



# Synthesis and stability of quasicrystalline phase in Al-Cu-Fe-Si mechanically alloyed powders

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## ABSTRACT

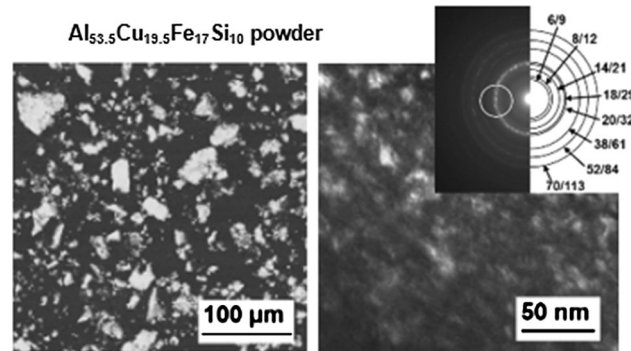
The effect of Si addition on a quasicrystalline phase formation in Al-Cu-Fe-Si alloys prepared by mechanical alloying has been investigated using X-ray diffraction and scanning and transmission electron microscopy. Two compositions containing 10 at.% of Si were selected to verify the influence of the  $e/a$  ratio on a sequence of phase formation during milling:  $\text{Al}_{58.5}\text{Cu}_{18}\text{Fe}_{13.5}\text{Si}_{10}$  ( $e/a = 1.98$ ) and  $\text{Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$  ( $e/a = 1.75$ ). A quasicrystalline icosahedral phase (i-phase) was found in both alloys after 10 h of milling in the form of nano-quasicrystallites with the size of 10–20 nm. Addition of Si stabilized the quasicrystalline phase being dominant after prolonged milling time, contrary to the reference ternary  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  powder, which apart of the quasicrystalline phase contained the cubic  $\beta\text{-Al}(\text{Cu}, \text{Fe})$  phase. Thermal stability of the quasicrystalline phase in the powders milled for 10 h was examined after annealing at 800 °C for 4 h. The i-phase was preserved partially in  $\text{Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$  and reference  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  powders (both with a ratio  $e/a = 1.75$ ), which coexisted with  $\beta\text{-Al}(\text{Cu}, \text{Fe})$  and  $\text{Al}_{13}\text{Fe}_4$  phase or  $\alpha\text{-Al}_{55}\text{Si}_7\text{Cu}_{25.5}\text{Fe}_{12}$  and  $\text{Al}_2\text{Fe}_3\text{Si}_3$  phases in  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  and  $\text{Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$ , respectively. For the  $\text{Al}_{58.5}\text{Cu}_{18}\text{Fe}_{13.5}\text{Si}_{10}$  powders ( $e/a = 1.98$ ), the annealing led to complete transformation of the i-phase to the cubic  $\alpha\text{-Al}_{55}\text{Si}_7\text{Cu}_{25.5}\text{Fe}_{12.5}$  approximant, forming crystallites with a size of 100–300 nm.

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## GRAPHICAL ABSTRACT



## Introduction

The stable quasicrystalline phase in the Al-Cu-Fe system was first identified in 1987 by Tsai et al. [1] in the massive  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  alloy cast by a conventional method and then annealed. This ternary alloy, characterized by low cost, easily accessible, recyclable and non-toxic constituent elements, has been extensively studied in the following years due to possibility of a number of applications [2–5]. In the Al-Cu-Fe system, the thermodynamically stable icosahedral phase exists in a narrow temperature range (750–850 °C) with composition near  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  and is usually accompanied by other crystalline phases [6–8]. It has been reported that the addition of a fourth alloying component has resulted in modification of the microstructure and forming a single-phase quasicrystalline alloy. In the quaternary  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{12}\text{M}_3$  alloys, in which iron atoms were partially replaced with other elements: Ti, V, Cr, Mn, Co, Ni, Si, Ge, Zr, Nb, only alloys containing Mn, Co and Si were characterized by a single-phase icosahedral structure [9].

The effect of addition of Si depends on the amount of element added, the content of other components and the method of preparation [10–13]. In the conventionally cast alloys, the volume fraction of the icosahedral phase decreased when silicon atoms replaced aluminum by up to 10 at.% [10, 11]. On the other hand, the research conducted by Sukhova et al. [14] showed that Al substitution by 4–7 at.% of Si in

the  $\text{Al}_{60}\text{Cu}_{25}\text{Fe}_{12}$  can promote the formability of i-phase, especially in the slow cooled alloys. It was also found that when the Si content increased up to 15 at.%, the icosahedral phase was replaced by the cubic approximant of AlCuFeSi [10]. This  $\alpha\text{-Al}_{55}\text{Si}_7\text{Cu}_{25.5}\text{Fe}_{12.5}$  phase with a cubic structure, a lattice constant  $a = 12.330 \text{ \AA}$  and the Pm-3 point group contains 135 atoms in the unit cell [15–17]. The formation of the  $\alpha\text{-Al}_{55}\text{Si}_7\text{Cu}_{25.5}\text{Fe}_{12.5}$  approximant can be supported by increasing the cooling rate during casting: moderate rate of solidification can improve the thermal stability of the quasicrystalline phase in the melt spun ribbon, while the higher quenching rates instigate the transformation of the quasicrystal into the cubic approximant [11]. Karaköse and Keskin [18] reported an increase of microhardness and reduction of the number of phases in the rapidly solidified  $\text{Al}_{64}\text{Cu}_{20}\text{Fe}_{12}\text{Si}_4$  ribbons compared to the conventionally cast alloys.

