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Magnetic hyperfine temperature dependence in Fe–Si crystalline alloys

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Abstract

Fe–Si crystalline alloys with different silicon contents (4.5, 12, 18 and 26 at.%) were investigated by ^{57}Fe Mössbauer spectrometry and a.c. magnetic measurements in order to get magnetic hyperfine data as a function of temperature and Curie temperatures as a function of silicon content at the different iron sites. The values of critical exponent β which are independent on the iron site are found close to 0.36, typical of Heisenberg ferromagnets, whatever the silicon content. The present results support the assumptions made in the literature to describe the magnetic and hyperfine properties of FINEMET nanocrystalline alloys and can further be considered.

Keywords: A. Magnetically ordered materials; E. X-ray and gamma-ray spectroscopies

1. Introduction

Both the structural and magnetic properties of Fe–Si crystalline alloys, with different silicon content lower than 25 at.%, have been previously studied [1]. The investigation of Fe–Si based nanocrystalline alloys has recently revealed the usefulness of hyperfine data versus temperature, which are not available yet in the literature, to our knowledge.

Indeed, great interest was devoted to FINEMET nanocrystalline ferromagnets in the recent years because these two magnetic and structural phase materials exhibit excellent soft magnetic properties which offer promising technological applications [2]. These nanocrystalline alloys result from the presence of ultrafine Fe–Si crystalline grains embedded in a residual amorphous matrix which occur after a subsequent annealing of the as-quenched precursor amorphous alloy [2,3]. It is now clearly established that the magnetic softening originates from the magnetic behaviour of Fe–Si crystalline grains [3]. Consequently, the modelling of the magnetic properties of these nanocrystalline alloys requires a detailed structural characterisation. Thus the two relevant structural parameters are the crystalline fraction and the atomic Si content within the crystalline grains. The latter is generally found between 12.5 and 21 at.% that corresponds to iron silicon alloys with the DO_3 crystal structure, characteristic of ordered stoichiometric Fe_3Si alloy (Fe-25 at.% Si) [4]. The cell consists of two cubic sublattices A and B: A contains Fe atoms, and B both Fe and Si atoms in equal proportions [5]. When the Si content is lower than 25%, Fe atoms occupy the D sites

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randomly giving rise to new non-equivalent iron sites, the populations of which can be derived from the binomial distribution [5]. Despite of complex hyperfine structures, Mössbauer spectrometry remains a valuable tool to partially resolve at least the main Fe contributions through the values of hyperfine parameters at Fe sites which are dependent on the silicon content and on the iron atomic neighbouring [1,6,7]. As the increasing number of silicon in the Fe vicinity induces both a decrease of the hyperfine field and an increase of the isomer shift at Fe sites, one may assign the different components to the Fe sites [1].

The X-ray diffraction and static magnetic measurements usually provide information concerning the silicon content of Fe–Si crystalline grains and the volumetric fraction of the crystalline phase, in the case of FINEMET alloys. It is, however, important to emphasise that the analysis of the X-ray patterns which consist of both a large feature due to the amorphous phase and broadened Bragg peaks due to the nanometre size of crystalline grains, may lead to some wrong estimations, especially on the volumetric fraction of the crystalline grains which is derived from its relative absorption area. In addition, the value of the lattice parameter which is linearly silicon content dependent in the case of bulk Fe–Si alloys, gives rise to the silicon content of Fe–Si nanometre size grains, assuming neither stresses nor preferential orientation.

The volumetric fraction may also be derived from the saturation magnetisation temperature dependence, assuming a weighted average of the magnetisation of two independent phases [8,9]. The silicon content is estimated from the Curie temperature extrapolated at high temperature, assuming that the FeSi magnetic nanocrystalline grains displayed as an Heisenberg ferromagnetic phase with a critical exponent $\beta = 0.36$ [8,9].

^{57}Fe Mössbauer spectrometry provides great advantage in investigating these nanocrystalline alloys because its atomic scale sensitivity allows to distinguish different kinds of resonating nuclei, in crystalline grains and in amorphous remainder. Nevertheless, fitting of Mössbauer spectra remains generally a very difficult task: indeed, the hyperfine structure results from both the broad lines sextet attributed to the amorphous residual matrix and the superimposition of several well defined sextets attributed to the different iron sites characteristic of Fe–Si ordered phase. High temperature spectra could provide more accurate information because their hyperfine structures are better resolved [10]. The refinement of the Mössbauer component attributed to the crystalline phase and its temperature dependence as well, could directly give an estimate of the silicon content. Consequently, we performed Mössbauer experiments at different temperatures on some Fe–Si alloys to get available magnetic hyperfine data because only those obtained at 300 K can be found in the literature. Also, Fe–Si crystalline alloys with different Si contents (4.5, 12, 18 and 26 at.%) were prepared and then investigated by means of X-ray diffraction, a.c. magnetic measurements and Mössbauer spectrometry. We report the temperature dependencies of Mössbauer spectra in order to get the available magnetic hyperfine data at different iron sites and their behaviours close to the Curie temperature to get an estimate of the value of the critical exponent β.

