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The influence of chemical disorder enhancement on the martensitic transformation of the $Ni_{50}Mn_{36}Sn_{14}$ Heusler-type alloy

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ABSTRACT

The effect of chemical disorder over the martensitic phase transformation of the $Ni_{50}Mn_{36}Sn_{14}$ Heusler-type alloy was systematically investigated by performing X-ray diffractometry (DRX), DC magnetization and ^{57}Fe-doping and ^{119}Sn-Mössbauer spectroscopy measurements. DRX patterns are characteristics of a $L2_1$-type chemically disordered structure, where the presence of this disorder was first evaluated by analyzing the relative intensity of the (1 1 1) DRX reflection, which varies in the case of Fe-doped and practically disappears for the milled samples. In consequence, the magnetic properties of Fe-doped well-milled samples related to the martensitic phase transformation change substantially. 300 K ^{57}Fe-Mössbauer spectroscopy data suggest that the changes in the magnetic properties related to the martensitic transformation are intrinsically correlated to the ferromagnetic and paramagnetic fractions, which are respectively associated with Fe atoms replacing Mn- and Sn-sites. In the case of milled samples, the drastic reduction of alloy magnetization was explained by the increase of the number of Mn atoms in the shell regions, which have a reduced magnetic moment comparatively to those in the grain cores. The magnetization change and the temperature transition in the martensitic transformation are governed by the grain core. The initial magnetic properties and martensitic transformation can be recovered by a subsequent annealing on the milled sample.

1. Introduction

X_2YZ full Heusler alloys have a body-centered cubic structure with a face-centered superlattice at room temperature, and may be thought as being formed by four interpenetrating face-centered cubic lattices A, B, C, and D, in which A and C are identical (typically $L2_1$-type structure) [1]. Generally, in the ordered X_2YZ Heusler alloys, the X atoms lie on lattices A and C, Y atoms on B and Z atoms on D (see $L2_1$-conventional cell in Fig. 1). The $L2_1$-type structure (*Fm*3*m*) is distinguishable either from the A2-type structure (*Im*3*m*) or from the B2-type structure (P*m*3*m*), in which lattices B and D are also identical, by reflections of odd superlattice Bragg peaks, if there is a sufficiently large difference in the scattering factors of the atoms on B and D. In addition, the A2-type structure does not show superlattice diffraction lines, e.g., the (2 0 0) Bragg peak.

Regarding the $Ni_{50}Mn_{25}Sn_{25}$ (or simply Ni_2MnSn) Heusler alloy, it has been reported that Mn atoms govern its magnetic properties, whereas Ni and Sn atoms are assumed to have small or negligible magnetic moments in their crystallographic sites [2–4]. No structure phase transition has been observed in a broad temperature range, from high (∼ 400 K) to low temperatures (∼ 4.2 K). However, changes in distances either between Mn–Mn or Mn-nearest neighbor species, caused by different conditions in sample preparation, can considerably modify the magnetic properties of that Heusler-type alloy. In addition, changes in the Mn chemical environment can be partially done by chemical substitution or out-of-stoichometric procedures where, for example, Mn-rich $Ni_{50}Mn_{50-x}Sn_x$ Heusler-type compounds can be formed [5,6]. It should be emphasized that these Mn-rich alloys have attracted special attention of researchers, essentially due to their intrinsic structural and magnetic properties found in experiments where the temperature is varied [5–26]. From the structural point of view, these alloys may exhibit a martensitic phase transformation (MPT) depending either on the Mn concentration or on the local chemical disorder between the constituents of B and D-lattices. In general,