Mechanical alloying, one-step procedure to obtain material in the form of powder, can lead to formation of a quasicrystalline phase in ternary Al-Cu-Fe alloys [19–24] and extends its composition range compared to the other methods. It was reported that substitution of 5 at.% of Fe by Si increases the stability of the i-phase and the cubic approximant in the mechanically alloyed and annealed  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  powder [12]. Murty et al. [13] showed that mechanical alloying of  $(\text{Al}_{60}\text{Cu}_{25}\text{Fe}_{12})_{100-x}\text{Si}_x$  alloys improves the quasicrystalline phase forming ability (QFA) in comparison to rapid solidification processing by extending the range of e/a ratio, over which the icosahedral phase

can be obtained. It was found also that thermal stability of the quasicrystalline phase in Si-containing alloys increases up to 1223 K.

In the present study, the influence of Si addition on the formation of the quasicrystalline phase in Al-Cu-Fe-Si alloys prepared by mechanical alloying has been investigated. To verify the effect of ratio of the number of valence electrons to number of atoms in unit cell ( $e/a$ ), an important parameter for the formation of quasicrystalline phases [25, 26], on the sequence of phase formation during milling process two alloy compositions (both containing 10 at.% of Si) were selected. The first composition with  $e/a$  ratio close to 2 corresponded to the alloy described by Murty et al. [13]; the second one with  $e/a$  equal 1.75 was identical as for the ternary  $Al_{65}Cu_{20}Fe_{15}$  alloy. Parameters of milling process were chosen based on our previous examination, where the single icosahedral phase formed in the  $Al_{65}Cu_{20}Fe_{15}$  powder directly after 10 h of milling at the speed of 350 rpm (revolution per minute) [24]. Additionally, the structural evolution induced by a subsequent annealing and thermal stability of the quasicrystalline phase was studied and compared to the reference ternary composition.

## Materials and methods

Elemental powders of aluminum, copper, iron and silicon (of purity at least 99.2% and the particle size in the range of 7–15  $\mu\text{m}$ , supplied by Alfa Aesar) were mechanically alloyed in a planetary high-energy ball mill Fritsch P5. Mixture of pure elements powder, corresponding to the compositions presented in Table 1, was milled in tungsten carbide (WC) vials together with WC balls under argon atmosphere (the ball to powder ratio was 10:1). Hexane was added as a process control agent to prevent oxidation and

**Table 1** Nominal composition (in at.%) of the investigated powders

Alloy designation	Composition of the alloy				$e/a$ ratio
	Al	Cu	Fe	Si	
Si0	65	20	15	–	1.75
Si1	58.5	18	13.5	10	1.98
Si2	53.5	19.5	17	10	1.75

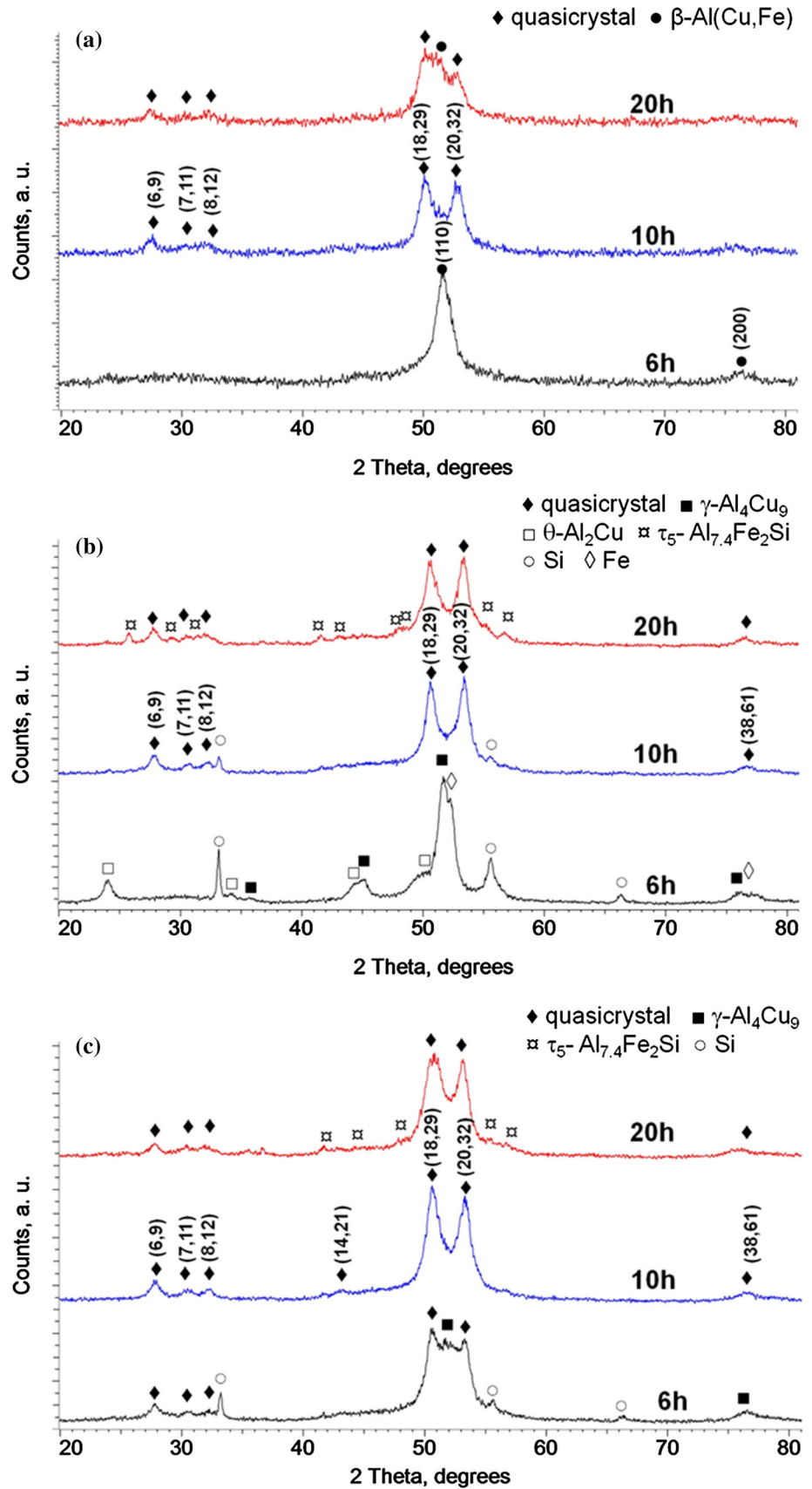
eliminates tendency to ignite of the powder during milling. Milling was performed at a rotation speed 350 rpm (revolution per minute) up to 20 h with intervals to cool down milled powders. The parameters of the milling process were chosen based on our experience in preparation of the ternary Al-Cu-Fe quasicrystalline powders [23, 24]. After milling, the selected powders were annealed at 800 °C for 4 h in quartz ampoules in vacuum. For the calculation of  $e/a$ , the nominal compositions were accepted, due to the results of the EDX microanalysis carried out in TEM showed similar chemical compositions of the milled powders as the initial values (see supplementary material).

