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THE EFFECT OF TRANSITION METALS ON QUASICRYSTALLINE PHASE FORMATION IN MECHANICALLY ALLOYED $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ POWDER

The effect of replacing iron with transition metals ($M = \text{Mn}, \text{Cr}, \text{Co}$) on the microstructure of mechanically alloyed $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ quasicrystalline powder was examined by X-ray diffraction and transmission electron microscopy methods. Powders of various compositions were milled in a high-energy planetary ball mill up to 30 hours at a rotation speed 350 rpm using WC milling media. The amount of the fourth additions was constant in all powders and Fe atoms were replaced with Mn, Cr or Co in a 1:1 ratio, while the content of the Al and Cu was selected in two ways: they remained the same as in the initial ternary $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy or changed to obtain e/a ratio = 1.75 (optimal for icosahedral quasicrystalline phase). Quasicrystalline phase formed in the quaternary $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{7.5}\text{M}_{7.5}$ powders, whereas in the second group of compositions only crystalline phases were identified.

Keywords: mechanical alloying, quasicrystal, Al-Cu-Fe, transition metals

1. Introduction

Different structure of quasicrystals compared to typical crystalline materials results in their unique chemical and physical properties such as: high hardness, low surface energy, good wear resistance, low friction coefficient, low coefficient of electrical and thermal conductivity. These properties make them materials promising for potential industrial applications as antiadhesive and protective coatings, reinforcement in metal matrix composites prepared by powder metallurgy technologies, or polishing material for soft metals [1-4].

One of the most attractive and most frequently investigated quasicrystal for these applications is Al-Cu-Fe ternary system due to low cost, easily accessible, recyclable and non-toxic components [5]. The phase diagram of this system is characterized by many intermetallic phases, which are close in composition to quasicrystalline phase [6]. The addition of a fourth alloying component can be an effective way of forming a single-phase quasicrystalline alloy more stable at elevated temperatures.

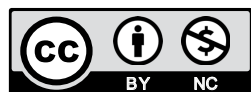
Shortly after the discovery of stable quasicrystals in the Al-Cu-Fe system [7] four-component $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{12}\text{M}_3$ alloys were tested, in which part of iron atoms were replaced with other elements: Ti, V, Cr, Mn, Co, Ni, Si, Ge, Zr and Nb [8]. It was found that alloys containing Mn, Co and Si were characterized by a single-phase icosahedral structure after annealing. Research

carried out in the next years showed that the effect of addition of Si is dependent on both: the amount of added element and the methods of preparation of the alloy [9-12]. Additions of transition metals like chromium, cobalt or manganese have good influence on formation of quasicrystalline phase, although in some cases its structure changes from icosahedral into decagonal quasicrystalline phase.

The Al-Cu-Fe alloys with the addition of cobalt and chromium may contain two types of quasicrystals: a phase with icosahedral and decagonal structure [13,14]. In the Al-Cu-Fe-Cr alloy containing 5 at.% of Cr a multiphase structure consisting of a mixture of quasicrystals and approximants was found, whose morphology and volume fraction depend on the content of other components and the cooling rate [13]. In the slowly cooled $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_8\text{Cr}_7$ alloy, a single-phase decagonal structure was obtained, which was unstable after milling in a high-energy ball mill and transformed into a fine-crystalline phase with regular structure due to defects generated during milling [14]. In rapidly cooled alloys with the addition of cobalt, with increasing Co content the icosahedral phase in the $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy disappears in favour of the decagonal phase [15]. Research by Sato et al. [16] showed that alloys with the addition of manganese $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15-x}\text{Mn}_x$ (for x in the range 0÷15, in at.%) contain quasicrystalline phases with icosahedral and decagonal structure as well as crystalline approximants of Al_3Mn and $\text{Al}_{13}\text{Fe}_4$,

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which form the modulated structure. In turn, Beauchesne et al. [17] received in $\text{Al}_{66.1}\text{Cu}_{21.3}\text{Mn}_{8.3}\text{Fe}_{4.3}$ rapidly cooled ribbons a single-phase icosahedral structure, which after heating gradually passed into a decagonal phase.

