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Endothermic quasicrystalline-to-crystalline phase transition in Al_6CuMg_4

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Abstract. Electron microscopic and differential scanning calorimetric (DSC) studies have been performed to investigate the phase transitions in the rapidly solidified Al_6CuMg_4 alloy system. We present evidence, for the first time, that an *endothermic* quasicrystalline to crystalline transition occurs in this system around 340°C. This is an unexpected feature—for conventional wisdom would lead one to expect exothermic behaviour as was seen in $Al_{86}Mn_{14}$—and points to the fact that stability of certain quasicrystalline phases may be much larger than hitherto expected. Some comments on the recently reported large quasicrystal for the Al_6CuLi_3 system are also made in the light of our observation.

Keywords. Quasicrystals; phase transition; thermal-study.

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Since the discovery of quasicrystalline phase with 532 symmetry in Al-Mn system by Shechtman *et al* (1984), a variety of other quasicrystals have been reported. Sastry *et al* (1986) produced a new quasicrystalline alloy, Al_6CuMg_4, which is an important member of a class (Ramachandrarao *et al* 1985) of quasicrystalline solids. More recently this class of quasicrystalline solids has also been predicted on the basis of quantum structural diagrams (Villars *et al* 1986). In this communication we report a study on the quasicrystalline to crystalline phase transitions in this system. Our study has interesting implication concerning the stability of the quasicrystalline phase.

The stoichiometric compound (Al_6CuMg_4) was prepared by melting constituent elements in pure form (99·99%) under argon atmosphere in a graphite crucible. Ribbon samples, of about 5 mm width and 30 μm thickness, for the present study were obtained by rapid solidification using the usual melt spinning method. The quasicrystalline character of these samples was confirmed (Dey *et al* 1986) by transmission electron microscopy (TEM) observations. Bright field electron micrograph showing the morphology of the icosahedral domains and selected area diffraction pattern showing five-fold symmetry are presented in figures 1a and 1b respectively. All other diffraction patterns were obtained from the same nodule at the expected angles characteristic of the $m\bar{3}\bar{5}$ point group. The three-fold pattern is shown in figure 3a.

Three DSC measurements were performed: one on the original crystalline material (out of which quasicrystalline ribbons were prepared), the second on as-grown quasicrystalline phase and the third on quasicrystal samples which were in situ heated to 400°C and then cooled to 30°C before the DSC scans were made. The

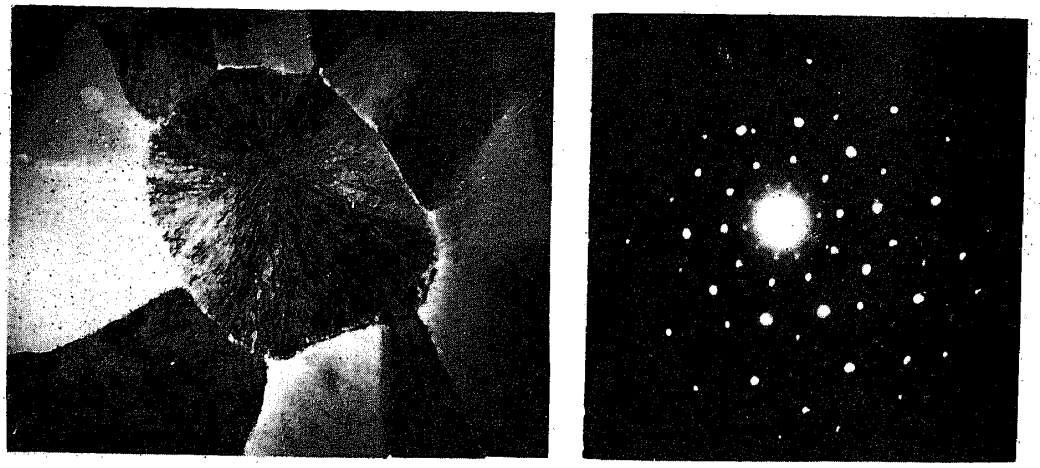

Figure 1. (a). The bright field electron micrograph is displayed showing the grain morphology. (b) Electron diffraction pattern exhibiting five-fold symmetry.

results for these three measurements are identified by the symbols I, II and III respectively and are displayed in figure 2. We performed the measurements several times with different portions of materials to confirm the repeatability of the results. All the DSC measurements were done on Mettler TA3000 thermal analysis system and the system was calibrated with pure indium. Further the DSC runs were conducted with two different heating rates viz 10 K/minute as well as 30 K/minute and it was confirmed that identical features were shown by both kinds of runs. In figure 2, however, only the results for 30 K/minute heating rate have been displayed.