The microstructure of the milled and heat treated powders was examined by X-ray diffraction (XRD) using D8 Discover Bruker diffractometer with  $Co\ K\alpha$  filtered radiation ( $\lambda = 0.17903\text{ nm}$ ), scanning electron microscopy (SEM) using E-SEM XL and analytical 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. For X-ray examination, powders were compacted in the mold to cylindrical form. Powders selected for SEM investigations were embedded in an epoxy resin, polished, and then, the specimen surface was coated with a conductive layer of carbon before examination. 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. The “ProcessDiffraction V-7.3.2Q” software developed by Labar [27] has been applied to measure interplanar spacing in the electron diffraction ring patterns.

## Results

The phase evolution during the milling process was investigated by XRD measurements. Initial powders contained the mixture of constituent elements: Al, Cu, Fe and additionally Si in Si1 and Si2 powders. At the first stage of milling (after 3 h), apart from the reflections of pure elements, Al-base phases started to form. For Si0 powder, the reflections of the cubic  $\beta$ -Al(Cu, Fe) phase were observed, while weak reflections of the  $\theta$ - $Al_2Cu$  phase appeared in the quaternary compositions.

**Figure 1** Sets of XRD patterns of Si0 a, Si1 b and Si2 c powders after 6, 10 and 20 h of milling.



The sets of XRD patterns after 6, 10 and 20 h of milling for the examined compositions are presented in Fig. 1. After 6 h of milling, the reflections of constituent elements disappeared completely in the Si0 powder with simultaneous increase in the intensity of reflections of  $\beta$ -Al(Cu, Fe) phase (Fig. 1a). The absence of (100) reflection indicates that the formed  $\beta$ -Al(Cu, Fe) phase is disordered. For Si1 powder, the  $\theta$ -Al<sub>2</sub>Cu phase coexists with  $\gamma$ -Al<sub>4</sub>Cu<sub>9</sub> phase, but the reflections of pure elements Si and Fe are still visible (Fig. 1b). The quasicrystalline *i*-phase dominates in the Si2 powder, accompanied by small amount of the  $\gamma$ -Al<sub>4</sub>Cu<sub>9</sub> phase and Si (Fig. 1c). Ten hours of milling resulted in the formation of *i*-phase in all powders, although for the Si1 powder the small amount of Si was also detected (Fig. 1b). The diffraction peaks of the *i*-phase were indexed using Cahn's scheme as a face-centered icosahedral quasicrystal (the superlattice reflection (7,11) is visible) [36, 37]. It can be seen that reflections of the *i*-phase in both Si-containing powders exhibit higher intensity compared to reference Si0 powder. Extending the milling time to 20 h led to reduction of the phase fraction of the *i*-phase and the formation of a disordered  $\beta$ -Al(Cu, Fe) phase in Si0 powder (Fig. 1a), while the *i*-phase was still dominant in the Si1 and Si2 with only a trace amount of the hexagonal  $\tau_5$ -Al<sub>7.4</sub>Fe<sub>2</sub>Si phase (Fig. 1b, c). The identified phases and their lattice parameters are presented in Table 2. The powders after 10 h of milling were selected for further microstructural investigations and subsequent heat treatment because of

the *i*-phase presence in all the examined compositions.

