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Preparation of a new Al–Cu–Fe quasicrystal with large grain sizes by rapid solidification

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Since a quasicrystal with an icosahedral structure was discovered in rapidly solidified $Al_{86}Mn_{14}$ alloy [1], the new type of nonequilibrium phase has been found in rapidly solidified alloys of Al–(Mn, Cr or V), Al–Mn–Si, $Mg_3Zn_2Al_2$, Mg_4CuAl_6, $(Ti, V)_2Ni$ and Al_6Li_3Cu, etc. More recently, the formation of the quasicrystal by rapid solidification has been reported in Al–Ge–Cr, Al–Ge–Mn, Al–Si–Cr and Al–Si–Mn alloys containing as much as ~15 to 25 at.% metalloid [2] as well as $Ga_{16}Mg_{32}Zn_{52}$ without aluminium [3]. Most of the icosahedral alloys have been formed in composition ranges where equilibrium phases are of the Frank-kasper type in which icosahedral coordination shells dominate in the structure and hence the formation of an icosahedral quasicrystal has generally been presumed to be related to the structural similarity in the equilibrium state. Thus, the number of alloy systems where the quasicrystal is formed by rapid solidification has steadily increased. However, there is no report on the formation of a mostly single quasicrystal containing a large amount of copper and/or iron, even though the formation of coexisting quasicrystalline and crystalline phases has been shown in rapidly solidified Ti_2Fe alloy [4]. It is very important from scientific and engineering points of view to find an alloy composition at which a quasicrystal including a large amount of ferromagnetic elements is formed. The aim of this letter is to present the composition range and microstructure of a new Al–Cu–Fe quasicrystal prepared by rapid solidification.

Al–Cu–Fe alloys including a ternary equilibrium compound composition $Al_7Cu_2Fe_1$ [5, 6] were used in the present work. The Al–Cu–Fe ingots were prepared by arc melting a mixture of pure aluminium (99.99 wt %), copper (99.99 wt %) and iron (99.9 wt %) in a purified argon atmosphere. The compositions are nominally expressed in atomic per cent. From the master alloy ingots, ribbons with a cross-section of about 0.02 mm × 1 mm were prepared by a single-roller melt-spinning technique. The as-solidified phase was identified by X-ray powder-diffraction using monochromatic Cu*Kα* radiation and transmission electron microscopy (TEM). The rapidly solidified ribbons had several electron transparent regions and consequently could be examined without further preparation.

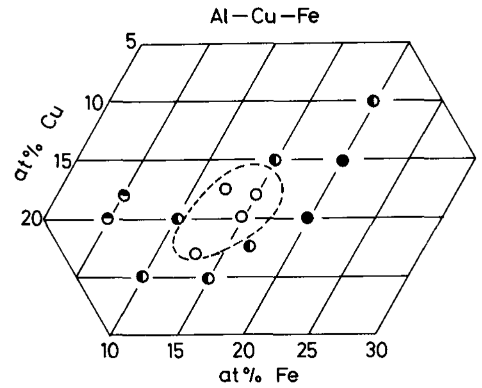

Figure 1 Composition range for formation of icosahedral quasicrystal in rapidly solidified Al–Cu–Fe alloys: (○) quasicrystalline; (◐) quasicrystalline + crystalline; (◓) amorphous + crystalline; (●) crystalline.

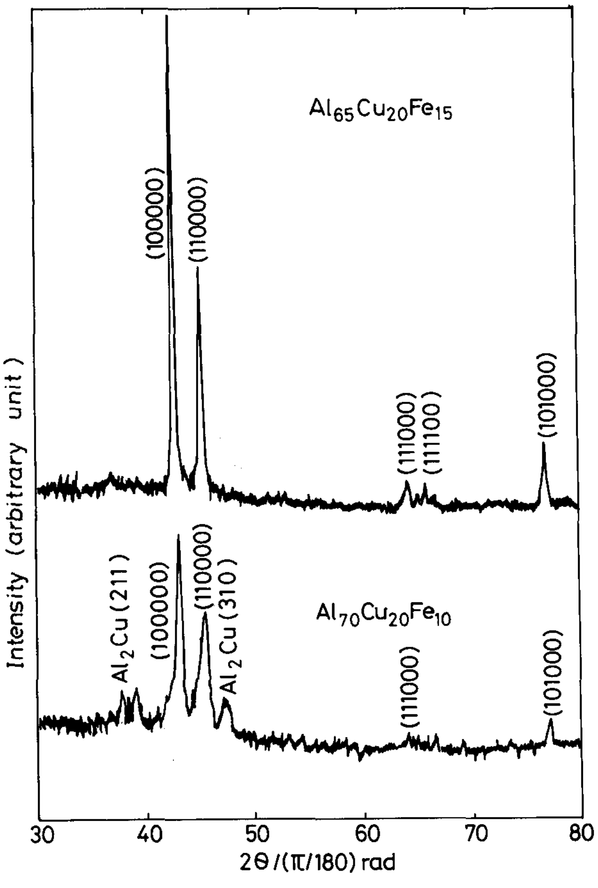

Figure 2 X-ray diffraction patterns of rapidly solidified $Al_{70}Cu_{20}Fe_{10}$ and $Al_{65}Cu_{20}Fe_{15}$ alloys.

