On the Nature of the Quasicrystalline Phase in Rapidly Solidified Al–Co–Si Alloys

By Jyothis Menon* and C. Suryanarayana†

An Al–20 at.% Co–5 at.% Si alloy was rapidly solidified from the liquid state and its structure in the as-quenched as well as transformed states was characterized through transmission electron microscopy techniques. Contrary to the expectation that an icosahedral phase will be produced, this rapidly solidified alloy contained only a decagonal quasicrystalline phase, probably due to the insufficient amount of silicon present to reduce the effective atomic size of the aluminum atoms. Diffraction patterns from this ternary alloy have been found to be more complex than those from the binary Al–Co alloy. The phenomenon of polytypism continues to be observed in the ternary alloy also. Formation of holes during transformation of the quasicrystalline phase has been interpreted on the basis of the lower density of the quasicrystalline phase in comparison to the equilibrium crystalline phases.

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1. Introduction

Ever since the discovery of a quasicrystalline phase exhibiting the icosahedral symmetry in rapidly solidified Al–14 at.% Mn, Cr or Fe alloys in 1984(1), there has been an intense activity in studies on the formation, characterization and transformation behavior of these novel phases(2–5). Two important categories of quasicrystalline phases have been detected so far. These include (i) the icosahedral phases exhibiting the five-fold symmetry in their electron diffraction patterns(6), and (ii) the decagonal phases exhibiting one-dimensional periodicity and ten-fold symmetry normal to it(7–9). One-dimensionally periodic quasicrystals with other symmetries have also been observed(9–12). The coexistence of both the icosahedral and decagonal phases has been reported so far only in the Al–Mn binary system.

Addition of a ternary (and/or a quaternary) element to a binary alloy has been found to modify the nature of the quasicrystalline phase in the rapidly-solidified alloys. In some cases, even though the constitution remained the same, subtle changes in the diffraction patterns (streaking, shape and sharpness of the spots, etc.) were noticed. Effect of addition of Si to binary Al alloys has been investigated in great detail although addition of other elements like Cu, Ge, Ru, etc. have also been studied(13–17). Bancel and Heiney(18) studied the effects of addition of Si and Ru to Al–Mn and Al–Cr alloys and observed an improvement in the icosahedral order. Addition of 2–11 at.% Ru to Al–Mn alloys has been shown to increase the stability of the icosahedral phase, although the diffraction peak widths have been found to be larger. Quaternary addition of Si sharpened the diffraction peaks without introducing any new additional phase.

Bendersky and Kaufman(13) reported that addition of Si to high-Mn content Al–Mn alloys resulted in the formation of an icosahedral phase instead of the usually observed decagonal phase. Chen and Chen(14) showed that partial substitution of Al by 6 at.% Si stabilized the icosahedral phase at the expense of the decagonal phase in an Al–20 at.% Mn alloy. Formation of a superlattice was also reported. Higher concentrations of Si progressively

* Department of Metallurgical Engineering, Banaras Hindu University, Varanasi-221 005, India.
† Present address: Wright Research and Development Center, WRDC/MLLS, Wright-Patterson Air Force Base, OH 45433-6533, USA.
resulted in the formation of the crystalline cubic \(\alpha\)-phase and an amorphous phase\(^{15}\). Dunlap and Dini\(^{19}\) studied the influence of Si addition on the quasicrystalline phase in aluminum-transition metal alloys and showed that an amorphous phase could be produced in Al–Co, Al–Cr, Al–Fe, Al–Mn and Al–Ni alloys provided that a minimum amount of Si was present. Schaefer\(^{20}\) also reported that addition of 6 at.\% Si to an Al–17 at.\% Mn–2 at.\% Fe alloy produced the icosahedral phase instead of the decagonal phase. Addition of Si to binary Al–Cr and Al–Ni alloys has been shown to result in the formation of a decagonal phase after rapid solidification while the binary alloys do not produce any quasicrystalline phase\(^{21}\). Preferential formation of the icosahedral phase in Si-containing alloys has been explained on the hypothesis that the effective average size of the Al atom decreased by the addition of Si\(^{20}\).

