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Formation of nano quasicrystalline phases by mechanical alloying of ternary systems $Al_{86}Cr_8Fe_6$ and $Al_{62.5}Cu_{25}Fe_{12.5}$

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ABSTRACT

The formation of the quasicrystalline ternary system $Al_{86}Cr_8Fe_6$ and the i-phase $Al_{62.5}Cu_{25}Fe_{12.5}$ by mechanical alloying technique have been investigated. The structural evolution during milling at various stages and after a subsequent annealing are examined by x- ray diffraction technique. No ternary intermetallic phase could be detected during the milling process in the AlCrFe system, but transit types of phases which eventually transformed to amorphous state at the end of milling process. The formation of $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystalline phase has been formed by mechanical alloying followed by thermal treatment which was mixed with intermetallic phase, which was formed during milling.

KEYWORDS

Mechanical alloying (MA);
Quasicrystalline (QC);
X-ray diffraction (XRD);
Differential thermal analysis (DTA);
Room-temperature resistivity.

INTRODUCTION

Since the discovery of the first quasicrystal in 1984 in Al Mn alloy[1] and then the discovery of first stable and perfect quasicrystal with high structural quality in Al Cu Fe alloy[2]. The quasicrystals have attracted considerable interest due to their unique atomic structure and extraordinary physical properties.

The quasicrystal phase formation has been observed for several alloys system mainly Al-base with a transition elements content and this mainly produced by liquid phase quenching[3,4]. However, a few attempts were carried out to produce the quasicrystalline phase using mechanical alloying technique from a ternary composition[5,6]. It is generally known that the crystalline state has a lower free enthalpy than the amorphous or the quasicrystalline phase respectively. However, for certain alloying compositions, icosahedral phase has been reported to be thermodynamically stable[7,8], but in general the majority of quasicrystalline phases are metastable.

For the Al-rich corner with Cr and Fe content between 10 to 20 at%, a rapidly solidified composition showed no ternary intermetallic phases in the structure, but rather the quasiphase in addition to the binary intermetallic phases in the structure[3].

The quasicrystalline Al Cu Fe phase (i – phase) was originally produced by rapid solidification from the liquid state[2,9,10]. Few years later, it was reported that, the quasicrystalline Al Cu Fe phase can be prepared by mechanical alloying (MA) process[11,12] which is of significant applied interest, Because it allows the production of quasicrystalline powders in an industrial scale and without very high costs, which are the advantages over the production of quasicrystals in the form of ribbon by rapid solidification technique.

The published results about the production of i – Al Cu Fe phase by MA show some apparent controversy. Eckert at al.[4] has reported that, it was not possible to obtain the i- phase for a composition $Al_{62.5}Cu_{25}Fe_{12.5}$ directly by milling process. On the other hand, Asahi at al.[11] has reported that, a p-type (meta-stable) i – phase was obtained directly by milling, which is transformed to F-type stable i-phase by further annealing. Salimon et. al.[12] has reported that, it was possible to obtain the i - phase as a secondary phase with very small volume fraction after milling and further annealing, while the predominance of another phase β - Al (Cu, Fe) was observed and have been related to a shift in composition due to contamination by iron as well as Al depletion. However, a combination of milling and subsequent annealing could enhance the formation of quasicrystalline phase in $Al_{65}Cr_{25}Fe_{15}$ at temperature above 600 C[13].

The first aim of the present work, is an attempt to find out whether it is possible to obtain quasicrystalline phase in Al-Cr-Fe system by mechanical alloying process. Secondly, is to study the possibility of producing the $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystalline phase by mechanical alloying and to try to deduce the mechanism involved and the factors affecting the milling and the annealing process.

EXPERIMENTAL PROCEDURE

Pure elemental aluminium (99.95 %), iron (97.7 %), Chromium (98 %), and Cu (99.9 %) are used as starting powders to make up the desired compositions, of $Al_{86}Cr_8Fe_6$ and $Al_{62.5}Cu_{25}Fe_{12.5}$. A 2 % organic surfactant (Stearic Acid) is added to the powders to act as a process control agent. The starting material mixture is charged into the attritor vial, and the ratio of ball to powders weight was 10 : 1 (100 gm of different diameter balls are used). To minimize contamination with oxygen and/or nitrogen, the mechanical alloying process is carried out under dry argon atmosphere.

X-ray diffraction study is carried out using a Siemens D5000 (computer controlled) powder diffractometer with a nickel filtered Cu-K_α radiation (wavelength $\lambda = 1.5406$ Å). The thermal stability of certain samples has been monitored with differential thermal analysis (DTA), Perkin-Elmer DTA7 (computer controlled). The sample is heated with a constant heating rate 15 K s^{-1} in static air as a furnace atmosphere.