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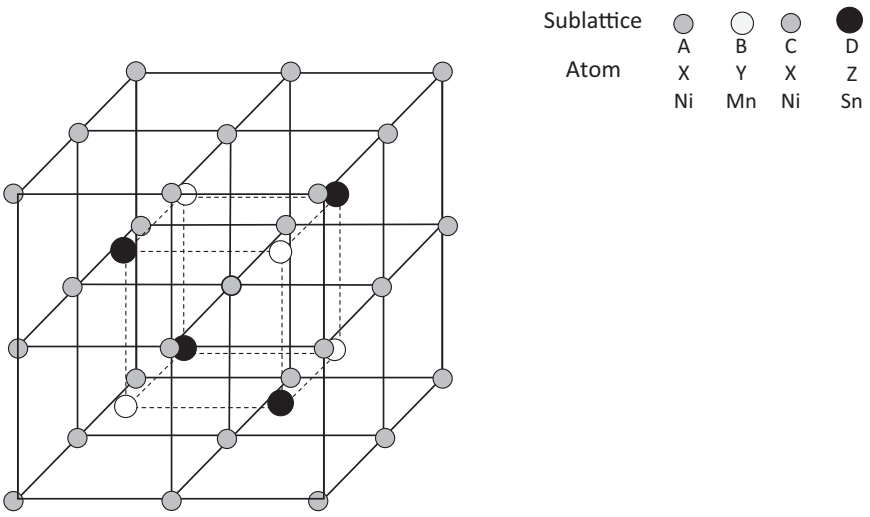

Fig. 1. Conventional cell for the X_2YZ full Heusler alloys.

this structural phase transformation seems to occur, in Mn-rich $Ni_{50}Mn_{50-x}Sn_x$ Heusler-type, from a highly symmetrical parent cubic phase ($Fm3m$) to a structure with lower symmetry ($Pmma$) [15].

Particularly, in the $Ni_{50}Mn_{36}Sn_{14}$ (or simply $Ni_2Mn_{1.44}Sn_{0.56}$) Heusler-type alloy, the martensitic transition temperature (T_M) value is about 220 K [15,20,21,23]. Above that, a ferromagnetic (FM) austenitic state is stable and the cubic crystal structure has a lattice parameter $a \approx 6$ Å [15]. Below T_M, in the martensitic phase, a FM orthorhombic four-layered structure is stabilized with a, b and c lattice parameters equal to 4.3 Å, 2.9 Å and 8.4 Å, respectively. On the other hand, due to the excess of Mn in the $Ni_{50}Mn_{36}Sn_{14}$, the crystal structure is not a pure $L2_1$-type structure found in the ordered $Ni_{50}Mn_{25}Sn_{25}$ ordinary Heusler compound. It is now a $L2_1$-B2-type disordered structure due to the extra Mn atoms occupying Sn-sites (D-lattices). Furthermore, while in the ordered $Ni_{50}Mn_{25}Sn_{25}$ compound the Mn atoms are ferromagnetically coupled, in the $Ni_{50}Mn_{36}Sn_{14}$ Heusler-type alloy, due the Mn excess, antiferromagnetic (AF) interactions also join to the ferromagnetic (FM) predominant phase, giving rise to the incipient AF compounds [5,6,24].

It has been reported that the partial substitution of Fe or Co in Ni or Mn sites results in a modification of T_M-values and the MPT disappears for large Fe doses [10,20]. This observation seems to be related to the chemical disorder effect (CDE), which causes changes in the Mn-neighborhood magnetic exchange interaction. Thus, the chemical disorder effect was studied by Fe-doping $Ni_{50}Mn_{36}Sn_{14}$ Heusler-type alloy with 1 at.% of ^{57}Fe tentatively occupying different sites of the $L2_1$-B2-type structure. It was also investigated the influence of milling on the magnetic properties of the iron-doped alloy samples.

^{57}Fe- and ^{119}Sn-Mössbauer spectroscopy measurements were performed in order to experimentally access the probe occupations in the lattice sites, as well as their chemical environments. These knowledge are essential to understand how magnetic properties are influenced by the new atomic arrangements modified by the chemical disorder of the $Ni_{50}Mn_{36}Sn_{14}$ Heusler-type alloy. These results will help to best comprehend the data from X-ray diffraction and magnetization measurements.

