Computational Materials Science 140 (2017) 89–94

Contents lists available at ScienceDirect

Computational Materials Science

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

Origin of the modulus anomaly over a wide temperature range of $Mn_{0.70}Fe_{0.25}Cu_{0.05}$ alloy

Yanguang Cui [a], Yunlong Guo [a], Yangxin Li [b], Jianfeng Wan [b,*], Jihua Zhang [b], Yonghua Rong [b], Nailu Chen [b], Dong Wang [c], Yunzhi Wang [d]

[a] UM-SJTU Joint Institute, Shanghai Jiaotong University, Dongchuan Road 800, Shanghai 200240, China
[b] School of Material Science & Engineering, Shanghai JiaoTong University, Shanghai 200240, China
[c] Center for Computational Study of Microstructure Evolution in Materials and Multi-Disciplinary Materials Research Center, Frontier Institute of Science and Technology, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
[d] Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210, USA

ARTICLE INFO

Article history:
Received 28 June 2017
Received in revised form 23 August 2017
Accepted 24 August 2017

Keywords:
Modulus anomaly
Antiferromagnetic transition
Phase-field method

ABSTRACT

To reveal the origin of modulus anomaly over a wide temperature range (about 240 K) observed in $Mn_{0.70}Fe_{0.25}Cu_{0.05}$ alloy, a phase-field model considering antiferromagnetic (AF) transition with doping Fe was established, in which the average modulus is considered as a functional of order parameter. Simulation reveals that the pining effect by doping Fe leads to the increase of low spin non-collinear AF domain walls (LS), meanwhile, the LS domain walls gradually evolve to high spin collinear AF domains (HS) with lowering temperature, accompanying the growth of HS domains and the decrease of modulus, and vice versa. Such a dynamic antiferromagnetic domain size (DAFDZ) effect gives rise to modulus anomaly, while the proper volume ratio of LS and HS is a crucial factor for the wide temperature range of modulus anomaly.

1. Introduction

Since discovery of Invar and Elinvar alloys by Guillaume, who was awarded the Nobel Prize of Physics in 1920 [1], physical properties of materials with abnormal temperature dependence have stimulated extensive experimental and theoretical studies for more than a century [2–10]. A lot of models have been suggested. Amongst these models, the 2γ-state model considering coexistence of two spin states is the most promising one, whose key idea was proposed by Weiss in 1963 [2]. In the theory, there are two possible states for FCC γ-Fe: the ferromagnetic high volume state and the antiferromagnetic low volume state. Thermal excitations between these two states are supposed to compensate for the usual lattice expansion related to anharmonic effects of the lattice vibrations. In the following decades, further development on various magnetic theories and models has been accelerating the step of research. Endoh and Ishikawa [11] proposed two spin structures in antiferromagnetic γ-FeMn alloy: collinear spin structure and non-collinear spin structure and roughly determined the Mn content range corresponding to the exchange of two spin structures. Besides, two antiferromagnetic (AF) states mentioned above existing in Mn-Ni alloys were reported [12,13]. Meanwhile, elastic modulus anomaly with wide temperature range was observed in these alloys [14]. In 1999, Schilfgaarde et al. presented *ab initio* calculations of the volume dependences of magnetic and thermodynamic properties for the most typical Invar system, in which non-collinear (canted) spin alignments lead to an anomalous volume dependence of the binding energy [6]. It is worthy to point out that non-collinear (canted) spin structure can have various spin directions and magnitude, which is different from non-collinear structure as unique spin state proposed by Endoh and Ishikawa [11]. Owning to the limited capability of *ab initio* calculations on larger scale, compositional fluctuation has not yet been considered in models reported. Although Elinvar effect was discovered in Invar alloy with doping 12Cr by Guillaume a century ago, the origin of modulus anomaly as a base of Elinvar effect has not been clarified from the viewpoint of magnetism, even though it has long been realized that the Elinvar effect is related to magnetism like Invar effect. Recently, a mechanism being independent magnetism was proposed by Cui and Ren [15], and they observed the Elinvar effect in Co-doped TiNi strain glass alloys and proposed the origin of Elinvar effect resulting from the coupling of dynamic size effect and size dependence of elastic modulus, in which strain glass transition between the critical temperature (T_{nd}) and glass temperature (T_g)

