Materials and Design 104 (2016) 327–332

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Annealing effects on the structural and magnetic properties of off-stoichiometric Fe-Mn-Ga ferromagnetic shape memory alloys☆

H. Yang [a,b,c], Y. Chen [b], H. Bei [d], C.R. dela Cruz [e], Y.D. Wang [a], K. An [b,*]

[a] Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang 110004, China
[b] Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[c] Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA
[d] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[e] Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ARTICLE INFO

Article history:
Received 20 February 2016
Received in revised form 22 April 2016
Accepted 28 April 2016
Available online 7 May 2016

Keywords:
Ferromagnetic shape memory alloy
Annealing
γ phase
Phase segregation

ABSTRACT

Annealing plays an important role in modifying structures and properties of ferromagnetic shape memory alloys (FSMAs). The annealing effect on the structures and magnetic properties of off-stoichiometric $Fe_{45}Mn_{26}Ga_{29}$ FSMA has been investigated at different elevated temperatures. Rietveld refinements of neutron diffraction patterns display that the formation of the γ phase in $Fe_{45}Mn_{26}Ga_{29}$ annealed at 1073 K increases the martensitic transformation temperature and reduces the thermal hysteresis in comparison to the homogenized sample. The phase segregation of a Fe-rich cubic phase and a Ga-rich cubic phase occurs at the annealing temperature of 773 K. The atomic occupancies of the alloys are determined thanks to the neutron's capability of differentiating transition metals. The annealing effects at different temperatures introduce a different magnetic characteristic that is associated with distinctive structural changes in the crystal.

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) exhibit both reversible martensitic and ferromagnetic transformations in response to the external magnetic, temperature and stress fields. The shape memory effect that is based on those integrated transformations thus becomes controllable, and it makes FSMAs viable for potential applications as actuators, sensors and electromagnetic devices. Since a large magnetically induced strain was confirmed in Ni_2MnGa alloys [1,2], extensive studies have been conducted in developing new ferromagnetic shape memory alloys, such as Ni_2FeGa [3,4], Co_2NiGa [5,6], CuAlMn [7,8] and Fe_2MnGa [9,10] alloys.

Among those, the Fe-Mn-Ga is a new system of FSMA since the martensitic transformation from paramagnetic cubic austenite phase to the ferromagnetic tetragonal martensite phase was firstly studied in $Fe_{43}Mn_{28}Ga_{29}$ in 2009 [9]. The Fe-Mn-Ga alloys gradually attracted great interests due to the exhibiting large difference in magnetization between the parent austenite and martensite phases and therefore a large shape memory strain up to 3.6% [10], in comparison with 1.5% in NiMnGa polycrystalline [11] and 0.1% in NiFeGa alloy [12]. The study of the Fe-Mn-Ga alloys has been extended to the magnetic, magnetotransport and optical properties [13,14] and then the correlation to the martensitic transformation [15,16]. The evolution of the magnetic domain structure in single crystals of a near the composition Fe_2MnGa was observed during phase transition by photoelectron emission microscopy [15]. A recent study of $Fe_{50}Mn_{23}Ga_{27}$ alloy found that the defects-induced local symmetry break suppressed the martensitic transformation without affecting the magnetic ordering [16].

However, most of the studies above had the sample prepared only through the process of homogenization treatment. The annealing treatments following, which are commonly used in the various alloy systems to tune the structures and the magneto mechanical properties in the development of FSMAs were barely reported in Fe-Mn-Ga alloys. In fact, although the annealing effects from structures to properties were intensively reported in other FSMAs, the results and the mechanisms were not consistent. The martensitic transformation temperature was found to increase with elevating the annealing temperature in $Ni_{55}Fe_{18}Ga_{27}$ [17], $Ni_{51}Fe_{22}Ga_{27}$ [18] and the $Ni_{50.6}Mn_{28}Ga_{21.4}$ microwires [19], while it could be remarkably decreased with longer annealing time in the $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloy [20]. In terms of the magnetic properties under annealing effects, the Curie temperature was increased in $Ni_{50.6}Mn_{28}Ga_{21.4}$ [19] but decreased in $Ni_{51}Fe_{22}Ga_{27}$ [20] and the

