych metodą „in situ" SHSB opatentowaną na Wydziale Odlewnictwa AGH. Największymi wadami powszechnie stosowanej metody „ex situ" są: mikroporowatość kompozytów, segregacja grawitacyjna oraz zła zwilżalność cząstek przez ciekłą osnowę metaliczną. Wad tych można uniknąć, stosując wybraną w niniejszej pracy metodę „in situ" syntezy węglików tytanu, wolframu, cyrkonu, niobu i tantalu drogą samorzutnej reakcji egzotermicznej w kąpieli stopu Ni_3Al. Wybór jako osnowy związku międzymetalicznego Ni_3Al podyktowany był między innymi możliwością jego uplastycznienia, wysoką odpornością na utlenianie w szerokim zakresie temperatur, a także wysoką odpornością na pełzanie i zużycie trybologiczne. Jako umocnienie kompozytów wybrano cząstki następujących węglików: TiC, WC, ZrC, NbC oraz TaC. Do badań strukturalnych otrzymanych materiałów wykorzystano metody mikroskopii skaningowej oraz mikroanalizy rentgenowskiej.

Słowa kluczowe: kompozyt „in situ", faza międzymetaliczna, proces SHSB, reakcja egzotermiczna, węgliki metali TiC, WC, ZrC, NbC, TaC

INTRODUCTION

Recent years have seen dynamic development of research on metal matrix composite materials, which due to a number of unusual properties can be successfully applied in many branches of industry such as: the automotive and aircraft industries, extraction of mineral resources, or, finally, sports and entertainment [1-4]. Among various MMCs, the most widely used are composite materials based on light metal alloys such as aluminium, titanium and magnesium, which guarantee high relative strength. As a reinforcing phase, the following materials are used: carbides (TiC, SiC, ZrC), oxides (Al_2O_3, TiO_2, MgO, ZrO_2), nitrides (BN, TiN, ZrN), borides (TiB_2, ZrB_2, SiB_2), silicides ($MoSi_2$), or fine particles of intermetalic compounds (Ni_3Al, NiAl, Fe_3Al, FeAl, Ti_3Al, TiAl) [5].

An original solution was to use as a matrix the Ni-Al alloy containing 87 wt.% nickel and 13 wt.% aluminium, solidifying as an intermetallic Ni_3Al phase.

The choice has been dictated by the very beneficial physical, chemical and mechanical properties offered by this phase. Numerous scientific studies have been devoted to the technology of making intermetallic phases and to the determination of their mechanical and tribological properties, as well as corrosion behaviour [6, 7]. Nickel aluminide Ni_3Al is characterised by high resistance to oxidation and stability of mechanical properties in a wide range of temperatures. The tensile strength of this compound increases with temperature and, depending on the grain size, reaches its maximum values in the range of 933÷1123 K. In contrast to many nickel-based superalloys, such materials also exhibit satisfactory compression strength in a temperature range of 923÷1373 K, as well as increased resistance to fatigue, which results from the alloy homogenity and lack of chemical segregations in the matrix. The Ni_3Al compound also exhibits high resistance to creep and mechanical wear. Against the background of these positive features, an undisputable drawback of the Ni_3Al phase is its insufficient ductility. However, this disadvantage can be overcome through the use of microalloying elements, boron in particular [8]. The choice of carbides for the reinforcing phase has been fully justified by their specific physical, chemical and mechanical properties. Metal carbides are a group of compounds characterised by a high melting point, high hardness, high Young's modulus, high resistance to abrasive wear and corrosion resistance at both ambient and high temperatures. Thus, processing a high-strength Ni_3Al phase into a composite reinforced with creep-resistant and hard carbides, creates a good opportunity for full utilisation of its mechanical and tribological properties. The manufacture of Ni_3Al/MeC type composites by the synthesis of TiC, WC, ZrC, NbC and TaC carbides in an SHSB process, the essence of which consists in direct in-bath processing of the Ni_3Al compound, gives the possibility for direct control of the volume fraction of the reinforcing phase and ensures the thermodynamic stability of the material, with the absence of chemical reactions at the matrix-particle interface and a high-degree of composite particles dispersion.