In the present study the effect of addition of transition elements (Cr, Mn, Co) on the quasicrystalline phase formation in the Al-Cu-Fe system prepared by mechanical alloying method was investigated. Mechanical alloying is one-step procedure to obtain quasicrystalline phase in the form of powder suitable for the applications. It could also be assumed that this alloy production method promotes the formation of a quasicrystalline phase and extends the range of its composition. The amount of the fourth element added into base $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy was selected in two ways: by partial replacing Fe atoms by one of transition metals keeping Al and Cu on the same level as in ternary composition or by calculation of electron/atom ratio to obtain optimal value for quasicrystalline phase formation.

2. Experimental

Elemental blends of aluminium, copper and transition metals (Fe, Mn, Cr, Co) powders (of purity at least 99.2% and the particle size in the range of 7-15 μm) were mechanically alloyed in planetary high-energy ball mill Fritsch P5. Mixture of pure elements powder of selected composition (Table 1) was loaded into tungsten carbide (WC) vials together with WC balls under argon atmosphere in glove box. The ball to powder ratio was 10:1. As a process control agent hexane was used. Hexane provides narrow distribution of particles size, prevents powder from oxidation during milling procedure and eliminates overheat of powder during milling. Milling was performed at a rotation speed 350 rpm (revolution per minute) up to 30 hours with intervals for cool down of milled powders. The conditions of the milling process were chosen based on our experience in preparation the ternary Al-Cu-Fe quasicrystalline powders [18,19].

TABLE 1

Nominal composition (in at.%) of the investigated powders

Alloy designation	Al	Cu	Fe	Mn	Cr	Co	Calculated e/a ratio
Mn1	65	20	7.5	7.5			1.676
Mn2	68.5	16.5	7.5	7.5			1.746
Cr1	65	20	7.5		7.5		1.601
Cr2	72	13	7.5		7.5		1.741
Co1	65	20	7.5			7.5	1.820
Co2	61	24	7.5			7.5	1.742

Phase composition of the milled powders was examined by X-ray diffraction (XRD) using D2 Phaser Bruker diffractometer with $\text{Cu K}\alpha$ filtered radiation ($\lambda = 0.15406 \text{ nm}$). For X-ray examination, samples of powders were compacted in the mold to cylindrical form. Microstructure of the powders was investigated by transmission electron microscope (TEM) using FEI Tecnai G^2 microscope at 200 kV equipped with high-angle

annular dark field scanning transmission electron microscopy detector (HAADF-STEM) combined with energy dispersive X-ray (EDX) EDAX microanalysis. The TEM observations were made for the transparent region near the thin edge of the powder particles, which were placed on a carbon film supported by a nickel grid.

3. Results and discussion

The base composition for preparation quaternary alloys was $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ icosahedral quasicrystalline phase. An important parameter for the formation of quasicrystalline phases in alloys is a ratio of the number of valence electrons to number of atoms in unit cell (e/a ratio). Tsai [20] shows that quasicrystalline phases exist in two narrow e/a ratios: 1.7-1.8 and at 2.1. Quasicrystals with e/a ratio 1.7-1.8 are built by Mackay icosahedron type clusters, while quasicrystals with e/a ratio 2.1 are built by Bergman triacontahedron type clusters. For Al-Cu-Fe quasicrystalline phase ideal e/a ratio is 1.75 [20]. Mizutani and Sato [21,22] suggest that transition metals have different e/a ratio when dissolved in polyvalent metals and new way to calculate optimal composition to obtain stable quasicrystalline phase was proposed. Their calculations have good correlation to experimental results and e/a ratio allow to determine new composition. Electron per atom ratio e/a for Mn, Cr, Co elements were 1.05, 0.92 and 1.11, respectively, when dissolved in polyvalent metals like Mg, Al, Zn, Cd and In [21].

In the quaternary compositions of investigated powders the amount of added transitions metals were constant and Fe atoms were replaced with Mn, Cr or Co in a 1:1 ratio, while the content of the remaining Al and Cu elements were selected according to two assumptions: 1) leaving the content identical as in the initial ternary $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy, what resulted in the decrease of e/a in the case of Mn and Cr additions and an increase in powder containing Co, 2) compositions were designed by calculation of e/a ratio to obtain close to ideal value 1.75 according to Tsai experiment [20]. Nominal compositions of the prepared powder were presented in Table 1.