Fig. 1 shows the compositional range of quasicrystal in rapidly solidified Al–Cu–Fe alloys. The mostly single quasicrystalline phase is formed in a composition range 16 to 24% Cu and 11 to 17% Fe. Additionally, alloys with coexisting quasicrystalline and crystalline structures are formed in the concentration region adjacent to the quasicrystal formation range. Here it appears important to point out that the formation range of the quasicrystalline single phase does not completely agree with the stoichiometric composition of an equilibrium tetragonal $Al_7Cu_2Fe_1$ compound

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TABLE I Interlattice spacing (d) and relative peak intensity (I_r) determined from X-ray diffraction pattern of the quasicrystalline phase in a rapidly solidified $Al_{65}Cu_{20}Fe_{15}$ alloy. The data of $Al_{77.5}Mn_{22.5}$, $Al_{60}Ge_{20}Mn_{20}$ and $Al_{60}Li_{30}Cu_{10}$ quasicrystals are also shown for comparison

Index	$Al_{65}Cu_{20}Fe_{15}$		$Al_{77.5}Mn_{22.5}$		$Al_{60}Ge_{20}Mn_{20}$		$Al_{60}Li_{30}Cu_{10}$	
	d(nm)	I_r (%)	d(nm)	I_r (%)	d(nm)	I_r (%)	d(nm)	I_r (%)
(1 0 0 0 0 0)	0.2111	100	0.2164	100	0.2149	100	0.2377	100
(1 1 0 0 0 0)	0.2000	67	0.2056	78	0.2043	94	0.2260	79
(1 1 1 0 0 0)	0.1448	9	0.1485	11	0.1481	9	0.1640	6
(1 0 1 0 0 0)	0.1239	22	0.1268	20	0.1265	14	0.1400	28

with lattice parameters of $a = 0.633$ nm and $c = 1.481$ nm [6] and is located in the ion-rich region of the equilibrium compound composition. There are no data available on equilibrium phases in the range where the quasicrystalline single phase is formed and hence the reason for formation of the icosahedral single phase in the vicinity of $Al_{65}Cu_{20}Fe_{15}$ remains unknown, even though it is thought to be closely related to the existence of the tetragonal $Al_7Cu_2Fe_1$ compound.

Fig. 2 shows X-ray powder-diffraction patterns as a function of diffraction angle for rapidly solidified $Al_{70}Cu_{20}Fe_{10}$ and $Al_{65}Cu_{20}Fe_{15}$ alloys. Identification of the X-ray diffraction peaks corresponding to the quasicrystal with an icosahedral structure was made by using six independent Miller indices as proposed by Bancel *et al.* [7]. As indexed in Fig. 2, the diffraction patterns consist of icosahedral quasicrystal and tetragonal Al_2Cu for $Al_{70}Cu_{20}Fe_{10}$ and icosahedral single phase for $Al_{65}Cu_{20}Fe_{15}$, indicating that the iron concentration in $Al_7Cu_2Fe_1$ compound is too low to form the quasicrystalline single phase by rapid solidification.

Table I summarizes the interlattice spacings and the relative intensities of the reflection peaks in rapidly solidified $Al_{65}Cu_{20}Fe_{15}$ alloy together with the data of quasicrystalline $Al_{77.5}Mn_{22.5}$ [8], $Al_{60}Ge_{20}Mn_{20}$ [2] and $Al_{60}Li_{30}Cu_{10}$ [9] alloys. The interlattice spacing is the smallest for the Al–Cu–Fe alloy and increases in the order of Al–Ge–Mn < Al–Mn < Al–Li–Cu. The small lattice spacing for Al–Cu–Fe alloy is probably because the atomic sizes of copper and iron are considerably smaller than those of aluminium, germanium and lithium. Thus the order is interpreted by taking the atomic size of the constituent elements into consideration. It is notable that the quasicrystalline single phase is formed even in Al–Cu–Fe alloys containing only copper and iron with atomic size smaller by 10.5 and 11.9%, respectively, than that of aluminium. The relative intensity of the reflection peaks for $Al_{65}Cu_{20}Fe_{15}$ quasicrystal decreases in the order of (1 0 0 0 0 0) > (1 1 0 0 0 0) > (1 0 1 0 0 0) > (1 1 1 0 0 0), in agreement with the order for the other aluminium-based quasicrystals.

