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Mechanically milled aluminium matrix composites reinforced with halloysite nanotubes

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Manufacturing and processing

ABSTRACT

Purpose: The present work describes fabrication of aluminium AlMg1SiCu matrix composite materials reinforced with halloysite nanotubes by powder metallurgy techniques and hot extrusion.
Design/methodology/approach: Mechanical milling, compacting and hot extrusion successively are considering as a method for manufacturing metal composite powders with a controlled fine microstructure and enhanced mechanical properties. It is possible by the repeated welding and fracturing of powders particles mixture in a highly energetic ball mill.
Findings: The milling process has a huge influence on the properties of powder materials, changing the spherical morphology of as-received powder during milling process to flattened one due to particle deformation followed by welding and fracturing particles of deformed and hardened enough which allows to receive equiaxial particles morphology again. The investigation shows that so called brittle mineral particles yields to plastic deformation as good as ductile aluminium alloy particles. That indicates that the halloysite powder can play a role of the accelerator during mechanical milling. 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. 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.
Research limitations/implications: Contributes to knowledge about technology, structure and properties of aluminium alloy matrix composite material reinforced with mineral nanoparticles.
Practical implications: Conducted research shows that applied technology allows obtaining very good microstructural characteristics.
Originality/value: It has been confirmed that halloysite nanotubes can be applied as an effective reinforcement in the aluminium matrix composites. Deformation, grain size reduction and dispersion conduce to hardening of the composite powders. Mechanical milling cause a high degree of deformation, decrease the grain size even to nanoscale and create an enormously uniform distribution of reinforcing phases or oxides in the structure of the metal.
Keywords: Aluminium matrix composites; Mechanical milling; Halloysite; Hot extrusion

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1. Introduction

For last few decades, composite materials have quickly progressed for industrial application and are now being successfully used to produce elements exposed to the impact of high temperature (pistons, engine blocks, combustion chamber inserts), for elements subjected to intensive wear (brake and clutch disks and drums), and also in power transmission systems ensuring low friction coefficient and high vibration damping capability [1]. Aluminium matrix composites reinforced with ceramic particles or fibres are used more and more mostly in the aviation-, machine-, automotive-, and electronic industries, and the most modern of them are adapted for the needs of the automotive and space industries, as well as for the professional sports equipment [2]. Among many manufacture methods of the metal matrix composites the significant role is played by the powder metallurgy methods [3]. Mechanical alloying/milling and following compacting and hot extrusion make fabrication of the nanostructural composite material possible with the constant cross-section, homogeneous distribution of the reinforcing mineral phase and size of its particles, and - resultant - improvement of the material mechanical proper-ties [4].

The unconventional reinforcement of the composites might be the nanotubes acquired from halloysite (Fig. 1a), being the clayey mineral of the volcanic origin, characteristic of high porosity, high specific surface (60-500 m^2/g), high ion-exchange, and ease of the chemical treatment and machining. Halloysite is composed of the flat surface lamellae, partially curled or in the form of tubes originating from the curled lamellae [5]. 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 [$Al_2Si_2O_5(OH)_4$•(H_2O)], belonging to the clayey silicates group - kaolinite group. Application of halloysite as the reinforcement of the metal composite materials is the original assumption of this paper and features and interesting challenge for the research team and will make it possible to use this mineral in the innovatory and economically reasonable way [6]. The purpose of this work was to obtain composite powders with enhanced halloysite reinforcement distribution by mechanical milling method and also to analyze this process by means of several process parameters and their influence on some of the material properties.

2. Material and method

2.1. Material and manufacture method

Composite materials were elaborated employing the air atomized powders of aluminium alloy - AlMg1SiCu from ECKA Company (Germany) - as a matrix (Fig. 1a) and the halloysite nanotubes (HNT) (Fig. 1b), delivered by NaturalNano Company (USA) as a reinforcement.