2. Experimental procedures

Fe-doped $Ni_{50}Mn_{36}Sn_{14}$-Heusler-type samples, namely $Ni_{50}Mn_{36}Sn_{14}$ (sample labeled 0% Fe), $Ni_{50}(^{57}Fe_{0.01}Mn_{0.99})_{36}Sn_{14}$ (1% ^{57}Fe–Mn), $(^{57}Fe_{0.01}Ni_{0.99})_{50}Mn_{36}Sn_{14}$ (1% ^{57}Fe–Ni) and $Ni_{50}Mn_{36}(^{57}Fe_{0.01}Sn_{0.99})_{14}$ (1% ^{57}Fe–Sn), were prepared in an arc-furnace from high graded chemicals of virtually pure Ni, Mn, Sn powder metals (better than 4N) and Fe metal isotopically 95%-enriched in ^{57}Fe. The main reason to use ^{57}Fe-rich instead of natural Fe is to trace and to get information about site occupation and local magnetism from ^{57}Fe placed in different sites of the $L2_1$-type structure using Mössbauer spectroscopy. The melted pellets were homogenized in a quartz evacuated tube at 1123 K for 48 h and after quenched in cold water (280 K). The powder samples used for X-ray analysis, Mössbauer spectroscopy and magnetization measurements were obtained by grinding pieces from the pellets, immersed in acetone, in an agate mortar. In addition, these alloys were also milled with a SPEX 8000 mill setup, for at maximum 4 min. The milling process has been done under argon atmosphere to prevent sample oxidation. More details of the milling tools and experimental procedures can be found in Ref. [27]. The milled samples were also annealed for 1 h at 1123 K and then they were characterized structurally and magnetically using the above experimental techniques.

Room temperature (RT; ~298 K) X-ray powder diffraction data were collected with a Rigaku diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The powder samples were evenly homogenized in a sample holder, in a care to avoid eventual texture effect. A Shimadzu SSX 550 scanning electron microscope (SEM) was used to confirm the phase formation and its composition, using the energy dispersive X-ray spectroscopy (EDX), from polished flat pieces obtained from the central part of the annealed pellets. As we previously reported for other set of samples similarly prepared [20,21], more than 99% of the SEM image areas can be associated with a single phase corresponding to the $L2_1$-B2-type structure in accord with the X-ray diffraction result. These EDX results confirm that the nominal compositions indeed correspond to the planned alloys. No Fe signal from the EDX was detected, as its content lies below the experimental detection limit. Mössbauer experiments were carried out with a standard constant acceleration spectrometer, under transmission geometry. A ^{57}Co:Rh source with a nominal activity of about 30 mCi, and a $Ca^{119}SnO_3$ source with about 3 mCi, were respectively used to obtain the ^{57}Fe and ^{119}Sn Mössbauer spectra. The powder samples were sealed in a sample holder of the Mössbauer set-up for RT experiments. The ^{57}Fe spectra were obtained with 512 channels, whereas the ^{119}Sn spectra were taken with 1024 channels. The Mössbauer spectra were analyzed using NORMOS Program in the distribution version. In general, the spectra were fitted using two subspectra: a magnetic hyperfine field distribution (MHFD) and a paramagnetic component (singlet). The isomer shift (δ) values are given relative to metallic α-Fe obtained at RT for the case of ^{57}Fe and relatively to the $CaSnO_3$ source, for ^{119}Sn spectra. Field cooled (FC) and field heated (FH) magnetization versus temperature [$M(T)$] curves were recorded between 70 and 320 K using a commercial physical property measurement system (Quantum Design PPMS) coupled to an Evercool model cryostat and under an applied DC magnetic field up to 50 kOe. These curves were obtained using protocols described elsewhere [21]. As previously reported, any thermal hysteresis observed between FC and FH $M(T)$ curves can directly be associated with the first-order character of the martensitic phase transition (MPT).

3. Results and discussions

In Fig. 2(a), it is displayed the X-ray diffraction patterns for the three samples prepared with 1 at.% ^{57}Fe replacing one of the chemical constituents (Ni, Mn or Sn) of the $Ni_{50}Mn_{36}Sn_{14}$ Heusler-type alloy (1% ^{57}Fe–X, X = Ni, Mn and Sn). For comparison, two other X-ray patterns are also plotted: (i) for the Fe un-doped sample (0% Fe) and (ii) a computer-simulated diffractogram for the $L2_1$-type struc-