Original Article

Formation of ethylene-vinyl acetate composites filled with Al–Cu–Fe and Al–Cu–Cr quasicrystalline particles

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Abstract

Icosahedral Al_{65}Cu_{23}Fe_{12} and decagonal Al_{73}Cu_{11}Cr_{16} quasicrystalline powders were synthesized by the mechanical alloying and subsequent annealing. Morphology evolution at mechanical alloying of Al-based powders was found to be determined by competition between cold welding and fracture mechanisms. Mechanical alloying results in formation of coarse agglomerates consisting of fine particles. The chemical binding between the polymer matrix and quasicrystals, destruction of agglomerated at extrusion, and the uniform distribution of quasicrystals over the polymer melt were provided by surface treatment of quasicrystalline particles with silanes. The highly filled (up to 60 wt%) ethylene-vinyl acetate/quasicrystals composites were obtained, and their rheological characteristics were studied. It was shown that the fluidity of the melt is retained at a high level providing uniform distribution of quasicrystalline particles over the polymer.

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1. Introduction

The properties of quasicrystals (QC) have been studied for more than 20 years. However, up to now, they have not found a wide industrial application. The quasicrystals possess the following practically important properties: high hardness and wear resistance, low surface energy, low friction coefficient, significant radiation and corrosion resistance, low electrical and thermal conductivity, and unusual optical properties [1–10]. Possible areas of application of unusual combination of thermal, electrical, and optical properties of quasicrystals were considered in [4,10–17].

The main drawback of quasicrystals, which limits their practical use, is a low fracture toughness (about 0.5–3.5 MPa m^{1/2}) [5,13,18], whereas, for metal materials, it is above 40 MPa m^{1/2}. Low toughness and crack propagation resistance at the temperatures below 450 °C limits the application of quasi-crystals in the form of bulk parts and thick film coatings.
At the same time, quasicrystals are very promising for use in the composites as the reinforcing phase [19-23]. One of the first proposed materials was martensitic aging steel SandvikBioluterik91. After hardening and aging of these steel, thermodynamically stable particles of icosahedral Mo–Fe–Cr phase were formed. The tensile strength of SandvikBioluterik91 steel is about 2500–3000 MPa, a Vickers hardness is about 730 HV [24]. This steel is proposed for the production of surgical needles.

Of interest is to use the Al–Cu–Fe and Al–Cu–Cr QC as reinforcements of aluminum alloys, due to the high hardness of the particles and a good combination with the matrix material [10,25–35]. Introduction of dispersed quasicrystalline particles 0.5–3 μm in size into the aluminum matrix can significantly increase the strength characteristics and improve hardness and abrasion resistance of the composite material. Al–Cu–Fe quasicrystals are considered as the promising fillers for the composites with polymer matrices, providing improved physical, mechanical, tribological and thermal properties [36–41]. Epoxy binders [36,37], polystyrene sulfide (FPS) [37], ultra-high molecular weight polyethylene (UHMWPE) [38,40], polyamide (PA) [39] and ethylene-tetrafluoroethylene [41] can be used as the matrix materials. The application of Al–Cu–Fe quasicrystals as a filling in epoxy resin and thermoplastic polymers allows one to increase the elastic modulus by two times and to improve heat resistance in relation to the unfilled matrix materials. The durability of the composites filled with QC is higher than that of composites filled with silicon carbide or aluminum oxide [36], which, in combination with a low coefficient of friction, allows one to fabricate the parts for dry friction bearings [37]. The composite materials based on QC Al–Cu–Fe and UHMWPE have been already tested in the manufacture of prostheses. The mechanical characteristics of such composites are higher than those of UHMWPE – hydroxyapatite composites. The biocompatibility and cytotoxicity of Al–Cu–Fe/UHMWPE composite are equal to those of pure UHMWPE [38]. Of interest is the use of compositions based on thermoplastic polymers filled with quasicrystals in rapidly developing technologies of additive manufacturing [39]. For example, the composite material PA + AlCuFeB, which is obtained by selective laser sintering, exhibits low porosity, low friction and wear.

An application of QC as fillers in the polymer matrix requires a high level of adhesion between the matrix material and quasicrystal. Moreover, it is important to provide the necessary dispersion of the filler, the absence of impurity phases with high surface energy, and uniform distribution of the filler over the matrix.

A promising method to obtain quasicrystals is the mechanical alloying and subsequent annealing. This method enables one to produce single-phase quasicrystalline powder, which satisfies the specified requirements. We have previously demonstrated the possibility of preparing quasicrystals of Al–Cu–Fe [42–44] and Al–Cu–Cr [45–47] systems using this method. However, for successful use of quasicrystalline powders as the fillers in the polymeric matrix it is necessary to ensure preparation of homogeneous, fine powder that can be uniformly distributed over the bulk polymer. Thermoplastic polymers, as well as quasicrystals, are sufficiently inert, and do not form chemical bonds. Therefore, the quasicrystalline surface modification of the filler is required to ensure the formation of chemical bonding of the filler to the matrix. Moreover, the fine powders of metal materials often form large aggregates, so it is necessary to ensure their deagglomeration for the uniform distribution over the molten thermoplastic substance. It should be noted that no investigations aimed at the development of the methods for uniform distribution of fine quasicrystalline powders over the polymer matrix are available from the literature. Our study was aimed to elaborate a route to create ethylene-vinyl acetate composites filled with Al–Cu–Fe and Al–Cu–Cr quasicrystals particles with homogeneous distribution of fillers in matrix.

2. Experimental

Metals powders 98.5–99.5 at. % pure were used as the starting components for the production of quasicrystals. According to a laser diffraction data, aluminum particles were about 498 μm in cut (d50) size. The particle sizes of other metals were close to each other, so for copper, d50 was about ~32 μm, for chromium, about 34 μm, and for iron, about 35 μm.

