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Structure and stability of rapidly quenched $Al_{86}Cr_{14-x}Fe_x$ alloys

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The structural and thermal properties of melt spun $Al_{86}Cr_{14-x}Fe_x$ alloys have been investigated using X-ray diffraction, transmission electron microscopy, electron diffraction and differential thermal analysis. Electron diffraction patterns indicate that all alloys contain quasicrystalline nodules with icosahedral symmetry in a matrix of fcc aluminium. Microscopically the alloys fall into two categories; those with $x \leq 6$ and those with $x > 6$. The first class alloys shows large (>1 μm) icosahedral crystallites with well defined dendritic crystallite growth and sharp quasicrystalline X-ray diffraction peaks. The latter alloys show quasicrystalline crystallites which are predominantly much smaller as well as considerably broadened X-ray diffraction peaks. Thermal analysis measurements indicate that the activation energy for crystallization in these alloys is about 1.5 eV.

1. Introduction

A quasicrystalline phase exhibiting icosahedral symmetry has been observed in a number of rapidly solidified alloys. The most commonly studied of these are various aluminium–transition metal alloys [1–3]. While the existence of the icosahedral phase in rapidly solidified alloys of aluminium with early 3d transition metal elements (e.g. vanadium, chromium and manganese) is well established [1, 2, 4–6], there is still some controversy concerning the structure of some alloys of aluminium with the late 3d transition metal elements (e.g. iron, cobalt, nickel) [1–4, 7, 8]. Al–Fe alloys near the stoichiometry Al_6Fe are a case in point. While some authors have reported these alloys to be of the icosahedral structure [3, 8] other measurements seem to indicate that these alloys are of the related decagonal phase [e.g. 10]. In any case it seems to be well established that the X-ray diffraction peaks resulting from the metastable phase in rapidly quenched Al–Fe (and other aluminium–late 3d transition metal alloys) are considerably broader than those from metastable Al–Mn (and other aluminium–early 3d transition metal alloys) [2, 3]. In the present work we have undertaken an investigation of the structure and stability of the rapidly quenched alloys $Al_{86}Cr_{14-x}Fe_x$ ($0 \leq x \leq 14$); a series covering the range of compositions from $Al_{86}Cr_{14}$, a well established icosahedral alloy with sharp X-ray diffraction peaks to $Al_{86}Fe_{14}$ a questionable icosahedral alloy with broad diffraction peaks.

2. Experimental methods

Alloys were prepared by first arc melting high purity elements under an atmosphere of argon. Rapidly solidified ribbons were prepared by ejecting melts from a 0.7 mm orifice using a 100 kPa over pressure of argon onto the surface of a single copper roller. The surface velocity of the roller was approximately 65 m sec^{-1} and all ribbons were quenched into air.

X-ray diffraction patterns of all as-quenched ribbons were obtained on either a Siemens powder diffractometer or a Rigaku RU300 rotating anode diffractometer using CuK_α radiation.

Differential thermal analysis (DTA) measurements were performed on a Fisher 260F thermal analyser (see reference [11] for further details). All alloys prepared in this work were tested using a heating rate of 20 K min^{-1}. $Al_{86}Cr_{14}$ and $Al_{86}Fe_{14}$ were further treated at various heating rates to determine the activation energy for crystallization. These data were analysed

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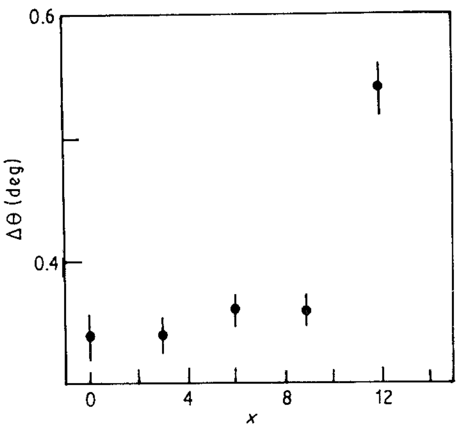

Figure 1 Line width of the (100000) diffraction peak as a function of composition for $Al_{86}Cr_{14-x}Fe_x$ alloys.

using Kissinger–Boswell plots [12, 13]. All DTA measurements were performed on samples of approximately 25 mg.

Transmission electron microscopy was carried out on a Phillips TEM/STEM electron microscope operating at 120 kV. Measurements were made on portions of the ribbons which were naturally thin enough (< 400 nm) to allow complete penetration of the electrons.

3. Results and discussion

3.1. X-ray diffraction measurements

X-ray diffraction patterns of all as-quenched alloys showed the presence of fcc aluminium as well as a second phase. The diffraction peaks for this latter phase were consistent with those of the quasicrystalline icosahedral phase reported by Bancel *et al.* [14] and Dunlap and Dini [2]. The varition of the linewidth of the (100000) peak with iron content is illustrated in Fig. 1. This figure shows the considerable line broadening which occurs for alloys near the iron-rich end of the series.