Electrical resistivity of the mechanically alloyed and annealed compacted powders of $Al_{62.5}Cu_{25}Fe_{12.5}$ has been studied using high current source, by examining the current passed on the sample – the sample coated by silver paint – and the corresponding voltage by using the sandwich method. The resistance "R" of the compacted sample was estimated by drawing the I – V curve, from which the resistivity "ρ" was calculated.

RESULTS AND DISCUSSION

The $Al_{86}Cr_8Fe_6$ system

For the ternary aluminum base mixture with 8 at% Cr and 6 at% Fe, a complete amorphization is only observed after 150 hs milling. XRD results, shown in Figure 1, suggested that after 30 hs milling α-Al (Cr) and/or α-Al (Fe) solid solution are formed.

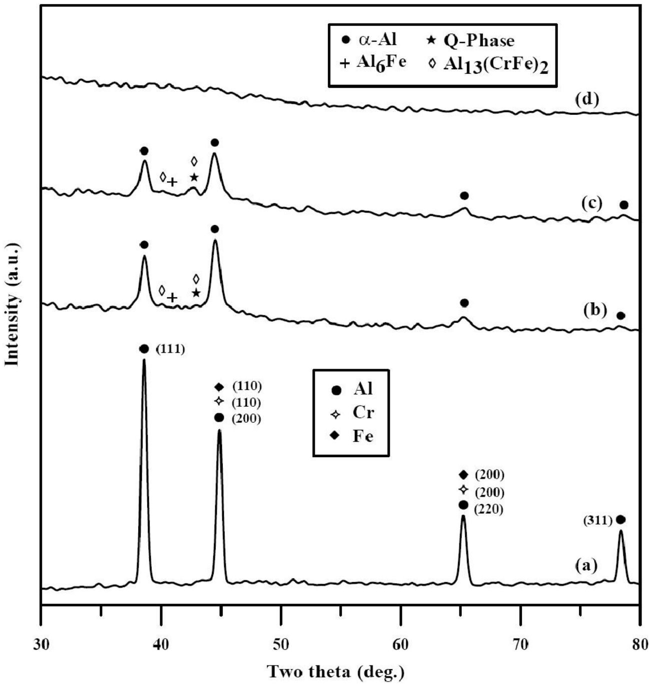

Figure 1 : XRD patterns of mechanically alloyed "$Al_{86}Cr_8Fe_6$" for: a) 0 h, b) 30 hs, c) 40 hs, d) 150 hs.

Such results are similar to that obtained for binary Al – Cr and Al – Fe systems, where a supersaturated α-Al solid solution phases are formed with milling time[14]. The observed peaks broadening with milling time is an indication of particular refining. The mean particle size for 40 hs milled powder ≅ 22 nm has been estimated using Williamson-Hall plot[15], as shown in Figure 2. Moreover, no ternary intermetallic phase could be detected after the milling process, which confirms early results by rapid quenching as well as a published ternary diagram of Al-rich corner with Cr and Fe, where no ternary phase is reported up to 600 C[16]. In the equilibrium conditions and for the present composition, three types of phases are expected to coexist; α-Al, $Al_{13}Cr_2$ and $Al_{13}Fe_4$. However, a quasiphase appears during rapid quenched of Al – 3Cr – xFe (x = 0, 1, or 3 at %)[3].

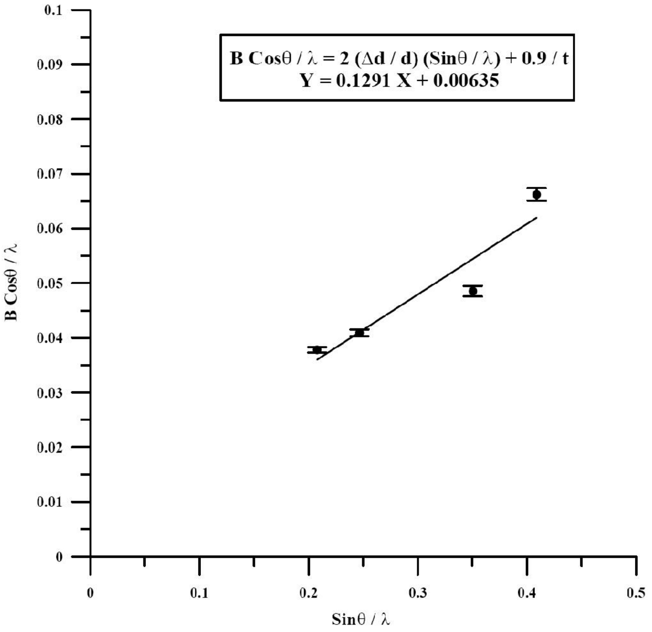

Figure 2 : Williamson-Hall plot for 40 hs milled powder for “$Al_{86}Cr_8Fe_6$”.

