Effect of milling time on XRD phases and microstructure of a novel Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ quasicrystalline alloy

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Abstract

The quasicrystalline materials represent a new materials group with definite crystallite structural characteristics, in which the AlCuFe(B) quasicrystalline alloys have been widely studied owing to its various technological advantages such as easily accessible in nature, thermal stability, affordability as well as not having toxic constituent elements. Although these materials can be achieved by different procedures, the synthesis of more extensive amounts of AlCuFeB quasicrystalline single-phase powders is more complicated. In this study, the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ quasicrystalline alloys were synthesized through the mechanical alloying process and afterward consolidated to the bulk specimens by cold isostatic pressing (CIP) technique. The structural and microstructural evolutions, as well as the morphology of as-milled powders and phase transformations, were studied during the ball milling process using field-emission scanning electron microscopy (FESEM) and x-ray diffractometry (XRD), while the thermal behavior was investigated using differential thermal analysis (DTA). The most fascinated result revealed that the stable AlCuFeB single quasicrystalline phase could be directly synthesized in short milling times (around ~4 h) by a high-energy planetary ball milling. It was appreciated that the icosahedral phase is stable up to 300 $^\circ$C, which is misplaced stability at superior temperatures and transforms into crystalline phases. The microhardness of consolidated ball-milled powders at various milling times was determined and it was figured out that the icosahedral phase has an extreme microhardness as much as 10.73 GPa.

1. Introduction

Nowadays, quasicrystalline (QC) alloys are increasingly attracting more attention due to their surface properties and unique structural features. QC forms a new class of solid materials that present non-periodic long-range order and differ from crystalline or amorphous materials [1, 2]. Although QC alloys exhibit attractive properties such as high hardness and stiffness, low thermal and electrical conductivities, minute friction coefficient, and high-grade corrosion, as well as wear resistance, they are so fragile at room temperature and their mechanical behavior is somehow similar to ceramic materials and intermetallic composites [3–6]. These specifications of QC alloys make them suitable for technological applications such as the automotive and aerospace industry in the form of surface coatings, thin films, and reinforcement particles in metal matrix composites (MMCs) [6–8]. Recently, the stable Al–Cu–Fe QC alloys have been widely investigated due to its numerous industrial benefits such as naturally effortlessly available, thermal stability, and affordability as well as not having toxic constituent elements [9–11]. The fabrication of Al–Cu–Fe QC alloys can be conducted via the two following processes; mechanical alloying (MA) and rapid solidification (RS) [10, 12]. MA of initially mixed powders, which is considered as an efficient method to obtain microscopically homogeneous materials [13], could be utilized to synthesize the metastable and stable QC alloys [12]. The MA method is based on the repeated welding,
fracturing, and re-welding of particles during high-energy milling [5]. Although the micro- and nano-QC alloy-forming ability and the composition range of the examined alloys was considerably improved, which needed to experience prolonged annealing to ensure stable QC alloys formation [14–16]. It has been shown that Al–Cu–Fe QC alloys are high intrinsic brittle [17, 18]. However, some evidence reveals that the use of boron (B) and chromium (Cr) elements, as additive agents, could modify their fragility and fortify of the mechanical properties [18, 19]. The principal intention of the present work is to examine the effect of milling time on the formation and structure of the mechanically alloyed Al_{67}Cu_{20}Fe_{10}B_{3} composition and development of stable icosahedral QC phase straightly through high-energy planetary ball milling without succeeding annealing as a single-phase and its transformations into other intermetallic compounds during ball milling (BM) and subsequent heat treatments. The outcomes would provide a better understanding of the correlation between milling time, crystallinity, stabilization of the QC phase, and microhardness.

2. Experimental procedure

In this endeavor, a metallic alloy was synthesized with a nominal composition of Al_{67}Cu_{20}Fe_{10}B_{3} (at%) corresponds to the desirable stable QC phase by BM technique of high purity raw materials powders (Aluminium–99%, Copper–99.7%, Iron–99.5%, Boron–99.9%) using a high-energy planetary BM machine and consolidated by a cold isostatic pressing (CIP) device. Noble quality of individual elemental powders was blended with average particle sizes not as much of than 200 μm in a glove box to obtain the desired alloys under a high purified argon atmosphere using appropriate stoichiometric proportions to provide the accurate nominal composition of Al_{67}Cu_{20}Fe_{10}B_{3} alloy. Afterward, approximately 300 g of balls and 10 g of coveted mixed elemental powder batch at a ball to powder weight ratio of 30 to 1 were charged into a 500 ml-volume hardened steel pot. The milling procedure was carried out at a rotation speed of 300 rpm through a Retsch PM 400 high-energy planetary BM device employing thirteen number of 20 mm (in diameter) hardened steel balls in each vial under a dry argon atmosphere to diminish oxygen and nitrogen pollution. Moreover, the MA process time was chosen between 1 h to 10 h to investigate structural evaluation of as-milled powders during BM. The adhering of the ductile powders into the milling medium (vials wall and milling balls) and excess cold welding of the elemental powders were minimized using 1 wt% stearic acid before mechanical milling as a process control agent (PCA). The milling process was periodically interrupted every 1 h for 30 min resting and started again subsequently to reduce the temperature of pots and prevent the mixture from overheating. The pots then were opened in an isolated glove box and a small amount of the as-milled powders (about 1 g) was extracted simultaneously for successive operations such as compactions, heat treatments, analyzes, and examinations. Succeeding annealing treatments were executed on the as-milled powders at selected temperatures to investigate the phase transformations. The mechanically alloyed powders at different milling times were used to prepare consolidated samples using a KJYc300 CIP apparatus at 400 MPa pressure and 25 °C temperatures, for assessing green density and microhardness of consolidated specimens.