2. Experimental section

Iron–silicon samples with different nominal compositions (4.5, 12, 18 and 26 at.% Si) were prepared by induction melting in a helium atmosphere using a water cooled copper crucible. The quenched materials were obtained by planar flow casting in a helium filled chamber using a quartz nozzle. The overheating (100°C above the melting point) was performed by r.f. induction. Such a second step leads to the obtention of crystalline iron silicon foils (kindly prepared by Dr P. Ochin and A. Dezellus—CECM/CNRS Vitry—Seine France). They were first characterised by the X-ray diffraction in order to check both their crystallinity and their homogeneity. Very sharp Bragg peaks in X-ray patterns are consistent with homogeneous microcrystalline Fe–Si alloys. Only on 4.5 at.% Si sample, one observes the presence of small peaks which are clearly attributed to iron oxide, probably due to a surface oxidation during preparation process. The value of the lattice parameter allows to an estimate of the Si content which is in good agreement with the nominal ones. Mössbauer experiments were performed in transmission geometry within the temperature range of 77–1000 K. The

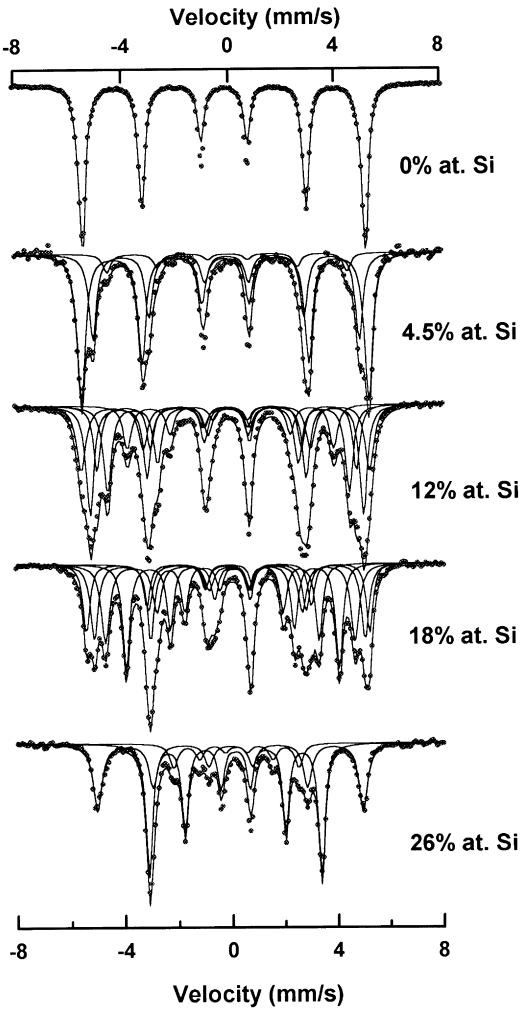

Fig. 1. Room temperature Mössbauer spectra recorded on different Fe–Si alloys.

samples were located either in a cryostat or in a furnace under vacuum. The hyperfine parameters were refined by using MOSFIT program [11]. The magnetisation of the samples was followed using an a.c. magnetic susceptometer (Bartington MS2) in the temperature range 300–1050 K.

3. Results and discussion

Fig. 1 shows the Mössbauer spectra recorded at room temperature on Fe–Si samples with different

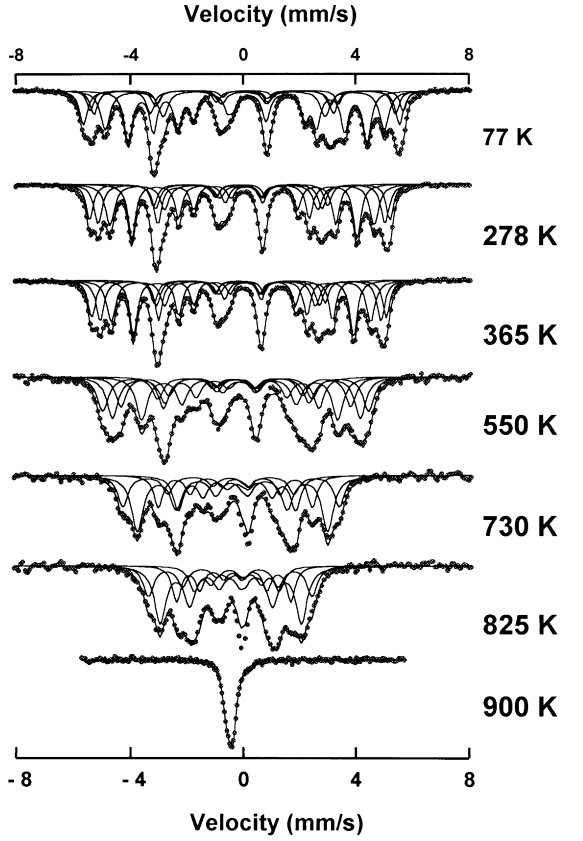

Fig. 2. Temperature dependence of the Mössbauer spectra recorded on Fe–Si with 18 at.% Si.

