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Chapter 6

# Fabrication, Composition, Properties and Application of the AlMg1SiCu Aluminium Alloy Matrix Composite Materials Reinforced with Halloysite or Carbon Nanotubes

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Additional information is available at the end of the chapter

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**Abstract**

In this chapter, the characterisation of the halloysite nanotubes (HNTs) and multiwalled carbon nanotubes (MWCNTs) as the reinforcement in the composite materials was described. The original and author technology of production of the aluminium AlMg1SiCu matrix composite materials reinforced with halloysite or carbon nanotubes using powder metallurgy techniques, including mechanical alloying and hot extrusion and the range of own research in the case to determine microstructure, as well as mechanical properties of those materials was present. It was investigated that the addition of carbon and halloysite nanotubes causes a significant improvement in mechanical properties of the obtained nanocomposites. The investigation results show that the technology used in manufacturing nanocomposite materials can find the practical application in the production of new light metal matrix nanocomposites.

**Keywords:** metal matrix composites, mechanical milling, carbon nanotubes, halloysite nanotubes

## 1. Overview of applications of halloysite and carbon nanotubes in composite materials

The diverse uses of composite materials with a matrix made of aluminium and aluminium alloys result most of all from the chemical and phase composition of reinforcing materials,

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as well as from their size and fraction. Aluminium composite materials are currently one of the most dynamically developing and most intensely investigated groups of engineering materials as confirmed, in particular, by the results of research into composite materials with an aluminium alloy matrix reinforced with ceramic particles [1–4] and intermetallic phases [5, 6].

Composite materials with an aluminium matrix reinforced with ceramic particles and/or fibres are finding increasingly extensive applications in the aviation, machine, automotive and electronic industry, and the most advanced ones are adapted to the needs of the arms and space sector and for professional sports equipment. Moreover—owing to their numerous advantages—they are used for parts exposed to high temperatures (pistons, engine blocks, combustion chamber inserts) in systems undergoing intensive friction (discs, clutch and brake drums), as well as in drive systems achieving a small friction coefficient and a high vibration absorption ability. Considering the numerous manufacturing methods of metallic composite materials, powder metallurgy and pressure infiltration methods play a special role. Mechanical alloying, mechanical milling, followed by compression and hot pressing, enable to fabricate nanostructured composite materials with a permanent cross section, with a uniformly distributed reinforcing intermetallic phase and with a uniform particle size and to consequently achieve enhanced mechanical properties of the material [7, 8]. Works have been conducted all the time to employ the new phases as reinforcements in composite materials with a matrix made of aluminium alloys. The aim is, most of all, to reduce defects caused by a conventional reinforcement, and to improve the functional properties of newly developed composite materials.

The latest publications show that graphite [9, 10] and carbon nanotubes [11, 12] are used as reinforcing phases in aluminium matrix composite materials. Carbon nanotubes are characterised by good mechanical, thermal and electric properties, unlike any others, i.e., engineering materials known to date [13, 14]. Carbon nanotubes, since they have been manufactured, have become the object of extensive investigations of many research institutions around the globe. Broad interest is signified by numerous publications concerning the studies of their structure, properties and application opportunities [15–18]. Carbon nanotubes have been used mainly as reinforcements of composite materials with a polymer [19, 20] and ceramic matrix [21]; however, growing interest in carbon nanotubes has been seen in the recent years as the reinforcement of composite materials with a matrix made of light metals and their alloys [22, 23].

An alternative and cheaper solution may be to use—as reinforcing phases in metallic composite materials—mineral halloysite nanotubes (HNTs) extracted from halloysite, which is a silty material of volcanic origin present, among others, in deposits located in Poland, as in one of three places globally apart from the USA and New Zealand. Halloysite has high porosity, a large specific area, high-ion exchange capacity and is easy to work chemically and mechanically. The scarce literature reports available so far concern only polymer nanocomposites reinforced with mineral halloysite nanotubes [22–25], however, own works indicate the purposefulness of investigating and applying this type of composite materials [26, 27]. Multiple novel technologies for using halloysite for scientific and industrial purposes have been developed as a result of works lasting many years pursued by research institutions [22,

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28, 29], among others, as a filler in polymer materials [30, 31]. The research works currently carried out, pertaining to composite materials with a polymer matrix [32, 33], point out that if several to more than 10% of mineral nanotubes are added, the strength, rigidity, hardness, thermal stability, and—in some cases—electric conductivity is enhanced. An important problem for production of such materials is difficulties in the uniform dispersion of nanotubes and the necessity to prevent aggregation, which is very disadvantageous for a composite material's strength [25]. Considering that the properties of the separation area of such phases have influence on the properties of a composite material, apart from the characteristics of its components, surface modification of halloysite becomes necessary by plasma or chemical functionalisation method, increasing surface energy and wettability [34, 35].

The second alternative reinforcement of composite materials can be carbon nanotubes which are used mainly as reinforcements of very light polymer nanocomposite materials [36, 37]. A nanocomposite material with a polyamide matrix with an addition of carbon nanotubes with the use of ultrasound mixing was produced in the work [36]. The authors have investigated the effect of the fraction of carbon nanotubes on the mechanical properties of the nanocomposite material. It was found that if a volume fraction of 0.01–0.5% of carbon nanotubes is added, the mechanical properties of the nanocomposite materials are improved. The Young's modulus of the nanocomposite material with the volume fraction of 0.05% of carbon nanotubes was increased by 110% in respect of pure polymer. In the work [38], the effect of the fraction of carbon nanotubes on electrical properties of the nanocomposite material with an epoxy resin matrix was discussed. If a volume fraction of 0.1% of carbon nanotubes is added, the electrical conductivity of the material is increased to $10^{-2}$ S $m^{-1}$ compared to resin conductivity. Carbon nanotubes are also applied as reinforcements of nanocomposite materials with a ceramic matrix. A nanocomposite material with an aluminium oxide matrix reinforced with carbon nanotubes using the pressure-free moulding method was fabricated in the work [39]. A material with enhanced mechanical properties was fabricated. The bending strength of the materials went up by 25%, while crack resistance by 45% vis-à-vis aluminium oxide without a fraction of carbon nanotubes. In the publication [40], the authors focused on investigating how the structure of functionalised carbon nanotubes (length and diameter) influences the degree of dispersion of nanofibers in an aluminium oxide matrix. The material was produced by spark plasma sintering (SPS). Growing interest has been seen in the recent years in carbon nanotubes as reinforcements of composite materials with a matrix made of light metals and their alloys [41, 42], and the amount of own works is also significant here [43, 44].

