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Nanoquasicrystalline Al–Fe–Cr-based alloys with high strength at elevated temperature

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ABSTRACT

Nanoquasicrystalline Al–Fe–Cr-based alloys have a microstructure composed of nanoquasicrystalline particles embedded in an α-Al matrix, and have high strength at elevated temperatures. However, the metastability of the quasicrystalline phase can limit the use of these alloys at elevated temperatures.

The microstructure, stability and mechanical properties at different temperatures on melt-spun nanoquasicrystalline Al–Fe–Cr-based alloys containing Ti, V, Nb or Ta have been studied and summarized in the present work.

The structural characterisation was carried out by means of X-ray diffraction, hot-stage transmission electron microscopy and scanning-transmission electron microscopy. The addition of a fourth element to the $Al_{93}(Fe_3Cr_2)_7$ alloy increases the thermal stability, in particular in the case of the Nb and Ta containing alloys, leading to the delay of the phase transformation towards the melting of the alloys.

The mechanical properties at elevated temperatures were studied by tensile tests at different test temperatures with different pre-heat treatments. All the alloys showed a very high strength up to 350 °C, more than five times the strength of the commercial Al alloys. These values and the enhanced thermal stability achieved in the quaternary nanoquasicrystalline Al–Fe–Cr-(Ti, V, Nb or Ta) alloys make these alloys very promising for industrial applications.

1. Introduction

An early work by Audebert et al. [1] compared the microstructure and the mechanical properties of several melt-spun Al-based alloys, nanocrystalline, nanogranular amorphous and nanoquasicrystalline. They found that the nanoquasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ alloy (compositions are in at% unless otherwise indicated), exhibited intermediate strength and ductility values at room temperature among the alloys studied and showed better microstructural stability at elevated temperatures. This alloy has a microstructure composed of quasi-spherical metastable icosahedral particles with sizes around 100 nm embedded in an α-Al matrix [2].

The authors' earlier work [3], on nanoquasicrystalline melt-spun $Al_{93}(Fe_3Cr_2)_7$ and $Al_{93}Fe_3Cr_2Nb_2$ alloys showed that the addition of Nb could have a stabilization effect on the icosahedral quasicrystalline phase, retaining the melt-spun microstructure at elevated temperature and providing promising applications at elevated temperatures, up to 400 °C, in the automotive and aeronautic industries. The understanding of the evolution of the microstructure with the temperature has been reported in detail in a previous paper by the authors [4] where it was analysed the effect of the addition of a fourth alloying element (Ti, V, Nb or Ta) to the $Al_{93}(Fe_3Cr_2)_7$ alloy on the microstructural evolution, using heat treatments and microstructural characterisation by a range of different techniques. A study on the mechanical properties at elevated temperature on melt-spun samples has also been reported recently by the authors [5].

This paper is therefore a review that builds on previous findings by the authors on the microstructure and mechanical properties, and on new results on microstructure stability carried out by means hot-stage TEM analysis and microstructure characterisation of heat treated samples. The analysis allows to conclude that the alloys studied can be produced in bulk shape by powder extrusion in a temperature range of 400–450 °C and obtain bars with a strength at 350 °C five times higher than commercial Al alloys [6,7]..

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Table 1
Identification code, nominal chemical compositions of the alloys studied.

Code	Nominal chemical composition (at%)
Al–Fe–Cr	$Al_{93}Fe_{4.2}Cr_{2.8}$
Al–Fe–Cr–Ti	$Al_{93}Fe_3Cr_2Ti_2$
Al–Fe–Cr–V	$Al_{93}Fe_3Cr_2V_2$
Al–Fe–Cr–Nb	$Al_{93}Fe_3Cr_2Nb_2$
Al–Fe–Cr–Ta	$Al_{93}Fe_3Cr_2Ta_2$

2. Experimental procedure

The code and the nominal chemical compositions of the melt-spun alloys studied are listed in Table 1

Master alloys were prepared in an arc furnace under a He atmosphere using pure elements and rapidly solidified ribbons, with thicknesses between 20 and 30 μm, were obtained by melt spinning in a reduced He atmosphere using BN coated quartz nozzles and with closed-loop controlled ejection temperature between 1200 and 1350 °C depending on the alloy.

