Structural Characterisation and Mechanical Properties of Nanocomposite Al-based Alloys

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Nanocomposite Al-based alloys can be obtained with a combination of amorphous, crystalline and quasicrystalline phases. In order to understand the correlation between the nanostructure and the mechanical behaviour, four nanocomposite alloys with different characteristics were studied: two alloys from the Al–Fe–Cr–Ti system consisting of a spherical nanoquasicrystalline phase in an \(\alpha\)-Al matrix; one alloy from the Al–Fe–V–Ti system consisting of a mixture of amorphous and \(\alpha\)-Al phases; and one alloy from the Al–Mn–Cr–Cu system consisting of nanocrystalline particles embedded in an \(\alpha\)-Al matrix. Melt-spun samples were prepared and the structure was characterised by means of X-ray diffraction and transmission electron microscopy. Differential scanning calorimetry was used to study the thermal stability and the transformation processes. Tensile tests, fractographic analysis and Vickers microhardness at room temperature were performed in order to evaluate the mechanical behaviour. A combination of solid solution, particle dispersion and grain refinement strengthening was responsible for the high strength of the alloys. The microstructure of the alloy Al\textsubscript{63}Fe\textsubscript{23}Cr\textsubscript{12}Ti\textsubscript{2} (\textsuperscript{at}\%) remained acceptably stable up to 703 K, due to the slow coarsening rate of the icosahedral phase.

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1. Introduction

Since the first non-brittle amorphous Al alloys were obtained in 1988\textsuperscript{1,2} several processes and new Al alloys have been developed. At present, it is possible to produce a wide variety of nanostructured Al-based alloys containing different combinations of amorphous, crystalline and quasicrystalline phases.\textsuperscript{3,4} Nanocrystalline Al-based alloys produced using rapid solidification and powder metallurgy techniques have been developed with improved mechanical properties in comparison to conventional crystalline alloys.\textsuperscript{5,6} One important route in the development of new high strength Al alloys has been focused on the concept of nanocomposite alloys.\textsuperscript{4,7}

One type of nanocomposite that has been studied intensively is amorphous nanocomposites composed of \(\alpha\)-Al nanocrystals finely dispersed in an amorphous matrix.\textsuperscript{8,9} The most important characteristic of these nanocomposites is their high strength, having up to 50\% higher tensile strength than the precursor amorphous alloy.\textsuperscript{8,9} In the Al–Ni–Y system, it has been shown that the strength is controlled by the solute concentration in the amorphous matrix.\textsuperscript{10} During the crystallisation process, which produces the dispersed \(\alpha\)-Al nanocrystals, the average chemical composition of the amorphous matrix changes resulting in an increase in the strength. The resulting strengths can be described by a simple rule of mixtures involving the strengthened amorphous matrix and \(\alpha\)-Al nanocrystals of ideal strength.\textsuperscript{11}

Another promising new type of nanocomposite that has been studied intensively is nanoquasicrystalline composites, composed of nanoquasicrystals dispersed in an \(\alpha\)-Al matrix.\textsuperscript{12,13} These alloys have higher microstructural stability and higher ductility than the amorphous nanocomposites.\textsuperscript{14,15} At present, three important groups of nanoquasicrystalline composites can be distinguished: (i) Al–(Mn/Cr)–Ln (Ln = lanthanides) based with very high strength;\textsuperscript{12,16} (ii) Al–(Mn/Cr)–Cu based with the best ductility;\textsuperscript{17,18} and (iii) Al–Fe–(Cr/V)–Ti based with the best stability.\textsuperscript{19,20} The deformation and strengthening mechanisms in the nanoquasicrystalline composites are still not well known. It has been proposed that an approximant interface phase may improve interfacial bonding between the Al matrix and the quasicrystalline particles, increasing the nanoquasicrystalline composite strength.\textsuperscript{12}

