## **Reactivity of metal-containing monomers** 71.\* Synthesis of nanosized quasicrystals and related metallopolymer composites

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The methods for the preparation of quasicrystalline intermetallic compounds in the protective matrix in the systems  $Al_{65}Cu_{22}Fe_{13}$  and  $Al_{54}Cu_9Mg_{37}$  were developed. They are formed both earlier and from elements during the formation of a metallopolymer composite material. Three methods of preparation are optimal: from low-dimensional powders of quasicrystals and film-forming polymers, by the *in situ* formation of quasicrystals during the thermal decomposition of the corresponding precursors, and *via* the thermal polymerization of metal-containing monomers (components of quasicrystals) followed by the controlled pyrolysis of the metallopolymers that formed. The metallopolymer composite obtained by the incorporation of  $Al_{63}Cu_{22}Fe_{13}$  into the high-density polyethylene or polyacrylamide matrix affords up to 10 wt.% cubic phase of  $\beta$ - $Al_{50}(Cu,Fe)_{50}$ . The products of thermal decomposition of the low-molecularweight precursors are a mixture of the quasicrystalline ( $Al_{65}Cu_{22}Fe_{13}$ ) and crystalline (cubic  $\beta$ - $Al_{50}(Cu,Fe)_{50}$  and tetragonal  $\omega$ - $Al_7Cu_2Fe$ ,  $Al_2Cu$ ) phases. The thermolysis of the metallopolymer composition yields a finely dispersed powder, whose main component is an alloy  $Al_7Cu_3Mg_6$  with an admixture of the  $Al_2CuMg$  phase.

Key words: quasicrystals, metallopolymer composite, thermolysis, metallopolymers.

Quasicrystals are intermetallic compounds including metal atoms (including noble and rare-earth), whose atomic structure is characterized by 5-, 7-, and higherfold symmetry axes. They have been found for the first time in the rapidly cooled alloy  $Al_{86}Mn_{14}$  with the 5-fold symmetry axis, which was confirmed by the electron microdiffraction data.<sup>2</sup> The sharp diffraction peaks indicate the presence of the far-range order in the atomic arrangement in the structure, which is characteristic of crystals. However, the symmetry of the observed diffraction pattern contradicts the fundamental concepts of classical crystallography.<sup>3</sup> The electron patterns of the new phase contain distinct quasiperiodical reflections, the distances between which are related by the exponents  $\tau = (\sqrt{5} + 1)/2$  (the socalled golden section), and their arrangement confirms the icosahedral point symmetry group incompatible with translational symmetry.

Owing to the non-periodical packing of atoms, quasicrystals have a series of properties that are not typical of usual alloys. They have high hardness, low friction coefficient (for example, for the quasicrystalline alloy  $Al_{62}Cu_{25.5}Fe_{12.5}$  the friction coefficient is 0.12–0.14), and high resistance to corrosion and oxidation. The quasicrystals Al–Cu–Fe have a low density  $(4-5 \text{ g cm}^{-3})$ , a high hardness  $(600-1000 \text{ kg mm}^{-2})$ , and a high elasticity modulus (70-100 GPa). They are characterized by low heat conductivity and high specific resistance.<sup>4</sup> The high force of resistance of dislocation movement in quasicrystals makes them less plastic and, hence, they can be used as efficient reinforcers in alloys.<sup>5</sup> Quasicrystals are classified as particular unusual solids combining the properties of both glasses and periodically ordered crystals, whose properties are determined by the aperiodical long-range order and the local atomic structure.