TABLE 1. **Carbides used for hardening of MMCs [6]**
TABELA 1. **Węgliki stosowane do umacniania kompozytów MMCs**

MeC	Density g/cm^3	Melting temperature °C	Microhardness μHV	Heat of formation kJ/mole
TiC	4.93	3250+/- 100	2850	183
SiC	3.21	up to 2800 then decomposes	3340	66
ZrC	6.73	3530	2920	184
VC	5.36	2830	2094	101
NbC	7.56	3760	2000	130
TaC	14.30	3880	1600	141
WC	15.60	2870	2080	35

From the group of carbides presented in Table 1 [9], the authors have chosen those for which the initiation of the exothermic reaction of synthesis seemed possible [10].

Composite synthesis by SHSB method

The SHSB method of composite synthesis is a modification of the SHS method, widespread in many areas of materials science. Generally it can be stated that the SHS method consists in the formation of a mixture of metal and non-metal powders, and in local surface heating of this mixture to initiate a spontaneously spreading, very strong exothermic reaction. The method was developed in the U.S. by the Martin Marietta Corporation, where research on this subject was carried out by Merzanov [11]. Merzanov's studies were continued by Anzelmi - Tamburini [10], who in the subsequent theoretical work focused their attention on a description of the exothermic reaction of synthesis taking place between metal and non-metal elements. In view of the very interesting possibilities offered by the SHS reaction, the said method has become the object of interest of many research centres. It allows the synthesis of various ceramic particles, including carbides, borides and nitrides. All these compounds are characterised by high hardness, high melting point and high Young's modulus, therefore the advantageous/beneficial properties of ceramic particles can be successfully used in designing composite materials.

In the process of creating a new composite material by SHS, a few important conditions should be taken into consideration. The reaction should be of a strongly exothermic character with the heat of formation reaching 170 kJ/mole. This ensures that a sufficient amount of thermal energy is transferred to the yet unreacted portions of material. Another important condition of the SHS process is that the rate of heat exchange must be lower than the rate of heat generation by the exothermic reaction, otherwise the risk exists that the reaction will extinguish itself.

The process of the SHS synthesis of materials is characterised by a high reaction temperature reaching even 5000 K, high-speed movement of the reaction front ranging up to 0.25 m/s, and a high temperature gradient of up to 10^7 K/m. The most important parameters of this process include the so called, adiabatic temperature T_{ad} and the velocity u of the reaction front movement. In the SHS process, the adiabatic temperature determines the maximum temperature that can be locally achieved by the reaction product from the initiation of the reaction up to its completion. It can be generally assumed that for the reaction written in its most general form

$$M + X = MX \tag{1}$$

where M, X and MX are the metal, non-metal and product of the solid state synthesis respectively, the adia-

batic temperature can be determined as a function of the upper limit of integration from the following relationship [10]:

$$\Delta H^{o}_{T_o} = \int_{T_o}^{T_{ad}} c_m(MX)dT \qquad (2)$$

where: $\Delta H^{o}_{T_o}$ - enthalpy of formation of MX compound at temperatures T_0 and T_{ad}, $c_m(MX)$ - molar heat of reaction product.

Figure 1 shows an example of temperature - time dependence which occurs in a standard SHS method during the synthesis of TiB_2. During the synthesis of titanium carbide, the adiabatic temperature is 3210 K. In practice, the thermodynamic system never reaches this temperature and the real temperature of the reaction is much lower. This is due to heat dispersion in the system in which the process is running.

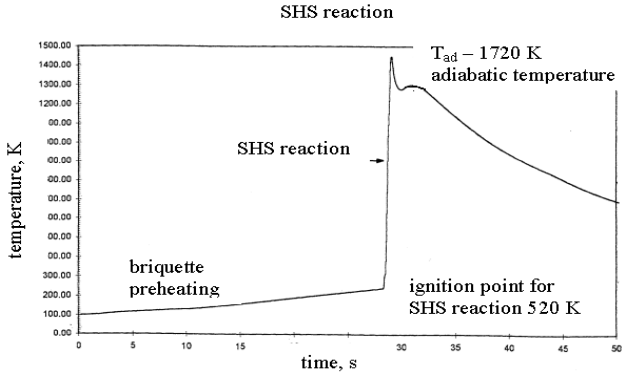

Fig. 1. Temperature - time relationship in standard SHS method during synthesis of TiB_2

