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Kinetics of tetrataenite disordering

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ABSTRACT

Tetrataenite is a chemically ordered $L1_0$-type $Fe_{50}Ni_{50}$ alloy detected for the first time in 1977 by ^{57}Fe Mössbauer spectroscopy studies in iron meteorites. The thermal history of meteorites, in particular short thermal events like those associated to hypervelocity impacts, can be constrained by tracing the presence of tetrataenite or its disordering into taenite. The knowledge of the disordering kinetics of tetrataenite, that is associated with changes in its magnetic properties, is still very fragmentary so that the time–temperature history of these meteorites cannot be constrained in details. Furthermore, knowledge of disordering kinetics is important due to potential technological application of tetrataenite as a rare-earth free strong magnet. Thus, this work provides the first time–temperature data for disordering reaction of tetrataenite. We have shown that disordering is not an instantaneous process but is a kinetic limited reaction. It was shown that disordering may take place at any temperature above the order–disorder transition for L_{10} superstructure phase (~320 °C) when the appropriate time-scale is considered. This result means that the apparent Curie point for tetrataenite is not an absolute property in the sense that any estimate of this parameter should be referred to a given time-scale.

1. Introduction

Tetrataenite is a chemically ordered $L1_0$-type $Fe_{50}Ni_{50}$ alloy detected for the first time in 1977 by ^{57}Fe Mössbauer spectroscopy in taenite lamellae extracted from Cape York and Toluca iron meteorites [1,2]. Soon after, also by Mössbauer spectroscopy, this ordered phase was detected in metal particles of chondrites and in the Santa Catharina iron meteorite [3,4]. It was recognized as a new mineral only in 1980 [5]. In nature, tetrataenite is found only in iron–nickel metals in meteorites that experienced slow cooling. It is noteworthy that tetrataenite is the natural analog of synthetic ordered FeNi, superstructure $L1_0$, which has been produced in 1962 by neutron irradiation of $Fe_{50}Ni_{50}$ alloys [6,7].

Because tetrataenite has peculiar magnetic properties (in particular very high coercivity) compared to other FeNi metallic minerals found in meteorites (kamacite, taenite, etc.), and because it disorders at high temperature, its presence has been recently shown to be a sensitive proxy for the thermal history of meteorites [8]. In particular, short thermal event like those associated to hypervelocity impacts can be detected by evidencing tetrataenite disordering into taenite. However, the knowledge of the disordering kinetics of tetrataenite, that is associated with changes in its magnetic properties, is still very fragmentary so that the time–temperature history of these meteorites cannot be constrained in details. Furthermore, knowledge of disordering kinetics is important due to potential technological application of tetrataenite. In the last years tetrataenite has received increased attention due to its applicability as a possible rare-earth free strong magnet, with a theoretical magnetic energy product exceeding 335 kJ m^{-3}, and therefore becoming a promising material for next-generation magnetic devices [9,10].

In this paper, we present time–temperature data concerning tetrataenite disordering and the implications for the interpretation of thermal history of meteorites. In addition, these data will be the background for a discussion related to the current apparent Curie temperature attributed to tetrataenite.

2. Tetrataenite: order–disorder reaction and magnetic properties

Tetrataenite forms through chemical ordering reaction from disordered taenite[1] phase, from now on referred only as taenite,

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[1] γ-Face centered cubic (γ-fcc) Fe–Ni alloy that may contain 20–50 wt% Ni. This phase is ferromagnetic at room temperature for Ni > 30 wt%.

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with 50 wt% Ni during slow cooling below 320 °C—the order–disorder transition temperature for L_{10} superstructure phase [5,6]. In this process, Fe and Ni atoms in the fcc taenite are rearranged on alternate (002) plans, producing a tetragonal distortion of fcc cell, and thus originating the tetragonal $L1_0$ structure. Due to its low order–disorder transition temperature, the ordered phase cannot be obtained artificially by annealing. Indeed, at temperatures below 320 °C, the diffusion rate of the Fe–Ni system is so low that it would take well over 10^4 years for ordering [11]. Essentially, as cooling occurs the diffusion coefficient of Ni decreases from $1.5\times10^{-16}\,\mathrm{cm^2\,s^{-1}}$ at 600 °C to $1\times10^{-21}\,\mathrm{cm^2\,s^{-1}}$ at 500 °C. Nevertheless, the chemical ordering reaction takes place in meteorites due to the extremely slow cooling experienced on their parent bodies, thus leading to the formation of tetrataenite. Tetrataenite has been detected in meteorites with cooling rates up to a few thousands °C/Myr in the 650–400 °C range [12]. It is worth mentioning that a synthetic analog of tetrataenite can be prepared by a number of non-conventional methods (e.g., mechanical alloying, neutron/electron irradiation) which are known to enhance diffusion, thus allowing equilibrium to be reached in short times [9,11]. Nevertheless, comparison between the meteoritic tetrataenite and its synthetic analog produced by electron irradiation showed that in spite of similar composition, the ordering degree is much higher in meteoritic tetrataenite [13].

