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Y_5Al_3; a new Y–Al compound

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Recent studies on the crystallization of Y–Al glasses have revealed the evolution of a new intermetallic compound. Transmission electron microscopy and X-ray diffraction have allowed identification of this phase as Y_5Al_3 with a $D8_8$ structure isomorphic with Mn_5Si_3.

1. Introduction

A recent study on crystallization characteristics of melt-spun Y–Al metallic glasses [1] has shown that crystallization in the composition range $Y_{60}Al_{40}$ to $Y_{80}Al_{20}$ produces a phase of hitherto unknown structure. This phase transforms on further heat treatment into the equilibrium phases [2]. From the composition dependence of the crystallization enthalpy, crystallization temperature and activation energy it was concluded that the composition was close to $Y_{62.5}Al_{37.5}$, i.e. Y_5Al_3.

In the present article we describe the result of further studies in which X-ray diffraction and electron microscopy have allowed us to determine both the composition and structure of this phase.

2. Experimental methods

Alloy buttons of 1.5 g were prepared by arc-melting the appropriate quantities of yttrium (99.9% purity) and aluminium (99.999% purity) under titanium-gettered argon. The glasses were produced by melt-spinning the buttons under helium at 15 kPa pressure. The resulting ribbons were examined by X-ray diffraction, electron beam microprobe and electron microscopy for crystallinity and homogeneity. The X-ray diffractometer was a computerized Nicolet L11 with a STOE goniometer and solid state detector using nickel filtered Cu$K\alpha$ radiation. The 2θ angular resolution was typically better than 0.05°.

Fully and partially crystallized samples were prepared, in the composition range $Y_{60}Al_{40}$ to $Y_{66.7}Al_{33.3}$, by heating at $40\,\mathrm{K\,min^{-1}}$ in a Perkin-Elmer DSC 2C differential scanning calorimeter. Upon reaching a certain point on the crystallization exotherm, the sample was cooled at $320\,\mathrm{K\,min^{-1}}$ to prevent any further transformations. Fig. 1 shows a representative exotherm for $Y_{62.5}Al_{37.5}$ with arrows marking the points to which the sample was heated.

Samples for transmission electron microscopy (TEM) were polished electrolytically at 245 K in a solution of 10% perchloric acid, 70% methanol and 20% glycerine and then thinned by ion-beam milling. The microstructure of these specimens was investigated by TEM in a Philips EM301 microscope operating at 100 kV. The electron diffraction patterns from selected areas were recorded with photographic plates. As a calibrant we used the 1 1 1, 2 0 0 reflection of an Al(2% Rh) vapour-deposited thin film resulting in an accuracy better than 2%.

A typical electron micrograph of glassy $Y_{66.7}Al_{33.3}$ is shown in Fig. 2a. The corresponding electron and X-ray diffraction patterns consisting of the main amorphous peak are shown in Figs 2b and c, respectively. More exhaustive studies were done on $Y_{62.5}Al_{37.5}$.

3. Results and discussion

Fig. 3 shows electron micrographs of partially (15%) and fully crystallized $Y_{62.5}Al_{37.5}$. Selected-area electron