Several methods of consolidation have been used to manufacture nanocomposite materials with a matrix made of aluminium and aluminium alloy reinforced with carbon nanotubes. The authors from the study [45–51] indicate that the following methods are in use: hot rolling [45], sintering [46], plasma spray forming [47], stir casting [48], semisolid powder processing (SPP) [49], spark plasma sintering (SPS) [50] and spark plasma extrusion (SPE) [51]. The methods of intensive plastic deformation, equal channel angular pressing (ECAP) [52] and friction stir processing were also employed to manufacture such nanocomposite materials [53]. Conventional hot pressing is considered to be a widely used consolidation method for producing

nanostructured composite material with an aluminium matrix and reinforced with carbon nanotubes [11, 54].

The main problem in manufacturing composite materials reinforced with halloysite and carbon nanotubes is their strong tendency to create agglomerates and difficulties in achieving their appropriate dispersion in the matrix material. The existence of reinforcement agglomerates in the case of nanocomposite material is limiting particles' ability to counteract the dislocation motion and is not effective in limiting grain growth. Both the uniform distribution of the reinforcing phase and its properties play an essential role in achieving improved material properties. One of the ways used for the uniform distribution of the reinforcing phase is to use mechanical synthesis methods, which have become one of the main ways to produce composite materials reinforced with carbon [55–57], and halloysite nanotubes [58, 59]. The manufacturing of nanostructured composite materials with a matrix of aluminium alloys reinforced with carbon and halloysite nanotubes can be divided into two phases. The first of them is the uniform distribution of nanotubes in an alloy matrix. The second is to consolidate the powders prepared in advance. This chapter presents the results of own investigations [43, 44, 60–62], although other chapter of the book discusses the possible uses of halloysite nanotubes for fabrication of a microporous skeleton acting as a preform for fabrication of aluminium matrix composites.

## 2. Fabrication and methodology of own research of composite materials with AlMg1SiCu alloy matrix reinforced with halloysite and carbon nanotubes

This chapter presents the method of fabrication using powder metallurgy techniques, including mechanical alloying and hot extrusion and the research methods of charge materials and the microstructure, as well as mechanical properties of aluminium alloy AlMg1SiCu matrix nanocomposites reinforced with multiwalled carbon nanotubes (MWCNTs) and halloysite nanotubes (HNTs).

The material for the investigations was prepared using, as a matrix material, a commercially available air-sputtered EN AW-AlMg1SiCu aluminium alloy powder (numerical designation EN AW-6061) manufactured by ECKA Company (Austria), whose nominal size of particles did not exceed 100 μm. The chemical composition is provided in **Table 1**. MWCNTs (supplied by Cheaptubes) and HNTs supplied by NaturalNano were used for the reinforcement of nanostructured composite materials with an EN AW-AlMg1SiCu alloy matrix (**Figure 1**).

| **Elements' concentration, wt.%** | | | | | | |
|---|---|---|---|---|---|---|
| **Mg** | **Si** | **Cu** | **Cr** | **Fe** | **Others** | **Al** |
| 0.97 | 0.63 | 0.24 | 0.24 | 0.03 | <0.3 | Balance |

**Table 1.** Chemical composition of the matrix–EN AW-AlMg1SiCu alloy powder.

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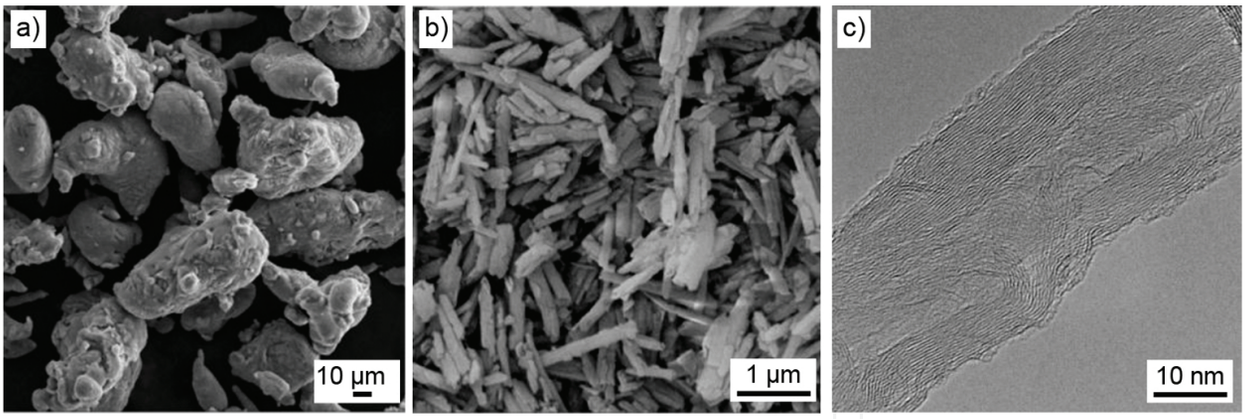



**Figure 1.** Morphology of the as-received (a) EN AW-AlMg1SiCu alloy powder, SEM, (b) halloysite nanotubes, SEM, (c) structure of the multiwalled carbon nanotubes, HRTEM.

