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Stage formation of quasi-crystals during mechanical treatment of the cubic Frank–Kasper phase $Mg_{32}(Zn, Al)_{49}$

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Abstract

Using high resolution electron microscopy, the stage formation of the icosahedral phase during the process of mechanochemical treatment of the cubic $Mg_{32}(Zn, Al)_{49}$ crystals has been studied. It has been shown that in the initial stages the icosahedral phase forms locally owing to the formation of rotation defects and disorder of the crystal planes due to the action of plastic deformation. The size of the disordered regions in the icosahedral phase increases with increase in the time of mechanical treatment. An orientation correspondence has also been revealed between the initial cubic and icosahedral phases; this is apparently due to the similarity in the structural designs of the cubic and icosahedral phases.

1. Introduction

Obtaining metastable and unusual crystalline structures by mechanochemical treatment of solids is at present an urgent problem of solid state chemistry [1–3]. One of the ways to solve this problem is mechanochemical synthesis of icosahedral structures in the Mg–Zn–Al and Mg–Cu–Al systems, which we have reported in refs. 4 and 5. Similar results have been obtained later by Eckert *et al.* [6] for the Al–Mn–Cu system.

It is considered that, from their structure, icosahedral phases are midway between the crystalline and amorphous states. A correlation is thereby revealed between the structure of the icosahedral phase and the structure of the corresponding phase in the equilibrium crystalline state. It is the existence of structural similarity that is responsible for the fact that icosahedral phases are most easily obtained in systems having intermetallic compounds with local icosahedral symmetry of structural elements in the crystalline state (Frank–Kasper and Laves phases etc.). Despite the fact that the structure of icosahedral phases has as yet been not fully clarified, it is considered in the literature that such phases may be obtained from crystalline phases by introduction of an ordered dislocation net and redistribution of atoms [7, 8].

Such a relation between the crystalline and quasi-crystalline state enables us to apply the mechanochemistry methods for the synthesis of icosahedral phases in the Mg–Zn–Al and Mg–Cu–Al systems [4, 5].

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However, up to now there has been no information in the literature on structural changes occurring during the transition from the crystalline to the quasi-crystalline state. It is not clear which types of defect play a decisive role in such a transformation. With the aim of elucidating these questions we have carried out investigations of the changes in the structure of the cubic $Mg_{32}(Zn, Al)_{49}$ crystals (Frank–Kasper type) during the process of mechanical treatment.

2. Experimental details

The synthesis of the cubic Frank–Kasper $Mg_{32}(Zn, Al)_{49}$ phase was performed according to a procedure described elsewhere [4, 5].

The mechanical treatment of samples was carried out in centrifugal planetary mills with an acceleration of 600 m s^{-2} in an inert gas atmosphere. During the mechanical treatment the phase composition was determined using an X-ray diffractometer with Cu Kα radiation.

High resolution electron microscopy and electron diffraction were performed with a JEM-2000FX II electron microscope, equipped with a side entry with a $\pm 20°$ double-tilt goniometer, operating at 200 kV. For the electron microscopy studies, thin specimens were obtained by mounting ground crystal fragments on holey-carbon-coated polymer films supported by a copper grid, using a suspension in ethanol. Images were obtained at or close to the Scherzer defocus condition.

3. Results and discussion

Microcrystals of powdered samples of the cubic $Mg_{32}(Zn, Al)_{49}$ phase are thin plates with a characteristic size across of 20–100 nm, and a linear dimension of the order of 1000 nm. Figure 1 presents the electron diffraction pattern and an electron micrograph showing an image of the (110) lattice planes with an interplanar spacing $d_{110} = 1.01$ nm. A characteristic feature of the starting samples of the cubic phase is the absence on the micrographs of edge dislocations.

Marked changes in the structure of the cubic $Mg_{32}(Zn, Al)_{49}$ phase are detected even at the very early stages of mechanical treatment, of the order of 1 min. In this case, as already noted in refs. 4 and 5, a decrease in the intensity and a broadening of peaks are observed in the X-ray diffraction patterns (Fig. 2). It is known that such a change in X-ray patterns may be associated both with decreased coherent diffraction blocks and with the formation of various types of defect in the crystal. It is commonly a rather difficult problem to separate these effects for samples subjected to mechanochemical treatment, since the processes of grinding and activation proceed simultaneously. Using electron microscopy it is possible to obtain further information about the course of each of these processes. Thus, in