The dependence of the q vector for the (100000) peak on valence concentration, V, is illustrated in Fig. 2. V is the average number of 3d and 4s electrons per transition metal atom. In this way, results are shown as well for $Al_{86}Mn_{14}$ as reported by Bancel *et al.* [14]. A reasonably linear increase in q is observed as a function of V. This is consistent with an expected decrease in the average Goldschmidt radius of the transition metal atoms and suggest a direct substitution of the iron for the chromium in the icosahedral phase.

It has been suggested that the broadening of the X-ray diffraction peaks of the quasicrystalline phase results from the effects of small crystalline sizes [3, 15]; about 6 nm.

3.2. Electron microscopy and electron diffraction measurements

Fig. 3 shows transmission electron micrographs (TEM) of the series of alloys studied here. All alloys show Al–Cr–Fe crystallites imbedded in a matrix of fcc aluminium. Convergent beam microdiffraction patterns of the crystallites show five-fold symmetry as described by Shechtman *et al.* [1] indicating the icosahedral phase. The quasicrystalline crystallites are

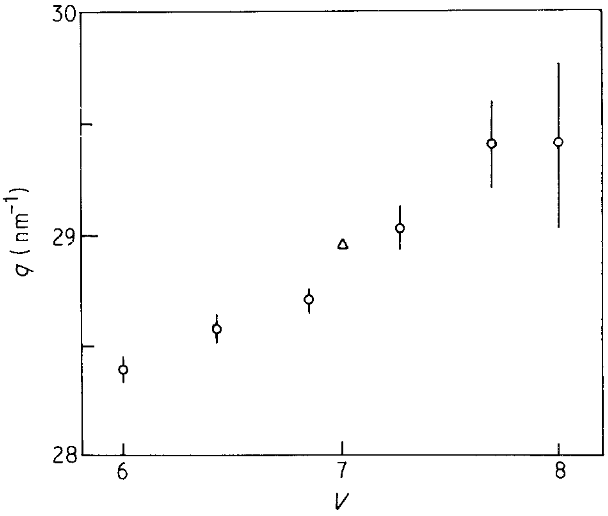

Figure 2 q vector of the (100000) peak for the $Al_{86}Cr_{14-x}Fe_x$ series. V is the average number of 3d and 4s electrons on the transition metal atoms. The value for $Al_{86}Mn_{14}$ from reference [14] is shown by Δ. The increase in the size of the error bars for larger x is the result of the increasing line width.

approximately 1–2 μm in diameter in the $Al_{86}Cr_{14}$ alloys and are all of a similar size. The figure shows that as the iron content of the alloys increases there are three significant changes in crystallite morphology: (1) the average size of the icosahedral crystallites increases slightly up to about 6 at.% Fe but decreases considerably for larger x; 2) the range of quasicrystal crystallites sizes for the $Al_{86}Fe_{14}$ alloy is considerably greater than for the chromium-rich alloys, and (3) crystallites in alloys with x up to about 6 at.% show well defined dendritic growth while their structure is not nearly so well defined in the alloys containing more iron. The size of the very small quasicrystal crystallites observed in the $x = 12$ and $x = 14$ alloys is consistent with the broadened X-ray peaks seen for these alloys (see Fig. 1).

The details of the fcc aluminium matrix are illustrated for the $Al_{86}Fe_{14}$ alloy in Fig. 4. The cell structure observed here indicates that this aluminium matrix is, in fact, a solid solution of Al–Fe. X-ray diffraction measurements of the lattice parameter of this phase by Dunlap *et al.* [8] show that the quantity of iron in solution is in the range of 2 at.%.

Convergent beam micro-diffraction patterns of all alloys showed that the nodules possessed five- three- and two-fold axes as are characteristic of the icosahedral phase. The diffraction pattern along the five-fold axis was indicative of the icosahedral phase rather than the decagonal phase (see reference [8]). We should point out that the quench rate which we have used is higher than has frequently been used by other workers in this area and it is known in Al–Mn that the preferential formation of the decagonal phase or the icosahedral phase can be a function of quench rate (see reference [16]).