X-ray diffractometry was carried out in a $\theta-2\theta$ diffractometer Philips 1810 using Cu-Kα radiation. Calorimetric studies at 40 K/min were carried out in a TA DSC.

Hot-stage TEM analysis was carried in a Philips CM20 TEM.

Tensile tests were carried out in vacuum at $\sim10^{-6}$ Torr, to prevent oxidation of the specimen while testing, in a tensile stage (20 kg tensile load cell, and a sensitivity of 0.001 g) designed for a JEOL 840 SEM by Oxford Instruments.

To compare the mechanical behaviour at different test temperatures tensile tests were performed at a constant strain rate of 10^{-4} s^{-1} and different test temperatures: room temperature, 300 °C, 315 °C, 330 °C and 350 °C. A 30 min heat treatment at a temperature 5 °C higher than the tensile test temperature was performed in each sample.

Considering that the rapid solidified material must be extruded at elevated temperature (400–450 °C) in order to obtain a bulk nanoquasicrystalline material for industrial applications, tensile experiments at 350 °C and a constant strain rate of 10^{-4} s^{-1} were carried out on samples heat treated at 450 °C for 30 min and then compared with those samples heat treated at 355 °C and tested at the same temperature and strain rate.

3. Results and discussion

3.1. Microstructure and stability

Fig. 1 shows the X-ray diffratograms obtained for the different as melt-spun samples. The presence of the α-Al in all the alloys was clearly seen and was indexed with reflections corresponding to: (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (4 0 0) planes in the range of $2\theta = 20–100°$. The icosahedral phase was indexed using Cahn's indexation scheme with reflections given individual (N/M) indexes [8]. Reflections corresponding to (6/9), (18/29), (20/32), (38/61) and (52/84) in the range $2\theta = 20–100°$ were indexed. Additional weak

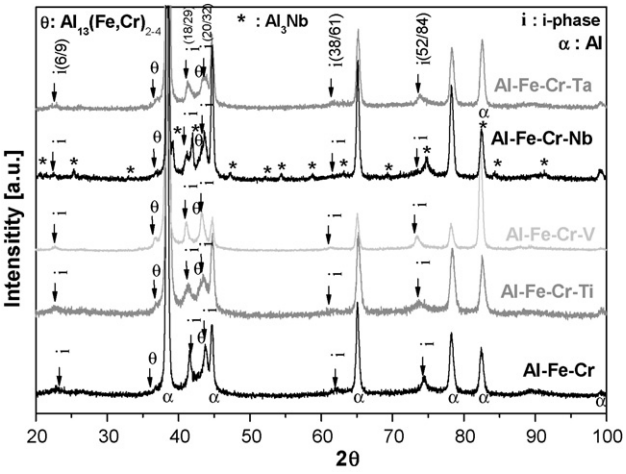

Fig. 1. X-ray diffractograms from the as melt-spun alloys.

X-ray peaks were observed at $2\theta \sim 36.7°$, 43.7°, 43.9°, 44.2°, 44.6° and 75.5° for all the as-spun alloys. These peaks were assigned to the metastable distorted θ-$Al_{13}(Cr,Fe)_{2-4}$ phase with chemical composition undetermined but in between the two stable monoclinic θ-phases (θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$) [4,9–11]. Thus, the XRD peaks of the distorted θ-$Al_{13}(Cr, Fe)_{2-4}$ were found to be weak and broad and overlapping with some peaks from both stable θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$ phases [9–11].

In particular, the Nb alloy exhibited the following additional reflections from the (0 0 2), (1 0 1), (1 1 0), (1 1 2), (0 0 4), (2 0 0), (1 1 4), (1 0 5), (2 1 3), (2 0 4), (1 1 6) and (2 2 0) planes of the stable tetragonal t-Al_3Nb phase. No other intermetallic compounds were identified in the Al–Fe–Cr, Al–Fe–Cr–Ti, Al–Fe–Cr–V and Al–Fe–Cr–Ta melt-spun alloys.

Fig. 2 shows representative bright field TEM micrographs showing the microstructure of the as melt-spun alloys for the Al–Fe–Cr alloy (Fig. 2a) and the Al–Fe–Cr–Ta (Fig. 2b). All the alloys showed similar microstructure containing quasicrystalline particles embedded in an α-Al matrix, however it was observed that the addition of a quaternary element led to a refinement of the quasicrystalline particles size of ~50%.

