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ALUMINIUM AlMg1SiCu MATRIX COMPOSITE MATERIALS REINFORCED WITH HALLOYSITE PARTICLES

MATERIAŁY KOMPOZYTOWE O OSNOWIE STOPU ALUMINIUM AlMg1SiCu WZMACNIANE CZĄSTKAMI HALOIZYTOWYMI

In this work selected results of investigations of the new AlMg1SiCu matrix composite materials reinforced with halloysite particles manufactured by powder metallurgy techniques including mechanical alloying and hot extrusion are present. The composite materials obtained as a result of mechanical synthesis and hot extrusion are characterized with the structure of evenly distributed, disperse reinforcing phase particles in fine-grain matrix of AlMg1SiCu alloy, facilitate the obtainment of higher values of strength properties, compared to the initial alloy. The nanostructural composite materials reinforced with halloysite nanotubes with 15 mass % share are characterized by almost twice as higher micro-hardness – compared to the matrix material.

Keywords: aluminium matrix composites, halloysite nanotubes, mechanical alloying, hot extrusion

W pracy przedstawiono wybrane wyniki badań materiałów kompozytowych o osnowie stopu AlMg1SiCu wzmacnianych cząstkami haloizytowymi wytworzonymi z wykorzystaniem metod metalurgii proszków, w tym mechanicznej syntezy i wyciskania na gorąco. Otrzymane w procesie mechanicznej syntezy i wyciskania na gorąco materiały kompozytowe charakteryzują się strukturą równomiernie rozłożonych, rozdrobnionych cząstek fazy wzmacniającej w drobnoziarnistej osnowie stopu AlMg1SiCu, sprzyjającą osiąganiu wyższych wartości właściwości wytrzymałościowych w porównaniu do stopu wyjściowego. Wytworzone nanostrukturalne materiały kompozytowe wzmacniane nanorurkami haloizytowymi o udziale masowym 15% charakteryzują się – w porównaniu do materiału osnowy – ponad dwukrotnie większą mikrotwardością.

1. Introduction

An advantage of composite materials is the possibility to combine the beneficial properties of the reinforcement and the matrix and the use of the advantages resulting from their interaction and thus the formation of the desired resultant properties. Among the numerous of such materials, the particular attention of scientists worldwide is focused on composite materials with matrix of aluminium and its alloys reinforced with discontinuous particles, which results in much better properties (including higher temperature stability and wear resistance) compare to the matrix material [1-6].

The mechanical synthesis, mechanical alloying and pressing and hot extrusion following them enable the production of nanostructural composite materials with constant cross-section, even distribution of the reinforcing intermetallic phase and the size of its particles, and – the consequent – improvement of the material mechanical properties. The use of new phases as reinforcement in composite materials with aluminum alloy matrix is most of all to restrict the defects caused by conventional reinforcement and the improvement of the usable properties of the newly developed composite materials [7-9].

The unconventional reinforcement of the metal matrix composites may be the halloysite particles. Halloysite [$Al_2Si_2O_5(OH)_4\cdot(H_2O)$] is the clayey mineral of the volcanic origin, characteristic of high porosity, high specific surface, high ion-exchange, and ease of the chemical treatment and machining. Halloysite is composed of the flat surface lamellae, partially coiled or in the form of tubes originating from the coiled lamellae [10]. The halloysite nanotubes are the polyhedral, empty inside, cylindrical objects with the diameter of 40÷100 nm and length even up to 1.2 μm. These nanotubes were extracted from halloysite, being the mineral produced in Poland in Dunino mine, as one of three locations in the world, in addition to New Zealand and USA. An important argument for their use is - therefore - existence in Poland of the big and very homogeneous halloysite deposit. Dunino mine has the exposed field with the depth of cover of 0.5÷1 m, which has an important effect on the relatively low and globally competitive mining costs of this raw material. The entire deposit is characteristic of composition homogeneity, high purity and trace amounts of heavy metals. As the result of the many years long investigations carried out in the research centres many novel technologies were developed of using halloysite both for the scientific and industrial purposes, among others,

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as a filler in the polymer materials, sorbents, or insulation mats. The ongoing research projects pertaining to composite materials with polymer matrix [11-13]. Employment of halloysite nanotubes as a dispersive reinforcement of the metal composite materials is the original assumption and features and will make it possible to use this mineral in the innovatory and economically justified way [14].

