Nanostructured icosahedral phase formation in Al 70 Cu 20 Fe 10 by mechanical alloying: Comprehensive study

P. Barua, B. S. Murty, B. K. Mathur, and V. Srinivas

Citation: Journal of Applied Physics **91**, 5353 (2002); doi: 10.1063/1.1464206
View online: http://dx.doi.org/10.1063/1.1464206
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/91/8?ver=pdfcov
Published by the AIP Publishing

Nanostructured icosahedral phase formation in $Al_{70}Cu_{20}Fe_{10}$ by mechanical alloying: Comprehensive study

P. Barua
Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur-721 302, India

B. S. Murty
Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur-721 302, India

B. K. Mathur and V. Srinivas[a)]
Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur-721 302, India

(Received 5 June 2001; accepted for publication 4 February 2002)

A systematic study on the formation and the stability of $Al_{70}Cu_{20}Fe_{10}$ quasicrystalline alloy has been carried out through mechanical alloying. The influence of the milling parameters, sequence of additive elements, and heat treatment on the formation of icosahedral phase has been investigated through x-ray diffraction analysis and transmission electron microscopy. A combination of milling and heat treatment of $Al_{70}Cu_{20}Fe_{10}$ composition resulted in the formation of a single icosahedral phase (*i*-phase) quasicrystal with face-centered structure. We present evidence that suggests the *i* phase is of a nanoquasicrystalline nature. From the present investigations, we propose an *i*-phase formation mechanism in Al–Cu–Fe system. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1464206]

I. INTRODUCTION

The discovery of thermodynamically stable quasicrystalline (QC) alloys has led to a series of interesting observations that make these alloys extremely valuable for developing a better understanding of structure and related physical properties of the icosahedral phase (*i* phase).[1–6] Among various QC alloys, the Al–Cu–Fe system is of special interest as it can be prepared with remarkable structural perfection and therefore allows one not only to understand microstructure but also the inherent properties of an *i* phase. A series of systemic investigations on the Al-rich part of the Al–Cu–Fe phase diagram showed that a pure *i* phase could only be obtained in a very narrow composition range.[4–9] Research on icosahedral structure and clarification of its growth morphology, as well as fundamental properties, are particularly important for the subsequent development of QC materials. There has been a number of investigations on the origin of the *i*-phase formation from the liquid state, though the exact mechanism of its formation is not yet clearly understood.[6–11] It was suggested that quasicrystals solidify via a peritectic reaction between $Al_{13}Fe_4$ and a residual melt in the Al–Cu–Fe system.[9] Other investigators have proposed a peritectic reaction involving β–Al(Cu,Fe), $Al_{13}Fe_4$, and liquid leading to the formation of the *i* phase.[7,8]

It is well known that the process of solid-state interdiffusion (SSID) reaction is a suitable method compared to solidification processes for the synthesis of metastable phase with good homogeneity. This method is also useful in understanding structural evolution of the *i* phase. Klein and Symko[12] have studied the growth of the *i*-phase in thin elemental layers of Al, Cu, and Fe by SSID and suggested a two-step process in which first, Al diffuses into the Fe forming Al_3Fe and later, the *i* phase grows by the diffusion of Cu into the Al_3Fe layer. Mechanical alloying (MA) is a SSID powder processing technique, allowing the production of large quantities of microscopically homogeneous materials starting from blended elemental powder mixtures.[13] Earlier experimental results on mechanically alloyed $Al_{65}Cu_{20}Fe_{15}$ showed that the QC phase with icosahedral symmetry does not form directly during ball milling.[14] Asahi *et al.*[15–17] observed the formation of the *i* phase along with an unknown impurity phase after subsequent heat treatment. But, most of these studies were restricted to $Al_{65}Cu_{20}Fe_{15}$ composition. Some attempts were made to study other compositions in order to understand the mechanism of the *i*-phase formation in Al–Cu–TM (TM=Mn,Cr, and V) system.[18–25] The studies on Al–Cu–Mn samples indicated that the *i*-phase formation is sensitive to the milling parameters and Al to the transition metal ratio.[14,19] However, such systematic studies on Fe containing samples are still missing in literature. However, it was thought that these studies would not only pave the way to the production of single-phase QC through SSID techniques but also help in understanding the underlying mechanism for its formation. More recently, synthesis of the disordered QC phase during MA of an elemental blend of $Al_{70}Cu_{20}Fe_{10}$ composition that is close to the equilibrium tetragonal phase (ω-phase) has been reported.[21,24] However, these results appear to be somewhat tentative, as the evolution of the *i*-phase has been investigated through x-ray diffraction studies alone. Apart from this, the *i*-phase formation mechanism in this system is still strongly debated. Therefore, a systematic study of $Al_{70}Cu_{20}Fe_{10}$ has been carried out in

[a)]Author to whom correspondence should be addressed; electronic mail: veeturi@phy.iitkgp.ernet.in

order to seek answers to the following questions.