The mechanical alloying (MA) process was performed using a water-cooled AFP-3 planetary ball mill. Elemental powders of Al52Cu23Fe12 and Al78Cu13Cr16 compositions (in at. %) were loaded into 900 ml steel vials. The rotation velocity of the carrier during the MA process was about 450 rpm. A mixture of ShKHo15 steel balls 7/8/9.5 mm in diameter in a ratio of 1:1.5:2 was used as the grinding bodies. The weight ratio of the processed material to the balls was about 1:10, a filling degree of the vial was about 40 vol. %.

The time of MA varied from 20 min to 180 min. Loading and unloading of the powders into the vials was provided in argon. Pure ethanol was used as process control agents (PCA) to prevent cold welding of powder particles to each other and to the walls of the vials and balls, which is a serious problem in case of milling of ductile metals, such as aluminum [48].

The annealing of the powders obtained by mechanical alloying (precursors of the quasicrystals) was carried out in a pure argon atmosphere in the temperature range of 400–850 °C.

Surface treatment of the obtained quasicrystals was carried out using the following silanes: triethoxyvinylsilane Geniosil GF 56, gamma-methacryloxypropyltrimethoxysilane Silquest A-174, and polydimethylsiloxane PDMS 200. Silanization of the quasicrystalline fillers was performed in 20% ethanol solution at a temperature of 40–45 °C for 6 h under intensive stirring.

Ethylene vinyl acetate Evatane 28-05 and Evatane 28-40 (Arkema) were used as the polymer matrix.

X-ray diffraction analysis was performed using an automated X-ray diffractometer DRON-4-07, with CoKα monochromatic radiation. The spectra were analyzed using software package described in [49].

The content of Al, Cr, Cu, and Fe in the alloys was measured using the atomic emission spectral method (atomic emission spectroscopy) with inductively coupled plasma (ICP-AES). The measurements were performed on an ICP 6300 Radial View spectrometer (Thermo Fisher Scientific Inc., USA).
A tap density of the powders was measured using Quantachrome Autotap in accordance with ASTM B527 – 15 (Standard Test Method for Tap Density of Metal Powders and Compounds). The samples weight was about 25 g. Three measurements were performed for each sample. The test parameters were as follows: the shaking amplitude of 3 mm, the frequency of about 260 beats per min. The maximum tap density of the powder was achieved after 1500 shaking operations.

The particle size analysis of the powders, depending on the time of mechanical alloying, was performed on a Fritsch Analysette 3 vibration shaker, in accordance with ASTM E2651 – 13 (Standard Guide for Powder Particle Size Analysis). The sample weight was about 100 g.

The distribution of the particle size was determined with a Fritsch Analysette Nanotech-22 laser analyzer according to the method ISO 13320:2009 (Particle size analysis – Laser diffraction methods).

The ethylene vinyl acetate based compounds were prepared by the extrusion using Thermo Scientific Haake MiniLab and Scientific LTE-16 laboratory extruders. The degree of polymer filling with the quasicrystals was about 10–60 wt.%. The mixing procedure was performed at the temperatures of about 110–130 °C, in a Haake MiniLab Thermo Scientific extruder. The time of the mixing was varied in the range from 3 to 15 min.

The resulting melt flow of compounds was measured with a CEAST MFT7025 rheometer, in accordance with ISO 1133:2011 (Plastics – Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics). The measurements were carried out at a temperature of 190 °C for the following set of loads: 1.2–2.16–3.8–5 kg.

The microstructure of the samples of the powder compositions and polymer concentrates was examined with Hitachi TM-1000 and Tescan Vega3 scanning electron microscopes. The microstructure of the extruded compounds was studied on the chips made in liquid nitrogen.

The FT-IR spectroscopy was performed using a Nicolet 380 IR-Fourier spectrometer (the spectral range of 4000–450 cm\(^{-1}\) with a resolution of about 0.9 cm\(^{-1}\), the accuracy of the wave number of 0.01 cm\(^{-1}\) in attenuated total reflection (ATR) mode.

### 3. Results and discussion

#### 3.1. Mechanical alloying

Figs. 1 and 2 show the variation in the morphology of the Al–Cu–Fe and Al–Cu–Cr powders depending on the mechanical alloying time. At the initial stage of mechanical alloying (within the first 30 min for the Al–Cu–Fe system (Fig. 1) and 45 min for the Al–Cu–Cr system (Fig. 2)), the size and morphology of the particles were determined by the peculiarities of the deformed aluminum particles. It is clearly seen, that there is a plastic deformation of the aluminum particles and the deformation introduction of other metals particles into the aluminum matrix. As a result, average particle size \(d_{50}\) increased from 280 to 290 \(\mu m\) for the starting mixture to 430–520 \(\mu m\) for the mechanically alloyed powders.

Fig. 3a gives the evolution of the particle size distribution curve of the Al–Cu–Cr and Al–Cu–Fe powders during MA. At the first stage of MA (0–20 min – Al–Cu–Fe, 0–45 min – Al–Cu–Cr), curve has bimodal distribution which contain large flake Al particles covered by fine Cu, Cr or Fe particles. At the second stage of MA (20–45 min – Al–Cu–Fe, 45–60 min – Al–Cu–Cr), curve has transformed from bimodal to unimodal asymmetric, the main peak shift from 430 to 60 \(\mu m\) for Al–Cu–Fe, from 515 to 50 \(\mu m\) for Al–Cu–Cr. Powders undergo significant changes in the size and morphology at the second stage of MA. Approaching to the third stage of MA (45–60 min – Al–Cu–Fe, 60–90 min – Al–Cu–Cr), the unimodal curve varies from asymmetric to symmetric, the main peak is shifted from 65 to 20 \(\mu m\) for Al–Cu–Fe, from 50 to 15 \(\mu m\) for Al–Cu–Cr. At the third stage of MA (60–180 min – Al–Cu–Fe, 90–180 min – Al–Cu–Cr) the particle size distribution curve does not change.