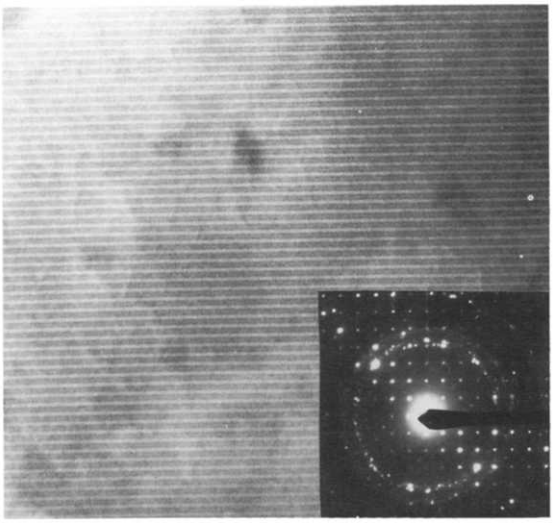


Fig. 1. High resolution electron image for the (100) planes of the initial $Mg_{32}(Zn, Al)_{49}$ crystal and the corresponding electron diffraction pattern.

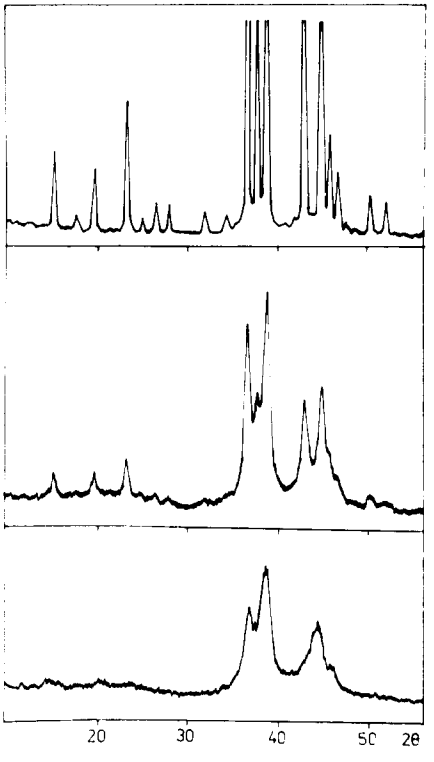


Fig. 2. X-ray diffraction patterns: (top) of the initial cubic $Mg_{32}(Zn, Al)_{49}$; (middle) after mechanical treatment for 30 s; (bottom) after mechanical treatment for 9 min.

the initial period time, no marked change in the size of the cubic $Mg_{32}(Zn, Al)_{49}$ crystals is observed. However, in electron high resolution micrographs, moiré patterns are observed in crystal regions 30–100 nm in diameter (Fig. 3). Moiré lines are thereby located at an angle to the lines from the $Mg_{32}(Zn, Al)_{49}$ crystal lattice with $d_{321} = 0.38$ nm; this indicates that the crystal lattice is rotated in these regions [9]. According to our estimates, the angle of rotation of the crystal lattices about each other changes from 2° to 15°.

During the process of mechanomechanical treatment, not only this type of defects is formed. The high resolution electron micrographs show small regions of the sample several tens of nanometres in size with a decrease in the contrast of crystallographic planes to complete disappearance, as shown in Fig. 4 for the (110) planes. Since the electron micrographs were taken at Δf for the optimal Scherzer defocusing corresponding to the density of electric charge distribution in the sample [10], the decrease in contrast is probably associated with a change in the order of occupation of atomic nets of the crystal lattice upon disordering of the crystallographic planes. The size of such disordered regions increases with increasing mechanical treatment time of the $Mg_{32}(Zn, Al)_{49}$ crystals and after treatment for 2 min it is 30–50 nm (Fig. 5).

The most interesting data were obtained on samples treated mechanically for 3 min. Figure 6 presents a high resolution electron micrograph of the mechanically treated $Mg_{32}(Zn, Al)_{49}$ crystal and electron diffraction patterns corresponding to different regions of the crystal. One part of the crystal has a cubic structure with a resolution of (110) planes. In this case, the axis of the $[44\bar{3}]$ zone for the cubic crystal is parallel to the electron beam. The second part of the crystal corresponds to an electron diffraction pattern with a three-fold axis, which unambiguously corresponds to the icosahedral

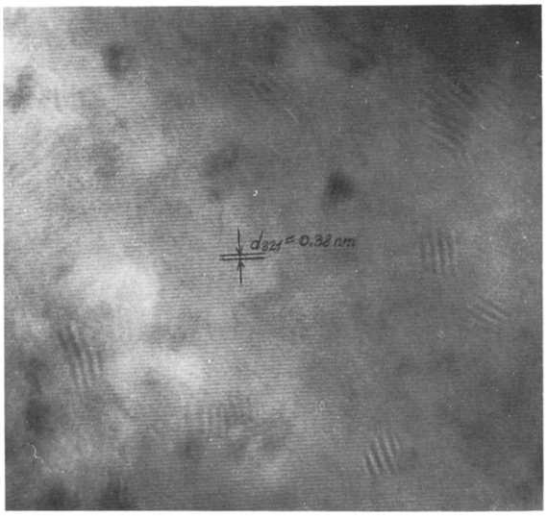


Fig. 3. Moiré image appearing after mechanical treatment for 1 min. Bands of the lattice with $d_{321} = 0.38$ nm are observed.