After 40 hs milling, in the diffraction range of 2θ = 35 to 55 shown in Figure 1, a few new low intensity peaks were observed in XRD pattern. The difficulties of indexing arose from peak overlapping of different phases, e.g., the (820) peak of $Al_{13}Cr_2$ of d = 0.207 nm is very close with the (20, 32) of quasiphase of d = 0.2007 nm. Also, the peaks (310) and (025) diffracted by Al_6Fe and $Al_{13}Fe_4$ of d = 0.206 and 0.205 nm, respectively. It is, therefore, within such limits the possible phases after 40 hs milling are the supersaturated α-Al as matrix, containing Al_6Fe, quasiphase and $Al_{13}(CrFe)_2$ phase. Difficulty exist to confirm the presence of the intermetallic $Al_{13}Fe_4$, and $Al_{13}Cr_2$ as separate phases because of the large possibility of Cr to be replaced by a considerable amount of iron atoms in the $Al_{13}Cr_2$ structure[17]. Such substitution process would only results in slight changes of the d-values of the $Al_{13}Cr_2$ phase. The overlapping between both intermetallic phase lines, make such separation by X-ray technique almost impossible.

A thermal treatment has been carried on the metastable phases that formed after 40 hs milling, in order to be evaluated. Figure 3 shows the DTA curve where three exothermic peaks can be observed, indicating various types of phases transformation.

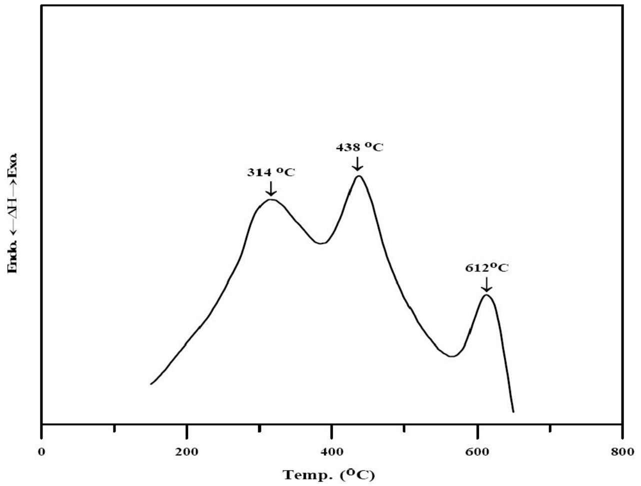

Figure 3 : DTA curve for 40 hs milled powder for “$Al_{86}Cr_8Fe_6$”.

Isothermal annealing for a long time up to 70 hs at a relative low temperature of 350 C is carried out. Following 10 hs annealing, XRD shown in Figure 4 indi-

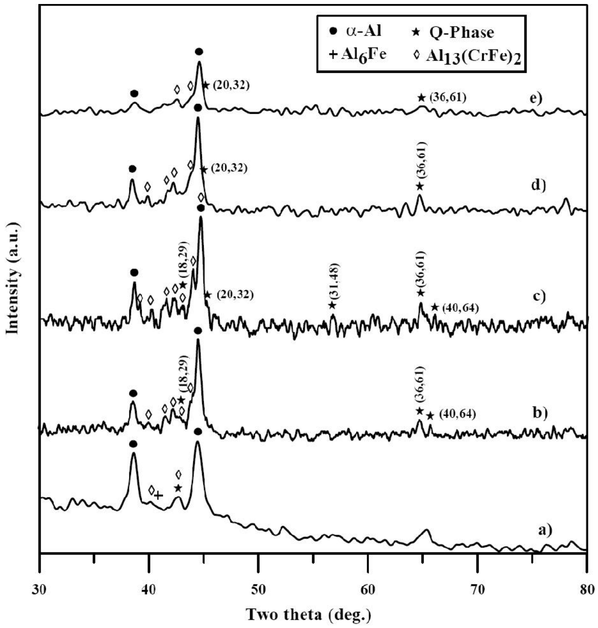

Figure 4 : XRD patterns for 40 hs mechanically alloyed “$Al_{86}Cr_8Fe_6$” annealed at 360 C for: a) as milled, b) 10 hs, c) 30 hs, d) 50 hs, e) 70 hs.

cated the presence of α-Al with a slight increase of the d-values which could be related to the dissolution of the supersaturated α-Al to the equilibrium solid solution concentration. It is also important to note that even increasing annealing times up to 70 hs, the metastable quasicrystalline phase continue to be present in structure of the sample.