Fig. 3b gives the dependence of \(d_{50}\) in the Al–Cu–Fe and Al–Cu–Cr systems on the time of MA obtained by laser diffraction method. Curves for both systems may be divided into three stages: on the first one the particle size gradually increases, on the second stage the \(d_{50}\) value drastically decrease, and, finally, on the third stage the steady-state condition was achieved. Such shape of the particle size vs. milling time dependence is typical for the case of ball milling of ductile alloys or to MA of several ductile metals [50–54]. According to [55,56], on the first stage of milling particles of ductile metals deform and change to flaky shape, and on the second stage the agglomerated particles become hardened, which results to the domination of fracture mechanism. Because of X-ray diffraction data shows nearly no new phases formations for both systems up to 60 min of milling (Table 1), we can propose that hardening in our case is promoted mainly by deformation and grain refinement. Comparing the \(d_{50}\) evolution with milling time for two investigated systems, one should note that transition from first to second stage occurs earlier for Al–Cu–Fe system than for Al–Cu–Cr system.

On the third stage of MA the steady-state condition, promoted by the equilibrium between fracture and cold welding processes [55,56], is achieved. As it is seen from Fig. 3b, \(d_{50}\) is practically unchanged and remains within 15–20 \(\mu m\) during the times of mechanical alloying over 90 min. Fig. 4 shows evolution of the fine and coarse fraction content with milling time obtained by sieve analysis. Both laser and sieve analysis show that steady-state condition achieved nearly at the milling time of 90 min. Sieve analysis (Fig. 4) also confirms that transition from first to second stage of MA occurs earlier for Al–Cu–Fe system than for Al–Cu–Cr system.

Fig. 5 shows the tap density dependences on the milling time. For both investigated systems obtained dependence represents a curve with minimum. The same shape of the powder density dependences on the milling time was observed for Al-based materials in [55,57–59]. As well as milling time dependences of particle size (Figs. 3b and 4), dependencies of tap density show that MA process consists of three stages. According to [57], the first stage consists of changes of the shape of ductile metal particles from initial equiaxiated to the flaky shape, which is accompanied with a decrease in powder density. On the second stage, due to the fracture mechanism predominance, the shape of particles changes from flaky against to equiaxial. The third stage, as well as for the
Fig. 1 – Evolution of Al_{65}Cu_{22}Fe_{12} powder morphology with increase in milling time (indicated at SEM micrographs in min).

dependences of the particles size on the milling times, reveals the approaching of the steady-stage condition of milling process. Comparing Fig. 5 with Figs. 3b and 4, one should note that transition from the one stage to the next proceeds later according to the tap density measurements than according to the particle size evolution. In the case of transition from first to the second stage of MA it means that the particle flattening continues even when the mean particle size starts to decrease due to fracture process. For the transition from the second to the third stage of MA it shows that average particle size achieves the steady-stage value earlier, then equiaxial shape.

Figs. 3–5 show that transition from the cold welding to fracture mechanism predominance at MA occurs earlier for Al–Cu–Fe system than for Al–Cu–Cr one. It may be associated with higher content of Al-based phase in Al–Cu–Cr. Taking into account that deformation at individual balls impact relates to the certain volume of materials, we should compare the volume fractions of Al-based phase in the MA systems. As it is seen from Table 1, for the MA time of 60 min, which is close to the transition point from cold welding to fracture, the volume fraction of Al-based phase in Al–Cu–Cr system is 82%, whereas for Al–Cu–Fe system this magnitude is only 69%. As it was observed in [55,58,59], an increase of the content of less ductile phase to the Al-based alloys results in the shift of the transition point between cold welding and fracture mechanisms predominance at MA to shorter times.

It is seen that, for both systems, the steady-state macroscopic condition of powders occurs at the MA time of 120 min. It should be noted that, in both systems, after 120 min of mechanical alloying, the powders are composed of the loosely coupled aggregates of equiaxed particles 1–2 µm in size (Fig. 6a and b). According to [55,56,59], such equiaxed shape of particles indicates that the steady-state condition of MA is reached.

The XRD analysis showed that no quasicrystalline phases form during MA. It should be noted that, at least in Al–Cu–Fe
Fig. 2 – Evolution of Al$_{73}$Cu$_{11}$Cr$_{16}$ powder morphology with increase in milling time (indicated at SEM micrographs in min).

Fig. 3 – Evolution of the particle-size distribution (a) and average particle size $d_{50}$ (b) of Al$_{65}$Cu$_{23}$Fe$_{12}$ and Al$_{73}$Cu$_{11}$Cr$_{16}$ powders during mechanical alloying.
Table 1 – The data of XRD phase analysis of as-milled and annealed powders. Phase fractions are given in vol. %.

