Revista de Metalurgia 51(4)
October–December 2015, e054
ISSN-L: 0034-8570
doi: http://dx.doi.org/10.3989/revmetalm.054

Quasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ alloys

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Submitted: 25 September 2015; Accepted: 30 October 2015; Available On-line: 03 November 2015

ABSTRACT: Aluminium alloy powder having a nominal composition of $Al_{93}Fe_3Cr_2Ti_2$ (at%) has been prepared using gas atomisation. The atomised powder present a microstructure of an aluminium matrix reinforced with a spherical quasicrystalline icosahedral phase, in the range of nanometre in size. The powder was consolidated into bars using warm extrusion. The microstructure of the extruded bars retains the quasicrystalline microstructure and the bars present outstanding mechanical properties, i.e. proof stress of 280 MPa at 300 °C. Upon heating the microstructure evolves towards the equilibrium. The thermal evolution was investigated by means of x-ray diffraction, differential scanning calorimeter, scanning electron microscopy and transmission electron microscopy. According to these observations a transformation in two steps is proposed. A first step consists in the decomposition of the supersaturated solid solution of the matrix and the quasicrystals, and a second step in the transformation of the quasicrystals into the equilibrium phases.

KEYWORDS: Aluminium alloy; Nanostructure; Powder metallurgy; Quasicrystal; Rapid solidification

Citation / Cómo citar este artículo: García-Escorial, A., Natale, E., Cremaschi, V.J., Todd, I., Lieblich, M. (2015) "Quasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ alloys". *Rev. Metal.* 51(4): e054. doi: http://dx.doi.org/10.3989/revmetalm.054.

RESUMEN: *Aleaciones cuasicristalinas $Al_{93}Fe_3Cr_2Ti_2$.* Se ha obtenido por atomización por gas polvo de la aleación $Al_{93}Fe_3Cr_2Ti_2$ (at%). Este polvo presenta una microestructura de una matriz de aluminio reforzada por precipitados icosaédricos de tamaño nanométrico. El polvo fue consolidado por extrusión en forma de barras cilíndricas. La microestructura de las barras retiene la microestructura cuasicristalina de las partículas de polvo. El material consolidado presenta propiedades mecánicas prometedoras, como un límite elástico de 280 MPA a 300 °C. Con los tratamientos térmicos, la microestructura evoluciona hacia el equilibrio. Esta evolución se estudia por difracción de rayos x, calorimetría diferencial de barrido, microscopías electrónicas de barrido y de transmisión. A la luz de los resultados obtenidos se propone que la transformación de las fases con el tiempo de tratamiento térmico ocurre en dos pasos. Primeramente, tiene lugar la descomposición de la solución solida sobresaturada, tanto en la matriz como en los cuasicristales, y posteriormente los cuasicristales se transforman en las fases de equilibrio del sistema: α-Al, $Al_{13}Fe_4$, $Al_{13}Cr_2$ y Al_3Ti.

PALABRAS CLAVE: Aluminio; Cuasicristal; Nanoestructura; Pulvimetalurgia; Solidificación rápida

1. INTRODUCTION

Nano-size quasicrystalline structures have been a subject of interest over recent years due to their potential use as reinforcement in advanced engineering alloys (Kimura *et al.*, 2000). The icosahedral phases are hard and brittle due to the difficulty of dislocation movement in the quasiperiodic lattice without long range periodicity. However, the use of such quasicrystalline phase as reinforcement of ductile matrix, such as aluminium alloys, offers the potential improvement of mechanical properties together with enhanced stability at elevated temperatures. Aluminium alloys for high temperature applications are of considerable interest, especially in the automotive and aerospace industries.

The $Al_{93}Fe_3Cr_2Ti_2$ extruded bars (Chlup *et al.*, 2003) show high strength at elevated temperatures, with a proof stress of 280 MPa at 300 °C and an elongation of 1.8%, Table 1. These good mechanical properties decrease with temperature. A combination of solid solution strengthening, precipitation strengthening and grain size refinement would be responsible for the high strength of this alloy (Galano *et al.*, 2009a).

Nanoquasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ powder was obtained by gas atomisation, the powder was sieved into well defined size fractions and consolidated into bars by warm extrusion. The stability and the evolution of bulk $Al_{93}Fe_3Cr_2Ti_2$ extruded bars upon thermal treatments is studied as a function of initial gas atomised powder particle size range, and therefore, of the solidification rate. Thermal treatments at 400 °C, which was the extrusion temperature, were performed up to 1000 hours.