The purpose of this work is to obtain composite powders with enhanced halloysite reinforcement distribution by mechanical alloying method and also to analyse this process by means of several process parameters and their influence on some of the material properties.

2. Experimental procedure

The microstructure of the investigated material was examined by the light microscope Leica MEF 4A and the transmission electron microscope S/TEM TITAN 80-300. To determine microhardness Vickers tests were performed in the parallel plane related to the extrusion direction.

3. Material for investigations

Composite materials were manufactured employing as a matrix the air atomized powders of AlMg1SiCu aluminium alloy and as a reinforcement the halloysite nanotubes (HNT). Composite powders of aluminium alloy matrix reinforced with 5, 10 and 15 wt.% of halloysite nanotubes were fabricated by two ways: by high energy mechanical alloying using a planetary mill with the following parameters: charge ratio: 20:1 (wt.); ball diameter: 20mm; AISI 420 stainless steel balls; rotation 400 rpm; milling time 6 hours; process control agent: 1 mass % of microwax, and alternatively - by low-energy mixing using the same planetary mill, with much smaller balls: 6 mm in diameter and milling time was only 30 minutes. No atmosphere control gaze was used. To find out the outcome of the inherence of brittle reinforcement particles in the high-energy mechanical alloying process, the aluminium alloy without reinforcement was also subjected to mechanical alloying. The obtained composite powders have been compacted in the cylindrical matrix 25 mm in diameter with 300 MPa pressure and then extruded at 480°C with caning and without additional vacuum degassing.

4. Results and discussion

The tests on the developed composite materials, made with the use of light microscopy, have not revealed discontinuity of structure in the form of pores or cracks, which proves that the powder consolidation carried out has been improved, particularly the appropriate desorption of gases from the dispersed forms' surface took place. Due to the fact that the agglomeration of particles constituting the composite materials' reinforcement causes deterioration of their mechanical properties, the basic requirement made to the materials composing them is to prove better properties through homogeneous distribution of the reinforcement material in the matrix. Although the plastic consolidation process through hot extrusion enhances the production of a homogeneous structure, without unfavorable concentrations of particles constituting reinforcement of composite materials, the agglomeration of such particles are created, depending on their size, geometry, electric charge concentrated on the surface, type of composite materials. It has been found that the process of low-energy agitation of the as-received powders causes relatively uneven distribution of irregular, mostly agglomerated reinforcement particles in the matrix (Fig. 1). The composite materials produced in the process of high-energy mechanical alloying are characterized with a different structure: the halloysite reinforcement particles are very evenly distributed, rarely forming any agglomerations (Fig. 2a). The evidence of correctly performed consolidation also is the obtainment of a highly dispersed structure material, without agglomerates of reinforcing particles. On some samples just a slight fibrosity of the structure in the section parallel to the extrusion direction could be observed, which is related to stretching the original limits of the disperse particles of the composite material (Fig. 2b). Such observations are identical to those presented in other publications [15-17].

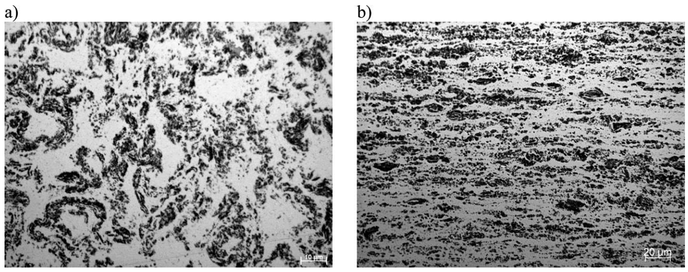

Fig. 1. Microstructure of the AlMg1SiCu matrix composite materials reinforced with 15 mass % halloysite nanotubes produced in the process of low-energy mixing: a) cross-section, b) longitudinal section, LM