The structural evolutions and phase analysis of the as-milled powders and heat-treated compacts were characterized by x-ray diffraction (XRD) test using a PHILIPS-PW 3710 device including Cu Kα radiation (λ_{Cu-Kα} = 1.54 Å), which operated at 40 kV and 30 mA. The evaluated XRD patterns were recorded within the Bragg angle range of 20°–70° at the step size of 0.01° and time per step of 0.6 s, which were investigated using PANalytical HighScore software. The microstructure, morphology, particle size, and quantitative element analysis of the as-milled powders were examined through a field-emission scanning electron microscope (FESEM) after applying standard metallographic preparation employing a TESCAN-MIRA3 appliance coupled with an energy dispersive x-ray microanalyzer (EDX). A dilute Keller’s reagent (194 ml H_{2}O, 3 ml HNO_{3}, 2 ml HCl) was applied as an etchant for a number of alloy compositions. Moreover, the particle size was appraised using Coulter counter model ZS6 and B with NaCl electrolyte, which computes the changes in electrical impedance generated by suspended non-conductive particles in an electrolyte [20]. A Coulter counter is an apparatus with one or more microchannels that separate two chambers containing electrolyte liquids. As a solution comprising particles was carried within an orifice, each particle induces a little change to the electrical resistance of the liquid, which is proportional to the volume of the particle. The counter detects these changes in electrical resistance. Also, a PERKINELMER SCIEX ELAN DRC-2 inductively coupled plasma mass spectrometry (ICP-MS) has been used to perceive the amount of boron and other elements in the examined powders. The thermal behavior of the as-milled powders was investigated through a BAHR-STA 503 differential thermal analyzer (DTA) at a heating rate of 10 °C.min^{-1} under a high purified argon atmosphere. Moreover, the microhardness and green density of the isostatically cold-pressed powders was measured. The microhardness of investigated samples, which is isostatically cold-pressed from the mechanically alloyed powders, was determined by utilizing a computer-controlled Akashi MVK-H1 Vickers microhardness tester with a tetrahedral diamond pyramid (the indentation size was about 9.8 μm) including an applied load of 10 g and 15 s dwell time. The
indentations diagonal and the microhardness were calculated using a digital video measuring system, which made assured that the preferred indentation regions are far from the borders. The Vickers microhardness was calculated by the corrected standard equation:\(^ \text{1}\)\(^ {\text{21}}\):

\[ H = 1.854 \times 9.81 \times \frac{P}{d^2} \]  \(\text{1}\)

Where \( P \) is the load (N), \( d \) is the diagonal length (\( \mu \text{m} \)) and \( H \) is the microhardness value (GPa).

3. Results and discussions

3.1. Crystallization and phase evolutions

Figure 1 demonstrates the XRD patterns of individual elemental powders Al (49 wt%), Cu (35 wt%), Fe (15 wt%), and B (1 wt%), subjected to MA in a high-energy planetary ball mill. The XRD pattern shows the sharp Bragg peaks of the constituent elements before milling.

The structural evolutions and phase composition of the as-prepared Al\(_{67}\)Cu\(_{20}\)Fe\(_{10}\)B\(_3\) elemental powder blend obtained by MA process for 1 h to 10 h period are shown in figure 2. As can be evidently seen from figure 2(a), the XRD pattern of Al\(_{67}\)Cu\(_{20}\)Fe\(_{10}\)B\(_3\) metallic alloy following 1 h BM illustrates the main diffraction reflections that could be corresponded to the unreacted initial elemental powders. There is generally no interdiffusion linking Cu and Fe as copper and iron are practically immiscible at this composition range under the current milling process situation. Al will react with Cu and Fe to make two intermetallics, a new tetragonal crystalline phase as named \( \theta \)-Al\(_2\)Cu, which is ordered and stable in common age-hardened aluminium alloys, and an approximant monoclinic crystal \( \lambda \)-Al\(_3\)Fe intermetallic compound with almost quasiperiodic distribution and local ordering of the atoms in the layers alike to an icosahedral AlCuFe and AlFe decagonal phases\(^ {\text{22, 23}}\). The existence of different metastable phases amongst the AlCuFe ternary alloy system identified by the melt-
spun procedure reported in [24]. For instance, the new Al$_3$Fe$_2$ phase, in which such alloys produced once have more than 20 at% Fe. Contrariwise, Al$_3$Fe is formed only with less iron content alloys about 12 at% Fe after the MA process and also subsequent heat treatment that confirm the formation of Al$_3$Fe intermetallics [25]. Moreover, it can be seen the alloying of the Al, Cu, Fe, and B during BM results in decreasing the intensity of Al, Cu, and Fe as well as the formation of Al$_3$Cu and Al$_3$Fe intermetallic compounds. The solubility of boron is not absolutely evident in the ternary AlCuFe alloy system since the weight ratio of boron is lower than 1% in the present alloy system, and therefore, it cannot be identified by XRD analysis [7, 19]. Additionally, it is obviously perceptible from the peak intensities of the MA XRD pattern that Al is the dominant phase at this point of BM and the Al$_3$Cu, Al$_3$Fe, and other raw materials are minor phases. As shown in figure 2(b), with escalating the MA process time to 2 h, the volume fraction of the Al$_3$Cu and Al$_3$Fe intermetallics was increased and the amounts of the other elements were reduced. It is also evident that the peak intensities of the Al$_3$Cu and Al$_3$Fe phases enhanced, and the diffraction peaks apparently have a propensity for broadening and clearly show a Gaussian profile. This behavior represents the reduction of the powder crystallite size and augmentation of the internal lattice strain, which causes the complexity of the XRD patterns of the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ alloy system after 2 h BM. Moreover, some defects such as ‘displacement’ and ‘disordering’ contribute to the broadening of diffraction peaks by rising milling time [23]. At this stage of the MA procedure, an insignificant amount of Al and the other preliminary elements still subsists in the mixed metallic powder, and no new phases can be identified in the as-milled product. It is observed from figure 2 that the peak intensities of the primary elements (Al, Cu, and Fe) dwindle with increasing milling time up to 2 h, indicating that the alloying process has been entirely completed and could be accomplished at higher milling times, in which depends on the BM intensity. Higher MA process time, up to 3 h, led to utterly diverse phase composition and dissolution of the Al$_3$Cu phase and other elemental powders, while an exclusive phase that identified as the icosahedral phase develops along with the Al$_3$-phase in the absence of the Al$_3$-phase. The composition of the AlCuFeB alloy system following 3 h BM has been investigated by an ICP-MS analyzer to distinguish the quantity of the Al, Cu, Fe, and B elemental powders.