Fig. 3 shows the DSC runs for the as-spun alloys. It can be observed that there was a shift of the main exothermic peak towards higher temperatures with the addition of a fourth element. Moreover, the Nb and Ta brought along a greater stability delaying

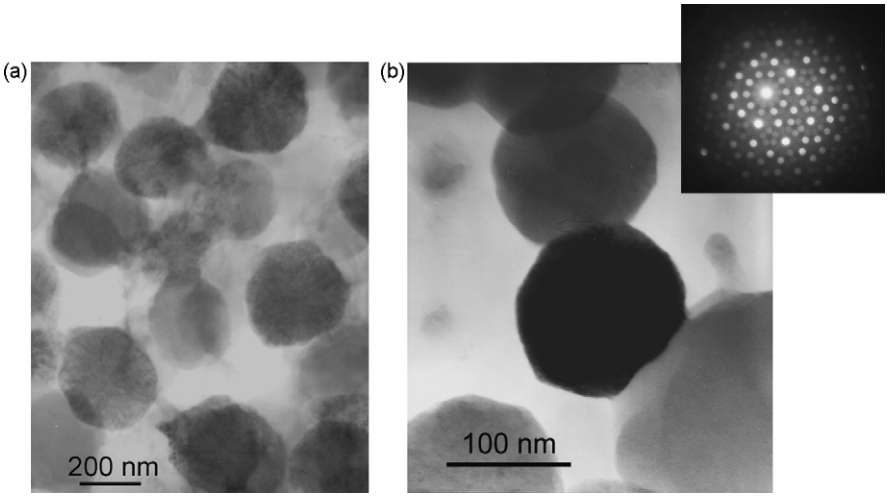

Fig. 2. Bright field TEM images showing the microstructure of the (a) Al–Fe–Cr and (b) Al–Fe–Cr–Ta alloys in the as-spun state.

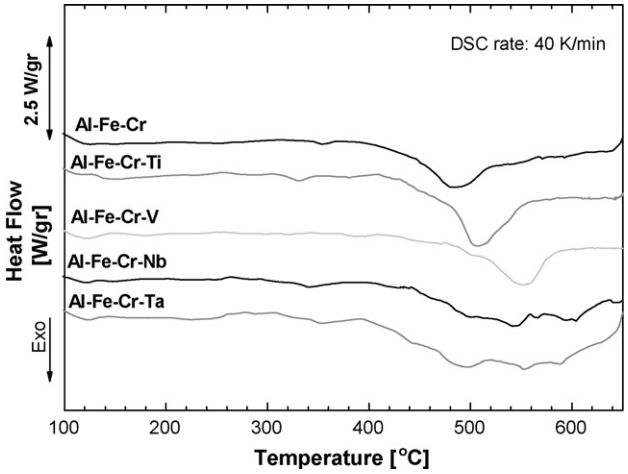

Fig. 3. DSC curves at 40 K/min of the Al–Fe–Cr, Al–Fe–Cr–Ti, Al–Fe–Cr–V, Al–Fe–Cr–Nb and Al–Fe–Cr–Ta alloys.

the transformation of the quasicrystalline phase until the onset of the melting of the alloy.

After heat treatment at 450 °C for 30 min, TEM analysis of the Al–Fe–Cr alloy, Fig. 4(a), showed that the quasicrystalline particles had grown in comparison with those in non-heat treated melt-spun samples. In particularly, this alloy shows large quasicrystalline particles with a rosette like shape with an average size of 500 nm. Quasicrystalline particles presenting that kind of shape have been previously observed by other authors in melt-spun Al–Fe–Cr and Al–Cr alloys, respectively [6,12,14,15].

A thorough analysis of the phases and chemical compositions was detailed in previous work by the authors [4,13]. In these works we found that the α-Al grain boundary precipitates in the heat treated samples, correspond to the metastable Al_6Fe and θ-$Al_{13}(Fe,Cr)_{2-4}$ phases. Fig. 4(b) shows that after the heat treatment at 450 °C for 30 min of the Al–Fe–Cr–Ta no new phases were observed and the quasicrystalline particles maintained a similar size and shape to that of the as melt-spun state. The lack of grain boundary particles observed in the heat treated quaternary alloy is due to the lower solute concentration in the α-Al matrix compared with the ternary alloy [4,13].

