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Mössbauer spectrometry of near equiatomic Fe–Cr alloys: Influence of preparation method

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Abstract

Mössbauer spectra reflect the strong sensitivity of the distribution of hyperfine magnetic field distributions (HMFDs) of near equiatomic Fe–Cr alloys to the method of preparation of samples. Whatever the way a bcc $Fe_{0.51}Cr_{0.49}$ alloy is prepared, powders produced from it by ball milling or by filing exhibit a unique HMFD at room temperature. The associated average hyperfine magnetic field, 16 T, is significantly smaller than those of alloys, which are cold-rolled and (/or) annealed at some stage of their preparation process (∼17–19 T).

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1. Introduction

Fe–Cr based materials possess a remarkable set of chemical, mechanical and magnetic characteristics [1–5]. The existence of a high-temperature solid solution region, in the central part of the Fe–Cr equilibrium phase diagram, was recently challenged by Ustinovshikov and Pushkarev [6] (and references therein). On the basis of microstructures observed by transmission electron microscopy, Ustinovshikov and Pushkarev claimed that the latter high-temperature region is actually a domain in which a tendency towards separation exists [6]. As discussed in a companion paper [7], the initial purpose of the present work was to check for the existence of that phenomenon in near equiatomic alloys by Mössbauer spectrometry at room temperature (RT) [4,8–14]. As explained below, the scope of the work was enlarged to study the effects of the preparation method of alloys and of plastic deformation on HMFDs.

2. Mössbauer spectrometry in concentrated Fe-rich Fe–Cr alloys

Foils of Fe–Cr alloys of a thickness of ∼15–30 μm are typically required to record high quality transmission Mössbauer spectra in reasonable times (a day to some days). Most Mössbauer studies of bcc Fe–Cr alloys were thus and are still performed on as-cast alloys, which are first cold-rolled, are then annealed for homogenization and to remove strain and are generally quenched. Small angle neutron scattering experiments evidence no signs of unmixing in alloys quenched in rather standard conditions. The literature results appear in that way as consistent between them. HMFDs $P(B)$ are extracted, most often at RT, from Mössbauer spectra of concentrated alloys, where $P(B)\,dB$ represents the fraction of Fe atoms whose field is between B and $B+dB$. The average of any parameter $Y(B)$ will be denoted as $\langle Y\rangle$. Different methods of sample preparation were used too. Kuwano and Ono [11] prepared for instance their powders by filing quenched bulk $Fe_{1-x}Cr_x$ ($0 \leq x \leq 0.96$).

Further, Dubiel and Zukrowski [10] investigated, among others, a $Fe_{0.55}Cr_{0.45}$ alloy for samples A and B which were prepared from as-cast alloys cold-rolled to a final thickness of 0.1 mm and homogenized. Samples A were then annealed for 6 h at 1140 °C and quenched while samples B were annealed at 900 °C for 5 h in argon and furnace-cooled down to RT. Foils were finally obtained by electropolishing. $\langle B\rangle$ values of 19.19 T and 23.46 T were reported for A and B, respectively. The changes of the latter fields were followed as a function of annealing time at 500 °C [10].

In the course of the present study, we measured significant shifts of the HMFDs for near-equiatomic alloys prepared in different conditions. As the influence of the successive steps of

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the preparation method on the HMFD's of concentrated Fe–Cr alloys is largely disregarded in the literature, we undertook a Mössbauer investigation of alloys prepared in the various conditions described below.

3. Experimental

Sets of as-cast alloys $Fe_{0.510(5)}Cr_{0.490(5)}$ with masses of 2 g and 21 g were prepared in Coimbra (C) and in Nancy (N), respectively. Fe (99.98, Aldrich) and Cr (99.99, Alpha) and Fe (99.99+, Goodfellow) and Cr (99.996, Aldrich) were used for N and C alloys, respectively. Alloys were isothermally annealed under vacuum in sealed quartz tubes and quenched into water rather slowly without breaking the tube (C) or more rapidly by breaking it (N). Some samples were cold-rolled (N) with a progressive reduction in thickness from about 1 mm to 2 mm down to 25–30 μm. Alloy compositions were measured by microprobe analysis. X-ray diffraction patterns were recorded on a Siemens D500 powder diffractometer using Co Kα1 radiation (λ = 0.17889 nm).