Figure 2. XRD patterns of the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ alloy after (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, (e) 5 h, (f) 6 h, (g) 7 h, and (h) 10 h BM.
The obtained results show that the examined specimen consists of about 66.89% aluminium, 19.28% copper, 12.85% iron, and 0.98% boron (atomic percent), reasonably close to the initial elemental blend. However, it is undoubtedly recognized that the iron contamination of the milling medium, has led to a minute increasing of the iron content in the mixed metallic powder. The XRD pattern of the as-milled power after 3 h (figure 2(c)) divulges the formation of almost AlCuFeB icosahedral QC phase with about only the XRD peaks related to that phase besides a few amounts of the residual \( \lambda \)-Al\(_3\)Fe intermetallic compound. The two major (211) (111) and (221) (001) [26, 27] diffraction peaks with 42.75° and 45.14° Bragg angles and five minor (111) (000), (311) (111), (111) (100), (222) (002), and (322) (111) reflections [26, 27] located at about 23.66°, 25.93°, 27.53°, 63.87° and 65.76°, respectively, are corresponding to the AlCuFeB icosahedral QC XRD pattern. This particular phase could be well-known as i-phase, which is stable with long-range ordering and could be a result of the dissolution of remaining Al and other elements and structural evolutions and mechanochemical interaction among the \( \theta \)-Al\(_3\)Cu and \( \lambda \)-Al\(_3\)Fe phases. It is obligatory to equilibrate the concentration of the QC component materials in the Al–Cu–Fe ternary phase diagram to produce thermodynamically stable AlCuFe icosahedral QC phase in the temperature range up to the peritectic transformation. A few deviations from the composition range could lead to the formation of crystalline intermetallics accompany with the QC phase. Accordingly, based on the phase diagram, the single QC i-phase is predominantly produced with compositions amid the Al\(_{60}\)Cu\(_{27}\)Fe\(_{13}\) and Al\(_{71}\)Cu\(_{16}\)Fe\(_{13}\) alloys [28]. In order to add boron to the Al–Cu–Fe ternary alloy system, it should be shortened the amount of aluminium and append the same amount of boron [7, 19]. It makes some new extra crystalline phases in the Al–Cu–Fe ternary system that improve the intrinsic brittleness, friction coefficient, and hardness advantages of the i-AlCuFeB phase in parallel with the conventional AlCuFe icosahedral phase [7, 19].

Continuing milling up to 4 h leads to form a single QC i-phase as a dominant phase notably, in which the volume fractions of the \( \lambda \)-Al\(_3\)Fe phase is almost negligible. Figure 2(d) represents the principle diffraction reflections that could be corresponded to the QC i-phase. Nevertheless, on analysis of the XRD pattern after further BM up to 5 h, a few weak peaks became visible amid the most intense peaks of the QC i-phase, correspond to the formation of a new cubic crystalline solid solution \( \beta \)-Al(Cu,Fe) phase with bcc structure (Cu:Al type) including lesser aluminium concentration \( \{ \text{Al}_{50-x} \text{(Cu,Fe)}_{50+x} \} \) [7], which is more thermodynamically stable than the QC i-phase [26]. Therefore, milling up to 5 h results in the formation of a metastable \( \beta \)-Al(Cu,Fe) phase, which is interrelated to the dissolution of the Cu and Al into the Al\(_3\)Fe layer through a solid-state diffusion progression [23]. Nevertheless, the depletion of the Al content of the initial powder batch causes the formation of the \( \beta \)-Al(Cu,Fe) phase in the mechanically alloyed powders [23]. Furthermore, the supersaturated solid solution \( \beta \)-Al(Cu,Fe) phase with little new short peaks, mostly in the low angle area (20° ~ 42°~44°), became visible in the XRD pattern. Moreover, the XRD pattern of the mixed metallic alloy at this time of BM (5 h) illustrates a typical mixture of the QC i-phase with a slight ternary solid solution \( \beta \)-Al(Cu,Fe) phase, as shown in figure 2(e).

Additional milling time (up to 6 h and 7 h) does not provide noteworthy changes in the XRD patterns; only the peak intensities of the \( \beta \)-Al(Cu,Fe) phase amplify and the volume fractions of the QC i-phase dwindle (figures 2(f), (g)). No fundamental variations in the QC i-phase reflection peaks has been detected for the duration of 2 h to 7 h BM, excluding the broadening of the principal peaks, which propose a refinement procedure of the mixed metallic alloy and reduction of the i-phase crystallite size as a result of peak broadening of a Lorentz peak profile based on XRD crystal theories. Figure 2(h) shows that later than a longer milling time of 10 h, the QC i-phase reflection peaks entirely vanish and the only reflection from the supersaturated solid solution \( \beta \)-Al(Cu,Fe) phase emerges on the XRD pattern. It is well-known that the single \( \beta \)-Al(Cu,Fe) phase is the only phase in the as-milled product after 10 h of BM with major (110) reflection (20° = 43.65°) and an ordered B2 structure based on the existence of a superlattice (100) peak (20° = 30.38°) as well as the basic (110) peak, which is comprised a homogenized chemical composition as a product of transformation and decomposition of the QC i-phase. The mechanochemical interactions during BM of the Al\(_{60}\)Cu\(_{27}\)Fe\(_{13}\)B\(_3\) alloy powder, including the formation and transformation of QC i-phase, can be expressed by the following equations (2) to (5):

\[
\text{Al} + \text{Cu} \rightarrow \theta - \text{Al}\(_3\)\text{Cu} \tag{2}
\]

\[
\text{Al} + \text{Fe} \rightarrow \lambda - \text{Al}\(_3\)\text{Fe} \tag{3}
\]

\[
\lambda - \text{Al}\(_3\)\text{Fe} + \theta - \text{Al}\(_3\)\text{Cu} + (\text{Al, Cu, Fe, B})_{\text{remain.}} \rightarrow i - \text{AlCuFeB} \tag{4}
\]

\[
i - \text{AlCuFeB} \rightarrow \beta - \text{Al}(\text{Cu, Fe}) \tag{5}
\]

Additionally, figure 2 shows a little shifting in the XRD peak position after 10 h BM, which could be related to the formation of a supersaturated solid solution phase of the Cu and Fe in the Al. There is limited solubility of Cu in Al and very limited dissolution of Fe in Al. The dissolution of the Cu and Fe into the Al leads to an increase in Al(Cu,Fe) lattice parameter (increasing of d-spacing) and consequently, peak shifting of the XRD pattern (decreasing of 20°) after 10 h BM based on Bragg’s law \( n\lambda = 2d\sin\theta \). Moreover, such increasing in lattice
distance can be attributed to the high concentration of point defects into interface due to heavy deformation of the powders upon BM [29].