An example of the microstructural evolution of the ternary alloy due to an isothermal heat treatment is shown in the bright field TEM micrographs in Fig. 5(a–c). These micrographs correspond to the hot-stage TEM analysis. The sample was heated from room temperature and stabilized at 474 °C. This whole procedure took ~10 min. Subsequently an isothermal experiment was carried out at 474 °C for 35 min. Fig. 5(a–c) refers to specific stages along the run. Different aspects in the microstructural evolution were observed. Fig. 5(a) shows the microstructure at 474 °C at the beginning of isothermal stage of the in situ experiment. The microstructure consisted of quasicrystalline particles and segregated particles in the matrix, probably $Al_6(Fe,Cr)$ or $Al_{13}(Cr,Fe)_2$ particles as deduced from XRD and EDX analysis on the ternary alloy heat treated at 450 °C for 30 min, which is detailed in ref. [4]. A few thin rod-like particles were also observed. After 13 min at 474 °C the small precipitates in the matrix had completely dissolved. At that stage, other rod-like

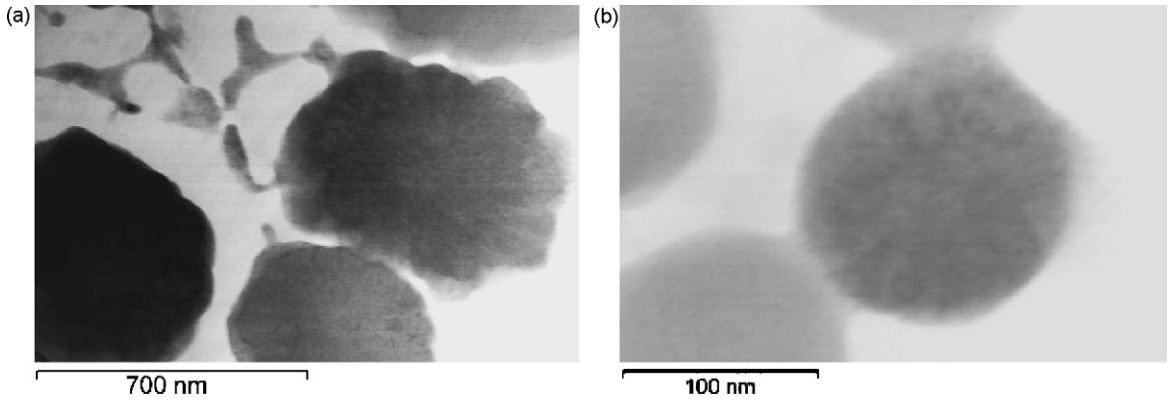

Fig. 4. STEM bright field micrographs of the (a) Al–Fe–Cr and (b) Al–Fe–Cr–Ta alloys after heat treatment at 450 °C for 30 min.

