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Synthesis and process characterization of mechanically alloyed icosahedral phase Mg–Zn–Al

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The formation process of the icosahedral i-Mg_{32} (Zn, Al)$_{49}$ phase during mechanical alloying has been studied. In the case of synthesis of i-phase from the metal powder mixture, the intermediate amorphous phase appeared during the first stages of mechanical alloying. In contrast the transformation of the cubic Frank–Kasper phase into the icosahedral one, was accompanied by progressive broadening and disappearance of the Bragg's peaks of the cubic phase without amorphization. These observations are discussed in terms of the structural relations of the amorphous, icosahedral and cubic Frank–Kasper phases, the formation and packing of icosahedral clusters during mechanical alloying of the metal powder mixtures and, on the other hand, the distortion of the cubic phase due to the formation of line defects.

1. Introduction

The discovery in 1984 of a new solid phase exhibiting five-fold symmetry by Schechtman *et al.* [1] has stimulated further progress in this field. The quasicrystals were mostly produced by the melt spinning technique [2] and only recently by thermodiffusion [3]. The published results are mainly concerned with the discovery of new phases, their structure and synthetic procedures. We have recently reported [4] the synthesis of the quasicrystalline Mg_{32} (Zn, Al)$_{49}$ and Mg_{32} (Cu, Al)$_{49}$ phases during mechanical alloying and the transformation of the Frank–Kasper cubic Mg_{32} (Zn, Al)$_{49}$ phase into the icosahedral phase upon mechanical treatment.

The most important problems involved in the study of icosahedral phases are some structural features, the possibility of defect formations in these phases, and their defect structures. This paper deals with the formation process of icosahedral phases during mechanical alloying. (As the technical procedure is the same, we shall use the term mechanical alloying (MA) both for the case of mechanical alloying of metal powder mixtures and for the mechanical treatment of the intermetallic compound.)

In contrast to the melt spinning technique, the use of MA enables a more detailed study of the formation of icosahedral phases. On the other hand, data on the formation of icosahedral phases can assist our understanding of the mechanical activation of solids. This is due to the unusual structure of i-phases – the absence of the translational symmetry and the presence of long-range order.

2. Experimental procedure

Powder mixtures of the stoichiometric composition 3 Mg:$(5 - x)$Zn:xAl with $x = 2$ to 4 or the intermetallic compound Mg_{32} (Zn, Al)$_{49}$, were mechanically alloyed under an argon atmosphere using a high-energy planetary ball mill with an angular velocity of 900 rev. min^{-1} (corresponding to a ball acceleration of 600 m sec^{-2}). The alloying time ranged from 30 sec to 60 min.

The cubic Mg_{32} (Zn, Al)$_{49}$ phase was obtained by annealing the MA icosahedral phase at 600 K for 1 h.

X-ray diffraction (Cu$K\alpha$), differential scanning calorimetry (DSC), SEM and TEM techniques were used to examine the resulting mechanically alloyed samples. The five-fold symmetry selected-area diffraction (SAD) pattern (Fig. 1) confirms the icosahedral structure of the final products.

3. Results

3.1. Mechanically alloyed i-Mg_{32} (Zn, Al)$_{49}$ from the elements

The X-ray diffraction patterns for a powder mixture with the nominal composition of 3Mg:2Zn:3Al recorded after several milling periods is given in Fig. 2. It is seen that the intensity of the Bragg reflections for the starting metals decreases and that a broad "halo" peak appears in the range $32 < 2\theta < 50°$. In some cases the amorphous "halo" appears instead of the metals Bragg reflections, even after 5 to 10 min MA. The broad peaks of the i-phase appear in the X-ray diffraction patterns when the MA time is increased to 10 to 15 min. Further increase in time leads to a narrowing of the Bragg peaks for the i-phase. This narrowing is not connected with any change in the specific surface area of the sample which does not differ much from 1 m^2 g^{-1} in the course of MA.

3.2. Formation of i-phase during MA of cubic Mg_{32} (Zn, Al)$_{49}$ phase

Just after 30 sec MA of the cubic Mg_{32} (Zn, Al)$_{49}$, the intensity of the Bragg reflections decreased which was

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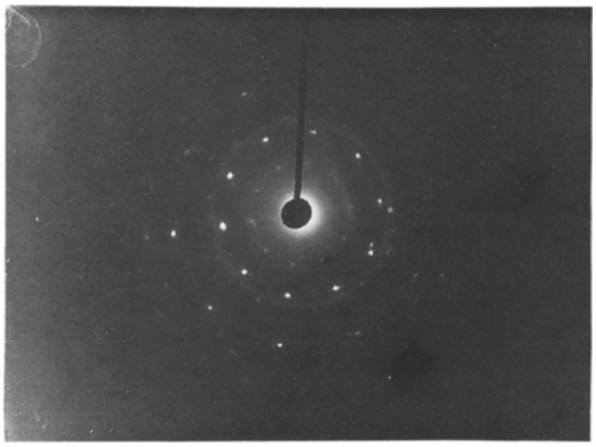

Figure 1 The five-fold symmetry SAD pattern of i-Mg_{32} (Zn, $Al)_{49}$.

accompanied by a significant broadening of the reflections. During the next 5 min of MA, (2 1 0), (2 2 0), (2 2 2), (3 2 1), (4 0 0), (4 1 1), (3 3 0), (4 2 0), (5 1 0), (4 3 1) and (5 2 1) reflections completely disappeared and other reflections became strongly broadened. After 6 min MA of the cubic phase, only the i-phase reflections could be seen in the X-ray diffraction patterns; these reflections did not change during further MA (Fig. 3).