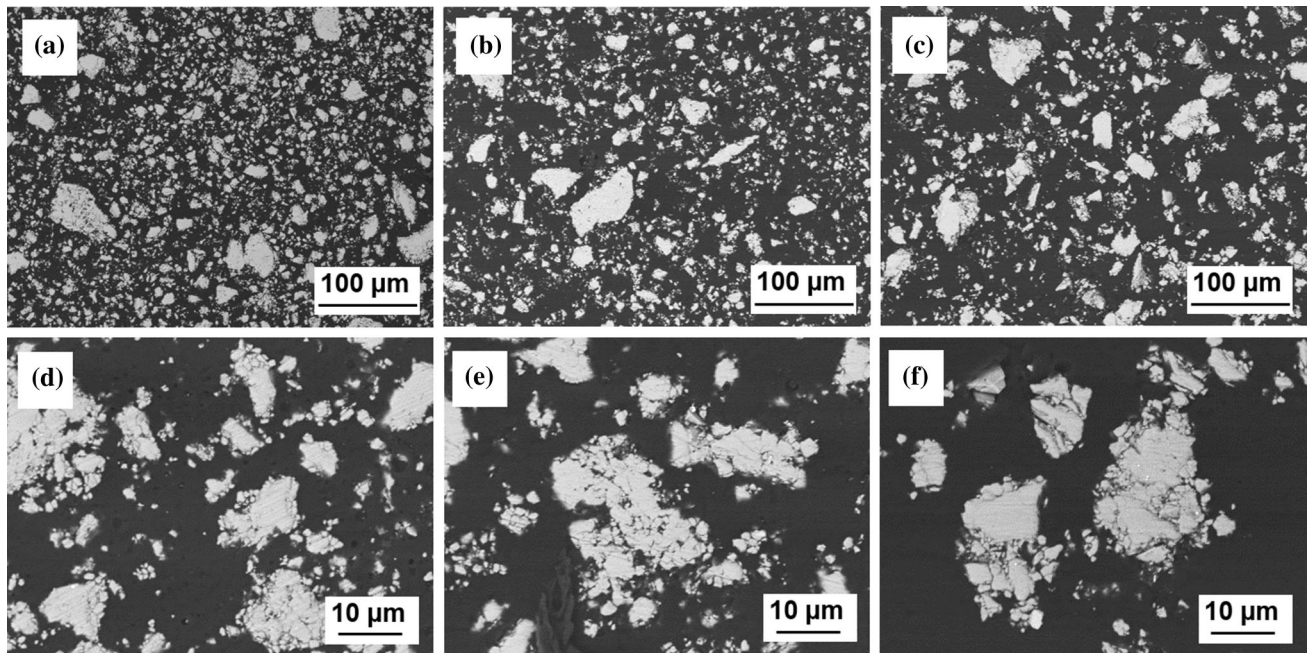
The SEM-BSE microstructures of the cross sections of the powders after 10 h of milling are given in Fig. 2. All powders contained particles with maximum dimension below 100  $\mu\text{m}$ ; however, most of the particles had a size of 10–20  $\mu\text{m}$ . The defragmentation of the particles was not finished and a lot of cracks can be seen at higher magnification in Fig. 2d–f. The cross sections of particles did not show differences in contrast, which may indicate their almost homogeneous structure.

The presence of the *i*-phase in the form of small crystallites was observed by TEM in all investigated powders. As an example, the bright (BF) and dark (DF) field images of the Si2 powder are shown in Fig. 3. The nanocrystallites of the *i*-phase with a diameter of the 10–20 nm are clearly visible in the DF microstructure. The selected area electron diffraction pattern (SADP) obtained from the area presented in Fig. 3a, b contains reflections lying along Debye–Scherrer rings; measured *d*-spacing values were indexed as the quasicrystalline *i*-phase (unlike the XRD diffraction, and the superlattice reflection (7,11) was not detected may be due to the local disordering of the *i*-phase).

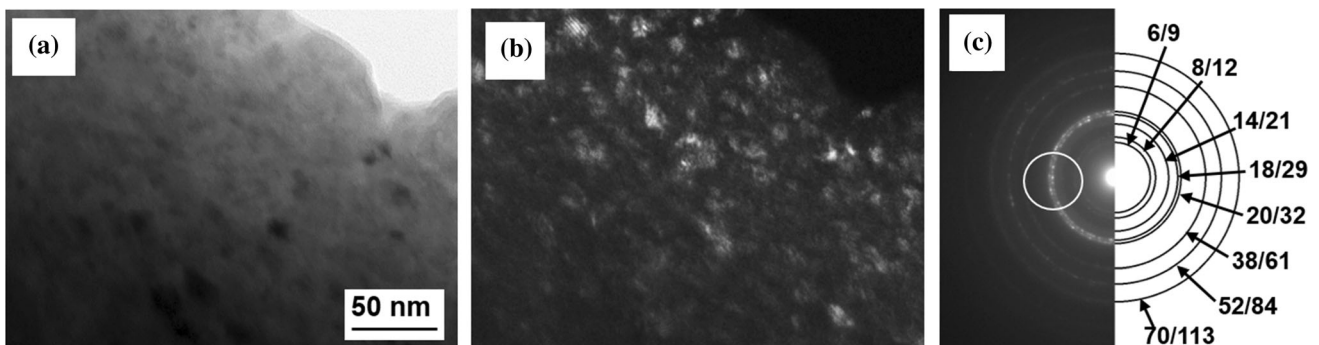
The stability of the quasicrystalline phase during annealing at 800 °C for 4 h in the powders milled for 10 h was examined by X-ray diffraction (Fig. 4). For the Si0 powder, in addition to the quasicrystalline phase, which was present in the as-milled powder,

