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EFFECT OF MILLING TIME ON MICROSTRUCTURE OF AA6061 COMPOSITES FABRICATED VIA MECHANICAL ALLOYING

WPŁYW CZASU MIELENIA NA MIKROSTRUKTURĘ KOMPOZYTÓW O OSNOWIE STOPU ALUMINIUM 6061 WYTWORZONYCH PRZEZ MECHANICZNE STOPOWANIE

The aim of this work is to determine the effect of manufacturing conditions, especially milling time, on the microstructure and crystallite size of a newly developed nanostructural composite material with the aluminium alloy matrix reinforced with halloysite nanotubes. Halloysite, being a clayey mineral of volcanic origin, is characterized by high porosity and large specific surface area. Thus it can be used as an alternative reinforcement in metal matrix composite materials. In order to obtain this goal, composite powders with fine microstructures were fabricated using high-energy mechanical alloying, cold compacting and hot extrusion techniques. The obtained composite powders of aluminium alloy reinforced with 5, 10 and 15 wt% of halloysite nanotubes were characterized with SEM, TEM and XRD analysis. It has been proven that the use of mechanical alloying leads to a high degree of deformation, which, coupled with a decreased grain size below 100 nm and the dispersion of the refined reinforcing particles–reinforces the material very well.

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

Celem niniejszej pracy było określenie wpływu warunków wytwarzania, w szczególności czasu mielenia, na strukturę i wielkość krystalitów nowo opracowanych nanostrukturalnych materiałów kompozytowych o osnowie stopów aluminium wzmacnianych nanorurkami haloizytowymi. Haloizyt, będący minerałem ilastym pochodzenia wulkanicznego, charakteryzuje się dużą porowatością, dużą powierzchnią właściwą, i może stanowić alternatywne wzmocnienie metalowych materiałów kompozytowych. W tym celu przy użyciu wysokoenergetycznego mechanicznego stopowania w młynie kulowym wytworzono rozdrobnione i trwale połączone proszki kompozytowe, które następnie poddano zagęszczaniu na zimno i wyciskaniu na gorąco. Tak opracowane materiały kompozytowe o udziale masowym haloizytowego wzmocnienia 5, 10, 15% zbadano metodami skaningowej i transmisyjnej mikroskopii elektronowej oraz rentgenowskiej analizy fazowej. Stwierdzono, że wywołane mechanicznym stopowaniem silne odkształcenie plastyczne i zmniejszenie rozmiaru ziarna poniżej 100 nm oraz dyspersja haloizytowych cząstek wzmacniających wpłynęła na znaczne umocnienie materiałów kompozytowych.

1. Introduction

The majority of research work in materials engineering is carried out in the field of materials strengthening. In general, metallic materials strengthening consists of applying actions which limit dislocation movements resulting in an increased yield strength. The numerous methods of metals and metal alloy strengthening include strengthening by: grain refinement, solid solution, particles, or cold working [1-6]. For several decades, numerous efforts have been made in the development of machinery and equipment constructions, including modern means of transportation, especially in the aviation and automotive sector, to replace steel components with other, namely non-ferrous metals such as light metal alloys, chiefly aluminium and magnesium [7,8]. In order to improve mainly mechanical properties, efforts have been made to introduce particles and fibres into such alloys, thus creating composite materials [9-12]. The mineral halloysite in the form of nanotubes may serve as an unconventional reinforcement of the composites. It is a clay-like aluminosilicate mineral of volcanic origin that boasts high porosity, high specific surface area, high ion-exchange, and simplicity in terms of chemical treatment and machining. Halloysite is composed of flat surface lamellae, partially curled or in the form of tubes originating from the curled lamellae [13,14].

The aim of this work was to determine the influence of manufacturing conditions, especially milling time, on the microstructure and crystallite size of newly developed nanostructural aluminium alloy matrix composites reinforced with halloysite nanotubes.

