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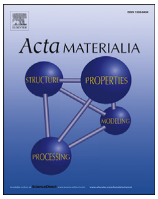

Full length article

Discovery of process-induced tetragonality in equiatomic ferromagnetic FeNi

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ABSTRACT

Synthesis of a new tetragonal phase at the equiatomic composition in the archetypal binary Fe-Ni phase diagram is reported. This new phase is proposed as a transitional phase linking cubic FeNi with the chemically ordered tetragonal $L1_0$ FeNi compound, tetrataenite, of interest as a new advanced permanent magnetic material. This new tetragonal phase was created in a selection of nominally equiatomic FeNi alloys, made either from natural Fe and Ni or from natural Fe combined with the ^{62}Ni isotope, via application of high-strain processing methods followed by an annealing protocol. High-resolution neutron diffraction affirms that all unprocessed samples adopt the A1-type cubic structure (space group $Fm\bar{3}m$) while all fully processed samples adopt the chemically disordered A6-type tetragonal structure (space group $I4/mmm$). Magnetic characterization documents a decrease in the initial magnetic susceptibility of deformed samples after annealing, evidencing a processing-induced increase in magnetic anisotropy that may be entirely accounted for by the measured tetragonal distortion. It is proposed that this new phase is a precursor to the formation of tetrataenite ($L1_0$ FeNi, space group $P4/mmm$), a meteoritic mineral of high magnetization and appreciable magnetocrystalline anisotropy that requires extraordinarily long cooling periods to form in nature. These results furnish new fundamental information as well as engineering insight for terrestrial synthesis of tetrataenite on industrial timescales, with high relevance for the creation of next-generation permanent magnets comprised entirely of easily accessible, earth-abundant elements.

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1. Introduction

Alloys comprised of iron and nickel have been essential to human civilization, with evidence of artifacts fashioned from meteoritic FeNi dated to the 5th millennium BCE [1,2], and from smelted FeNi alloys dated as early as the 3rd millennium BCE [3]. Further, modern metallurgy has been built, in large part, on these alloys, which all adopt cubic crystal structures. However, a lower-symmetry tetragonal phase of FeNi, known as tetrataenite, has been identified by the planetary science community as a component of many stony, stony-iron, and iron meteorites and has rekindled interest in this historic alloy system. The mineral tetrataenite features a high magnetization and a room-temperature magnetocrystalline anisotropy energy density in the range 1.0–1.3 MJ/m^3 [4]. This appreciable anisotropy energy value, attributed to tetrataenite's chemically ordered tetragonal crystal structure (space group $P4/mmm$, $L1_0$ Strukturbericht designation), advances $L1_0$-type FeNi as a promising permanent magnet candidate with a technologically relevant theoretical maximum energy product of 335 kJ/m^3 (42 MGOe) [4], approximately 66% of that of NdFeB-based supermagnets. As indispensable technologic materials, permanent magnets permit interconversion of mechanical and electrical energy to enable critical technologies in alternative energy, communications systems and military applications, among

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others. In support of the global energy challenge [5,6], special attention has been devoted to the development of new magnetic materials, such as $L1_0$-type FeNi, with the potential to supplement and/or replace rare-earth-based permanent magnets for energy transformation and generation. However, enthusiasm for incorporation of $L1_0$ FeNi-based magnets in technological applications is considerably tempered by its formidable synthesis requirements: natural formation of tetrataenite in meteorites requires extraordinarily long cooling periods of up to one billion years [7]. Engineering the development of tetragonality and long-range chemical ordering in the chemically disordered face-centered cubic (fcc or A1, space group $Fm\overline{3}m$) parent phase to form tetrataenite has proven to be very challenging [8].

It is within this context that we describe here the synthesis of a new FeNi phase with a chemically disordered tetragonal crystal structure that may be considered as a precursor to the elusive tetrataenite phase. This new phase has been realized in a selection of FeNi-based alloys subjected to severe plastic deformation and post-deformation treatments that allow access to kinetically hindered but thermodynamically accessible states. The existence of this new phase in specifically processed FeNi-based samples is confirmed through analyses of high-resolution neutron diffraction data that unambiguously demonstrate the presence of tetragonality that is unaccompanied by detectable chemical order, describing the A6-type structure (space group $I4/mmm$). The absence of chemical order is confirmed through exploitation of the isotopic dependence of neutron scattering amplitudes in the materials of this study consisting of natural Fe alloyed with the isotope ^{62}Ni. It is postulated that this chemically disordered tetragonal A6-type structure constitutes a transitional phase linking the ordinary disordered cubic A1 structure with the chemically ordered tetragonal $L1_0$-type compound, tetrataenite. Overall, these results provide enabling insight into the conditions and processes necessary to favor the formation of tetrataenite, as well as inform the microstructural aspects of this material in its potential transition from a research material to a commercial magnet.