Rys. 1. Zależność temperatury od czasu w klasycznej metodzie SHS uzyskana podczas syntezy TiB_2

RESEARCH METHODS

The specific character of the melting process of the intermetallic compound Ni3Al is due to a large difference between the melting temperatures of aluminium and nickel, and to the occurrence of an exothermic reaction during the formation of this phase. The rapid increase in temperature up to about 1800 K immediately after the occurrence of the exothermic reaction between Al and Ni in the atmosphere of air, followed by rapid oxidation of aluminium and the formation of slag make precise control of the alloy chemical composition extremely difficult. Therefore, the Ni-Al alloy was manufactured in a vacuum (in a Balzers vacuum furnace) using an argon atmosphere at a negative pressure of 0.05 MPa. After the melting of the aluminium and the occurrence of the exothermic reaction, an addition of boron was introduced to the liquid alloy in the form of an Al-B3% master alloy. Then, in the bath of the base Ni-Al-B alloy, during successive operations, the carbides of titanium, tungsten, zirconium, niobium and tantalum (in an amount of 5% volume fraction) were produced by the SHSB technique. The procedure was as follows: to the melt of the base alloy at a temperature of 1700 K, titanium and carbon (for example) were introduced in the form of a Ti-C-Al powder briquette, compacted at a pressure of 500 MPa. As soon as the briquette came in contact with the surface of the metal bath, the exothermic reaction of titanium carbide synthesis started. After 5 minutes, the ready suspension of Ni3Al + TiC was cast in a ceramic mould [8]. A similar method was used for the synthesis of other carbides, i.e. WC, Zr, NbC and TaC. From the thus fabricated composites, specimens were taken and prepared for metallographic examinations, scanning microscopy and structure examinations.

As already mentioned, the starting point for the development of a new method of composite synthesis was the previously described SHS process. Preliminary analysis of the thermodynamic data of this process showed that the process of synthesis of the reinforcing phase should also occur in a liquid medium, which is the metal bath. Hence emerged the idea of a new method called SHSB (self-propagating high-temperature synthesis in bath), which assumed the use of liquid metal as an initiator of the SHS reaction.

On the surface of molten metal in an induction furnace, a package with a stoichiometric mixture of metal/non-metal powders was introduced. Then, as a result of heat exchange in the package, the reaction of synthesis was initiated, the product of which were the particles of carbides (for example TiC). At the next stage of the process, the fluid motion induced by eddy currents in the electromagnetic field evenly distributed the suspension of the synthetic particles within the whole volume of the metal bath. Additionally, the liquid metal also played the role of a "cooling" system for the exothermic reaction.

RESULTS

The above described method enabled the fabrication of the following composite materials: Ni_3Al/TiC Ni_3Al/WC, Ni_3Al/NbC, Ni_3Al/ZrC and Ni_3Al/TaC. In this part of study, the results of the investigations of these materials are presented.

Ni_3Al/TiC composite

The microstructure of the obtained Ni_3Al/TiC composite is shown in Figure 2a, while Figure 2b shows the scanning topographic image of a sample of this material.

A photomicrograph of the Ni_3Al/TiC composite (Fig. 2a) shows the precipitates of titanium carbide of up to 10 μm dimensions distributed in the interdendritic spaces. The Ni_3Al/TiC phase boundary is presented in Figure 2b. Good coherence of the alloy matrix and ceramic particles caused destruction of the reinforcing phase during fracture of the Ni_3Al/TiC composite sample.