2. EXPERIMENTAL TECHNIQUES

Atomised powder particles of composition $Al_{93}Fe_3Cr_2Ti_2$ (at %) were produced by helium atomisation of pure Al and Ti, and master Al-Fe and Al-Cr alloys. The $Al_{93}Fe_3Cr_2Ti_2$ melt was superheated in a crucible up to above the liquidus, and then teemed via a refractary tundish through a confined nozzle. Atomisation of the melt was achieved at the nozzle exit by an annular jet of argon. Figure 1 presents a squeme of the gas atomiser employed.

The atomised powder was separated by sieving into three −25, 25–50 and 50–100 μm powder particle size fractions.

TABLE 1. Tensile strength and proof stress of the quasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ alloy at room temperature and 300 °C

	Tensile strength (MPa)	Proof stress (MPa)	Elongation (%)
Room temperature	600	520	
300 °C	300	280	1.8

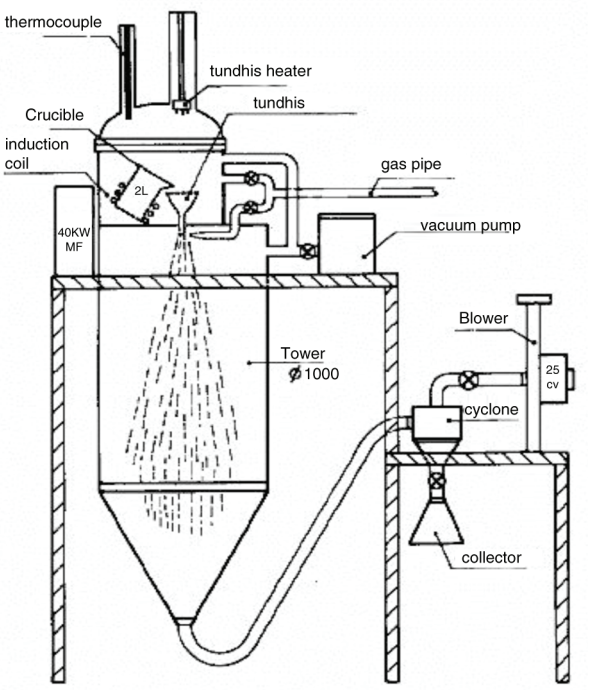

FIGURE 1. Gas atomiser.

Consolidation of the different powder particle size fractions, PPSF, −25, 25–50 and 50–100 μm, was performed without prior degassing by means of a horizontal warm extrusion press with a container diameter of 42 mm and maximum available pressure of 1600 MPa. After several trials at different temperatures and extrusion ratios (Todd *et al.*, 2004), the extrusions were carried out at 400 °C, extrusion ratio 10 to 1 and extrusion ram velocity 0.3 mm s^{-1}. Prior to the extrusion, the encapsulated powder batches were submitted to heating at the extrusion temperature for 15 minutes.

The extruded bars, that have a diameter of 14 mm, were heat treated for 1, 10, 100 and 1000 hours at 400 °C. The powder, the as-extruded and the heat treated bars were characterised by means of X-Ray Diffraction (XRD), using Cu Kα radiation, Differential Scanning Calorimeter (DSC), under argon flow at a constant rate of 40 °C min^{-1} from room temperature up to 600 °C, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM), equipped with Energy Dispersive X-ray analysis units (EDX).

3. RESULTS AND DISCUSSION

Direct observations of powder particle surfaces in the SEM showed they are spherical in shape (Fig. 2). The surface of powder particles is smoother the smaller the particle size (Fig. 3). Cross section observations of the powder particles by scanning electron

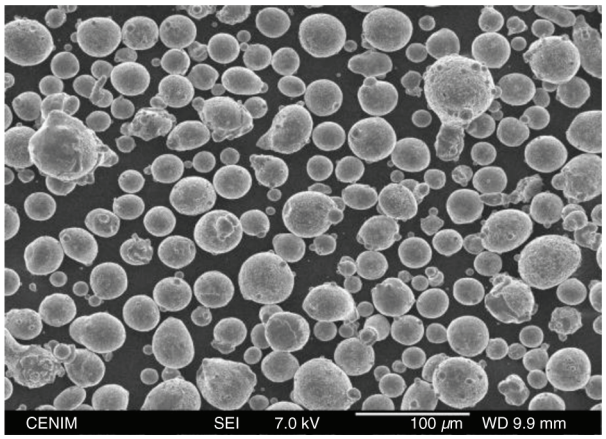

FIGURE 2. Atomised powder.