Annealing is also carried at relative higher temperatures of 500 and 650 C for a period of time from 5 to 15 hs for the 40 hs milled specimens. XRD results are shown in Figures 5, 6 for both temperatures in respective manner. The quasicrystalline phase continues to be present following such treatments. However, following the peaks intensities it is possible to indicate that a smaller amount of the quasicrystalline phase is present at higher temperature and annealing times. Therefore, this transformation is a time and temperature dependent and could indicate a self diffusion mechanism, where the amount of defects plays a controlling role. On the other hand, lines intensity increases after such treatment could suggest an increase of the intermetallic phase $Al_{13}(CrFe)_2$. Further quantitative analysis is needed to exactly determine the volume fraction of both quasi and intermetallic phases after the annealing treatment.

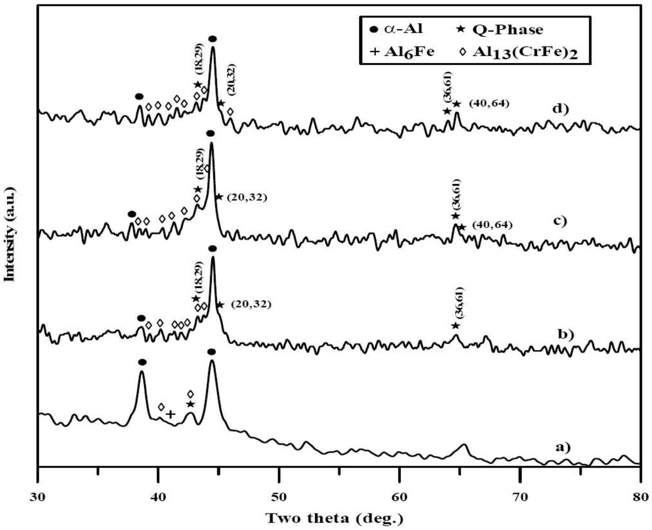

Figure 5 : XRD patterns for 40 hs mechanically alloyed "$Al_{86}Cr_8Fe_6$" annealed at 500 C for: a) as milled, b) 5 hs, c) 10 hs, d) 15 hs.

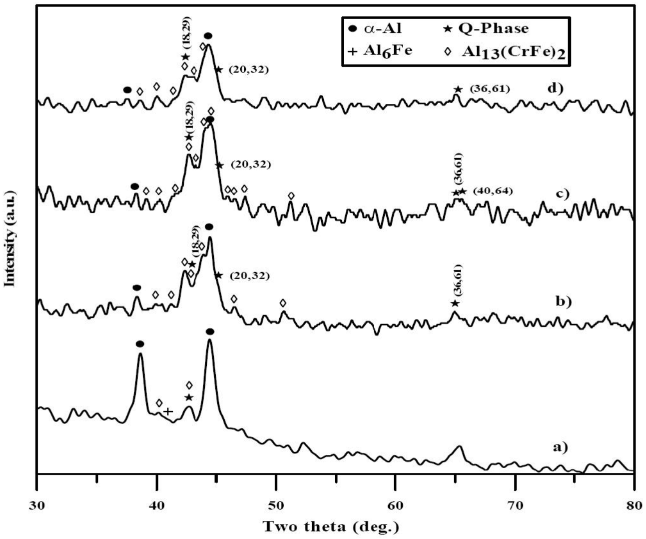

Figure 6 : XRD patterns for 40 hs mechanically alloyed "$Al_{86}Cr_8Fe_6$" annealed at 650 C for: a) as milled, b) 5 hs, c) 10 hs, d) 15 hs.

The room-temperature resistivity (ρ) measurement after various annealing times at 350 C "as an example", is shown in Figure 7. The observed changes in ρ-values can be considered as indication of the continues changes of both the number and the type of phases evaluation during the isothermal treatment, as indicated previously by the X-ray results.