A centrifugal ball mill, Pulverisette 5, by Fritsch Company, was used to produce crushed and permanently joined composite powders. The manufacturing conditions of composite powders are listed in **Table 2**. A slip additive, MA7050 (micronized ethylene-bis-stearamide-wax), reducing adhesion between the charge material and the mill material [process control agent (PCA)] with the mass fraction of 1%, was used for all the powders.

| **Reinforcement** | **MWCNTs** | **HNTs** |
|---|---|---|
| Ball-to-powder weight ratio | 20:01 | |
| Ball diameter | 20 mm | |
| Ball material | AISI 420 quenched stainless steel | |
| Time of milling | 5; 10 h | 3; 6 h |
| Reinforcement contents | 0.5; 2; 3.5; 5 wt.% | 5; 10; 15 wt.% |

**Table 2.** Milling process parameters.

Five sets of materials were prepared containing, respectively, 5, 10 and 15% of halloysite nanotubes by mass and 2 and 5% of multiwalled carbon nanotubes by mass. The composite powders obtained in mechanical milling were cold pressed in a mould with the socket diameter of 26 mm and under the pressure of 300 MPa, and then extruded at 460–480°C using a graphite suspension in oil as a slip substance, without degassing, in a shield jacket. Direct extrusion of the cold pressed rod-shaped composite materials consisted of placing a moulding in a thick-wall sleeve closed from one side with a punch, and from the other side—with a die with a forming opening. At elevated temperature, under the influence of pressure exerted by a punch, the material was moulded through a die opening, and a rod with the desired shape and dimension was achieved and with density near the theoretical density. A die was used allowing to extrude material with the deformation degree of 10.57. The heating temperature of the charge material and the tools used was optimised; the best results were achieved for the charge

material temperature of 460–480°C (**Figure 2a**). A higher temperature led to the occurrence of the liquid phase and surface defects such as cracks and skinning (**Figure 2b** and **c**), while the lower temperature—led to the lack of appropriate connection between particular composite material grains and the related disadvantageous properties of the ready product.

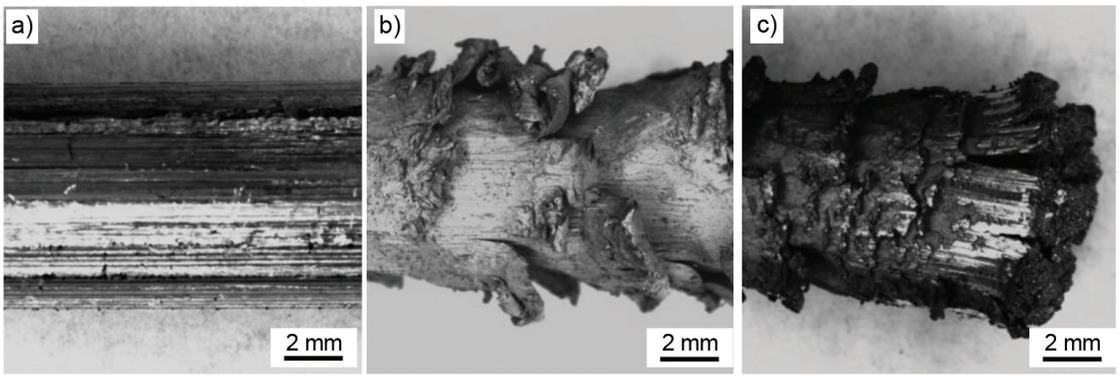



**Figure 2.** Macrofractography of the extruded bars at (a) 460 °C (b) and (c) 500 °C.

Complex and complementary investigations were performed to establish a dependency between the fraction of the reinforcement material in the matrix, structure and properties of the composite material produced. The morphology of EN AW-AlMg1SiCu alloy powders, halloysite and composite powders, as well as the structure of the manufactured composite materials was examined in a scanning electron microscope (SEM) SUPRA 35 by ZEISS. Secondary electron (SE) detection and back scattered electron (BSE) detection with the accelerating voltage of 7–20 kV and the maximum magnification of 50,000 times was used for obtaining the images of the examined materials. Metallographic examinations were performed for composite materials mounted in conductive phenol resin with a carbon filler. They were ground with a Tegramin-20 grinder-polisher by STRUERS with SiC sandpapers with the grain size of 120–500 μm/mm$^2$, and then were subjected to polishing using three suspensions of polycrystalline diamond and a colloidal silica suspension. Microsections were made in the direction perpendicular and parallel to the direction of extrusion. Metallographic observations of composite materials were carried out with a LEICA MEF4A light microscope equipped with a computer image analysis system with the magnification of 500 and 1000 times. A qualitative phase composition analysis of powders and composite materials was carried out with an X'Pert PRO X-ray diffractometer by PANalytical with an Xcelelator band detector, using filtered radiation of a copper and cobalt lamp with the voltage of 40 kV and a filament current of 30 mA. Radiation intensity measurements were made within the angle range 2θ of 5–140°. Diffraction examinations and examinations of the structure of thin foils were performed with an S/TEM TITAN 80-300 high-resolution transmission electron microscope (HRTEM) by FEI Company. The high-resolution transmission electron microscope is equipped with BF, DF and HAADF scanning transmission detectors, a Cs condenser spherical aberration corrector, an electron energy filter, electron energy-loss spectrometer EELS, energy dispersion spectrometer EDS. The distribution of grain composition of the powders used was analysed with an ANALYSETTE 22 MicroTec analyser by FRITSCH. The measurements were made at room temperature

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for equivalent grain diameter of 80 nm to 2 mm, using water as a dispergating liquid, with a small addition of a surfactant. Powders were dispergated with ultrasounds prior to and during a measurement. The microhardness of powders and composite materials was examined on the ground microsections with a FUTURE TECH hardness tester by the Vickers method for the pressure of 0.98 ($HV_{0.1}$) and 0.49 N ($HV_{0.05}$).

## 3. Structure and properties of composite materials with AlMg1SiCu alloy matrix reinforced with halloysite and carbon nanotubes

This chapter presents the results of investigations determining the microstructure, as well as mechanical properties of aluminium alloy matrix nanocomposites reinforced with multiwalled carbon nanotubes (MWCNTs) and halloysite nanotubes (HNTs) fabricated using powder metallurgy techniques, including mechanical alloying and hot extrusion. AlMg1SiCu aluminium alloy powder was used as a matrix of the nanocomposites.