Another type of nanocomposite is that obtained in the Al–(V/Ti)–Fe systems, composed of a very fine nanogrannular amorphous phase embedded in an \(\alpha\)-Al matrix. The formation of the nanogrannular amorphous phase has been related to the presence of icosahedral clusters in the liquid before solidification.\textsuperscript{21,22}

The different types of Al-based nanocomposites are all metastable alloys with good mechanical properties and potential for structural application. It is important therefore to develop a fundamental understanding of the microstructure formation, stability and mechanical properties of the different types of alloy. In the present work, four nanocomposite alloys from three different alloy systems were studied. One alloy from the Al–Mn–Cu–Cr system was selected for good ductility;\textsuperscript{17} another from the Al–Fe–V–Ti system\textsuperscript{20} was selected for its fine-scale nanogrannular amorphous composite structure, and two alloys from the Al–Fe–Cr–Ti system\textsuperscript{19} were selected as nanoquasicrystalline composites with high thermal stability.
2. Experimental

Table 1 shows the nominal chemical composition, the measured composition determined by WDX and the code number of the rapidly solidified alloys. Master alloys were prepared in an arc furnace under He atmosphere using pure elements, Al(99.99%), Cr(99.99%), Fe(99.98%), Mn(99.98%), Cu(99.99%), V(99.7%) and Ti(99.7%). Rapidly solidified samples were obtained by melt spinning onto a rotating copper wheel (40 m/s) in a reduced He atmosphere (200 KPa) using a quartz nozzle, and with a closed-loop controlled ejection temperature of 1200°C. As can be seen in Table 1, a small amount of Si contamination from the quartz nozzle was detected.

The microstructures of ribbon samples were characterised by X-ray diffraction (XRD) in a θ–2θ diffractometer (Philips 1810) using Cu–Kα radiation, and by transmission electron microscopy (TEM) using a Philips CM-20 microscope. The thin foils for TEM were prepared by electropolishing in 20 vol% nitric acid in methanol at 233 K and a voltage of ~15 V. The structural stability and the transformation processes were monitored by differential scanning calorimetry (DSC) in a TA Instruments model 2200 thermal analyser fitted with a 2010 DSC, using a heating rate of 40 K/min under a dynamic Ar atmosphere. The structural evolution was analysed by means of XRD and TEM on samples heat treated for 45 min at selected temperatures representative of the end of each transformation step as determined by DSC.

In order to study the mechanical behaviour, tensile tests on the melt spun samples were carried out using a microtensile machine (Oxford Instruments). The tests were performed on ribbons with an initial length of 10 mm at a strain rate of $10^{-3}$ s$^{-1}$ at room temperature. Fractographic analysis was carried out by scanning electron microscopy (SEM) in a JEOL JSM-840F, and Vickers microhardness was measured in a Leitz Miniload instrument with a load of 100 g. The microhardness was measured at room temperature on samples in both as-spun and heat treated states.

3. Results

3.1 As melt-spun alloys

All melt-spun samples were obtained with a thickness of approximately 30 μm and with the exception of the Ti-1 alloy, could be hand bent up to 180° without fracture, which implies good ductility.

3.1.1 XRD analysis

XRD traces from the as melt-spun samples are shown in Fig. 1. The presence of the α-Al phase was confirmed in all four alloys. In the XRD traces from the Ti-1 and Ti-2 melt spun alloys, in addition to the α-Al phase, between the two main peaks of the α-Al phase, there was a broad, low intensity peak, corresponding to an amorphous phase, between the two main peaks of the α-Al phase. The α-
Al peaks for the V-1 melt spun alloy were broader than those for the other melt spun alloys, perhaps indicating a high level of crystal distortion caused by residual stresses.