2. Experimental procedure

The qualitative analysis of the phase composition of powders and composite materials was carried out on an X'Pert PRO X-ray diffractometer produced by PANalytical, equipped

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with the Xccelerator strip detector, filtered radiation of the copper tube at the voltage of 40 kV and 30 mA incandescence. Reflected ray measurements were performed within the angular range of 2θ from 5° to 140°. To determine the size of crystallites of sizes below 100 nm, the methods based on diffraction line profile analysis were applied. The peak reflex widths were determined as FWHM (Full Width Half Maximum). The silicon standard was applied to eliminate the impact of apparatus function width on the diffraction reflex width. The theoretical functions, i.e. Gauss-type ($y = \exp(-ax^2)$), in the approximation methods were used for the experimental description of diffraction line intensity distribution, due to factors caused by apparatus, as well as physical ones. According to Scherrer's relation, the widening of the diffraction line resulted from the small size of crystallites is expressed by the formula [15]:

$$\beta_k = \frac{K \cdot \lambda}{D_{hkl} \cdot \cos\theta}. \tag{1}$$

where: β_k is the width of peak depending on crystallite size, radian; K – constant (assumed K=0.9); λ – radiation wavelength, nm; D_{hkl} – crystallite size perpendicular to (hkl), nm; Θ – Bragg's angle, radian.

Widening of the diffraction line, resulting from lattice deformations is expressed by Taylor's dependency [15]:

$$\beta_z = 4e \cdot tg\theta. \tag{2}$$

where e is lattice deformation.

The total of β_k and β_z widening is the overall widening of the diffraction line. The diffraction line profiles were described by Gauss type function (Halder – Wagner method):

$$\beta^2 \cdot \cos^2\theta = \left(\frac{\lambda}{D}\right)^2 + 16e^2 \cdot \sin^2\theta \tag{3}$$

with the assumption that:

$$\beta^2 = B^2 - -b^2. \tag{4}$$

where: B is the width of the peak measured for analysed sample, radian; b – the width of the peak measured for a standard sample, radian.

The width of the peaks were determined as FWHM, matching each reflex to the curves determined based on the Lorentz function in the FITYK software, both for the $K\alpha_1$ and $K\alpha_2$ components. Powders microstructural characterization was conducted using a scanning electron microscope Zeiss SEM SUPRA 35. The microstructure of the investigated extruded composites was examined by the transmission electron microscope FEI S/TEM TITAN 80-300.

3. Material for investigations

Air atomized 6061 aluminium alloy powder (ECKA Co, Germany) was mixed with 5, 10 and 15 wt. % of halloysite nanotubes (NaturalNano, USA). The powders were then subjected to mechanical alloying in the planetary Fritch mill Pulverisette 5 for up to 12 hours in steel container, rotational speed of 400 rpm, AISI 420 steel balls of 20 mm diameter and ball-to-powder weight ratio of 20:1 (1000g:50g) were utilized. Subsequently, the milled powders were compacted in the hydraulic uniaxial press in a mould of 25 mm in diameter, the with 300 MPa pressure and then extruded at 480°C with caning and without degassing. Extruded bars of 8 mm diameter and near theoretical density have been produced.

4. Results and discussion

Investigations using the SEM BSE allowed an analysis of the powder particles' microstructure. The cross section of AA6061 alloy powder particles in the initial state with spherical shape (Fig. 1a) is distinguished by the arrangement of fine, light precipitates rich in iron with the distinctive dendritic form on the grain boundaries (Fig. 1b). In agreement with the literature [16], it is likely an intermetallic phase from the group $Al_{12}Fe_3Si$, Al_8Fe_2Si, $Al_{15}Fe_3Si_2$ or Al_5FeSi created as a result of rapid cooling during atomization. In the first stage of mechanical alloying the majority of particles are deformed, but the degree of deformation is quite diverse (Fig. 2a). The deformed particles, besides of the shape changes to a plate-like form, contained refined precipitates (Fig. 2b). The flat particles were welded many times as a result of further milling the particles create plate structures with much bigger dimensions (Fig. 3a). A specific boundary between the aluminium alloy matrix particles joined as a result of welding induced by high-energy collisions of milling balls is represented by refined particles of halloysite and aluminium oxides coming from the particles' surface (Fig. 3b). The large particles formed in the process became harder as a result of strain hardening as compared to the initial state, hence very predisposed to cracking (Fig. 4a). Powder fragmentation occurring at the following stage is – apart from the hardening suggested above – also caused by the size of large particles. Large flat particles are sensitive to cracking, and this is related to the fact that the appearance probability of a nucleus of cracking is directly proportional to the particle size.