A decagonal quasicrystalline phase was produced in rapidly solidified Al–Co alloys containing 14 to 25 at.\% Co\(^{22,23}\). Formation of an icosahedral phase was not detected in any composition range in this alloy system (although Dunlap and Dini\(^{25}\) have erroneously interpreted their X-ray data on the basis of an icosahedral phase). With a view to investigate whether addition of Si to binary Al–Co alloys results in the formation of an icosahedral phase (similar to the case of the Al–Mn alloy), rapid solidification studies have been undertaken on an Al–Co–Si ternary alloy and the results obtained constitute the subject matter of this paper.

II. Experimental Procedure

A ternary Al–20 at.\% Co–5.3 at.\% Si alloy was prepared from high-purity components in an argon arc melting furnace. The alloy was repeatedly remelted to ensure homogenization. Small pieces were melted and rapidly solidified from the liquid state using the technique of melt spinning. The resultant ribbons were thin enough for direct observation in the transmission electron microscope without further thinning. A JEOL JEM 200CX electron microscope operating at 200 kV and fitted with a goniometer stage and a hot-stage was used to characterize the foils in the microscopic, diffraction and analytical modes. A W–5\% Re/W–26%Re thermocouple was used to measure the temperature during in-situ heating, and a heating rate of 10 to 15 K/min was employed.

III. Results

1. As-quenched structure

Figure 1 shows a bright-field electron micrograph recorded from the as-spun ternary alloy foil. The microstructure can be characterized by the presence of rosettes in a crystalline matrix and as such this microstructure is very similar to the one observed in the binary Al–14 at.\% Co alloy foil\(^{22,23}\). High magnification photographs of these rosettes indicate that these are made up of overlapping dendrite branches. The rosettes are 1 to 2 \(\mu\)m in size and give rise to quasicrystalline diffraction patterns as shown in Fig. 2. The arrangement of diffraction spots in an aperiodic manner suggests that the phase is quasicrystalline. However, the observation of strict periodicity in one direction in the 2-fold pattern unambiguously confirms that only a decagonal phase is produced in the ternary alloy also.

Occasionally, a nodular-type morphology of the microstructure has also been observed (Fig.

![Fig. 1 Electron micrograph of the as-quenched Al–Co–Si alloy foil showing the rosette morphology of the quasicrystalline phase.](image-url)
3(a)). This type of morphology, observed frequently in the icosahedral-type quasicrystals (and only rarely in decagonal phases) does not show dendritic branches even at high magnifications; but, cellular boundaries can be seen. A dark-field electron micrograph (Fig. 3(b)) recorded using one of the intense spots in the aperiodic direction in Fig. 3(c) clearly shows the presence of speckle contrast, which has been earlier thought to be a characteristic feature of the icosahedral phase. Thus,
although *microstructurally* the phase produced shows features similar to those of the icosahedral phase, the periodic arrangement of spots in one direction is irrefutable evidence for the presence of only a decagonal phase.

2. **Decomposition behavior**

The quasicrystalline decagonal phase transformed on *in-situ* heating in the electron microscope. A similar observation was made on external heating also, even though the temperature at which it transformed to the equilibrium phases was lower because of the sustained long time (1 h) allowed at that temperature. Holes started forming when the transformation was about to begin and in this respect it is similar to the binary Al–Co alloys\(^{(26)}\). On continued heating, the size and number of holes increased resulting in agglomeration of holes at a sufficiently high temperature. Figure 4 shows a typical micrograph obtained after cooling the specimen to room temperature from about 900 K. The holes are about 150 to 200 nm in size and their volume fraction works out to only about 7%.