The peaks corresponding to the $\alpha$-Al phase in the XRD traces from the Mn-1 melt spun alloy showed a small displacement towards the high angle side. In addition, two small peaks which could not be indexed were present. Several phases, such as icosahedral and approximant phases, have reflections in these positions.26, 27)

### 3.1.2 TEM observation

Figure 2 shows bright field (BF) TEM images of each alloy in the as melt spun state. The Ti-1 melt spun alloy had a uniform distribution of small near-spherical quasicrystalline particles 10–20 nm in diameter embedded in an $\alpha$-Al matrix with grains $\sim 0.5–2 \mu m$ in size (Fig. 2(a)). The Ti-2 melt spun alloy (Fig. 2(b)), had a lower volume fraction distribution of coarser near-spherical quasicrystalline particles 50–80 nm in diameter embedded in an $\alpha$-Al matrix. Some non-spherical small particles were observed but could not be identified, possibly the intermetallic compounds detected by XRD (Fig. 1). The inset of Fig. 2(b) shows a nano beam electron diffraction pattern, taken from a near-spherical particle, that denotes a five-fold symmetry characteristic of an icosahedral phase, in agreement with the XRD profiles (Fig. 1).

The V-1 melt spun alloy (Fig. 2(c)) had the finest scale microstructure. A large, dark-imaging $\alpha$-Al grain ($\sim 0.7–1.5 \mu m$) is shown with a high fraction of 5–10 nm embedded particles. In agreement with the XRD traces, corresponding selected area electron diffraction patterns showed a continuous diffraction halo corresponding to the nanogranular amorphous phase and diffraction spots corresponding to the $\alpha$-Al matrix (see inset of Fig. 2(c)).

The Mn-1 melt spun alloy (Fig. 2(d)) had the most conventional microstructure of $\sim 1–2 \mu m$ sized $\alpha$-Al grains with 20–40 nm intermetallic particles decorating the grain boundaries and a low fraction of 10–20 nm precipitates within the $\alpha$-Al grains. The presence of the i-phase could not be verified in this alloy by TEM observation.

### 3.2 Structural stability

#### 3.2.1 DSC runs

DSC traces from the melt spun Ti-2, V-1 and Mn-1 alloys are shown in Fig. 3. Each alloy studied showed two exothermic transitions corresponding to two transformation steps: the first one very sluggish and broad with relatively low heat release, and the second one strong and sharp with relatively high heat release. The weak peak of the first transition was centred around 595 K and 600 K for the Mn-1 and V-1 alloys respectively. The Ti-2 alloy showed a first transition centred at a higher temperature of 670–690 K. The second transition showed a much stronger heat release, and had a different shape for each alloy. The Ti-2 alloy showed a second transition apparently composed of only one peak at approximately 773 K, some 35–40 K higher than those of the other two alloys. The V-1 alloy showed a second transition composed of two sharp overlapping peaks at 729 K and 743 K, whereas the Mn-1 alloy showed a second transition with a broad peak at $\sim 739 K$.

#### 3.2.2 XRD analysis of heat treated alloys

The temperatures of the heat treatments are indicated in Fig. 3 and were chosen in order to analyse the structure developed in each transformation step as determined by DSC. Figure 4 shows XRD traces from the Ti-2 alloy, as melt spun
and after heat treatment for 45 min at 703 K and 823 K. After heat treatment at 703 K, i.e. at the end of the first transformation step, the structure remained similar to the as melt spun alloy, still consisting of a mixture of i-phase, $\alpha$-Al$_{13}$Cr$_2$ and $\alpha$-Al$_3$Ti embedded in an $\alpha$-Al matrix. The peak corresponding to (103)$t$-Al$_3$Ti at $2\theta = 39.2^\circ$ increased in intensity. Moreover, three new peaks were observed, two of which were close to peaks corresponding to the icosahedral phase. These peaks could be indexed as the distorted $\theta$-Al$_{13}$(Cr,Fe)$_2$x phases, which has been observed in Al-Fe-Cr alloys obtained by rapid quenching.24,25,26 This structure is a metastable state which forms prior to transformation to the stable $\theta$-Al$_{13}$Cr$_2$ and $\theta$-Al$_{13}$Fe$_4$ phases. After higher temperature heat treatment at 823 K, $\alpha$-Al, $\alpha$-Al$_{13}$Cr$_2$, $\theta$-Al$_{13}$Fe$_4$ and $\theta$-Al$_3$Ti phases were all identified by XRD.