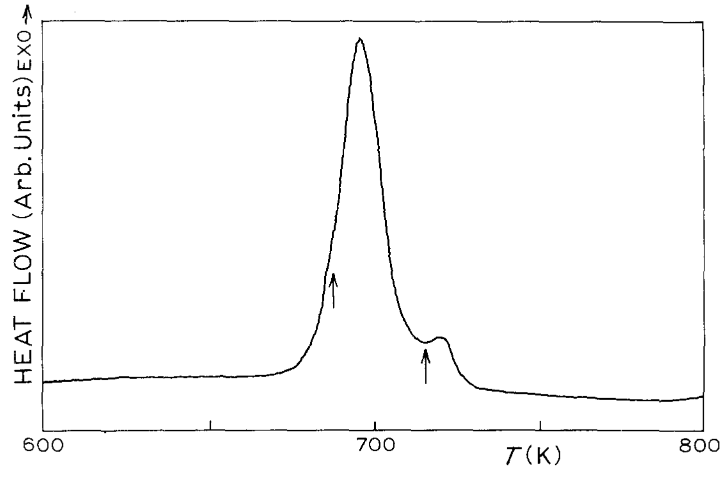
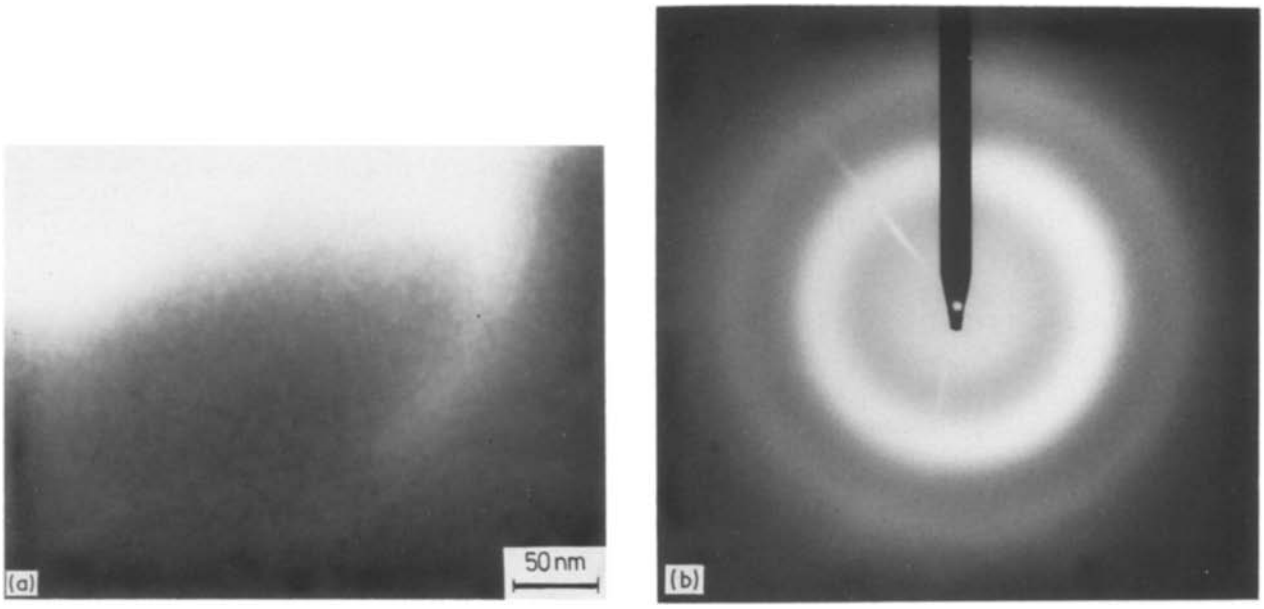


Figure 1 DSC scan of glassy $Y_{62.5}Al_{37.5}$ at a heating rate of $40\,\mathrm{K\,min^{-1}}$. Arrows indicate the temperatures where heating was stopped.



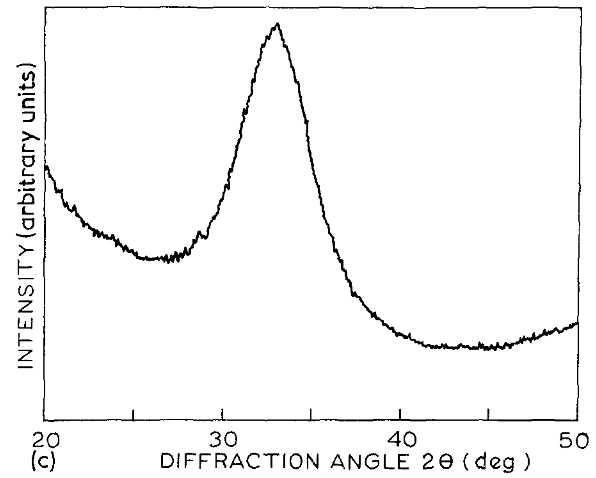


Figure 2 (a) Typical electron micrograph, (b) electron diffraction pattern and (c) X-ray diffraction graph of glassy $Y_{66.7}Al_{33.3}$.