(1) Is it possible to obtain a single *i* phase in $Al_{70}Cu_{20}Fe_{10}$ during milling?

(2) Do the *i*-phase formation and intermediate phase(s) depend on the sequence of addition of constituent elements?

(3) What are the intermediate phases that help in the development of the *i* phase during milling and also on subsequent heat treatment?

(4) What is the effect of milling parameters on the *i*-phase formation?

(5) Can we prepare nanoquasicrystals by mechanical alloying? How stable they are compared to bulk quasicrystals?

(6) Are these microstructural results consistent with their electrical behavior?

II. EXPERIMENTAL DETAILS

Elemental blends of Al, Cu, and Fe (99.9% purity) powders of <45 μm size, corresponding to the nominal composition of $Al_{70}Cu_{20}Fe_{10}$ have been mechanically alloyed in a low energy planetary ball mill (LEM), at a milling speed of 200 rpm in three different processing routes.

(a) *Route 1*: Elemental blend of Al, Cu, and Fe of the aforementioned composition has been milled up to 60 h.

(b) *Route 2*: An Al and Fe powder blend has been mechanically alloyed up to 20 h in the stoichiometric ratio of 3:1, aimed at the formation of Al_3Fe. At this stage, additional Al and Cu powders have been added to the mill and the milling was continued for 40 h to yield the desired final composition, $Al_{70}Cu_{20}Fe_{10}$.

(c) *Route 3*: Initially Cu and Fe powder blend has been mechanically alloyed up to 20 h in the stoichiometric ratio 2:1. Further milling in this case up to 40 h has been done with the addition of Al to make $Al_{70}Cu_{20}Fe_{10}$ composition.

Milling has been performed in toluene using hardened steel media (11 mm diameter balls) and a ball to powder weight ratio of 10:1. In order to investigate the effect of milling parameters on the *i*-phase formation mechanism and to identify the intermediate phases during milling process, milling experiments were carried out in two different types of mills. In addition to LEM, another high-energy planetary ball mill (HEM), Fritsch Pulverisette-5, with tungsten carbide (WC) milling media (10 mm diameter balls) has also been used and the details were given elsewhere.[21] The calculation of energies imparted to the powder blends during ball milling was performed on the basis of the earlier work.[26–28] The total energy transferred was 3.9×10^6 and 1.6×10^6 J/kg/h for HEM and LEM, respectively. The milled powders have been annealed at elevated temperatures after encapsulating them in quartz tubes under a vacuum of 3×10^{-5} Pa. The as-milled and heat-treated samples were characterized with a Philips 1710 x-ray diffractometer (XRD) using Co $K\alpha$ radiation, Philips CM20 transmission electron microscope (TEM), and an Oxford–Link energy dispersive x-ray (EDX) microanalyzer attached to a JEOL JSM 5800 scanning electron microscope. The powder samples were cold compacted using an eight-ton press for low temperature electrical resistivity measurements. The resistivity of the samples has been measured by a conventional four-probe dc technique in the temperature range from 85–300 K.

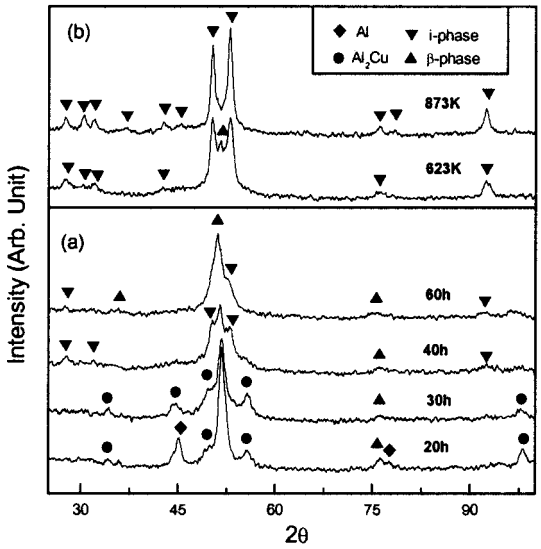

FIG. 1. XRD profiles of mechanically alloyed $Al_{70}Cu_{20}Fe_{10}$ prepared by route 1 (a) as a function of milling time and (b) subsequently heat treated for 4 h after 40 h of MA.