^{57}Fe Mössbauer spectra were recorded at RT in transmission geometry by a constant acceleration type spectrometer using a ^{57}Co source in Rh with a strength of ∼10 mCi. Isomer shifts IS are referenced to α-Fe at RT. HMFDs were obtained [15] employing Lorentz lines. All Fe–Cr spectra were nicely fitted (Fig. 1) using the following IS(B) relationship explained in [14], namely: IS = −0.118 mm/s for $B \leq 1$ T, IS (mm/s) = $-0.142 + 0.00169B$ for $1 \leq B \leq 12.8$ T and IS (mm/s) = $-0.195 + 0.00586B$ for $B \geq 12.8$ T. Mössbauer samples, either in foil form or powdered, were finally obtained from alloys prepared in different ways. Texture effects were taken into account when necessary (cold-rolled samples; Fig. 1).

Cold-rolled alloys were most often vacuum annealed for 1 h up to some tens of hours at a temperature T_a where 900 °C ≤ T_a ≤ 1200 °C (some samples were instead cold-rolled after annealing). Another way of obtaining foils was by progressive mechanical thinning, with metallographic abrasive papers, of bulk alloys, which were most often annealed at T_a (one face was polished before and one after the heat-treatment). Diamond files were used to prepare powders by gently filing either bulk alloys (most often annealed) or the previous foils. Finally, powders were prepared from high-energy ball milling of bulk alloys. Pieces of bulk alloys were milled under an argon atmosphere in a planetary ball-mill (Fritsch Pulverisette 7) using seven steel balls and vials. The powder-to-ball weight ratio was 1/20.

4. Results

All X-ray diffraction patterns show only a single set of intense diffraction peaks due to a bcc phase. The coherent domain size d of filed samples is typically of the order of 250 ± 50 nm while d = 25 ± 5 nm for samples milled for 4 h.

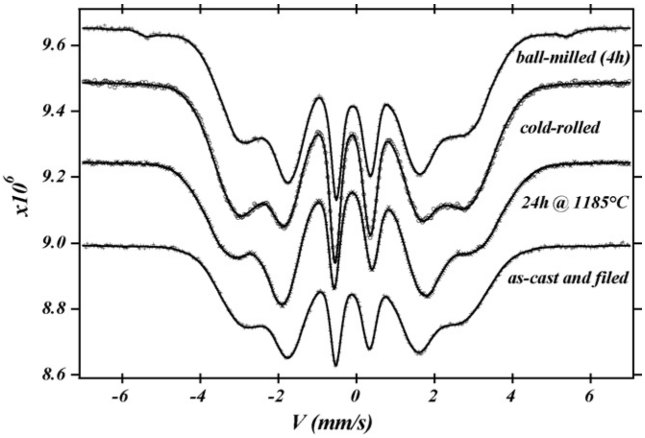

Fig. 1. RT ^{57}Fe Mössbauer spectra of as-cast $Fe_{0.51}Cr_{0.49}$ alloys further treated as indicated (solid lines = fits). The sample annealed at 1185 °C was mechanically thinned (30 μm).

