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Thermal stability of a supersaturated Fe-Ge-Nb solid solution produced by ball milling

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Abstract. Thermal evolution of Fe neighbourhood in a supersaturated bcc Fe(Ge,Nb) solid solution, obtained as the final product of mechanical alloying of Fe₇₅Ge₂₀Nb₅, was studied. No changes in Fe neighbourhood were detected after heating up to 473 K, although differential scanning calorimetry shows a clear deviation of the baseline at 400 K. After heating up to 723 K, a similar nanocrystalline microstructure is derived from X-ray diffraction. However, Mössbauer spectra evidence changes in the Fe neighbourhood. A proposed deconvolution of the hyperfine field distribution yields a Ge content of ~10 at. %, in agreement with the maximum solubility of Ge in bcc Fe in thermodynamical equilibrium.

1. Introduction

Mössbauer spectroscopy is found to be a useful tool in order to study the local Fe environment in Fe containing alloys. In this work, the evolution of microstructure and local Fe environments of the supersaturated bcc Fe(Ge,Nb) solid solution obtained as the final product of mechanical alloying of Fe₇₅Ge₂₀Nb₅ [1] is reported. X-ray diffraction (XRD) shows that, at the end of milling process (150 h at 350 r.p.m), powders show a single phase: nanocrystalline bcc Fe(Ge,Nb) supersaturated solid solution with a lattice parameter $a = 2.894 \pm 0.003$ Å and a minimum crystal size of ~6 nm. The as-milled sample was heated up to 473 and 723 K in order to study its thermal stability.

2. Experimental

Fe₇₅Ge₂₀Nb₅ alloy was prepared by mechanical alloying from pure powders in a planetary ball mill Fritsch Pulverisette 5. Details of milling parameters can be found elsewhere [1]. Crystalline structure was studied by XRD using Cu K α line and the local Fe environment was analyzed by Mössbauer spectroscopy (MS) at room temperature in a transmission geometry using a ⁵⁷Co(Rh) source. The values of hyperfine parameters were obtained by fitting with NORMOS program [2]. Thermal characterization of the samples was studied by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7.

3. Results and Discussion

MS spectra were fitted using a hyperfine field distribution ($0 \leq HF \leq 36$ T). In figure 1(a) the MS spectrum along with HF distribution for as-milled and heated samples are shown. The average hyperfine field $\langle HF \rangle \sim 27$ T and the average isomer shift $\langle IS \rangle \sim 0.15$ mm/s (slightly increasing with heating temperature) are similar for all samples and different to those of pure bcc Fe, which agrees with the existence of the supersaturated bcc Fe(Ge,Nb) solid solution observed by XRD.

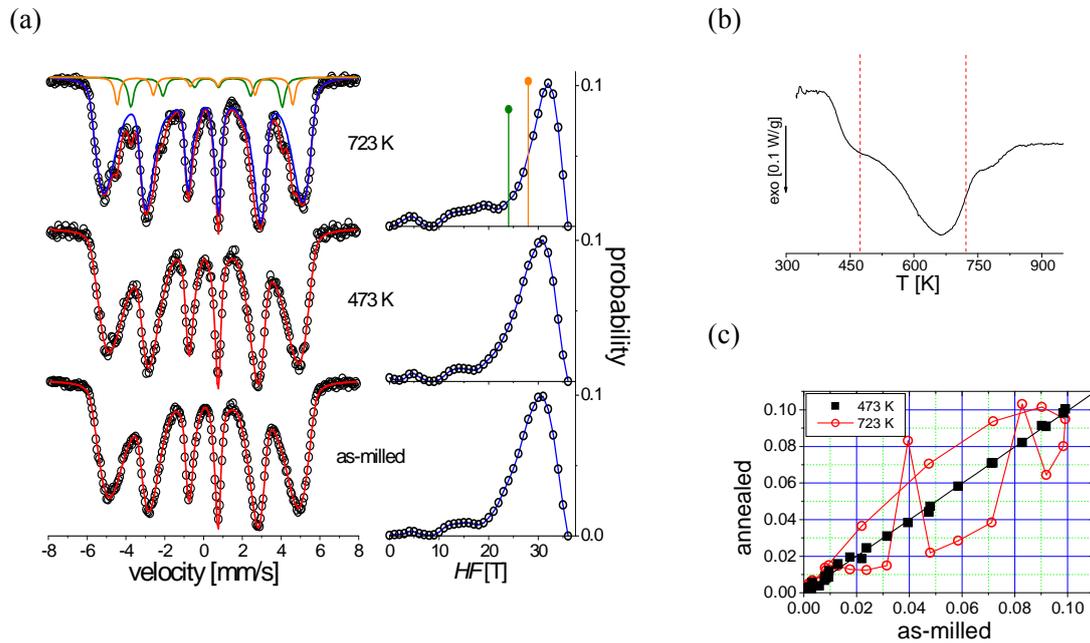


Figure 1. (a) Mössbauer spectra and HF distributions at 300 (as-milled), 473 and 723 K; (b) DSC scan of as-milled sample; (c) correlation between HF distributions of as-milled and heated samples.

The broad exothermic process (from 400 up to 800 K) shown in figure 1(b) ascribed to structural relaxation does not affect the microstructure or HF distribution after heating up to 473 K (first dotted line in figure). However, for the sample heated up to 723 K, two new site contributions ($HF \sim 28$ and ~ 24 T) are necessary to fit the spectrum, indicating an evident evolution of Fe environments in the solid solution. In fact, figure 1(c) shows a good correlation of the probabilities of each HF contribution between the samples heated up to 473 K and the as-milled one. In the case of the sample heated up to 723 K the lost of correlation is clearly observed.