In order to examine whether or not a small amount of second phase precipitates along the grain boundaries of the quasicrystalline matrix, in addition to clarification of morphology and grain size of the icosahedral quasicrystal, TEM observation was carried out for a rapidly solidified $Al_{65}Cu_{20}Fe_{15}$ alloy. Fig. 3 shows a bright-field electron micrograph (a) and a selected-area diffraction pattern (b) taken from the region surrounded by a circle in (a). The diffraction pattern reveales a five-fold symmetry and is indexed as $[1\,0\,0\,0\,0\,0]_q$. As shown in the bright-field micrograph, the quasicrystal consists of large grains with a size of about 3.5 to 8.0 μm and the contrast revealing radiating branches, that stem from a site near the grain boundary, is seen in each grain. Neither subgrain boundaries nor clearly appreciable second phase are seen. It is notable that the grain size of $Al_{65}Cu_{20}Fe_{15}$ quasicrystal

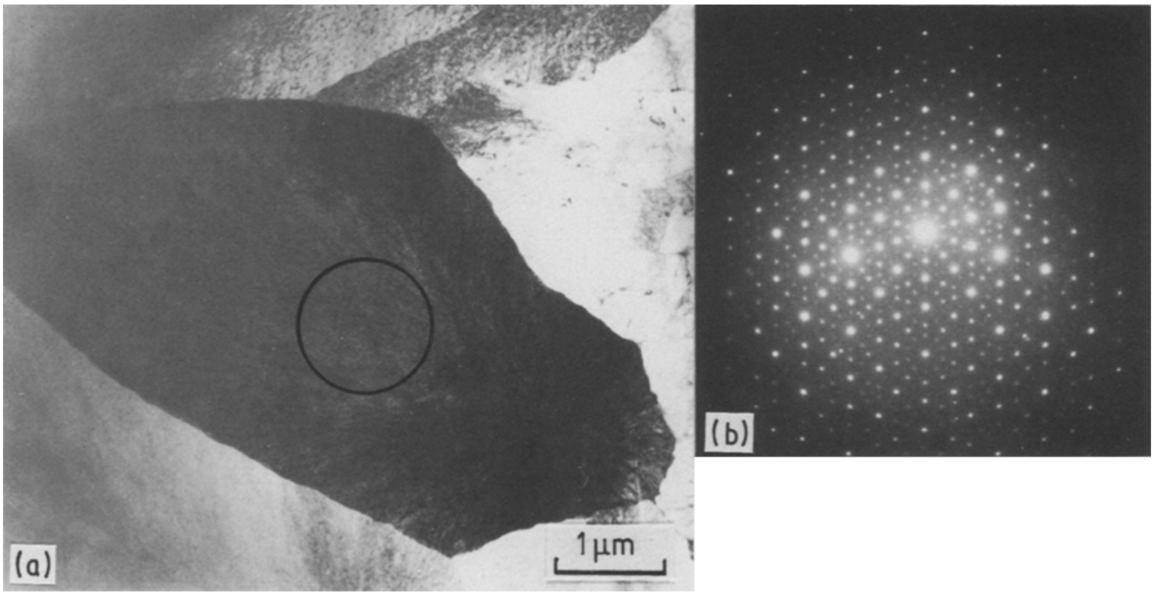

Figure 3 (a) Bright-field electron micrograph and (b) selected-area diffraction pattern of a rapidly solidified $Al_{65}Cu_{20}Fe_{15}$ alloy.

is 7 to 40 times larger than that (0.2 to 0.5 μm) of the quasicrystals in Al–Mn [1, 8] and Al–Cr [10] systems prepared in the same melt-spinning condition and hence the grain growth of quasicrystal from liquid is thought to be much faster for Al–Cu–Fe alloy. Considering the results that the average grain size of the $Al_{65}Cu_{20}Fe_{15}$ quasicrystal is as large as about 6 μm and no trace of second phase is seen even on the grain boundaries, the formation of the new quasicrystalline single phase at $Al_{65}Cu_{20}Fe_{15}$ is concluded to be much easier than that for the previously reported aluminium-based quasicrystals except the Al–Cu–Li [11] system. Subsequent investigation of the preparation, structure and properties of the Al–Cu–Fe quasicrystal with larger grain size is at present underway.

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