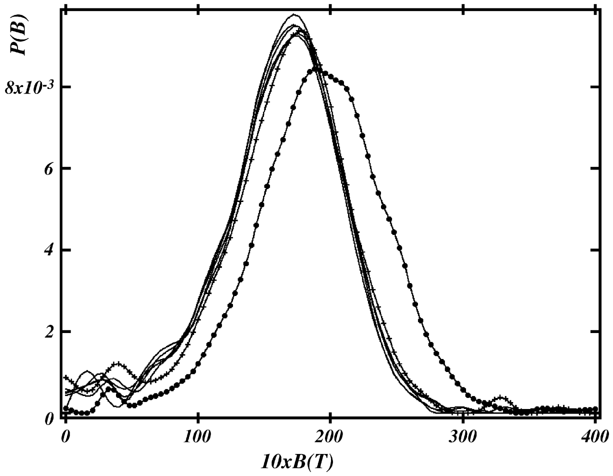

Fig. 2. Various HMFDs of as-cast $Fe_{0.51}Cr_{0.49}$ alloys. The six HFMDs, which are hardly differentiated, are obtained from as-cast samples treated in different conditions and finally filed to obtain powdered Mössbauer samples: (1) as-cast, (2) annealed 18 h at 900 °C, (3) annealed 18 h at 900 °C, quenched and annealed 11 h at 550 °C, (4) annealed 23 h at 1000 °C, (5) annealed 23 h at 1180 °C, (6) annealed 24 h at 1200 °C. The distinct HMFD (solid line and points) is that of an as-cast alloy annealed 24 h at 1000 °C, quenched, annealed 24 h at 1200 °C and finally mechanically thinned. For convenience, the distributions are shown as $P(B)$ vs. 10 times B, where B in Tesla.

Apart from eventual texture effects and from their global extent, all RT Mössbauer spectra are alike (Fig. 1) with "gaussian-shaped" $P(B)$ (Figs. 2 and 3). All Mössbauer samples, which were obtained by filing a bcc alloy, have basically identical HMFDs (Fig. 2) whatever the preparation method of the alloy (see Section 3). The average field calculated from 36 Mössbauer spectra of samples obtained by filing alloys prepared in different ways is $\langle B\rangle_{\text{filed}} = 16.2 \pm 0.2$ T with an average

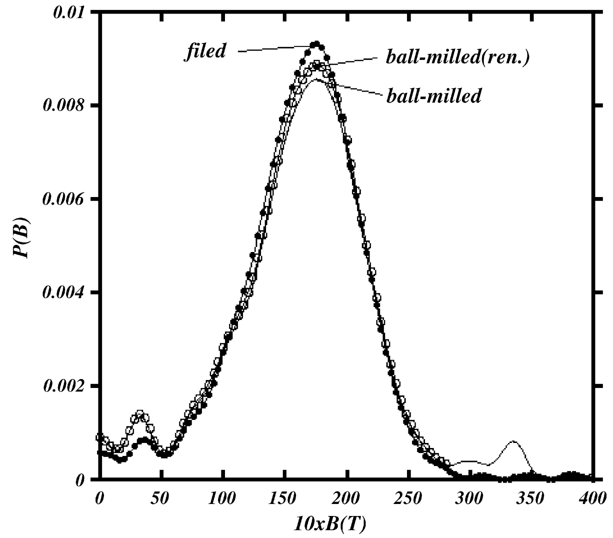

Fig. 3. HMFDs of an as-cast $Fe_{0.51}Cr_{0.49}$ alloy: (1) filed and (2) ball-milled for 4h. In the latter case, a distribution renormalized between 0 and 28 T is also shown (ren.). For convenience, the distributions are shown as $P(B)$ vs. 10 times B, where B in Tesla.

Table 1
Average hyperfine magnetic fields and the associated standard deviations of the HMFDs of $Fe_{0.51}Cr_{0.49}$ as-cast alloys treated in different conditions

