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Manufacturing of EN AW6061 matrix composites reinforced by halloysite nanotubes

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ABSTRACT

Purpose: The core of the work consists in the elaboration of composite materials of aluminium alloy matrix, manufactured with the use of powder metallurgy technologies, including mechanical milling and hot extrusion and in determining the influence of the share of halloysite nanotubes – as the reinforcing phase on the structure and mechanical properties of fabricated composites.
Design/methodology/approach: Mechanical milling and hot extrusion are considering as a method for fabricating composite metal powders with a controlled fine microstructure. It is possible by the repeated fracturing and re-welding of powders particles mixture in a highly energetic ball mill.
Findings: It has been confirmed that halloysite nanotubes can be applied as a effective reinforcement in the aluminium matrix composites. High energy ball milling as a method of mechanical milling improves the distribution of the halloysite reinforcing particles throughout the aluminium matrix, simultaneously reducing the size of particles.
Research limitations/implications: Contributes to research on structure and properties of aluminium alloy matrix composite material reinforced with mineral nanoparticles.
Practical implications: The apparent density changes versus milling time can be used to control the composite powders production by mechanical milling and the presence of halloysite reinforcements particles accelerates the mechanical milling process. Conducted research shows that applied technology of composite materials production allows to obtain very good microstructural characteristics.
Originality/value: The application of halloysite nanotubes as the reinforcing phase of metal composite materials is a novel assumption of the discussed work and an interesting challenge whereof realization would enable to use this mineral clay in an innovative and cost effective way.
Keywords: Aluminium matrix composites; Halloysite nanotubes; Mechanical milling; Hot extrusion

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1. Introduction

Aluminium matrix composites represents a group of engineering materials which for decades have been investigated in numerous scientific centres worldwide [1-3]. The conducted research involves mainly the manufacture of materials in industrial environment which show repeatability of properties. The properties of composite materials are not the resultant total of the properties of their components, that is why the designing of technological processes is difficult and therefore the fabrication of such materials should be supported by strong scientific background, high engineering skills and very accurate realization of technological process of their fabrication [4, 5]. The aluminium matrix composite materials reinforced with the ceramic particles or fibres are becoming more well-liked and are broadly used in aircraft and automotive industry, electronic sectors of machine-building industry, and the most advanced ones are adapted for the requirements of armaments and aerospace industries or advanced sports equipment [6-8]. Moreover, due to many advantages, they are applied on elements working in elevated temperature (engine blocks, pistons, inserts into combustion chamber), in systems exposed to intensive wear (drums in brakes or clutches, discs) as well as in driving systems providing the obtainment of low friction factor and high vibration absorption [9, 10]. From among many manufacture methods of metal matrix composite materials the powder metallurgy play a exceptional role. Mechanical milling and following pressing and hot extrusion enable the fabrication of nanostructural composite materials of defined section, homogeneous distribution of the reinforcing phase and size of its particles, which lead itself into raised mechanical properties of the material [11-13].

In many areas of modern industry, including also contemporary modes of transport and especially in aviation or automotive industry, there is a growing tendency to replace steel parts with elements manufactured from light metal alloys, mostly aluminium and magnesium. The ecological and economic aspects are enforcing the search for solutions which would minimize the mass of particular elements and of the complete products, in particular in vehicles where better performance coupled with lower fuel consumption is most desirable. In comparison to steel, light metal alloys, including aluminium alloys, are characterized by lower Young modulus, lower strength, rigidity and worse tribological properties. Apart from heat treatment processes, new technologies where particles or fibres are brought into these alloys have been elaborated to improve mechanical properties [14, 15].

Chemical and phase composition of reinforcing particles in metal matrix composite materials as well as their size and shape, determine type of application. Metal matrix composites are presently one of the most quickly increasing and expansively investigated groups of engineering materials, what has been confirmed by the research results on aluminium matrix materials reinforced by ceramic particles [16], intermetallic phases [17], and most recently also with carbon nanotubes [18]. The application of carbon nanotubes as the reinforcing of composite metal material improve their mechanical properties and also increase their electric and thermal conductivity. The parallel effect should be exhibited by mineral nanotubes, although the literature reports involving this problem are not satisfactory. Independently of the fact that a certain drop in price of carbon nanotubes is expected, the price of mineral nanotubes is unbeatable lower, which, regardless of the access to raw materials, grounds the interest in this group of materials, even though very scanty and most recent literature reports involve purely polymer nanocomposites reinforced by halloysite nanotubes [19, 20].