More than a hundred of quasicrystal-forming systems based on various metals have been found to the present time. Substantial progress was achieved in the area of development of novel methods for their preparation, study of the structure and properties, and possible practical use.<sup>5</sup> Diverse methods are used to obtain monophase quasicrystalline alloys: vapor condensation, solidification at high pressure, devitrification of amorphous substances or decomposition of oversaturated solid solutions, and mechanical activation. "Mechanical smelting" in a ball vibrating mill is most popular.<sup>6</sup> For this purpose, components of the Al<sub>70</sub>Cu<sub>20.3</sub>Fe<sub>9.7</sub> alloy are mixed in an experi-

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mentally selected ratio, and after dividing for may hours the obtained mixture is heated to 800 °C in an argon atmosphere and stored for 10-20 min. One of the most abundant methods for the preparation of metastable and stable quasicrystalline phases of the fast quenching of liquid melts with cooling rates of  $10^4 - 10^6$  K s<sup>-1</sup>. The methods for sputtering and controlled thermolysis of the amorphous phase were developed. The methods of cold gasodynamic sputtering with surging of a supersound flow of a matrix material mixture on the metal surface,<sup>7</sup> mechanical smelting, and others are used for the production of composite materials with tribological properties. For instance, stable decagonal quasicrystals of Al<sub>70</sub>Ni<sub>15</sub>Co<sub>15</sub> were grown from the melt using the Czochralski technique.<sup>8</sup> Decagonal quasicrystals of Al72.5Ni7.5Co20 were obtained after prolong annealing (20 days at 950 °C) and standard quenching of an alloy.9 Monophase decagonal quasicrystals of Al<sub>72</sub>Ni<sub>12</sub>Co<sub>16</sub> were grown using a special levitation setup by the crystallization of overcooled melts<sup>10</sup> and laser treatment of alloys.<sup>11</sup>

Methods of solid-phase syntheses, <sup>12,13</sup> in particular, self-propagating high-temperature synthesis, <sup>14</sup> are promising from the technological point of view. The approach based on the preparation of nanometer quasicrystals by sol-gel reactions seems interesting.<sup>15</sup> Nanoparticles of the Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> quasicrystal 15±1.8 nm in size dispersed in the silica gel matrix were thus synthesized.

However, the products obtained by these methods contain a considerable amount of other compounds along with the quasicrystalline phase. Therefore, additional annealing is used for the preparation of a material with a perfect structure (for instance, for the monophase alloy Al—Cu—Fe, annealing at 730 °C for 24 h is carried out).<sup>16</sup>

Investigation of quasicrystals is an intensively developed field of science: our concepts about their preparation are extended, new types of compositions are revealed, their structure is refined, and new areas of application are searched for.

The purpose of the present work is the synthesis of metallopolymer composites from nanosized quasicrystalline intermetallic compounds and the study of diverse variants of their formation.

## **Experimental**

The following reagents were used: aluminum nitrate  $Al(NO_3)_3 \cdot 9H_2O$  (pure, Khimmed, Russia), iron nitrate nonahydrate (98%) (PANREAC, Spain), copper(11) formate (pure, Vekton, Russia); magnesium nitrate (pure), Mg(NO\_3)\_2 \cdot 6H\_2O, iron formate Fe(HCOO)\_3, acrylamide 98.5 (Acros Organics, New Jersey, US); polyethylene with high density (965 kg m<sup>-3</sup>, HDPE), melt flow index MFI = 4.5 g/(10 min) with a specific surface of 10 m<sup>2</sup> g<sup>-1</sup> and the degree of crystallinity 64%.

The starting powders  $Al_{65}Cu_{22}Fe_{13}$  (0.01 µm < d < 3 µm, distribution maximum 0.5 µm) were presented by the FGUP VIAM (Russia). The metallopolymer composite material was prepared

as follows. A mixture preliminarily homogenized in a porcelain mortar and consisting of quasicrystals (8 g) with an average particle size of 0.5  $\mu$ m and HDPE (5 g) (volume ratio 1 : 2.5) was placed in a sealed agate 0.5-L beaker. A dark homogeneous mixture was obtained after stirring for 15 min with an average rate of 500 rpm. When the monomer was used as a stabilizing agent at the stage of the preparation of the polymer composite, the Al<sub>65</sub>Cu<sub>22</sub>Fe<sub>13</sub> system (17 g) was approved, which represented solid polymerized monomer acrylamide (10 g, volume ratio 1 : 2.5). After mixing and preliminary triturating in a porcelain mortar, the mixture was placed in a sealed agate beaker of a Pulversette 6 planetary mill (Fritsch GmbH, Germany) and stirred for 30 min in the presence of polished agate balls with an average rotation rate of 550 rpm. The mixture was loaded out and analyzed.

