Phase transitions in quasicrystalline Al$_6$CuMg$_4$

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Calorimetric and electron diffraction studies reveal that the quasicrystalline-to-crystalline phase transition in Al$_6$CuMg$_4$ is endothermic, in contrast to the exothermic crystallization in quasicrystalline Al-Mn reported earlier. This finding indicates that the stability of certain quasicrystalline phases may be much larger than that of the Al-Mn system. This finding is in agreement with the prediction based on quantum structural diagrams. From a kinetic study the activation energy of this phase transition was found to be 260 kJ/mole.

Since the discovery of a quasicrystalline phase with a fivefold symmetry (point-group symmetry $m\bar{3}\bar{5}$) in Al-Mn by Shechtman, Bloch, Gratias, and Cahn[1] great interest has been aroused in this class of materials. The quasicrystalline phase is regarded by some as a new "metastable" phase of solid matter intermediate between crystals and glasses[2] and efforts to study properties of quasicrystals has picked up momentum. In a study of the thermal properties it was observed[3] that transition of the quasicrystalline Al-Mn system to its orthorhombic crystalline state is similar to crystallization of metallic glasses. In particular, differential-scanning-calorimetric runs for this transition revealed a broad exothermic structure (below 680 K) followed by a sharp exothermic peak at 780 K.

Recently[4,5] a new class of quasicrystalline alloys has been predicted and produced which has opened up the possibility of producing large-sized quasicrystals (dimension of a few millimeters) for experimental investigations. The crystalline state of these alloys, which is isostructural with the compound Mg$_{32}$(Al,Zn)$_{49}$, contains a large number of atoms grouped in clusters associated with each lattice point of the bcc unit cell. These clusters which exhibit the icosahedral symmetry over several states of their formation are postulated[5] to provide the "embroyos" for the formation of quasicrystalline phases upon rapid solidification. Al$_6$CuLi$_3$ and Al$_6$CuMg$_4$ alloys are two important members[4] in this class of quasicrystals. It has been observed[6] that for Al$_6$CuLi$_3$ one can grow larger sized single quasicrystals. In this Rapid Communication we focus our attention on the other alloy, viz. Al$_6$CuMg$_4$ and report an *endothermic* quasicrystalline-to-crystalline transition in this system. First we will discuss the differential-scanning-calorimetric (DSC) and transmission-electron-microscopy (TEM) observations and then we will present our finding relating to the kinetics of this transformation.

The stoichiometric compound (Al$_6$CuMg$_4$) was prepared by melting constituent elements in pure form (99.99%) under argon atmosphere in a graphite crucible.

Quasicrystalline 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 by TEM observations. Bright field electron micrograph showing the morphology of the icosahedral domains and selected area diffraction pattern showing fivefold symmetry are presented in Figs. 1(a) and 1(b), respectively. All other diffraction patterns were obtained from the same nodule at the expected angles characteristic of the quasicrystalline phase. X-ray diffraction pattern (which will be communicated separately) does not show presence of aluminum peaks. This is in contrast to the case of rapidly solidified Al-Mn alloys in which the precipitates of quasicrystalline nodules are embedded in an aluminum matrix. The ribbons are entirely composed of grains of quasicrystalline Al$_6$CuMg$_4$, and probably as a consequence our ribbons are extremely brittle.

Differential scanning calorimetric (DSC) measurement of icosahedral Al$_6$CuMg$_4$ samples was performed on a Mettler TA3000 thermal analysis system. The system was calibrated with pure indium. We conducted the DSC
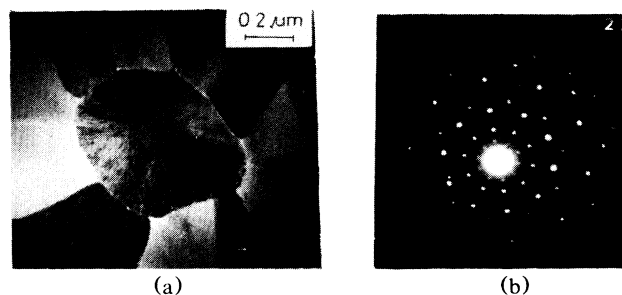

(a)   (b)

FIG. 1. (a) The bright-field electron micrograph is displayed showing the grain morphology and (b) electron diffraction pattern exhibiting fivefold symmetry.

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runs with different heating rates. Data collected in this system were directly transferred to a modular instruments computer for further processing. The kinetics of transformation was found from these data. Details of all these experiments are discussed below.