Figure 5 shows XRD traces from the V-1 alloy, as melt spun and after heat treatment at 683 K and 823 K.

and after heat treatment for 45 min at 703 K and 823 K. After heat treatment at 703 K, the microstructure again showed high volume fraction of intermetallic phases of different sizes, as can be seen in Figs. 7(b), 8(b) and 8(c). In addition to the nucleation of some additional crystalline phases, a continuous diffraction halo was still present which confirmed the continuing presence of the amorphous phase as shown in the inset of Fig. 7(b). After heat treatment at the higher temperature of 823 K, the microstructure was similar to that of the Ti-2 alloy heat treated at the same temperature again consisting of a high volume fraction of intermetallic phases of different sizes, as can be seen in Figs. 8(a) and (b).

TEM observation of the microstructure of the V-1 alloy after heat treatment for 45 min at 628 K showed no change with respect to the as melt spun microstructure, as can be seen by comparing Figs. 7(a) and 2(b). There was little evidence of the formation of intermetallic compounds, in agreement with the XRD traces in Fig. 4. The near-spherical quasicrystalline particles remained without apparent grain coarsening as shown in Fig. 7(a). After heat treatment at the higher temperature of 823 K a high volume fraction of intermetallic phases of different sizes was observed as shown in Fig. 8(a).

Figure 6 shows XRD traces from the Mn-1 alloy, as melt spun and after heat treatment for 45 min at 603 K and 823 K. The unidentified peaks present in the as melt spun alloy (see arrow in Fig. 6) disappeared after heat treatment at 603 K, confirming that the peaks corresponded to a metastable phase. In addition there was some evidence of the initial stages of formation of $\theta$-Al$_{13}$Cr$_2$ during the first exothermic transition as shown in Fig. 6. After higher temperature heat treatment at 823 K, $\alpha$-Al, $\theta$-Al$_{13}$Cr$_2$ and O-Al$_{11}$Cu$_5$Mn$_3$ phases were all identified by XRD.

### 3.2.3 TEM of heat treated alloys

TEM observation of the microstructure of the Ti-2 alloy after heat treatment for 45 min at 703 K showed little change with respect to the melt spun microstructure, as can be seen by comparing Figs. 7(a) and 2(b). There was little evidence of the formation of intermetallic compounds, in agreement with the XRD traces in Fig. 4. The near-spherical quasicrystalline particles remained without apparent grain coarsening as shown in Fig. 7(a). After heat treatment at the higher temperature of 823 K, the microstructure was similar to that of the Ti-2 alloy heat treated at the same temperature again consisting of a high volume fraction of intermetallic phases of different sizes, as can be seen in Figs. 8(a) and (b).

TEM observation of the microstructure of the V-1 alloy after heat treatment for 45 min at 628 K again showed no change with respect to the as melt spun microstructure, as can be seen by comparing Figs. 7(b) and 2(c). A continuous diffraction halo was still present which confirmed the continuing presence of the amorphous phase as shown in the inset of Fig. 7(b). After heat treatment at the higher temperature of 823 K, the microstructure was similar to that of the Ti-2 alloy heat treated at the same temperature again consisting of a high volume fraction of intermetallic phases of different sizes, as can be seen in Figs. 8(a) and (b).