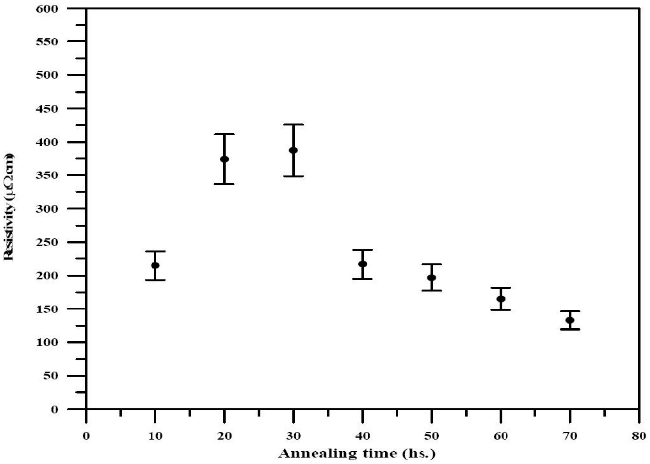

Figure 7 : Resistivity changes with the annealing tine for 40 hs. milled powder "$Al_{86}Cr_8Fe_6$" annealed at 350 C.

Similar processing sequence is reported by Eckert et. al.[18], on the nature of phase synthesized in Al-Cr-Mn which depends on the intensity of milling and the quasi-phase appears at an intermediate stage between the solid solution phase formation and the equilibrium intermetallic structures. This has been explained to be due to a rise in milling temperature with higher milling intensity. The increase of milling intensity could be thought been equivalent to the sequence of milling with the subsequent thermal treatment used with the present ternary system.

In a previous study[14] on both binary $Al_{86}Cr_{14}$ and

$Al_{84}Fe_{16}$ processed by MA, it has been indicated that the quasi-phase can only be obtained for Al-Cr system after thermal treatment following the milling stage however; Al-Fe only yields various types of intermetallic phases. It is, therefore, possible that the presence of iron atoms in the ternary system would result in a higher milling intensity with all other factors been equivalent. The harder iron atoms in the ternary system will compensate the required thermal energy for the binary system Al-Cr to increase the milling intensity which is required for the formation of the quasi-phase in the ternary system.

The $Al_{62.5}Cu_{25}Fe_{12.5}$ system

The as-milled samples

Figure 8 shows the x ray diffraction pattern of the milled sample after different milling times, line broadening and reduced intensities of essential elemental lines are observed, which become more pronounced with the increasing of milling time Figures 8.b, 8.c and 8.d, in addition to gradual disappearance of certain diffracting lines. At this stage, it is also possible to detect the formation of the first intermettalic phase Al_2Cu, where the strongest peak of this phase at $2\theta = 47.78\,^{o}$ appears relatively weak in intensity in addition to some diffused peaks, indicating that only a small amount of this phase is formed. The intermettalic formation at this early stage could be possibly related to in homogeneity in the composition distribution.

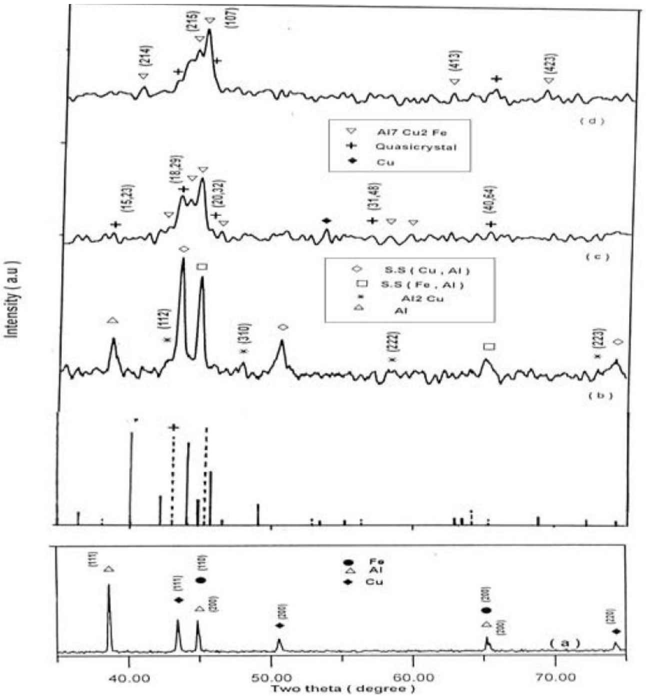

Figure 8 : XRD patterns of mechanically alloyed "$Al_{62.5}Cu_{25}Fe_{12.5}$" sample for: a) mixed elements (0 h), b) 10 hs, c) 20 hs, d) 30 hs.

Moreover, the observed increase of the measured d-values of the elemental lines of both Cu and Fe and reduced intensities of Al lines can be an indication of solid solution formation, based on atomic radii differences of the elements (r (Fe) > r (Cu) > r (Al)) it is possible to obtain more than one solid solution such as Al (Cu) and Al (Fe) solid solutions. However, it is necessary to stress on the fact that, not all the elements are consumed in the formation of both solid solution phases.

