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Phase formation and stability of quasicrystal/α-Mg interfaces in the Mg–Cd–Yb system

S. Ohhashi [a], K. Suzuki [a], A. Kato [b], A.P. Tsai [a,*]

[a] Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan
[b] Advanced Materials Engineering Div., Toyota Motor Corporation, Shizuoka 410-1193, Japan

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Abstract

Phase formation involving icosahedral quasicrystals (iQc) in the Mg–Cd–Yb system was investigated. The phase diagrams obtained revealed that the iQc is in equilibrium with either $(Mg, Cd)_2Yb$ or an α-Mg phase over a wide composition range at 673 K. A eutectic reaction, where the melt decomposed to a rod-like lamella structure consisting of iQc and α-Mg phases was observed for $Mg_{68}Cd_{24}Yb_8$ at 735 K. High-angle annular dark-field scanning transmission microscopy observation of the iQc in $Mg_{96}Cd_3Yb_1$ verified the atomic positions of the Yb icosahedra and confirmed that the i-MgCdYb is isostructural to the i-CdYb. The formation of the eutectic structure is responsible for the high stability of the iQc/α-Mg interfaces because of good lattice matching; which is coincident interplanar spacing over several planes for the two phases. This coincidence in interplanar spacing was further confirmed in the real atomic structure, for which the twofold planes of the iQc, and the [0002] and [2−1−10] planes of α-Mg are dominant factors in determining the stability of the interfaces.

Keywords: Quasicrystal; Magnesium; Eutectic structure; Lattice matching

1. Introduction

Despite their lack of translational order, quasicrystals (Qc) diffract electrons and X-rays, showing sharp Bragg spots with rotational symmetries (fivefold, eightfold, tenfold or 12-fold), which are forbidden in classical crystallography. The first reported Qc was a metastable phase in the Al–Mn system [1]. The first stable Qc with high structural perfection was verified in the Al–Cu–Fe system [2], after which Qc were identified in several alloy systems [3–6]. The first stable binary icosahedral Qc was reported in the Cd–Yb system, in which an unknown $Cd_{5.7}Yb$ alloy was verified to be a stable Qc [7]. It turns out that the discovery of this stable i-$Cd_{5.7}Yb$ Qc was a milestone, which led to a new group of stable Qc as well as a large number of approximants that exhibit interesting properties. Moreover, since there are only two constituent elements, and there is no chemical disorder in the structure, i.e. Cd and Yb occupy different atomic sites, structural analysis of the Qc is relatively simple. Consequently, the first precise structural solution of i-$Cd_{5.7}Yb$ was obtained by means of single-grain X-ray structure analysis [8]. Three building units with unique atomic decorations; acute rhombohedron (AR), obtuse rhombohedron (OR) and rhombic triacontahedron (RTH), fill the space to form a quasi-periodic structure in three dimensions. These same three building units were also identified for the Cd–Yb family in all known approximants except for the 1/1 approximant, which was composed only of the RTH. The structural model of the i-$Cd_{5.7}Yb$ is chemically feasible, and provides a structural understanding to enable

* Corresponding author.
E-mail address: aptsai@tagen.tohoku.ac.jp (A.P. Tsai).

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discussion of the physical properties and theoretical calculation based on the structure.

The Mg–Cd–Yb system [9] was developed from the Cd–Yb system by replacing Cd with Mg. The iQc phase forms over a wide compositional range of $Mg_xCd_{(85-x)}Yb_{15}$ ($x = 0$–60), even extending into the Mg-enriched region, which led to the formation of the first stable iQc in Mg-based alloys. The coexistence of the iQc and α-Mg phases in the Cd–Mg–Yb system was first observed by Singh and Tsai [10], who reported nanoparticles of the iQc phase embedded in an α-Mg matrix for the alloy $Mg_{70}Cd_{15}Yb_{15}$. The Cd–Mg–Yb system, in which the present authors have confirmed that the iQc and α-Mg phases coexist over a certain compositional range, is a promising system for studying the phase equilibrium between the iQc and α-Mg phases [11,12]. Except for the iQc phase, no other phase coexists with the α-Mg at selected compositions in Mg-enriched region, which enables one to develop the iQc reinforced Mg alloys where the sole contribution from the iQc could be derived. However, no phase diagram is available for the Mg–Cd–Yb system, although a phase diagram is available for the Mg–Cd–Y system [13]. The other interesting question regarding this system is how the equilibrium between the iQc and α-Mg phases is maintained over such a wide compositional range. The phase equilibrium implies that the iQc/α-Mg interface is stable or energetically low. This raises a fundamental question: how can a periodic lattice match along a quasiperiodic lattice to form a stable interface? This is a significant concern not only in terms of the metallurgy, but also from a mathematical point of view. The present authors believe that this is the first system to enable experimental investigation of these topics. In the present work, the phase formation of the iQc is investigated in a two-phase region around $Mg_xCd_{(85-x)}Yb_{15}$ ($x = 50$–) with three related motives. First, the intention is to determine the isothermal section of the phase diagram covering Mg 40–100 at.%, Cd 0–60 at.% and Yb 0–35 at.% at 673 K and the composition–temperature relationship of the pseudo binary iQc/α-Mg system. Then, a promising composition will be determined at which a microstructure with iQc particles dispersed in an α-Mg matrix can be obtained by conventional solidification. Finally, the geometrical relationship between iQc and α-Mg phases is studied using transmission electron microscopy (TEM) in order to understand the relationship between interface stability and lattice matching.