For all prepared compositions the X-ray diffraction investigations were performed. Measurements were made after the designated milling time to determine the sequence of the phase formation. Figure 1 shows the XRD profiles of the $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{7.5}\text{Mn}_{7.5}$ (Mn1) and $\text{Al}_{68.5}\text{Cu}_{16.5}\text{Fe}_{7.5}\text{Mn}_{7.5}$ (Mn2) powders after different milling time. For both compositions the reflections of constituent elements are identified after 3 hours of milling, however the broadening and reduction of their intensity could be noticed. Simultaneously, the reflections corresponding to the $\lambda\text{-Al}_{13}\text{Fe}_4$ phase appear and their intensity increase with milling time at the expense of initial elements. After 10 hour of milling, in the both powders, the copper rich $\gamma\text{-Cu}_9\text{Al}_4$ phase coexists with the $\lambda\text{-Al}_{13}\text{Fe}_4$ phase. After 20 hour of milling, the quasicrystalline i-phase was predominant in the Mn1 powder and prolonged milling time led to small peaks shifts, but no other phases are observed. The mixture of $\gamma\text{-Cu}_9\text{Al}_4$ and $\omega\text{-Al}_7\text{Cu}_2\text{Fe}$

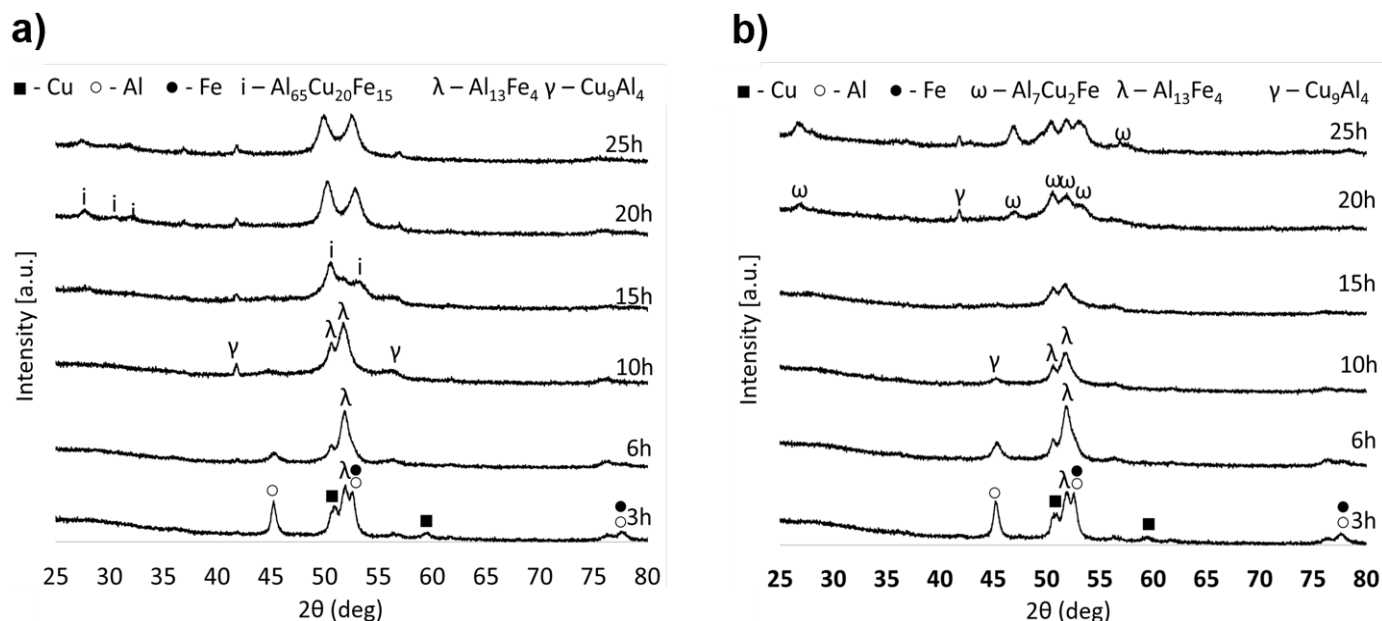


Fig. 1. XRD patterns of the powder (a) Mn1 and (b) Mn2, after milling for 3, 6, 10, 15, 20 and 25 hours

phases was visible in Mn2. The broadening of the peaks increase with the milling time, which indicated the grain refinement and lattice strain.