Halloysite nanotubes, being a clayey mineral of volcanic origin which is characterized by high porosity, large specific surface, high ion exchange and easy chemical and mechanical treatment can be used as alternative reinforcement of metal matrix composite materials. Halloysite is built from flat surface plates, partially curled, or shaped like tubes made from curled plates [21]. Halloysite nanotubes are in the shape of polyhedron, hollow inside, cylindrical objects of the diameter 40-100nm and length of up to 1.2μm. The discussed nanotubes have been extracted from halloysite $Al_2Si_20_5(OH)_4{\cdot}(H_20)$ belonging to a coalinite group of clayey silicates. The fact that deposit of halloysite is available in Poland (at the Dunino mine, one of three places in the world apart from New Zealand and the USA) is a strong argument justifying its application. The overall resources are big and homogeneous of at least 10-12 mln tones whereof exploitable resources prepared so far are around 500000 tons. The mine has an openpit deposit of the overburden thickness of 0.5-1 m, which is important in view of relatively low and competitive extraction costs of this mineral in the world. The thickness of halloysite seam is up to 20 m. The whole deposit is characterized by uniform composition, high purity and trace amount of heavy metals. Presently, the mineral extracted in the mine is applied to produce a wide range of mineral sorbents in the form of granulate, for the absorption of acid, basic substances, crude oil derivatives and various emulsion mixtures [21].

The application of halloysite as the reinforcing of metal composite materials is a novel assumption of the discussed work and an interesting challenge whereof realization would enable to use this mineral in an innovative and cost effective way. The profit brought about by the extraction of this deposit when we assume technological application of these halloysite would be supposedly several times higher as compared to the current application. Hence it was most desirable to initiate elementary studies aiming to find out the application potentials of these nanotubes in line with the assumptions of this scientific problem.

In many research centres all over the world, many novel technologies have been developed for the application of halloysite nanotubes both for scientific and industrial purposes, e.g. as filler in polymer materials. The research works implemented currently involving polymer matrix composite materials [19, 20] reveal that putting in a few percent of halloysite nanotubes results in a significant rise of hardness, rigidity, strength, thermal stability and, in sometimes, also electric conductivity. A major problem taking place during the manufacture of these composites create difficulties with providing uniform dispersion of nanotubes and the necessity to prevent their aggregation, very adverse in terms of the strength of composite material. So far, there have been no information from international research centres confirming the application possibility of halloysite nanotubes as the reinforcing material in metal composite materials, which betoken of the originality of the undertaken issue.

The main aim of this work is to descript the effect of the high energy milling processes on manufacture of aluminium alloy matrix composite powders, reinforced with a uniform dispersion of halloysite nanotubes.

2. Material and methods

Newly elaborated composite materials were fabricated employing the air atomized powders of aluminium alloy – EN AW6061 from ECKA Company (Germany). The chemical composition of the alloy is given in Table 1. Morphology evaluated by scanning electron microscope of the initial aluminium powder particles used are given in Fig. 1. The particle size of the powder was < 150 μm with the volume size distribution median $q_{0.5}$ = 62.3 μm.

Table 1.
Chemical composition of the matrix – aluminium alloy powder EN AW6061

Elements' concentration, weight %						
Mg	Si	Cu	Cr	Fe	Others	Al
0.97	0.63	0.24	0.24	0.03	<0.3	Bal.