It was revealed with electron scanning microscopy that the primary circular particles are deformed, flattened and have a plate-like form in the initial stage of mechanical synthesis. A tendency to join the earlier deformed particles prevails when milling the powders further, leading to increasingly larger composite material components being formed (**Figure 3a**). Changes in the shape and size of the ground powders result from individual particles being welded due to collisions with grinding mediums or with the mill walls. The conglomerates of flattened particles formed as a result of welding are becoming much more reinforced, harder, and hence susceptible to cracking. As milling advances, the particles are fragmented and rejoined, and this finally contributes to the random orientation of the welded particles' boundaries. A relatively equiaxial shape of the milled powder's particles informs that the process has reached the predefined status. As opposed to the EN AW-AlMg1SiCu alloy powder being ground, it was found for the composite material powder that the deformed particles were tightly joined, thus creating a homogenous structure free of pores and discontinuities.

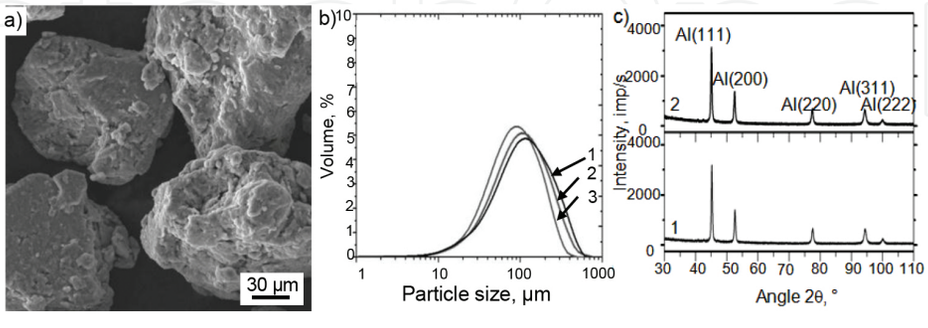



**Figure 3.** (a) Morphology of the composite powders AlMg1SiCu reinforced with 10% of HNTs after 6 h of mechanical milling, (b) comparison of the grain distribution of AlMg1SiCu alloy powder (1) and AlMg1SiCu alloy powder with 5% (2) and 10% (3) volume fraction of HNTs subjected to high-energy milling for 6 h and (c) X-ray diffraction pattern of AlMg1SiCu alloy powder milled with volume fraction of 10% of HNTs for 6 h (1), unmilled AlMg1SiCu (2) alloy powder.

The findings of microscopic observations are strengthened by an analysis of results of measurements carried out for the size of composite materials' powder particles (**Figure 3b**). The size distribution of the particles in the initial stage is characterised by two apexes and this is explained by the fact that the investigated powders are a mixture of particles with a largely differentiated size, but also by the measurement method itself. The thin, flat particles prevailing at the beginning of grinding may distort the measurement results depending on the angle between the laser beam and the measured irregular particle. On the other hand, it is suggested in the work [63] that—due to a larger number of the investigated particles—ultrasound mixing of the suspension during measurement and the fact that the angle between the measured particle and the measuring beam is completely accidental, the value measured indeed corresponds to the average particle diameter. As the grinding time is extending, according to the changes in morphology and structure as described earlier, a particle size distribution curve is becoming broader, thus confirming that a phenomenon exists of joining the deformed particles. The distribution curve is characterised in the next stage by an asymmetric deviation signifying a higher fraction of large particles formed as a result of multiple welding. The existing asymmetry is gradually disappearing and this is related to the cracking of large particles described earlier. It is suggested by a symmetric, relatively narrow distribution curve and a median value larger than the initial state by 50%, that the process has reached the set condition, showing the state of balance between the mechanisms of joining and fragmentation.

Mechanical synthesis, apart from the proven impact on the morphology and structure of the developed composite powders, also has an effect on their phase composition. The phase composition analysis results, shown in **Figure 3c**, depending on the milling time of a composite material reinforced with halloysite nanotubes prove that after 10 min of milling, low-angle reflections coming from mineral halloysite crystals disappear, and reflections identified as $\alpha$-Al are only left on the diffraction pattern. The observed amorphisation of the halloysite reinforcing phase takes place as a result of disruptions in the packet structure, which is consistent with the observations included in the works [64–66].

The influence of a fraction of brittle reinforcement on the progress of the mechanical synthesis process can be explained in two ways [63]. Cold plastic deformation is the driving force of a welding process occurring during mechanical milling. It should be noted, though, that a deformation smaller than a critical value does not cause welding, and the presence of reinforcing particles between the matrix particles during joining them is increasing the local degree of deformation, therefore, a critical value enabling welding is exceeded. In addition, local growth in the degree of deformation caused by reinforcing particles arranged in the matrix is also causing local strain hardening which is supporting fragmentation in the next stage. The reinforcing phases accelerating the cracking mechanisms are also expediting the process of mechanical milling. The presence of fine, hard and brittle particles acting as 'micro grinding mediums' largely increasing the process energy is another phenomenon that may be decisive for an increased deformation, thus for acceleration of structural changes in mechanical milling. To summarise, the presence of reinforcing particles is supportive to a higher degree of deformation and thus accelerates milling.

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As shown, the use of mechanical milling leads to a high degree of deformation, which–coupled with a decreased size of grain below 100 nm and the dispersion of the reinforcing refined particles—is reinforcing the material, as best illustrated by increased hardness of powders of composite materials [67, 68]. Evolution in the morphology and size of particles of milled composite powders in the initial phase does not differ between the applied types of reinforcement. Because of higher plasticity of AlMg1SiCu powder alloy and, potentially, because of dynamic recrystallisation, the cold welding mechanism is a dominant mechanism during milling in a ball mill, leading to the formation of large particles (**Figure 4a**). If MWCNTs are added, powders are more reinforced, hence particles are produced with a much smaller size. The difference in the size and shape of particles is decreased with longer milling time. **Figure 4b** compares the grain distribution of AlMg1SiCu aluminium alloy powder with a 5% volume fraction of MWCNTs subjected to high-energy milling after 10 h of milling. All the analysed distributions are unimodal. As the milling time is increasing, the range of particle size (distribution curve shape) is decreasing because the cracking of particles was the dominant mechanism during mechanical milling. The particles are smaller and smaller, the quantile value q0,9 for the ground AlMg1SiCu alloy powder decreases from 291 μm for 5 h of milling to 224 μm for 10 h of milling. Analogously, the quantile value q0,9 for the ground alloy powders with the volume fraction of 2 and 5% of MWCNTs is decreasing in the range of, respectively, 184–153 μm and 77–75 μm. The average size of particles is decreasing as the fraction of MWCNTs is increasing. Powders with the volume fraction of 5% of MWCNTs have the smallest particle size. An X-ray analysis of the milled powders of nanocomposite materials has shown the occurrence of phase $\alpha$-Al only (**Figure 4c**). No visible reflections coming from carbon structures were identified despite a high maximum volume fraction of MWCNTs (5% vol.) in AlMg1SiCu alloy powders subjected to mechanical synthesis. The reflections coming from carbon structures were identified in the extruded composite materials. The $Al_4C_3$ phase was identified (**Figure 5a, b**).

