Journal of Alloys and Compounds 717 (2017) 214–218

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Crystal structure and mechanical properties of a new ternary phase in Mg-Zn-Y alloy solidified under high pressure

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ARTICLE INFO

Article history:
Received 11 April 2017
Received in revised form
5 May 2017
Accepted 8 May 2017
Available online 10 May 2017

Keywords:
Metals and alloys
Phase transition
Crystal structure
X-ray diffraction
Computer simulations
Mechanical properties

ABSTRACT

A new ternary phase, $Mg_{64.093\pm0.004}Zn_{15.355\pm0.002}Y_{20.552\pm0.005}$ (at. %) was found in a Mg-Zn-Y alloy prepared by high pressure solidification. A full set of crystal structure parameters including the atomic coordinates of this new phase were determined using X-ray diffraction with Rietveld refinement and electron probe micro-analysis. Furthermore, the mechanical properties of this phase, including the Young's modulus and hardness were reported by nanoindentation test. Theoretical elastic constants, bulk modulus, shear modulus, Young's modulus, Poisson's ratio of this phase were calculated by first-principles. Results indicate that this phase is a ductile materials phase.

1. Introduction

As a low-density structural material, Magnesium-based Mg-Zn-Y alloy systems have received considerable interest over the past decade for producing high strength products, bulk metallic glasses, and hydrogen storage materials [1]. So far, a number of ternary and binary phases found in Mg-Zn-Y alloy system have been reported: I-phase Mg_3Zn_6Y, 14H-phase $Mg_{12}YZn$, 18R-phase $Mg_{10}YZn$, W-phase $Mg_3Y_2Zn_3$, Z-phase $Mg_{28}Y_7Zn_{65}$ [2–5], etc. Some of these phases introduce excellent properties to the alloys. Different ternary phases can be obtained by either tuning the element composition ratio [6], or by adopting different preparation approaches, especially preparation under extreme conditions. When the Mg-Zn-Y ternary alloys are prepared by rapid solidification, they can exhibit superior mechanical properties, with the yield strength higher than 600 MPa and elongation of 5%. These unique tensile properties are reportedly due to the formation of nanoscale intermetallics of a long-period stacking ordered (LPSO) structure [7–9]. When studying these systems, it is of overwhelming importance to understand the containing phases and the structure-properties relationship. In addition, controlling the formation of specific phases in the system is also critical. However, the phase composition and crystal structures for Mg-Zn-Y ternary system are not widely studied and understood yet due to its complicated phase composition.

High pressure has been found to be a powerful tool for controlling the element distribution and phase composition [10]. The ever increasing chamber dimension and maximum allowable pressure in the high-pressure manufacturing equipment make high-pressure manufacturing became an appealing solution for preparing materials with superb properties nowadays [11,12]. Zhou et al. [13], Dong et al. [14] and Fan et al. [15] investigated the effect of high pressure solidification on the microstructure, phase transformation and mechanical properties of Mg-Zn-Y alloys. Their works show that the high pressure can significantly affect the Mg-Zn-Y alloy system.

In this work, a new ternary phase $Mg_{64.093\pm0.004}Zn_{15.355\pm0.002}Y_{20.552\pm0.005}$ (at. %) was discovered in the high pressure solidified Mg-Zn-Y alloy. The crystal structure of this unique phase

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http://dx.doi.org/10.1016/j.jallcom.2017.05.088
0925-8388/

was determined by a combination of X-ray diffraction and Rietveld refinement. In addition, the mechanical properties were measured by nanoindentation. And the theoretical elastic properties such as elastic constants, bulk modulus, shear modulus and Young's modulus of this new phase were calculated by first-principles.

2. Materials and experimental techniques

A Mg-Zn-Y alloy with 33 wt % Y and 17 wt % Zn was prepared by conventional casting from 99.99 wt % pure Mg, Y and Zn. The whole casting process was protected by SF_6 and CO_2 gas mixture. The samples for high-pressure solidification were cut into cylinders 20 mm in diameter and 18 mm in length. The high pressure experiments were carried out using a six-anvil apparatus with pressures of 3 GPa and the temperature was 773 K. Temperature was measured at the side of the sample using Platinum-Rhodium thermocouples. The pressure was added before increasing the temperature. Samples were heated for 1 h at relatively stable temperature. In the end of the process, the samples were cooled by chilled water to room temperature and then the applied pressure was released. The chemical composition of the phase was determined by the electron probe micro-analysis using a CAMECA SXFive. The surface of the sample was polished before test. The pure Mg, Zn and YAG(Y: 44.9304 at.%, Al:22.7261 at.%, O: 32.3436 at.%) were selected as standard, respectively. Morphology was examined by Field Emission Scanning Electron Microscopy (FESEM) using Zeiss Sigma. The crystal structure was determined by X-ray diffraction on a PANalytical Empyrean X-ray diffractometer (Cu Karadiation, step size 0.026°2Th., scan step time 96.39s), using the JADE 2010 software. Rietveld refinement was performed using the Jade 2010. Load-controlled nanoindentation testing was performed employing a calibrated HYSITRON 900 TRIBOINDENTER with a diamond Berkovich tip. Testing was performed five times on the target phase. Prior to the nanoindentation tests, the surface of the sample was polished to mirror-finish. Structural optimizations and elastic constants calculations are performed with CASTEP code [16]. The generalized gradient approximation (GGA) with the PW91 [17] is used as the exchange-correlation potential. The Mg $2p^6 3s^2$, Zn $3d^{10}4s^2$ and Y $4s^2 4p^6 4d5s^2$ electrons are treated as valence electrons. The integrations over the Brillouin zone are performed using the Monkhorst–Pack set [18] for new phases and the 600 eV energy cutoff is used. The structural parameters of the new phase are obtained from our experimental data, the values of the k-point meshes are $8 \times 8 \times 8$. The tolerances for geometry optimization are set as the difference in total energy being within 10^{-6} eV/atom.