<table>
<thead>
<tr>
<th>Milling time</th>
<th>As-milled</th>
<th>Annealing temperature, °C</th>
<th>400</th>
<th>600</th>
<th>650</th>
<th>700</th>
<th>750</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 min</td>
<td>Al – 69.0</td>
<td>α-Fe(Al,Cu) – 39.1</td>
<td>Al – 15.8</td>
<td>Al – 4.7</td>
<td>Al – 22.1</td>
<td>Al – 54.2</td>
<td>Al – 2.3</td>
<td>Al – 12.9</td>
</tr>
<tr>
<td></td>
<td>Cu – 17.0</td>
<td>α-Fe(Al,Cu) – 30.3</td>
<td>Cu – 5.3</td>
<td>Cu – 4.6</td>
<td>Cu – 25.1</td>
<td>Cu – 46.3</td>
<td>Cu – 3.1</td>
<td>Cu – 9.5</td>
</tr>
<tr>
<td></td>
<td>Cr – 1.0</td>
<td>α-Fe(Al,Cu) – 31.0</td>
<td>Cr – 7.6</td>
<td>Cr – 7.6</td>
<td>Cr – 10.0</td>
<td>Cr – 14.5</td>
<td>Cr – 3.6</td>
<td>Cr – 9.5</td>
</tr>
<tr>
<td>120 min</td>
<td>Al – 63.0</td>
<td>α-Fe(Al,Cu) – 28.3</td>
<td>Al – 60.8</td>
<td>Al – 11.9</td>
<td>Al – 14.0</td>
<td>Al – 20.1</td>
<td>Al – 20.1</td>
<td>Al – 20.1</td>
</tr>
<tr>
<td></td>
<td>Cr – 1.0</td>
<td>α-Fe(Al,Cu) – 30.3</td>
<td>Al – 11.9</td>
<td>Al – 11.9</td>
<td>Al – 11.9</td>
<td>Al – 11.9</td>
<td>Al – 11.9</td>
<td>Al – 11.9</td>
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<tr>
<td></td>
<td>Cu – 7.0</td>
<td>α-Fe(Al,Cu) – 31.0</td>
<td>Al – 22.9</td>
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<td>Al – 22.9</td>
<td>Al – 22.9</td>
<td>Al – 22.9</td>
<td>Al – 22.9</td>
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<tr>
<td></td>
<td>Cr – 1.0</td>
<td>α-Fe(Al,Cu) – 31.0</td>
<td>Al – 22.9</td>
<td>Al – 22.9</td>
<td>Al – 22.9</td>
<td>Al – 22.9</td>
<td>Al – 22.9</td>
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<tr>
<td></td>
<td>Cr – 9.0</td>
<td>Cr – 4.1</td>
<td>Al – 3.4</td>
<td>Al – 3.4</td>
<td>Al – 3.4</td>
<td>Al – 3.4</td>
<td>Al – 3.4</td>
<td>Al – 3.4</td>
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<tr>
<td>120 min</td>
<td>Al – 79.0</td>
<td>Cr – 2.1</td>
<td>Cr – 78.0</td>
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<td></td>
<td>Cu – 5.0</td>
<td>Cr – 2.1</td>
<td>Cr – 1.0</td>
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<td></td>
<td>Cr – 14.0</td>
<td>Cr – 2.1</td>
<td>Al – 2.7</td>
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<td>Al – 2.7</td>
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<tr>
<td></td>
<td>Al – 6.8</td>
<td>Cr – 2.1</td>
<td>Al – 95.4</td>
<td>Al – 95.4</td>
<td>Al – 95.4</td>
<td>Al – 95.4</td>
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<tr>
<td>180 min</td>
<td>Al – 72.0</td>
<td>Cr – 2.1</td>
<td>Cr – 2.1</td>
<td>Cr – 2.1</td>
<td>Cr – 2.1</td>
<td>Cr – 2.1</td>
<td>Cr – 2.1</td>
<td>Cr – 2.1</td>
</tr>
<tr>
<td></td>
<td>Cu – 2.0</td>
<td>Cr – 2.1</td>
<td>Al – 2.1</td>
<td>Al – 2.1</td>
<td>Al – 2.1</td>
<td>Al – 2.1</td>
<td>Al – 2.1</td>
<td>Al – 2.1</td>
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<tr>
<td></td>
<td>Cr – 17.0</td>
<td>Cr – 2.1</td>
<td>Al – 3.0</td>
<td>Al – 3.0</td>
<td>Al – 3.0</td>
<td>Al – 3.0</td>
<td>Al – 3.0</td>
<td>Al – 3.0</td>
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<tr>
<td></td>
<td>Al – 9.0</td>
<td>Cr – 2.1</td>
<td>Al – 5.5</td>
<td>Al – 5.5</td>
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</table>
system, QC phase can generally be obtained directly by MA [60–64]. However, formation of QC directly by MA requires a complicated optimization of milling process, at that considerable amount of other phases was observed in as-milled powders [63]. Moreover, QC phase obtained directly by MA is unstable and transforms into other phases both by subsequent milling and by annealing [64]. That is why synthesis of QC phase by MA with subsequent annealing, as it was reported in [42–47,65,66], seems to be more appropriate, especially taking into account that our powders will undergo both mechanical and thermal treatment during extrusion process.

Table 1 gives the phase composition of as-milled powders. Up to 60 min of MA, only phases of initial elements were observed by XRD. Formation of Al2Cu intermetallic phase in both investigated systems starts after 60 min of MA. Further increase in milling time results in the increase in Al2Cu phase fraction; additionally, for Al–Cu–Fe system increase in milling time results in the increase in the Fe phase content due to formation of α-Fe-based solid solution, see also discussion in Section 3.2. Fraction of Cu phase decrease with milling time for both systems, and fraction of Cr phase for Al–Cu–Cr system even increases with milling time. Equilibrium solubility of Cu in solid Al is about 2.5 at.%, whereas solubility of both Fe and Cr in solid Al is less than 1 at.% [67], thus we can suppose that preferential solution of Cu in Al occurs at MA. Formation of Al-based solid solution is evidenced by decrease in lattice constant of Al at milling. Whereas lattice constant of pure Al is of 0.4050 nm, after 60 min of milling it is of ~0.4048 nm for both systems, increase in milling time up to 180 results in a decrease in lattice constant down to 0.4041 nm for both systems. On the base of the results of XRD investigations we can suppose that formation of Al2Cu intermetallic phase at MA proceeds via diffusion of Cu into the body of Al with subsequent nucleation and growth of new phase.