☆ Notice: This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

* Corresponding author
E-mail address: kean@ornl.gov (K. An).

http://dx.doi.org/10.1016/j.matdes.2016.04.098
0264-1275/

saturation magnetization was enhanced in both $Ni_{49.5}Mn_{29.3}Ga_{21.2}$ [21] and $Ni_{50.6}Mn_{28}Ga_{21.4}$ [19]. For whatever the trend is, the authors claimed the correlation with the atomic ordering in the ternary systems [18,19,22]. Moreover, the precipitation may form after the thermal treatment to alter the phase structure. The $Ni_{49.5}Mn_{29.3}Ga_{21.2}$ alloy after annealing at 1173 K with presence of γ phase precipitation possesses good ductility and enhanced saturation magnetization [21]. Increased annealing time results in the formation of Ni_3Ti precipitates as observed in the $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloy, and after annealing, the formed five-layer martensitic structure of the alloy improves its ductility at room temperature [23]. Additionally, the decomposed Co-rich precipitates in the $Co_{46}Ni_{27}Ga_{27}$ martensite [24] and the secondary phase in the $Ni_{55}Fe_{18}Ga_{27}$ alloy [25] were respectively observed after annealing treatment. Apparently, the properties of the FSMAs have been tuned through the structure modification, as many reports claimed. However, the annealing effects may differ from case to case, the specific study of the phase structure evolution and the complex atomic ordering in a ternary Fe-Mn-Ga system under the annealing treatment is essential to understand the structural mechanism of the material behaviors that are closely related to the FSMA performance.

The neutron diffraction is a suitable technique for the phase structure investigation of Fe-Mn-Ga alloys. The large cross-section of all components make it possible to differentiate multiple phases, and the large penetration depth of neutrons further reflect the behavior of the bulk instead of the surface. Neutron diffraction enables deciphering the site occupancies in the crystal structure of a complex FSMA system, owing to the differentiable scattering contrasts of transition metals elements [26–29]. Utilizing the advantages of the neutron diffraction for the material structure characterization, in this paper, we select the $Fe_{45}Mn_{26}Ga_{29}$, an off-stoichiometric Fe_2MnGa, as the model material to report the significant temperature-dependence of the phase composition and the atomic ordering under the annealing. The annealing effects on the martensitic transformation and the magnetic properties of this FSMA system is to be revealed.

1.1. Sample preparation and measurements

The polycrystalline button ingot with a nominal composition of $Fe_{45}Mn_{26}Ga_{29}$ was prepared with high-purity iron (99.99%), manganese (99.99%) and gallium (99.99%) by melting three times in an arc-melting furnace under a high-purity argon atmosphere. According to the process reported before [9,10,13], the ingot was homogenized at 1273 K for 24 h and quenched in water and then cut into three sections (named as Sample I–III). Sample I was homogenized at 1273 K, Sample II and III were annealed 2 h at temperatures of 1073 K and 773 K, respectively. All the three samples were water quenched after thermal treatment to explore crystal structure evolutions and magnetism behaviors.

The bulk magnetic properties were examined using a superconducting quantum interference device magnetometer with heating and cooling rates of 2 K min^{-1}. The magnetization measurements were performed in the temperature range of 4 K–300 K with an applied magnetic field up to 6.5 T. The temperature dependence of the magnetization was measured in zero field cooling (ZFC) and in field cooling (FC) modes. The crystal structures of Sample I were investigated by neutron diffraction at the POWGEN diffractometer at 300 K and 20 K. The neutron diffraction measurements of Sample II and III were collected at the VULCAN instrument [30] at the Spallation Neutron Source (SNS). The neutron diffraction under 3 T magnetic field were measured at the HB2a powder diffractometer at High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory. The neutron diffraction patterns were analyzed by performing Rietveld refinement using the GSAS software [31] and EXPGUI interface [32], which extract the refined lattice parameters, site occupancies and weight fraction of each phase.