4. Discussion

The synthesis of the icosahedral Mg_{32} (Zn, $Al)_{49}$ phase from the elements proceeds by formation of an intermediate amorphous phase, in contrast to the synthesis of the i-phase by MA of the cubic Mg_{32} (Zn, $Al)_{49}$ phase. The following speculations should be taken into account when discussing these two different processes.

The cubic Mg_{32} (Zn, $Al)_{49}$ crystals are considered [5] to represent the result of maintaining the icosahedral packing. Starting with an icosahedron, spheres are added in successive shells in such a manner as always to be at the centre of the triangles of previous shells. A complex of 117 atoms can be built up, with 72 atoms in the outermost shell lying on the faces of a cubo-octahedron. The complex can be then packed in the body-centred-cubic lattice. The introduction of structural defects may disorder this cubic lattice into the amorphous structure or non-translational icosahedral structure. The amorphous structure exhibits the icosahedral short-range packing, as do icosahedral quasicrystals [6].

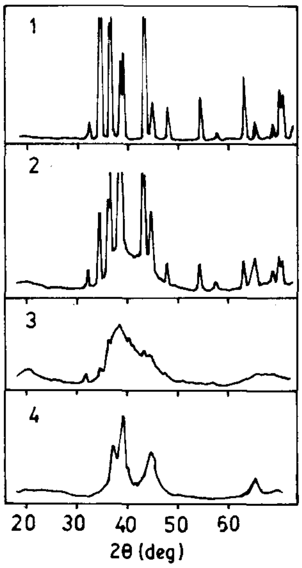

Figure 2 The sequence of the diffraction patterns of the mechanically alloyed mixtures. (1) Original mixture of metal powders, (2) 6 min MA, (3) 12 min MA, (4) 20 min MA.

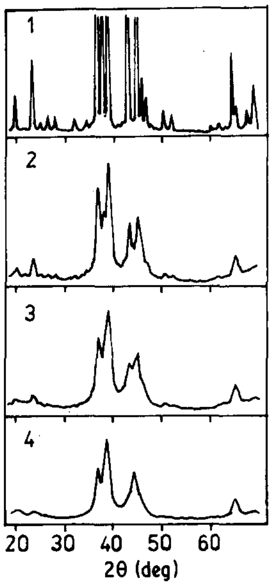

Figure 3 The cubic to icosahedral phase transformation during MA. Diffraction patterns of (1) cubic Mg_{32} (Zn, $Al)_{49}$, (2) after 30 sec MA, (3) after 3 min MA, (4) after 12 min MA.

The data presented above suggest that the initial stage of the mechanochemical synthesis of the icosahedral Mg_{32} (Zn, $Al)_{49}$ involves the formation of short-range icosahedral packing. These icosahedral clusters, consisting of elementary metals, can first form the amorphous structure. Further MA of the amorphous solid intensifies the mass transfer processes and thus leads to the crystallization of the non-translational, but more ordered and more thermodynamically stable, icosahedral structure. The process seems to be similar to the formation of the close-packed structure of stainless steel spheres in a vibrating volume. Because the icosahedral phase is metastable and transforms into the cubic one when heated, it is possible to suppose that the i-phase can be transformed into the cubic phase by more severe mechanical treatment, due to an increase in either ball diameter or mill revolution speed. This process is not in contradiction to the reverse process when the cubic Frank–Kasper phase transforms into the i-phase during MA.

The mechanical alloying of the elements involves the formation of the icosahedral clusters, whereas during the mechanical treatment of the cubic phase, these icosahedral clusters already exist in the structure. Henley and Elser have demonstrated [7] that the icosahedral structure can be derived from the cubic one by introducing the disclination network into it. Different defects and dislocations can be introduced into the crystal structure by severe plastic deformation

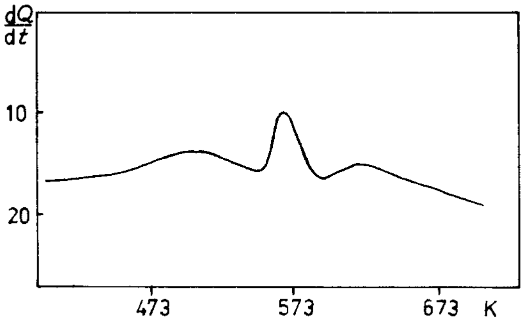

Figure 4 DSC curve of i-Mg_{32} (Zn, Al)$_{49}$.

caused by MA. The broadening of the Bragg reflections during the first stages of MA of the cubic phase, points to the formation of defects, presumably dislocations. The longer the duration of MA the more dislocations can form. The dislocations can then collapse into disclinations and thus the cubic phase can transform directly into the icosahedral one without the formation of the intermediate amorphous phase.

It should be noted that the mechanically alloyed icosahedral phase Mg_{32} (Zn, Al)$_{49}$ is characterized with broad X-ray Bragg reflections which can be narrowed by annealing at 500 K (see the exothermic effect on the DSC curve, Fig. 4). This seems to be evidence for the defect structure in the icosahedral phase obtained by MA.

Conclusions

The following mechanism for the synthesis of the icosahedral phase by MA from the elements is proposed. First, icosahedral clusters form and build the disordered (amorphous) phase. The energy input during MA leads to enhanced mass transfer processes and thus increases the possibility of formation of the more thermodynamically stable icosahedral phase. We suppose that the nucleation and growth of the non-translational icosahedral phase can proceed by a cluster-by-cluster mechanism. The formation of a large nucleus of the cubic lattice which contains 162 atoms seems to be possible only in long-term regions of high mass transfer, say, in the case of severe plastic deformation.

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