**Table 2** The phases identified in the Si0, Si1 and Si2 powders after milling and after annealing

Phase	Structure, space group	Lattice parameters [nm, deg]	Reference
(Al)	Cubic, Fm-3 m	$a = 0.4049$	[28]
(Cu)	Cubic, Fm-3 m	$a = 0.3614$	[28]
$\alpha$ -Fe	Cubic, Im-3 m	$a = 0.2866$	[28]
(Si)	Cubic, Fd-3 m	$a = 0.5431$	[28]
$\beta$ -Al(Cu, Fe)	Cubic, Pm3m	$a = 0.2941$	[29]
$\theta$ -Al <sub>2</sub> Cu	Tetragonal, I4/mcm	$a = 0.6067, c = 0.4877$	[30]
$\gamma$ -Al <sub>4</sub> Cu <sub>9</sub>	Cubic, P-43 m	$a = 0.8703$	[31]
<i>i</i> -Al <sub>65</sub> Cu <sub>20</sub> Fe <sub>15</sub>	Icosahedral phase	–	[32]
$\tau_5$ -Al <sub>7.4</sub> Fe <sub>2</sub> Si	hexagonal	$a = 1.234 \text{ nm}, c = 2.621 \text{ nm}$	[33]
$\lambda$ -Al <sub>13</sub> Fe <sub>4</sub>	Monoclinic, C2/m	$a = 1.5492, b = 0.8078, c = 1.2471, \beta = 107.69^\circ$	[34]
$\tau_1$ -Al <sub>2</sub> Fe <sub>3</sub> Si <sub>3</sub>	Triclinic, P-1	$a = 0.4651, b = 0.6326, c = 0.7499, \alpha = 101.37, \beta = 105.92, \gamma = 101.24$	[35]
$\alpha$ -Al <sub>55</sub> Si <sub>7</sub> Cu <sub>25.5</sub> Fe <sub>12.5</sub>	Cubic, Pm-3 1/1 approximant	$a = 1.2321$	[17]



**Figure 2** SEM-BSE microstructures of the cross section of the Si0 (a, d), Si1 (b, e) and Si2 (c, f) powders after 10 h of milling.



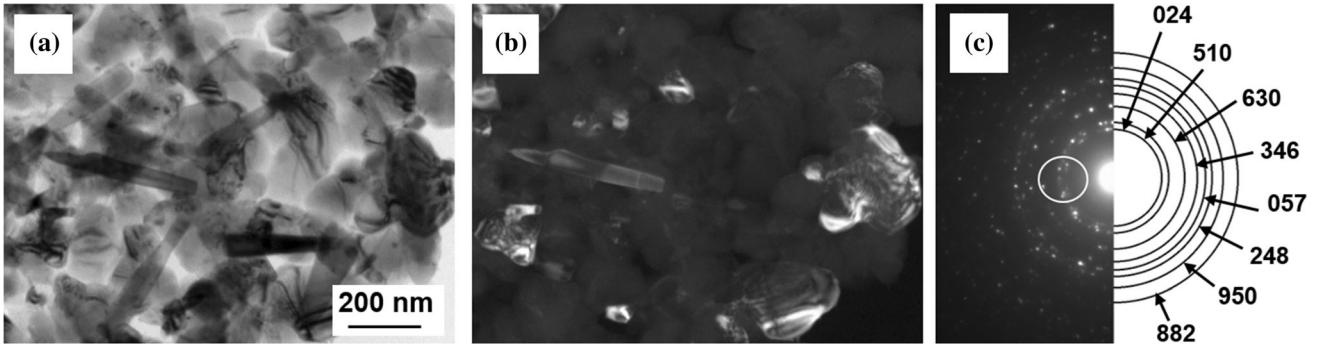
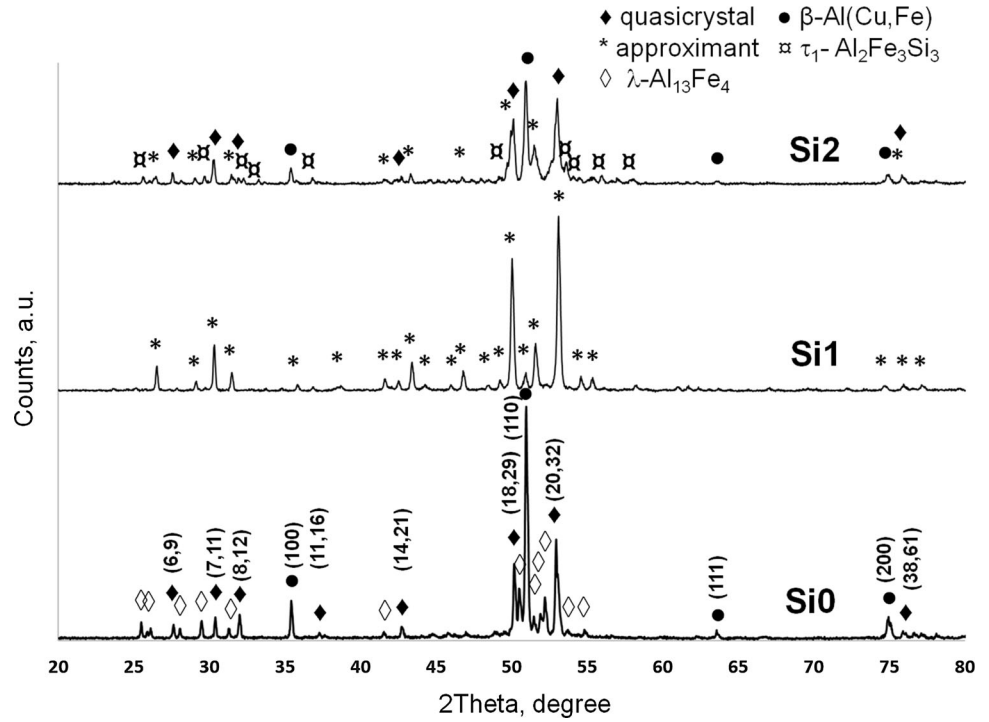
**Figure 3** TEM **a** bright- and **b** dark-field microstructures and **c** corresponding SADP (the position of the objective aperture for DF image is marked) of the Si2 powder milled for 10 h.