**Quasicrystalline alloy**  $A_{17}Cu_2Fe$ . The starting mixture of powders (3.26 g of AlH<sub>3</sub>, 6.12 g of Cu(HCOO)<sub>2</sub>, and 3.99 g of Fe(HCOO)<sub>3</sub>) with a component ratio Al—Cu—Fe (at.%) of 65 : 22 : 13 was stirred according to a stepped scheme: iron and copper formates in an agate mortar were stirred for 15 min, AlH<sub>3</sub> was introduced into the prepared mixture under an inert atmosphere, and then this mixture was mechanically stirred additionally for 15 min in a closed tube. The obtained mixture was subjected to thermolysis at 500, 600, and 700 °C for 1 h.

**Quasicrystalline alloy**  $Al_7Cu_3Mg_6$ . The starting mixture of powders  $AlH_3$ —Cu(HCOO)<sub>2</sub>—Mg (finely dispersed powder) was stirred at a ratio of components Al—Cu—Mg of 54.2 : 9.2 : 36.6 (at.%) or 50 : 20 : 30 (wt.%). All procedures were carried out in an inert atmosphere. The obtained mixture was subjected to thermolysis at 500 and 650 °C under the isothermal conditions *in vacuo* for 1 h. A dark gray finely dispersed powder was obtained.

**Quasicrystal**  $Al_{68}Cu_{21}Fe_{11}$ . A mixture of  $Al(NO_3)_3 \cdot 9H_2O$ (10 g), 2.13 r Cu(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  3H<sub>2</sub>O (2.13 g), and Fe(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  9H<sub>2</sub>O (2.1 g) was triturated with acrylamide (13 g). The reaction accompanied by the evolution of water of crystallization and formation of a light green paste-like substance. After the end of the reaction, the product was washed with benzene and ether to remove an excess of acrylamide and water and the resulting mixture of acrylamide complexes was dried *in vacuo*. At the initiation temperature 50 °C *in vacuo*, the monomeric mixture underwent frontal polymerization in the condensed phase to form metallopolymer as a finely dispersed dark brown powder, which was subjected to thermolysis *in vacuo* at 500, 600, and 700 °C.

Quasicrystalline sample Al54Cu9Mg37 was obtained by the combination of polymerization of the acrylamide complex of Mg<sup>II</sup> nitrate with the assembling method. The complex  $Mg(NO_3)_2(CH_2=CHCONH_2)_4 \cdot 2H_2O$  was synthesized by the substitution of water of crystallization in crystalline hydrate  $Mg(NO_3)_2 \cdot 6H_2O$  for molecules of the acrylamide ligand. Found (wt.%): C, 31.71; H, 5.46; N, 18.09; Mg, 5.8. Calculated (%): C, 30.75; H, 5.16; N, 17.93; Mg, 5.19. The acrylamide complex of Mg<sup>II</sup> nitrate was mixed in an agate mortar with other metal-containing components of the synthesized alloy: AlH<sub>3</sub> and Cu(HCOO)<sub>2</sub> with the ratio of components Al : Cu : Mg equal to 54.2 : 9.2 : 36.6 (at.%) or 50 : 20 : 30 (wt.%). The obtained mixture was subjected to thermolysis at 500 °C under the isothermal conditions in vacuo for 2 h to form the product as a homogeneous dark gray finely dispersed powder. The composition and morphology of the obtained alloys were studied by chemical analysis and scanning electron microscopy on a Tescan Vega TS5130MM scanning electron microscope with an INCA Energy 350 energy-dispersive X-ray spectral analyzer. X-ray phase analysis was carried out on a DRON-UM2 diffractometer in the reflection mode of detection of diffraction patterns using an X-ray tube with a BSV-27 copper anode (voltage U = 30 kV, current I = 25 mA) and a 1,3BSV-29 chromium anode (U = 35 kV, I = 35 mA) and on a D8 Advance X-ray setup (Bruker AXS) in the copper radiation detection mode (U = 40 kV, I = 40 mA). The qualitative X-ray phase analysis of the obtained diffraction patterns was performed using the DIFFRACplus BASIC EVA 10.0 software. Quantitative phase analysis was carried out by the Rietveld method using the Topaz 3.0 program. IR spectra were recorded on a Specord M-80 instrument (Carl Zeiss Jena, Germany).