TEM observation of the microstructure of the Mn-1 alloy after heat treatment for 45 min at 603 K showed significant particle coarsening, as can be seen by comparing Figs. 7(c) and 2(d). After heat treatment at the higher temperature of 823 K, the microstructure again showed high volume fraction of coarse intermetallic particles (Fig. 8(c)).
3.3 Mechanical properties

3.3.1 Tensile testing of melt spun alloys

Figure 9 shows typical examples of stress-strain curves obtained from tensile tests of the four as melt spun alloys at room temperature. The Ti-1 alloy was very brittle and fractured at low tensile stress, in the range of 200–250 MPa. The Ti-2 alloy, with a lower volume fraction of the icosahedral phase than the Ti-1 alloy, had higher ultimate tensile strength and showed a small plastic deformation zone, with fracture stresses and total strains (elastic and plastic) typically of 510–575 MPa and 3–3.5% respectively. The V-1 alloy had the highest strength but without showing macroscopic ductile behaviour. Conversely, the Mn-1 alloy had comparatively good ductility, with a parabolic behaviour similar to conventional ductile Al alloys, albeit with a low yield strength, with fracture stresses and strains typically of 210–300 MPa and 3.5–4.5% respectively.

3.3.2 Fractography of melt-spun alloys

The fracture surfaces of the as melt spun Ti-1 samples showed no evidence of plastic flow. They were flat with some undulations as a consequence of catastrophic brittle fracture in a stressed material (Fig. 10(a)). On the other hand, the fracture surfaces of the as melt spun Mn-1 samples exhibited necking and a dimpled fracture surface characteristic of plastic deformation in crystalline Al alloys, as shown in Fig. 10(b). The fracture surfaces of the as melt spun Ti-2 samples showed the characteristic ribs of ductile fracture, as shown in Fig. 10(c) (see details in the inset of Figure) with slip bands close to the fracture surface. The fracture surfaces of the as melt spun V-1 samples, that had not shown macroscopic plastic deformation, again showed ribs and vein patterns characteristic of a ductile fracture (Fig. 10(d)) similar to those found in ductile amorphous or partially amorphous alloys.29,30) Furthermore typical shear bands, as are observed in glassy metals,30) were found near the fracture surface.

3.3.3 Microhardness as a function of heat treatment

Figure 11 shows microhardness results for Ti-2, V-1 and Mn-1 alloys as melt spun and after heat treatment at the different temperatures corresponding to the end of each transformation step. The Ti-2 and V-1 alloys had similar microhard-
ness values in the as melt-spun state and again after heat treatment at high temperature (823 K). The microhardness values of the Ti-2 and Mn-1 alloys decreased continuously, whereas the microhardness of the V-1 alloy increased initially, after heat treatment at intermediate temperature (628 K), before decreasing, after heat treatment at higher temperature (823 K). The Mn-1 alloy had the lowest microhardness values and decreased faster with the increasing heat treatment temperature in comparison with the other alloys.

4. Discussion

4.1 Structure and stability

All samples had the α-Al phase as a matrix, although the alloys of the different systems showed different microstructures. The Ti-1 and Ti-2 alloys had finer microstructures than observed previously for a melt spun sample with a composition close to the icosahedral phase,20) and for the same composition produced in bulk by warm extrusion of atomised powders.31) The XRD profiles of both Ti-1 and Ti-2 showed only the P-type i-phase peaks, and no other peaks related to the F-type ordered i-phase found previously by Inoue et al.20) in similar alloys containing Fe. The weakness of the (18/29) and (20/32) i-phase peaks may be related to the presence of a disordered P-type i-phase, and reflections from the distorted planes of approximant phases, such as monoclinic θ-Al–(Cr, Fe).24, 25, 28) The two other small peaks in XRD traces of the Ti-2 alloy could be assigned to t-Al,Ti and θ-Al–(Cr, Fe). The sample heat treated at 703 K showed clearer peaks from θ-Al–(Cr, Fe), and after heat treatment at 823 K all the equilibrium phases were formed following decomposition of the i-phase. The i-phase at higher alloy content than Ti-1 or Ti-2, i.e. with a composition close to Al41.2Fe2Cr0.3Ti2.5 (at%), has been shown previously to transform via two DSC peaks at ~850 K and ~925 K.19) The Ti-2 sample, of the present study has a lower alloy content, and also shows two peaks, although at lower temperatures (Fig. 3). The difference in transformation temperatures results from the lower alloy content and the P-type disordered structure of the i-phase.

