Research Article

Direct Preparation of Nano-Quasicrystals via a Water-Cooled Wedge-Shaped Copper Mould

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We have successfully synthesized multicomponent Mg-based nano-quasicrystals (nano-QCs) through a simple route by using a water-cooled wedge-shaped copper mould. Nanoscale QCs are prepared directly on tip of wedge-shaped castings. The further study shows that nano-QCs in the $\text{Mg}_{71}\text{Zn}_{26}\text{Y}_2\text{Cu}_1$ alloy show well microhardness of greater than HV450. Electrochemical properties of three kinds of quasicrystal alloys are investigated in simulated seawater. The $\text{Mg}_{71}\text{Zn}_{26}\text{Y}_2\text{Cu}_1$ nano-QC alloy presents the best corrosion resistance in this study for the formation of well-distributed nano-QC phases (1~5 nm) and polygonal $\text{Mg}_2(\text{Cu,Y})$ nanophases (40~50 nm).

1. Introduction

Quasicrystals (QCs) are aperiodic solids whose atomic arrangements have symmetries (typically five- or tenfold) that are forbidden for conventional crystallography [1] and have long been thought forbidden in nature. It brings about a paradigm shift in solid-state physics when the first QC example is obtained in a rapidly solidified Al-Mn alloy [2]. The unexpected discovery of QCs presents scientists with a new, puzzling class of materials and involves hundreds of researchers in this realm. In the past nearly thirty years, QCs in various systems have been synthesized in laboratories [3, 4] and have also been discovered in natural minerals [5]. These QCs possess a host of unusual mechanical and physical properties [6]. Though they cannot be applied directly as structural materials for their innate brittleness, they present high microhardness which makes them used as good strengthening phases for some flexible matrix. Accordingly, diverse QC master alloys have been successfully synthesized and added into different commercial alloys [7, 8].

Usually, nano-quasicrystals (nano-QCs) can be synthesized through two kinds of ways. Nano-QCs are known to form in annealed [9, 10] or ball-milled [11] metallic glasses. Moreover, they can also be fabricated in extruded [12, 13], rolled [14], or wrought [15] Mg-based alloys

at high temperature. These nano-QC alloys exhibit better mechanical properties compared with their corresponding glasses or conventional crystalline alloys [16]. So, the nano-QC alloy is a kind of very promising material. In this study, we have synthesized nano-QC alloys through a new and simple route instead of traditional heat treatment and texturing process. Thus, the forming process of nano-QC alloy can strongly be simplified. At the same time, the costing of manufacture equipment can highly be cut down.

On the other hand, magnesium alloys present poor corrosion resistance. They can easily be eroded either in acid, neutral, or alkali solutions, even in pure water [17]. So, their further applications are restrained. Considering the excellent corrosion resistance of QCs [18], we manage to in situ synthesis Mg-based nano-QCs in Mg-Zn-Y alloys which are hopeful to show their improved corrosion resistance.

In past work, we have synthesized quaternary spherical Mg-Zn-Y-based QC phase [19] by controlling compositions and undercooling conditions of the melts. In order to fabricate nanoscale QCs, we improve the cooling condition in this paper by using a water-cooled wedge-shaped copper mould [20]. Multicomponent spherical nano-QCs are successfully synthesized and their electrochemical properties are investigated in simulated seawater.

TABLE 1: Nominal composition of the experimental alloys.

Alloy No.	Alloy compositions (at. %)				
	Mg	Zn	Y	Cu	Ni
1#	72.0	26.0	2.0	—	—
2#	71.0	26.0	2.0	1.0	—
3#	71.0	26.0	2.0	0.5	0.5

2. Experimental

The experimental alloys (Table 1) were produced by a reformed crucible electric resistance furnace (SG₂-5-10 A, China), melted under the mixture of CO₂/0.5vol.%SF₆ protective atmosphere, using Mg(99.95%) and Zn(99.90%) ingots, Ni(99.99%) and Cu(99.99%) powder, and Mg-29.05%Y master alloy. Stirring for 2 min by impellor at 1073 K and holding for 5 min above 1053 K, the melt was poured and cooled in a water-cooled wedge-shaped copper mould. Samples were taken on tip of castings as shown in Figure 1.