the ordered  $\beta$ -Al(Cu, Fe) and  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub> phases were identified. In the case of Si1 powder, i-phase transformed completely during annealing into the cubic  $\alpha$ -Al<sub>55</sub>Si<sub>7</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> approximant. The Si2 powder contained the mixture of the i-phase and the ordered  $\beta$ -Al(Cu, Fe) as dominant phases, and traces of triclinic  $\tau_1$ -Al<sub>2</sub>Fe<sub>3</sub>Si<sub>3</sub> phase and the  $\alpha$ -Al<sub>55</sub>Si<sub>7</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> approximant.

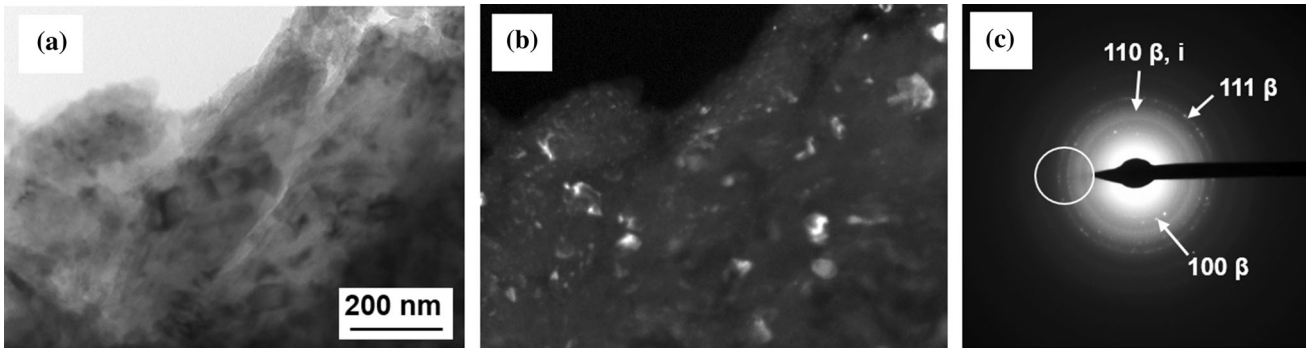
The Si1 powder particles consisted of randomly distributed crystallites of 100–300 nm, what means that the size of the crystallites after annealing increased significantly (Fig. 5). The corresponding SADP was in the form of rings that can be identified as the  $\alpha$ -Al<sub>55</sub>Si<sub>7</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> approximant, confirming the XRD results.

In the Si2 powder, the growth of the crystallites during annealing was not as significant as in the case of the Si1 powder. Grain growth up to about 100 nm could be seen in the TEM bright- and dark-field microstructures presented in Fig. 6a, b. The corresponding SADP (Fig. 6c) contains reflections of the ordered  $\beta$ -Al(Cu, Fe), which was identified in the XRD pattern as one of the prevailing phases (Fig. 4). The weaker reflections of the i-phase, which overlap with or lie close to reflections of  $\beta$ -Al(Cu, Fe) phase, are also visible in the presented SADP.

**Figure 4** Set of XRD patterns of Si0, Si1 and Si2 powders after 10 h of milling and subsequent annealing at 800 °C for 4 h.



**Figure 5** TEM **a** bright- and **b** dark-field microstructure and **c** corresponding SADP (the position of the objective aperture for DF image is marked) of the Si1 powder milled for 10 h and annealing at 800 °C for 4 h.



**Figure 6** TEM **a** bright- and **b** dark-field microstructures and **c** corresponding SADP (the position of the objective aperture for DF image is marked) of the Si2 powders milled for 10 h and annealing at 800 °C for 4 h.