III. RESULTS AND DISCUSSION

A. Formation of nanoquasicrystalline phase

1. Route 1

Figure 1(a) shows the selected XRD patterns of the alloy prepared by route 1 as a function of milling time. The XRD pattern of 20 h milled sample shows the presence of residual Al along with cubic solid solution, Al(Cu,Fe) (β-phase) and Al_2Cu phase. After 30 h of milling, Al is dissolved and the XRD pattern consists of β and Al_2Cu phase, while β-phase is observed to be dominant. Milling up to 40 h has resulted in the evolution of a particular phase along with the β-phase at the expense of Al_2Cu. This phase could be identified as the *i* phase, using the indexing scheme of Bancel *et al.*[29] The volume fraction of the *i* phase has been calculated to be ~0.45 after 40 h of MA. Continued milling up to 60 h has led to the decrease of the intensity ratio of *i* phase to β-phase significantly. The fractional volume of *i* phase is observed to be small (0.17) at this stage. The composition after 40 h of milling has been analyzed by an EDX microanalyzer and found to be 70.0 at. % Al, 19.8 at. % Cu, and 10.2 at. % Fe, which is very close to the starting elemental blend. It is clearly evident that the volume fraction of the *i* phase is maximum after 40 h of MA and starts decreasing upon further milling, which is similar to that observed by Asahi *et al.*[15] in the case of $Al_{65}Cu_{20}Fe_{15}$.

We carried out an annealing study of the 40 h mechanically alloyed sample at different temperatures for 4 h. Annealing at 623 K induces a marginal increase in the relative intensity of the *i* phase (~0.66) peaks compared to β-phase [Fig. 1(b)]. At the same time, a superlattice diffraction peak at around 30.4° has been detected, which is the characteristic of the *i*-phase quasicrystal with F-type structure.[2] The sample

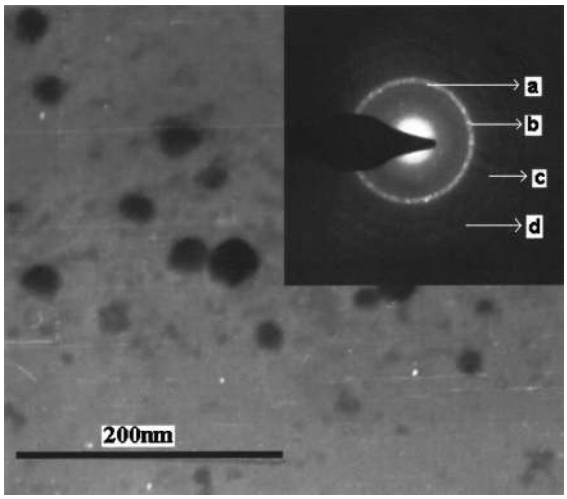

FIG. 2. TEM microgarph of 4 h heat treated (873 K) sample after 40 h of MA. Inset: the corresponding SAD pattern.

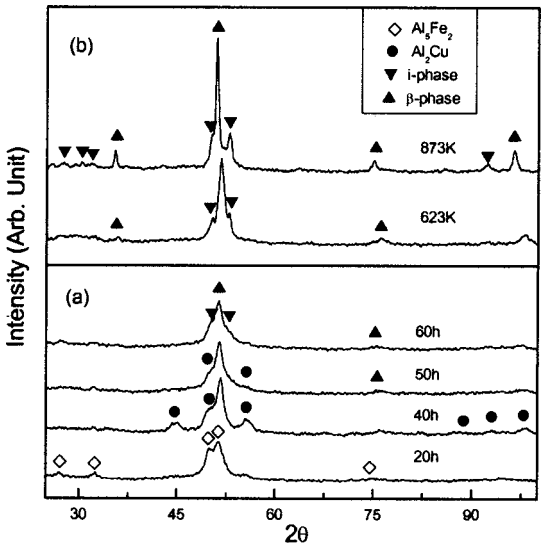

FIG. 3. XRD profiles of mechanically alloyed $Al_{70}Cu_{20}Fe_{10}$ prepared by route 2 (a) as a function of milling time and (b) subsequently heat treated for 4 h after 60 h of MA.

annealed at 873 K for 4 h shows the significant development of the peaks of the *i* phase and gives rise to the single *i*-phase F-type quasicrystal with a sharp intense peak. The volume fraction of the *i* phase is estimated to be ~1.00. A typical TEM micrograph of the 40 h milled and subsequently heat treated (873 K) sample is shown in Fig. 2. The average particle sizes of as-milled and annealed samples have been estimated to be 20 nm and 30 nm, respectively. The corresponding selected-area electron diffraction (SAD) pattern is shown inset of Fig. 2. The rings indicated as $a-d$ in Fig. 2 are identified as those belonging to the *i* phase. The ratio of the radii of the fourth (d ring) and second (b ring) rings is found to be equivalent to the golden mean (1.618) confirming icosahedral symmetry.