diffraction patterns (Fig. 4) of single crystallites exhibit a single phase. No evidence for any other phase was found and no excess material between the crystallites was seen in any of the micrographs taken. Thus we conclude that the new phase is formed by a polymorphic crystallization reaction and is indeed at or close to Y_5Al_3.

From the single-crystal electron diffraction patterns for $Y_{62.5}Al_{37.5}$ and $Y_{66.7}Al_{33.3}$, as shown in Fig. 4, it is likely that the lattice of the new phase is hexagonal. All electron diffraction patterns were succesfully indexed to a hexagonal lattice with $a = 0.888 \pm 0.008$ nm and $c = 0.671 \pm 0.03$ nm. Fitting to detailed X-ray powder diffraction scans of partially and fully crystallized $Y_{62.5}Al_{37.5}$ (see Fig. 5) the lattice spacings were determined to be $a = 0.8787$ nm and $c = 0.6435$ nm in agreement with the above results. Based on the measured density of $4.02\,\mathrm{g\,cm^{-3}}$ the hexagonal unit cell can accommodate two formula units of Y_5Al_3 ($= Y_{62.5}Al_{37.5}$). It is possible to accommodate ten Y atoms and six Al atoms in this unit cell in the following way: three Y and three Al can be packed in a plane perpendicular to the c-axis as shown in Fig. 6. An additional three Y and three Al can be packed in a plane which is obtained by rotation of π and translation by $c/2$ of the plane shown in the figure. The four remaining Y atoms are then located at the positions P (see Fig. 6) at $\pm c/4$ from the plane.

This structure belongs to the $P6_3/mcm$ space group and is the most symmetric of the three space groups, i.e. $P6_3/mcm$, $P6_3cm$ and $P6c2$, which are allowed by the observed absence of the (0 0 0 1) and ($hh0l$),

TABLE I Experimental and calculated d-spacings and relative intensities for Y_5Al_3.

d (exp) (nm)	I/I_0(exp)	hkl	I/I_0(calc)	d (calc) (nm)
0.4392	6	1 1 0	9	0.4394
0.3806	14	2 0 0	21	0.3805
0.3630	17	1 1 1	23	0.3629
0.3218	5	0 0 2	8	0.3218
0.2964	25	1 0 2	43	0.2964
0.2876	48	2 1 0	49	0.2876
0.2625	100	2 1 1	100	0.2626
0.2599	56	1 1 2	75	0.2596
0.2537	29	3 0 0	29	0.2537
0.2460	1	2 0 2	2	0.2457
0.2197	2	2 2 0	2	0.2197
0.2111	1	3 1 0	2	0.2111
0.2079	4	2 2 1	5	0.2079
0.2002	3	3 0 2/3 1 1	4	0.1992
0.1924	3	1 1 3	4	0.1928
0.1903	7	4 0 0	4	0.1902
0.1816	10	2 2 2	24	0.1814
0.1765	4	3 1 2	8	0.1765
0.1745	5	3 2 0	4	0.1746
0.1719	8	2 1 3	28	0.1720
0.1685	11	3 2 1	11	0.1685
0.1661	15	4 1 0	21	0.1661
0.1638	13	4 0 2	24	0.1638
0.1609	8	0 0 4/4 1 1	10	0 1609
0.1522	5	5 0 0	3	0.1522
0.1504	1	3 1 3	< 1	0.1504
0.1483	3	2 0 4/4 1 2	4	0.1482
0.1439	7	4 2 0	6	0.1438
0.1428	10	3 3 1	10	0.1428
0.1401	5	2 1 4	11	0.1404
0.1375	8	5 0 2	17	0.1376

Note: The diffraction peaks from planes with $l \geqslant 2$ are broad (see also Fig. 5), indicating that the agreement with calculated values is much better if integrated intensities are considered.