The morphology observation of QCs was conducted using transmission electron microscopy (TEM, DEOL JEM-2010FEE, Japan). Microhardness of QC alloys was examined by microhardness tester (HXD-1000, China). The electrochemical properties of specimens were tested in simulated seawater (2.73% NaCl, 0.24% MgCl₂, 0.34% MgSO₄, 0.11% CaCl₂, 0.08% KCl, and 96.5% deionized water, vol.%) by an electrochemical workstation (Gamry, PCI4-750, USA) with a sweep rate of 10 mV/s. A saturated calomel electrode (SCE) was used for the reference electrode.

3. Results and Discussion

TEM photos of QC alloys in different sample positions are shown in Figure 2. Three kinds of componential micro-/nano-QC phases are synthesized on tip of wedge-shaped castings. Energy-dispersive spectroscopy (EDS) analysis (Figure 3) shows that micro-/nano-QC phases in Position B of Alloy 1~ Alloy 3 are Mg-Zn-Y phase, Mg-Zn-Y-Cu phase, and Mg-Zn-Y-Cu-Ni phase, respectively. The selected area electron-diffraction (SAED) patterns with typical fivefold rotational symmetry identify that these micro-/nano-QC phases are icosahedral QCs. Among all QCs, QCs in Position A of Alloy 1 show petal-like morphology, while others show spherical morphology. From the further analysis in Table 2, we can see that in alloys with same components, QCs in Position B are smaller than those in Position A, while QC microhardness in Position B is greater than that in Position A. After introducing Cu(-Ni) into Mg-Zn-Y alloys, we can see in the same sample position, QC size of Alloy 2 and Alloy 3 is obviously smaller than that of Alloy 1. QC size of Alloy 2 in Position A is close to that of Alloy 1 in Position B. Nano-QC spheres about 8~30 nm and 1~5 nm are synthesized in Position B of Alloy 3 and Alloy 2, respectively. It shows from the microhardness testing that the smaller the QC spheres, the greater their value of microhardness. Furthermore, the microhardness of nano-QC spheres in Position B of Alloy 2 exceeds HV450, which shows fascinating properties.

FIGURE 1: Sketch map of a wedge-shaped casting (mm).

Figure 4 shows the potentiodynamic polarization curves of QC alloys (Position B) measured in simulated seawater open to air at room temperature. We can see that Mg₇₁Zn₂₆Y₂Cu₁ nano-QC alloy presents high corrosion resistance in simulated seawater and its corrosion resistance is much better than that of Mg₇₂Zn₂₆Y₂ and Mg₇₁Zn₂₆Y₂Cu_{0.5}Ni_{0.5} QC alloys. The further study shows that this result can be ascribed to the existence of well-distributed nano-QC phases (shown in Figure 5 by red arrows) and polygonal Mg₂(Cu,Y) phases [21]. These high-corrosion resistance phases decrease the anodic passive current density, improve the polarization resistance, cut down the corrosion rate (Table 3), and finally improve the corrosion resistance of the Mg-Zn-Y-based alloy markedly. Cu and Ni have long been considered as harmful elements for improving corrosion resistance of Mg-based alloy [22], however they are used to synthesize nano-QC spheres in this paper. Due to high-corrosion resistance of QC phases, Mg₇₁Zn₂₆Y₂Cu₁ and Mg₇₁Zn₂₆Y₂Cu_{0.5}Ni_{0.5} nano-QC alloys present better corrosion resistance than Mg₇₂Zn₂₆Y₂ QC alloy. Moreover, the corrosion resistance of Mg₇₁Zn₂₆Y₂Cu₁ nano-QC alloys is higher than Mg₇₁Zn₂₆Y₂Cu_{0.5}Ni_{0.5} nano-QC alloys for the higher damage level of Ni to the corrosion resistance of magnesium alloy than that of Cu when they have same contents [22].