2. Route 2

Figure 3(a) shows the XRD patterns of the mechanically alloyed samples obtained by route 2 as a function of milling time. The MA of $Al_{75}Fe_{25}$ powder blend has resulted in the formation of an Al_5Fe_2 phase within 20 h milling. It is interesting to note that the expected Al_3Fe phase could not be observed in the present study. This could be attributed to a marginal loss of Al due to oxidation during MA, which increases the Fe content of the elemental blend. In addition, since Al_5Fe_2 is a congruent melting phase with more negative enthalpy of formation compared to Al_3Fe, the former is likely to have a higher driving force for its formation during MA. Continued milling up to 40 h, after the addition of Cu and remaining Al to yield a nominal composition of $Al_{70}Cu_{20}Fe_{10}$, leads to the formation of Al_2Cu and β-phase, the latter being the major phase. No significant change has been observed except the decrement of the peak intensity of Al_2Cu phase after 50 h of milling. However, on inspection of the XRD pattern after further milling (total milling period of 60 h), a few weaker peaks appeared around the most intense peak of the β-phase. Deconvolution of this broad peak showed that it consisted of peaks of β-phase and *i* phase. The fractional volume of the *i* phase is observed to be small (~0.14) compared to the β-phase at this stage. The composition of the blend after 60 h of milling, analyzed by an EDX microanalyzer has been found to be 69.64 at. % Al, 19.85 at. % Cu, and 10.51 at. % Fe.

The subsequent heat treatment results of the 60 h milled samples are shown are in Fig. 3(b). The sample heat treated at 623 K for 4 h shows a marginal increase in the intensity of β-phase and *i*-phase peaks compared to the as-milled (60 h) sample. Annealing at 873 K for 4 h has resulted in the diminution of the *i*-phase peaks while a significant increase in the peak intensity of β-phase and the shift in β-phase peak position to lower angles has been observed, indicating an increase in its lattice parameter. The volume fraction of the *i* phase (0.29) is less than the β-phase at this stage.

3. Route 3

Figure 4(a) shows the XRD pattern of the composition prepared by route 3 as a function of milling time. No change in elemental peaks has been observed except for the broadening of the elemental peaks after 20 h of milling, which suggests a refinement process of the elemental blends (not shown). It also indicates that Cu and Fe are immiscible at this composition under the present milling conditions. Upon further milling for 20 h (total milling period of 40 h), after the addition of Al to yield the desired composition leads to the formation of two crystalline phases (Al_2Cu and β) along with residual Al while β is the dominant phase. Continued milling up to 30 h (total milling period 50 h), leads to the dissolution of residual Al. The evolution of the *i* phase has been observed along with β-phase after 60 h of milling. The volume fraction of the *i* phase at this stage is ~0.48. The composition of the blend after 60 h of milling has been analyzed by an EDX microanalyzer to be 69.78 at. % Al, 19.27 at. % Cu, and 10.95 at. % Fe.

The heat treatment results of the XRD pattern after 60 h of MA are depicted in Fig. 4(b). The sample annealed at 623 K for 4 h shows the appearance of F-type *i*-phase quasicrystal with sharper peaks compared to the β-phase suggesting

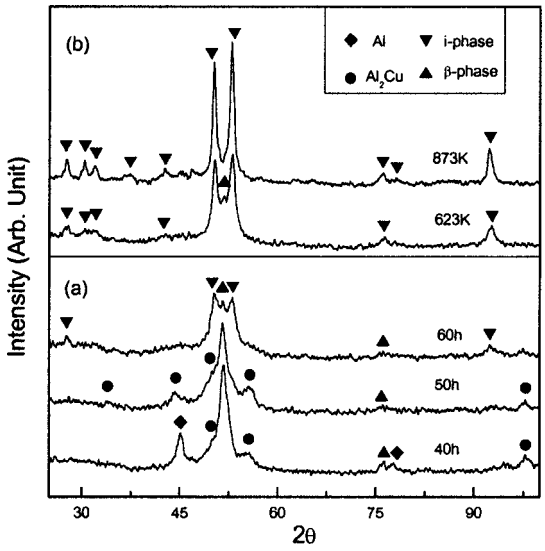

FIG. 4. XRD profiles of mechanically alloyed $Al_{70}Cu_{20}Fe_{10}$ prepared by route 3 (a) as a function of milling time and (b) subsequently heat treated for 4 h after 60 h of MA.

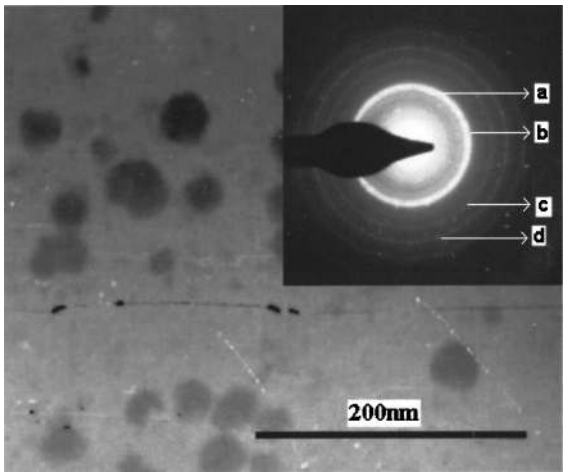

FIG. 5. TEM microgarph of 4 h heat treated (873 K) sample after 60 h of MA. Inset: the corresponding SAD pattern.

grain coarsening of the *i* phase. Further annealing at 873 K for 4 h clearly indicates the formation of almost single *i*-phase quasicrystal with F-type structure similar to that we observed in the case of route 1. The volume fraction of the *i* phase observed in this route is ~1.00. Figure 5 is the TEM micrograph obtained from the sample milled for 60 h and subsequently annealed at 873 K for 4 h. The average particle sizes of milled and annealed samples have been estimated to be around 15 nm and 35 nm, respectively. This suggests that no significant grain growth has occurred during heat treatment even at 873 K. The corresponding SAD pattern is shown in the inset of Fig. 5. Measurements of the radii of the d ring (101000) and b ring (110000) exhibit that their ratio is equal to $\tau=1.618$, the golden mean corroborating the interpretation of the x-ray results in terms of a quasicrystalline structure.