As the milling time increases up to 20 h. Figure 8.c, it is observed that only a few weak intensities of the elemental powders are observed, and the expected increase of the intermetallic Al_2Cu intensity with milling is not observed. This could indicate that, further homogeneity and powder interaction took place. This is mainly observed in 2θ rang of $40 - 44^0$ where it is possible to suggest the presence of a quasicrystalline phase in a primitive form, i.e., a metastable quasicrystalline, p-type, phase. At this stage, a high rate of diffusion is expected with a nanoprticle size formation during milling, Therefore, interdiffusion between early formed phases Al_2Cu, solid solutions and remaining elementals are likely to contribute to quasicrystalline phase formation. In addition, the dissolution of Al_2Cu could be responsible of the observed new intermetallic, which is indexed to be the tetragonal Al_7Cu_2Fe (ω – phase) structure, These results confirm an early idea of possible formation of a quasi - phase in this material which can be related to certain milling intensities[6].

After longer sitting of milling up to 30 h. a significant distortion can be introduced to existing structures by milling effects, such as phason or dislocation type of defects, mainly to quasicrystalline structure and consequently prevent the enhancement of such phase, but rather tend to its dissolution. XRD after 30h. Milling confirms such mechanism, where a reduction of quasicrystalline phase intensities and lines is observed and the $Al_7\,Cu_2\,Fe$ phase (ω– phase) becomes dominant phase Figure 8.d. It is to be noted that a complete dissolution of the quasicrystalline phase is not observed for this stage of milling.

The formation of $Al_7\,Cu\,_2\,Fe$ phase with milling represents a small deviation from phase expected with ternary phase diagram of Al Cu Fe at room temperature[19], the nominal used powder composition should give a quasicrystalline (i – phase) at equilibrium. Moreover, with milling a possible small depletion in both Fe and Cu in the composition might lead to the formation of the observed ω - phase, which is the closest to i– phase in the equilibrium phase diagram on the lower Cu and Fe side. The possibility of forming another close phase, such as β - Al (Cu, Fe) type[19], is also examined, but it is excluded in the present work, since the formation of such phase needs a higher degree of in homogeneity of the composition during milling, as well as relatively higher Cu and Fe content.

Moreover, with increasing milling time, a high local temperature may induce thermal relaxation that can contribute to the dissolution of the metastable quasicrystalline phase. Milling of elemental powders of $Al_{62.5}Cu_{25}Fe_{12.5}$ composition reveals that up to 30 hours processing time, no single phase of quasicrystals can be obtained, but rather a mixture of various phases formed depending on the setting time.

Thermal treated samples

Thermal analysis is carried out after 10h milling up to 800^0 C, and the DTA results indicated the existence of three extended exothermic peaks at 220^0 C, 438^0 C and 590^0 C respectively as shown in Figure 9. The fact that those peaks appears extended over a wide range of temperature could be related to a continuous type of reactions taking place with heating, they are likely to be diffusion dependent reactions. It is difficult at this stage to attribute certain peaks to a specific type of reactions.

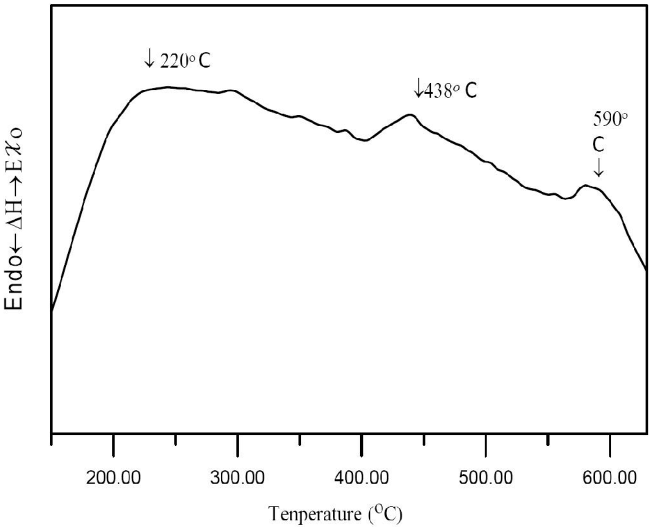

Figure 9 : DTA curve for 10 hs milled powder for “$Al_{62.5}Cu_{25}Fe_{12.5}$”

The effects of thermal isothermal heating on the produced mechanically alloyed structures are examined in function of setting time, where different structure evolution are to be expected.