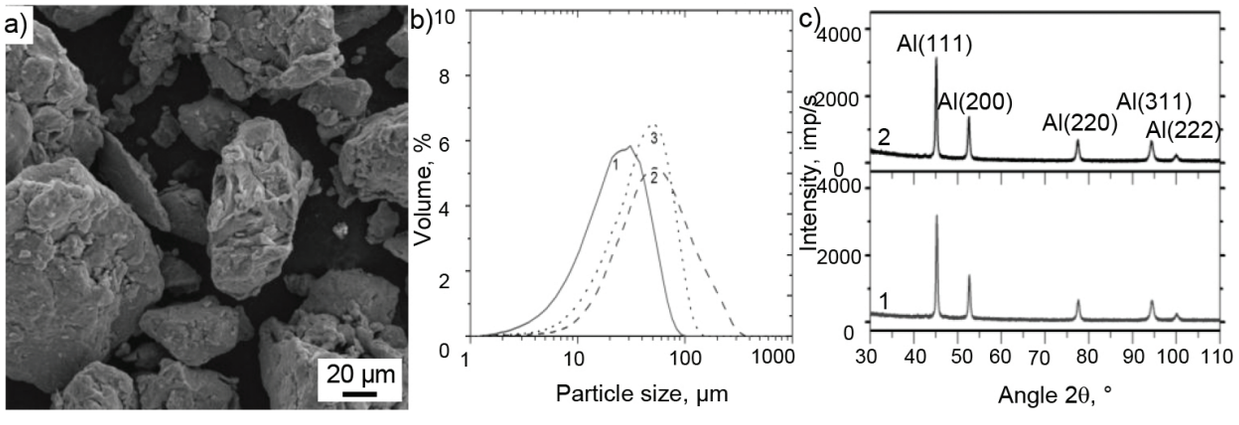



**Figure 4.** (a) Morphology of AlMg1SiCu alloy powder with fraction of 5% of MWCNTs by mass subject to high-energy milling for 10 h, (b) comparison of the grain distribution of AlMg1SiCu (1) alloy powder and AlMg1SiCu alloy powder with 2% (2) and 5% (3) volume fraction of MWCNTs subjected to high-energy milling for 5 and 10 h, (c) X-ray diffraction pattern of unmilled AlMg1SiCu alloy powder, milled with volume fraction of 2% (1) and 5% (2) of MWCNTs for 10 h.

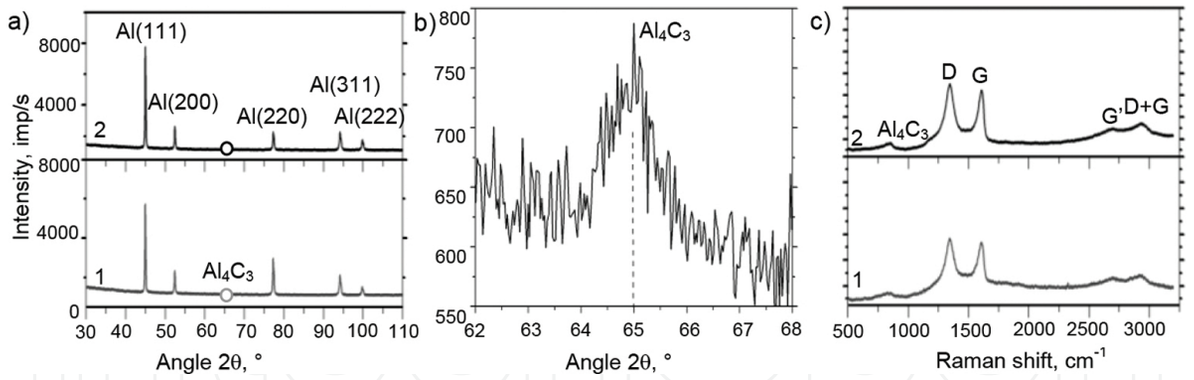



**Figure 5.** (a) X-ray diffraction pattern of nanocomposite material with volume fraction of 2% (1) and 5% (2) of MWCNTs for 10 h, (b) magnification of the peak of $Al_4C_3$ phase, (c) Raman spectrum of nanocomposite material with volume fraction of 2% (1) and 5% (2) of MWCNTs milled for 10 h.

**Figure 5c** shows Raman spectra of nanocomposite material powders with the volume fraction of 2 and 5% of MWCNTs subjected to high-energy milling for 10 h. The bands (D and G, G′) distinctive for MWCNTs confirm the presence of carbon nanotubes in AlMg1SiCu alloy powder. It was found as a result of a spectral analysis that the intensity of band D is higher for all powders as compared to the band existing for MWCNTs themselves, which signifies a higher number of defects, carbon impurities with $sp^3$ bonds and defects on the side walls as a result of breaking $sp^2$ bonds created in high-energy mechanical milling. The intensity of the G′ bands has decreased significantly as a result of defects. Moreover, the Raman spectra show the presence of the $Al_4C_3$ phase.