* Corresponding author.
E-mail addresses: jfwan0909@hotmail.com, jfwan@sjtu.edu.cn (J. Wan).

http://dx.doi.org/10.1016/j.commatsci.2017.08.040
0927-0256/

lead to the modulus anomaly. Whether this mechanism is suitable for FCC Mn-Fe-Cu alloys with antiferromagnetic domains needs be examined.

In this work, we established a phase-field model considering antiferromagnetic (AF) transition with doping Fe in $Mn_{0.95-x}Fe_xCu_{0.05}$, in which the average modulus is considered as a functional of order parameter, to clarify the effect of doping on collinear AF state (CAF) and non-collinear AF state (NCAF) related to origin of the modulus anomaly over a wide temperature range.

2. Material and methods

The MnFeCu alloys with different composition were prepared from electrolytic manganese, copper, and pure iron by medium-frequency induction melting in an argon atmosphere. All ingots were forged into blocks, annealed at 1100 °C for 12 h and quenching in water. Then the bars were reheated at 950 °C for 0.5 h and quenched in water to retain the metastable γ phase. The final chemical compositions of the specimens (in at.) were $Mn_{0.80}Fe_{0.15}Cu_{0.05}$, $Mn_{0.70}Fe_{0.25}Cu_{0.05}$, and $Mn_{0.60}Fe_{0.35}Cu_{0.05}$.

Specimens with dimension 30 mm × 5 mm × 1 mm were cut from the block. Modulus-temperature curves of three $Mn_{0.95-x}Fe_xCu_{0.05}$ specimens were measured by dynamic mechanical analysis (DMA) using multi-frequency and single cantilever mode. Temperature range of the measurement was from −100 °C to 250 °C.

3. Theory and model

According to previous results of AF structure in Mn-based FCC alloys [8–10,16–19], an exchange from CAF to NCAF happens at the composition of about 20%Fe∼40%Fe, as is shown in phase diagram proposed by Endoh and Ishikawa (inset of Fig. 1a) [11]. For a CAF, it means that spin of each atom parallels to one of ⟨1 0 0⟩ axis of the FCC lattice and for a NCAF, spin is canted from those directions.

To study the coexistence effect of two AF structure, a phase field model concerning antiferromagnetic transition with doping Fe is established. As a start, a 2D model of CAF evolution from paramagnetic state without doping was considered in a FCC solid solution. Magnetic moments of CAF in FCC lattice are known to be alternately pointed upward and downward at distances half of a unit cell along the ⟨1 0 0⟩ axis. Therefore, CAF state can be defined by a vector, whose direction is same as magnetic moment of one sublattice and transverse to the other. Such a vector, $\boldsymbol{\eta}$, is named as antiferromagnetic vector in this work and served as the order parameter in the model. Although CAF is theoretically defined along <1 0> directions, in the simulation $\boldsymbol{\eta}$ with canted angle less than 0.01 rad to one of four <1 0> axes is defined as CAF state, and the rest is treated as NCAF state. The vector module $|\boldsymbol{\eta}|$ stands for average magnetization intensity.

