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Leaching of rapidly quenched $Al_{65}Cu_{20}Fe_{15}$ quasicrystalline ribbons

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Abstract. In the present work, $Al_{65}Cu_{20}Fe_{15}$ alloy has been synthesized by melting of pure elements (e.g., Al (99.96%), Cu (99.99%) and Fe (99.98%)), using a radiofrequency induction melting furnace. The as-prepared alloy was subjected to rapid solidification by melt spinning technique at $\sim$3500 rpm speed on a copper disk of diameter 14 cm. As a result of the melt spinning, nearly 2 mm wide, 30−40 μm thick and 4–5 cm long ribbons were formed. The structural and microstructural characterizations were carried out by X-ray diffraction and transmission electron microscopy techniques. We have performed leaching operation using 10 mol NaOH aqueous solution on the surface using a pipette. Leaching was performed for various durations ranging from 30 min to 8 h. After leaching, the reflectivity reduces and the surface looks reddish brown. The microstructure of the 8 h leached sample shows a breakdown of the quasicrystalline phase but with the evolution of other metallic phases. Copper (Cu) particles are found to be present on the surface of quasicrystal after 4 h of leaching and relatively more iron (Fe) evolves during further leaching of 8 h. This low-cost method to prepare a distribution of nano-Cu/Fe metal particles encourages their uses in catalytic reactions, indicating the possibility of use of quasicrystals as the industrial catalysts.

Keywords. Quasicrystal; rapid solidification; leaching; catalyst.

1. Introduction

Rapid solidification processing (RSP) of alloys is of immense interest to materials scientists because of the unique opportunity to synthesize a variety of materials with different microstructures and consequent physical properties [1]. While studying the metastable phase formation in rapidly solidified aluminium transition metal alloys for high strength applications, quasicrystal (QC) phase was discovered and the Nobel Prize in Chemistry for the year 2011 was awarded to Professor Danny Shechtman for this revolutionary discovery [1]. It is now understood that QCs are translationally as well as orientationally ordered structures (but not periodic) exhibiting classically forbidden rotational symmetries such as five-fold, eight-fold, ten-fold and twelve-fold [2–6]. The Al–Mn QC exhibiting a simple icosahedral (i) symmetry ($Pm\overline{35}$), however the ordered QC was showing face-centred icosahedral (FCI) symmetry ($Fm\overline{35}$) reported in annealed Al–Cu–Fe rapidly solidified alloy [7,8]. A stable (i) Al–Cu–Fe ternary QC has been discovered, which is a part of the equilibrium phase of Al–Cu–Fe [9]. It is generally understood that Al–Cu–Fe QC also presents an FCI structure similar to that observed after annealing of rapidly solidified Al–Mn quasicrystalline alloys [8–10]. The Al–Cu–Fe QC alloys are important due to the absence of toxicity, easy availability and favourable costs of their alloying elements and concerned processing. These structural features of Al–Cu–Fe QC are linked to their special property combination such as poor electrical and thermal conductivity, low surface energy and low coefficient of friction as well as high brittleness, work softening tendency and high hardness. When prepared by conventional melting and casting, the QC phase in Al–Cu–Fe system exhibits a peritectic reaction among AlFe, Al_3Fe and the remaining liquid. However, crystalline phases often coexist with the stable quasicrystalline phase in the as-cast products. Additional annealing may be utilized, or the material may be synthesized by rapid solidification techniques, e.g., melt spinning and gas atomization, or by mechanical alloying in order to obtain single-phase QC materials. Perhaps due to the aperiodicity, these materials exhibit different properties from those of conventional metallic materials, which can be exploited for industrial applications [11,12]. QCs based on Al–Cu–Fe have been considered as the most promising candidate for the surface catalysis because of their thermal stability, easy forming ability of the metallic nanoparticles on the surface. Some intermetallic compounds are known to have good catalytic selectivity and activity for increased production of hydrogen gas at a temperature lower than that required to begin the decomposition reaction of methanol [13]. Due to the unique structure and presence of metallic components in

QC, it has been anticipated that QCs would exhibit intriguing physical and/or chemical properties. It was subsequently found that they are promising precursors for the fabrication of high-performance nano-composite catalysts when they are subjected to a leaching treatment. The catalytic activity can be further improved by selective leaching of intermetallic compounds in a concentrated NaOH solution [14]. For QC intermetallic alloy ribbons, studies on the catalytic properties are very limited [15,16] and thus it will be interesting to see the leaching effect on QC surface, especially to see the evolution of phases and consequent microstructures.