The atomic emission spectral method measurement of the content of Al, Cr, Cu, and Fe elements in the samples, which were obtained by the mechanical alloying, showed that the deviations in the composition from the initially given level did not exceed 0.5 at.%. This is important in view of a narrow range of homogeneity of the QC phases. The content of Fe in the Al–Cu–Cr powders increased with the milling time, but did not exceed 0.5 at.% even after 180 min. of MA.

3.2. Annealing

Powders, obtained by the mechanical alloying, were annealed in the argon atmosphere for 1h. Recently [68] phase transformations in these powders at heating were studied by differential thermal analysis. It was found that formation of quasicrystalline phases in mechanically alloyed Al–Cu–Fe and Al–Cu–Cr under heating may include liquid state eutectic and peritectic reactions finally resulting in gradual homogenization [68]. Here on the base of XRD data we will mainly discuss solid state processes proceeding all relatively low temperatures.

In Al–Cu–Fe system, for which icosahedral quasicrystalline phase is thermodynamically stable, phase transformation at heating proceeds in accordance with equilibrium phase diagram. An important specific feature of ternary Al–Cu–Fe system is high solubility of both Al and Cu in α-Fe based solid solution. Up to 55 at.% Al and up to 30 at.% Cu can be dissolved in α-Fe at 600 °C [69]. Thus, whereas in binary Fe–Cu systems components are nearly immiscible in solid state, solubility of Cu in α-FeAl) solid solution is significant. α-Fe(Al,Cu) solid solution in equilibrium state may either exist as disordered bcc solid solution with A2 structure (α phase) or form ordered structure such as α2 phase with B2 structure and α1 phase with D03 structure [67,69]. Moreover, some other types of α phase ordering may be realized by annealing of MA Al–Cu–Fe powders. Previously [42–44] we observed a transformation of D03 structure into D8.3 one at heating of MA Al65Cu23Fe12 powder. In [70] phase with simply cubic structure, which is a superstructure of B2 phase, was observed after annealing of MA Al65Cu23Fe12 powder. In Table 1 α-Fe based phases are designated as α-Fe(Al,Cu) regardless of the type of ordering.

Table 1 shows that for Al–Cu–Fe powder milled for 60 min after annealing at 400 °C amount of α-Fe(Al,Cu) and Al2Cu phase increases significant in relation with as-milled powder, however, a certain amount of residual elemental Al and Cu phases retained in the sample. Small amount of QC phase was
also observed in sample annealed at 400 °C. Increase in the annealing temperature up to 600-650 °C results in total disappearance of elemental Al and Cu phases, and Al<sub>12</sub>Cu phase transforms into Al<sub>12</sub>Cu<sub>2</sub>Fe intermetallic phase. It was reported, then Al<sub>12</sub>Cu<sub>2</sub>Fe may be obtained immediately at MA by using of severe (ball-to-powder ratio of 70:1) milling regime [63], but commonly Al<sub>12</sub>Cu<sub>2</sub>Fe appears in MA Al-Cu-Fe powders only after annealing [42-44,61,66,71-74]. Further increase in the annealing temperature up to 700 °C results in disappearance of Al<sub>12</sub>Cu<sub>2</sub>Fe phase, however, Al<sub>12</sub>Fe<sub>4</sub> phase forms at this temperature. Al<sub>12</sub>Fe<sub>4</sub> phase was observed in a few works both in as-milled Al–Cu–Fe powders [73] and after heating of MA powders [63,71-73]. Amount of QC phase gradually increases with the annealing temperature, its maximum amount is achieved at 750 °C. However, for powders milled for 60 min both α-Fe(Al,Cu) and Al<sub>12</sub>Fe<sub>4</sub> phases coexist with QC in the annealing temperature range of 700–800 °C.

For Al–Cu–Fe powders milled for 120 and 180 min., no residual elemental Al and Cu phases retained after annealing at 400 °C. Al–Cu<sub>2</sub>Fe phase in this cases forms at the temperatures below 400 °C and, as well as for powder milled for 60 min, disappears after heating to the temperature above 650 °C. However, it should be noted that in powders milled for 120 and 180 min no formation of Al<sub>12</sub>Fe<sub>4</sub> phase was observed. Increase in milling time from 120 to 150 min results in the phase transformation processes rate at the temperatures below 700 °C. It should be noted that phase transformations at the temperatures below 700 °C proceeds, in accordance with the previously proposed scheme [43,44], via gradually approaching of the chemical composition of phases to the average chemical composition of the alloys. In the annealing temperature range of 700–800 °C only α-Fe(Al,Cu) phase coexists with QC. Increase in the annealing temperature above 700 °C lead to a slight decrease in the amount of the QC phase in the powder. It
may be associated with a partial oxidation of aluminum by adsorbed oxygen, which leads to the withdrawal from the region of stability for QC phase.