The presence of the quasicrystalline *i*-phase in the Mn1 powder milled for 25 hours was confirmed by TEM observations. This phase in the form of fine crystallites about 10-20 nm in size is visible in the bright- and dark-field images in Fig. 2a and 2b, respectively. The selected area electron diffraction pattern (SADP) obtained from the area shown in Fig. 2a, b contains sharp Debye-Scherrer rings (Fig. 2c). The measured *d*-spacing values are indexed as the icosahedral *i*-phase, using the scheme of Cahn [23].

The sequence of phase formation in the initial milling stages of powders with the addition of Cr and Co were similar to those for powders with the addition of Mn. Therefore, Fig. 3 and 4 show only the selected XRD patterns obtained after 3, 10 and 25 hours of milling. After 10 hours of milling, in both

powders $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{7.5}\text{Cr}_{7.5}$ (Cr1) and $\text{Al}_{72}\text{Cu}_{13}\text{Fe}_{7.5}\text{Cr}_{7.5}$ (Cr2) (Fig. 3) three phases: $\theta\text{-Al}_2\text{Cu}$, $\gamma\text{-Cu}_9\text{Al}_4$ and Fe_3Al were identified, contrary to the single icosahedral phase, which formed in ternary $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ composition [18, 19]. An increase milling time to 25 hours led to the formation of quasicrystalline *i*-phase in the Cr1 powder, which was accompanied by small amounts of $\gamma\text{-Cu}_9\text{Al}_4$ phase, while in the Cr2 powder only crystalline phases: $\gamma\text{-Cu}_9\text{Al}_4$, $\omega\text{-Al}_7\text{Cu}_2\text{Fe}$ and $\theta\text{-Al}_2\text{Cu}$ are visible.

The XRD patterns (Fig. 4) for $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{7.5}\text{Co}_{7.5}$ (Co1) and $\text{Al}_{61}\text{Cu}_{20}\text{Fe}_{7.5}\text{Cr}_{7.5}$ (Co2) powders differ significantly. In Co1 powder, the weak reflections of the *i*-phase coexisting with the AlFe_2Co -phase were observed after 10 hours of milling (Fig. 4a). The amount of AlFe_2Co -phase reduces after 25 hours of milling and the *i*-phase becomes dominant. In the case of Co2 powder (Fig. 4b) the single AlFe_2Co -phase, which forms after 10 hours of milling persists with prolonged milling time.

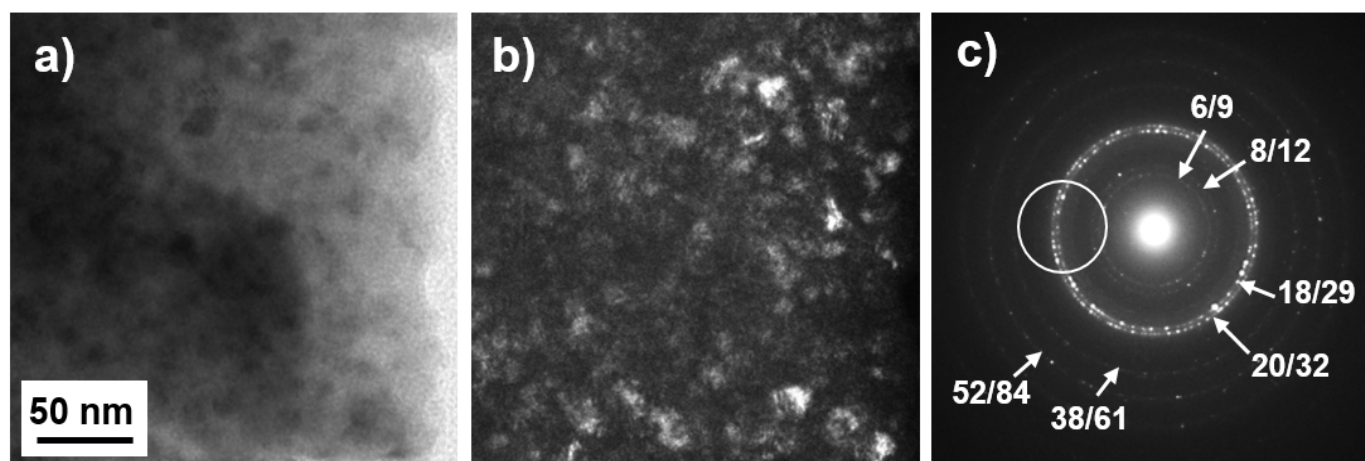


Fig. 2. TEM images of the Mn1 powder milled for 25 hours, (a) bright-field, (b) dark-field and (c) corresponding SADP with indexing of the *i*-phase (the position of the objective aperture for obtaining dark-field is marked)