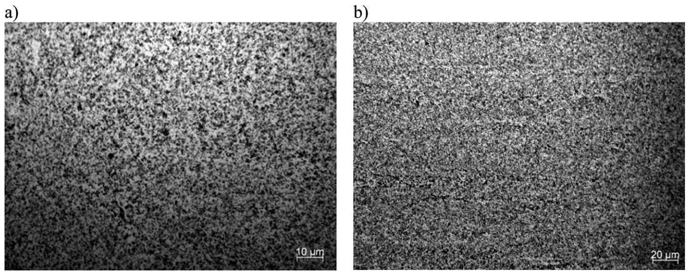

Fig. 2. Microstructure of the AlMg1SiCu matrix composite materials reinforced with 15 mass % halloysite nanotubes produced by high-energy mechanical alloying: a) cross-section, b) longitudinal section, LM

One of the key purposes of this paper was to define the dispersion of the reinforcing particles in the composite material. Due to the approximate chemical composition of the disperse amorphous or quasi-crystalline form of reinforcement, high extent of plastic deformation causing a strong deformation of the crystallographic net, the explicit identification of the structure in classic TEM mode is challenging. The specified factors and high extent of structure dispersion determined the necessity to use advanced methods of high-resolution transmission electron microscopy. The observations performed in STEM mode, enabling a more explicit and reliable interpretation, showed that – in addition to a strongly disperse structure

– the composite materials examined consist of two phases of contrasting structure (Fig. 3b). The phase, relatively homogeneous and compact, corresponds to the metal matrix, while the spongy and non-homogeneous one – is the halloysite reinforcement. The lack of pores, empty spaces and close adherence of the phases to each other proves the good amalgamation between the matrix and reinforcement particles during both the mechanical synthesis and plastic consolidation. The structural differences defined in STEM mode, identifying the specific phases, were confirmed with the use of energy dispersive spectroscopy. The analysis of distribution of elements has proved that the area examined of the aluminium alloy produced is characterized with almost homogeneous distribution of Al and Si, while Fe, Cr and Mn are concentrated in several areas creating primary intermetallic precipitations. However, in the composite material reinforced with halloysite (Fig. 4a), in addition to precipitations rich with iron (Fig. 4f), manganese (Fig. 4g) and chromium (Fig. 4e), areas with significantly higher concentration of silicon (Fig. 4d) and oxygen (Fig. 4c), i.e. elements that compose halloysite, in addition to aluminium (Fig. 4b) have been recognized. The observations of samples after spectroscopic examination surprisingly provided additional information on the resistance of phases examined to the electron beam effect, high-energy electron beam interaction with the sample material depends on several factors, of which the most significant ones are: electron energy, chemical composition and material structure. The phenomena accompanying the interaction between the electron beam and metals and semi-conductors are usually reversible and cause no defects to the material examined. In case of aluminum alloys, the knock-on processes (interactions between electrons and nucleons) are exceptional and may lead to Frenkel defects, however the collision cross-section of this process is scarce. In case of materials other than metals or semi-conductors the frequency of defects produced is higher. Therefore, the specific traces of electron material interaction with the thin foil material were observed in the fragments containing a mineral reinforcing phase, which may be defined in this way as sensitive to the electron beam impact (Fig. 5). Due to TEM mode tests, the occurrence of solid solution of aluminum with nanometric grains (Fig. 6), primary intermetallic phases $AlFe_3$ (Fig. 7a) and $Al_4(Fe,Cr,Mn)Si_{0,74}$ (Fig. 7b) have been identified.