2. Experimental

Mg–Cd–Yb alloys were prepared from pure elemental Mg (99.99%), Cd (99.999%) and Yb (99.9%) with the purities given in parentheses. These pure elements were encapsulated in a stainless tube 10.5 mm in diameter and 70 mm long by arc welding. Then, this stainless tube was sealed within a quartz tube to protect from oxidation. The atmosphere inside the stainless tube was replaced with argon gas. Alloying and homogenization were performed in an electric furnace, which was first heated up to 1123 K and then kept at 673 K for over 140 h, and finally water quenched.

Phase identification was carried out using powder X-ray diffractometry (XRD; Mac science M03XHF22, Cu). Fine particles for high-resolution XRD measurement were placed in a 0.2-mm-diameter glass capillary, which was then exposed to a synchrotron photon factory source ($\lambda = 0.0653$ nm at SPring-8, NIMS beam line BL-15XU). Microstructure observation and composition analysis were carried out using an electron probe micro analyzer (JEOL JXA-8621MX) equipped with a wavelength dispersive X-ray spectrometer. The orientation relationships and interface between the iQc and α-Mg phases were studied by electron diffraction in a Topcon EM-02B and using a high-resolution image from an FEI Titan electron microscope, respectively. Mechanical thinning and ion milling (Fischione 1010) were used to prepare the TEM specimens. Thermal analysis was performed with a differential thermal analyzer (DTA, Rigaku thermo plus TG8120).

3. Results

3.1. Formation of the iQc

iQc phase formation has been reported previously for the Mg–Cd–Yb system, in which all alloys were in as-prepared states without further homogenization treatment. In order to approach the equilibrium state, all samples in this study were treated at 673 K for a long enough time up to 140 h. Table 1 gives nominal and analyzed compositions for some selected samples from this work. Fig. 1 shows the scanning electron microscopy (SEM) backscattering images of samples with the two- or three-phase regions listed in Table 1. Only three phases were observed

Table 1
Nominal alloy compositions and analyzed compositions of the phases examined in this study.

Nominal composition	Analyzed compositions (phase)
(a) $Mg_{55}Cd_{27}Yb_{18}$	$Mg_{56.4}Cd_{26.5}Yb_{17.1}$ (iQc)
(b) $Mg_{55}Cd_{10}Yb_{35}$	$Mg_{58.8}Cd_{8.3}Yb_{32.8}$ (Lv)
(c) $Mg_{60}Cd_{20}Yb_{20}$	$Mg_{51.1}Cd_{21.5}Yb_{27.4}$ (Lv), $Mg_{66.3}Cd_{18.0}Yb_{15.7}$ (iQc)
(d) $Mg_{70}Cd_{12}Yb_{18}$	$Mg_{56.6}Cd_{15.3}Yb_{28.1}$ (Lv), $Mg_{97.6}Cd_{2.2}Yb_{0.3}$ (α-Mg)
(e) $Mg_{57}Cd_{35}Yb_{8}$	$Mg_{41.8}Cd_{44.0}Yb_{14.1}$ (iQc), $Mg_{76.6}Cd_{23.3}Yb_{0.1}$ (α-Mg)
(f) $Mg_{80}Cd_{10}Yb_{10}$	$Mg_{53.6}Cd_{19.3}Yb_{27.1}$ (Lv), $Mg_{68.9}Cd_{16.0}Yb_{15.1}$ (iQc), $Mg_{96.7}Cd_{3.1}Yb_{0.2}$ (α-Mg)

Lv: Laves phase.