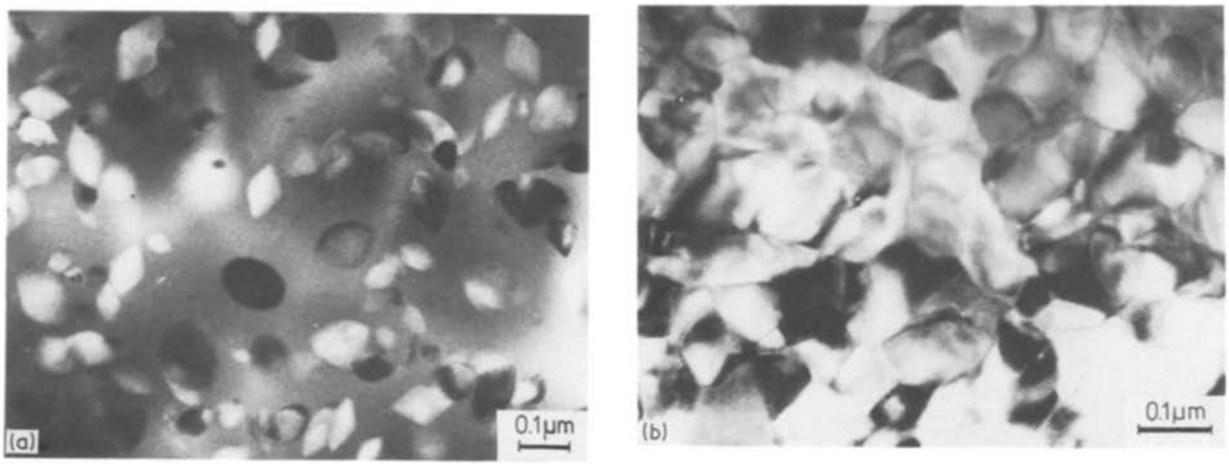


Figure 3 Electron micrograph of (a) partially and (b) fully crystallized $Y_{62.5}Al_{37.5}$.

reflections with l = odd, and the presence of the (0 0 0 2) and $(h h \overline{2h} l)$, reflections with l = odd. This structure is also known as the $D8_8$ structure. Six Y and six Al atoms are located at the g positions with x(Y) = 0.234 and x(Al) = 0.600, respectively [3]. The remaining four Y atoms are located at the d position. The calculated d-spacings and intensities are compared with the experimental X-ray powder diffraction data in Table I; the agreement is excellent.

It is interesting to note that these Y atoms form chains parallel to the c-axis with an Y–Y distance of 0.322 nm which is 10% shorter than the Y–Y distance