However, the diffraction peaks were noticeably broadened by the rising BM process time up to 10 h, which indicates a decrease of crystallite size and an increase of lattice parameter and microstrain during BM. In other words, peak broadening is an effect of diminishing particle size and introducing microstrain during BM, in which the crystallite size and microstrain were calculated in the ensuing research. Furthermore, the BM process is followed by decreasing of Bragg peak intensity and increment of Bragg peak width attributed to increasing the internal lattice strain and crystallite size refinement. Accordingly, the crystallite size and microstrain were calculated based on the best Rietveld refinement of the corresponding patterns after the formation of the QC phase beyond 3 h BM. For this purpose, the fitting process was repeated continuously until the parameter $R_b$ became smaller than 10%. Figure 3 shows a plot of crystalline size and microstrain components of inherent diffraction peak profile as a function of milling time using Rietveld structure analysis of entire pattern fitting structure refinement in favor of broadened peaks, which employs powder diffraction step-scanned intensities as a replacement for integrated powder intensities. The peak broadening of the diffraction profile is commonly affected by the crystallite size and microstrain, together, which is considered in the present estimations and the values extracted simultaneously from the XRD peak patterns.

Moreover, the crystallite size, microstrain, lattice parameters, and weight percentage of the QC/crystalline phases were estimated and exhibited in Table 1. It is obviously apparent that the weight percentage of the QC i-phase is maximum following 4 h of the BM and begins diminishing by increasing the milling time. Therefore, it can be concluded that the optimum time of BM to achieve the maximum weight percentage of i-phase, is 4 h for the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ alloy system. Figures 3(a), (b) indicates the evolutions of the crystallite size and microstrain for the QC/crystalline phases with the milling time. It was found that the computed crystallite size of the corresponding phases was to be exceptionally low and the related microstrain and lattice parameters were estimated to be so high by increment of milling time, which is an ordinary behavior of the entire metallic alloy systems synthesized by the MA process [30]. It becomes visible from figure 3 that the crystallite size and microstrain have reached the saturation values after 10 h BM, and it is complicated to attain any alterations by the further milling process. Indeed, it has been scrutinized that extended milling time beyond 10 h even through an elevated milling intensity increases the existence probability of the crystalline cubic phase ($\beta$-phase) with bcc structure besides the diminution of the crystallite size and augmentation of the microstrain [31–33]. Furthermore, it seems that the rate of grain refinement is so fast at the beginning, and gradually, decreases toward the end of the milling procedure. This effect can be owing to a balance between the increased dislocation density caused by severe plastic deformation and the recovery process governed by the annihilation of the dislocations [34]. As can be observed, the crystallite size of the QC i-phase reaches a nanometer regime following 3 h BM. Consequently, it is noticeably apparent that the QC i-phase acquired by the MA process is naturally nano-QC and the QC size declined with milling time from 3 h to 7 h and arrives at around 23 nm after 7 h BM, while the internal microstrain and lattice parameter increase with progressing of milling time up to 10 h and get to 1.1365% and 2.991 Å$^\circ$, respectively. Hence, the slight variations of the crystallite/QC size, internal
microstrain, and lattice parameters of powders during the BM process could be due to the increase of surface temperature of the powders during extended milling time [30].

3.2. Thermal behavior of as-milled powders
A differential thermal analysis (DTA) examination of the as-milled powders indicates the existence of several exothermic peaks at a range of 200 to 600 °C, as shown in figure 4. The isothermal annealing treatments for various periods of the BM powders were carried out to study the promising phase metamorphoses during annealing. Therefore, the XRD analysis was accomplished to point out every single one of major transmutations. Furthermore, different progressions of phase transformation also have been investigated by several studies [35, 36], such as processing conditions and annealing temperature, which could be affected by the ultimate structure that synthesized by the BM process and subsequent annealing treatment. In order to evaluate the effect of thermal treatments on the various ball-milled powders, the samples were annealed up to 600 °C, and afterward, quenched in the water promptly. Figure 4 shows the DTA curves of the as-milled powders following 1 h, 2 h, 4 h, and 6 h BM while heating up to 600 °C.

The particular specimens for the XRD analysis were heat-treated at the analogous temperatures to identify the most relevant phenomena corresponded to thermal analysis results and understand major phase transformations that occurred during annealing of the as-milled powders. Figure 5 shows the XRD patterns of the as-milled Al_{67}Cu_{20}Fe_{10}B_{3} specimens after annealing at preferred temperatures in which the Phase transformations were readily observed.

The Al_{67}Cu_{20}Fe_{10}B_{3} DTA curve following 1 h BM, as shown in figure 4(a), designates two exothermic peaks at around 375 °C and 480 °C. The first exothermic peak could be related to annealing out the defects created throughout the milling procedure as well as the interaction among raw materials and formation of a new ω-Al_{2}Cu_{2}Fe phase besides the θ-Al_{3}Cu and λ-Al_{13}Fe intermetallic compounds, as shown in figure 5(a). According to the XRD pattern of the annealed specimen at 375 °C, it could be perceived following annealing process leads to the interaction among an enormous amount of the θ-Al_{3}Cu phase with the λ-Al_{13}Fe and transform to the more stable ω-Al_{2}Cu_{2}Fe phase, as reported in [5, 14], i.e. the amount of θ-Al_{3}Cu phase decrease while the ω-Al_{2}Cu_{2}Fe phase creates by increasing the annealing temperature to 375 °C. As shown in figure 5(b), the second exothermic peak at around 480 °C could be due to the chemical interactions among the ω-Al_{2}Cu_{2}Fe, θ-Al_{3}Cu, and λ-Al_{13}Fe intermetallics and formation of the AlCuFeB QC i-phase and precipitation of a supersaturated solid solution (β-AlCuFe) phase besides a little amount of residual λ-Al_{13}Fe intermetallic compound. The XRD pattern also confirms that the XRD peaks of the ω-Al_{2}Cu_{2}Fe phase decrease in their intensity and disappears completely at around 480 °C by increasing the annealing temperature. On the other hand, interdiffusion among the components intensifies by increasing the milling time, which induces the solid-state reactions and leads to the formation of two new phases θ-Al_{3}Cu and λ-Al_{13}Fe during BM. When such

| Milling time (h) | Phase(s) | Weight (%) | Crystallite size (nm) | Microstrain (%) | Lattice parameters (Å) |
|-----------------|----------|------------|----------------------|----------------|-------------------|
| 3               | QC       | 92         | 44.325               | 0.4678         | —                 |
|                 |          |            |                      |                | a = 15.532        |
|                 |          |            |                      |                | b = 8.2591        |
|                 |          |            |                      |                | c = 12.509        |
|                 |          |            |                      |                | β = 110.31°       |
| 4               | QC       | 95         | 40.394               | 0.5674         | —                 |
|                 |          |            |                      |                | a = 15.357        |
|                 |          |            |                      |                | b = 8.2791        |
|                 |          |            |                      |                | c = 12.534        |
|                 |          |            |                      |                | β = 110.41°       |
| 5               | QC       | 85         | 32.703               | 0.6716         | —                 |
|                 |          |            |                      |                | a = 2.934         |
| 6               | QC       | 68         | 29.986               | 0.7968         | —                 |
|                 |          |            |                      |                | a = 2.963         |
| 7               | QC       | 53         | 23.125               | 0.8652         | —                 |
| 10              | β        | 100        | 13.125               | 1.1365         | a = 2.991         |

* Debye-Scherrer equation, where D is the crystal size, λ is the wavelength of x-ray, θ is the Braggs angle in radians, and β is the full width at half maximum of the peak in radians.