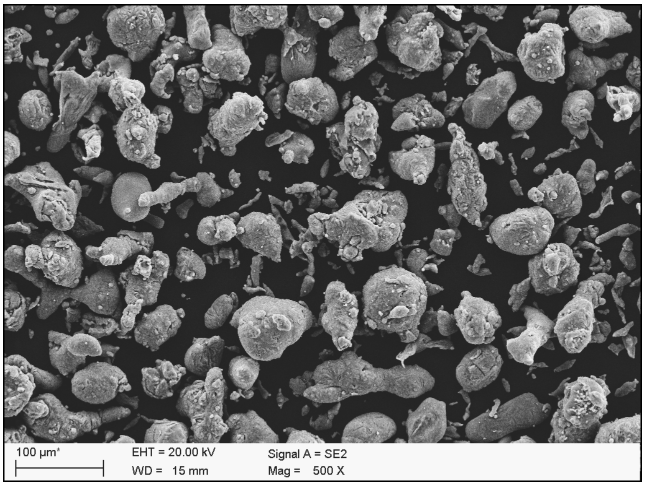

Fig. 1. Morphology of powder particles of EN AW 6061 alloy as received, SEM

As a reinforcement the halloysite nanotubes (HNT), delivered by NaturalNano Company (USA), have been used. SEM morphology of the initial halloysite particles used are given in Fig. 2. Particles size was less than 25 μm with the volume size distribution median $q_{0.5}$ = 2.6 μm. Parameters of particle size analysis are given in Table 2 and particles size distribution is shown in Fig. 3.

Table 2.
Particle size parameters of powders in initial state

Powder name	Specific surface area, m^2/g	Quantile $q_{0.1}$, μm	Median $q_{0.5}$, μm	Quantile $q_{0.9}$, μm
ENAW6061	0.129	31.819	62.296	106.579
Halloysite Nanotubes	6.000	0.367	2.577	11.329

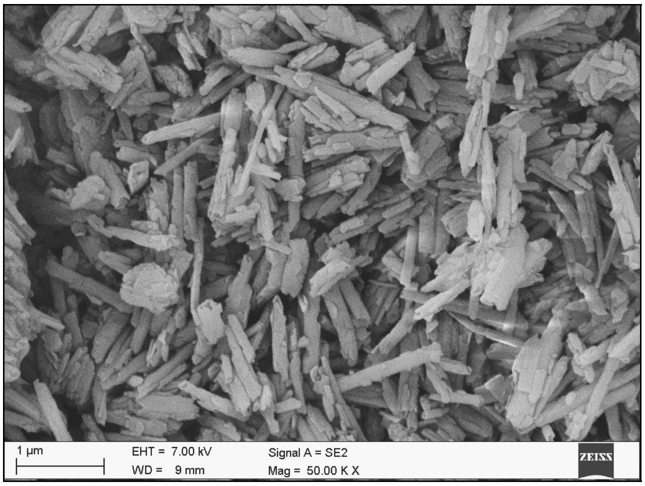

Fig. 2. Morphology of halloysite nanotubes as received, SEM

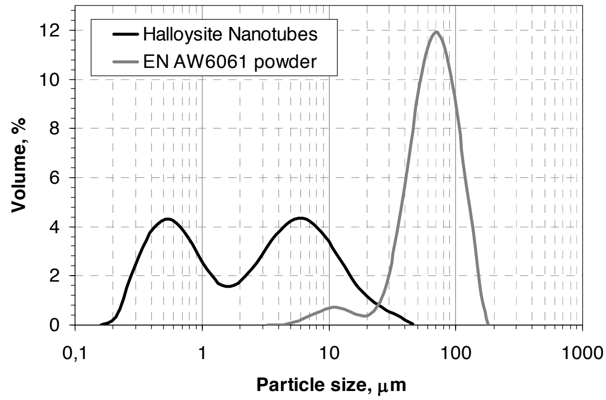

Fig. 3. Particles size distribution of powders in initial state

Composite powders of EN AW6061 aluminium matrix reinforced with 5-15wt.% of halloysite nanotubes were produced by high energy ball milling using a planetary mill (Fritsch). Parameters of the milling process are given in Table 3.

Table 3.
Milling process parameters

Ball-to-powder weight ratio	10:1
Ball diameter	20 mm
Ball material	AISI 420 quenched stainless steel
Time of milling	24 h
Process control agent	Microwax wt. 1%
Reinforcement contents	5, 10, 15 wt. %

The mechanically milled powders have been characterized by their apparent density (MPIF Standard 28). The obtained powders have been cold pressed in the cylindrical matrix 25 mm in diameter with 300 MPa pressure and then extruded at 480°C without caning and degassing (Fig. 4). To protect a mould against undesirable influence of friction graphite lubricant has been used. Extruded bars of 8 mm diameter and near theoretical density have been obtained.