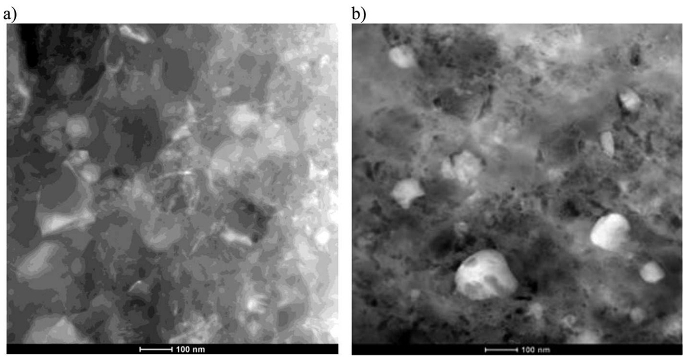

Fig. 3. Microstructure of the AlMg1SiCu alloy (a) and composite material reinforced with 15 mass % halloysite nanotubes (b) produced by high-energy mechanical alloying, HAADF-STEM images

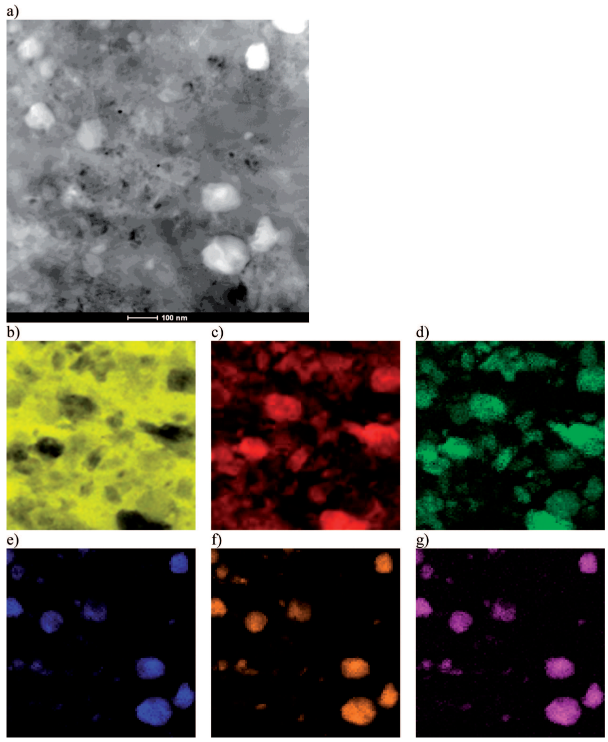

Fig. 4. a) Microstructure of the composite material reinforced with 15 mass % halloysite nanotubes produced by high-energy mechanical alloying: HAADF-STEM image (a); elemental maps extracted by EDS spectroscopic imaging in STEM : Al (b) O (c) Si, (d), Cr (e),Fe (f) and Mn (g)

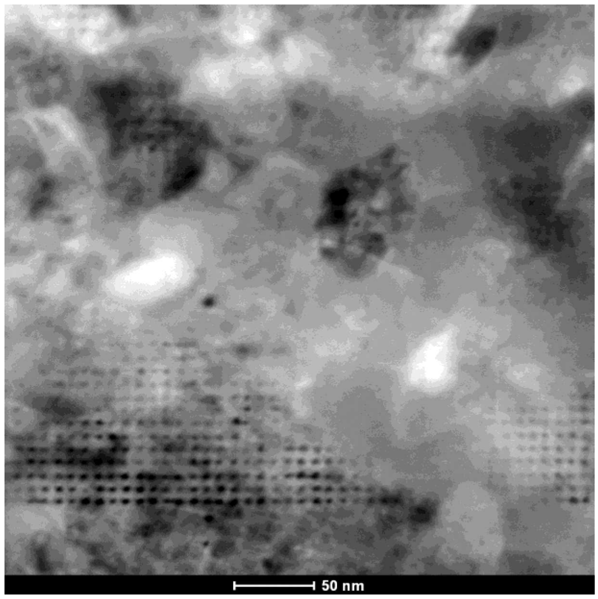

Fig. 5. Microstructure of the composite material reinforced with 15 mass % halloysite nanotubes produced by high-energy mechanical alloying, HAADF-STEM image (observations after spectroscopic examination)

The high extent of plastic deformation, dispersion of the structure to nanometric sizes and dispersive reinforcement with halloysite and oxide particles, caused by mechanical alloying, brings about almost triple growth of micro-hardness. However, after plastic consolidation a 30% reduction of micro-hardness of the materials produced was observed in comparison to the powders ground, which may be related to the recovery and partial recrystallization caused by increased temperature impact during extrusion. Nevertheless, the composite materials produced are characterized with micro-hardness of the range 110÷140 $HV_{0,1}$ which largely exceeds the values obtained for AlMg1SiCu alloy, even after thermal processing carried out correctly (Table 1).