In the present work, $Al_{65}Cu_{20}Fe_{15}$ QC ribbons have been synthesized by melt spinning technique. The aim of the present work is to examine the influence of leaching with 10 mol of NaOH on the surface of melt spun QC ribbons and to understand the evolution of the various phases.

2. Experimental

A stable QC of nominal alloy composition the $Al_{65}Cu_{20}Fe_{15}$ has been prepared from 99.98 wt% purity Al, 99.99 wt% of Cu and 99.98 wt% of Fe. Powder (10 g) of individual elements in the required stoichiometry was pelletized in the form of circular buttons under hydraulic pressure. The pellets were taken in a silica crucible in continuous inert Ar gas flow through a silica tube for 30 min. The pellet was melted in a radio frequency induction furnace (18 kW). The argon flow was maintained throughout the melting. After melting, the material was subjected to rapid solidification by the melt-spinning technique. To achieve this, the ingot was melted in a silica crucible having an orifice of 1 mm diameter and ejected on the copper wheel rotating fast at the speed of 3500 rpm. As a result, ribbons of nearly 1–2 mm width, $30-40$ μm thickness and a few centimeters length were obtained. As-quenched ribbons were leached with 10 mol NaOH aqueous solution for 30 min, 1, 2, 4 and 8 h; then they were carefully washed with distilled water and methanol until no alkali was detected in the filtrate. Structural and microstructural characterizations of the samples are analysed by transmission-electron microscopy (FEI-TECNAI-20G2 operating at 200 kV), scanning electron microscopy (QUANTA-200) and X-ray diffraction (XRD) by employing CuK_α radiation ($\lambda = 1.5402$ Å) using an X'Pert PRO (PANalytical). To prevent contamination of the samples in air or moisture during XRD measurement, the specimen holder was covered by parafilm (Pechiney plastic packing).

3. Results and discussion

In order to unravel the different phases after leaching of (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbons, structural characterization was carried out by XRD techniques. The XRD patterns of as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon on figure 1a confirm the presence of the icosahedral phase, as this can be indexed based on the data available for this phase [17]. Figure 1b shows the XRD patterns obtained from the sample leached for 8 h with 10 mol NaOH aqueous solutions. As shown in figure 1b, it is evident that leaching with the NaOH solution results in the broadening of the peak as well as appearance of some new peaks arising out of Cu and Fe particles, while the QC phase survives even in the 8 h leached ribbons. In the present experiment, no visible peaks from copper oxides–iron oxides were observed after leaching treatment (figure 1b). The common oxidized iron, i.e., α-Fe_2O_3 phase (haematite, JCPDS Number 24-0072), which has a rhombohedral structure with the lattice parameters of $a = 5.03$ Å and $c = 13.76$ Å, and the cubic Fe_3O_4 (magnetite, JCPDS Number 65-3107), with lattice parameter $a = 8.39$ Å, have not been observed. The reflections of the XRD pattern of iron (figure 1b) can be attributed to the body centred cubic (bcc) phase of Fe (JCPDS Number 87-0721), without indication of the common oxidized iron phase. Further, the elemental compositions of the unleached and leached surfaces have been verified by energy-dispersive X-ray (EDX) analysis along with scanning electron microscopy. The EDX spectra have been presented in the inset of figure 1a and b, correspondingly. A nominal $Al_{65}Cu_{20}Fe_{15}$ composition is observed from the melt spun ribbon as shown in the inset of figure 1a; however, after 8 h of leaching, a significant change in their chemical composition is observed as shown in the inset of figure 1b. The typical chemical composition ratio of the transition metals (Cu–Fe) on unleached surface was 1.27, whereas on the leached surface it was 1.44. A small amount of oxygen was observed on both unleached and leached surfaces; however, it was nearly same, i.e., 2.15 and 2.75 at%, respectively. Therefore, the leached surface is oxygen deficient, and moreover the chemical compositions of Cu and Fe become key factors after leaching of the QC ribbon surface. It should be mentioned that the amount of Al dissolved during the NaOH leaching and the amount of Cu and Fe have increased simultaneously. It is interesting to note that the precipitation rate of Fe is lower than that of Cu.