The tetragonal $L1_0$ structure of tetrataenite provides a uniaxial magnetic character and an associated magnetocrystalline anisotropy that leads to high coercivity [9,14]. Nagata et al. [14] report coercivities in the range of 110–400 mT for tetrataenite from a wide variety of meteorites, but no correlation between these values and the meteoritic microstructure was established. Since coercivity depends closely on the magnetic domain state, and therefore depends on mineral size, it is useful to know the microstructure in which tetrataenite is found in meteorites. For instance, tetrataenite grains within plessite[2] have lower coercivity than the smaller tetrataenite grains in the cloudy zone [16,17]. The cloudy zone is a microstructure found in meteoritic FeNi metals with submicron-sized tetrataenite precipitates within low-Ni martensite matrix [18]. Nowadays, this microstructure is being the subject of ongoing debates, e.g. Bryson et al. [17] claim that the matrix in CZ is the magnetically soft ordered Fe_3Ni phase rather than low-Ni martensite [19]. In addition to magnetocrystalline anisotropy, the tetragonal distortion creates an anisotropic charge distribution around each Fe atom in tetrataenite, producing an electric-field gradient that creates the quadrupole shift in the Mössbauer spectrum, and therefore making the identification of this phase by Mössbauer spectroscopy easy in various types of meteorites [20].

Several works show that saturation magnetization (M_S) vs. temperature (T) plots, i.e. thermomagnetic curves, for tetrataenite are essentially flat in a temperature range below 500 °C, and drop sharply at ~550 °C (the apparent Curie point). Such curves exhibit a typical square-shape and are characteristic of tetrataenite [14,21]. The heating to apparent Curie point destroys the magnetic anisotropy of tetrataenite, i.e. complete disordering takes place and the ordered phase tetrataenite is transformed into taenite. Upon cooling from apparent Curie point to room temperature, the thermomagnetic curve is no longer square-shaped but is convex and characteristic of taenite. Thus, thermomagnetic experiments for tetrataenite are thermally irreversible. Unfortunately, in all these previous thermomagnetic experiments there was no information about heating rate. Furthermore, even works dealing with techniques other than thermomagnetic measurements report tetrataenite disordering at ~530 °C but without any explicit information about time-dependence of disordering. For instance, Lewis et al. [9] using the differential scanning calorimetry technique have shown that tetrataenite extracted from NWA 6259 iron meteorite undergoes an irreversible transition starting at 530 °C corresponding to conversion of tetrataenite into taenite.

3. Materials and methods

3.1. Samples

In the absence of synthetic tetrataenite, we selected two meteorites (Santa Catharina and Guidder) whose magnetic properties are dominated by tetrataenite.

Santa Catharina is an iron meteorite with bulk Ni content (~35 wt%) typical of the Invar alloys. Danon et al. [4] using ^{57}Fe Mössbauer spectroscopy were the first to observe tetrataenite in Santa Catharina meteorite, along with a Ni-poor Fe–Ni phase. Rancourt and Scorzelli [22] proposed that the Ni-poor phase is an antiferromagnetic low-spin γ-fcc Fe–Ni phase (25–30 at% Ni) with low saturation hyperfine field at low temperatures and high stability against martensitic transformation, as a consequence of its low-spin structure. This phase has been proposed as a new meteoritic mineral, called antitaenite, that is never observed alone but always in close microstructural association with tetrataenite, forming a typical intergrowth (tetrataenite/antitaenite—TT/AT) indicative of low-temperature equilibrium state in the Fe–Ni system at compositions ~20–40 at% Ni. For Santa Catharina, Mössbauer data indicate that tetrataenite and antitaenite have equal relative areas (50%) [4]. Although these areas represent the atomic fractions of Fe (at%) for each phase, taking into account the molecular formula for tetrataenite ($Fe_{50}Ni_{50}$) and antitaenite ($Fe_{100-x}Ni_{x}$, $x=25$–30), the relative weight fraction for these phases can be estimated as ~60 wt% and ~40 wt%, respectively. It is worth mentioning that the intergrowth tetrataenite/antitaenite has also been observed by Mössbauer spectroscopy in a wide variety of meteorites [22].

As shown in previous papers [4,23,24], tetrataenite is the main ferromagnetic phase in the non-oxidized samples from Santa Catharina ataxite. As a result, chemical treatment is not needed for tetrataenite extraction and, therefore we used the non-oxidized bulk sample to characterize the magnetic behavior of tetrataenite. In some cases, when the meteorite bulk is dominated by ferromagnetic kamacite (α-phase, bcc structure, ~ < 5 wt% Ni), chemical treatments are needed. For instance, as pointed out by Kotsugi et al. [25], in order to perform magnetic and structural characterization of tetrataenite from Toluca meteorite (whose bulk mineralogy is mainly kamacite), chemical etching in a 5% aqueous HCl solution is needed to preferentially dissolve kamacite and to obtain tetrataenite rich fractions.

Detailed investigations of the microstructural features of the metal in Santa Catharina meteorite have been carried out by several authors [23,26,27] using a variety of electron optical techniques. Therefore, only a brief summary will be given here. The metallic regions of Santa Catharina have a microstructure described as islands of ordered phase (tetrataenite) in a honeycomb matrix phase attributed to antitaenite. The islands are typically 20–40 nm in diameter, 29 ± 2 nm average, whereas the intervening antitaenite walls are typically only 5 nm wide or less [28,29]. According to Nagata et al. [14] and Scorzelli et al. [23], tetrataenite has nominal composition close to $Fe_{50}Ni_{50}$, in the non-oxidized samples of Santa Catharina meteorite.

In addition, we selected Guidder, a stony meteorite fallen in Cameroon in 1949 and classified as an LL5 ordinary chondrite. Since a general description of this meteorite, including microscopic examinations of thin sections and chemical analyses can be

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[2] Plessite is a mixture of kamacite, taenite and/or tetrataenite [15].