* The error is around 1%.
powders are incessantly heated up another new phase that named as \( \omega \)-Al\textsubscript{7}Cu\textsubscript{2}Fe generates. Moreover, the lattice deficiencies such as dislocations and point defects increase the interdiffusion of Al, Cu, and Fe atoms and activate the solid-state phase transformations. The chemical interactions during the annealing of the Al\textsubscript{67}Cu\textsubscript{20}Fe\textsubscript{10}B\textsubscript{3} alloy powder after 1 h BM procedure, based on thermal analysis, can be described as follows (6 to 8):

\[
\begin{align*}
\text{Al} + \text{Cu} + \text{Fe} + \text{B} \rightarrow & \quad \theta - \text{Al}_{3}\text{Cu} + \lambda - \text{Al}_{3}\text{Fe} + (\text{Al}, \text{Cu}, \text{Fe}, \text{B})_{\text{remain}}. \\
\theta - & \quad \text{Al}_{3}\text{Cu} + \lambda - \text{Al}_{3}\text{Fe} + (\text{Al}, \text{Cu}, \text{Fe})_{\text{remain}}.
\end{align*}
\]

\[
\begin{align*}
375 \degree C \quad \omega - & \quad \text{Al}_{3}\text{Cu}_{2}\text{Fe} + \theta - \text{Al}_{3}\text{Cu} + \lambda - \text{Al}_{3}\text{Fe} \\
480 \degree C \quad i - & \quad \text{AlCuFeB} + \beta - (\text{AlCuFe}) + \lambda - \text{Al}_{3}\text{Fe}
\end{align*}
\]

Figure 4 (b) indicates the Al\textsubscript{67}Cu\textsubscript{20}Fe\textsubscript{10}B\textsubscript{3} DTA curve after 2 h BM, including two broad exothermic peaks in the vicinity of 360 \degree C and 475 \degree C with approximately different nature from 1 h milled powder. The XRD patterns of the samples subjected to 2 h BM and annealed at 360 \degree C and 475 \degree C are shown in figures 5 (c), (d). The as-milled powder almost consists of \( \theta \)-Al\textsubscript{3}Cu and \( \lambda \)-Al\textsubscript{3}Fe phases before annealing at 360 \degree C, which coexisted with the remaining aluminium and a little amount of other elemental powders. However, two main phases, including AlCuFeB QC i-phase and \( \beta \)-Al(Cu,Fe) solid solution, can be observed after annealing treatments. It could be scrutinized that the \( \theta \)-Al\textsubscript{3}Cu and \( \lambda \)-Al\textsubscript{3}Fe phases dissolved and faded thoroughly and transformed into the QC i-phase and cubic \( \beta \) intermetallic compound after annealing at 360 \degree C, which indicates that the formation of the QC phase depends on the processing route [14]. It seems that the amount of \( \beta \)-Al(Cu,Fe) solid solution increases, the volume fraction of the QC i-phase decreases, and the \( \lambda \)-Al\textsubscript{3}Fe phase precipitates by rising the annealing temperature to 475 \degree C. Moreover, the structure and behavior of the annealed sample at 475 \degree C, based on the acquired data from the XRD and DTA measurements, is comparable to the one obtained after 1 h BM and resultant annealing at 480 \degree C, i.e. the structures are almost stable beyond about 475 \degree C, just before 600 \degree C. Consequently, only two most important transformations occur in the annealing of 2 h ball-milled powder, which is exposed in the following equations (9) to (11):

\[
\begin{align*}
\text{Al} + \text{Cu} + \text{Fe} + \text{B} \rightarrow & \quad \theta - \text{Al}_{3}\text{Cu} + \lambda - \text{Al}_{3}\text{Fe} + (\text{Al}, \text{Cu}, \text{Fe}, \text{B})_{\text{remain}}. \\
\theta - & \quad \text{Al}_{3}\text{Cu} + \lambda - \text{Al}_{3}\text{Fe} + (\text{Al}, \text{Cu}, \text{Fe})_{\text{remain}}.
\end{align*}
\]

\[
\begin{align*}
360 \degree C \quad i - & \quad \text{AlCuFeB} + \beta - (\text{AlCuFe}) \\
475 \degree C \quad i - & \quad \text{AlCuFeB} + \beta - (\text{AlCuFe}) + \lambda - \text{Al}_{3}\text{Fe}
\end{align*}
\]
The QC phase was recognized in the XRD pattern following 3 h BM and continues to increase in its amount up to the 4 h BM process. It is almost a single-phase after 4 h BM procedure, which its thermal behavior was estimated and presented in figure 4(c) that indicates an extremely broad exothermic peak at around 400 °C. The XRD pattern of the Al67Cu20Fe10B3 alloy close to 400 °C, as shown in figure 5(e), contains two crystalline phases as well as a little amount of the QC i-phase. The first most relevant crystalline phase, can be indexed as the β-Al(Cu,Fe) solid solution, is the product of the QC i-phase transformation and could be formed in the as-quenched Al67Cu20Fe10B3 alloys and the second one is the λ-Al3Fe phase including a complex monoclinic structure with a huge unit cell, which is expected to be provided by the milling procedure under the current situations. Therefore, the results confirmed that the stability of the QC i-phase is below 300 °C and the feasible existence of the QC i-phase in the 4 h ball-milled powders followed by annealing accomplishment, could be above 400 °C. On the basis of the results mentioned above, the foremost solid-state reactions occurring in the annealing of the Al67Cu20Fe10B3 alloy can be explained by the following equations (12) to (13):

\[
\text{Al} + \text{Cu} + \text{Fe} + B \xrightarrow{4\text{ h MA}} \text{i} \rightarrow \text{AlCuFeB} \tag{12}
\]

\[
\text{i} \rightarrow \text{AlCuFeB} \xrightarrow{\text{above } 400^\circ\text{C}} \beta - (\text{AlCuFe}) + \text{i} \rightarrow \text{AlCuFeB} + \lambda - \text{Al}_3\text{Fe} \tag{13}
\]