Figure 2a shows the scanning electron micrograph (SEM) in secondary electron image mode of (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon. After 2 h of leaching with 10 mol NaOH, the surface reveals deep etching, and the contours of melt-spun tracks formed during melt spinning are clearly visible (figure 2b). The ribbon produced after leaching for 4 h with 10 mol NaOH solution showed different microstructural features (figure 2c) and elongated grains with small particles, as observed in figure 2c. In the 8 h leached ribbon, the surface is covered by cube-like microstructure, which is clearly recognizable in figure 2d. Homogeneous distributions of small particles together with very small particles on and around the large particles have been observed. The development of the particular microstructure is related to the leaching duration and concentration of NaOH, as well as the type of QC materials [16]. It is interesting to note that a single grain of (i) Al–Cu–Fe shows a pentagon-like microstructure after 8 h of leaching [18,19]. The size of homogeneously distributed small particle precipitates on the surface of 8 h leached ribbons has been calculated from SEM

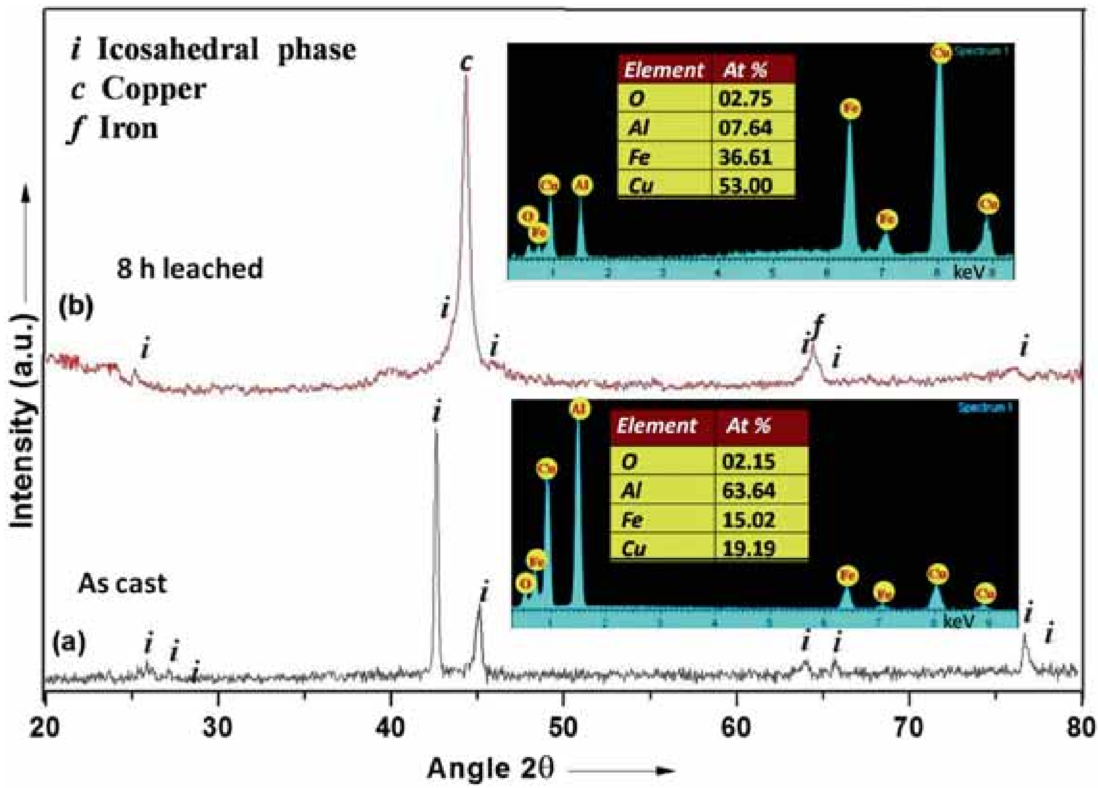