The free energy density, $f(\eta_i)$, is described as follows:

$$f(\eta_1,\eta_2,\ldots,\eta_p)=\Delta f(T)\left[\sum_{i=1}^{p}\left(\frac{1}{2}A\eta_i^2+\frac{1}{4}A\eta_i^4\right)+\frac{1}{2}B\sum_{i=1}^{p}\sum_{j>1}^{p}\eta_i^2\eta_j^2+\frac{1}{6}C\left(\sum_{i=1}^{p}\eta_i^2\right)^3\right]\quad(p=2) \tag{1}$$

where $A=-1$, $B=1$ and $C=1$ are phenomenological parameters; $\Delta f(T)$ is defined as the driving force coefficient and as a function of temperature between T_N and Ms. The above free energy form is a classic multiple well potential and $f(\eta_i)$ has constant minimum points at $\pm\eta_0, 0$ and $(0,\pm\eta_0)$, corresponding to four equivalent collinear AF variants with AF vector along $[\pm1,0]$ and $[0,\pm1]$ in FCC matrix, respectively. By this setting, fewest coefficients are required to preserve the basic characteristics of symmetry change with respect to the transition. The introduction of $\Delta f(T)$ ensures that only depth of $f(\eta_i)$ changes upon cooling(increasing Δf) and heating (decreasing Δf) while minimum point sites of $f(\eta_i)$ is kept unchanged, and such an introduction would be more convenient for the following analysis of simulation results. Evolution of η_p satisfies Allen-Cahn equation:

$$\frac{\partial\eta_p(\boldsymbol{r},t)}{\partial t}=-L\frac{\delta F}{\delta\eta_p}+\xi_p(\boldsymbol{r},t) \tag{2}$$

where L is the kinetic coefficient for the microstructure evolution, F total energy of the system, and $\xi_p(\boldsymbol{r},t)$ Langevin noise term. F has form of follows:

$$F=\int_V\left[f(\eta_1,\eta_2,\ldots,\eta_p)+\beta\sum_{i}^{p}(\nabla\eta_i)^2\right]d^3r \tag{3}$$

here $\beta=\beta_0\left(\frac{\eta_0}{2}\right)$ is taken as a gradient (domain wall) energy coefficient. Long range interactions including elastic interaction and mag-

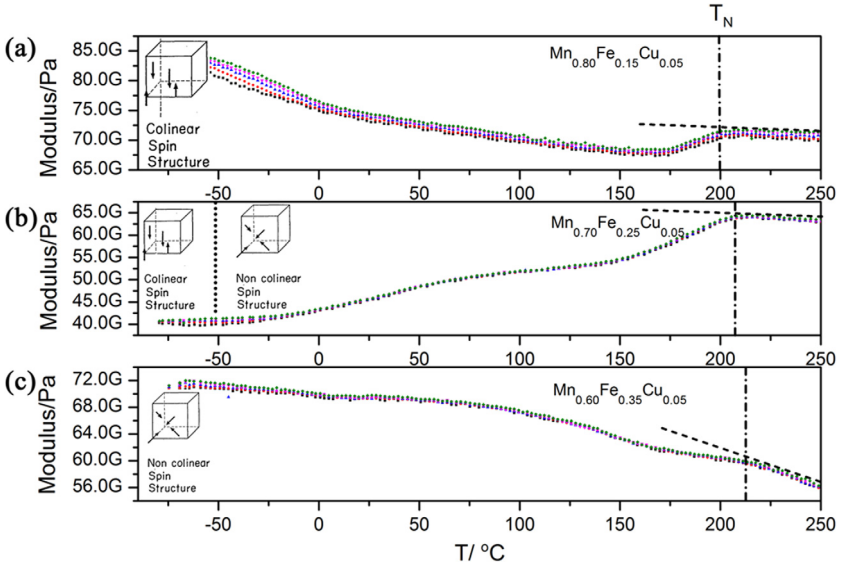

Fig. 1. Modulus variation of γ-$Mn_{0.80}Fe_{0.15}Cu_{0.05}$ (a), γ-$Mn_{0.70}Fe_{0.25}Cu_{0.05}$ (b) and γ-$Mn_{0.60}Fe_{0.35}Cu_{0.05}$ (c) with temperature measured by DMA at multi-frequency mode (0.2, 1, 4, 10, 20 Hz); inset is AF structure proposed by Endoh and Ishikawa in rough compositional range [11].