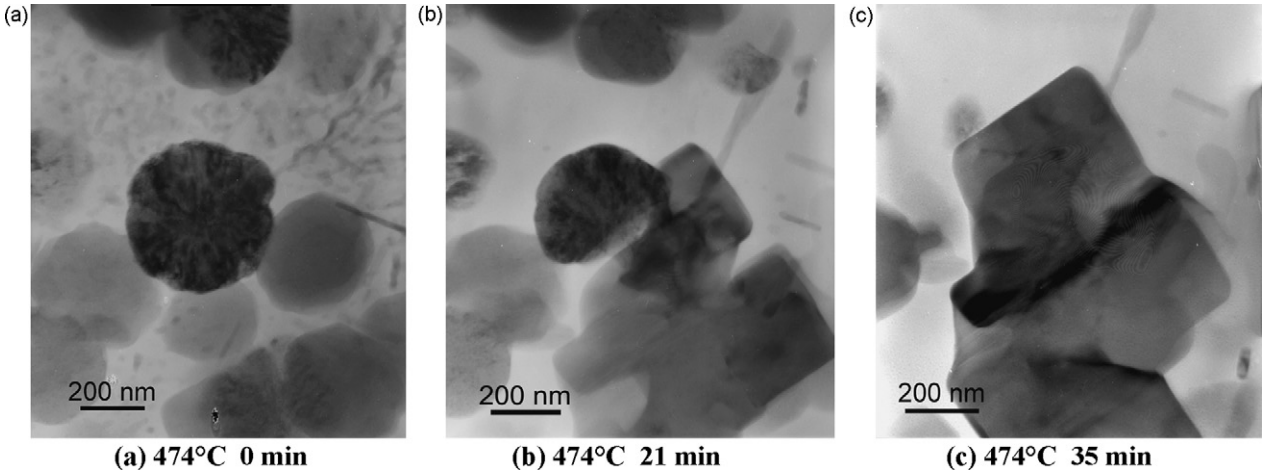

Fig. 5. (a–c) Hot-stage TEM bright field micrographs of the Al–Fe–Cr alloy during an in situ isothermal experiment at 474 °C. The sample was pre-treated for 10 min up to 474 °C. The times indicated below the micrographs do not include the pre-treatment.

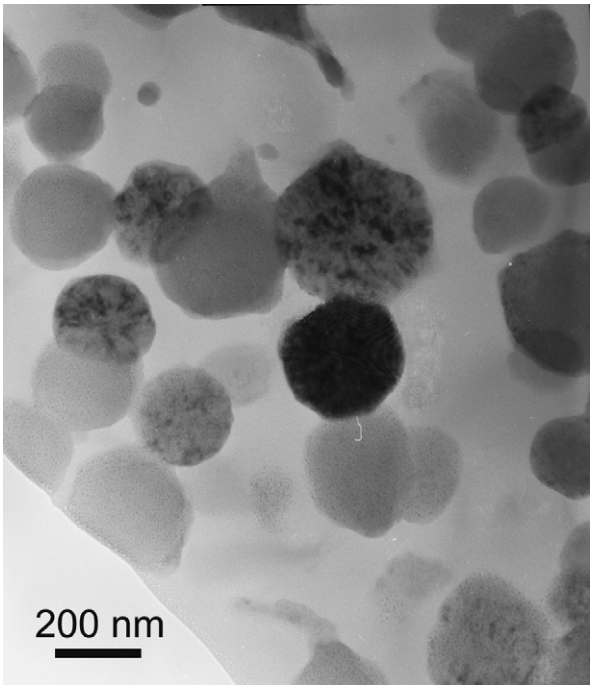

Fig. 6. Bright field TEM micrograph of the Al–Fe–Cr–Ta after heat treatment at 522 °C for 30 min.

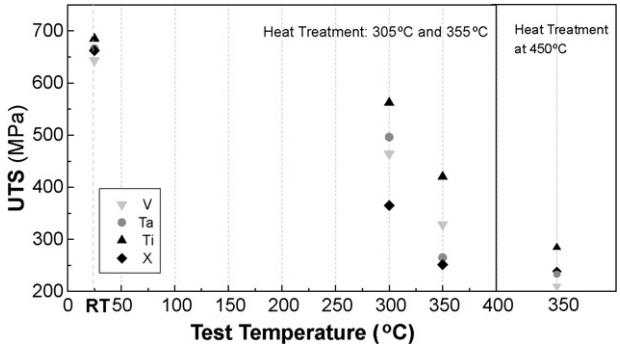

Fig. 7. Ultimate tensile strength vs test temperature (room temperature, 300 °C and 350 °C). The effect of the heat treatment temperature on the ultimate tensile strength at 350 °C can also be observed. The graph shows the ultimate tensile strength values for each of the alloys heat treated at 355 °C (left hand side of the graph) and at 450 °C for 30 min (right hand side of the graph) and tested at 350 °C. The corresponding tensile curves are shown in Fig. 8.

particles had appeared. The quasicrystalline particles have started to dissolve and a square-like particle formed and grew up close to the quasicrystal.