## **Results and Discussion**

Three different methods were developed for the synthesis of metallopolymer composites. The methods are based on the formation of a polymer stabilizing matrix around quasicrystals or their precursors followed by the controlled thermolysis of the obtained materials leading to the formation of the quasicrystal phase stabilized by the polymer shell. The variants of the synthesis used can be classified as environmentally appropriate "dry" methods, because solvents are used at none of the stages of this multistage process. These approaches can be described as follows.

(1) Assembling method: the *in situ* formation of quasicrystals during the thermal decomposition of the corresponding precursors taken in stoichiometric amounts. This method often results in the formation of nanosized particles, which are stabilized by the stabilizing polymer matrix appeared due to polymerization transformations of the ligand fragments of the precursors.

(2) Introduction of low-dimensional powders of quasicrystals in a composition with the matrix of film-forming polymers (both from the ingredients and by the combined dispersion of powders of quasicrystals and polymers on high-performance planetary matrices).

(3) Thermal polymerization of metal-containing monomers (components of quasicrystals) followed by the controlled pyrolysis of the metallopolymers than formed. In this case, nanocrystals stabilized by the polymer shell are always formed. The properties of such multicomponent systems are controlled by the synthesis and thermolysis conditions. The polymer matrix formed in the synthesis prevents the formation of large particles, and the stabilizing shell is the product of thermal destruction of the polymer fragments.

Solid-phase thermolysis (both *in vacuo* and in a medium of gaseous transformation products: self-generated atmosphere)<sup>16</sup> possesses the most potent possibilities for the formation of metallopolymer composites. The temperature of thermal transformation can be maintained constant (isothermal conditions) or subjected to programmable changes (non-isothermal conditions, thermal analysis mode). The rate of the processes is monitored by both the amount of evolved gaseous products and the change in the weight of the initial or accumulated product using the spectral or other characteristics of the reacting systems.

Assembling of quasicrystals from metal-containing precursors. The thermal transformations of carboxylates, in particular, metal formates, are accompanied by the formation of highly dispersed (for example, the average Cu<sup>0</sup> particle size is 60 nm) metals stabilized by the hydrocarbon matrix.<sup>17,18</sup>

Quasicrystalline alloys  $Al_{65}Cu_{22}Fe_{13}$  and  $Al_7Cu_2Fe$  were obtained from the low-molecular-weight metal-containing precursors: AlH<sub>3</sub> and iron Fe(HCOO)<sub>3</sub> and copper Cu(HCOO)<sub>2</sub> formates. The thermolysis results in a finely dispersed powdered substance. According to the X-ray phase analysis, at 500 °C the thermolysis product contains Al<sub>65</sub>Cu<sub>22</sub>Fe<sub>13</sub> and crystalline phases of cubic  $\beta$ -Al<sub>50</sub>(Cu,Fe)<sub>50</sub> and tetragonal  $\omega$ -Al<sub>7</sub>Cu<sub>2</sub>Fe (Fig. 1) alloys. An increase in the thermolysis temperature to 600 and 700 °C decreases the content of  $\omega$ -Al<sub>7</sub>Cu<sub>2</sub>Fe and the growth of the cubic phase  $\beta$ -Al<sub>50</sub>(Cu,Fe)<sub>50</sub>. At 700 °C the content of the quasicrystalline phase in the thermolysis product reaches 30 wt.%.

Particles of the thermolysis products are densely packed agglomerates consisting of cut crystals with an average diameter of  $10 \,\mu\text{m}$  and particular pentagonal prisms formed at different angles (Fig. 2).