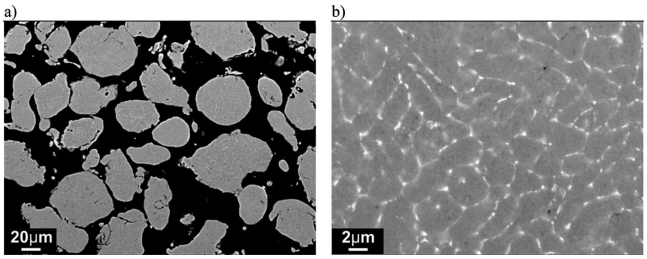

Fig. 1. Microstructure of the as-received air atomised AA6061 powder: a) mag. 1000x, b) 10000x, SEM

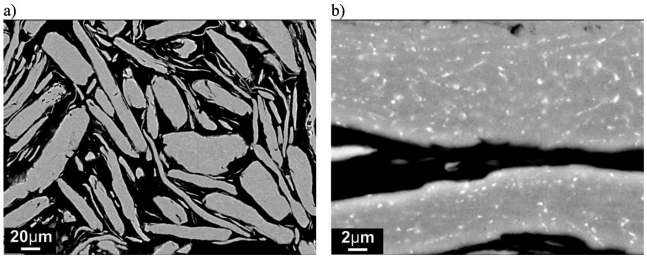

Fig. 2. Microstructure of the composite materials reinforced with 10% halloysite nanotubes after 1 h of mechanical alloying: a) mag. 1000x, b) 10000x, SEM

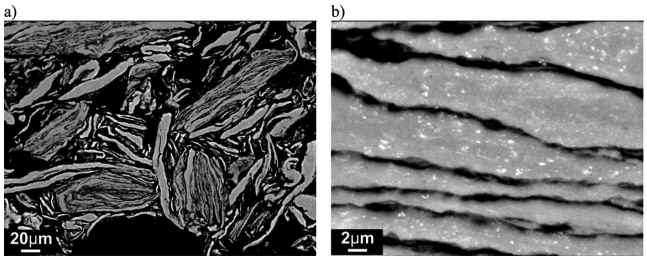

Fig. 3. Microstructure of the composite materials reinforced with 10% halloysite nanotubes after 2 h of mechanical alloying: a) mag. 1000x, b) 10000x, SEM

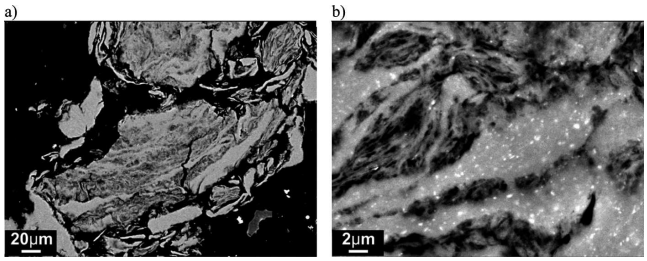

Fig. 4. Microstructure of the composite materials reinforced with 10% halloysite nanotubes after 3 h of mechanical alloying: a) mag. 1000x, b) 10000x, SEM

Large, non-equiaxial plate-like particles formed as a result of overlapping and welding are – regardless of their hardness – more sensitive to cracking as compared to their correspondents with small size and irregular shape. Fine particles are characterised by the absence of nuclei of cracks and hence they are stronger and exhibit a tendency of inter-welding. The occurrence of cracking is accompanied by re-welding (Fig. 5a) and, as a result, this influences the random orientation of the welded particles' boundaries (Fig. 5b). A layer-like or plate-like structure from the earlier stage of milling, particular particles is consequently becoming more random due to such multiple welding and cracking, without continuous boundaries between the joined particles. The equiaxial shaped particles (Fig. 6a) with uniformly distributed fine reinforcing particles (Fig. 6b) indicate that the process has reached steady state. Further milling does not affect significantly the powder structure and resulted properties. It only causes the unwanted sticking of particles to the mill walls and milling balls themselves. The observed changes in powder morphology and structure are the same as the outcomes presented in the work [17] thus confirming the correct preparation of composite powders. It also should be noted that the changes described in the structure of powders