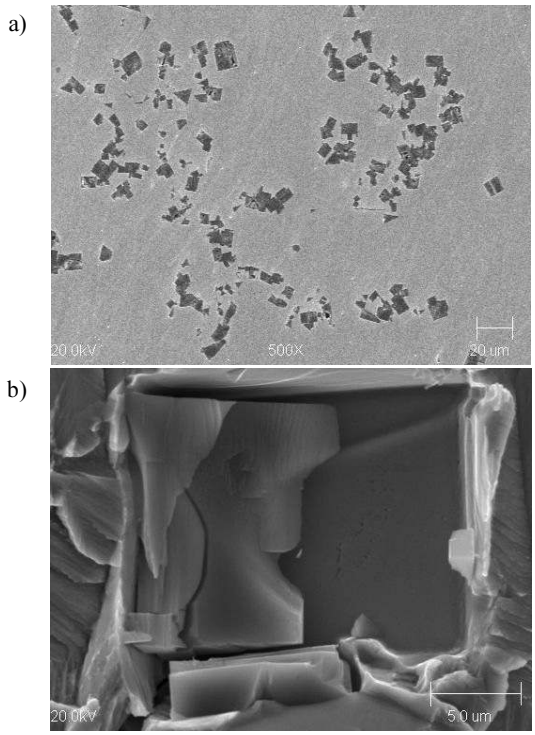

Fig. 2. Microstructure of Ni_3Al/TiC composite, 500x, (a), and scanning image of Ni_3Al/TiC composite fracture, 5000x (b)

Rys. 2. Mikrostruktura kompozytu Ni_3Al /TiC, 500x, (a), obraz skaningowy przełomu kompozytu Ni_3Al/TiC, 5000x (b)

Ni_3Al/WC composite

The fabricated composite was initially subjected to metallographic examinations. Figure 3a shows its microstructure.

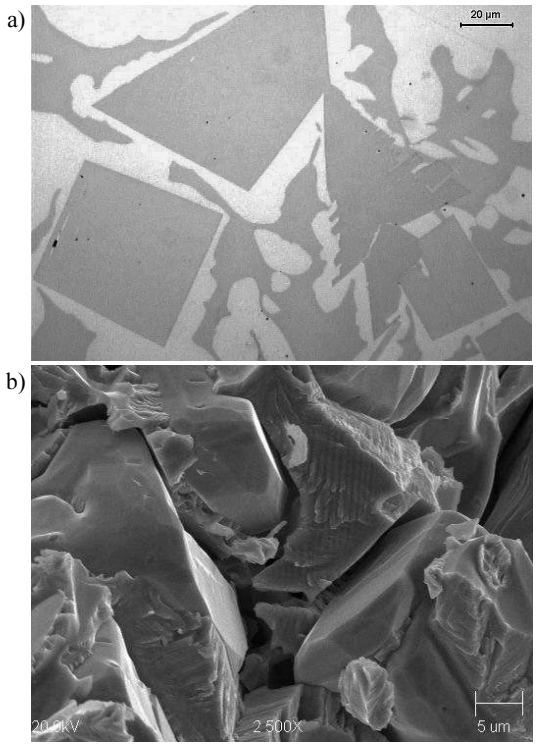

Fig. 3. Microstructure of Ni_3Al/WC composite, 500x, (a) and scanning image of Ni_3Al/WC composite fracture, 2500x (b)

Rys. 3. Mikrostruktura kompozytu Ni_3Al/WC, 500x, (a), obraz skaningowy przełomu kompozytu Ni_3Al/WC, 2500x (b)

The particles of WC carbides of dimensions from 20 to 80 µm are distributed in the interdendritic spaces of the matrix. The next step was examination of the matrix-reinforcing particle phase boundary in the Ni_3Al/WC composite done by scanning the specimen fracture as illustrated in Figure 3b. No foreign phases were detected on the Ni_3Al matrix - WC reinforcing particle phase boundary.

Ni_3Al/ZrC composite

As in the case described above, also in this composite, attention was focused on metallographic and scanning tests and X-ray microanalysis of the matrix--reinforcing particle phase boundary. The microstructure of the Ni_3Al/ZrC composite sample is shown in Figure 4a, while the results of the X-ray microanalysis of the Ni_3Al matrix-reinforcing particle phase boundary are shown in Figure 4b.