By increasing the milling time exceeding 4 h, a supersaturated β-Al(Cu,Fe) solid solution initiates adjacent to the QC i-phase and augments its amount by developing the milling time, in which could become a single-phase following the 10 h BM process. The 6 h ball-milled Al67Cu20Fe10B3 alloy powder DTA curve, as exposed in figure 4(d), points out an enormously broad exothermic peak at around 400 °C after the isothermal heat treatment. As shown in figure 5(f), by pursuing the XRD pattern of the annealed specimen at 400 °C, it is observed that the QC i-phase disappeared partially and a large amount of that phase transforms into the β-Al(Cu,Fe) and λ-Al3Fe phases after annealing treatment, in which the quantity of the β-Al(Cu,Fe) phase increases to an immense extent. On the basis of the data information founded on the XRD and DTA results, the instability

Figure 5. XRD patterns of the Al67Cu20Fe10B3 as-milled powders after subsequent annealing: (a) 1 h-375 °C, (b) 1 h-480 °C, (c) 2 h-360 °C, (d) 2 h-475 °C, (e) 4 h-400 °C, and (f) 6 h-400 °C.
and transformation of the QC i-phase by increasing temperature during heat treatments are well-known, by which it could dissolve and transform to the more stable $\beta$-Al(Cu,Fe) phase. However, it is acknowledged the structural evolutions and thermal characteristics of the 6 h ball-milled powder are relatively the same as the one after 4 h BM and subsequent annealing till 600 °C, as shown in the following equations (14) to (15):

$$
\begin{align*}
\text{Al} + \text{Cu} + \text{Fe} + \text{B} & \xrightarrow{6 \text{ h MA}} \text{i-AlCuFeB} + \beta - (\text{AlCuFe}) \\
\text{i-AlCuFeB} + \beta - (\text{AlCuFe}) & \xrightarrow{\text{above 400 °C}} \beta - (\text{AlCuFe}) + \lambda - \text{Al}_2\text{Fe} + \text{i-AlCuFeB}
\end{align*}
$$

A differential thermal analysis (DTA) study of the as-milled powders is done, and its result indicates the presence of one or two exothermic peaks after the isothermal heating of the samples. The XRD analysis is carried out to assess the phase evolutions and the possible existence of the QC i-phase during annealing. The XRD outcome signifies the changes generally in the metastable $\theta$-Al$_2$Cu phase, as reported in [14], and the formation of the complex intermetallic compounds such as the $\omega$-Al$_5$Cu$_2$Fe, $\lambda$-Al$_3$Fe, $\beta$-Al(Cu,Fe), and AlCuFeB i-phase, which transform into each other through the interaction with the primary elements and also between themselves. The crystalline phases, indexes as the $\theta$-Al$_2$Cu and $\lambda$-Al$_3$Fe, are expected to be produced thanks to the interaction flanked by the remaining Al, Cu, and Fe elements during BM, while the $\beta$-Al(Cu,Fe) supersaturated phase, enriched in copper and iron, is formed throughout a long time BM. Likewise, outcome data additionally confirmed the doable existence of the $\omega$-Al$_5$Cu$_2$Fe, as a third phase in the annealed samples, and could be created by the interaction between the $\theta$-Al$_2$Cu, $\lambda$-Al$_3$Fe and remaining elemental powders by subsequent annealing treatment, which is also reported in [13] to coexist with the $\theta$-Al$_2$Cu and $\lambda$-Al$_3$Fe phases in the quickly quenched Al–Cu–Fe ternary system. Also, it was noted that the $\lambda$-Al$_3$Fe intermetallic compound could be more stable in comparison with both $\omega$-Al$_5$Cu$_2$Fe and $\theta$-Al$_2$Cu phases. Moreover, the present results of these interactions and phenomena agreed to some efforts related to Al–Cu–Fe intermetallic alloy systems produced utilizing MA [23, 25]. The QC phase formation was identified by the XRD investigations in both as-milled powders besides heat-treated samples. Although the broadening of the QC i-phase peaks is expected by enhancing the milling time due to the mechanical straining during the milling process [14, 37], the QC peaks began to sharpening by annealing procedure and continue to increase with further elevating annealing temperature caused by stress relaxation [29]. Thermal stability assessments were indicated the presence of one or two exothermic peaks at around 300 °C to 600 °C, as shown in figure 4. Therefore, annealing treatment was carried out at corresponding temperatures for further thermal stability appraisal. Accordingly, following 4 h BM just about a single QC i-phase is generated in the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ alloy system, which is worthy to mention by succeeding annealing treatment at 300 °C even for three consecutive days no changes have been made, and almost a single QC i-phase is acquired for the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ composition (as shown in figure 6). After an isothermal annealing treatment at around 360 °C to 600 °C, the QC i-phase still subsists, and its amount keeps on to decrease until it almost becomes extinct and only the $\beta$-Al(Cu,Fe) phase could be existent through elevating the milling process time up to 10 h. On the other hand, by growing the milling process time, subsequent annealing treatments lead to decreasing the QC i-phase amount, although it is still existed in a trivial volume fraction, in a way that, it could be contemplated that the BM procedure has a propensity to dwindle the QC i-phase formation. However, further studies should be carried out to estimate the precise volume fraction of the QC i-phase following annealing treatments. The annealed structures comprise a variety of the crystalline phases nearby the AlCuFeB QC i-phase, in which the $\beta$-Al(Cu,Fe) cubic type can be the most important one that could be generated in the as-quenched and mechanically alloyed AlCuFeB alloy system [23, 38]. It could be expected that the QC phase will make among the interaction between the $\theta$-Al$_2$Cu and $\lambda$-Al$_3$Fe phases with the remaining Al and the other elements during the milling and annealing procedures. It is also generated by the interaction between the $\omega$-Al$_5$Cu$_2$Fe, $\theta$-Al$_2$Cu, and $\lambda$-Al$_3$Fe phases for the period of annealing treatment. It was identified that the current corollary is in contrast to several parallel studies on Al–Cu–Fe-(B) processed by the MA and some other techniques [13, 39]. Nonetheless, it is considerably clear that the milling conditions, e.g. the intensity of planetary BM, milling rotation speed, purity of elemental powders, and media contamination, could be a reasonable explanation for the differences in such reported upshots, besides obtained following complex structures employing a high energy planetary ball mill [14]. However, the other routes were utilized to synthesis the icosahedral QC phase in the AlCuFe alloy system throughout the MA and annealing progress [15] are comparable with the current processing sequence.