It was reported that a large negative enthalpy of mixing and/or existence of Frank-Kasper-type phases appear to be the crucial criteria for the formation of nano-quasicrystalline phase in any system [23]. Meanwhile, Mg-Zn-Y-based QCs just belong to Frank-Kasper-type phases [24] and have a certain negative enthalpy of mixing. So theoretically, Mg-Zn-Y-based nano-QCs can be formed in a proper cooling conditions. The past cooling rate the researchers made to produce QCs was whether too high or too low, and

FIGURE 2: TEM photos of micro/nano-QC alloys and QC typical selected area electron-diffraction (SAED) patterns on Position B of different alloys.

was not content with the forming conditions of nano-QCs. This route just meets the demands for forming nanoscale QCs. So, nano-QCs are successfully produced in this paper. Moreover, the additions of Cu and Ni improve the degree of constitutional supercooling of Mg-Zn-Y melts and reduce the crucial criteria radius for forming spherical QCs. However, increasing thermodynamics undercooling coming

from water-cooled wedge-shaped copper mould makes it still possible to form spherical QCs. At the same time, the alloy components designed for this study is based on the three empirical rules [25] for the formation of metallic glass. It has been widely accepted that quasicrystals and at least some metallic glasses are built up with icosahedral clusters [26]. The short-range atomic configuration is very similar

FIGURE 3: Energy-dispersive spectroscopy (EDS) analysis of QCs in Position B.

FIGURE 4: Potentiodynamic polarization curves of QC alloys (Position B) measured in simulated seawater open to air at room temperature.

FIGURE 5: Pentagonal nanophase in Alloy 2 (a) TEM photo. (b) Magnifying TEM photo and (c) its fast Fourier transform (FFT) pattern.

TABLE 2: Comparisons of the quasicrystals (QCs).

Alloy	Sample position	QC size(diameter)/nm	QC morphology	Microhardness /HV
1	A	650–900	Petal-like	324
	B	330–340	Spherical	375
2	A	370–400	Spherical	367
	B	1.0–5.0	Spherical	459
3	A	20–55	Spherical	412
	B	8–30	Spherical	438

TABLE 3: Corrosion parameters obtained from potentiodynamic polarization curves for Position B of QC alloys in simulated seawater.

Specimen	$I_{\text{corr}}/\mu\text{A}/\text{cm}^{-2}$	$R_p/\text{k}\Omega$	Corrosion Rate/mpy
1	11.09	6.925	19.298
2	2.035	14.76	1.522
3	3.762	8.105	3.084

I_{corr} : corrosion current; R_p : polarization resistance.

between the quasicrystal and amorphous phases [27]. On the tip of the wedge-shaped ingots, its cooling conditions is just suitable for these icosahedral clusters to be nucleation of QCs. And then, it leaves very short time for quasicrystal growth. So, it is nano-QCs that form in this route instead of metallic glasses.

4. Conclusions

After introducing Cu(-Ni) into Mg-Zn-Y alloys, spherical nano-quasicrystals (nano-QCs) are directly prepared on tip of wedged-shaped castings. Nano-QCs in the $\text{Mg}_{71}\text{Zn}_{26}\text{Y}_2\text{Cu}_1$ alloy show well microhardness of greater

than HV450. At the same time, the $\text{Mg}_{71}\text{Zn}_{26}\text{Y}_2\text{Cu}_1$ nano-QC alloy presents high corrosion resistance in simulated seawater for the formation of well-distributed nano-QC phases (1~5 nm) and polygonal $\text{Mg}_2(\text{Cu},\text{Y})$ nanophases (40~50 nm).

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