Quasicrystals Al-Cu-Mg. Magnesium-containing quasicrystalline systems are interesting from the viewpoint of preparation of materials that efficiently absorb dihydrogen.<sup>19</sup> For the preparation of the quasicrystalline alloy Al-Cu-Mg, we used the solid-phase synthesis from the metal-containing precursors. The X-ray phase analysis data indicate that the main component of the product is the alloy Al<sub>7</sub>Cu<sub>3</sub>Mg<sub>6</sub> and also admixtures of the Al<sub>2</sub>CuMg phase (Fig. 3, Table 1). An increase in the thermolysis temperature to 650 °C results in the disappearance of the Al<sub>7</sub>Cu<sub>3</sub>Mg<sub>6</sub> phase and the appearance of phases of metallic aluminum, magnesium, and magnesium oxide (Fig. 4).

Introduction and stabilization of polymetallic quasicrystals  $Al_{65}Cu_{22}Fe_{13}$  in polymer matrices. The polymer shell separates metallic particles from each other and from the external medium and thus performs functions of the stabilizing agents and improves the properties of the metallopolymer composite. The methods of coacervation, precipitation with a non-solvent or evaporation of the solvent, physical adsorption, extrusion (the particles of covered with the shell upon forcing of the quasicrystalline intermediate compound through the film-forming material), sputtering in the fluidized bed, vapor condensation, polymerization on the particle surface, and others. The results of studies of the starting powder by the X-ray phase method are presented in Fig. 5 and in Table 2.



**Fig. 1.** X-ray diffraction pattern of the products of thermal transformations of a mixture of the metal-containing precursors  $AlH_3$ -Cu(HCOO)<sub>2</sub>-Fe(HCOO)<sub>3</sub> at 500 (*a*) and 700 °C (*b*).

The preliminary studies on the formation of the protective shell on quasicrystals from polystyrene (PS) solutions with various concentrations in aromatic solvents showed that this way is not promising. This is because of the surface properties of the polymer that are not optimal for this application, namely, poor wettability at the interface, a low energy of the quasicrystal—PS interaction, *etc.* This results in the low stabilizing effect in this case. For instance, for the composite based on the quasicrystal Al<sub>65</sub>Cu<sub>22</sub>Fe<sub>13</sub> with an average particle size of 0.5  $\mu$ m and PS, the efficiency of stabilization of the polymetallic particles turned out fairly low.

The methods of mechanochemical mixing of quasicrystals with the polymer matrix or its precursor are more attractive from the technological point of view. Depending on the character of motion of the ball loading (polished agate balls), there are three modes of dividing of the polymer matrix: sliding (abrasion), rolling (impact), and









**Fig. 2.** Images of particles of the products of thermolysis at 500 °C of a mixture of the metal-containing precursors  $AlH_3 - Cu(HCOO)_2 - Fe(HCOO)_3$ : general view (*a*) and pentagonal crystals (*b*, *c*).



Fig. 3. X-ray diffraction pattern of the product of thermolysis at 500 °C of a mixture of the metal-containing precursors  $AlH_3-Cu(HCOO)_2-Mg$ .



Fig. 4. X-ray diffraction pattern of the product of thermolysis at 650 °C of a mixture of the metal-containing precursors  $AlH_3$ -Cu(HCOO)<sub>2</sub>-Mg.

2θ/deg	<i>d</i> /nm	$I_{\rm rel}(\%)$	Phase	2θ/deg	<i>d</i> /nm	$I_{\rm rel}(\%)$	Phase
15.20	5.829	5	_	49.40	1.845	5	Al <sub>7</sub> Cu <sub>3</sub> Mg <sub>6</sub>
19.10	4.647	20	Al <sub>2</sub> CuMg	51.30	1.781	15	Al <sub>2</sub> CuMg
25.00	3.562	16	Al <sub>2</sub> CuMg	53.75	1.705	11	Al <sub>2</sub> CuMg
27.20	3.278	26	Al <sub>2</sub> CuMg	55.30	1.661	5	
31.60	2.831	7	Al <sub>2</sub> CuMg	62.40	1.488	14	Al <sub>2</sub> CuMg
35.00	2.564	37	Al <sub>2</sub> CuMg	64.40	1.447	26	$Al_7Cu_3Mg_6$
36.55	2.458	45	$Al_7Cu_3Mg_6$	66.85	1.399	6	
38.05	2.365	100	$Al_7Cu_3Mg_6$	68.85	1.364	5	$Al_7Cu_3Mg_6$
38.75	2.324	90	Al <sub>2</sub> CuMg	70.65	1.333	7	Al <sub>7</sub> Cu <sub>3</sub> Mg <sub>6</sub>
40.85	2.209	16	Al <sub>2</sub> CuMg	72.95	1.297	4	$Al_7Cu_3Mg_6$
42.80	2.113	47	Al <sub>2</sub> CuMg	75.30	1.262	5	
44.25	2.047	43		77.45	1.232	23	_
44.85	2.021	49	Al <sub>7</sub> Cu <sub>3</sub> Mg <sub>6</sub>	78.90	1.213	6	Al <sub>7</sub> Cu <sub>3</sub> Mg <sub>6</sub>
45.40	1.998	34	Al <sub>2</sub> CuMg	81.15	1.185	6	Al <sub>2</sub> CuMg
46.65	1.947	13	Al <sub>2</sub> CuMg				2 0
				-			