XRD (Fig. 1) and TEM (Fig. 2(c)) show that as melt-spun V-1 has a microstructure composed of a nanogranular amorphous phase embedded in an α-Al matrix. The formation of this kind of microstructure is related to glass formation in icosahedral alloys.32–34) These alloys have, in the liquid, an icosahedral short range order around the transition metal atoms which provides a barrier to the formation of crystalline phases.33, 35) Therefore, an icosahedral phase can form composed of interpenetrating clusters of icosahedral symmetry.36) When the transition metal in the i-cluster has low atomic diffusivity in the Al liquid (such as Ti and V), quasicrystalline formation becomes difficult and a nanogranular amorphous region with icosahedral short range order can be retained in the α-Al matrix. It has been reported34, 37) that a decrease in cooling rate allows the formation of the quasicrystalline phase. The subsequent annealing of the V-1 alloy shows a first heat treatment step where no microstructural changes are observed (Figs. 5 and 7(b)), perhaps caused by structural relaxation. On the other hand, the second transformation step is characterized by two exothermic DSC peaks around 729 K and 743 K (Fig. 3). Similar behaviour has been observed for the ternary nanogranular amorphous alloys Al93Fe7Ti4 and Al93Fe2V432, 38) although at lower temperature, which confirms the higher stability of the quaternary alloy. After the second heat treatment step, only the crystalline stable phases are observed (Fig. 5).

The as melt spun Mn-1 alloy has a conventional microstructure with fine particles in the grain boundaries and inside the α-Al grains. The presence of the i-phase could not be confirmed. Haas et al.17) have reported the presence of the i-phase for a sample with a similar composition produced by warm extrusion. That means that the formation of the i-phase in this alloy is very sensitive to the chemical composition and the kinetic conditions. The lower alloy content of the Mn-1 alloy with respect to Ti-1, Ti-2 and V-1, and the higher solubility of Cu in α-Al (3 to 8 times higher than Fe, Cr, Mn and Ti) may hinder the formation of the i-phase. In agreement with this hypothesis, there is a small displacement in the positions of the α-Al peaks observed in the XRD profiles (Fig. 1), indicating that the α-Al matrix has a higher solute content. The first heat treatment step (Fig. 2) is characterised by intermetallic coarsening (Fig. 7(c)) and decomposition of the unindexed metastable phase (Fig. 6). The second DSC step, with a broad exothermic peak at ~740 K is associated with the formation of coarse intermetallic compounds (Fig. 8(c)). The decomposition of the quasicrystalline particles was reported by Haas et al.,17) to occur at ~700 K at 10 K/min. Considering the peak displacement with the DSC scan rate,19) that means that the stability of the metastable alloy is reached at a similar temperature for the decomposition of either the metastable crystalline or quasicrystalline precursor phase.

4.2 Mechanical properties

4.2.1 Al–Fe–Cr–Ti system

The tensile stress-strain curves in Fig. 9 and the SEM fractographs in Fig. 10, show that the volume fraction of
the icosahedral phase has a great influence on mechanical properties in the Al–Fe–Cr–Ti system (Ti-1 and Ti-2). The less highly alloyed Ti-2 material shows a tensile strength (~550 MPa) similar to that reported by Inoue et al. on a bulk warm extruded sample, although the failure strain (~3.5%) is slightly lower. The volume fraction of particles can be estimated, assuming that particles are arranged like points of a fcc lattice, from the relationship:

\[ f = \frac{r_p^2}{\langle \lambda \rangle^2} \]

where \( r_p \) is the mean planar particle radius and \( \lambda \) is the mean distance between the centres of the planar particles. From TEM observation the average values are \((2r_p) \sim 65\,\text{nm} \) and \( \langle \lambda \rangle \sim 100\,\text{nm} \) for the Ti-2 alloy, giving \( f \sim 0.42 \), similar to the value of 0.45 reported by Inoue et al. Similar calculation for the more highly alloyed Ti-1 material gives \( f \sim 0.46 \).