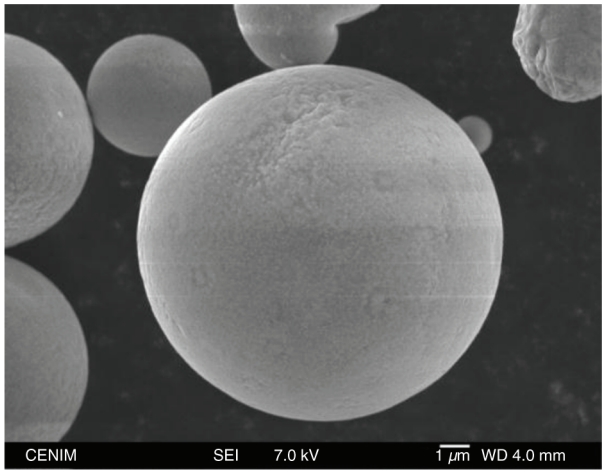

FIGURE 3. SEM micrograph of atomised $Al_{93}Fe_3Cr_2Ti_2$ powder.

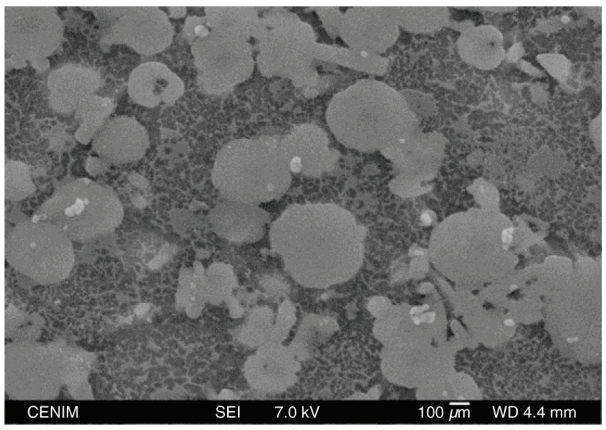

FIGURE 4. SEM micrograph of a cross section of atomised $Al_{93}Fe_3Cr_2Ti_2$ powder.

microscopy (Fig. 4) show the copious presence of near spherical precipitates into the Al matrix. As it was shown in previous work (Todd *et al*., 2004), x-ray diffraction patterns of the powder showed mainly signal of the α-Al phase together with peaks indexed as an icosahedral phase, i-phase, by using the indexation scheme for icosahedral quasiperiodic crystals (Bancel *et al*., 1985). In the 25–50 and 50–100 μm powder particle size ranges, some smaller peaks corresponding to the intermetallic $Al_{23}Ti_9$ were also identified. The DSC traces revealed a large exothermic peak around 500 °C (Todd *et al*., 2004), which was attributed to the transformation of the i-phase.

Figure 5 collects the XRD patterns of the bars processed with the −25 μm powder particle size fraction, in the as-extruded and the heat treated states, in the most representative range of 2θ between 35° and 50°. In the as-extruded state, signals of α- Al and the i-phase are seen. In the bars extruded with larger powder size fraction, some peaks of Al_3Ti are also detected. The XRD pattern of the bar treated 1 hour at 400 °C is similar to that of the as-extruded bar. In the 10 and 100 hours treated bars the Al_3Ti phase grows, and appears the metastable Al_6Fe phase, which gets its maximum with the 100 hours treatment at 400 °C, and disappears afterwards. Meanwhile, the bar treated for 1000 hours presents the equilibrium phases: α- Al, Al_3Ti, $Al_{13}Cr_2$ and $Al_{13}Fe_4$.

The thermal evolution of the as-extruded bars was followed by differential scanning calorimeter (García Escorial *et al*., 2015). The DSC traces showed a large exothermic reaction at around 500 °C, which was larger the smaller the particle size and occurred at a slightly lower temperature, in a similar way to the DSC traces of the powder.

The presence of the icosahedral i-phase in the $Al_{93}Fe_3Cr_2Ti_2$ as-extruded bar was confirmed by TEM (García Escorial *et al*., 2007). Selected area diffraction patterns revealed the two, three and five fold reflection spots as can be seen in Fig. 6. Quasicrystals in the atomised powder as well as in the extruded bars of $Al_{93}Fe_3Cr_2Ti_2$ have the clear and characteristic spherical shape shown in Fig. 4 and Fig. 6. TEM observations reveal the presence of Al_3Ti, also in the −25 μm size powder bar. This phase was not observed in this bar through XRD probably due to its small volume fraction.