3.3. Thermal analysis measurements

The temperature of the onset of crystallization, T_x for the Al–Cr–Fe alloys is shown in Fig. 5. Data are again plotted as a function of the number of 3d and 4s

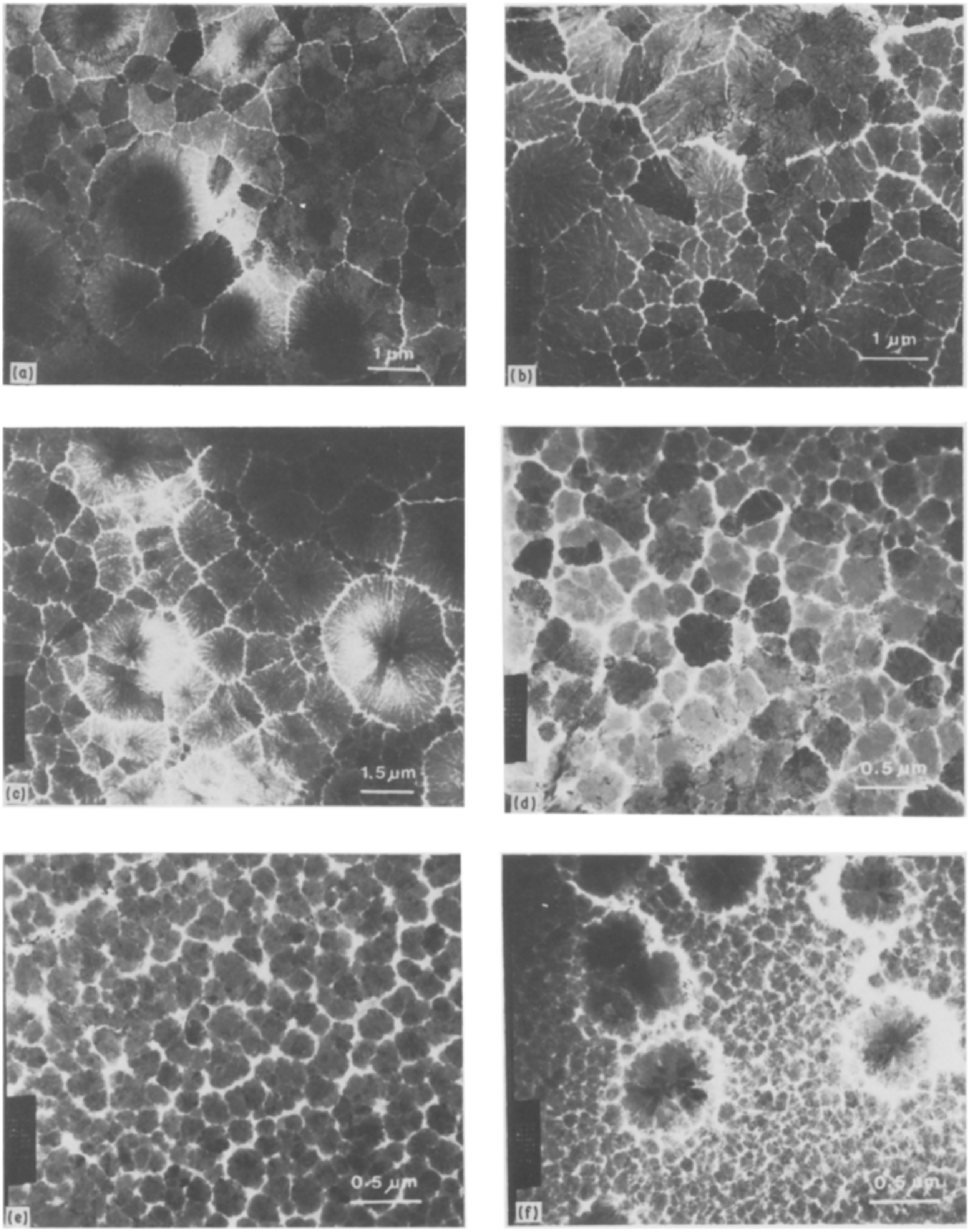

Figure 3 TEM of $Al_{86}Cr_{14-x}Fe_x$ for (a) $x = 0$, (b) $x = 3$, (c) $x = 6$, (d) $x = 9$, (e) $x = 12$ and (f) $x = 14$.

electrons. The T_x values show a significant peak near the middle of the series and are in contrast to Al–Mn results for alloys with similar V [15].

The activation energy, ΔE, for crystallization was obtained from DTA scans made at different rates, $r = \partial T/\partial t$, for the $Al_{86}Cr_{14}$ and $Al_{86}Fe_{14}$ alloys. ΔE is found from a linear fit to $\ln(r/T_m)$ as a function of $1/T_m$. T_m is the temperature of the peak of the crystallization exotherm. Analysis of the data in Fig. 6 gives $\Delta E = 1.53 \pm 0.05$ eV and 1.46 ± 0.05 eV for $Al_{86}Cr_{14}$ and $Al_{86}Fe_{14}$, respectively.