The importance of the volume fraction of the second phase in nanocomposites has been demonstrated by Scanlon et al. They observed in nanoscale mixtures of a pure plastic metal and hard oxide nanoparticles, that the microhardness has a different relationship with respect to the volume fraction after the percolation threshold of ~0.5. A similar concept has been proposed to explain the ductile-brittle transition as a function of chemical composition in heterogeneous amorphous metals and nanocomposites containing hard nanocrystals.

The high volume fraction Ti-1 alloy has the highest microhardness value (μHV₁₀₀ ~ 450 kg/mm²) and shows completely brittle behaviour (Fig. 9) without traces of microplasticity or evidence of second phase particles on the fracture surface. This mode of fracture results presumably from the presence of pre-existing internal or surface flaws or cracks, so that crack nucleation is not necessary. The stress is concentrated progressively ahead of the pre-existing flaws or cracks, crack propagation takes place throughout the matrix between the high volume fraction of hard quasicrystalline particles as soon as it is accompanied by reduction in total system energy, leading to brittle fracture. Neither sheared nor cleaved quasicrystalline particles have been observed on fracture surfaces in other nanoquasicrystalline Al-based alloys.

The low volume fraction Ti-2 alloy, shows significant ductility (Fig. 9), and shear flow associated with heterogeneous microscopic plasticity can be seen clearly on the fracture surface (inset of Fig. 10(c)). The lower volume fraction of second phase particles allows plastic deformation and prevents catastrophic brittle failure at pre-existing flaws or cracks. Fracture is initiated at higher stress level than the more brittle Ti-1 alloy, when the applied stress is sufficient to activate multiple slip or twinning leading to formation of microcracks. The enlarged view of the high stress region of plastically deformed Ti-1 alloy, when the applied stress is sufficient to activate multiple slip of twinning leading to formation of microcracks. This yield stress is that required to nucleate and grow slip bands which propagate until specimen failure by crack propagation throughout the Al matrix, as can be deduced by the rib marks with small grains in the fracture surface (inset of Fig. 10(c)).

Two different regions can be observed in the fracture surface (inset of Fig. 10(c)) that can be explained as follows: (i) The surface of the ribbon is unable to support a stress, deforms under plane stress conditions, and produces shear lips. (ii) The central portion of the ribbon is subjected to plane strain conditions and the cracks advance faster as a result of a smaller plastic zone size and a triaxial stress state. This results in a reduced fracture toughness but with a ductile fracture.

Heat treatment for 45 min at 703 K, i.e. after the first transformation step, on the Ti-2 alloy produces ~40% reduction in the microhardness from ~396 to ~240 kg/mm². This softening is related to the relaxation of residual stresses in the α-Al matrix, and the reduction of solute content in the matrix, as intermetallic particles are formed. The decomposition of the icosahedral phase and the coarsening of the intermetallic particles reduces the microhardness value still further, by ~28% to ~173 kg/mm² (Fig. 11).
4.2.2 Al–Fe–Cr–V system

The V-1 alloy has around 0.5 volume fraction of the nanogranular amorphous phase, which acts as a strengthening agent. The homogeneous distribution of a high volume fraction of very fine hard particles is a well known alloy strengthening mechanism.\(^{43}\) In agreement, V-1 alloy shows a very high ultimate tensile strength, \(\sigma_{\text{UTS}} \sim 650\text{ MPa}\) (Fig. 9). This value is higher than that reported by Kimura et al.\(^{20}\) for an alloy with the same composition produced by warm extrusion of atomised powders (\(\sigma_{\text{UTS}} \sim 500\text{ MPa}\)), with a microstructure of 120 nm sized icosahedral particles distributed in an \(\alpha\)-Al matrix. The larger icosahedral particle size (120 nm compared with the 5 to 10 nm sized amorphous regions) may explain the difference in \(\sigma_{\text{UTS}}\) values between the extruded and the present melt-spun alloys.