Composite powders of aluminium alloy matrix reinforced with 5, 10 and 15 wt.% of halloysite nanotubes were manufactured by high-energy ball milling using a planetary mill (Fritsch) with the parameters listed in Table 1. Process control agent was added to prevent sticking of the powders to ball and mill surface. Milling process was stopped every 30 minutes to prevent a powder heat effect which is connected with high energy type of balls collisions. No atmosphere control gaze was used. The high-energy milling time was determined for each composition independently. Table 2 shows the average particle size parameters of powders in initial state. To analyse the effect of the inherence of brittle reinforcement particles in the high-energy milling process, the AlMg1SiCu aluminium alloy without reinforcement was also subjected to this kind of milling. 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 degassing. To keep a mould against undesirable influence of friction graphite lubricant has been used. Extruded bars of 8 mm diameter and near theoretical density have been achieved.

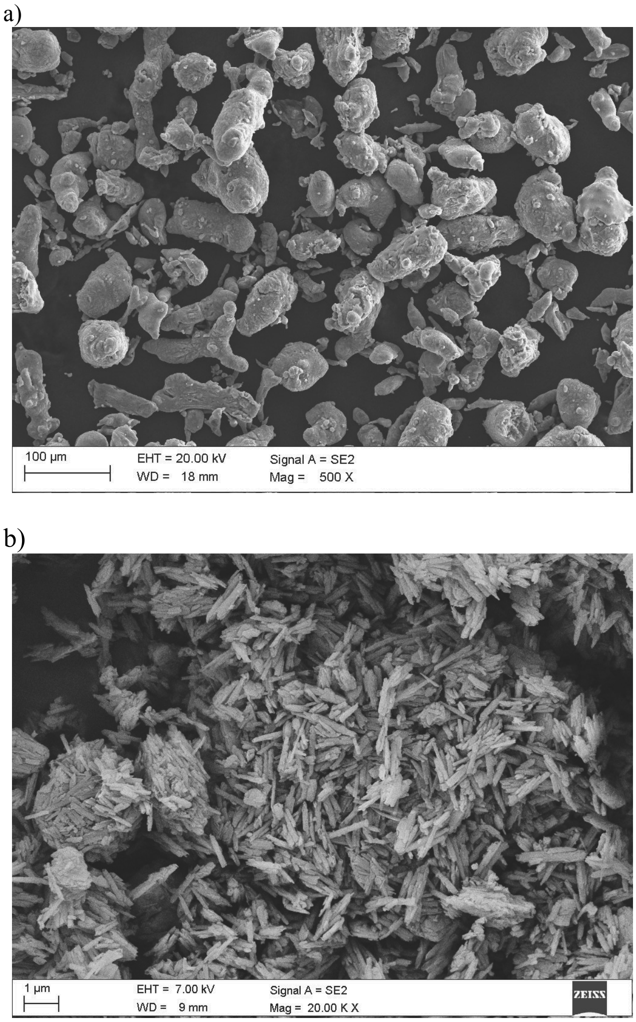
a)
b)


Fig. 1. Morphology of as received powder particles used in the experiment: a) halloysite nanotubes, b) AlMg1SiCu alloy

Table 1.
Mechanical milling process parameters

Charge ratio	20:1
Ball diameter	20 mm
Ball material	AISI 420 stainless steel
Speed	400 rpm
Process control agent	1% (wt) microwax

Table 2.
Particle size parameters of as-received powders

Powder	Quantile Q_{10}, µm	Median Q_{50}, µm	Quantile Q_{90}, µm
AlMg1SiCu	31.8	62.3	106.6
HNT	0.3	2.6	11.3

2.2. Investigation procedure

Elaborated composite powders were characterized for their apparent density (MPIF Standard). Investigation of particles size distribution has been realized on Fritsch laser particle size analyser - Analysette 22 MicroTec Plus based on dual laser diffraction particle sizing system. Five measurements were carried out for each sample and the measurement has been done in the equivalent diameter range from 0.08 mm up to 2000 mm.

Microstructural and morphological characterization was made by optical microscopy Leica MEF 4A and scanning electron microscope SEM SUPRA 35 Zeiss using the secondary electron detection at the 7-20 kV accelerating voltage. To determine microhardness suitable tests were performed with a use of the Vickers hardness tester FUTURE-TECH FM-700 under load of 50 G.