Table I shows the crystallite sizes of the *i* phase (d_i) and volume fraction of the *i* phase (f_i) after milling and annealing at different elevated temperatures. The crystallite sizes (d_i) of the *i* phase, calculated using Voigt function,[30] were found to be exceptionally low after milling and annealing at different elevated temperatures. Thus, it is apparent that the *i* phase obtained by MA is nanoquasicrystslline in nature and its rate of grain coarsening is reasonably low which is supported by TEM micrographs depicted earlier.

From these observations, it appears that the *i* phase evolves directly during MA in all the routes, though the fractional volume of the *i* phase obtained during MA in route 2 is much less. However, it appears that the mechanism of the *i*-phase formation is same for all the routes. From the present

TABLE I. Crystallite sizes (d_i) and fractional volume (f_i) of the *i* phase for various processing conditions.

Processing routes	Milling duration			Heat treated for 4 h		
				623 K	723 K	873 K
Route 1	20 h	d_i	⋯	⋯	⋯	~51 nm
		f_i	⋯	⋯	⋯	~0.57
	30 h	d_i	⋯	⋯	⋯	~34 nm
		f_i	⋯	⋯	⋯	~0.70
	40 h	d_i	~9 nm	~11 nm	~14 nm	~18 nm
		f_i	~0.45	~0.66	~0.85	~1.00
Route 2	40 h	d_i	⋯	⋯	⋯	~10 nm
		f_i	⋯	⋯	⋯	~0.83
	50 h	d_i	⋯	~10 nm	~12 nm	~15 nm
		f_i	⋯	~0.28	~0.42	~1.00
	60 h	d_i	~8 nm	~11 nm	~13 nm	~17 nm
		f_i	~0.14	~0.19	~0.38	~0.29
Route 3	40 h	d_i	⋯	⋯	⋯	~49 nm
		f_i	⋯	⋯	⋯	~0.58
	50 h	d_i	⋯	⋯	⋯	~35 nm
		f_i	⋯	⋯	⋯	~0.68
	60 h	d_i	~11 nm	~14 nm	~18 nm	~21 nm
		f_i	~0.48	~0.7	~0.88	~1.00

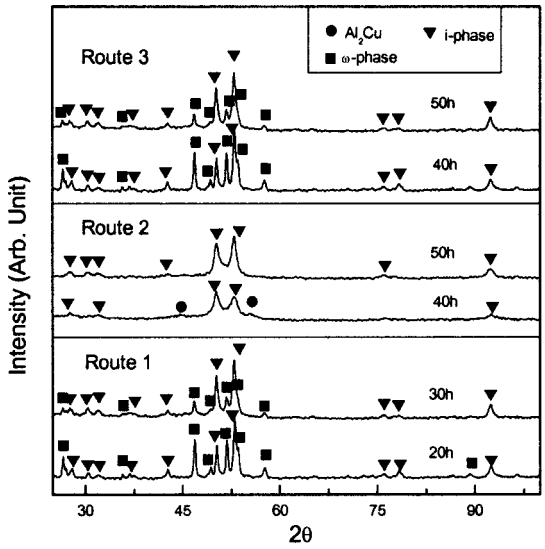

FIG. 6. XRD patterns of the milled and heat treated (873 K for 4 h) samples prepared by different processing routes.

results, it is clear that the β- and Al_2Cu phases are the essential components for the formation of the *i* phase, which appear in all three routes discussed herein. The *i* phase seems to develop through a reaction between Al_2Cu and β phase and this conclusion is in agreement with our earlier work.[21] It is interesting to point out here that Tsai *et al.*[10] reported a reaction between β- and ω- (T-Al_7Cu_2Fe) phase leading to the formation of *i* phase, in their short time milling and heat treated experiments on a mixture of Al and β-phase. However, the ω-phase has not been observed during milling or subsequent heat treatment of longer duration milled samples of the present study. In order to further examine, we carried out heat treatment experiments on short duration milled samples.