Several \(\sigma_{\text{UTS}}\) values have been reported for Al-based alloys with a microstructure similar to the V-1 alloy: 1000 MPa for \(\text{Al}_{93}\text{Fe}_{2}\text{V}_{4}\text{Si}_{2}\),\(^{25}\) 1350 MPa for \(\text{Al}_{93}\text{Fe}_{2}\text{V}_{4}\text{Cr}_{2}\),\(^{21}\) 1320 MPa for \(\text{Al}_{92}\text{Fe}_{2}\text{V}_{4}\text{Ti}_{4}\),\(^{21}\) and 760 MPa for \(\text{Al}_{92}\text{Fe}_{2}\text{V}_{4}\text{Si}_{2}\).\(^{34}\) The latter alloy has the same Al concentration as the V-1 alloy, and has a \(\sigma_{\text{UTS}}\) value closer to that of the V-1 alloy than the other alloys. The similarity in behaviour between \(\text{Al}_{93}\text{Fe}_{2}\text{V}_{4}\text{Si}_{2}\) and V-1 may be related to a similar volume fraction of hard particles with similar macroscopically brittle failure mode (Fig. 9).

Fractographic investigation shows that fracture in V-1 is a ductile process, resulting in a fracture surface with rib marks and vein patterns (Fig. 10(d)) characteristic of adiabatic fractures in fully or partially amorphous metals.\(^{8,29}\) A vein pattern on the fracture surface of nanogranular amorphous Al-based alloys has been observed previously by Inoue et al.\(^{38}\)

The V-1 alloy also has an acceptable ductility in bending tests, but nanocomposites obtained by crystallisation with a similar (solid solution, grain refinement and dispersion particles) was observed to be responsible for the high strength of the different microstructures obtained by the different processing routes. Haas et al.\(^{17}\) reported a microstructure composed of icosahedral particles embedded in an \(\alpha\)-Al matrix, whereas the Mn-1 alloy, produced by liquid quenching, exhibits a fine scale distribution of particles at the \(\alpha\)-Al grain boundaries which can decrease the toughness and hence the strength and the ductility.\(^{46}\)

After heat treatment for 45 min at 603 K, the microhardness of the Mn-1 alloy decreases by about 60%, from \(\sim 340\) to \(\sim 124\text{ kg/mm}^2\), which could be related to the formation of additional incoherent precipitates in the \(\alpha\)-Al matrix and coarsening of the particles (Fig. 7(c)). After the second stage of heat treatment for 45 min at 823 K, the Mn-1 alloy shows a microstructure of rod-shaped submicron intermetallic compounds in an \(\alpha\)-Al matrix, and the microhardness decreases further, by \(\sim 33\%\) to \(\sim 78\text{ kg/mm}^2\).

5. Conclusion

Four Al-based nanocomposite alloys with different kinds of microstructure composed of crystalline, amorphous or quasicrystalline phases dispersed in an \(\alpha\)-Al matrix have been studied.

The Ti-2 alloy contained icosahedral particles in an \(\alpha\)-Al matrix, and exhibited a high strength and a very stable microstructure during heat treatment, with the icosahedral particles resistant to coarsening prior to decomposition into crystalline phases. The V-1 alloy contained a nanogranular amorphous phase in an \(\alpha\)-Al matrix, and exhibited a highest strength with a moderately stable microstructure up to 628 K, but relaxation in the amorphous structure made the alloy harder and more brittle. The Mn-1 alloy contained strengthening crystalline intermetallic particles in the \(\alpha\)-Al matrix, and exhibited a high ductility, with a significant decrease in strength during heat treatment caused by incoherent precipitation and particle coarsening.

A combination of classical strengthening mechanisms (solid solution, grain refinement and dispersion particles) was observed to be responsible for the high strength of the different kinds of nanocomposites studied.

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REFERENCES