As-cast $Fe_{0.51}Cr_{0.49}$ alloy with subsequent treatments for preparing samples for transmission Mössbauer spectrometry	Average hyperfine magnetic field (T) $\langle B\rangle$	Standard deviation (T) $< (B - \sigma = \langle (B - \langle B\rangle)^2\rangle 1/2$
The as-cast alloy is mechanically thinned	19.2 (0.1)	5.1 (0.1)
The as-cast alloy is cold-rolled	17.3 (0.2)	4.6 (0.1)
The as-cast alloy is annealed for 18 h at 900 °C, quenched and finally cold-rolled	17.1 (0.2)	4.6 (0.15)
As-cast alloys are cold-rolled, annealed for times t at temperatures T_a and quenched: $T_a = 1000\,°C$: (1) $t = 44$ h, (2) $t = 48$ h, (3) $t = 1$ h; $T_a = 1180\,°C$: (4) $t = 8$ h average parameters are finally obtained from the corresponding RT Mössbauer spectra	18.5 (0.25)	4.6 (0.1)
The as-cast alloy is annealed for 24 h at 1185 °C, quenched and mechanically thinned	18.6 (0.1)	4.4 (0.1)
The as-cast alloy is annealed for 22 h at 1000 °C, quenched and mechanically thinned	18.1 (0.1)	4.4 (0.1)

standard deviation $\sigma_{\text{filed}} = 5.0 \pm 0.2$ T. The latter field differs significantly from the average field $\langle B\rangle_{\text{calc}} = 18.0 \pm 0.1$ T expected at RT for $x = 0.49$ from the published $\langle B\rangle(x)$ values [7–10] for alloys which were cold-rolled at some stage of the preparation process. A filed powder annealed for 5 h at 1185 °C and quenched has $\langle B\rangle = 18.9(0.1)$ T and $\sigma = 5.1(0.2)$ T, a field consistent with those seen in Table 1. The maximum $\langle B\rangle$ reached in the present work is found to be about 19.2 T (Table 1).

The RT Mössbauer spectrum of an as-cast alloy, broken into pieces at liquid nitrogen temperature and ball-milled for 4 h, shows a small contribution, ∼2–3% of the total Fe, possibly due to a contamination by steel of milling tools (Fig. 1). The HMFD's parameters are $\langle B\rangle = 16.6$ (0.1) T and $\sigma = 6.0$ (0.2) T. When renormalizing $P(B)$ between 0 and 28 T to remove the 'steel' contribution, the parameters become, $\langle B\rangle_{\text{ren}} = 16.0$ (0.1) T and $\sigma_{\text{ren}} = 5.3$ (0.2) T. In any case, both sets are basically the same as those of filed samples (Fig. 3). Additional HMFDs of alloys, either cold-rolled or mechanically thinned, annealed for different times at 1000 °C and at 1185 °C is shown in Ref. [7].

5. Discussion and conclusions

The most striking result of the present work is the existence of a reference HMFD both for filed and for ball-milled samples with a $\langle B\rangle$ smaller by ∼1 T than that of cold-rolled as-cast alloys, by ∼2 T than the field, 18 T, expected from the literature for the studied alloy composition and by ∼3 T than the maximum $\langle B\rangle$ observed here. Plastic deformation cannot solely explain these differences. Both filed and ball-milled samples have respectively ultrafine and nanosized domains. Filing and ball-milling tend likely to better mix Fe and Cr in bulk than does cold-rolling and than do the various preparation methods used here. It is however difficult to know how close the final distribution is to a random one. The low-field parts of HMFDs of ball-milled nanocrystalline materials, in particular those of concentrated nanostructured Fe–Cr alloys, are often attributed in the literature to Fe atoms belonging or close to grain boundaries. The present results show that care must be taken before concluding on the existence of a separate contribution of GB Fe atoms to HMFDs as the $P(B)$'s are basically the same for filed and ball-milled Fe–Cr samples despite domain sizes which differ by an order of magnitude. We performed calculations of HMFDs from computer simulations of atomic configurations of bcc $Fe_{0.51}Cr_{0.49}$ alloy generated with the Gehlen–Cohen method [16]. They show that $\langle B\rangle$ decreases when changing chemical order from an unmixing trend to an ordering trend, with a concomitant significant decrease of σ. However, the fluctuations of B, as measured by σ, depend here only weakly on the preparation conditions (Table 1). More detailed results about changes of magnetic properties with the preparation method will be published elsewhere. The present results confirms the strong sensitivity of the chemical order to the details of sample preparation, a fact which calls for more refined theoretical models of chemical order in concentrated Fe–Cr alloys, in particular at high temperature.

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