B. Effect of milling time on *i*-phase formation

Short time milling and subsequent heat treatment also resulted in *i*-phase formation.[15,24] In order to investigate the *i*-phase formation mechanism, we carried out a further annealing study of short time milled samples of all the three routes, which are depicted in Fig. 6. The evolution of ω-phase along with the *i* phase has been observed when the 20 and 30 h-milled samples of route 1 were annealing at 873 K for 4 h. It can be seen that the peak intensity of the ω-phase decreases and the *i* phase emerges as dominant phase with increasing milling time. As shown in Fig. 1(a), the 20 h-milled sample of route 1 contains residual Al in addition to the Al_2Cu and β-phase, compared to 30 h-milled sample. This indicates that the presence of excess Al during milling may lead to the formation of ω-phase. These results may be compared with 40 h (20 h milling after Al is added) and 50 h (30 h milling after Al is added) milled and annealed samples of route 3, as there was no alloying which took place during the first 20 h of milling the Cu and Fe. The presence of residual Al in the 40 h milled sample of route 3 is quite clear from Fig. 4(a), and, hence the development of more intense ω-phase peaks on heat treatment. It is clear from the Fig. 6 (see routes 1 and 3) that the peak intensity of the ω-phase decreases with increasing milling time and the formation of the β-phase has been circumvented in the short period milled samples of routes 1 and 3. These observations are consistent with the results of Saliman *et al.*[24] and Tsai *et al.*[10] It is also apparent that the β-phase gets stabilized with the increase in milling time, suppressing the ω-phase formation during subsequent heat treatment. This could be due to the change in composition of the β-phase with an increase in milling time, which probably makes the nucleation of the ω-phase more difficult. Clearly, the systematic shift of the peak position in the XRD pattern to the left-hand side with an increase in milling time during MA and subsequent annealing suggests a change in its composition. More interestingly, in route 2, the appearance of an essentially single *i*-phase ($\sim$1.00) quasicrystal has been observed in the case of 50 h (30 h of milling after the addition Cu and remaining Al) milled sample annealed at 873 K for 4 h. On the other hand, the annealing study of a relatively short time (40 h) milled sample at the same temperature led to the formation of the *i* phase ($\sim$0.83), which is associated with a small trace of the Al_2Cu phase. In this route, no sign of ω-phase was observed during heat treatment and no traces of residual Al during milling. This observation further supports our earlier conclusion. From these studies of three different processing routes, we propose that route 2 is the pragmatic way to get the *i* phase with short time milling assisted by thermal treatment. This also supports the hypothesis that the Al and Fe react first to give a binary phase and latter Cu diffuses into this binary phase leading to the formation of the *i* phase through the reaction of the β-phase and Al_2Cu phase, while annealing occurs at elevated temperatures.[9,12] It is shown that a single *i*-phase quasicrystal with F-type structure has been observed after additional heating at 873 K for 4 h in all the three routes. From these findings, it can also be suggested that, milling helps in the formation of a layered microstructure with clean interfaces between the different components. The heat produced during milling and an optimum postmilling heat treatment helps in the evolution of the *i*-phase quasicrystal with F-type structure through SSID. Although it appears that the sequence in which the different constituent elements were added during milling seem to play an important role in increasing the reaction rate. The equation of the *i*-phase formation may be written as follows:

$$\beta + Al_2Cu \xrightarrow{\text{Heat}} i \text{ phase}$$

$$\beta + Al_2Cu + Al_{\text{residual}} \xrightarrow{\text{Heat}} i \text{ phase} + \omega\text{-phase}.$$

C. Effect of milling energy

As seen, heat treatment of the short time milled sample gives rise to an *i*-phase and ω-phase, while prolonged milling results in a β-phase. Hence, an optimum milling and subsequent heat treatment is very much necessary for obtaining single-phase quasicrystals. One would expect such changes due to milling energy and milling media. In order to investigate this, we have carried out the aforementioned experi-

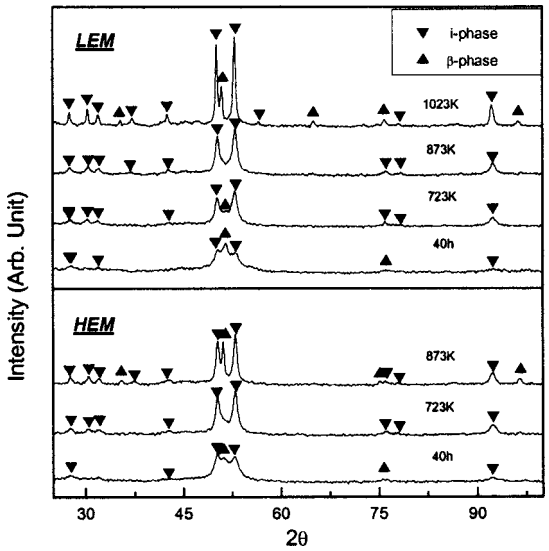

FIG. 7. Comparative study of development of the *i* phase obtained through route 1 in two different mills.