Two DSC measurements were performed; one on the as-grown quasicrystalline phase and the second on quasicrystal samples which were heated to 400 °C *in situ* in the DSC setup then cooled to 30 °C, before the DSC scans were made. Above 360 °C and below 300 °C, the results for both the samples are similar, and both of them show a strong endothermic peak at 474.9 °C. However, between 300 and 360 °C the spectra are very different. In Fig. 2, we have displayed the results for these two measurements, over the range 300–370 °C, taken at a heating rate of 30 K/min. The symbols I and II in Fig. 2 are identified in the caption. While for the as-grown quasicrystalline material (I), the heat out vs temperature shows a broad endothermic structure around 340 °C, followed by two sharp peaks at 351.01 and 356.45 °C, respectively. (These are designated as *A, B, C* in Fig. 2.) For the quasicrystalline samples first heated to 400 °C (II) and then cooled to 30 °C before recording the DSC run from 30 °C upwards, there is only a sharp endothermic peak at 356.45 °C coinciding with the peak of *C* of II, and neither the broad structure *A* nor the peak *B* is seen. So we believe that *A* and *B* are both associated with the quasicrystalline-to-crystalline transition. The 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 heated *in situ* to 400 °C and then DSC runs were performed at a cooling rate of 30 K/min. It was found that the peak *C* reappears (as an "exothermic" peak) at the same temperature confirming the reversibility of this transition. Indeed, this transition can be reproduced always by going back and forth across the transition point.

To confirm the quasicrystalline-to-crystalline phase transition, electron diffraction patterns were recorded. These are displayed in Fig. 3. In Fig. 3(a) the threefold pattern for the on-grown quasicrystalline phase is shown, and in Fig. 3(b) we display the pattern of the as-grown quasicrystal after heat treatment at 340 ± 1 °C for 1 h. In the latter case the sample was removed from the furnace and allowed to cool to room temperature before taking the electron diffraction patterns. As can be seen from a comparison of Figs. 3(a) and 3(b), the separation of spots in Fig. 3(a) is related to "golden ratio," while those in Fig. 3(b) exhibit a periodicity. This leads to the conclusion that once the quasicrystalline phase is annealed for 1 h at 340 °C it transforms to a crystalline state. In order to further elucidate the nature of peaks *A* and *B* the as-grown quasicrystalline samples were isothermally kept in DSC at peak *A* (340 °C) for 1 h. Subsequent DSC scan through higher temperature (above 340 °C) did not show peak *B*. In view of this finding peak *A* was used for studying the kinetics with nonisothermal method, which is discussed below.

Study of kinetics of solid-state transformation can be carried out using either isothermal or nonisothermal methods.[7] In the study of the kinetics of crystallization of amorphous material using nonisothermal methods, one seeks a linear relation[7,8] between $\ln(Q/T_p^2)$ and $1/T_p$, where T_p is the temperature of the DSC peak corresponding to the heating rate Q. One can determine the parameters characterizing the devitrification process, namely activation energy and Arrhenius frequency, from the plot of $\ln(Q/T_p^2)$ vs $1/T_p$ (known as Kissinger's plot). We have applied this approach to our case of quasicrystalline-to-crystalline phase transition through a study of the shift in position of the peak *A* of Fig. 2 for five different heating rates. The experiments were repeated to check the consistency of the result; 5 to 7 mg of sample was used in each run. It was observed that for 10, 15, 30, 45, and 60
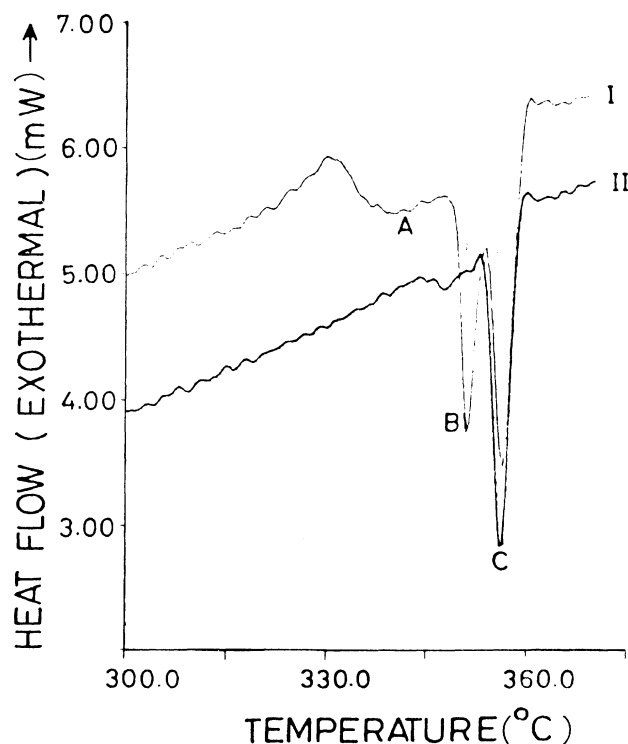