Above 400°C, the results for all the three are similar, in that there is a strong endothermic peak at 474·9°C and the enthalpy change is 230·92 J/g. However, below 360°C the spectra are very different as shown in figure 2. While for the original crystalline material (I), the heat out vs temperature shows no peaks and for the as-grown quasicrystalline phase (II) we see a broad endothermic structure

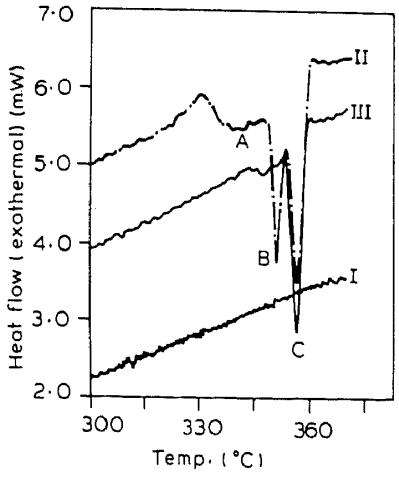

Figure 2. As-recorded DSC data (I) for original crystalline material (10 mg of sample), (II) for as-grown quasicrystalline phase (5 mg of sample) and (III) for in-situ annealed quasicrystalline sample.

around 340·06°C followed by two sharp peaks at 351·01°C and 356·45°C respectively. These are designated as A, B, C in figure 2 and the enthalpy changes associated with these peaks are 2·2, 1·47 and 2·5 J/g respectively. For the quasicrystalline samples first heated to 400°C (III), there is only a sharp endothermic peak at 356·45°C coinciding with the peak C of II, and neither the broad structure A nor the peak B is seen.

It was observed that arresting a phase, from a region between the two peaks A and B, at room temperature is not possible. If the as-grown quasicrystalline sample was kept at peak A (340°C) for a few minutes, and then the subsequent DSC scan through higher temperature (above 340°C) did not show the presence of peak B. In view of this finding the electron diffraction pattern of the quasicrystalline sample, which was heat-treated at 340°C for one hour, was recorded and compared with that of the as-grown quasicrystalline sample (refer figure 3). In figure 3a the three-fold pattern for the as-grown quasicrystalline phase is shown and in figure 3b we display the pattern of the heat-treated quasicrystalline sample. As can be seen from a comparison of figures 3a and 3b the separation of spots in (3a) is related to the 'golden ratio', while those in (3b) exhibit a periodicity, which confirms crystallization. This is analogous to what was observed (Chen *et al* 1985) in the case of $Al_{86}Mn_{14}$, wherein a broad exothermic structure (below 680 K) precedes a sharp exothermic peak at 780 K and an icosahedral to crystalline transformation can be brought about by annealing the samples at 650 K for 30 minutes (or at 700 K for 20 minutes). So we believe that A and B are both associated with the quasicrystalline to crystalline transition. Peak C is connected with a reversible (polymorphic) crystalline phase transition. This was confirmed through the following experiment. The as-grown quasicrystalline samples were first in situ heated to 400°C and then DSC runs were performed at a cooling rate of 30 K/min. It was found that peak C reappears (as an exothermic peak) at the same temperature confirming the reversibility of this transition.

In conclusion, we have found that quasicrystalline to crystalline phase transition in Al_6CuMg_4 system is an *endothermic* process as compared to exothermic crystallization in the Al-Mn system. This indicates that Al_6CuMg_4 forms a stabler quasicrystal than the Al-Mn system. Better stability of this alloy system was

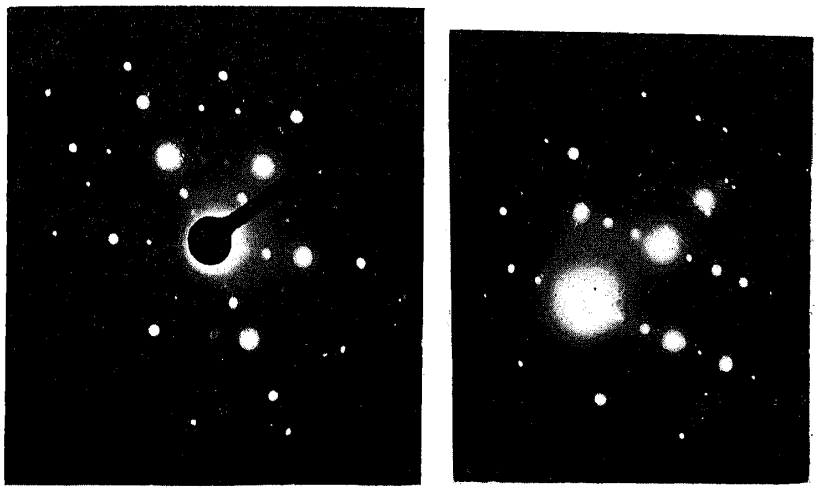

Figure 3. Electron diffraction pattern (**a**) for quasicrystalline phase and (**b**) for annealed sample as detailed in the text.

predicted on the basis of quantum structural diagram (Villars *et al* 1986) and the result of this communication confirms that prediction. Our observation suggests that, by judicious choice of cooling rate, it should be possible to grow large-sized quasicrystals, akin to what has been found possible (Dubost *et al* 1986) in the Al_6CuLi_3 system. Subsequent x-ray diffraction study (details will be published separately) of this quasicrystalline to crystalline transition shows that the transformed crystalline phase is not the same as that of the equilibrium alloy phase. Although both the crystalline phases have the space group of Im3-T_h^5, their atomic positional parameters are different.

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