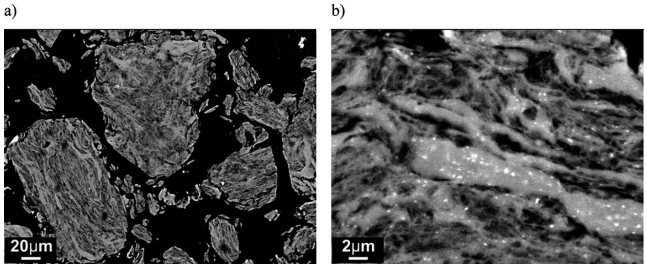

Fig. 5. Microstructure of the composite materials reinforced with 10% halloysite nanotubes after 4 h of mechanical alloying: a) mag. 1000x, b) 10000x, SEM

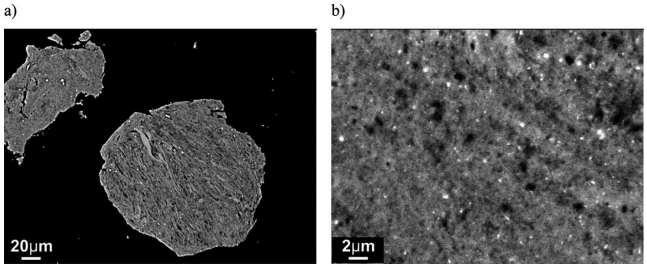

Fig. 6. Microstructure of the composite materials reinforced with 10% halloysite nanotubes after 6 h of mechanical alloying: a) mag. 1000x, b) 10000x, SEM

in a mechanical milling process has of the statistical nature: each of the milled particles is subjected to a unique process of deformation and is characterised by an individual degree of structure refining and reinforcement.

The mechanical alloying, besides the influence on the microstructure of the composite powders, also affects their phase composition. The phase composition depended on the milling time of the halloysite nanotubes reinforced the composite material. Fig. 7 shows that after more than a dozen of minute milling, low-angle reflexes originating from the halloysite mineral crystals fade, leaving only reflexes identified as α-Al on the diffractograms. The amorphization of the halloysite reinforcing phase takes place as a result of the destruction of the multi-layer structure. Similar observations were reported in the works of [18-20]. The milling time affected not only the phase composition of the processed powders, but also the refinement of the grains. The high-energy mechanical milling is a process generating a large number of defects and causes refinement to the crystalline structure. The size of the milled powder particles usually ranges from a few to several tens of micrometers, however, their structure is characterized by size range of the crystallites in the nanometer range, i.e. areas coherently dispersing X-ray radiation. To determine the impact of the process on the refinement of the composite materials structure, a crystallite size analysis using X-ray methods, for particular milling times, was carried out (Table 1).

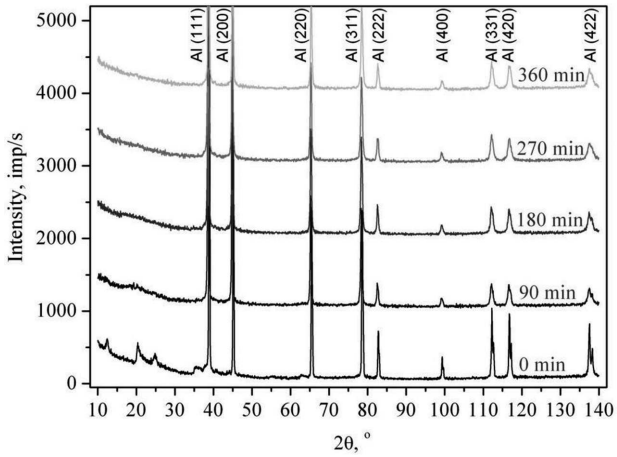

Fig. 7. XRD results of the AA-6061 matrix composite powders reinforced with 10% of halloysite nanotubes for selected milling times