Al–Cu–Cr equilibrium phase diagram, in contrast to Al–Cu–Fe, contains no wide area of solid solutions existence [75], which may be one of the reasons of the observed difference between Al–Cu–Fe and Al–Cu–Cr MA powders behavior at annealing. Table 1 shows that in MA Al–Cu–Cr powders no new phase formation was observed after annealing up to 400 °C. For all samples, regardless the milling time, annealing at 400 °C results in total disappearance of pure Cu phase, simultaneously, the amount of Al_{2}Cu and Cr phases increases at annealing. Because of equilibrium solubility of Al in Cr at room temperature is about 25 at.% [67], we proposed that increase in Cr phase amount is associated with dissolution of Al in Cr at heating. Increase in the annealing temperature up to 600 °C results in formation of two new phases – decagonal QC and Al_{4}Cu_{9} phase. It should be noted that some amount of residual unreacted Cr kept in the samples even after annealing at 600 °C; at that, no binary Al–Cr phases formation was observed neither at MA nor at heating. The same peculiarities were observed previously in [45, 46], where phase formation at MA and subsequent annealing was investigated for Al–Cu–Cr alloys of various compositions. Formation of binary Al–Cu phases at annealing of MA powders was observed for all studied composition, whereas binary Al–Cr phase, namely, Al-rich Al_{45}Cr_{7} compound, formation was found for one composition only [46]. It may be proposed that the formation of binary Al–Cr phases at annealing of MA powders is hampered by kinetic factors. It is known that diffusion coefficient of Cr in solid Al is by several orders lower than diffusion coefficient of Cu in solid Al [76], which may prevent Al–Cr binary phases formation at low-temperature annealing.

Increase in milling time results in the increase in decagonal QC phase and in decrease in residual Cr content in samples after annealing at 600–700 °C. Further increase in annealing temperatures up to 750–800 °C results in the disappearance of Al_{2}Cu phase, after annealing at 800 °C only decagonal QC and small amount of Al_{4}Cu_{9} phase kept in Al–Cu–Cr samples. For Al–Cu–Cr samples milled for 60 min maximum amount of QC phase was observed after annealing at 800 °C, and for samples milled for 120 and 180 min maximum amount of QC phase was observed after annealing at 750 °C. Fig. 7 shows X-ray diffractograms of nearly single phase QC samples of Al–Cu–Fe (a) and Al–Cu–Cr (b) systems obtained by MA and subsequent annealing, as it was described above. Beside of lines of QC phases, only weak peaks related to residual intermetallic phases are present in the diffractogram.

As it was described above, as-milled powders represent loosely coupled aggregates, representing the plate-shaped
particles consisting of alternating layers of thin metal foils, which are formed as a result of repeated high-energy impact exposure (Fig. 6a and b). The quasicrystalline phases, which form in the course of annealing, occur in the local regions of these particles. The optimal structure after annealing, for the purpose of filling the thermoplastic polymers, may be achieved by annealing at 700–800 °C, as it is presented in Fig. 6c and d. It consists of weakly bound agglomerates of quasicrystalline particles with the thickness of about 20–30 µm and length size of about 300–400 µm, whereas the individual particles are 1–3 µm in size. As it will be shown below, during the extrusion mixing under the action of shear, these agglomerates decompose into individual particles and are distributed over the polymer.

Further increase in the annealing temperature up to 850 °C results in the formation of faceted quasicrystalline particles 10–50 µm in size, which forms coarse agglomerates 300–500 µm in size, Fig. 6e and f. Such faceted particles can form in MA [73] or cast [77] Al–Cu–Fe alloys as a result of partial melting and subsequent crystallization of initial lamellar (layered) structure of alloy. Growth of mentioned above coarse-grained particles at the annealing of our powders was studied and discussed in detail in [78], obtained peculiarities of quasicrystals growth are in good agreement with recently published data [79,80]; here we should note that such coarse particles seem to be not suitable for using as fillers for polymer matrix.

The optimal conditions for the synthesis of QC powders were determined from the results of laser granulometric analysis of the changes in the shape and size of the particles during the mechanical alloying, the change in the tap density, and the data on the fine fraction and coarse fraction according to the sieve analysis, XRD and SEM study of annealed powders. Finely, for the Al_{65}Cu_{23}Fe_{12} composition, the mechanical alloying time should be performed for about 120 min with subsequent annealing in the argon atmosphere for about 1 h at a temperature of 700 °C. For the Al_{73}Cu_{12}Cr_{15} system, the mechanical alloying time should be of about 120 min, followed by the annealing in the argon atmosphere for about 1 h at a temperature of 750 °C. Powders treated as it was described above were used for the investigations that will be considered in the next sections.

3.3. Silanization

Organic functional silanes contain the hydrolyte functional groups, which make possible for them to be incorporated in the inorganic or mineral surfaces or to be solidified due to Si–O–Si bridges formation. The presence of the organic functional groups, connected with the alkoxyc group through the hydrocarbon chain bridge allows silanes to interact with the organic polymers and to be connected with them. Organic functional silanes are used to create the molecular bridge between the inorganic fillers, such as glass fibers and mineral fillers, and organic polymer matrix.

Arun Prakash et al. produced E-glass fiber and iron(III) oxide particles with varying size by high energy ball milling and sol-gel methods and used surface modification process on both fiber and filler by an amino functional silane 3-Aminopropyltrimethoxysilane (APTMS) to enhance better dispersion of particles and improve adhesion of fibers and fillers with epoxy matrix [81]. Khosravi et al. explored the effects of 3-glycidoxypropyltrimethoxysilane (3-GPTS) modified Na-montmorillonite (Na-M) nanoclay addition on mechanical response of unidirectional basalt fiber (UD-BF)/epoxy composite laminates under tensile, flexural and compressive loadings [82].

To improve the binding between the quasicrystalline fillers and the polymer matrix, the surface treatment was performed using the following silanes: triethoxyvinylsilane Geniosil GF 56, gamma-methacryloxypropyltrimethoxysilane Silquest A-174, and polydimethylsiloxane PDMS 200. A hydrolysable group OR in these silanes, like an alkyl group (e.g., methoxy, ethoxy) can react with various forms of hydroxyl groups present in oxidized surface of QC phases. These groups can provide the linkage with inorganic or organic substrates. Organosilanes served as bridges between inorganic QC filler and polymeric matrix and, hence, can dramatically improve adhesion between them [83].