3. Results and discussion

3.1. Apparent density

Powder technological characteristic such an apparent density is strongly dependent on milling time which can be observed on Fig. 2. In the beginning of milling the apparent density is constantly decreasing and for reinforced with 5% of halloysite nanotubes aluminium alloy it reaches a minimum value after about 2 hours of milling, then commences to increase together with increasing milling time. Moreover, milled powder with flattened particles has caused a lot of technological problems, especially with flow and fulfilment of the mould. After longer milling, the apparent density of the reinforced AlMg1SiCu reaches a steady state, similar or even a little bit higher to that of the as-received powder. Flattened particles have worse packing ability opposite to equiaxial powders in initial state or after achievement of steady state as an outcome of mechanical milling. Changes of apparent density with the milling time of the composite powders is analogous to that observed with the pure powder alloy: an initial decline followed by an increase and stabilization. On the other hand, the apparent density behaviour occurs in a shorter time with the addition of reinforcement particles. In fact, an addition of 15% halloysite nanotubes brings about this apparent density behaviour in half the time it takes with the unreinforced AlMg1SiCu powder alloy.

3.2. Powder morphology and microstructure

Assuming that changes of powders apparent density during milling process are determinate by changes in the shape of particles, powder morphology and microstructure investigation have been also realised. Fig. 3 presents the morphologies of the composite particles with 5, 10, 15% HNT after 1, 2, 3 and 4 h of milling. Generally globular shape of the as received AlMg1SiCu particles, characteristic for atomized powder, enables fine powder packing, which is linked with the relatively high initial apparent density values. In the initial stage of the mechanical alloying process, powders can be characterized by small apparent densities representing a laminar shape, what is connected with weak powder packing ability. Afterwards, in a later stage of the milling process, the morphology of the particles is changing again to more equiaxial one, characterized by better powder packing and higher value of the apparent density.

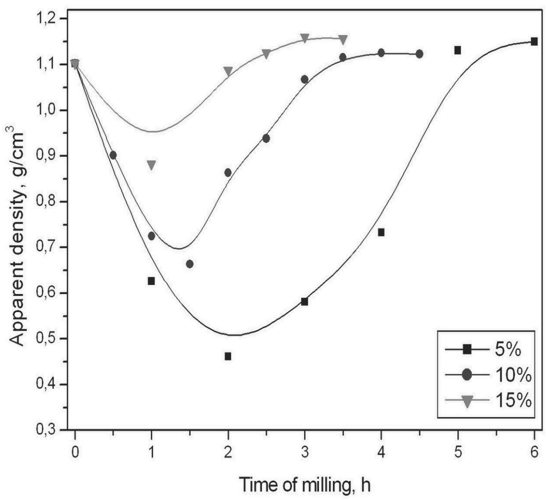


Fig. 2. Apparent density of milled powders

To analyse the impact of milling process on the powders microstructure, an optical metallographic analysis of the powder particles was carried out. Figs. 3 and 4 present the structural progress of composites with high-energy milling time. The as-received AlMg1SiCu powder has a spherical morphology (Fig. 1a). In the initial stage, after 1 h of milling, there is a superiority of flattened powder particles (Figs. 3a and 4a). After 2 h of milling time, welded oblate particles can be easily noticed (Figs. 3b and 4b), which suggests that welding is the main occurrence at this stage of the process. In the next stage, particles created from more than a few flattened, welded oblate particles can be observed. Changes in the particles morphology are consequence of flattened particles micro-welding which enable creation of bigger and more bulked particles. Nevertheless, micro-welded conglomeration of the particles as a result of strong plastic deformation become relatively hard and disposed to fracture

(Fig. 4c). After 3 h of milling simultaneously particles micro-welding process and fracture of the welded particles causes creation of more and more equiaxial particles (Fig. 4c). In this stage the interfacial boundaries are randomly oriented, but after 4 h of milling (Fig. 4d) they are not visible by optical metallography. These interpretations are in accordance with literature [7,8,9]. 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. To describe the effect of the reinforcement on mechanical alloying process, analyse of small reinforcing particles behaviour during deformation and micro-welding has to be done.