4. Conclusions

Electron diffraction studies have shown that alloys of the series $Al_{86}Cr_{14-x}Fe_x (0 \leqslant x \leqslant 14)$ form icosahedral nodules in a matrix of fcc aluminium. There is no evidence of a decagonal phase as has been reported by some authors (e.g. reference [10]). Since it

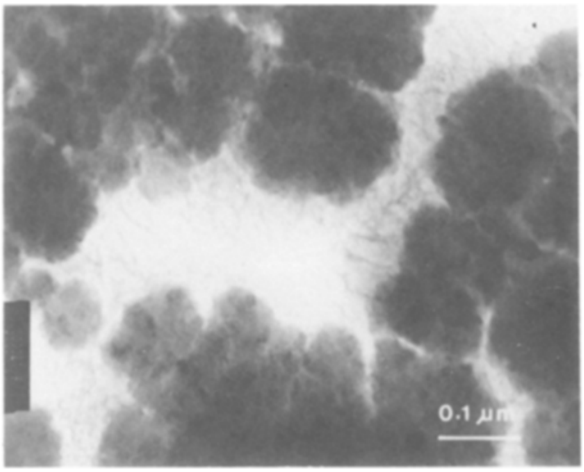

Figure 4 Details of the aluminium matrix in the $Al_{86}Fe_{14}$ alloy.

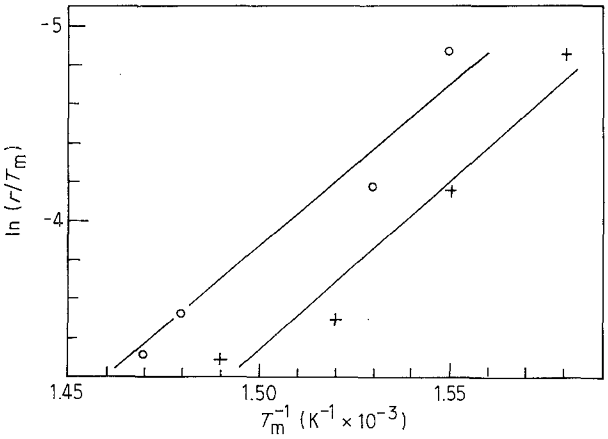

Figure 6 Kissinger–Boswell plots of the peak of the crystallization exotherm as a function of heating rate, *r*, for $Al_{86}Cr_{14}$ (+) and $Al_{86}Fe_{14}$ (○).

is well known that alloys of aluminium and manganese can form either an icosahedral phase or a decagonal phase when quenched using different conditions [16], it is also not surprising that different results may be obtained for Al–Fe alloys of the same nominal composition that have been prepared under different conditions.

For small concentrations of iron the crystallite size is seen to increase slightly with x. Above $x = 6$ the crystallite size decreases significantly. Corresponding to the decrease in crystallite size there is a pronounced broadening of the icosahedral X-ray diffraction peaks. This broadening may be caused by the small average size of the quasicrystal crystallites. If this is the case the X-ray line width for the (100000) peak in $Al_{86}Fe_{14}$ would suggest a crystallite size of about 6 nm. It is difficult to either confirm or refute this interpretation on the basis of the TEM in Fig. 4f.

The anomalous increase in T_x between $x = 0$ and $x = 6$ is not easy to explain in any straightforward way. The general trend of crystallization temperatures in aluminium–transition metal quasicrystals correlates well with the average interatomic spacing (i.e. $1/q$). This trend is consistent with those observed in amorphous alloys and has been explained in terms of changes in the interatomic spacing [17] or in terms of the number of 3d electrons [18]. These are, in general, equivalent explanations and it is difficult to say which is more fundamental. Clearly, as shown in Fig. 2, the expected relationship between q and V holds for the present series of alloys. The TEM measurements presented here indicate that there are significant changes in the grain structure of the alloys across the series. A consideration of these effects may be important as well in a description of the crystallization processes.

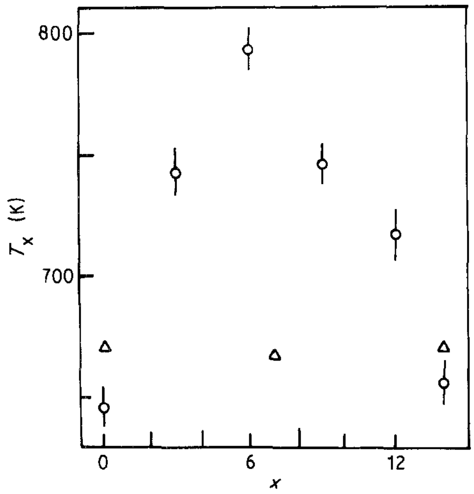

Figure 5 Temperature of the onset of crystallization for the $Al_{86}Cr_{14-x}Fe_x$ series (○). Also shown are results from reference [15] for $Al_{86}C_{14}$, $Al_{86}Mn_{14}$ and $Al_{86}Fe_{14}$. (△) Measurements are for heating rate of $20\,K\,min^{-1}$.

Finally, the activation energy for crystallization in these alloys is found to be somewhat less than that in most transition metal glasses.

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