Some interesting observations have been made on the diffraction patterns during *in situ* heating operation. Figure 5(a) shows the diffraction pattern recorded from the as-quenched ternary alloy foil. It may be noted that the distance between two intense spots in the periodic direction is divided into 8 parts giving rise to a periodicity of 1.6 nm for this decagonal phase. After *in situ* heating up to a temperature of 450 K (Fig. 5(b)), the arrangement of spots in the periodic direction seems to

![Fig. 5](image-url) Diffraction patterns recorded during *in situ* heating of the Al–Co–Si alloy foil. (a) Starting diffraction pattern with the neighboring intense spots in the periodic direction divided into 8 parts giving rise to a periodicity of 1.6 nm. (b) At 450 K, streaking and mixture of periodicities of 1.6 nm and 1.2 nm can be noticed. (c) Division of intense periodic spots into 6 parts on further heating.

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Fig. 4 A micrograph showing the formation of holes when the foil is heated *in situ* up to 900 K and then cooled down to room temperature.
be modified. For example, one can notice a mixture of two periodicities of 1.6 nm and 1.2 nm and some sort of streaking. While the row through the transmission spot shows a periodicity of 1.2 nm prominently (although weak spots corresponding to 1.6 nm periodicity also can be seen) the non-zero layers show a periodicity of 1.6 nm. On further heating, the periodicity becomes clearly 1.2 nm (Fig. 5(c)). From this observation, one can infer that the periodicity has changed from 1.6 nm to 1.2 nm during heating, but before transforming to the crystalline phase(s).

Figure 6 shows the microstructure of the specimen after it had been completely transformed to the crystalline state and then cooled down to room temperature. Extremely fine grains with a size ranging from 0.5 to 1 μm and fine holes at the bottom left side of the micrograph are worth noticing. The corresponding diffraction pattern is shown in Fig. 6(b). This diffraction pattern could not be indexed on the basis of any of the known binary Al–Co phases or pure Si. Available literature does not show the presence of any ternary equilibrium Al–Co–Si phase. Attempts to index this phase on the basis of homologous cubic α-AlFeSi phase have not been successful and work is in progress to characterize the crystal structure of this phase.

IV. Discussion

1. Atomic size effect

The basic objective of Si addition to the binary Al–Co alloys was to explore the possibility of producing an icosahedral quasicrystalline phase in place of the decagonal phase observed in the binary alloys containing 14 to 25 at.% Co. However, in contrast to the Al–Mn–Si system, even in the ternary Al–Co–Si alloy with about 5 at.% Si, only a decagonal phase was produced.

Table 1 lists the atomic radii of the elements involved in the formation of the quasicrystalline phases and also the ratio of atomic radii of the aluminum and the transition metal atoms. Since Si can substitute for Al

<table>
<thead>
<tr>
<th>Element / Alloy</th>
<th>Effective atomic radius ratio of (Al+Si)/TM</th>
<th>Nature of the quasicrystalline phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.143 nm</td>
<td>—</td>
</tr>
<tr>
<td>Mn</td>
<td>0.132 nm</td>
<td>—</td>
</tr>
<tr>
<td>Co</td>
<td>0.128 nm</td>
<td>—</td>
</tr>
<tr>
<td>Si</td>
<td>0.102 nm</td>
<td>—</td>
</tr>
<tr>
<td>Al–14 at.% Mn</td>
<td>6.655</td>
<td>Icosahedral</td>
</tr>
<tr>
<td>Al–20 at.% Mn</td>
<td>4.333</td>
<td>Decagonal</td>
</tr>
<tr>
<td>Al–20 at.% Mn–6 at.% Si</td>
<td>4.240</td>
<td>Icosahedral</td>
</tr>
<tr>
<td>Al–20 at.% Co</td>
<td>4.469</td>
<td>Decagonal</td>
</tr>
<tr>
<td>Al–20 at.% Co–5 at.% Si</td>
<td>4.389</td>
<td>Decagonal</td>
</tr>
</tbody>
</table>

Table 1 Effect of average atomic size ratios* on the nature of the quasicrystalline phase in rapidly solidified aluminum-transition metal (TM) systems with and without silicon.