### 3.3. Microstructure and morphology of as-milled powders

Figure 7 shows the field-emission scanning electron micrographs (FESEM) of the mechanically alloyed Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ samples, which demonstrates the microstructure, morphology, and grain size of the as-milled powders at different milling time durations (1 h, 2 h, 4 h, and 10 h). It is well-known that the grain size of mechanically alloyed particles decreases during the BM process, and the milling time is noticeably affected the particle size and morphology. The morphology variations of the particles have been investigated by the FESEM.
for the duration of the alloying process in which the powder particles covered on the milling medium (vials and balls) at the early steps of the alloying procedure that resulted in the reactions and interdiffusion among the powder particles [20]. The covered powder particles take out from the milling medium and crush into undersized particles by increasing the milling time and exceeding the alloying process and provide a more uniform microstructure of grains mixture. It is considered that the morphology of the mechanically alloyed powders is appreciably diverse at different milling time stages and could be agglomerates of diminutive crystals and even featureless particles in various districts of the mixed metallic powder in which the particles shape uniformity considerably improved by increasing the milling time. Figure 7(a) shows the electron micrograph of the as-received powders, subjected to 1 h BM with a shape and irregular morphology, in which the particle size distribution is quite inhomogeneous and the average particle size of powders is estimated around 95 μm. Moreover, figure 7(a) clearly illustrates grains and pointed grain boundaries, whereas increasing the milling time result in decreasing the grain boundaries sharpness. In this regard, figure 7(b) shows the FESEM image of 2 h ball-milled powder, which indicates the agglomerated particles of the θ-Al2Cu and λ-Al3Fe intermetallic phases and remaining primary elements with, heterogeneous and disorder tangled shape distribution, instead of separately sharp grain border particles. Additionally, it can be seen the grain refinement and decreasing the particle size in comparison to 1 h ball-milled powder (∼60 μm), whilst the irregularity temperament of the particles is still visible in the short-term milling times. Nevertheless, the particles have a propensity to achieve a higher uniformity and homogeneity through the development of the milling process and rising the milling time in which the shape of the particles is more similar to each other. As shown in figure 7(c), by increasing the milling time up to 4 h, the morphology of the as-milled product is modified and the particle size considerably reduced and achieved to about 800 nm in some areas. Moreover, the particle size distribution homogenizes much better, while the morphology of some particles is still featureless, and agglomeration existed, and it could be supposed that each particle in the agglomerates is a single QC [23]. Figure 7(d) represents the relatively uniform distribution of Al67Cu20Fe10B3 powders after 10 h BM with an average particle size of 460 nm, which points out only a little agglomeration of the particles. It is interesting to note that the average particle size of the powders, as measured by the FESEM image analyzer is relatively comparable to that calculated by the Coulter counter model.

It is realized that during the MA process, the solid-state reactions increase by intensifying the milling time, which results in the formation of large luminant particles with fine ‘lamella’ structures (as shown in figure 7(e)) including slaty featureless crystals in the as-milled product. Accordingly, the big luminant particles, comprising lattice imperfections (dislocations and point defects), clearly illustrate the interdiffusion of the primary elements (Al, Cu, Fe, and B atoms) and the solid-state phase transformations for the period of the BM process. Inset of
Figure 7. FESEM of the mechanically alloyed Al67Cu20Fe10B3 powders after (a) 1 h, (b) 2 h, (c), (e), (f) 4 h, and (d) 10 h and the EDX of 4 h mechanically alloyed powder (g).

Figure 7(e), the chemical analysis was carried out using the EDX technique to identify the nature of the luminant particles following 4 h BM, which is recognized that the QC i-phase being the dominant phase of these particles and confirmed the nominal elemental composition of the Al67Cu20Fe10B3 QC i-phase under the current investigational conditions. Furthermore, figure 7(f) reveals one distinctive image of the as-milled powder subjected to 4 h BM that containing a single nano QC i-phase particle with the faceted pentagonal dodecahedral morphology that reflects the icosahedral symmetry of the QC phases [40] in which confirms the existence of QC i-phase. Moreover, as shown in figure 7(g), the EDX examination fallout confirms the composition of the QC i-phase particle. Nevertheless, a little amount of iron contamination from milling medium (vials and balls) was detected (about 1.89 at%) based on the obtaining data from the EDX interpretation corresponding to 4 h MA, in which any type of other pollutions was not identified promisingly, besides a few losses of the Al component. Figure 8 shows the backscattered FESEM images of the mechanically alloyed samples, indicating the microstructure of the as-milled powders following 1 h, 2 h, 4 h, and 10 h BM. Figures 8(a), (b) demonstrate the microstructure of 1 h and 2 h BM powders with irregular shapes and inhomogeneous distributions that illustrate the presence of the elemental powders mixture and two other crystalline intermetallic compounds (θ-Al2Cu and λ-Al3Fe). Figure 8(c) shows the FESEM image of the Al67Cu20Fe10B3 alloy system subjected to 4 h BM that containing the faceted pentagonal dodecahedral QC particles in some regions in which the composition of the proper particles comprising the QC i-phase was investigated using the EDX analyzer. Inset of figure 8(e), it is
found that the composition of the synthesized powder following 4 h BM is reasonably adjacent to the nominal composition corresponding to the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ alloy system. Furthermore, figure 8(d) represents the moderately homogeneous dispersion of the $\beta$-Al(Cu,Fe) solid solution phase as a single-phase after 10 h BM of the Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ alloy system.