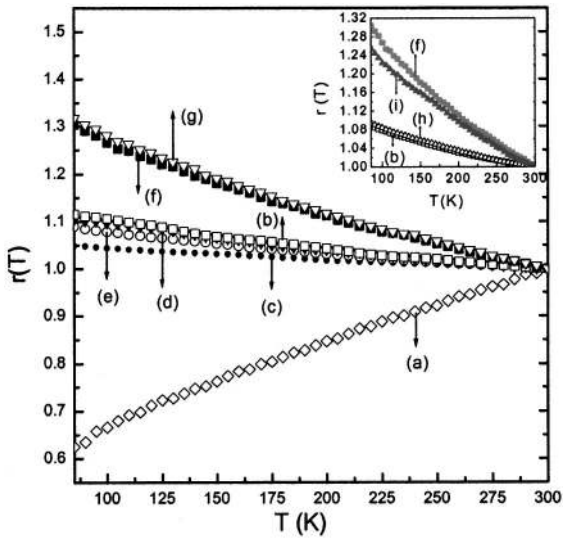

FIG. 8. Normalized resistivity, $r(T)$ as a function of temperature of: (a) unmilled; (b) 40 h (route 1); (c) 60 h (route 2); (d) 60 h (route 3) LEM milled samples; (e), (f), and (g) are the heat treated samples of (b), (c), and (d), respectively. Inset: (h) and (i) are 40 h HEM milled (route 1) and heat treated samples, respectively. All the heat treated samples mentioned annealed at 873 K for 4 h.

ments in two different mills. Although the *i*-phase formation mechanism observed during MA and subsequent annealing at elevated temperatures in both LEM and HEM is similar, there seem to be certain differences that can be noticed in Fig. 7. A single *i* phase has been observed when a 40 h milled sample annealed at 723 K in HEM and 873 K in LEM. However, partial dissolution of the *i* phase into β-phase has been observed when these samples were annealed at 873 K and 1023 K, respectively (see Fig. 7). These observations suggest that the *i* phase obtained from LEM is more stable compared to that of HEM and this could be attributed to the defects generated during the milling process. Although the total energy transfer per kg per hour is higher in the case of HEM compared to that of LEM, which seems to be not critical to the final microstructure but, of course, the kinetics of the process are dependent on the energy, and times for attaining the same microstructure can be obtained with longer periods of milling in the LEM.

D. Temperature dependence of electrical resistivity

Thermodynamically stable QC phases of high quality have various physical properties, which are very distinct from their crystalline counterparts and help in identifying the QC phase. It has been established that the electrical resistivity (ρ) of QC alloys is quite sensitive to the sample quality. The existence of a small amount of crystalline secondary phase reduces the ρ and also changes its temperature dependence drastically because the crystalline phase has orders of magnitude more conductive than QC phase. The existence of phason strain (disorder) in the QC phase also reduces the resistivity values quite significantly. Thus, the temperature dependence of ρ can be considered as good measure of quasicrystallinity. Earlier reports[5,12,31] suggest that the *i* phase shows a much higher resistivity with a negative temperature coefficient of resistivity (TCR) in comparison with crystalline and amorphous states, suggesting that it has a semiconductor-like behavior. We have carried out low temperature (85–300 K) electrical resistivity measurements on the compacts of the mechanically alloyed and annealed samples prepared through various routes. However, in order to avoid the effect of porosity to the tune of ~15% and to have a clear comparison of the resistivity under different routes, normalized resistivity, $r(T)=\rho(T)/\rho(300\,\mathrm{K})$, as a function of temperature is plotted in Fig. 8. The $r(T)$ showed a significantly higher value in the nanoquasicrystalline state at 85 K in comparison with the unmilled sample. It should be mentioned that during annealing, there must be a tendency for grain coarsening of the nanoquasicrystalline phase, though negligible in the present study (see Figs. 2 and 5), which is expected to lower the resistivity. However, the increase in the resistivity due to the increase in the volume fraction of the *i* phase appears to overcome this contribution from grain coarsening. Interestingly, an increase of the normalized resistivity and negative TCR with the increase in the volume fraction of the *i* phase has been clearly observed. These observations are consistent with our earlier report.[21] Further, we compare the $r(T)$ data obtained for samples which are prepared by different intensity mills but with the same route (route 1). As is seen from the inset of Fig. 8, that the samples produced by LEM show larger values of ρ and TCR. This is very much consistent with the structural investigations presented in the earlier section, where it was mentioned that the samples produced by LEM and subsequent optimum heat treatment gives essentially a better QC phase compared to HEM.

IV. CONCLUSIONS

(1) Icosahedral quasicrystalline phase has been synthesized with $Al_{70}Cu_{20}Fe_{10}$ alloy composition through LEM and subsequent heat treatment. The icosahedral phase formed

during MA transformed into an almost single *i*-phase quasicrystal with F-type structure after additional heating at elevated temperatures.

(2) Two of the essential intermediate phases that seem to contribute in the formation *i* phase are Al_2Cu and β-phases. Our results also strongly suggest that the *i* phase appears to form by the peritectic reaction between these two phases.