The inherence of halloysite particles between the aluminium particles during micro-welding process enhances local deformation in the area of the reinforcement particles. Local deformation improves deformation hardening, which effects an enhancement of the fracture process. Furthermore, very small brittle halloysite particles during the process behave as a small milling agents which result in enhancement of the energy of the milling system. It can be concluded that the more of halloysite reinforcements particles addition will result in an acceleration of the mechanical milling process. On the grounds of the analysis of received composite powders, it can be summary 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.

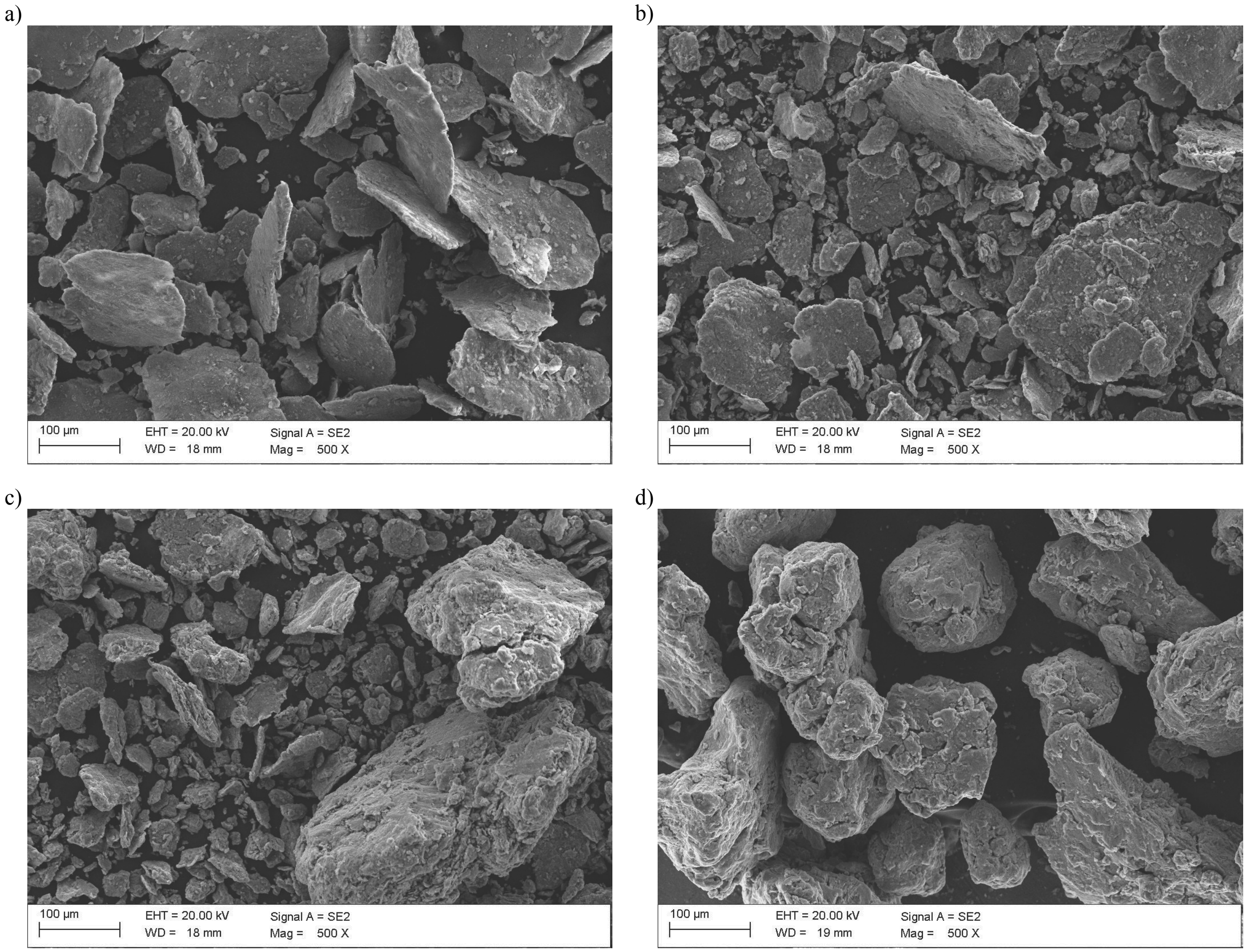


Fig. 3. Morphology of the composite AlMg1SiCu +10% HNT powder particles after a) 1h, b) 2h, c) 3h and d) 4h; SEM