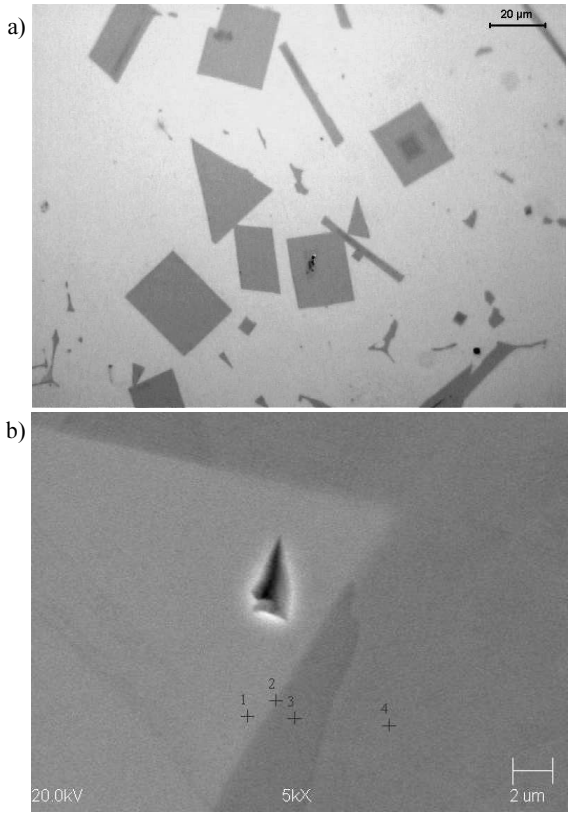

Fig. 4. Microstructure of Ni_3Al/ZrC composite, 500x, (a), scanning topographic image of Ni_3Al/ZrC composite, 5000x (b)

Rys. 4. Mikrostruktura kompozytu Ni_3Al/ZrC, 500x, (a), skaningowy obraz topograficzny kompozytu Ni_3Al/ZrC, 5000x (b)

The observed particles of zirconium carbide are several times smaller than the particles of the WC carbide. Also in this case, no chemical reactions were observed to have occurred on the matrix-reinforcing particle phase boundary.

In the Ni_3Al/ZrC composite, at selected points of the phase boundary, a local analysis was made and its results are given in Table 2.

TABLE 2. **Chemical composition of carbides and matrix in Ni_3Al/ZrC composite, measured using EDX**
TABELA 2. **Analiza chemiczna w mikroobszarze na granicy węglik-osnowa kompozytu Ni_3Al/Zr (metoda EDX)**

Chemical composition, wt.%				
Point	C	Al	Ni	Zr
1	46.7	0.1	1.0	52.1
2	47.1	3.1	13.4	36.5
3	-	23.7	75.4	0.8
4	-	15.5	83.6	0.8

Ni_3Al/NbC composite

The metallographic examinations have shown that niobium carbides NbC present in the composite occur in two forms, i.e. as individual particles and, more often, as large aggregates (Fig. 5a). Their size ranges from 10 to 20 μm.

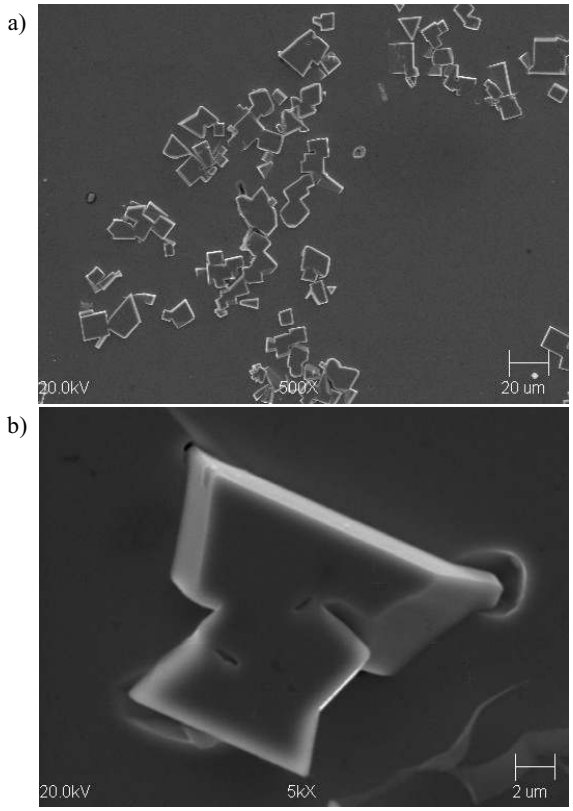

Fig. 5. Scanning image of Ni_3Al/NbC composite, 500x, (a) and topographic image 5000x (b).