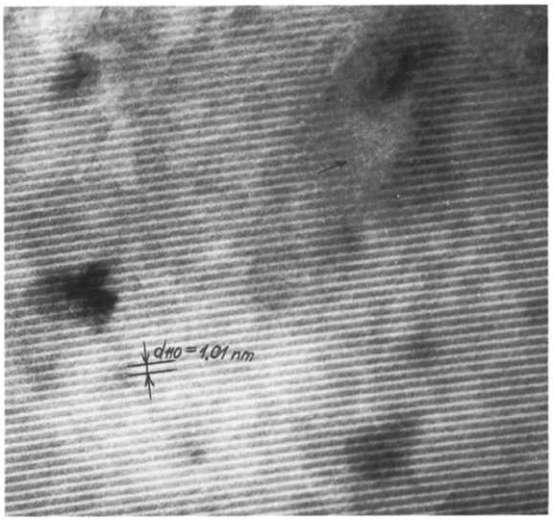


Fig. 4. High resolution electron image of the cubic crystal with (100) planes after a 1 min mechanical treatment. A defect region can be observed at the top of the micrograph.

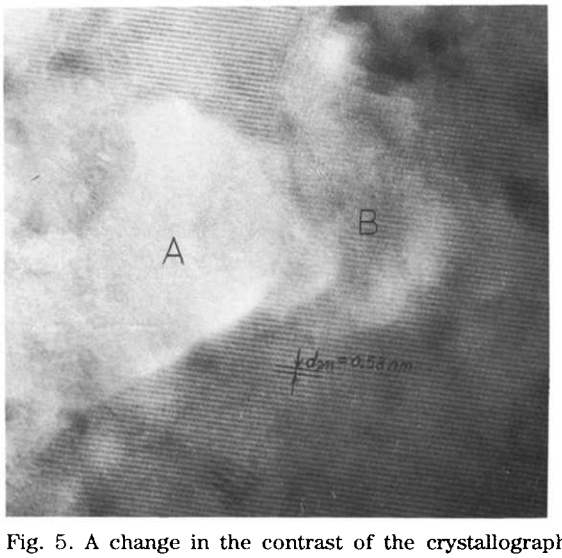
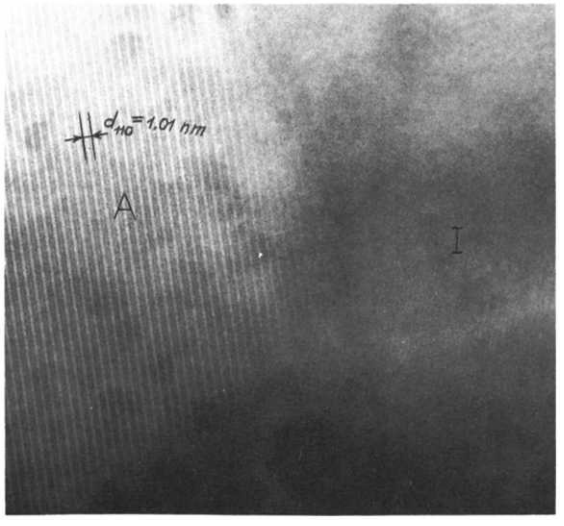
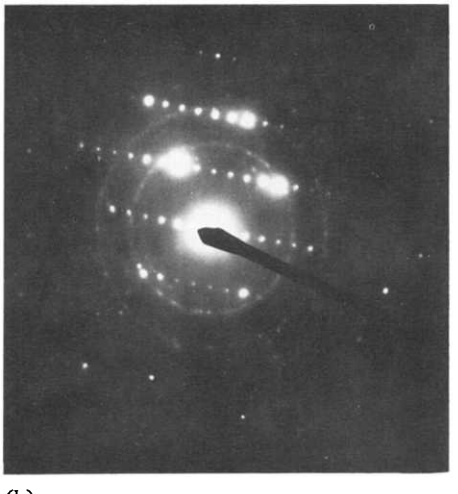


Fig. 5. A change in the contrast of the crystallographic planes of the $Mg_{32}(Zn, Al)_{49}$ after a 2 min mechanical treatment. No resolution of the lattice bands is observed in the region A; region B shows softened contrast.