Therefore, the acquired experimental consequences verified that the usage of the MA method could lead to the formation of a stable AlCuFeB icosahedral QC phase, which proves that the phase composition of the as-milled Al$_{67}$Cu$_{20}$Fe$_{10}$B$_3$ products primarily relies on the milling time and secondly, the heat treatment procedure. Likewise, the as-milled powders include not only the QC phase but also a small amount of other crystallite intermetallic phases, which could be made by changes in the chemical composition of the powders during the BM process that can be attributed to the iron contamination at long times of BM, as a result of the grinding media and jar abrasion. The EDX results demonstrate this phenomenon by increasing iron content (about 3–4 atomic percent) and indicate a little amount of pollution from the BM medium and also an increase in the oxygen content in the as-milled powders.
3.4. Cold isostatic pressing of as-milled powders

The consolidation of the powders into bulk specimens of 30 mm in diameter was carried out under the pressure of 400 MPa at 25 °C with the soaking time of 5 min. The as-milled powders initially were blended separately once more to attain homogeneous composition utilizing a low energy ball mill with a rotation speed of 100 rpm and ball to powder ratio of 5:1 for 1 h. The blended samples subsequently were loaded into a cylindrical elastomeric mold and consolidated through a CIP apparatus, which is intended to fabricate a green density with maximum value based on the compressibility of the mechanically alloyed powders. Moreover, the green density of each specimen principally depends on its composition and compaction conditions such as pressure factors [41] in which the samples with the practically similar compositions have almost the same green density. Accordingly, table 2 shows the densities of consolidated as-milled powders, besides figure 9 exhibits the relative green density of that samples in the histogram, which can readily compare the density of each sample and observe the similarity. The density variations of the as-received samples are owing to the experimental operations in which the as-received samples subjected to 1 h BM have the most amount of elemental powders, and consequently, have the highest density amongst the others (as shown in figure 9).

3.5. Microhardness measurements

The astonishing characteristics of the electron configuration of QCs lead to atypical advantages such as high strength and hardness, which could be practical for industrial applications [42, 43]. The Young’s modulus of the QCs is about 100–200 GPa, and the hardness of the AlCuFe QC alloy is around 10 % of Young’s modulus, which is nearby the values for diamonds and several ceramics [42, 44]. It was perceived that an enhancement in temperature results in a momentous decrease in the hardness of the QC phases [42, 44]. The Vickers microhardness was computed by the amended standard equation (1). Figure 10 shows the microhardness of the CIP consolidated specimens calculated through a Vickers indentation, which is employed a tetrahedral diamond pyramid with a load of 10 g and dwell time of 15 s. As shown in figure 10, the microhardness of the samples significantly depends on milling time and composition of the as-milled powders in which the microhardness magnitude notably changed by progressing the milling time. In this regard, the compositional changes at various time of milling procedure affected the microstructure and mechanical properties of the materials such as the microhardness in which the microhardness examination has been extensively used to characterize the effect of composition on the mechanical properties of fabricated samples [45–47].

However, the microhardness of consolidated specimens considerably amplifies by increasing the milling time up to 4 h, and subsequent enhancement in the milling time generally causes a decrease in the microhardness in which escalating the time of holding pressure under CIP process particularly leads to a substantial augment in the microhardness. The maximum microhardness values were observed for consolidated samples subjected to 4 h BM after a 5 min holding under pressure since the main phase of the consolidated samples is the QC i-phase. Furthermore, the 4 h ball-milled sample shows a notable higher microhardness value rather than the others. The microhardness variations apparently can be attributed to the presence of different phases and the texture of the above-mentioned specimens. The differences in the microhardness of AlCu2Fe0.5B3 are related directly to their crystallite size [33] and also the amount of the QC phase formation, which depends on the milling time. Inset of figure 10, the variation of microhardness of consolidated ball-milled powders as a function of milling time noticeably demonstrated. It is manifest that the microhardness increased significantly at the beginning stages of the milling process, and the microhardness of the initial sample (4.54 GPa, 1 h ball-milled) increases with milling time in three steps, i.e., after 2 h, 3 h, and 4 h attain to 6.52 GPa, 9.26 GPa, and then 10.73 GPa, respectively. Moreover, owing to the softening behavior and chemical composition of the as-milled powders, the microhardness decreases into 8.80 GPa, 7.21 GPa, and 6.86 GPa following 5 h, 6 h, and 7 h MA, respectively after achieving the maximum value of 10.73 GPa. The softening of the QCs as brittle materials is an illustrous approach to improve the performance of these materials by refining the grain size from micrometer to nanometer, which is well-known as Hall-Petch relationship that provides a semi-empirical correlation between the grain size and yield stress, and can be expressed by the following equation [33]:

\[ \sigma = \sigma_0 + k_d^{-\frac{1}{2}} \]  \hspace{1cm} (16)

Where \( \sigma_0 \) is the frictional stress, which is the general resistance of crystalline lattice to dislocation movement, \( k \) is the locking parameter that measures the relative hardening contribution of the grain boundaries, and \( d \) is the average diameter of the grains, characterizing the crystallite size. A parallel expression can be presented for the hardness of the materials as [33]:

\[ H = H_0 + k_H d^{-\frac{1}{2}} \]  \hspace{1cm} (17)

Accordingly, the microhardness of the consolidated sample noticeably intensifies and reaches 8.55 GPa through increasing the milling time up to 10 h. Moreover, the microhardness test is carried out at room
Table 2. Densities of consolidated as-milled powders.

| Milling time (h) | Density (g cm\(^{-3}\)) |
|------------------|--------------------------|
| 1                | 2.99 ± 0.47              |
| 2                | 2.94 ± 0.45              |
| 3                | 2.85 ± 0.37              |
| 4                | 2.79 ± 0.34              |
| 5                | 2.65 ± 0.28              |
| 6                | 2.54 ± 0.26              |
| 7                | 2.45 ± 0.23              |
| 10               | 2.21 ± 0.17              |
temperature to show a relationship involving the chemical composition and the intensity of Cu and Fe dissolved in diverse phases of the AlCuFeB alloy system on the distinctive microhardness of the fabricated samples.

4. Conclusions

The QC alloys are novel materials, which can be used in several regions of highly developed technology. In this paper, the QC i-phase was in situ synthesized by the MA procedure and consolidated through a CIP apparatus. The structural and microstructural evolutions, thermal behavior, and microhardness of the AlCuFeB QC alloys were estimated.
The stable icosahedral phase could be formed instantly by a high-energy planetary ball milling process, in which 4 h milling resulted in the formation of almost a single QC phase, while a long-time BM induced the formation of a supersaturated solid solution $\beta$-Al(Cu,Fe) cubic phase.

The stability of the icosahedral phase was about 300 °C, which was misplaced stability at superior temperatures and transforms into crystalline phases and decreases its volume fraction, but a proper milling procedure promoted the formation of the QC i-phase besides the crystallite phases after subsequent annealing treatment at a suitable temperature.

The microhardness of the consolidated as-milled powders at various milling times was determined, and it is well-known that the 4 h ball-milled compact in which the QC i-phase is dominant, has an enormous microhardness of about 10.73 GPa.

Although almost a single QC phase was acquired, following the BM process in the present study, a high weight percentage of the QC phase could be obtained by optimizing the milling time and annealing temperature.

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