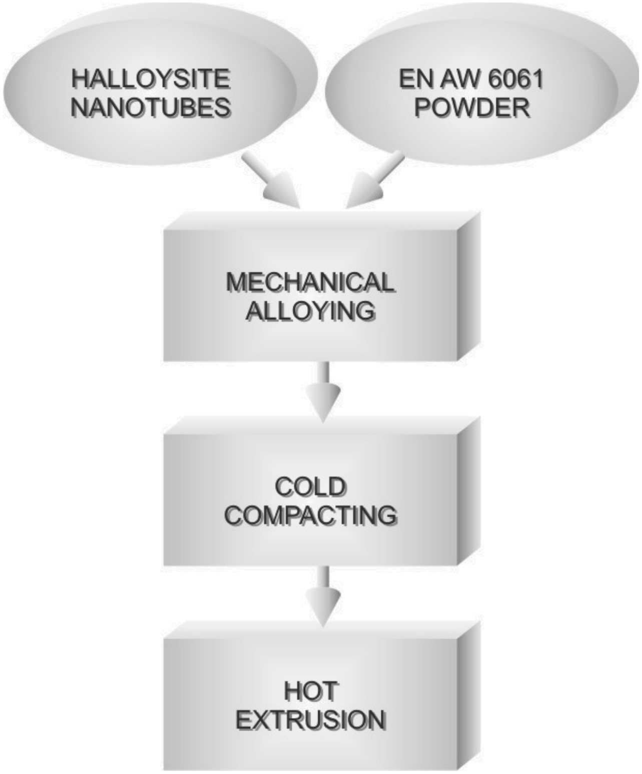

Fig. 4. Diagram of the technological operations for manufacturing aluminium composite materials reinforced by halloysite nanotubes

Analysis of grain size distribution has been realized on Mastersizer 2000 analyser based on laser diffraction particle sizing system. The measurement has been done in the equivalent diameter range up to 2000 μm. As a dispersing agent deionised water has been used, and the measurements have been carried out in constant temperature taking into consideration viscosity and density of liquid. To avoid particles agglomeration, dispersion of the samples has been done using ultrasonic probe.

To determine microhardness suitable tests were performed in the parallel plane related to the extrusion direction with a use of the Vickers hardness tester FUTURE-TECH FM-700 under load of 100 G. Microstructure observations were made by optical microscopy Leica MEF 4A and scanning electron microscope SEM DSM 940 OPTON using the secondary electron detection at the 20 kV accelerating voltage.

3. Description of achieved results of own research

The implementation of powder metallurgy makes possible fabrication of composite materials with broad range of reinforcing particles content without the necessity of supplementary treatment and without segregation, which is characteristic in the case of casting processes. On the basis of observations the structure of powders milled in planetary mill, it can be supposed, that this kind of milling change the morphology of powders and moreover enables more uniform distribution of reinforcing particles in the matrix.

Applied process of mechanical milling, from its nature, has induced crushing of microstructure and generation of high number of defects. The process has been realised in solid state and mechanically induced reaction between particular components has played main role in this process. As a effect of long-lasting mechanical milling unstable structure of solid solution, ceramic phases, mixture of components or even amorphous material nature has been produced. Modification of the microstructure of material as well as in chemical composition of initial material can be obtained at the end of the process. The process hinge on properties of the mechanically treated powders to a great degree, and for that reason three basic cases are distinguished: each powders are plastic, both are brittle or one powder is plastic and the second one is brittle. In analyzed case third option has taken place – plastic aluminium alloy and brittle halloysite nanotubes. Accomplished investigations of microstructure and morphology of the formed composite material powder bears out the fact of receiving homogeneous distribution of brittle particles in plastic matrix resulting from mechanical milling. While milling grains of plastic aluminium powder has succumb collisions in systems grinding ball – powder – grinding ball or grinding ball – powder – wall of mill, resulting in strong plastic strain causing significant strengthening of the powder. Accomplishment of the process in quasi-protective atmosphere has enabled protection of the surface of powders against unreasonable destructive oxidation, what has favoured particle fusion. In the initial stage of the process propensity to lamellar structure formation has prevailed. Those flat and thin structures have put on each other creating bigger and more strengthened particles; because of high strengthening those particles have cracked above critical strengthening and the cycle has taking place again. It has been simplified by cracking and high size reduction of the powder of brittle nature, and owing to that, grains with reduced size have penetrated or even embed into fused surfaces of the plastic powders leading to its further fissuring. In the end, vulnerability of milled particles to cracking and fusion has been compensated and – what is related to that – its size has remained constant in some range. Analyze of grains size and shape, shows that the process of mechanical synthesis can be divided into four basic stages (Fig 5.):