Figure 7a shows a SEM micrograph of an as-extruded bar, which present bands of different precipitation density formed by the elongation that suffered each powder particle during the extrusion process, with a copious presence of nearly spherical precipitates, identified by TEM as icosahedral phase. Figure 7b shows a TEM micrograph of an icosahedral quasicrystal and the selected area diffraction pattern. The quasicrystals are quite enriched in alloying elements, as determined by EDX analysis which pointed out to a composition around the $Al_{84.5}Fe_7Cr_6Ti_{2.5}$ in agreement with other studies (Kimura *et al*., 2000; Galano *et al*., 2009b). With the 1 hour treatment, the microstructure hardly changes with respect to that of the as-extruded bars. After the

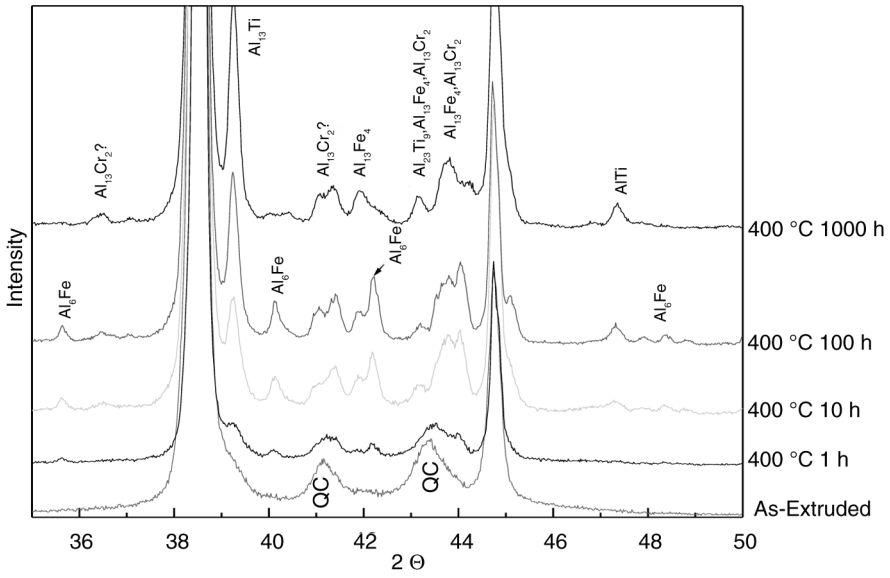

FIGURE 5. XRD patterns of as-extruded and heat treated bars obtained with −25 μm powder particle size fraction.

10 hours and 100 hours thermal treatments the spherical QC are mostly substituted by less spherical and larger precipitates (Fig. 8), which resemble the previous QC with darker regions of several shapes as tie-bow, helix, triangle and cross (Fig. 8a), Ti enriched according with EDX analysis. Figure 8b shows a corresponding TEM micrograph. After heating for 1000 hours at 400 °C, (Fig. 9), numerous Fe enriched needle-like precipitates are seen, together with large agglomerates of Cr and Ti rich precipitates.

The atomised powder particles contain α-Al and QC and the extruded bars retain this structure, with an increasing amount of Al_3Ti as particle size increases. Upon heating the Al_3Ti phase grows, and the metastable Al_6Fe phase appears. With the 1000 hours annealing, the metastable QC transforms into the equilibrium phases: $Al_{13}Fe_4$, $Al_{13}Cr_2$ and Al_3Ti.

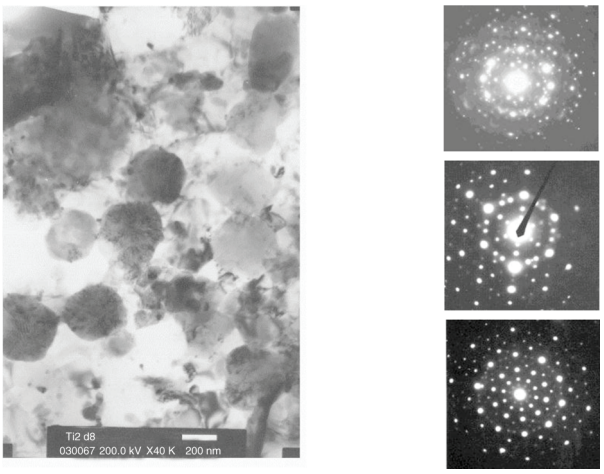

FIGURE 6. TEM micrograph of quasicrystals in an as-extruded $Al_{93}Fe_3Cr_2Ti_2$ bar and the corresponding selection diffraction patterns.