Fig. 8 shows the FTIR spectra of the Al_{65}Cu_{23}Fe_{12} quasicrystalline powders treated with silanes obtained by the technology proposed in the present work. The absorption after 790 cm\(^{-1}\) is associated with Al–O symmetric stretching [84]. The broad absorption in the 1200–900 cm\(^{-1}\) range indicates the formation of Al–O–Si and Si–O–Si bonds [85–87]. The OH bending vibrations near 930–970 cm\(^{-1}\) can be associated to the OH bending of Al–OH bond [88–90].

The strongest line of asymmetric stretching vibration of Al–O–Si and Si–O–Si is observed in the case of Geniosil GF 56. In the case of silane Silquest A174, the peaks, which are characteristic of silane, remain, but the intensity of the main peaks decreases (Fig. 8), pointing to a weak interaction between silane and quasicrystals. In case of silane PDMS 200, the strong peaks of silane are observed, and their intensity remains almost unchanged. In the course of silanization, the formation of suspension of the quasicrystalline particles was observed, when triethoxyvinylsilane and gamma-methacryloxypropyltrimethoxysilane were used. This is also the evidence for the interaction between silanes and the quasicrystals. It should be noted that the observed spectra of icosahedral Al_{65}Cu_{23}Fe_{12} phase and decagonal Al_{73}Cu_{12}Cr_{15} phase treated by silanes are identical (Fig. 9). This confirms the fact that the bond with the silane is carried out through Al–O–Si.

Fig. 10 shows the microstructure of the processed Al_{65}Cu_{23}Fe_{12} quasicrystalline powders. For powders treated with Geniosil GF 56 or Silquest A174 silanes, where formation of Al–O–Si and Si–O–Si bonds was observed from FTIR data, SEM shows the visible layers of silane on the particle surfaces and on the intergranular boundaries (Fig. 10b–d). SEM micrograph of powders treated with PDMS 200 shows no formation of silane layer on the powder surface (Fig. 10a).

It is shown from FTIR and SEM data that the best results were obtained in the case of the treatment with Geniosil GF 56 silane. Therefore, quasicrystalline powders treated with Geniosil GF were used in further extrusion experiments. The presence of the silane layers on the grain boundaries of quasicrystalline powders allows to destroy powder agglomerates more effectively and to achieve a more homogeneous
Fig. 8 – FTIR spectra of the Al$_{65}$Cu$_{23}$Fe$_{12}$ powders milled for 120 min, annealed for 1 h at 700 °C, and treated with triethoxyvinylsilane Geniosil GF 56, gamma-methacryloxypropyltrimethoxysilane Silquest A-174, and polydimethylsiloxane PDMS 200.

Fig. 9 – FTIR spectra of the Al$_{65}$Cu$_{23}$Fe$_{12}$ and Al$_{73}$Cu$_{11}$Cr$_{16}$ powders milled for 120 min and annealed for 1 h at 700 °C (Al$_{65}$Cu$_{23}$Fe$_{12}$) and at 750 °C (Al$_{73}$Cu$_{11}$Cr$_{16}$) treated with triethoxyvinylsilane Geniosil GF 56.
distribution of filler in the polar polymer matrix during extrusion mixing.

### 3.4. Extrusion

Fig. 11 shows the process of the aggregated particles destruction in the extrusion machines (Evatane 28-05 polymer was used). During extrusion blending, large agglomerates of quasicrystals (see Fig. 6c and d) destroyed into separate particles with an average size of 3–5 μm. The destruction of large aggregated particles under a high shear stress started within 3–5 min in the course of mixing with the polymer, this process is completed by 12–15 min. SEM micrographs relating to 3–5 min of extrusion, presented in Fig. 11, allow to associate the process of coarse agglomerates crushing with the silane layers formations on the intergranular boundaries in the agglomerates. SEM micrograph of polymer/quasicrystal mixture extruded for 12 min shows homogeneous distribution of quasicrystal fillers through polymer matrix. After 12 min of extrusion quasicrystalline particles take the almost spherical shape and are covered with a layer of polymer, which is an evidence of good adhesion between polymer and quasicrystalline fillers (Fig. 11). Additionally, we tried to extrude ethylene-vinyl acetate together with no silanized Al-Cu-Fe powder. In this case relative weak destruction of aggregates was observed, no spherical particles of filler were observed in extruded composite. This experiment confirms the above mentioned conclusion about the role of silane layer in aggregates destruction process.

To confirm the spatial distribution and uniformity of the quasicrystals, a distance between particles on various blending times were calculated by using SEM images. The cumulative distribution curves were plotted. Fig. 12 shows the evolution of the distance between Al₆₅Cu₂₃Fe₁₂ quasicrystalline particles during extrusion blending with polymer
Evatane 28-05. We may see that a distance between quasicrystalline particles reduced significantly during extrusion process due to destruction of large aggregated particles under a high shear. As result, after 12 min of extrusion distribution of distance between quasicrystalline particles becomes significantly more uniform in comparison with 3–5 min of extrusion.

Fig. 13 shows the concentration dependences of the melt mass-flow rate of Evatane 28-05 and Evatane 28-40 based melts filled with quasicrystalline particles. The differences in the melt flow of the polymers filled with Al_{65}Cu_{23}Fe_{12} and Al_{23}Cu_{11}Cr_{16} powders are statistically insignificant. Increase in applied load results in the increase in melt mass-flow rate by the same way for filled and unfilled polymers. The MFR of the polymers reduced slowly with increase in filler content up to 40 wt.%, for this filler content decrease in melt flow does not exceed 10% of the melt flow for the pure polymers. Further increase in filler content results in the drastically drop in the melt flow of filled polymer.