Figure 1. X-ray diffraction patterns (**a**) as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon and (**b**) ribbon leached for 8 h with 10 mol of NaOH solution; insets show the corresponding EDX spectra.

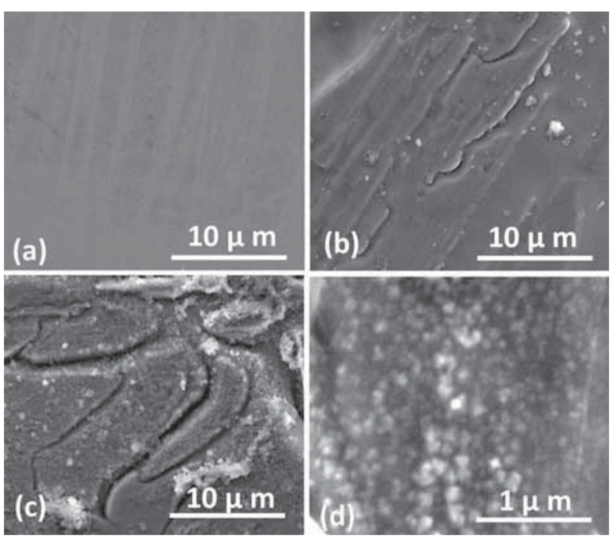

Figure 2. Scanning electron microscopy of (**a**) as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon, (**b**) as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 2 h with 10 mol NaOH solution, (**c**) as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 4 h with 10 mol NaOH solution and (**d**) as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 8 h with 10 mol NaOH solution.

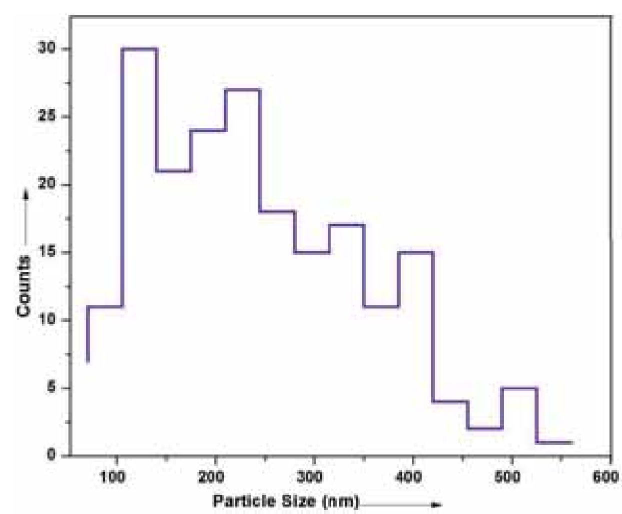

Figure 3. Histograms of crystallite size distribution measurements on SEM microstructure of as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 8 h with 10 mol NaOH solution.

micrographs, which yields an average grain size of ~100 nm as shown in figure 3. The distribution of grain sizes determined by SEM was normalized to unit area and standard deviation of the size distributions was calculated to be ~5 nm. The histograms of the crystallite size distribution show a very narrow dispersion in the size of precipitates obtained in the present experimental conditions.