## Discussion

The presented studies have shown that mechanical alloying is a method that can lead to the formation of face-centered icosahedral quasicrystalline phase for all investigated powder compositions. In the case of ternary Al-Cu-Fe powder, the *i*-phase has been observed in milled powders of similar composition [21–23, 38–40]. It was also revealed, as in our research, that the *i*-phase after a longer milling time transformed into the disordered cubic  $\beta$ -Al(Cu, Fe) phase. The same transition was also found in the Al-Cu-Fe [41, 42] and Sn reinforced Al-Cu-Fe [43] powders during ball milling of a cast, annealed and crushed alloy containing the stable *i*-phase, which after milling, transformed into the cubic  $\beta$ -Al(Cu, Fe) phase. The transition was explained by occurrence of a quasilattice strain introduced during milling (phase distortion and phonon distortion component), when the grain size of the quasicrystalline phase decreased to  $\sim 10$  nm.

In both quaternary Al-Cu-Fe-Si powders, despite the identical silicon amount of 10 at.%, the formation of a quasicrystalline phase during milling took place in a different way. The *i*-phase started to form in the Si2-Al<sub>53.5</sub>Cu<sub>19.5</sub>Fe<sub>17</sub>Si<sub>10</sub> powder ( $e/a = 1.75$ ) faster than for the Si1-Al<sub>58.5</sub>Cu<sub>18</sub>Fe<sub>13.5</sub>Si<sub>10</sub> powder ( $e/a = 1.98$ ) and pronounced reflections of this phase coexists with small amount of silicon and Al<sub>4</sub>Cu<sub>9</sub> phase after 6 h of milling. After the same milling time, the Si1 powder contained, apart from pure elements Si and Fe, the Al<sub>2</sub>Cu and Al<sub>4</sub>Cu<sub>9</sub> phases, while the *i*-phase was not observed. The formation of binary phases containing Al and Cu at initial stage of milling is related to the higher diffusion coefficient of Cu in aluminum compared to Si and Fe.

A quasicrystalline structure has been observed after 10 h of milling in both Si1 and Si2 compositions. For the Si2 powder, the *i*-phase was detected as a single phase, while for the Si1, it was accompanied by a small amount of silicon. This can be explained by the fact that Al content in Si1 powder was higher than that in Si2, and since Si atoms replaced Al atoms, only a part of Si was consumed to form the quasicrystalline phase for this composition (the Al: Cu: Fe ratio in Si1 corresponds to the *i*-phase). It was also found that the *i*-phase in the Si1 powder appeared after a shorter milling time compared to the results obtained by Murty et al. [13], where 30 h was needed to form the quasicrystalline phase (together with  $\beta$ -Al(Cu,

Fe)) for the same powder composition. This may be due to differences in milling conditions, in particular high milling speed and using WC milling media in our experiments, which led to an increase in the total energy transferred to the powder during milling process.

SEM and TEM observations have shown that the *i*-phase was visible in the form of small crystallites in all investigated powders after 10 h of milling. Similar size and distribution of the crystallites of the *i*-phase inside the powder particles was reported by Murty et al. [13] in the sample after 40 h of milling for composition analogous to Si1. Nanocrystallites of the *i*-phase are also observed in the previous studies of the mechanically milled powder [11, 24, 44, 45].

The quasicrystalline phase is not stable and prolonged milling resulted in its partial transformation. In contrast to the Si0 alloy, where the  $\beta$ -Al(Cu, Fe) single phase appeared, a small fraction of  $\tau_5$ -Al<sub>7.4</sub>Fe<sub>2</sub>Si phase except dominated the *i*-phase was identified in both Si-containing alloys. It should be noted that the face-centered icosahedral quasicrystalline phase was detected through the whole milling process. The traces of the  $\tau_5$ -Al<sub>7.4</sub>Fe<sub>2</sub>Si phase, one of a ternary  $\tau$ -type phases enriched in Fe and Si [46], has been observed in multilayered Al/Cu/Fe thin films deposited onto Si substrate in the Al-deficient samples, together with the dominating  $\alpha$ -Al<sub>55</sub>Si<sub>7</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> approximant [47].

The quasicrystalline *i*-phase identified in all investigated powders milled for 10 h underwent different transformations during annealing at 800 °C for 4 h to form various phases. For the ternary Si0-Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> powder, the dominant ordered  $\beta$ -Al(Cu, Fe) phase is accompanied by the *i*-phase and small amount of the  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub>. In the XRD pattern, the strong and sharp reflections of the both main phases are clearly visible, due to the increased size of the crystallites compared to the as-milled state. This result is consistent with our previous experiments for an annealed Al-Cu-Fe powder, which also contained the  $\beta$ -Al(Cu, Fe) and the *i*-phase, regardless of the phases identified in the powders after milling [24]. Similar, two-phase microstructure of annealed Al-Cu-Fe powders has also been reported by other researchers, e.g., [44, 48, 49].

The conditions of the milling process and the milling time influence the phase composition of as-milled powders, and thus are of decisive importance for the formation of the quasicrystalline phase after



annealing. The synthesis of a powder with a high volume fraction of the quasicrystal phase could be achieved by combination of a short milling time and subsequent annealing [19, 44, 49–51]. The formation of the quasicrystalline phase in Al-Cu-Fe powders containing  $\beta$  and  $\theta$  phases in as-milled state after non-isothermal annealing above 750 °C was reported by Nicula et al. [50]. Salimon et al. [51] showed that the as-milled powder consisting of a mixture of solid solutions of starting elements and the  $\text{Al}_2\text{Cu}$  phase transformed into an almost single icosahedral quasicrystalline phase after annealing at 700 °C. Ali et al. [52] studied the phase evolution during milling and subsequent annealing of the quasicrystalline phase and concluded that the formation of the ordered  $\beta$ -Al(Cu, Fe) phase was promoted with increasing milling time. The stored internal energy reduced the activation barrier for nucleation of the crystalline  $\beta$ -Al(Cu, Fe) phase in the icosahedral structure (samples milled for longer time require lower thermal energy for transformation).