- Development of thin layers and formation of bigger and smaller particles of powders than initial one resulting in decrease of bulk density is observed (3-6 h).
- Increase of coarse-grained fraction of powder with lamellar structure, parallel to the milling balls occurs, hardness of milled material also increase (12 h).
- Formation of equiaxial particles – disintegrated free particles forms equiaxial ones, bulk density increases (18 h).
- Terminal – random orientation of particles binding, when decrease of particles size and change in phase composition in relation to initial composition is found, microstructure is reduced in size and the particles are rigid (24 h).

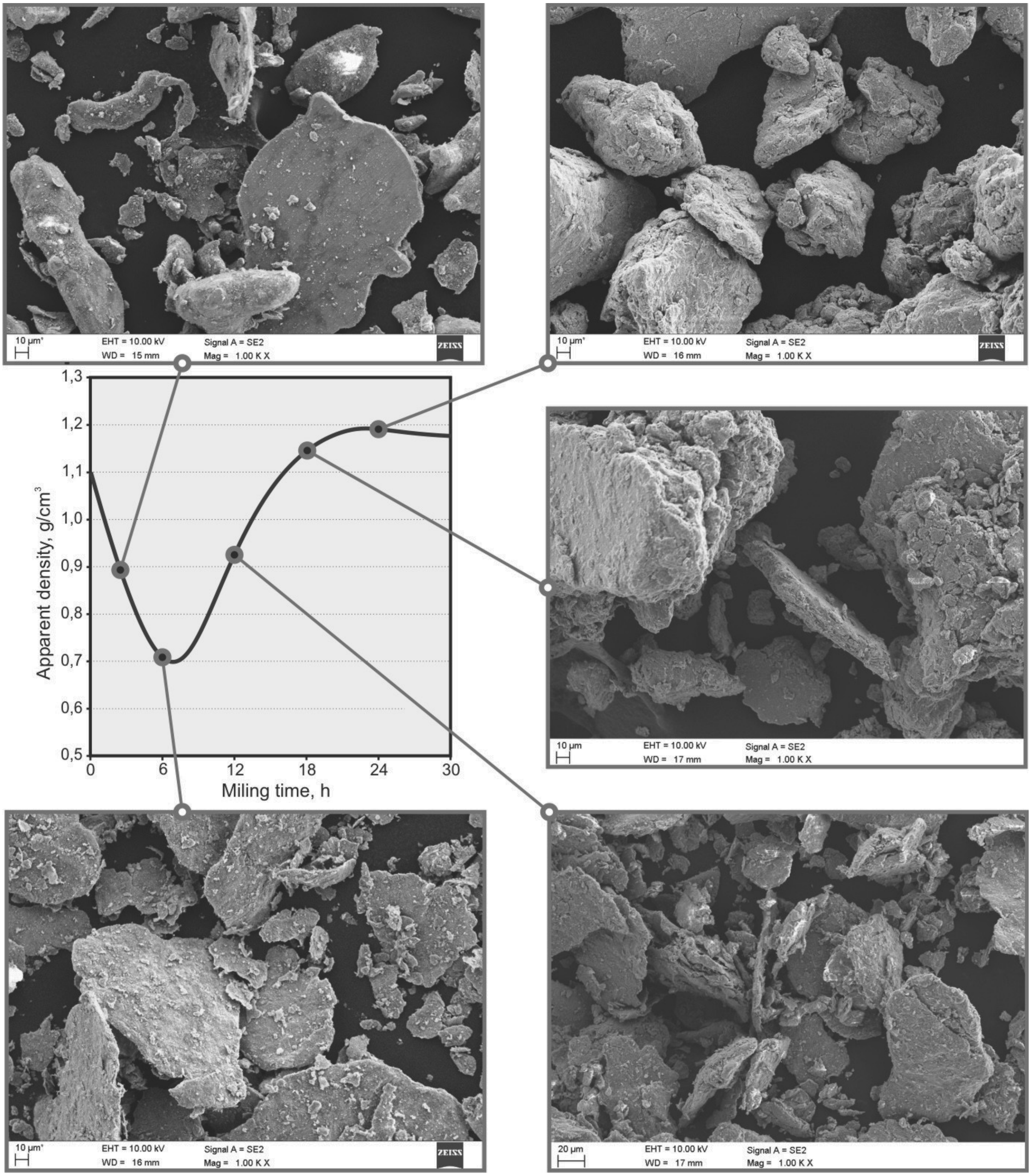

Fig. 5. Dependence of milling time on apparent density and morphology of EN AW6061 matrix composite reinforced by 10% of halloysite nanotubes, SEM

Additional quantity, that reveals steady state of mechanical milling process is apparent density of milled powders. Oblate particles possess lower packing ability opposite to equiaxial powders in initial state or after achievement of steady state as an outcome of mechanical milling.

The apparent density can be formulate by mass per unit volume of a material, or the apparent density express the density without the application of pressure, with the exception of atmospheric pressure. Dependence of milling time on apparent density of EN AW6061 matrix composite reinforced with 10% of halloysite nanotubes is given in Fig. 5. The apparent density in the beginning of milling is constantly decreasing and it reaches a minimum value after about 6 hours of milling. After longer milling, from 12 to 24 hours, apparent density achieves a steady value, a little bit higher than as-received aluminium powder. Table 4. shows results of apparent density measurements and flow rate for powder at steady state, after 24 hours of mechanical