Fig. 5(b) shows the microstructure after 21 min; the rod-like particle had almost fully dissolved, whereas the rod-like particles that precipitated during the experiment were still undissolved. The quasicrystal was touched by the square particle and had reduced in size and become flattened on the side toward the square particle. Moreover, the dissolution of the quasicrystal seemed to have accelerated at the side nearer to the growing square particle. After 24 min the square particle was still growing and the quasicrystal continued dissolving apparently at a fastest rate at the closest part to the square particle. The quasicrystal had dissolved completely after 35 min where a completely new microstructure can be seen with no outlines of the quasicrystalline particles.

A sample of the Al–Fe–Cr–Ta, observed in the hot-stage TEM, was pre-treated by increasing the temperature from room temperature to 522 °C in 52 min. Fig. 6 shows the microstructure at 522 °C, in which spherical quasicrystalline particles embedded in the α-Al matrix can be observed together with refined microstructure even after heat treatment at high temperature.

This result is in agreement with those from TEM observation at room temperature of samples heat treated at 450 °C and 550 °C

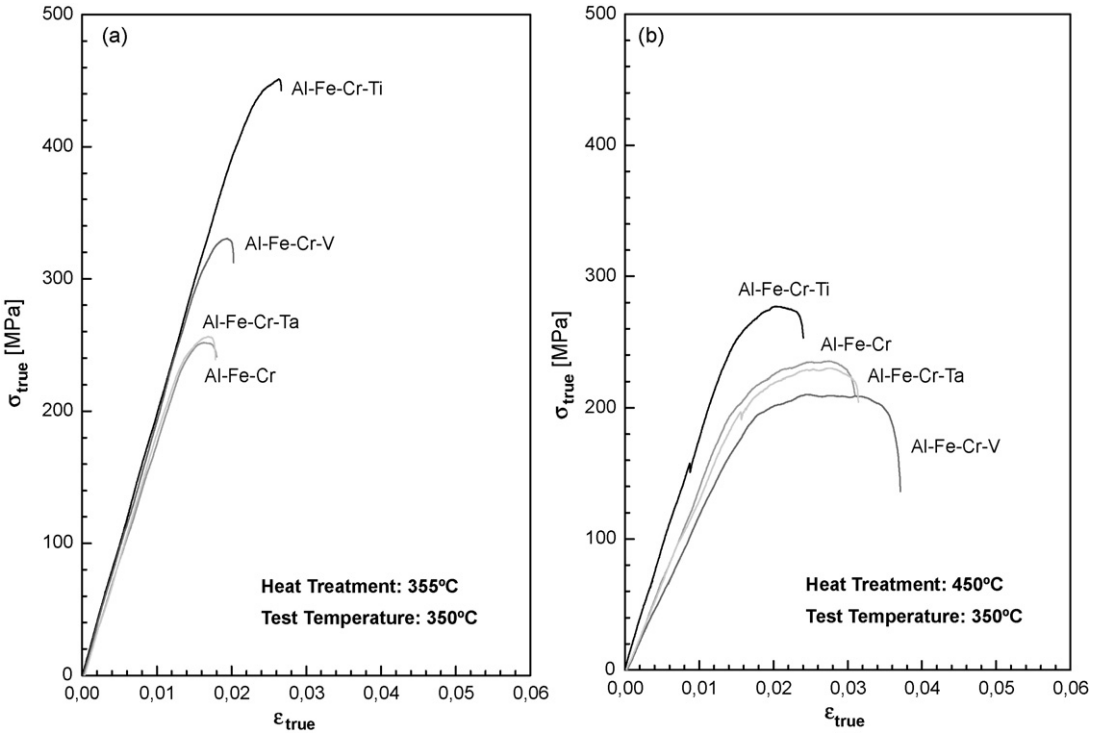

Fig. 8. True stress vs true strain for the Al–Fe–Cr, Al–Fe–Cr–Ti, Al–Fe–Cr–V, and Al–Fe–Cr–Ta alloys. The curves in (a) and (b) were pre-treated for 30 min at 355 °C and 450 °C, respectively. The test temperature was 350 °C in both cases.

for 30 min (see ref. [4]) which implied a higher stability for the Al–Fe–Cr–Ta alloy in comparison with the Al–Fe–Cr, Al–Fe–Cr–V and Al–Fe–Cr–Ti alloys.