Due to the calculative error of the method and the dependency on numerous physical factors (the crystallite size, lattice strain) and apparatus, the results were compared to an approximation

function, describing the diffraction line profile. The crystallite size and lattice deformations showed significant differences in the calculated values, depending on the assumptions made and calculation method applied [15]. Based on the obtained results, it was shown that the most adequate method of calculations is the Halder-Wagner method. In analysing the particular results, it was observed that depending on the milling time, the average crystallite size decreases from the initial value of 499 nm – for the powder at the initial state – down to 65 nm for the powder of composite material after 6 hours of milling.

TABLE 1

Crystallite size and lattice strain for AA-6061 matrix composite powders reinforced with 10% of halloysite nanotubes determined by the application Halder-Wagner method for selected milling times

Milling time [min]	0	60	120	180	240	300
Crystallite size [nm]	499	105	80	74	81	70
Lattice strain [%]	0.01	0.04	0.03	0.03	0.05	0.05
Pearson's correlation	95.47	98.89	98.86	96.96	96.95	96.66

TABLE 2

Crystallite size for extruded AA-6061 matrix composite reinforced with different fractions of halloysite nanotubes determined by the application Halder-Wagner method

Mass fraction of halloysite particles, %	0	5	10	15
Crystallite size [nm]	158	95	98	83
Pearson's correlation [%]	94.76	97.32	98.54	96.73

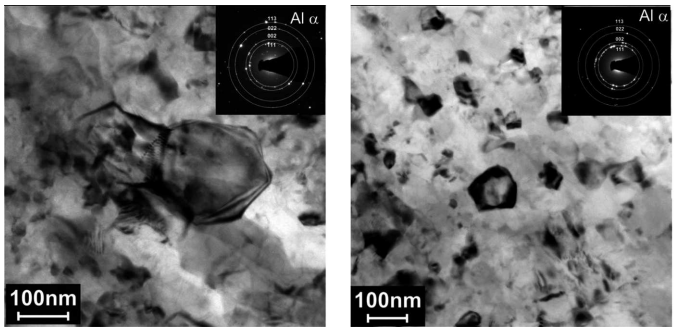

Fig. 8. Microstructure of the AA-6061 alloy (a) and composite material reinforced with 15% halloysite nanotubes (b) produced by high-energy milling; TEM

Characteristics for nanostructural metallic materials low thermal stability of their structure. Results from the small size of grains and high density of the accumulated dislocations. The growth of grains may occur under a significantly lower temperature, compared to the conventional materials. Therefore, in case of powders produced by mechanical milling methods, their consolidation conditions are immensely important. In the case of the plastic consolidation by extrusion, the temperature of around 500°C and, the short time of the material annealing might retards recrystallization and overgrowth of grains [21]. Another measurement of the crystallite size and lattice deformation for the extruded halloysite reinforced composite materials, showed a slight growth of the crystallite size to ca. 100 nm (Table 2). This shows that the plastic consolidation guarantees the maintenance of the improved mechanical properties, resulting from the nanostructure of the produced composite materials. The XRD analysis results have been confirmed by TEM observations (Fig. 8). The structure of thin foils of composite materials can be generally described as subgrain solid solution of aluminium. No convincing diffraction evidence of amorphous or crystal structure of halloysite reinforcing phase has been obtained.

5. Conclusions

It can be concluded by analysing of microstructure of the milled powders, that a longer milling time leads to a homogenous distribution of reinforcing particles into equiaxial composite powders particles. It also should be noted that halloysite, being a reinforcing phase of the newly developed composite materials, is subjected to brittle cracking and is strongly crushed. The composite materials obtained as a result of mechanical alloying and hot extrusion are characterized with the structure of uniformly distributed, disperse halloysite particles in a fine-grain matrix of AA6061 alloy. It has been shown that the crystallite size decreases from the initial value of 499 nm to 65 nm for composite powder in the steady state.

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