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Mössbauer spectrometry of near equiatomic Fe–Cr alloys: Phase separation at high temperature?

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Abstract

Mössbauer spectrometry shows that a bulk bcc $Fe_{0.51}Cr_{0.49}$ alloy annealed between 1000 and 1200 °C and quenched at ambient temperature is not phase-separated in contradiction with recent claims. Despite small differences in the various hyperfine magnetic field distributions, none shows the features expected for phase separation. The latter differences, which are discussed in a companion paper, reflect the sensitivity of the Fe–Cr chemical order to the alloy treatments.

Keywords: Metals and alloys; Hyperfine interactions; Mössbauer spectroscopy

1. Introduction

Numerous investigations and applications of Fe–Cr based materials, from bulk alloys to multilayered materials, are rooted in a notable set of characteristics among which a high-corrosion resistance, good mechanical properties and a diversity of magnetic behaviors [1–7]. Further, a broad miscibility gap exists at low-temperature in the central part of the binary equilibrium phase diagram [1–4]. Bulk Fe–Cr alloys exhibit a wide variety of metastable phases whose structures depend on composition and preparation ([8–11] and references therein). Amorphous and metastable Fe–Cr phases were described recently and electronic properties of Fe–Cr alloys with various structures were calculated theoretically [8–13]. Since the first publication of Treitschke and Tammann in 1907 [14], the basic features of Fe–Cr alloys might then be considered to be understood.

In a sequence of papers, Ustinovshikov et al. have however suggested that some regions of equilibrium phase diagrams of various binary Fe–T systems (T = Ti, V, Mn, Co, W), and more importantly of Fe–Cr alloys [15–19], which are considered as 'solid solution regions' are actually domains in which a tendency towards separation exists. A modified Fe–Cr diagram was then proposed on the basis of microstructures observed by transmission electron microscopy (TEM) for $Fe_{1-x}Cr_x$ ($x \leq 0.5$) alloys heat-treated at different temperatures and quenched [16–19]. A high temperature, oval-shaped, phase separation domain ($T_1 \approx 1100\,^\circ C \leq T \leq T_2 \approx 1450\,^\circ C, x_1 \approx 0.19 \leq x \leq x_2 = 0.50$) is added inside the classical solid solution region of concentrated alloys ($x \leq 0.5$) [17–19].

Mössbauer studies of bcc Fe–Cr alloys ([4,20–28] and references therein) were and are still most often performed on as-cast alloys which are first cold-rolled, are then annealed for homogenization and to remove strain and are generally quenched. Various small angle neutron scattering experiments evidenced no signs of unmixing in alloys quenched in rather standard conditions. Hyperfine magnetic field distributions (HMFDs) are extracted from Mössbauer spectra recorded most often at room temperature (RT). Consistent results are published in that way in the literature. In the course of the present study, we measured significant shifts of the HMFDs of near equiatomic alloys prepared in different conditions which are described in a companion paper [28].

The purpose of the present work was to check for the existence of an eventual high-temperature phase separation by Mössbauer spectrometry at RT which is a well-established technique of investigation of such a phenomenon in Fe–Cr alloys [4,20–27].

2. Experimental

Sets of as-cast alloys $Fe_{0.510(5)}Cr_{0.490(5)}$ were prepared from Fe (99.99+, Goodfellow) and Cr (99.996, Aldrich). Alloys were isothermally annealed under

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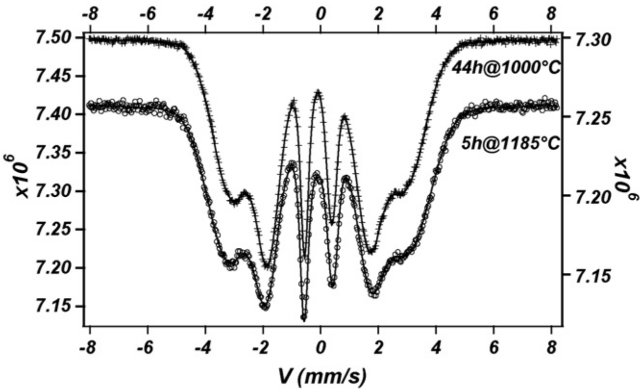

Fig. 1. Two RT ^{57}Fe Mössbauer spectra of as-cast $Fe_{0.51}Cr_{0.49}$ alloys further treated as indicated (solid lines = fits, additional spectra are shown in Ref. [28]).