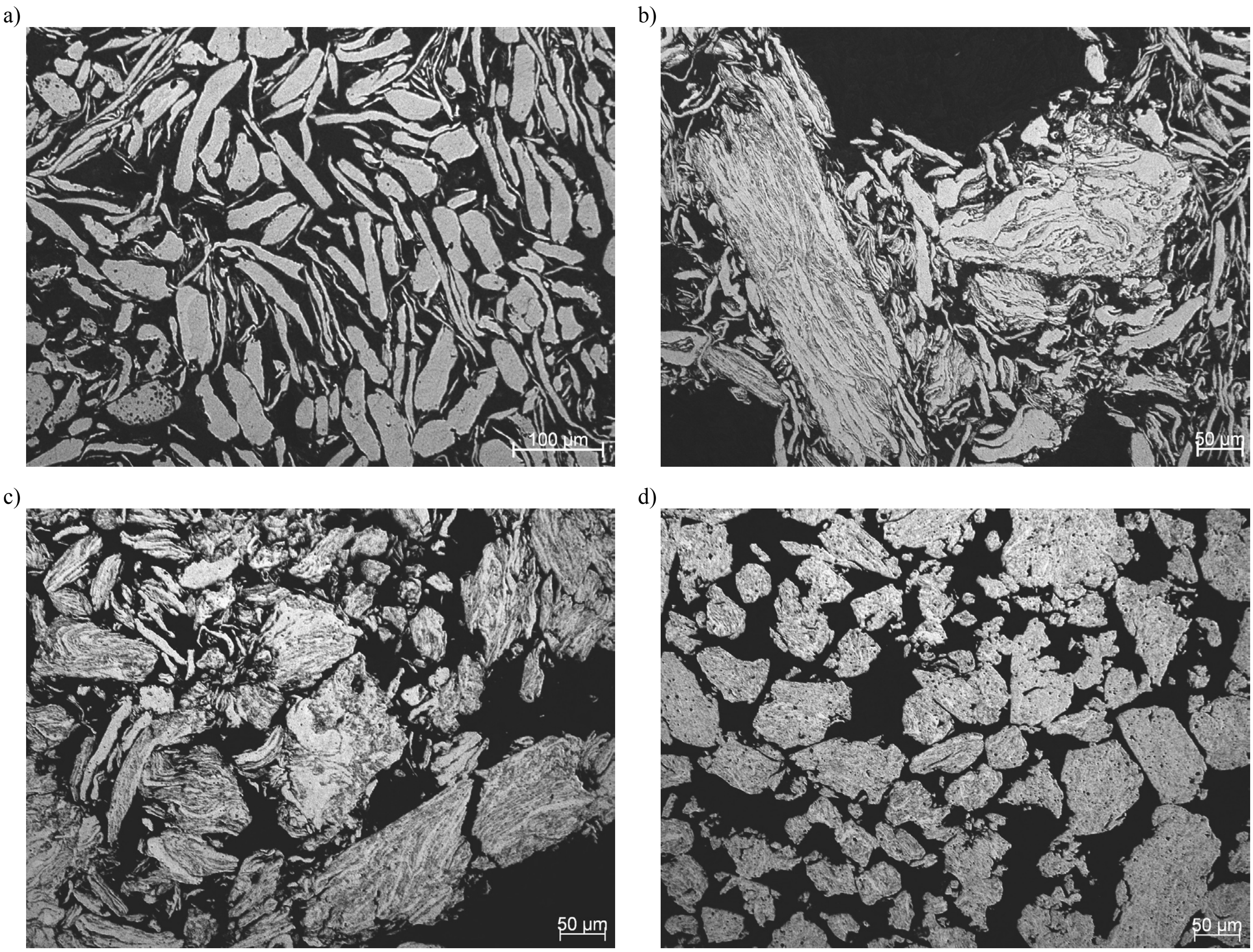


Fig. 4. Microstructure of cross-section of the composite with 10% of HNT powder particles after a) 1h, b) 2h, c) 3h and d) 4h; LM

Table 3.
Particle size distribution values of AlMg1SiCu reinforced with 10% of halloysite nanotubes for selected milling times