Several authors have studied the transformation of quasicrystalline Al-based alloys upon thermal treatments mainly on melt-spun ribbons and by TEM (Lui and Köster, 1991; Galano *et al.*, 2010) and report different ways of transformations: continuous and discontinuous transformations, as peritectoid, polymorphic, eutectoid and precipitation. In this work the evolution of bars, which is a bulk material, has been studied by SEM and TEM at 400 °C as a function of holding time, up to 1000 hours. Similarly to the microstructural evolution observed by other authors in other QC-Al base alloy ribbons, the i-phase seems to be supersaturated, since thermal treatment leads to a precipitation reaction of Al_3Ti inside the QC, relaxing the QC prior to decomposition, meanwhile the supersaturated matrix leads to the precipitation of Al_6Fe and Al_3Ti. So, the quaternary QC-AlFeCrTi would evolve towards ternary QC-AlFeCr, because Fe and Cr are QC formers and they would reject Ti to form Al_3Ti precipitates, although the presence of an intermediate phase of the type of $Al_{13}(Fe,Cr)_{2\text{-}4}$ should be also considered, because Fe and Cr replace each other. With further thermal treatments the remaining QC particles may transform eutectoidcally to $Al_{13}Fe_4$ and $Al_{13}Cr_2$ and the Al_6Fe phase evolves to the equilibrium $Al_{13}Fe_4$ phase.

As has been seen above, the QC phase present in the alloy studied in this work is quite stable, and thus, it would contribute to the high mechanical properties of this alloy at high temperatures (Chlup *et al.*, 2003; Galano *et al.*, 2009a; Todd *et al.*, 2004). Effectively, Fe and Cr are quasicrystal formers in Al base alloys, and Ti produces a significant

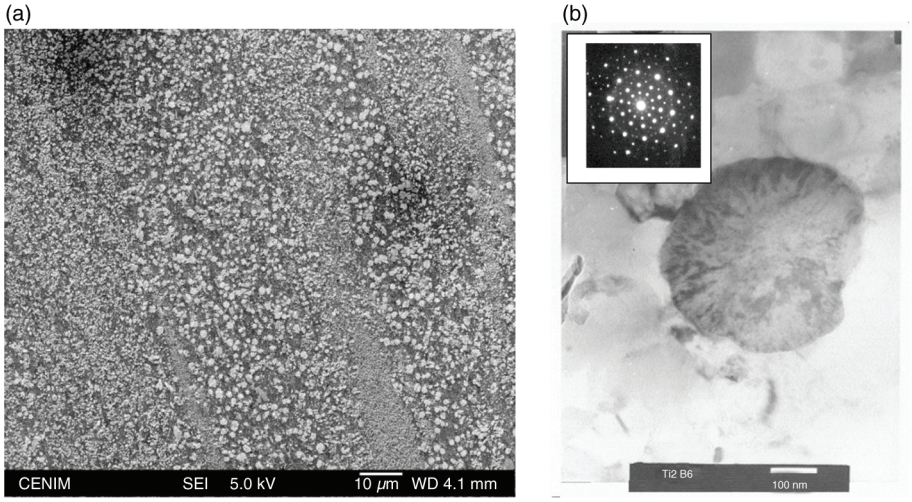

FIGURE 7. Micrographs of an $Al_{93}Fe_3Cr_2Ti_2$ as-extruded bar: a) SEM and b) TEM, in the inlet the selected diffraction pattern.