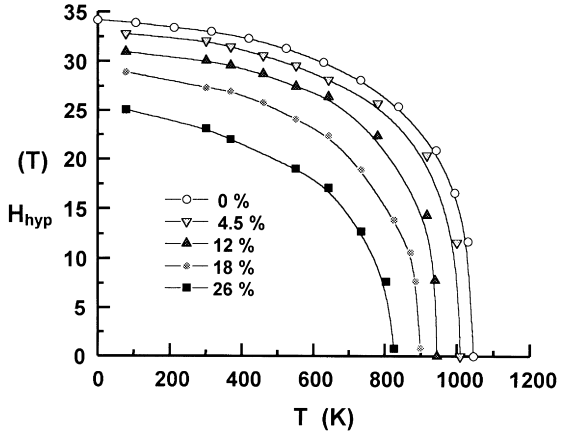

Fig. 3. Temperature evolution of the mean values of hyperfine fields characteristic of the different Fe–Si samples.

Table 1
Magnetic characteristics of Fe–Si alloys for different silicon contents

at.% Si	T_c (K) magnetic measurements	T_c (K) Mössbauer spectrometry	β
0	1047	1047	0.36
4.5	1030	1030 ± 10	0.37 ± 0.02
12	972	982 ± 5	0.36 ± 0.01
18	900	899 ± 5	0.36 ± 0.01
26	820	825 ± 3	0.36 ± 0.01

Si contents. One observes the magnetic sextets whatever the silicon content is, but the hyperfine structures are strongly silicon content dependent. The spectrum of the 26 at.% Si can be clearly decomposed into two components with proportions 3:1, as expected for the stoichiometric Fe_3Si alloy. For low silicon content (typically below 10 at.% which corresponds to the limit of solubility of silicon in bcc-iron), silicon atoms randomly substitute iron atoms: the three main components correspond to the Fe sites surrounded by 8, 7, 6 next nearest Fe neighbours and their relative absorption area are close to those expected by a binomial distribution (65:30:5 compared to 70:25:5, respectively) [1]. In the intermediate content range which corresponds to that encountered in nanocrystalline Fe–Si grains, the spectra are fitted by means of 5, 6 or 7 magnetic components, according to the Si content. Their relative proportions are proportional to the absorption area, assuming the same values of f recoilless factor. The present results, i.e. the hyperfine field, the isomer shift, the quadrupolar shift and the relative absorption area, are fairly consistent with those previously discussed by Rixecker et al. at 300 K [5].

Series of the Mössbauer spectra were recorded at several temperatures on the different FeSi alloys: an example with 18 at.% Si is illustrated in Fig. 2. It is important to note the same characteristics as a function of the silicon content. One clearly observes the better resolved hyperfine structure within a large temperature range whereas the magnetic sextets progressively collapse at high temperatures towards quadrupolar spectra which consist of broad non-lorentzian singlets. The fitting procedure developed at room temperature and involving several magnetic components according to the silicon content (see Section 2), was successfully, i.e. with physical temperature dependence for each hyperfine parameter, applied to spectra recorded at different temperatures, except those obtained within the close vicinity of the Curie temperature. Indeed, due to the lack of resolution and to the number of hyperfine parameters, some fitting constraints have to be introduced during the fitting procedure. The values of the hyperfine parameters versus temperature are available on request.[†] Nevertheless, from the temperature dependence of the mean values of hyperfine fields (see their evolution for the different silicon contents in Fig. 3), we calculated both the critical exponent β and the Curie temperature which are listed in Table 1. The values of the critical exponent show that these alloys display as Heisenberg ferromagnets and the Curie temperatures are in agreement with those observed by the magnetisation measurements. Thus, we only estimated β values at the different Fe sites in the case of Fe–Si 18 at.%: the values are found close to 0.36 and remain rather independent on the iron sites.

4. Conclusion

The present results supports well the assumptions previously made to analyse the magnetisation temperature dependence in nanocrystalline alloys favouring the emergence of Fe–Si crystalline grains, i.e. FINEMET alloys, and the present hyperfine data can be used to fit the Mössbauer spectra versus temperature on such alloys, in order to improve the validity of both the volumetric fraction and silicon content. It is also important to emphasise that the present hyperfine data can lead to a significant disagreement with high temperature Mössbauer spectra. Such a feature suggests the presence of high

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temperature superparamagnetic effects, originating a reduction of hyperfine fields at iron sites, consistent with the presence of non-interacting magnetic Fe–Si crystalline grains, i.e. a low volumetric fraction [9,12].

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