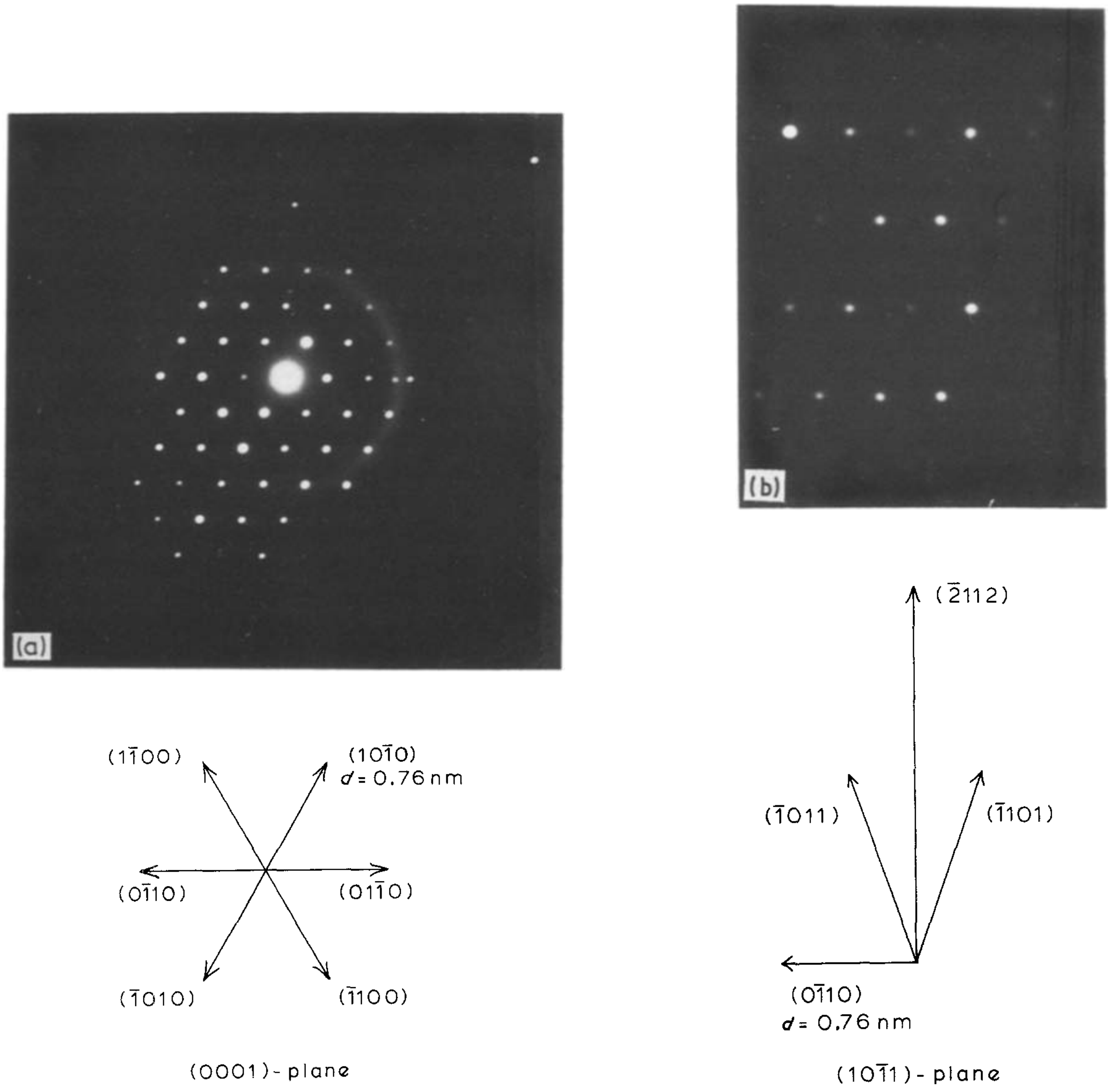


Figure 4 Typical electron diffraction patterns of Y_5Al_3 in partially crystallized (a) $Y_{62.5}Al_{37.5}$ and (b) $Y_{66.7}Al_{33.3}$. The indexing is according to a hexagonal lattice discussed in the text. The smallest point-to-point distance corresponds to a lattice spacing of d = 0.76 nm, i.e. $hkil = 10\bar{1}0$.