At first, a short annealing time of one minute at 450 C is performed for a compacted powder after 10 h milling. XRD pattern of such treatment is shown in Figure 10.a and an important phase transformation can be noticed. The starting solid solutions, Al_2Cu and the few elemental lines have changes to a quasicrystalline structure, the Al_2Cu phase continues to be present (with reduction in its peaks intensities and numbers) with the presence of few peaks corresponding to elemental Al lines. The reduction of Al_2Cu peaks intensities and numbers can be taken as sign of the phase dissolution through an active interdiffusion mechanism in which those elements are likely to react with some of the remaining powder elements forming the observed quasicrystalline structure.

As the annealing time increases to 15 min. at 450 C it is possible to observe further reduction of Al_2Cu phase peaks, i.e. reduction in its volume fraction, the quasicrystalline phase shows reduction in its volume fraction too, as shown in Figure 10.b. Further increases of annealing time to 45 min. confirm the previous results, where the quasicrystalline phase continue to decrease, giving way to the domination of Al_7Cu_2Fe phase, Figure 10.c.

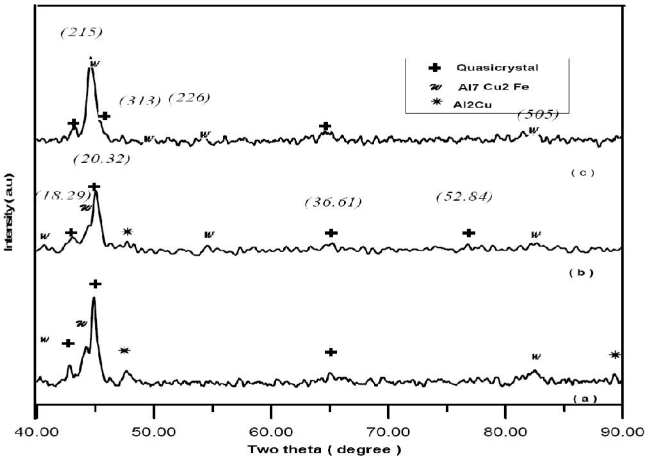

Figure 10 : XRD patterns of “$Al_{62.5}Cu_{25}Fe_{12.5}$” milled for 10 hs. followed by annealing at a) 450 C for 1 min., b) 450 C for 15 min., c) 450 C for 25 min.

For the 10h. milled specimen, annealing was carried out for 1 min at 600 C, the results show the presence of small volume fraction of quasicrystalline phase in addition to a dominating of Al_7Cu_2Fe phase, Figure 11.b. In general, it is clear that for low sitting milling time, the metastable quasicrystalline phase can be obtained only by annealing for a short period of time mainly at 450 C which will easily be transformed with increasing both annealing temperature and time to a more stable Al_7Cu_2Fe (ω–phase).

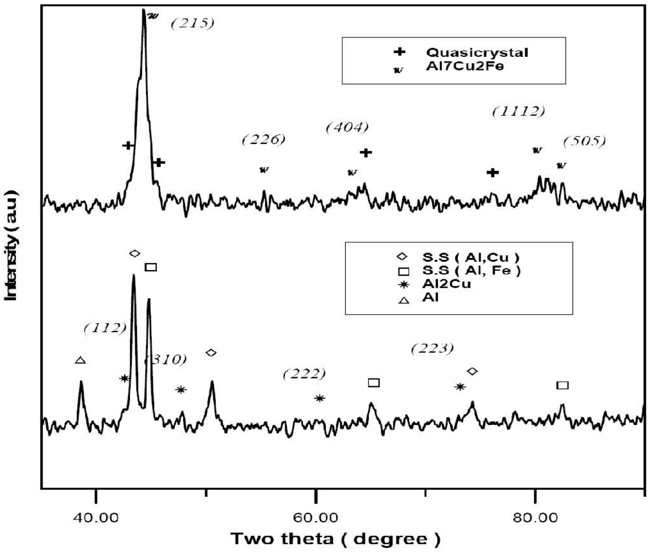

Figure 11 : XRD patterns of “$Al_{62.5}Cu_{25}Fe_{12.5}$” a) milled for 10 hs., b) milled for 10 hs. followed by annealing at 600 C for 1 min.

For higher setting milling time of 20 h. and 30 h., the obtained structures differ from the low sitting one, as indicated before. Annealing is carried out at 450 C, 500 C and 600 C for short period of time (1 min.) for each setting, their XRD are shown in Figures 12, 13. The dissolution of the quasicrystalline phase which is obtained during milling can be observed to take place gradually with increasing annealing temperature, enhancing the formation of the already existing Al_7Cu_2Fe phase. Nevertheless, traces of the quasicrystalline phase continue to appear up to 600 C annealing.