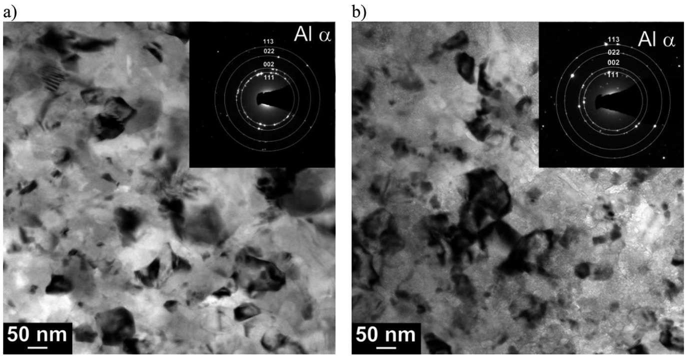

Fig. 6. Microstructure of the AlMg1SiCu alloy (a) and composite material reinforced with 15 mass % halloysite nanotubes (b) produced by high-energy mechanical alloying, TEM bright field image with diffraction pattern

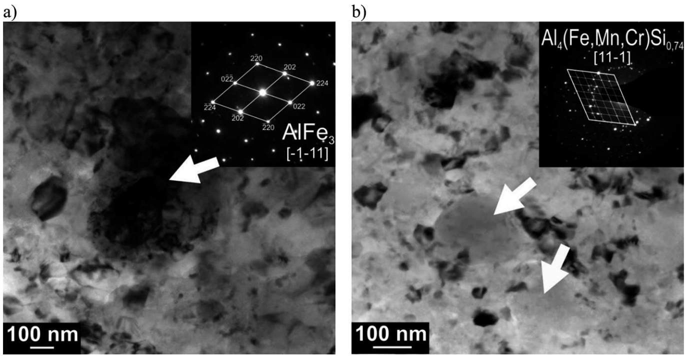

Fig. 7. Microstructure of the composite material reinforced with 15 mass % halloysite nanotubes produced by high-energy mechanical alloying, a,b) TEM bright field images with diffraction patterns

TABLE 1

Microhardness of obtained materials

Composite material		High-energy mechanical alloying		Low-energy mixing	
		Averadge micro-hardness	Standard deviation	Averadge micro-hardness	Standard deviation
AlMg1SiCu		112	3	67	7
HNT	5 mass %	122	6	72	9
	10 mass %	130	5	74	7
	15 mass %	142	4	73	12

5. Conclusions

The composite materials obtained as a result of mechanical alloying and hot extrusion are characterized with the structure of evenly distributed, disperse mineral phase particles in fine-grain matrix of AlMg1SiCu alloy, facilitate the obtainment of higher values of strength properties, compared to the initial alloy. The nanostructural composite materials reinforced with halloysite nanotubes with 15 mass % share are characterized by almost twice as higher micro-hardness – compared to the matrix material.

It has been proven that low-energy mixing of the as-received powders causes relatively uneven distribution of irregular, mostly agglomerated reinforcement particles, however the composites after high-energy mechanical alloying are characterized with homogeneous distribution of halloysite reinforcement particles are very evenly distributed, rarely forming any agglomerations. Furthermore mechanical alloying of the composite powders effects on the grain refinement of the extruded composites. Occurrence of solid solution of aluminum with nanometric grains has been confirmed. Additionally, unexpected sensitiveness to the electron beam impact of the halloysite reinforcing phase has also been observed.

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