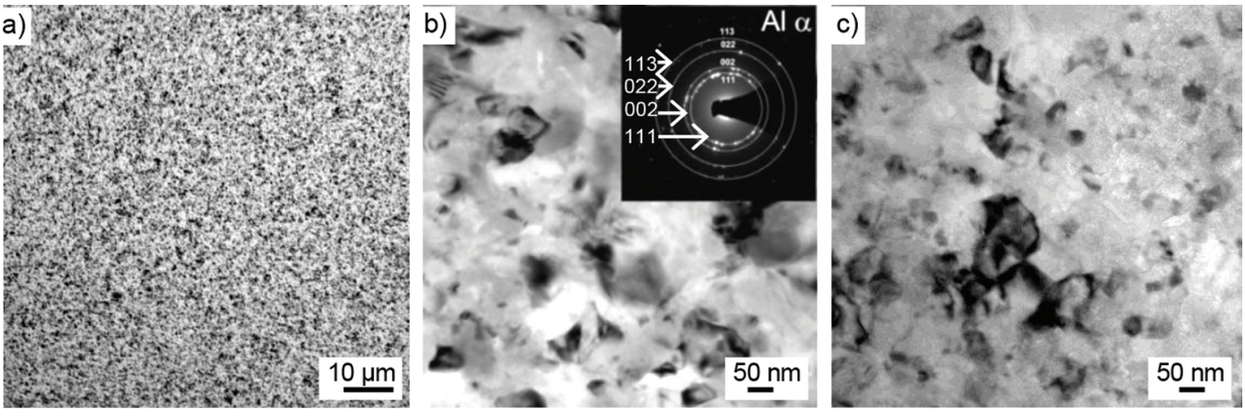



**Figure 6.** (a) Structure of nanocomposite material produced from AlMg1SiCu alloy powder with volume fraction of 5 and 10% of HNTs after 6 h of mechanical milling (light microscope), (b, c) structure of thin foils of materials produced by mechanical milling for 6 h and by hot pressing of (b) AlMg1SiCu alloy (c) composite material reinforced with 10% volume fraction of HNTs.

Due to the fact that the agglomeration of particles being the reinforcement of composite materials deteriorates their mechanical properties, the basic requirement posed for materials being their components is to demonstrate better properties by distributing the reinforcing

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material uniformly in the matrix [69, 70]. Although the process of plastic consolidation by hot pressing supports the formation of a homogenous structure free of any unfavorable clusters of particles being the reinforcement of composite materials, the agglomerations of such particles are formed depending on their size, geometry, the electric charge collected on the surface, the type of material, as well as differences in their density, which are the most frequent reasons why composite materials lose their properties [63]. Halloysite reinforcing phases in the achieved composite materials are distributed very uniformly, and rarely create clusters, which only exist for composite materials reinforced with fossil halloysite. The proof that consolidation is carried out correctly is also the material achieved with a very fine structure (**Figure 6a**), deprived of any agglomerates of reinforcing particles. Slight structural fibrousness in the cross section parallel to the direction of extrusion exists in some cases only, which is associated with the extension of the original boundaries of dispersed particles of the composite material. The observations are the same as presented in the works [71, 72].

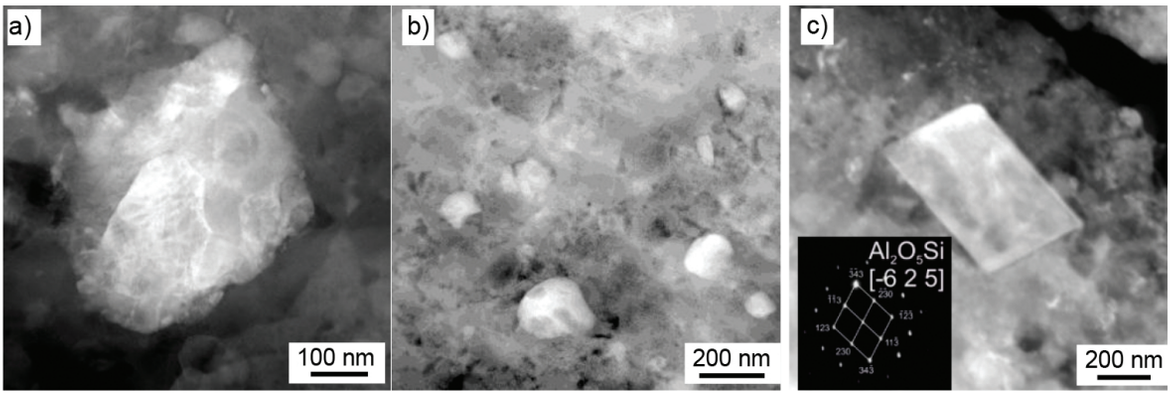



**Figure 7.** The structure of the aluminium alloy AlMg1SiCu composite material with reinforcement of the 15% halloysite nanotubes with the primary intermetallic phases: (a) $AlFe_3$, (b) $Al_4(Fe, Cr, Mn)Si_{0.74}$, (c) $Al_2O_5Si$ (TEM).

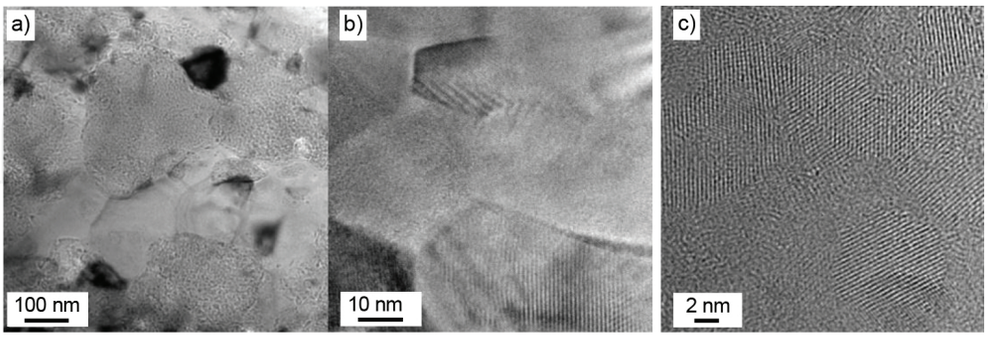



**Figure 8.** The structure of the aluminium alloy AlMg1SiCu composite material with reinforcement of the 15% halloysite nanotubes: (a) after mechanical alloying (STEM mode using the energy-filtered TEM microscopy technique), (b) and (c) with the occurrence of nanometric grains even 5–10 nm in the matrix (HRTEM).