3. Results and discussion

3.1. Microstructure evolution

Fig. 1 shows the microstructure of the samples synthesized at conventional casting and high pressure. It can be seen that high pressure can lead to dramatic microstructural changes as well as phase in the alloy. As indicated in the SEM images and XRD pattern, the alloy was mainly composed by lath14H ($Mg_{12}ZnY$), W phase ($Mg_3Y_2Zn_3$) and Mg solid solution after the alloy solidified under normal pressure. The bright spots in the Fig. 1(a) are the concentrated Y_2O_3. Whereas in Fig. 1(b), (c), the entire alloy was filled by white bright “flower-like” phase and eutectic structure which around the white “flower” after the alloy was solidified under 3 GPa. The eutectic structures are composed of new flower phase (bright parts) and Mg solid solution (black parts). A handful square-shaped Y_2O_3 phases were scattered around the major phase. In order to confirm the chemical composition of the new “flower” phase, we measured the phase by Electron Probe Micro-Analysis. The tests were performed on the different regions in the flower-shape phase of the sample for five times. The test result showed that the total atomic percent for each test was 100%, and the lowest total wt% is 99.63%, with the highest at 101.732%. According to the EPMA testing benchmarks, the result could be assessed as very good. Average multiple tests, the electron probe micro-analysis (EPMA) showed that the chemical composition of the bright “flower” phase was $Mg_{64.093\pm0.004}Zn_{15.355\pm0.002}Y_{20.552\pm0.005}$ (at. %), to the best of author's knowledge, there is no known phase in Mg-Zn-Y alloy that matches or closes to this composition [1,19–21].

3.2. Rietveld refinement and crystallographic data

Fig. 2 shows the observed and calculated (Rietveld) XRD patterns of sample synthesized under 3 GPa, and the difference plot is shown in the lower part of figure. As shown in the observed pattern, a number of peaks can be well described by α-Mg. There are some minor lines, which are assigned to be the Y_2O_3 (space group *I*213 (No.199), corroborated by the SEM-EDS. Despite the two phases mentioned above, it's clear that the main diffraction pattern don't match any ternary Mg-Y-Zn phase in the database. As shown in the lower part of Fig. 2, the peak positions of some common ternary Mg-Y-Zn phases are listed by vertical bars. Combined with the SEM microstructure, it is concluded that these peaks belong to the new “flower” phase. What we need to do is setting up a model of crystal structure according to the peak position and intensities. In the first step, we employed Peakfit to precisely locate the peaks in the XRD pattern. Throughout the process, we combed all locations for this new phase, and obtained a series of accurate peak positions. Those positions were subsequently calculated in DICVOL06, and yielded several sets of lattice parameters. Then, those lattice parameters were further calculated in check cell to give the theoretical corresponding peak locations. After examining the pattern obtained in the experiment, we could verify the calculated peak positions and determine the space group of this phase. Once the peak positions were verified, we got the primitive crystalline model. We further used Rietveld analysis to refine this model, which ultimately gave precise parameter for this phase. Rietveld analysis of the newly-built crystal structure shows the reliability factors are: R-WP = 5.68% and E = 1.32%. The calculation showed that the alloy contains the $Mg_{64.093\pm0.004}Zn_{15.355\pm0.002}Y_{20.552\pm0.005}$ phase (68.5%) and Mg solid solution (30.9%), yttrium oxide (0.6%) after high pressure solidification. The refinement parameters, such as the lattice parameters, the atomic coordinates, occupancies and the peaks list of the $Mg_{64.093\pm0.004}Zn_{15.355\pm0.002}Y_{20.552\pm0.005}$ phase are given in Table 1. A schematic illustration of the crystal structure of this new phase is shown in Fig. 3. The different color proportions in the same atomic position represent the occupancy of different atoms at the same spot, Mg, Y and Zn atoms are represented in gray, green and blue colors respectively. Among these independent sites in the unit cell, only one site (0.5, 0.5, 0.5) is fully occupied by the Mg element. While the other sites, (0, 0, 0), (0.25, 0.25, 0.25) belong to mixed sites, composed of Y/Mg and Zn/Mg with the occupancy ratio of 0.822/0.178 and 0.307/0.693, respectively.

3.3. Mechanical properties and first-principles calculation

The mechanical properties of this phase were measured by nanoindentation technique. Young's Modulus is a measure of material's stiffness or resistance to elastic deformation. If the Young's modulus of metal is greater, it's stiffer. The smaller the value of Young's Modulus is, the better the plasticity is. It is an important design factor for metals elastic deflections. Oliver and Pharr [22]