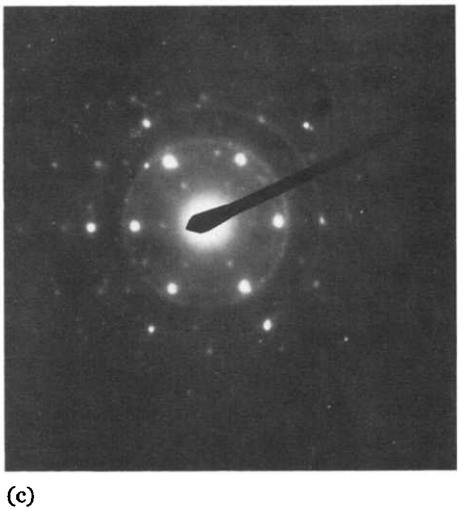
$Mg_{32}(Zn, Al)_{49}$ phase. In this electron diffraction pattern reflections located on one vector of the inverse lattice are related to each other as $d_i = d_{i+1}\tau$, where $\tau = (1+5^{1/2})/2$ is the golden ratio. The absence of resolution of the crystallographic planes of the quasi-crystal in Fig. 6 appears to be associated with the small values of interplanar spacing and the large thickness of the sample. This formation of the icosahedral phase upon the mechanical treatment



(a)



(b)



(c)

Fig. 6. (a) High-resolution electron micrograph of the $Mg_{32}(Zn, Al)_{49}$ crystal after a 3 min mechanical treatment. The micrograph shows two regions: A, cubic crystal with a resolution for the (100) planes, to which electron diffraction pattern in (b) corresponds; I, quasi-crystalline region (electron diffraction pattern in (c)). (b) Selected-area diffraction pattern of the cubic $Mg_{32}(Zn, Al)_{49}$ crystal corresponding to region A in (a). The axis of the $[4\bar{4}\bar{3}]$ zone is parallel to the electron beam. (c) Selected-area diffraction pattern corresponding to region I in (a). There is a threefold axis for the icosahedral $Mg_{32}(Zn, Al)_{49}$ phase.

of the cubic $Mg_{32}(Zn, Al)_{49}$ crystals indicates the existence of orientation correspondence between the starting phase and the phase formed; the axis of the $[4\bar{4}\bar{3}]$ zone of the cubic crystal is parallel to the three-fold axis of the quasi-crystal.

An increase in the mechanical treatment time of the cubic phase (more than 10 min) leads to a decrease in the size of the crystals of both the cubic and the icosahedral phase. At the same time, a transition of the cubic crystal to the quasi-crystalline state is observed. After 20 min mechanical treatment, the X-ray patterns and electron diffraction patterns show peaks of the icosahedral phase only (Fig. 2(c) and Fig. 7). The quasi-crystal size is 20 nm.

Thus the data obtained show that the transition of the cubic $Mg_{32}(Zn, Al)_{49}$ crystal to the quasi-crystal proceeds by formation of defects in its structure, namely rotations of the crystal lattice, and crystal plane disordering. During this, the formation of the icosahedral phase upon mechanical treatment appears to proceed as follows: (1) in the initial stages of transformation the icosahedral phase is formed locally as a result of the formation of rotary defects under the action of plastic deformation and crystal plane disordering; (2) as the mechanical treatment time of the $Mg_{32}(Zn, Al)_{49}$ is increased, the size of such disordered regions increases to give the icosahedral phase. It should be noted that an analogy is observed with the development of topochemical reactions which has been well studied in solid state chemistry; first, the nucleation of a new phase occurs and then the growth of nuclei. An even more surprising fact revealed in this work is that during mechanical treatment an orientation correspondence may occur between the initial cubic phase and the icosahedral phase, *i.e.* the three-fold axis of the quasi-crystalline phase appears to be parallel to the axis of the $[44\bar{3}]$ zone of the cubic crystal. That is, when making analogies, the phenomenon of topotaxy is observed. The similarity of the structural designs of the cubic and icosahedral phases seems to be a pre-condition for the topotaxy, which supports the hypothesis set up previously that the icosahedral phase should be considered as the cubic phase disordered in a definite manner.

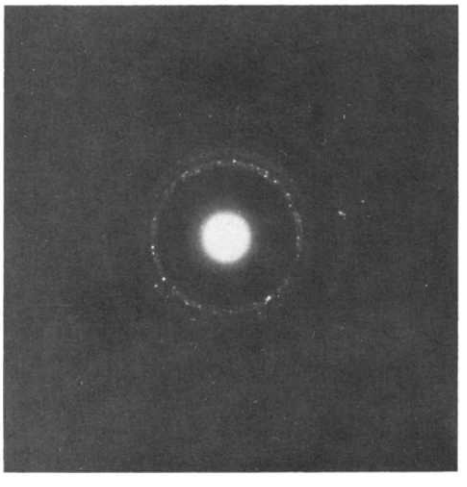


Fig. 7. Electron diffraction pattern of the forming icosahedral $Mg_{32}(Zn, Al)_{49}$ phase after a 20 min mechanical treatment.

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