Rys. 5. Skaningowy obraz kompozytu Ni_3Al/NbC, pow. 500x, (a) oraz obraz topograficzny, 5000x (b)

Besides the two basic phases of Ni_3Al and NbC, the X-ray microanalysis did not reveal any products of reaction at the matrix-reinforcing particle phase boundary (Fig. 5b).

Ni_3Al/TaC composite

The metallographic examinations of the Ni_3Al/TaC composite showed that tantalum carbides occurred in the form of large clusters (Fig. 6a), spread over the entire surface of the examined sample. The size of the precipitates was in the range of 4÷10 μm (Fig. 6b).

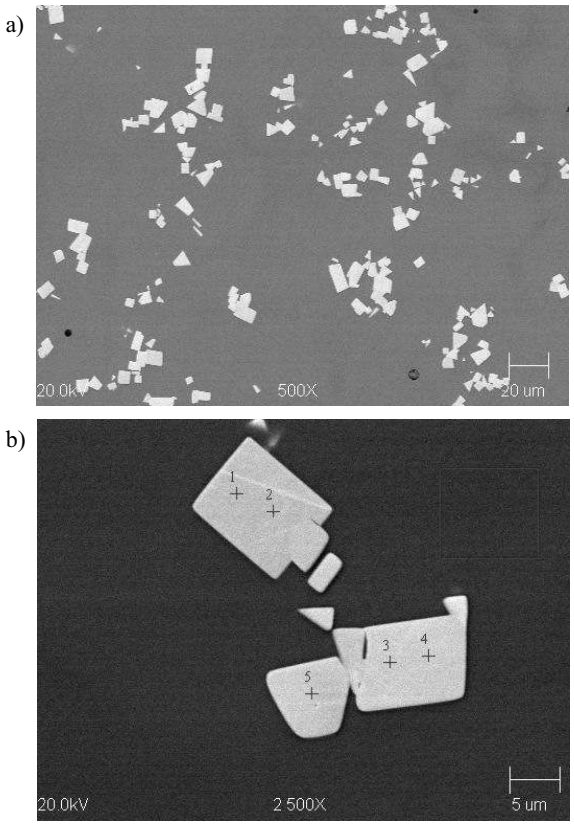

Fig. 6. Microstructure of Ni_3Al /TaC composite, 500x, (a), image with marked points of chemical analysis, 2500x (b).

Rys. 6. Mikrostruktura kompozytu Ni_3Al /TaC, 500x, (a), obraz z zaznaczonymi punktami analizy chemicznej, 2500x (b)

To check the nature of the formed ceramic phases, the chemical composition was examined by EDX analysis at selected points on the sample cross-section marked in Figure 6b. The measurement results are summarised in Table 3.

TABLE 3. **Chemical composition of carbides and matrix in Ni_3Al/TaC composite, measured using EDX**
TABELA 3. **Wyniki pomiarów składu chemicznego cząstek TaC i osnowy w kompozycie Ni_3Al/TaC, metoda EDX**

Chemical composition, wt.%				
Measuring point	C	Al	Ni	Ta
1	36,9	0,0	1,7	61,2
2	36,5	0,1	1,4	61,9
3	36,3	0,1	1,4	62,0
4	36,6	0,0	1,6	61,6
5	37,4	0,0	1,7	60,7
6	-	24,9	86,7	-

CONCLUSIONS

The SHSB method has proved to be an effective tool in the synthesis of five composites, i.e. Ni_3Al/TiC,

Ni_3Al/WC, Ni_3Al/Zr, Ni_3Al/NbC and Ni_3Al/TaC. The size of the TiC and TaC particles was comprised in the range of up to 10 μm. The carbides of TaC and ZrC had the size of 20 μm, while WC carbides were the largest (20 to 80 μm).

The X-ray microanalysis did not reveal any products of reaction at the matrix-reinforcing particle phase boundary in any of the examined composites (total absence of oxides, other precipitates, and cracks, as well). These are the major problems that occur when composites are fabricated by an in situ method.

The mechanical and tribological properties of Ni_3Al/TiC, Ni_3Al/WC, Ni_3Al/Zr, Ni_3Al/NbC and Ni_3Al /TaC will be the object of further research.

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