Particle size distribution values	Milling time			
	1h	2h	3h	4h
Quantile Q_{10}, µm	4.77	12.06	17.70	29.31
Median Q_{50}, µm	72.27	53.00	58.46	98.84
Quantile Q_{90}, µm	138.59	145.97	217.95	268.12

3.3. Particle size analysis

Fig. 5 presents the particle size distributions for AlMg1SiCu matrix composite reinforced with 10% halloysite nanotubes for several milling times. Perpendicular lines relate to the equivalent diameter size marked as Q_{50}, which is known as median diameter or medium value of particle diameter.Q_{50} is particle diameter value in case cumulative distribution percentage reaches 50%. Table 3 shows statistical values of size distribution analysis results. In the beginning of milling process particle size distribution is characterized by two peaks, which is strongly connected with the way of the laser analyser. Laminar particles gives distort values of particle size distribution, depending on the angle between laser beam and measure flat particle. In the next stage, after 2 hours of the milling process realisation, particle size distribution became a bit broadens, which confirm that micro-welding process take place in this stage. According to morphology and microstructure analysis, after 3 hours of milling asymmetric aberration especially in the region of big particles have been noticed.

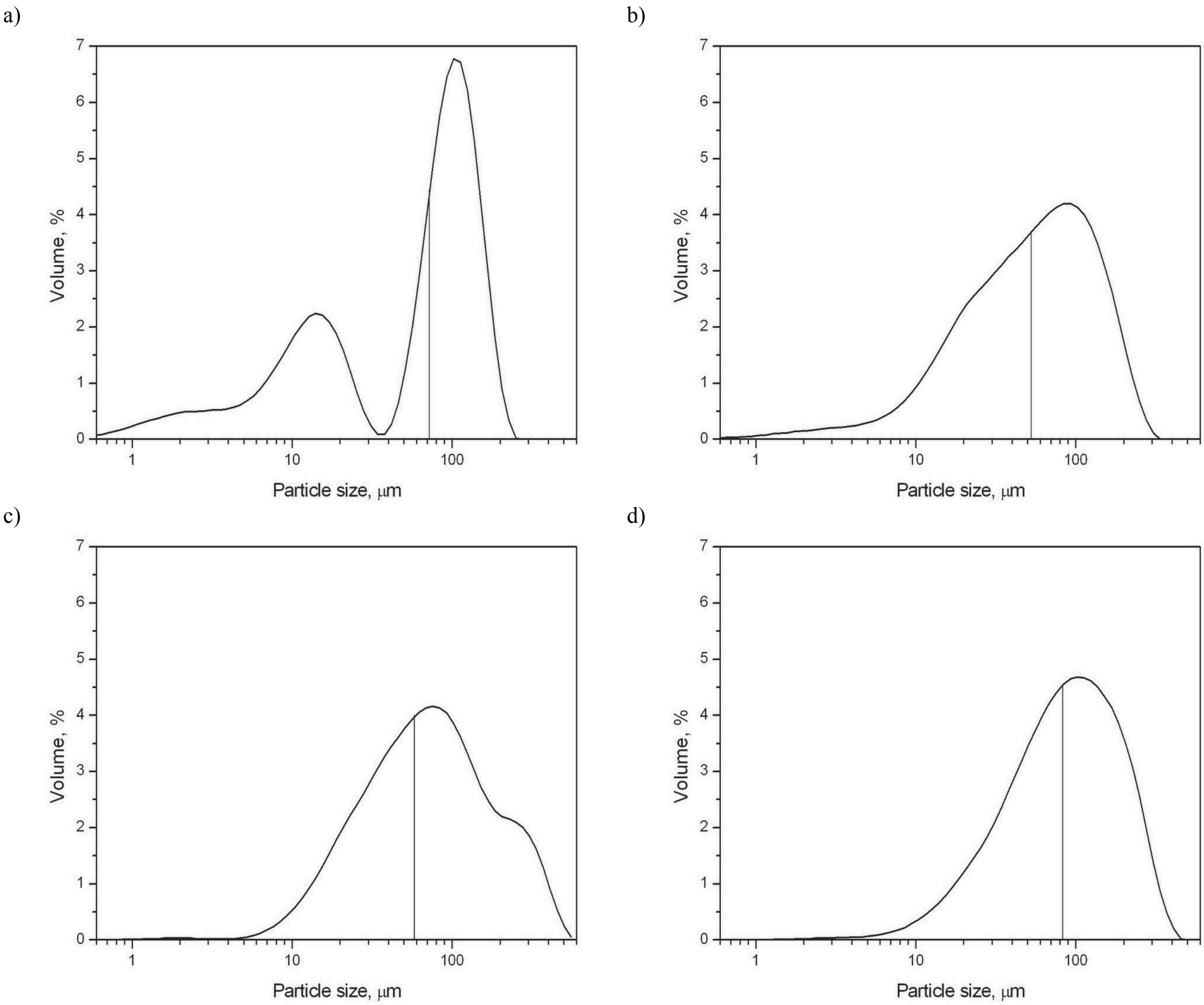


Fig. 5. Particle size distributions for the AlMg1SiCu matrix composite reinforced with 10% halloysite nanotubes after milling times: a) 1h, b) 2h, c) 3h, d) 4h

This phenomenon is connected with creation large particles as a outcome of progressive micro-welding process. In the end, distribution curve become almost symmetric and the final Q_{50} is 1.5 times bigger in comparison with initial state. In this stage particle distribution is narrower, which can be explained by powder steady state achievement related with balance between fracture and micro-welding mechanism.

3.4. Microhardness