3.2. Mechanical properties

Fig. 7 shows the results for the ultimate tensile strength (UTS) as a function of the tensile test temperature. It can be observed that at room temperature (RT) all the as-spun alloys had UTS values in the range of 650–690 MPa, around the maximum value given by Inoue et al. [6,15] for the Al–Fe–Cr–Ti in bulk form. All the alloys studied presented a continuous decrease in UTS with increasing test temperature but these UTS values were higher than that of the bulk Al–Fe–Cr–Ti alloy throughout the entire temperature range. This is expected considering that the bulk alloy was extruded at 400 °C and thus the microstructure should have undergone changes in comparison with the rapidly solidified alloys [6,15] which can affect the mechanical properties.

The Al–Fe–Cr–Ti alloy had the highest UTS value in comparison with the rest of the alloys over the entire temperature range studied. The lowest UTS values were found for the ternary alloy for all the temperatures; moreover this alloy had the greatest decrease of the UTS from RT to 300 °C. Between the temperature range of 300 °C and 350 °C, the Al–Fe–Cr–Ta alloy showed the greatest decrease in UTS.

Fig. 7 also represents the UTS values for the different alloys tested at 350 °C but with different prior heat treatments (for 30 min at 355 °C and at 450 °C, right hand side of the graph), hence with different changes in the microstructures. The alloys have a very similar behaviour to the one reported by Inoue et al. for bulk Al–Fe–Cr–Ti alloys [6,15]. The highest strength values were achieved by the Ti containing alloy while the ternary alloy generally had the lowest strength values. After 450 °C all the alloys suffered from an over-aging effect. However all the values remained higher than the ones for conventional Al alloys and higher that the Al–Fe–Cr–Ti alloy tested by Inoue et al. [6,15]. Fig. 8 shows a comparison of the tensile curves of the samples with heat treatments at 350 °C and heat treated 30 min at 450 °C.

The microstructural analysis of the heat treated samples, after 30 min at 450 °C showed that all the alloys had significant changes in the microstructure compared to the microstructure at lower temperatures [2]. Those changes consisted mainly in grain bordering precipitates and quasicrystals coarsening, in different grade for each alloy (see ref. [4]). Therefore, as a result of the microstructural evolution after the heat treatment at 450 °C all the alloys had very similar UTS at 350 °C. These values for the alloys heat treated at 450 °C are in accordance with those reported by Inoue [2] for the bulk nanoquasicrystalline Ti containing alloy extruded at 400 °C. These results on melt-spun nanoquasicrystalline Al–Fe–Cr-(Ti, V, Nb or Ta) alloys suggest that bulk extruded bars of these alloys would have a very high strength around 250 MPa at 350 °C which is more that five times higher than the commercial Al alloys [16].

4. Conclusions

The addition of Ti, V, Nb or Ta to the $Al_{93}(Fe_3Cr_2)_7$ alloy produced by melt spinning leads to a refined microstructure composed of near-spherical icosahedral particles in an α-Al matrix. Moreover, the addition of those elements increases the stability of the icosahedral quasicrystal. Both Nb and Ta showed the highest effect delaying the dissolution of the icosahedral quasicrystal particles at the melting of the alloy.

All the quaternary melt-spun $Al_{90}Fe_3Cr_2(Ti, V, Nb \text{ or } Ta)_2$ alloy have higher tensile strength than the ternary melt-spun $Al_{93}(Fe_3Cr_2)_7$ alloy up to 350 °C. The Ti containing alloy has the highest tensile strength in that temperature range when the melt-spun alloy is heat treated by 30 min at 5 °C above the test temperature.

When the melt-spun $Al_{93}(Fe_3Cr_2)_7$ and $Al_{93}Fe_3Cr_2(Ti, V \text{ or } Ta)_2$ alloys are heat treated for 30 min at 450 °C the microstructure is affected by grain bordering precipitates and quasicrystals coarsening, to a different extent in each alloy, leading to all the alloys to have a tensile strength value close to 250 MPa at 350 °C.

It is expected these alloys can be obtained in bulk shape by hot extrusion in a range of 400–450 °C with a strength more that five times higher that the corresponding to the commercial alloys, which make the nanoquasicrystalline $Al_{93}Fe_3Cr_2(Ti, V \text{ or } Ta)_2$ alloys very promising for industrial application in the automotive and aeronautical sectors.

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