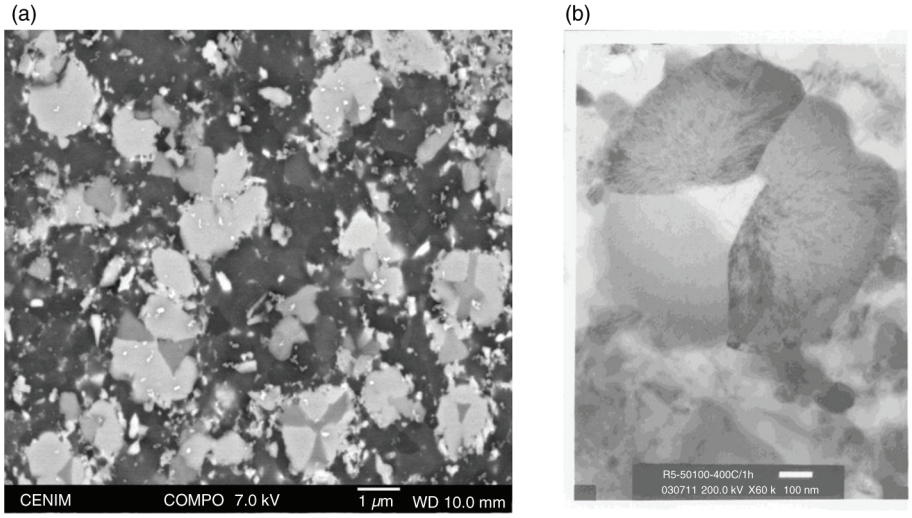

FIGURE 8. Micrographs of an $Al_{93}Fe_3Cr_2Ti_2$ bar heat treated 100 h at 400 °C: a) SEM and b) TEM.

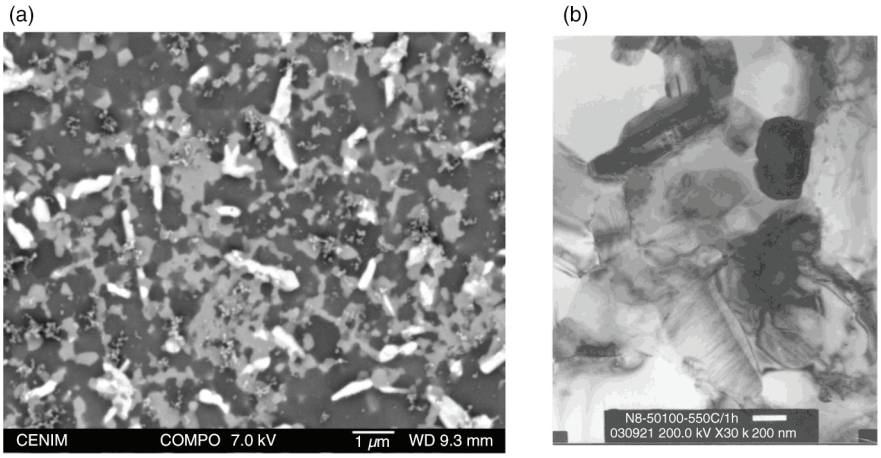

FIGURE 9. Micrographs of an $Al_{93}Fe_3Cr_2Ti_2$ bar heat treated 1000 h at 400 °C: a) SEM and b) TEM.

refinement of the icosahedral particle size as well as an increase of the stability (Galano *et al*., 2004). With enough time of permanence at high temperature, i.e. 1000 hours at 400 °C in our case, the metastable QC phase transforms into the equilibrium ones, with the result of the decay of mechanical properties.

At the present, we are studying composites of QC $Al_{93}Fe_3Cr_2Ti_2$ matrix with Al fibres to improve ductility, which is one of the properties that should be improve in this type of materials.

4. CONCLUSIONS

- As-atomised $Al_{93}Fe_3Cr_2Ti_2$ powder particles exhibit a microstructure of an aluminium matrix reinforced with a spherical nanometric icosahedric phase.
- Bars obtained by warm extrusion at 400 °C of as-atomised −25, 25–50 and 50–100 μm powder particle size fractions retain the nanoquasicrystalline microstructure.
- The QC are enriched in alloying elements, with a composition around $Al_{84.5}Fe_7Cr_6Ti_{2.5}$.
- The as-extruded bars evolve upon heating through two steps. During the first one the supersaturated solid solution of the matrix and the QC decomposes, forming Al_6Fe and Al_3Ti in the matrix and Al_3Ti precipitates in the QC, as observed after 10 and 100 hours at 400 °C. In the second step the QC are fully transformed into equlibrium phases, $Al_{13}Fe_4$, $Al_{13}Cr_2$ and Al_3Ti, as observed after 1000 hours at 400 °C.

ACKNOWLEDGEMENTS

We want to acknowledge specially to Prof. M. Torralba for his guidance and support. This work was carried out into the project "Nano-Al" funded by the European Union (Proyecto HPRN-CT-2000-00038).

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