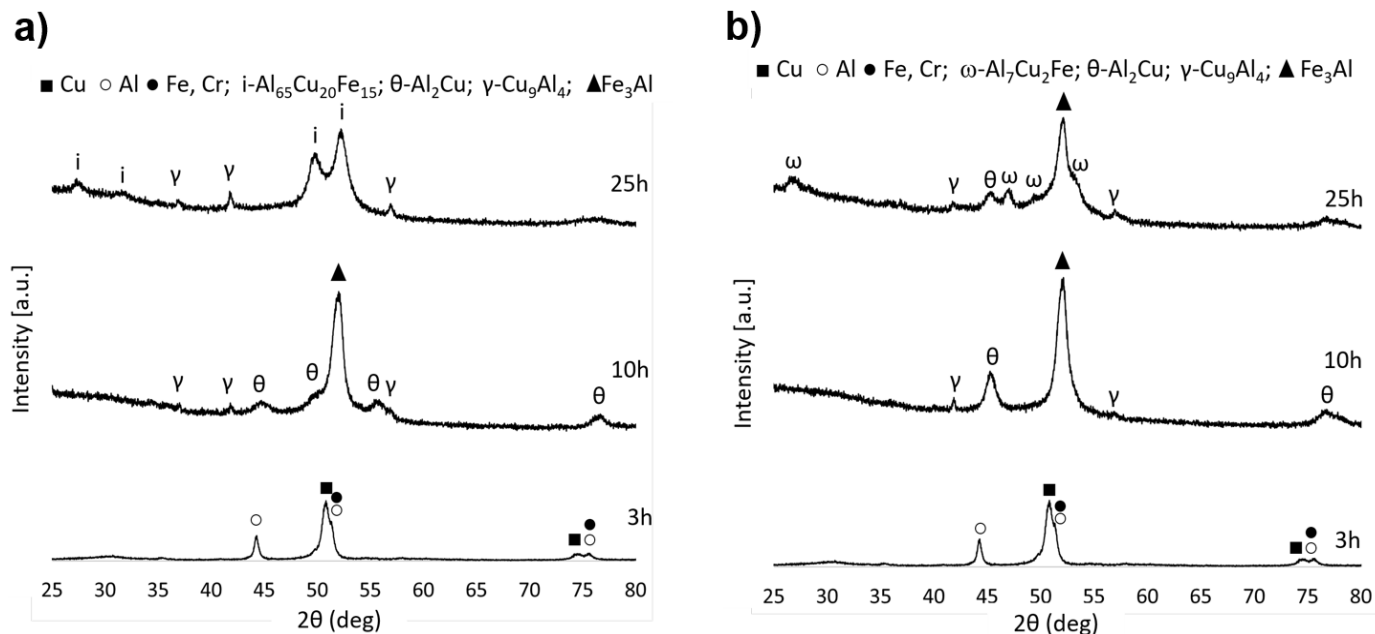


Fig. 3. XRD patterns of the powder (a) Cr1 and (b) Cr2, after milling for 3, 10 and 25 hours