2. Results

2.1. The influence of annealing on microstructure of $Fe_{45}Mn_{26}Ga_{29}$

The crystal structures were obtained by performing Rietveld analysis on the neutron diffraction patterns. For example, Fig. 1 shows the refined patterns of Sample I at 20 K and 300 K. The $Fe_{45}Mn_{26}Ga_{29}$ has a pure austenitic cubic phase ($Fm\bar{3}m$ space group) at 300 K [14], while at 20 K both the martensite phase (I4/mmm space group) [9] and the austenite phase co-exist in it. The lattice parameter *a* of the austenite is ~5.874 Å at 300 K and ~5.842 Å at 20 K. The lattice parameters of the martensite are ~3.790 Å for *a* and ~7.083 Å for *c* at 20 K, respectively.

In order to reveal the chemical ordering of Fe, Ga and Mn in the austenite lattice and in the martensite lattice, their occupancies at the three lattice sites were calculated with Rietveld refinement. In the refinement, the arbitrary exchanges of two elements between two sites were allowed with the full site occupancy constraint and the composition constraint, and the process was repeated throughout the three elements and all three sites until the stable minimum χ^2 was reached. The determined atom occupancies in the austenite (300 K) and martensite (4 K) are presented in Tables 1 and 2.

At 300 K, the results show that in the austenite unit cell, the Fe, Ga and Mn atoms mainly occupy the Wyckoff Position 8c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4a (0, 0, 0), respectively. However, as an off-stoichiometric composition, the structure is not fully ordered because there are multiple species of atoms in each site. The excess Ga atoms (Ga_{Mn}) occupy the Mn sites and some Mn atoms (Mn_{Fe}) shift to the free Fe sites as the result of the defect pair of Ga_{Mn} and Mn_{Fe}. The Fe and Mn atoms also have a certain degree of exchange between 8c and 4a sites. Therefore, the $Fe_{45}Mn_{26}Ga_{29}$ has a partial ordered atomic arrangement in the cubic austenite at 300 K.

The martensite and austenite phases co-exist at 20 K. The weight fractions of martensite and austenite phases are 69% and 31%, respectively, as extracted from the Rietveld refinement using GSAS. The martensite phase is not fully ordered as shown by the atom site occupancy in Table 2. The low-temperature austenite phase lattice monotonically shrinks upon cooling, not showing any anomalous changes.

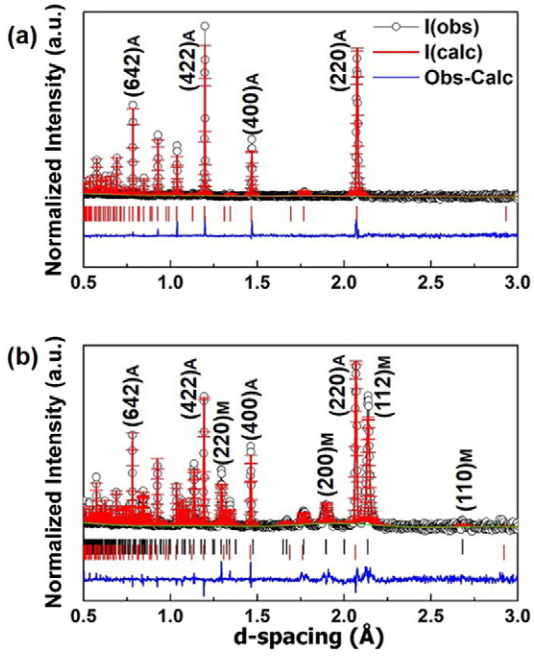

Fig. 1. Neutron diffraction patterns of Sample I homogenized at 1273 K for 24 h (a) the austenite ($Fm\bar{3}m$) phase at 300 K and (b) the martensite (I4/mmm) and austenite phases co-exist at 20 K.