milling. Presented outcome suggest better packing capacity of composite powders as opposed to EN AW6061 powder without reinforcement. Furthermore precisely scientific and technological methods of assigning optimum milling time, there exist occurrence of sticking the milled particles to the bottom and internal walls of mill. Longer time of realized process does not give increase of technological properties as well as mechanical ones, but causes losses connected with occurrence already described.

Table 4.
Results of apparent density and flow rate measurements

Powder type	Apparent density, g/cm^3	Flow, s
EN AW6061	1.10	not flowing
EN AW6061+5% HNT	1.23	15
EN AW6061+10% HNT	1.26	15
EN AW6061+15% HNT	1.28	15

On the grounds of the analysis of received composite powders, it can be concluded that the longer milling time has enable reduction of particles size as well as homogenous reinforcement particles distribution throughout the whole blend and has formed equiaxial morphology (Figs. 6-8). In order to indicate an influence of milling time on microstructure, microphotographs of obtained composites after 12 hours of milling has been shown in Fig. 9 (cross section) and Fig. 10 (longitudinal section). Usage of a composite powder after only 12 hours of milling with thin and flat particles, has induced non homogenous microstructure and lower values of mechanical properties. Moreover, milled powder with flattened particles has caused a lot of technological problems, especially with flow and fulfilment of the mould. It should be pointed out also that halloysite nanotubes, that are reinforcing phase, have undergone strong fragmentation, what is not possible to reach in low-energetic process.

Microhardness tests and compression tests results of mechanically milled composites after hot extrusion, with different volume fraction of reinforcing particles powders, are presented in Table 5.