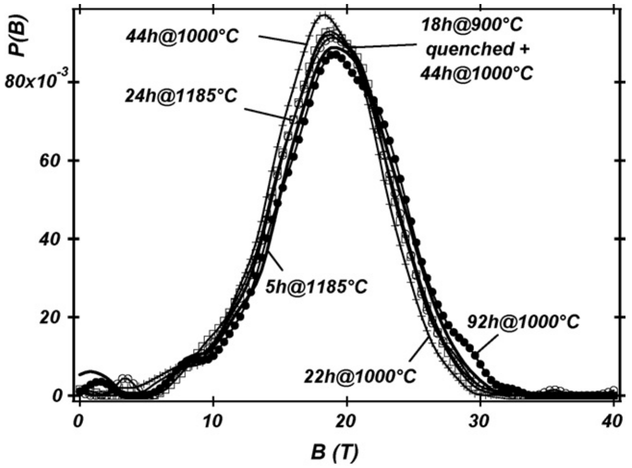

Fig. 2. HMFDs of as-cast $Fe_{0.51}Cr_{0.49}$ alloys further treated as indicated and quenched.

vacuum in sealed quartz tubes and quenched into water. Some samples were cold-rolled with a progressive reduction in thickness from about 1–2 mm down to 25–30 μm. Cold-rolled alloys were vacuum annealed for 1 h up to some tens of hours at a temperature T_a where $1000\,°C \leq T_a \leq 1200\,°C$. Another way of obtaining foils was by progressive mechanical thinning, with metallographic abrasive papers, of bulk alloys which were annealed at T_a (one face was polished before and one after the heat-treatment).

Alloy compositions were measured by microprobe analysis. X-ray diffraction patterns were recorded on a Siemens D500 powder diffractometer using Co Kα$_1$ radiation (λ = 0.17889 nm).

^{57}Fe Mössbauer spectra of samples in foil form 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 $P(B)$ were obtained [29] employing Lorentz lines. $P(B)$ 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 $\langle Y \rangle$. All Fe–Cr spectra were nicely fitted (Fig. 1) using the following IS(B) relationship explained in Ref. [27], 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. Texture effects were taken into account when necessary (cold-rolled samples, Fig. 1 of Ref. [28]).

3. Results

All X-ray diffraction patterns show only a single set of intense diffraction peaks due to a bcc phase. Apart from eventual texture effects (Fig. 1 of [28]) and from their global extent, all RT Mössbauer spectra are alike (Fig. 1). All $P(B)$ look essentially "gaussian-shaped" and are similar, apart from shifts and broadenings (Fig. 2). As described in Ref. [28], all Mössbauer samples, 36 in total, which were obtained by filing a bcc alloy with a diamond file have basically identical HMFDs, *whatever the preparation method of the alloy*. Their average field is $\langle B \rangle_{\text{filed}} = 16.2 \pm 0.2$ T with a standard deviation of 5.0 ± 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 [20–22] for alloys which were cold-rolled at some stage of the preparation process (e.g.: $\langle B \rangle(x) = 33.55 - 31.794x$ [20], $\langle B \rangle(x) = 33.36 - 30.071x - 2.8686x^2$ [22]). 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. As Mössbauer spectra of filed samples are independent of the annealing treatment, they will not be further discussed (see Ref. [28]). Fig. 2 presents HMFDs of different samples, either cold-rolled or mechanically thinned, annealed for different times at 1000 and 1185 °C.

4. Discussion and conclusions

The TEM samples investigated by Ustinovshikov et al. [16–19] were taken from as-cast alloys forged into square bars of 12 mm × 12 mm (in conditions which are not described) and annealed for 2 h at 1000 °C. The latter bars were further annealed for some hours, typically from 1 to 22 h, at various temperatures $550\,°C \leq T_a \leq 1400\,°C$ and then water-quenched. No information is given on the location of TEM samples in the quenched bar and on the method used to prepare them. Despite small differences in the various $P(B)$'s (Fig. 2) which are discussed in Ref. [28], none shows the features expected for phase-separated alloys [20–27]. In that case, $P(B)$ would reveal a main peak due to the Fe-rich Fe–Cr bcc phase, centered at a field ranging

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 $\langle B \rangle$ (T)	Standard deviation $\sigma = \langle (B - \langle B \rangle)^2 \rangle^{1/2}$ (T)
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 1000 °C, quenched and mechanically thinned	18.1 (0.1)	4.4 (0.1)
The as-cast alloy is annealed for 22 h at 1185 °C, quenched and mechanically thinned	18.6 (0.1)	4.4 (0.1)

between ∼26 T ($x = 0.25$) and ∼27 T ($x = 0.20$) for $T_a \sim 1200\,^\circ$C according to the phase diagram proposed in Refs. [16–19] and a second one at small fields due to the Cr-rich Fe–Cr bcc phase (the miscibility gap being expected to extend beyond $x > 0.5$). The field of the expected main peak, ∼26 T, exceeds thus the field of the observed main peak, ∼18, by ∼8 T. The latter field is further fully consistent with that expected from the literature (∼18 T) for bcc alloys prepared in a similar way and showing no sign of unmixing. A difference of ∼8 T is significantly larger than those due to the preparation method which vary from a negative value of ∼−2 T for filed or ball-milled alloys (16 T) to ∼1 T for as-cast alloys (19 T) [28].

We conclude that bulk phase separation does not occur in near equiatomic Fe–Cr alloys at high temperature. The question of a surface-induced phase separation observed by TEM is raised among others. The sensitivity of ^{57}Fe hyperfine magnetic fields to the details of sample preparation is however evidenced as discussed in Ref. [28], a fact which calls for more refined theoretical models of chemical order, in particular at high temperature.

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