The observations carried out in the scanning-transmission mode (**Figure 6b, c**) showed that —apart from a highly fine structure—the studied composite materials consist of two phases

with a contrasting structure. The lack of pores, voids and the tightly adhering phases signify that the matrix and reinforcement particles are well bonded during mechanical synthesis as well as in plastic consolidation. Examinations in the transmission mode also allowed to identify the presence of a solid aluminium solution with nanometric grains, intermetallic primary phases $AlFe_3$ and $Al_4(Fe,Cr,Mn)Si_{0.74}$ and $Al_2O_5Si$ phase (**Figure 7**) created most probably during the mechanical milling process. Convincing evidence of diffraction signifying the existence of other primary or secondary phases was not achieved. A highly fine structure, especially the existence of grains with the size of several nanometres, was shown by means of high-resolution electron microscopy (**Figure 8**).

| HNT content in Al alloy powder, vol.% | Milling time, h | Microhardness, $HV_{0.1}$ |
|---|---|---|
| AlMg1SiCu | Unmilled | 61 |
| AlMg1SiCu/5% HNT | 3 | 97 |
| | 6 | 122 |
| AlMg1SiCu/10% HNT | 3 | 103 |
| | 6 | 130 |

**Table 3.** Microhardness of the extruded composites reinforced with HNTs.

A high degree of plastic deformation, a fine structure with nanometric sizes, as well as dispersive reinforcement with particles of halloysite and oxides, all caused by mechanical milling, have an obvious effect on a nearly threefold growth of microhardness. It was found, however, that after plastic consolidation, microhardness of the created materials fell by 30% compared to the milled powders, which may be connected with recovery and partial recrystallisation caused by the effect of higher temperature in extrusion. Nevertheless, the produced composite materials are characterised by microhardness ranging between 110 and 150 $HV_{0.1}$ (**Table 3**), which clearly exceeds the values attained for a conventional EN AW-AlMg1SiCu alloy even after correct heat treatment [73, 74].

The same as for composite materials reinforced with halloysite nanotubes, the materials reinforced with MWCNTs produced in high-energy mechanical milling and hot pressing are characterised by the lack of matrix structure discontinuities (**Figure 9a**). The lack of structure discontinuities and cracks means that powder consolidation was performed correctly.

Structure examinations in a high-resolution transmission electron microscope were carried out on a nanocomposite material with the fraction volume of 5% vol. of MWCNTs fabricated from powder milled for 10 h. The examined material has a homogenous, nanocrystalline structure. This is confirmed by images obtained in the transmission mode. Grains are symmetric, nearly ball-shaped, and their size is about 50–70 nm (**Figure 9b, c**). A diffraction SAED image is characteristic for polycrystalline (nanocrystalline) materials. Two lines are present, characteristics for aluminium carbide, which do not exist in aluminium. **Figure 10** shows well-dispersed MWCNTs in the matrix of the extruded AlMg1SiCu matrix composite as well as the structure of the $Al_4C_3$ carbides formed as a result of the interaction between the outer shells of carbon

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nanotubes (CNTs) and the Al matrix during mechanical alloying in the extruded AlMg1SiCu matrix composite reinforced with MWCNTs.

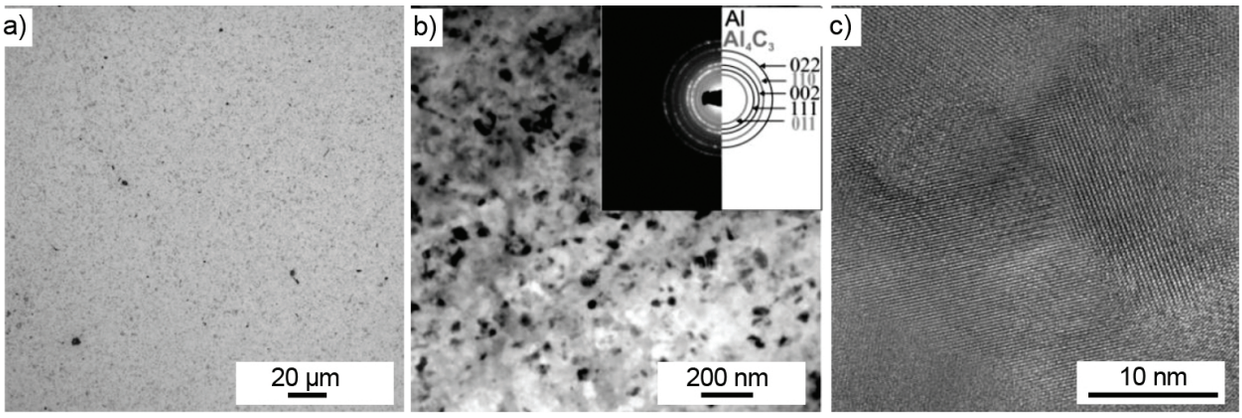



**Figure 9.** (a) Structure of nanocomposite material produced from AlMg1SiCu alloy powder with volume fraction of 5% of MWCNTs after 10 h of mechanical milling (light microscope), (b) structure of thin foil of nanocomposite material reinforced with 5% vol. of MWCNTs after 10 h of mechanical milling (TEM), (c) nanostructural grains in the matrix.

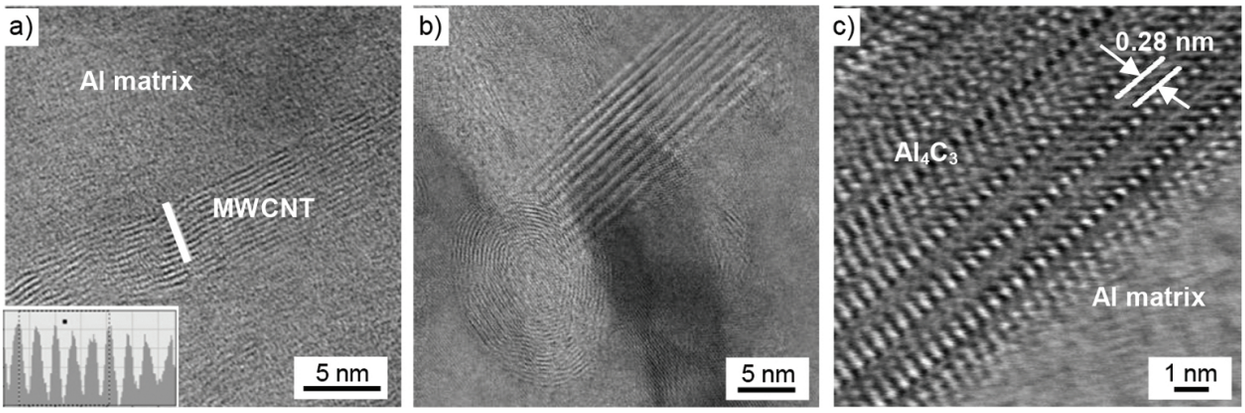



**Figure 10.** The structure of the extruded AlMg1SiCu matrix composite reinforced with MWCNTs, (a) well-dispersed MWCNTs in the matrix of the extruded AlMg1SiCu matrix composite, (b) and (c) the $Al_4C_3$ carbides formed as a result of the interaction between the outer shells of CNTs and the Al matrix during mechanical alloying in the extruded AlMg1SiCu matrix composite reinforced with MWCNTs (HRTEM).