Fig. 6 shows the milling time dependence of composite powder microhardness. Deformation, grain size reduction and dispersion conduce to hardening of the composite powders. Mechanical milling cause a high degree of deformation, decrease the grain size even to nanoscale and create an enormously uniform distribution of reinforcing phases or oxides in the structure of the metal. Fundamentally as-received particles and un-deformed particles are relatively softer than deformed particles after mechanical milling. Besides standard deviation of the microhardness examination hardly changes especially between 1.5-2.5 hours of milling (Table 4). This observation can be explained by occurring difference in deformation level of particular particles. After 3 hours of milling particles deformation level starts to be more uniform and standard deviation is decreasing. Summary increase of the hardness due to the mechanical milling process has been noticed. Addition of the halloysite nanotubes to the aluminium matrix increased hardness of obtained composite materials. The significant hardness increases in comparison with row aluminium alloy was observed in case of milled composites.

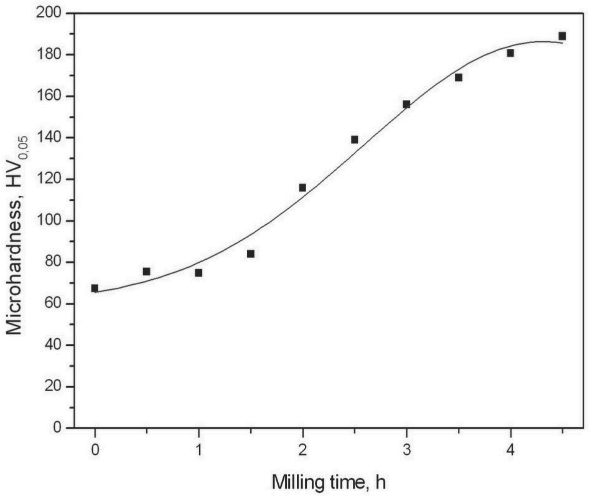


Fig. 6. Microhardness of obtained composite powders

Table 4.
Microhardness of obtained composite powders

Milling time, h	Microhardness $HV_{0.05}$	Standard deviation
0	67.50	3.65
0.5	75.46	7.74
1	74.90	5.62
1.5	83.99	12.98
2	115.97	16.10
2.5	139.09	30.01
3	156.06	7.23
3.5	169.02	8.30
4	180.85	5.82
4.5	188.99	4.51

4. Conclusions

The analysis of the investigation results of morphology and microstructure composite powders based on AlMg1SiCu aluminium alloy 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 composites powders it has been concluded that composite materials are characterized by a very homogeneous distribution of halloysite particles. The absence of any reaction and good cohesion at the matrix - particle interfaces has been also noticed;
- 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.

Acknowledgements

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