It is noticed that, annealing even up to 600 ^{0}C, did not produce sharp peaks of the final phases. This can be due to either or both effects of mechanical straining, which is not relieved by short annealing and / or a rather stable smaller particle size in the order of nanosize, i.e. no particle coarsing with annealing is obtained. It is most likely that the presence of few free iron atoms in structure during annealing will be a determining factor for delaying coarsing process through the “drag effect” mechanism, which is due to slow rate of Fe atom diffusion.

The high defect concentration introduced to composition during milling is expected to contribute to the observed high rate of phase transformation during annealing, knowing the close structure relation between the transformed phases[20]. In that respect, nanosize particles are also likely to enhance the elements rate of diffusion[21]. Another important factor which will be active during annealing is that, at certain temperatures, chemical affinity is expected to play a leading role during phase

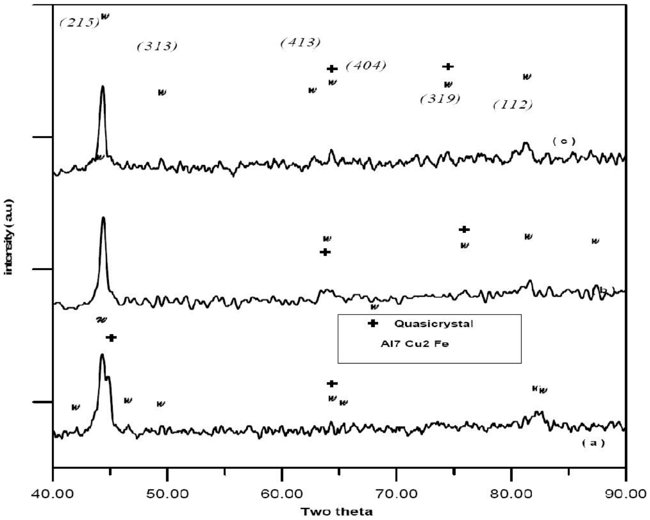

Figure 12 : XRD patterns of “$Al_{62.5}Cu_{25}Fe_{12.5}$” milled for 20 hs. followed by annealing for 1 min. at 450 C, 500 C, and 600 C respectively in upward way.

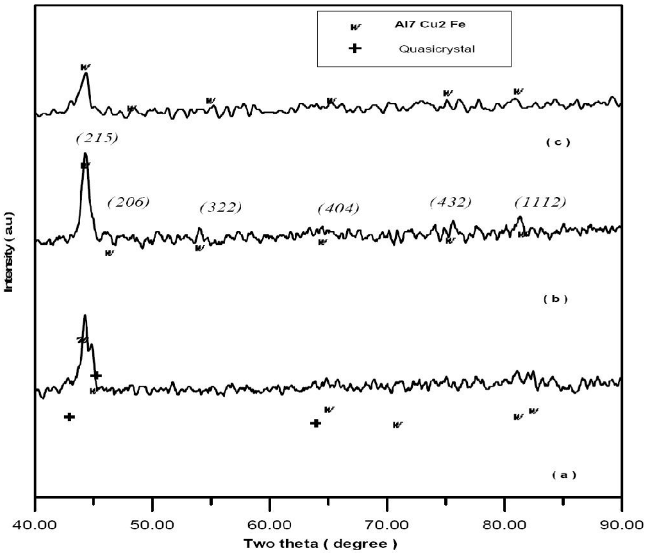

Figure 13 : XRD patterns of “$Al_{62.5}Cu_{25}Fe_{12.5}$” milled for 30 hs. followed by annealing for 1 min. at a) 450 C, b) 500 C, and c) 600 C.

transformation, although during mechanical alloying process, this role is suppressed by entropy factor[12].

CONCLUSION

The ternary $Al_{86}Cr_8Fe_6$ powders mixture when processed by mechanical alloying as well as various thermal treatments resulted in the following phases formation. A supersaturation of $\alpha - Al$ (Cr) and / or $\alpha - Al$ (Fe) formed after 40 hs milling, in addition to quasi-phase and intermetallic $Al_{13}(CrFe)_2$. Isothermal heating up to 70 hs at 350 C enhanced the existence of both quasi and intermetallic phases. Those phases are continue to be present at higher annealing temperatures of 500 and 650 C.

It is possible to conclude that, the process of mechanical alloying can be used to produce the quasicrystalline phase (i-phase) in AlCuFe alloys. The i-phase is not obtained as a single phase, but rather as a dominant phase after subsequent annealing at certain temperature and time. Further increase of the annealing temperature or time resulted in i-phase transformation into a more stable ω-phase.

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