Nanocomposite materials with a matrix made of AlMg1SiCu aluminium alloys reinforced with carbon nanotubes exhibit—in relation to a pure alloy acting as a matrix—much better mechanical properties, including compressive strength (**Figure 11**). **Table 4** shows the results of microhardness measurements of the achieved nanocomposite materials depending on the fraction of a reinforcing phase and milling time.

Nanocomposite hardness is increasing along with the growing fraction of carbon nanotubes, as well as milling time. The microhardness of nanocomposite materials reaches values higher than the microhardness of the input alloy. The hardness of nanocomposite materials is rising as the fraction of a reinforcing phase is rising. It was found that the addition of MWCNTs with

the fraction of 5% by vol. increases hardness by nearly 200% as compared to the hardness of material produced from the input, unmilled powder. The highest microhardness of 168 ± 7 HV is seen for a nanocomposite material reinforced with 5% vol. of MWCNTs, fabricated from powder milled for 10 h and is higher by 55% than the hardness of the extruded AlMg1SiCu alloy produced from powder milled over the same time.

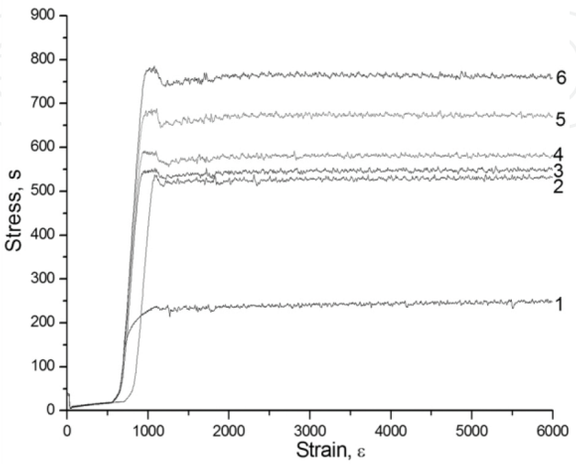



**Figure 11.** Compression test curves of the aluminium alloy EN AW-AlMg1SiCu composite materials with reinforcement of the different concentrations of carbon nanotubes: 1—AlMg1SiCu, 2—AlMg1SiCu/0%MWCNTs, 3–AlMg1SiCu/0.5%MWCNTs, 4–AlMg1SiCu/2%MWCNTs, 5—AlMg1SiCu/3.5%MWCNTs, 6—AlMg1SiCu/5%MWCNTs.

| MWCNT content in Al alloy powder, vol.% | Milling time, h | Microhardness, $HV_{0.1}$ |
|---|---|---|
| AlMg1SiCu | Unmilled | 61 |
| AlMg1SiCu/2% MWCNT | 5 | 132 |
| | 10 | 157 |
| AlMg1SiCu/5% MWCNT | 5 | 158 |
| | 10 | 168 |

**Table 4.** Microhardness of the nanocomposites.

## 4. General remarks

Nanocomposite materials with a matrix made of AlMg1SiCu aluminium alloys, reinforced with carbon or halloysite nanofibers, manufactured by high-energy mechanical synthesis or low-energy mixing, cold consolidation and hot pressing, according to the developed custom original technology, exhibit much better mechanical properties in relation to the matrix alloy. Microhardness and compressive strength of the materials containing 5% of multiwalled carbon nanotubes during high-energy milling is rising nearly threefold. If 15% of halloysite nanotubes is added, this leads to a nearly threefold reduction in volume loss in abrasion tests. Strong

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plastic deformations and a grain size reduction below 100 nm and the dispersion of reinforcing particles, all caused by mechanical milling, is substantially reinforcing the composite materials reinforced with carbon and halloysite nanotubes. A structure of nanograins, crushed even to the size of 5–10 nm, is particularly a structural cause of enhanced mechanical properties. This is explained using a high-resolution transmission electron microscope (HRTEM). In the case of carbon nanotubes, the matrix is reinforced with such nanotubes. Moreover, as a result of interactions between the external layer of carbon nanotubes and Al during mechanical alloying, the degree of defects of carbon nanotubes is increased as a result of interactions at the matrix-reinforcement boundary. Needle-like precipitates of $Al_4C_3$ carbide also occur, which are then crystallised during plastic consolidation at an elevated temperature. $Al_4C_3$ carbide is most probably not influencing positively the ductility of the composite material. Additional reinforcement with primary intermetallic phases, i.e., with $AlFe_3$ and $Al_4(Fe,Cr,Mn)Si_{0.74}$ and with the $Al_2O_5Si$ phase, which is created most certainly during mechanical milling, is taking place in the nanocomposite materials reinforced with halloysite nanotubes. The composite materials produced in mechanical synthesis and hot pressing are characterised by a structure of uniformly arranged, fine reinforcing phase particles in a fine-grained matrix of AlMg1SiCu alloy. The examinations of the structure of the newly developed nanostructured composite materials reinforced with halloysite and carbon nanotubes prove that a mechanical milling process allows to improve the arrangement of reinforcing particles in the matrix material. A homogenous structure with uniformly arranged reinforcing particles can be achieved by applying a reinforcement with halloysite and carbon nanotubes, if short time of milling is used, thus eliminating an issue of their agglomeration; it also allows to achieve more advantageous functional properties.

## 5. Additional information

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