Fig. 6. Microstructure of extruded EN AW6061 with 5% addition of halloysite nanotubes after 24 h of milling

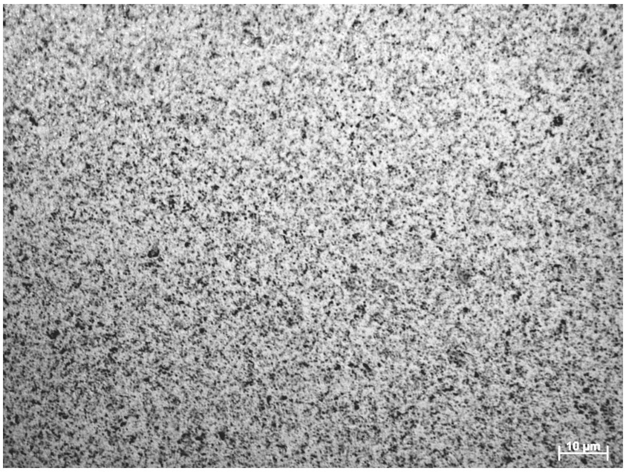

Fig. 7. Microstructure of extruded EN AW6061 with 10% addition of halloysite nanotubes after 24 h of milling

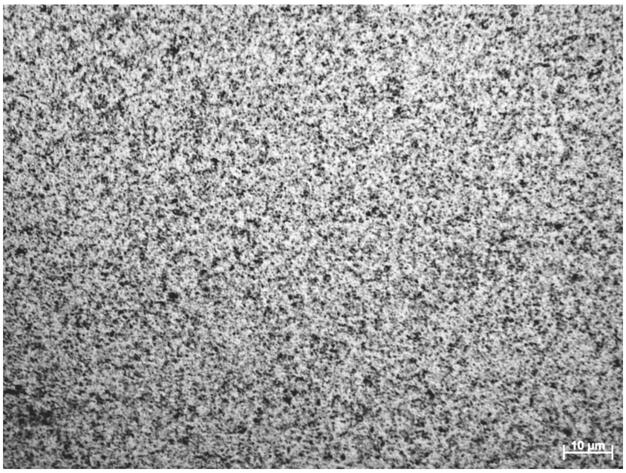

Fig. 8. Microstructure of extruded EN AW6061 with 15% addition of halloysite nanotubes after 24 h of milling

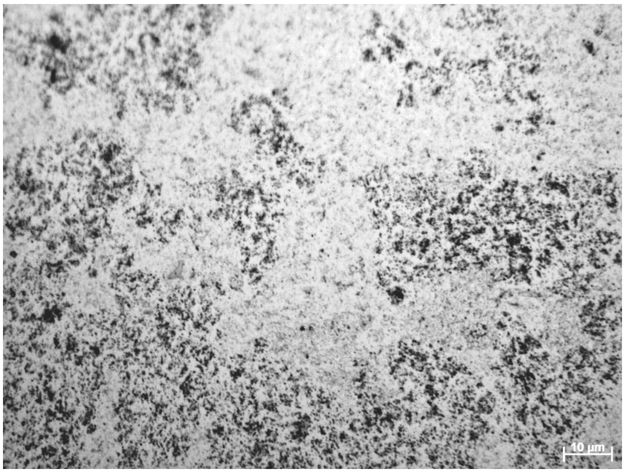

Fig. 9. Microstructure of extruded EN AW6061 with 15% addition of halloysite nanotubes after 12 h of milling

Fig 10. Microstructure of extruded EN AW6061 with 15% addition of halloysite nanotubes after 12 h of milling

Table 5.
Results of microhardness and compressive yield stress measurements of obtained composite materials

Powder type	Microhardness $HV_{0.1}$	Yield stress MPa
EN AW6061	111.55	276.0
EN AW6061+5% HNT	122.31	448.4
EN AW6061+10% HNT	130.23	481.6
EN AW6061+15% HNT	141.70	460.1

4. Conclusions

The analysis of the investigation results of microstructure of hot extruded composite materials based on EN AW6061 aluminium reinforced with halloysite nanotubes shows that:

- It has been affirmed that halloysite nanotubes can be applied as a effective reinforcement in the aluminium matrix composites.
- Based on metallographic examination of extruded composites are characterized by a very homogeneous distribution of halloysite particles and the absence of any reaction and with good cohesion at the matrix – particle interfaces.
- High energy ball milling leads to uniform distribution of the halloysite reinforcing particles throughout the aluminium matrix and simultaneously reducing the size of particles.
- Dependence between the apparent density and milling time can be employ to regulate the composite powders manufacturing by mechanical milling.
- The addition of halloysite reinforcements particles accelerates the mechanical milling process.
- Observed microstructural changes influence on the mechanical properties, especially microhardness and compression yield.

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