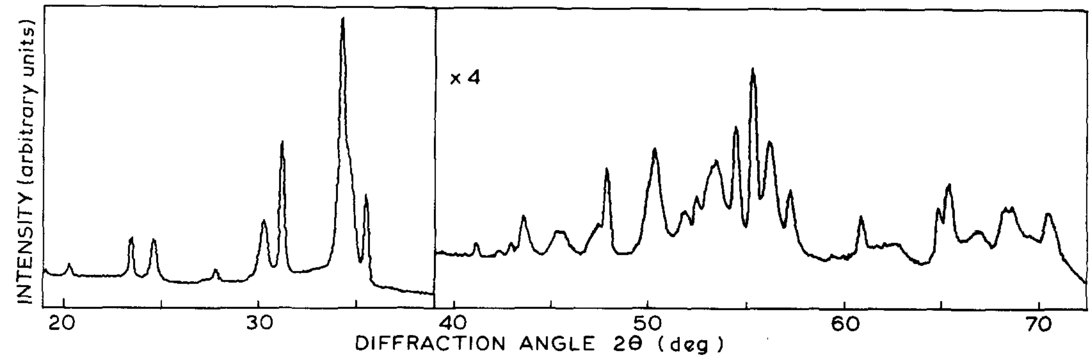


Figure 5 X-ray powder diffraction pattern of crystallized $Y_{62.5}Al_{37.5}$.

for the in-plane atoms, and 18% shorter than the distance between a Y atom in the plane and one on the chain. This suggests that the physical properties of Y_5Al_3 may be highly anisotropic.

The structure of Y_5Al_3 is by no means uncommon; there exist many other isomorphic intermetallic compounds such as Mn_5Si_3, Hf_5Al_3, Y_5Ga_3 as listed in Pearson [4]. There is evidence in the literature that for some alloys this $D8_8$ structure may be stabilized by oxygen, nitrogen, carbon or boron impurities (see for example, [5]). We shall not go so far as to assume that Y_5Al_3 is stabilized by impurities, but it is certainly possible that its precipitation from the glass is catalysed by oxygen impurities. Even nominally high-purity yttrium can contain as much as 1 or 2 at % oxygen depending on the method of preparation. The idea of a new phase being catalysed from the glass by oxygen impurities is not new; it has already been reported for Fe–Zr, Co–Zr and Ni–Zr glasses [6, 7]. The structure of Y_5Al_3 has sufficient space to accommodate oxygen atoms at $c/4$ and $3c/4$ above the triangular yttrium configuration shown in Fig. 6. The local oxygen site symmetry is similar to that of oxygen dissolved in hexagonal α-Y. If all these sites were filled, an oxide with the formula Y_5Al_3O would result. The yttrium–oxygen distance in this structure would be 0.261 nm, compared with 0.227 nm in Y_2O_3. In the absence of oxygen there is, in consequence, a rather large gap between successive triangles of Y. This may lead to a reduced conduction electron density in the $c/4$, $3c/4$ plane and thus explain the increase in the electrical resistivity when the glass crystallizes into Y_5Al_3 [1]. Once again a similar phenomenon is observed for the oxygen catalysed phases in Ni–, Co– and Fe–Zr [7].

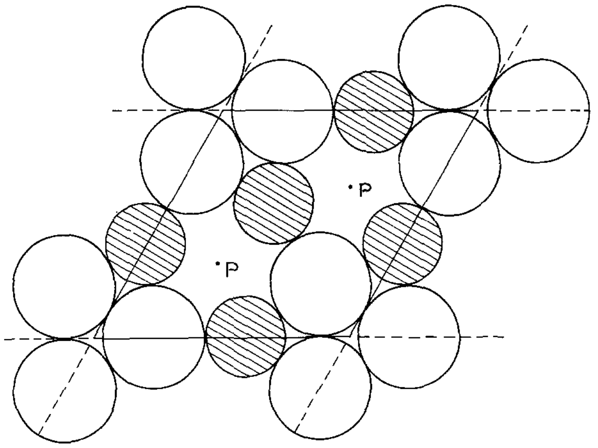


Figure 6 Basal plane of Y_5Al_3, i.e. perpendicular to the c-axis. Aluminium atoms are shaded, yttrium atoms are not. Further yttrium atoms sit at $c/4$ above the P positions.

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