(3) The icosahedral phase formation mechanism is the same for all the routes but appears to be sensitive to the milling intensity, time, and the way the nominal composition is reached during MA.

(4) The icosahedral phase obtained by MA is nanoquasicrystslline in nature and its rate of grain coarsening is quite low.

(5) A better quality *i* phase with higher stability could be obtained through LEM.

ACKNOWLEDGMENT

One of the authors (P.B.) is grateful to ICCR, Delhi for financial support.

[1] A. P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys., Part 2 **26**, L1505 (1987); *ibid.* **27**, L1587 (1988); the 1872th *Report of the Institute of Materials Research, Tohoku University*, Sendai, Japan, 99 (1991).
[2] T. Ishimasa, Y. Fukano, and M. Tsuchimori, Philos. Mag. Lett. **58**, 157 (1988); T. Ishimasa and M. Mori, *ibid.* **62**, 357 (1990).
[3] S. Ebalard and F. Spaepen, J. Mater. Res. **4**, 39 (1989); Z. Zhang, N. C. Li, and K. Urban, *ibid.* **6**, 366 (1991).
[4] Y. Calvayrac, A. Quivy, M. Bessiere, S. Lefebvre, M. Cornier-Quiquandon, and D. Gratias, J. Phys. (France) **51**, 417 (1990).
[5] S. J. Poon, Adv. Phys. **41**, 303 (1992) and references therein.
[6] F. Faudot, A. Quivy, Y. Calvayrac, D. Gratias, and M. Harmelin, Mater. Sci. Eng., A **181**, 841 (1994).
[7] T. A. Lograsso and D. W. Delaney, J. Mater. Res. **11**, 2125 (1996).
[8] G. Rosas and R. Perez, Mater. Lett. **36**, 29 (1998).
[9] C. Dong, M. De Boissieu, J. M. Dubois, J. Pannetier, and C. Janot, J. Mater. Sci. Lett. **8**, 827 (1989).
[10] A. P. Tsai, T. Tsurui, A. Memezawa, K. Aoki, A. Inoue, and T. Masumoto, Philos. Mag. Lett. **67**, 393 (1993).
[11] D. M. Follstaedt and J. A. Knapp, Phys. Rev. Lett. **56**, 1827 (1986).
[12] T. Klein and O. G. Symko, Appl. Phys. Lett. **64**, 431 (1994).
[13] C. Suryanarayana, Prog. Mater. Sci. **46**, 1 (2001).
[14] J. Eckert, L. Schultz, and K. Urban, Acta Metall. Mater. **39**, 1497 (1991).
[15] N. Asahi, T. Maki, S. Masumoto, and T. Sawai, Mater. Sci. Eng., A **181**, 841 (1994).
[16] N. Asahi, T. Maki, T. Kishida, and T. Tatsugawa, J. Non-Cryst. Solids **156**, 927 (1993).
[17] N. Asahi, Mater. Sci. Eng., A **226**, 67 (1997).
[18] J. Eckert, L. Schultz, and K. Urban, Appl. Phys. Lett. **55**, 117 (1989).
[19] J. Eckert, L. Schultz, and K. Urban, J. Alloys Compd. **167**, 143 (1990).
[20] P. Barua, B. S. Murty, B. K. Mathur, and V. Srinivas, J. Mater. Res. **17**, 653 (2002).
[21] P. Barua, V. Srinivas, and B. S. Murty, Philos. Mag. A **80**, 1207 (2000).
[22] V. Srinivas, P. Barua, and B. S. Murty, Mater. Sci. Eng. A **294**, 65 (2001).
[23] P. Barua, B. S. Murty, and V. Srinivas, Mater. Sci. Eng., A **304**, 863 (2001).
[24] A. I. Salimon, A. M. Korsunsky, E. V. Shelekhov, and T. A. Sviridova, Mater. Sci. Forum **321**, 676 (2000).
[25] A. M. Korsunsky, A. I. Salimon, I. Pape, A. M. Polyakov, and A. N. Fitch, Scr. Mater. **44**, 217 (2001).
[26] N. Burgio, A. Iasonna, M. Magini, S. Martelli, and F. Padella II, Nuovo Cimento D **13**, 459 (1991).
[27] M. Abdellaoui and E. Gaffet, Acta Metall. Mater. **43**, 1087 (1995).
[28] B. S. Murty, M. Mohan Rao, and S. Ranganathan, Acta Metall. Mater. **43**, 2443 (1995).
[29] P. A. Bancel, P. A. Heinry, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2422 (1985).
[30] T. H. de Keijser, J. I. Langford, E. J. Mittemeijer, and A. B. P. Vogels, J. Appl. Crystallogr. **5**, 308 (1982).
[31] S. Roche, G. Trambly de Laissardiere, and D. Mayou, J. Math. Phys. **38**, 1794 (1997) and references therein.