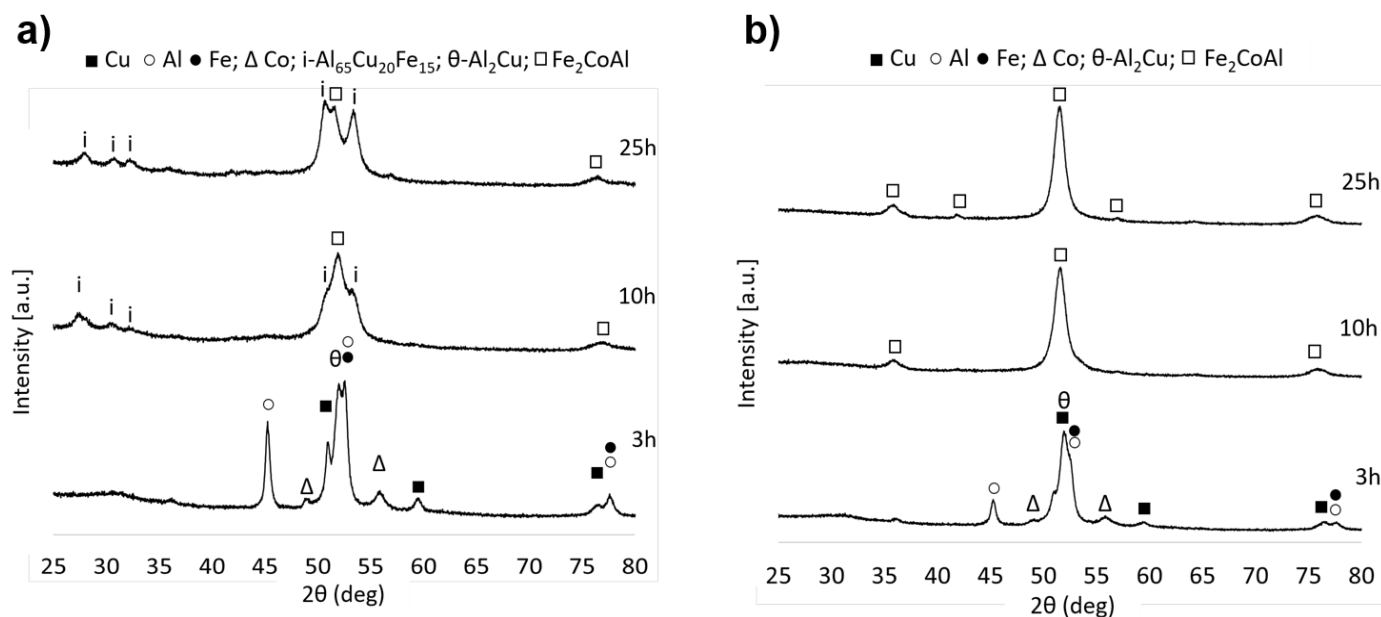


Fig. 4. XRD patterns of the powder (a) Co1 and (b) Co2, after milling for 3, 10 and 25 hours

Based on the conducted research, it can be stated that the formation of the quasicrystalline phase in the investigated mechanically alloyed powders is possible for compositions, where Fe atoms are replaced by Mn, Cr and Co without changing the content of Al and Cu. The icosahedral phase is formed in these powders after 25 hours of milling, i.e. after longer time than in the ternary $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ powder, in which a single-phase quasicrystal was observed after 10 hours [18,19]. It was found also that the cell parameters of i-phase in quaternary powders extended in comparison to the theoretical values. In the case of powders with compositions designed based on the calculation e/a , quasicrystalline phase was not found, even after the longest milling time. Instead, a mixture of crystalline phases was formed.

4. Conclusions

1. The nano-crystallites (10-20 nm) of icosahedral i-phase formed in $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{7.5}\text{M}_{7.5}$ ($M = \text{Mn}, \text{Cr}, \text{Co}$) powders mechanically alloyed in high-energy planetary ball mill. Quasicrystalline phase coexists with small amount of crystalline phases for all compositions. The milling time needed to obtain the quasicrystalline structure in quaternary powders increase up to 25 hours, compared to 10 hours for ternary $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$.
2. In the powders with compositions designed according to the formula $e/a = 1.75$, the quasicrystalline phase did not form even after 25 hours of milling. Mixture of phases: γ - Cu_9Al_4

and ω -Al₇Cu₂Fe or γ -Cu₉Al₄, ω -Al₇Cu₂Fe and θ -Al₂Cu formed in the powders with Mn and Cr additions, respectively. In the powder containing Co single phase AlFe₂Co structure was observed.

Acknowledgments

Financial support from the Polish National Science Centre NCN, research projects no 2015/19/N/ST8/01036 is gratefully acknowledged. Samples were examined in the Accredited Testing Laboratories at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in Cracow.

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