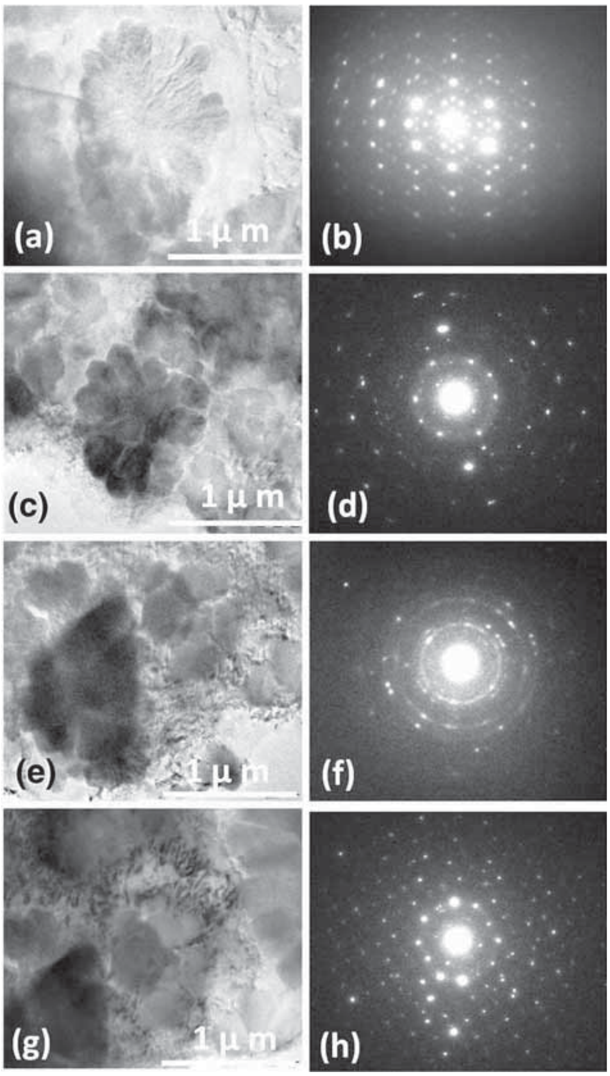

Figure 4. Transmission electron micrograph of as-synthesised (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon, (**b**) corresponding selected-area diffraction (SAD), (**c**) microstructure of as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 2 h with 10 mol NaOH solution, (**d**) corresponding SAD patterns, (**e**) microstructure of as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 4 h with 10 mol NaOH solution, (**f**) corresponding SAD patterns, microstructure of as-synthesized (i)-$Al_{65}Cu_{20}Fe_{15}$ ribbon surface leached for 8 h with 10 mol NaOH solution and (**g**) corresponding SAD pattern.