The *i*-phase was partially preserved also in  $\text{Si}_2\text{-Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$  powder, although the volume fraction of the ordered  $\beta$ -Al(Cu, Fe) was lower compared to the  $\text{Si}_0$ . It should be noted that the calculated *e/a* ratio for both powders is identical and equal 1.75, what may be the reason for similar phase composition after annealing (Si-containing phases,  $\alpha$ - $\text{Al}_{55}\text{Si}_7\text{-Cu}_{25.5}\text{Fe}_{12.5}$  approximant and  $\text{Al}_2\text{Fe}_3\text{Si}_3$  phase, replaced  $\lambda$ - $\text{Al}_{13}\text{Fe}_4$  phase in  $\text{Si}_2$  powder). In the case of the  $\text{Si}_1\text{-Al}_{58.5}\text{Cu}_{18}\text{Fe}_{13.5}\text{Si}_{10}$  powder, the *i*-phase completely transforms during annealing to the cubic  $\alpha$ - $\text{Al}_{55}\text{Si}_7\text{-Cu}_{25.5}\text{Fe}_{12.5}$  approximant, which is associated with significant increase of the grain size up to about 300 nm. The transformation of the quasicrystalline phase into the cubic approximant was also found in the gas atomized powder of a similar composition ( $\text{Al}_{57}\text{Cu}_{17.75}\text{Fe}_{14.75}\text{Si}_{10.5}$ ) after heating to a temperature above 600 °C [53]. A different result for the powder of identical composition was obtained by Murty et al. [13], wherein a mixture of the *i*-phase and the  $\beta$ -Al(Cu, Fe) was obtained during annealing at 600 °C (it should be mentioned that the as-milled powder before annealing also contained these phases). The different phase composition obtained after milling as well as after annealing can be caused by different parameters used during milling, as well as different annealing temperature.

Based on the results obtained, it can be concluded, that addition of 10 at.% of Si, irrespective of the

mutual content of other components and the *e/a* ratio, has a positive effect on the formation of the icosahedral phase in Al-Cu-Fe powders produced by mechanical alloying. The quasicrystalline phase in both  $\text{Si}_1$  and  $\text{Si}_2$  powders was more stable and retained after a longer milling time as compared to the reduced volume fraction of this phase in favor of the  $\beta$ -Al(Cu, Fe) phase in the reference ternary  $\text{Si}_0$  alloy. These results may be important for application of the powders with a quasicrystalline structure. Due to their high hardness and brittleness, these powdered materials can be used, for example, as a reinforcement in composites. The stability of the quasicrystalline phase is highly dependent on the *e/a* ratio in the powders during annealing. It was found that *i*-phase in the  $\text{Si}_2$  and  $\text{Si}_0$  powders, with the *e/a* ratio equal to 1.75, is partially preserved, while the  $\text{Si}_1$  powder with *e/a* = 1.98 was completely transformed to the cubic approximant.

## Conclusions

The quasicrystalline icosahedral *i*-phase formed in the  $\text{Al}_{58.5}\text{Cu}_{18}\text{Fe}_{13.5}\text{Si}_{10}$ ,  $\text{Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$  and the reference  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  mechanically alloyed powders after 10 h of milling at the speed of 350 rpm and using WC milling media. Particles of the powder consisted the fine 10–20 nm crystallites of the *i*-phase for all investigated compositions. Addition of Si stabilized the quasicrystalline phase being dominant after extended milling time, contrary to the reference ternary powder, which apart of quasicrystalline phase contained the cubic  $\beta$ -Al(Cu, Fe).

Annealing of the powders milled 10 h at 800 °C for 4 h maintained partially the *i*-phase in  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  and  $\text{Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$  powders (*e/a* ratio was 1.75 for both compositions) accompanied by an increase of crystallites sizes up to 100 nm. The *i*-phase coexisted with  $\beta$ -Al(Cu, Fe) and small fraction of  $\text{Al}_{13}\text{Fe}_4$  or  $\alpha$ - $\text{Al}_{55}\text{Si}_7\text{-Cu}_{25.5}\text{Fe}_{12.5}$  and  $\tau_1\text{-Al}_2\text{Fe}_3\text{Si}_3$  phases in  $\text{Al}_{65}\text{-Cu}_{20}\text{Fe}_{15}$  and  $\text{Al}_{53.5}\text{Cu}_{19.5}\text{Fe}_{17}\text{Si}_{10}$ , respectively. For the  $\text{Al}_{58.5}\text{Cu}_{18}\text{Fe}_{13.5}\text{Si}_{10}$  powders (*e/a* = 1.98) the annealing led to the complete *i*-phase transformation to the cubic  $\alpha$ - $\text{Al}_{55}\text{Si}_7\text{-Cu}_{25.5}\text{Fe}_{12.5}$  approximant in the form of 100–300 nm crystals.

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## Declarations

**Conflict of interest** There are no conflicts of interest to declare.

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