The impressive permanent magnetic properties of tetrataenite are derived from, in part, its lower-symmetry tetragonal $L1_0$-type crystal structure that may be described as a low-temperature crystallographic derivative of a face-centered cubic lattice. This anisotropy contributes to a large magnetic remanence which significantly amplifies the amount of magnetic energy that may be stored in a magnet. The $L1_0$ crystal structure consists of alternating layers of constituent elements stacked along the tetragonal c-axis, creating a natural superlattice, Fig. 1. The c-axis also defines the uniaxial easy direction of magnetization and of the accompanying uniaxial magnetocrystalline anisotropy. The $L1_0$ phase is believed to form by nucleation and growth processes through a thermodynamically first-order chemical disorder-order phase transformation from a parent low-anisotropy fcc (A1-type) phase below a critical chemical order-disorder temperature T_{OD} [9,10]. While isothermal annealing at temperatures below T_{OD} is usually sufficient to promote $L1_0$ phase formation in related systems such as FePd and FePt [11], the task of obtaining the $L1_0$ phase in the FeNi system is quite difficult due, in part, to its very low T_{OD} of 320 °C [12] and to the extremely sluggish diffusion rate of Ni in the iron host at that temperature [8,13]. For comparative purposes, T_{OD} for the $L1_0$-type ferrous compounds FePd and FePt are 680 °C and 1300 °C, respectively [14], temperatures at which atomic mobilities are much greater.

Twentieth-century scientific literature contains hints of the presence of unexpected bonding in the Fe-Ni binary system. The existence of a low-temperature superlattice in the Fe-Ni system in the vicinity of the equiatomic composition was first suggested by Dahl in 1936 [15]. Dahl reported exceptional changes in the resistivity of FeNi alloys, including equiatomic FeNi, subjected to different processing conditions that was reminiscent of similar behavior exhibited by phases in the Au-Cu system which was confirmed to contain low-temperature superstructured compounds. The presence of preferential interatomic interactions in FeNi suggesting the existence of a lower-symmetry structure was also reported by Wakelin and Yates in 1953 [16] and later by Jiang and coworkers [17] in laboratory-synthesized alloys. Petersen confirmed the existence of a metallic phase with a superstructure in an iron meteorite in 1977 [18], with the first positive identification of tetrataenite in meteoritic material attributed to Clarke and Scott in 1980 [19]. However, laboratory synthesis of the $L1_0$ FeNi phase has only been substantiated in materials subjected to non-scalable processing techniques as neutron and electron radiation [20–23] or synthesized by monatomic layer-by-layer deposition processes to produce ultra-thin films [24,25]. Ordered phase formation in irradiated samples was attributed to enhancement in the rate of phase transformation fostered by a high density of extrinsic lattice defects.

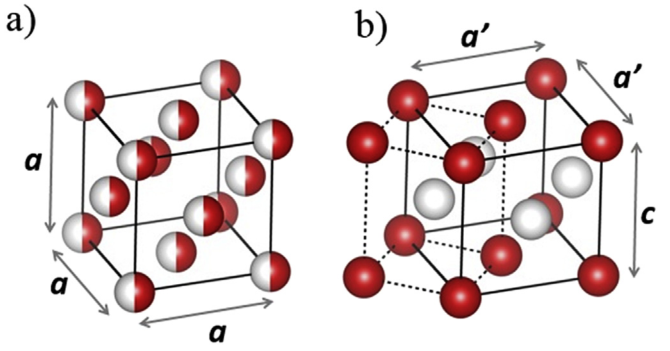

Fig. 1. *Representations of the cubic (A1) unit cell and the tetragonal ($L1_0$) unit cell.* The unit cells of a) the disordered face-centered cubic (fcc) and b) the tetragonal chemically ordered $L1_0$ crystal structures. The lattice parameters are identified, and the half-shaded spheres of depiction a) indicate an equal probability of lattice site occupancy for either Fe or Ni. For clarity, depiction b) shows the same orientation of the basis vectors of the cubic unit cell and a non-standard, C-centered tetragonal unit cell to indicate the $L1_0$ structure, with the primitive unit cell delineated by the dashed black lines.

The $L1_0$-type FeNi phase is very challenging to detect in scattering experiments due to the extremely small difference of both neutron scattering lengths and X-ray scattering factors between natural Fe and natural Ni. This small difference results in Bragg superstructure peaks – which signal the presence of chemical order in the $L1_0$ structure – of exceedingly low intensities. Indeed, a sample of single-phase, untextured $L1_0$ FeNi with perfect chemical order would provide an intensity of the strongest superstructure peak (*001*) that is approximately 0.3% of that of the most intense fundamental (*111*) Bragg reflection (as seen in Fig. S1). While there have been reports of $L1_0$ superlattice peak detection in X-ray diffraction experiments for bulk FeNi processed samples [26,27], it remains an open question as to whether the detected peaks are signatures of $L1_0$-type chemical order or if they correspond to other phases with Bragg reflections overlapping the $L1_0$ FeNi superstructure peaks of interest. For example, easily produced oxides such as Fe_2O_3, Fe_3O_4 and $NiFe_2O_4$ are confirmed to exhibit a high-intensity Bragg reflection at a d-spacing that coincides with the (*110)* $L1_0$ FeNi superlattice peak. To meet the challenge of assessing the existence of chemical order in these materials, in this work the isotopic element ^{62}Ni has been used in place of naturally occurring Ni to manipulate the geometric structure factor for Bragg neutron diffraction reflections. Natural Ni has a positive neutron scattering length while that of ^{62}Ni is large and negative; therefore employing the scattering lengths for natural Fe and for ^{62}Ni yields geometric

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