Comparing obtained results with known data for ethylene-vinyl acetate and related polymers filled with various types of inorganic fillers, one can conclude that quasicrystalline fillers alloys keep melt flow of the composites close to those for pure polymer even at high content of fillers. For instance, addition of 40 wt.% of magnesium hydroxide [91] or magnesium sulfate [92] results in the decrease in the MFR more than two times. Addition of 30 wt.% of starch results in the decrease in MFR by 20% [93], addition of even 10 wt.% of organoclay carbonate leads to the decrease in MFR by 30% [94], addition of 10 wt.% of calcium carbonate leads to the decrease in MFR by 10% [95] in relation to pure ethylene-vinyl acetate. Filling of ethylene-vinyl acetate with 30 wt.% of carbon black results in the decrease in the MFR in three times [96], and 10 wt.% of multiple walled carbon nanotubes results in the drop of ethylene-vinyl acetate based polymer blend MFR down nearly to zero [97]. It should be noted that rheological behavior of polymer composite melts generally correlates not with the weight, but with the volume fraction of inorganic fillers [98], however, correct conversion from weight to volume fraction is hampered because the real density of inorganic fillers can be varied due to agglomeration/deagglomeration processes during composite formation. That is why the real difference in melt flow concentration dependences between quasicrystalline powders and inorganic fillers discussed above may be less than it follows from the comparison of rheological

Fig. 11 – Evolution of extruded Evatane 28-05 filled with 20 wt.% of Al_{65}Cu_{23}Fe_{12} powders milled for 120 min, annealed for 1 h at 700 °C, and treated with Geniosil GF 56 silane composition with extrusion time.

Fig. 12 – Evolution of the distance between Al_{65}Cu_{23}Fe_{12} quasicrystalline particles during extrusion blending with polymer Evatane 28-05.
Fig. 13 – Filler concentration dependences of melt mass-flow rate (MFR) at 190 °C of the extruded for 12 min ethylene-vinyl acetate based compounds containing (a) Al₆₅Cu₂₃Fe₁₂ powders milled for 120 min, annealed for 1 h at 700 °C and treated with Geniosil GF 56 silane, and (b) Al₇₃Cu₁₁Cr₁₆ powders milled for 120 min, annealed for 1 h at 750 °C and treated with Geniosil GF 56 silane. 1 – Evatane 28-05 based compounds, loading 1.2 kg; 2 – Evatane 28-05 based compounds, loading 3.8 kg; 3 – Evatane 28-05 based compounds, loading 5.0 kg; 4 – Evatane 28-40 based compounds, loading 1.2 kg; 5 – Evatane 28-40 based compounds, loading 2.16 kg.

behaviors of composites by using weight fraction of fillers. Nevertheless, we can state with assurance that our composites possess a stable rheological behavior with increase in filler content.

Concentration stability of MFR, shown in Fig. 13, may be a result of several factors. Firstly, as it is shown in Fig. 11, after extrusion quasicrystalline particles take the almost spherical shape. It is known that rheological behavior of polymer composites melts depends on the filler particles geometry. Using of spherical particles as fillers allows to keep low viscosity up to high filler content, whereas rod and plate shape of fillers particles results in drastically increase in viscosity at relative low content of fillers [99]. Secondly, the chemical nature of substance used for surface treatment of fillers can affect the MFR magnitude strongly. As it was shown in [99], surface treatment of magnesium hydroxide
with ammonium stearate results in the increase in MFR of ethylene-vinyl acetate based compounds, whereas treatment with \( \gamma \)-aminopropiltriethoxysilane results in drastically drop in MFR. We can propose that silanization used in this study has a positive effect on rheological behavior of composite melts. One more factor resulting in high MFR of quasicrystal filled polymer melts may be associated with very low surface energy of quasicrystals; for instance, the magnitude of surface energy for Al–Cu–Fe quasicrystals is of 28 kJ/mole [4]. Generally, we can conclude that the used route for quasicrystalline fillers formation and treatment allows to obtain ethylene-vinyl acetate based compounds with good workability with extrusion method.

4. Conclusions

The application of quasicrystal particles as the filler for the polymer-matrix composite materials requires the fulfillment of the following conditions: the filler particles less than 5 \( \mu \)m in size, an acceptable level of adhesion between the components providing uniform distribution of the filler, the absence of impurities and phases with high surface energy, and a low production cost. In the present work, we proposed an approach to the future preparation of composite materials based on polyethylene and polypropylene extruded using a pre-prepared ethylene-vinyl acetate-quasicrystal concentrates, which are chemically compatible with the polyolefin matrix.

Quasicrystals, which have a low surface energy, do not interact with the polymer matrix. This leads to chipping of very hard particles and a substantial increase in the wear during the operation, for example, in the case of tribological applications of these materials. As for the quasicrystals based on Al, it should be noted that Al\(_2\)O\(_3\) films on the surfaces are always involved in the problem of adhesive interaction. This problem was solved using silanes, which provide an interaction between the organic compounds and metallic materials.

As a result, the formation method of the polymer composite with optimal morphology and distribution of the quasicrystalline particles is developed. The method involves the mechanical alloying treatment and subsequent heat treatment of quasicrystalline powders in an inert atmosphere. The resulting concentrates based on highly filled ethylene-vinyl acetate and silane-treated quasicrystalline powders, make possible to produce composite materials based on polyolefins, providing a uniform distribution of the fillers and avoiding aggregation of the particles. Possible areas for application of these materials are the composite coatings on the pipes with a reduced rate of deposition of organic deposits due to a low surface energy of the reinforcing quasicrystalline phase, which is comparable to that of pure polymers.

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Conflicts of interest

The authors declare no conflicts of interest.


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