FIG. 2. As recorded DSC data (I) for as-grown quasicrystalline phase (5 mg of sample) and (II) for *in situ* annealed quasicrystalline sample.
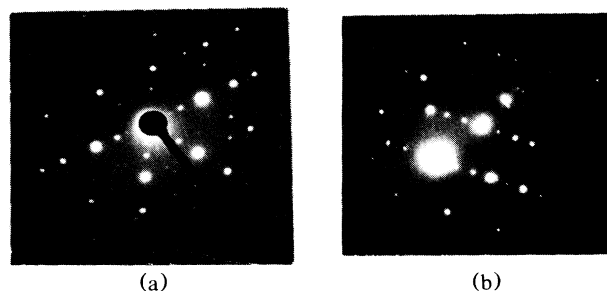

(a)   (b)

FIG. 3. Electron diffraction pattern (a) for quasicrystalline phase and (b) for annealed sample as detailed in the text.
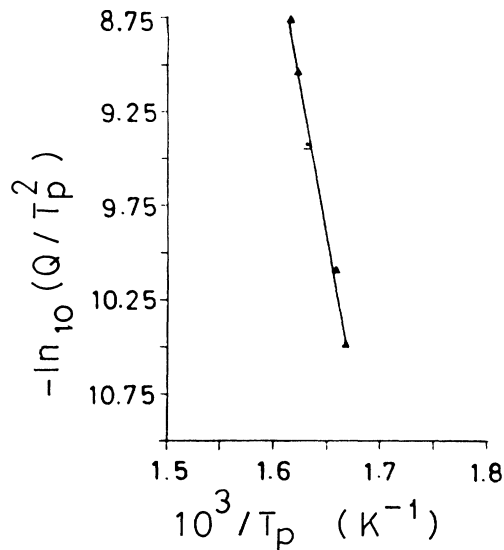
FIG. 4. Kissinger's plot of quasicrystalline-to-crystalline phase transition (correlation coefficient =0.985).

K/min the positions of peak A were 326.81, 329.78, 340.06, 343.26, and 345.83 °C, respectively. Kissinger's plot[7] obtained with this data is shown in Fig. 4. The activation energy for crystallization and Arrhenius frequency factor were found to be 260.03 kJ/mole and 3.51×10^{22} min^{-1}, respectively. The value of activation energy ob-

tained here is similar to that observed in the crystallization of conventional glass (209.7 kJ/mole) (Ref. 8) and in quasicrystalline-to-crystalline transition in Al-Mn (221.76 kJ/mole).[3] The value of Arrhenius frequency factor is exceedingly higher than that for conventional glass (3.41×10^9 min^{-1}), but surprisingly it is close to that obtained in the crystallization in a gel system (10^{24} min^{-1}).[8]

We have found that quasicrystalline-to-crystalline phase transition in Al$_6$CuMg$_4$ system is an endothermic process as compared to exothermic crystallization in Al-Mn. This indicates that Al$_6$CuMg$_4$ forms a stabler quasicrystal than Al-Mn. It is possible that other alloy systems which are electronically and compositionally similar[4,5] will also show similar behavior. Study is under way to confirm this prediction. Better stability of these alloy systems was predicted on the basis of quantum structural diagrams[4] and the result of this Rapid Communication confirms that prediction. Endothermic crystallization implies that at some temperature below the range of the present experiments, the quasicrystalline phase of this ternary alloy is more stable than the crystalline phase [isostructural to (Al,Cu)$_{49}$Mg$_{32}$]. This suggests that, by judicious choice of cooling rate, it should be possible to grow large sized quasicrystals of Al$_6$CuMg$_4$.

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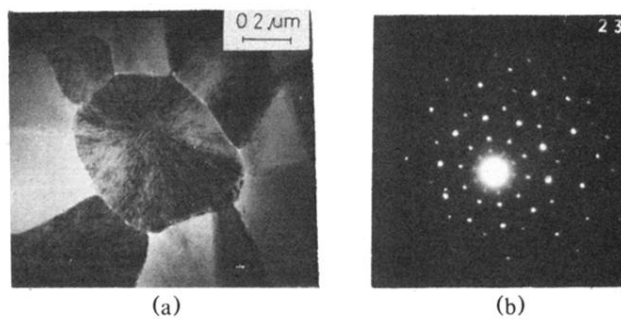
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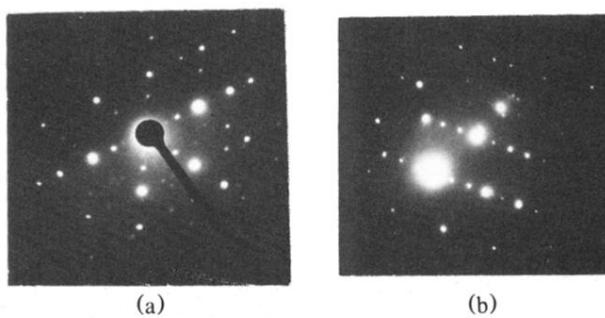
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