**Table 1.** X-ray phase data for the product of thermolysis at 500 °C of a mixture of the metalcontaining precursors  $AlH_3$ -Cu(HCOO)<sub>2</sub>-Mg

vortical (predominantly impact). Impact and shift loads result in dispersion and efficient rolling of quasicrystals into the polymer matrix of HDPE. The combined milling also affects the structure of the polymer matrix. For instance, HDPE undergoes partial destruction and crosslinking, insignificant amorphization of the crystalline phase occurs, and the crystalline phase of extended PE appears (d = 3.55 and 2.55 Å) (Fig. 6, Table 3). It should be mentioned that, according to the X-ray phase analysis data, the introduction of  $Al_{63}Cu_{22}Fe_{13}$  into the HDPE matrix results in the appearance of up to 10 wt.% of the cubic phase  $\beta$ -Al<sub>50</sub>(Cu,Fe)<sub>50</sub>. The necessary ratio between the phases of the quasicrystal and polymer matrix is monitored both at the stage of charge preparation and during the subsequent controlled thermolysis of the obtained product.

Variants of the preparation of metallopolymer composites are especially interesting in the cases where the



Fig. 5. X-ray diffraction pattern of the quasicrystalline alloy  $Al_{65}Cu_{22}Fe_{13}.$ 

polymer matrix is formed from the adsorbed monomer directly on the quasicrystal surface.<sup>20</sup> In this case, the degree of conversion of the monomer into polymer depends on the dispersion intensity. Freshly formed juvenile metal surface serve as initiators of polymerization: an electron is transferred by the surface metal atoms to the monomer to form initiating particles of the radical ion type. The solid monomer acrylamide and quasicrystal Al<sub>65</sub>Cu<sub>22</sub>Fe<sub>13</sub> were approved as media at the stage of formation of the polymer matrix for the preparation of the polymer matrix. Unreacted acrylamide in the obtained composite was washed off with benzene in which the polymer product is insoluble. According to the data of IR spectroscopy, the spectrum of the metallopolymer composite retains absorption bands in the region of stretching ( $v_s(NH)$ ) and  $v_{as}(NH)$ ) and out-of-plane bending ( $\delta(NH)$ ) NH vibrations at 3198, 3350, and 1613  $cm^{-1}$ , as well as bending and stretching vibrations of  $CH_2$  and CH (1428 and 1280 cm<sup>-1</sup>). The absence of the  $\delta$ (=CH) absorption bands at 962 cm<sup>-1</sup> confirms the conversion of the C=C bonds during polymerization. The optimization of the concentration ratios quasicrystal: monomer and the conditions of the conversion of the latter to polymer require further studies, as well as the molecular weight characteristics of the polymers formed.

Table 2. X-ray phase data for the quasicrystalline alloy  $Al_{65}Cu_{22}Fe_{13}$ 

2θ/deg	<i>d</i> /nm	$I_{\rm rel}(\%)$	20/deg	d/nm	$I_{\rm rel}(\%)$
23.75	3.746	13	45.25	2.004	100
26.15	3.408	14	64.10	1.453	12
27.60	3.232	8	65.85	1.418	7
42.90	2.108	95	76.90	1.240	27



**Fig. 6.** X-ray diffraction patterns of the quasicrystalline alloy Al-Cu-Fe in the composite on the polyethylene matrix (*a*) and the initial polyethylene (*b*).