* Effective atomic radius ratio here is defined by

\[
\text{at.% of Al} \times r_{\text{Al}} + \text{at.% of Si} \times r_{\text{Si}}
\]

\[
\text{at.% of TM} \times r_{\text{TM}}
\]
in its lattice sites, the effective atomic radius ratio of (Al+Si) relative to that of the transition element is also calculated. It can be noticed from this table that the effective atomic radius ratio for the Al–14 at.% Mn alloy works out to 6.655 (for the icosahedral phase), while it is only 4.333 for an Al–20 at.% Mn alloy producing the decagonal phase. With substitution of 6 at.% Si for Al, the effective atomic radius ratio for the Al–20 at.% Mn–6 at.% Si is reduced to 4.240 and this composition produces an icosahedral phase on rapid solidification. In the case of the Al–Co system, it may be noticed that the radius ratio for the Al–20 at.% Co alloy is 4.469 and it decreases to 4.389 on substituting 5% Al with Si. However, this value is higher than 4.333 for the binary Al–Mn or 4.240 for the ternary Al–Mn–Si alloy producing the icosahedral phase. Furthermore, since Co atom is smaller than Mn, one can expect that the average size of the Al and Si atoms required to stabilize the icosahedral Al–Co–Si phase would be even less than that required to stabilize the icosahedral phase in the Al–Mn–Si system. This suggests that a much higher percentage of Al atoms should be substituted with Si (at least up to 10 at.%). Thus, the insufficient reduction in the radius ratio of the atoms maybe responsible for the non-occurrence of the icosahedral phase in the Al–Co–Si ternary alloy.

Earlier investigations on rapidly solidified Al–Co–Si alloys reported on producing an amorphous phase in alloys containing more than 8 at.% Si\(^{(19)}\). Although it was not made clear in that paper, it can be assumed that only the decagonal phase continued to be present at lower Si contents in conformity with our results. From these observations, it also appears that it may be difficult to produce an icosahedral phase in the Al–Co–Si system because less than 8 at.% Si produces a decagonal phase, while at higher concentrations of Si, formation of an amorphous phase dominates. It may be interesting to see if controlled crystallization of the amorphous phase produces an icosahedral phase.

2. Morphology and speckle contrast

The morphology of the decagonal phase in the ternary alloy is quite similar to that observed in the binary Al–14 at.% Co and Al–20 at.% Co alloys. These include the rosettes and the nodules. The nodular morphology is rather uncommon even in aluminum-base icosahedral phases and not at all reported for the decagonal phases. The dark-field micrographs from the nodular grains show the typical speckle contrast which has also been shown to be true in the binary alloys\(^{(29)}\). Several reasons have been put forward to explain the speckle contrast. Urban *et al.*\(^{(29)}\) noted that the details in the speckle depended on the size of the objective aperture used, the objective lens focus and the type of reflections. Subsequently, they\(^{(30)}\) suggested that this contrast arose from internal strains in regions some 10 nm in size, which caused local lattice misorientations. Robertson *et al.*\(^{(31)}\) suggested that the motting on a 2 to 5 nm scale could be related to the peak broadening observed in X-ray powder diffraction patterns. The speckle contrast was also found to be dependent on both the diffraction vector and electron beam direction\(^{(32)(33)}\). These attributed the contrast to a spinodal-type decomposition in the alloy and showed that the form of the contrast exhibited in dark-field images of icosahedral Al–Mn and Al–V alloys is consistent with that expected from a material with inherent compositional inhomogeneity and concluded that these do not arise from dislocation strain fields or multiply twinned particles. It has been recently suggested\(^{(34)}\) that the speckle contrast is a necessary consequence of quasicrystalline organization and should therefore be expected even for a chemically uniform structure.