The results of TEM investigation on the microstructure of as-synthesised (i)-$Al_{65}Cu_{20}Fe_{15}$ QC ribbon along with leached ribbon have been presented in figure 4, which shows a typical microstructure of the synthesised alloy, which is present throughout the specimen. It shows a rosette and coral-like morphology and the corresponding selected-area diffraction (SAD) patterns exhibiting two-fold symmetries corresponding to icosahedral phase are shown in figure 4b. The microstructure and corresponding SAD patterns of 2 h leached ribbon are displayed in figure 4c and d, respectively. It is interesting to note that the leaching operation changes the shape and size of the quasicrystalline grains. A faceted type of morphology has been observed around the rosette-like morphology. The extra spots expected between the transmitted spot and the most intense spots may be due to evolution of the new phases around the leached area. Rather diffuse scattering along these reciprocal directions can be identified, indicating the development of disorder in QC phase due to compositional changes in the present case. The microstructure and corresponding SAD of the 4 h leached as-synthesised $Al_{65}Cu_{20}Fe_{15}$ ribbons are shown in figure 4e and f. Two different types for the leached ribbon and a homogeneous distribution of small particles have been observed. This is due to the presence of two different phases such as Cu and Fe in the leached ribbon. The bright field image and its corresponding SAD pattern for the ribbon leached for 8 h have been shown in figure 4g and h, respectively. In the 8 h leached ribbon, volume fraction of (i)-phase microstructure is relatively less in amount. This can be attributed to the fact that only the Al concentration is changed drastically, rather reduced, due to leaching. Thus, the change in local structure could be attributed to the Al deficiency, leading to collapse of icosahedral structure. After the leaching of a (i)-$Al_{65}Cu_{20}Fe_{15}$ QC ribbon with 10 mol NaOH, we find that the majority of transition metal particles are present in the leached area, whereas Al, which is the major element in the as-grown QC alloy (before leaching), has disappeared. The dissolution behaviours of the QCs can be attributed to the quasiperiodicity in atomic arrangements [20,21] as well as affinity of Al for reaction with NaOH. The effect of quasicrystallinity may have some role while controlling the leaching behaviour. Thus, during leaching with NaOH, the dissolution kinetics of Al is relatively high compared with other elements, leading to the formation of $NaAlO_2$ and subsequently to Al_2O_3, Cu and Fe. After thorough washing of the leached surface with methanol and distilled water in ultrasonic bath, most of the Al_2O_3 precipitates are removed due to low density and weak bonding of Al_2O_3 compared with that of Cu and Fe [22]. Thus, the microstructure in 8 h leached QC phase obtained by a chemical method is dominated by the removal of the Al atoms. A schematic diagram of the leaching process on Al–Cu–Fe QC ribbon surfaces and precipitated Cu and Fe nanoparticles has been shown in figure 5. Figure 5a shows ideally pentagonal dodecahedron-shaped grains of Al–Cu–Fe QCs. After leaching of the surface with NaOH (figure 5b), grains of Al_2O_3, Cu and Fe that have precipitated on the surface and the density of Al_2O_3, Cu and Fe particles are relatively high at the defect sites. After the thorough washing of the leached surface with methanol and distilled water in ultrasonic bath, most of the Al_2O_3 precipitates came out due to its low density and weak bonding to QC surface compared with the Cu and Fe nanoparticles (figure 5c). Since kinetics of leaching at the defect site will be more compared with that of the defect-free surface, some areas of deep leaching have been observed on the surface QC ribbon and they exhibit Cu and Fe nanoparticles on the surface. These QCs decorated by transition metals can be a good catalyst for potential application of QCs for catalysis [23].

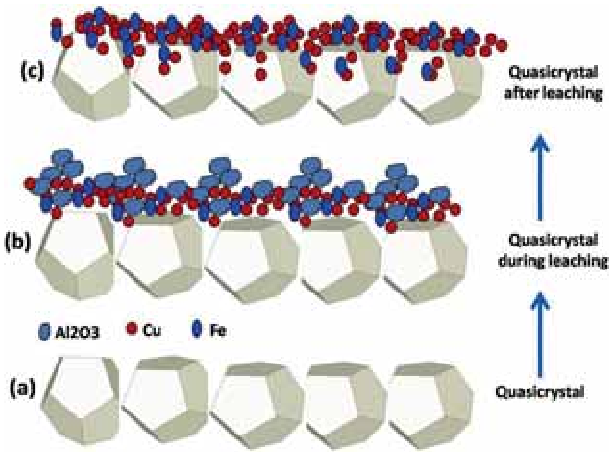

Figure 5. A schematic diagram of the leaching process on Al–Cu–Fe QC ribbon surfaces and precipitation of Cu and Fe nanoparticles.

4. Conclusions

From the experimental observation, it can be stated that the single-phase icosahedral quasicrystalline $Al_{65}Cu_{20}Fe_{15}$ ribbon prepared by melt spinning technique has gone through gradual changes in the composition of quasicrystalline phases and subsequently leads the collapse of icosahedral structure due to depletion of Al after leaching with 10 mol NaOH aqueous solution up to 8 h. Consequently, small particles corresponding to Cu and Fe have been identified to evolve on the surfaces replacing the QC phases. It is known that Cu and Fe do not form any solid solution or any compound and accordingly they maintain their individual identities. Al has been dissolved from the surface due to the formation of Al_2O_3 while reacting with NaOH solution. It has been noticed that the colour of the surfaces is altered from shiny metallic surface to reddish brown due to the presence of nano-size Cu/Fe particles.

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