**Preparation of quasicrystalline alloys by the polymerization of metal-containing monomers.** Metal complexes, whose ligand environment contains a substituents with the multiple bond capable of polymerization transforming are named metal-containing monomers.<sup>21</sup> These precursors are rather frequently used for the synthesis of polymetallic alloys (for instance, YCuBa— or BiCaSrPbCu— HTSC ceramic<sup>22</sup>). It could be assumed that they would be convenient precursors for the polymer-assisted synthesis of quasicrystals: assembling of quasicrystals from elements with the simultaneous formation of the stabilizing polymer shell.

Quasicrystalline alloy  $Al_{68}Cu_{21}Fe_{11}$ . The typical experiment included the *in situ* solid-phase synthesis of the acrylamide complexes Al—Cu—Fe at the ratio of components 65 : 22 : 13 (at.%) or 45.23 : 36.05 : 18.72 (wt.%). The composition and morphology of the thermolyzed products were studied by scanning electron microscopy with an energy-dispersive X-ray spectral analyzer. The scanning electron spectroscopic data indicate that the thermal

**Table 3.** X-ray phase data for the quasicrystalline alloy Al—Cu—Fe in the composite on the polyethylene matrix

2θ/deg	<i>d</i> /nm	$I_{\rm rel}(\%)$	Phase
29.15	4.552	13	PE
31.90	4.168	27	PE
35.55	3.752	13	PE
41.45	3.237	10	$Al_{13}Cu_4Fe_3$
55.50	2.460	9	$Al_{13}Cu_4Fe_3$
65.75	2.110	91	$Al_{13}Cu_4Fe_3$
69.90	2.007	100	$Al_{13}Cu_4Fe_3$
83.30	1.724	6	$Al_{13}Cu_4Fe_3$
104.00	1.454	18	$Al_{13}Cu_4Fe_3$
108.00	1.416	9	$Al_{13}Cu_4Fe_3$

transformations of the acrylamide complexes with a specified ratio of the components result in the formation of nanosized particles of the alloys uniformly distributed in the polymer matrix. The elongation of the annealing duration (to 5 h) leads to a more structured nanocomposite. According to the energy-dispersive X-ray spectral analysis data, the quasicrystalline phase has the composition  $Al_{68}Cu_{21}Fe_{11}$ .

Synthesis of quasicrystalline  $Al_{54}Cu_9Mg_{37}$  was carried out in several stages. At the first of them, the acrylamide complex of magnesium nitrate Mg(NO<sub>3</sub>)<sub>2</sub>-(CH<sub>2</sub>=CHCONH<sub>2</sub>)<sub>4</sub>·2H<sub>2</sub>O was obtained by the substitution of water of crystallization in the crystalline hydrate Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for acrylamide molecules. At the second stage, the complex was mixed with the calculated amount of other metal-containing components of the alloy (AlH<sub>3</sub> or Cu(HCOO)<sub>2</sub>) followed by thermolysis at 500 °C. The composition of the obtained alloy was examined by X-ray phase analysis.

Thus, in the present work, we approved for the first time different variants of the preparation of the metalcontaining composites using the low-dimensional powders of quasicrystals and film-forming polymers: adsorption of polymers from their solutions and combined dispersion of powders of quasicrystals and polymers, as well as their monomeric precursors. It was shown that particles of quasicrystals Al<sub>65</sub>Cu<sub>22</sub>Fe<sub>13</sub> and Al<sub>54</sub>Cu<sub>9</sub>Mg<sub>37</sub> can be stabilized by the polymer matrix during polymer composite formation. The quasicrystals are stabilized in all cases studied; however, the most promising direction of preparation of materials of this type seems to be the polymerization of monomers and formation of polymer composites from the calculated amounts of the ingredients of quasicrystals capable of further polymerizing. This method requires no use of beforehand prepared quasicrystals, whose synthesis is a labor-consuming process.

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