From the foregoing, it becomes clear that the origin of speckle contrast is not very clear and could be due to the inherent quasicrystalline nature, compositional inhomogeneity, dislocation strain field or some other factors. Noting that a similar speckle contrast is observed in the decagonal binary Al–Co and ternary Al–Co–Si alloys, it may be concluded that the speckle contrast could be an inherent characteristic of the quasicrystalline phase irrespective of whether it is icosahedral or decagonal in nature. The observation of non-uniform fringe spacing in the lattice resolu-
tion photographs suggesting a compositional inhomogeneity complicates the situation further. It should, however, be pointed out that the speckle contrast has not been reported frequently in quasicrystalline alloys and rarely in a decagonal phase.

3. Diffraction patterns

The diffraction patterns from the decagonal phase in the ternary alloy presented in Fig. 2 show some special features. Firstly, the density of diffraction spots is high in both the 10-fold and pseudo 3-fold patterns. Secondly, the patterns do not appear to be “clean”. The additional number of spots present in a ternary Al–Mn–Si alloy were interpreted by Chen and Chen as due to the formation of a superlattice. In our case, however, we cannot explain the presence of extra spots as due to a superlattice because the arrangement of spots is not very symmetric. However, one could notice rows of spots resembling streaking and the corresponding lattice resolution photographs show a variety of faults. These include Moiré fringes, terminating fringes indicating the presence of dislocation-like defects and semicoherent interfaces. In some regions one could also observe variations in fringe spacing suggesting a compositional change. Thus, it is understandable that due to the combined effects of all these irregularities the diffraction patterns are complex. A similar observation was made in the Al–Mn icosahedral phase by Krishnan (private communication) and in the Al–Mn decagonal phase.

4. Transformation behavior

It is interesting to note that during in-situ heating of the alloy foil, it has been observed that the periodicity of the decagonal phase changes from 1.6 nm to 1.2 nm. This transformation passes through a stage where the stacking layers get disordered in the aperiodic directions as suggested by streaking in the diffraction pattern. Additional spots other than those showing 1.2 nm periodicity in the diffraction pattern of the transformed structure suggest that there is enhanced intra-layer disorder. From these observations one can conclude that 1.2 nm may be the more “stable” periodicity for this ternary decagonal phase. This phenomenon where one periodicity of the metastable decagonal phase transforms into another periodicity can be compared to the phenomenon of polytypism in crystals, where the number of layers stacked along any direction can vary resulting in different unit cell sizes along that direction. This aspect of “polytypism” in quasicrystalline phases has been discussed in detail elsewhere.

Like in the binary alloys, we were able to observe the formation of holes during the transformation of the quasicrystalline phase to the equilibrium constitution. It has been suggested that the holes form to account for the volume difference between quasicrystalline and crystalline phases. Earlier investigators have clearly shown that the quasicrystalline phase is about 2 to 6% less dense than its crystalline counterpart. This additional volume is accommodated through the formation of holes. It should be clarified in this context that although a primary crystalline phase is present along with the decagonal quasicrystalline phase, one could clearly observe the formation of holes. In the binary alloys, the formation of holes is not very prominent in alloys containing a mixture of crystalline and quasicrystalline phases. For example, the hole formation was most prominent only in the Al–20 at.% Co alloy and not prominent enough in the other compositions.

V. Conclusions

Based on the above observations, the following conclusions can be drawn.

1. Substitution of Al by 5 at.% Si reduces the effective atomic size of Al in the ternary Al–Co–Si alloy, but not sufficient enough to produce an icosahedral phase. It is estimated that at least 10 at.% Si is required to produce the icosahedral phase. However, formation of an amorphous phase may dominate at these higher silicon contents.

2. The diffraction patterns from the ternary decagonal phase are more complex than those from the binary alloys.

3. The phenomenon of polytypism continues to exist in the ternary alloy and transfor-
formation of one polytype with 1.6 nm periodicity to another with 1.2 nm periodicity has been observed during in-situ heating.

(4) Hole formation has been observed during transformation from the quasicrystalline to the crystalline state to accommodate the difference in density between the two states.

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REFERENCES


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