Taken into account the effect of Ge [3] and Nb [4] on HF for Fe-Fe interactions, it is possible to estimate the impurity content in the bcc Fe phase [1]. In order to reduce the huge amount of possible configurations for Ge and Nb as nearest neighbours, NN, (n and p , respectively) and next nearest neighbours, NNN, (m and q , respectively) of a central Fe atom, average reductions on HF can be considered. In the case of Nb, both NN and NNN has been averaged to $\langle HF_{pq} \rangle$, and for Ge as NNN, $\langle HF_m \rangle$ was calculated. Finally, HF can be expressed as a function of Ge atoms as NN:

$$HF = 34.54 - 2.36n^{1.5} - \langle \Delta HF_{pq} \rangle - \langle \Delta HF_m \rangle. \quad (1)$$

Table 1. Average reduction due to Nb as NN and NNN and Ge as NN.

% at. Nb	1	2	3	% at. Ge	10	15	20
$\langle \Delta HF_{pq} \rangle$ [T]	0.45	0.90	1.35	$\langle \Delta HF_m \rangle$ [T]	1.07	1.61	2.15

Table 1 shows the reduction in HF of Fe atoms due to Nb as NN and NNN and Ge as NN for different concentrations of these elements in the crystals. Fixing $HF(n)$ to the corresponding values from expression (1) and table 1, experimental HF distributions were fitted with a set of 5 contributions ($n=0, 1, 2, 3, 4$ and >4). Figure 2(a) shows an example of the deconvolution of HF distribution for the spectrum of as-milled sample.

From deconvolution results, it is possible to obtain an experimental probability for each atomic environment and compare its value with the theoretical probability calculated for a totally disordered bcc Fe(Ge,Nb) phase, for known Ge and Nb contents, as is shown in figure 2 (b). It can be observed that for a composition of ~15 at.% Ge and between 1 and 2 at.% Nb, the experimental probability agrees with the theoretical one, and a Fe_{83.5}Ge₁₅Nb_{1.5} composition can be estimated for the solid solution of as-milled sample (with error bar of 2.5 at.% Ge and 0.5 at.% Nb), for which a lattice parameter between 2.896 < a < 2.900 Å can be calculated considering an increase of $1.7 \cdot 10^{-3}$ Å per at.% Ge [5] and $\sim 4.4 \times 10^{-3}$ per at.% Nb [6] in the bcc Fe lattice, in agreement with XRD, $a = 2.894$ Å.

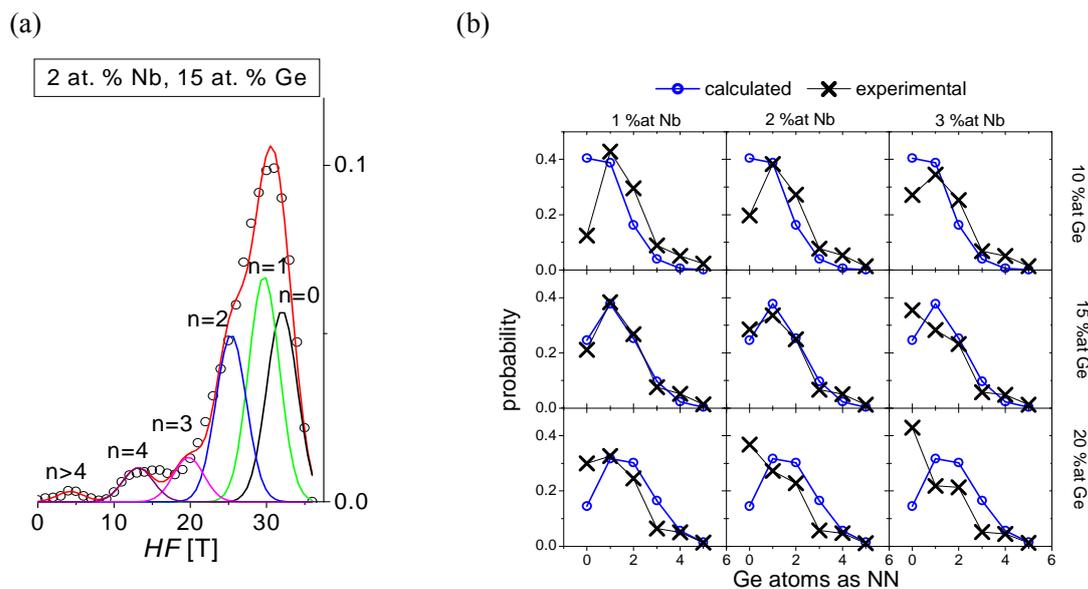


Figure 2. (a) Deconvolution of HF distribution at room temperature for 2 at% Nb, 15 at.% Ge in bcc phase; (b) Experimental and calculated probabilities for different Ge and Nb contents in crystals.

In the case of sample heated up to 723 K, the microstructure evolves mainly due to the rejection of Nb atoms to the grain boundaries. Therefore, the HF distribution was fitted considering 0 at.% Nb in the crystals and keeping free the different $HF(n)$ contributions (due to the numbers of Ge atoms as NN) as is shown in figure 3(a). Considering $HF(0,0) = 34.54$ T [3] as the hyperfine magnetic field of a Fe atoms with no Ge in the first and second shells and plotting $HF(0,0) - HF(n)$ as a function of $n^{3/2}$, a linear trend is observed in figure 3(b). The slope is 2.3 ± 0.2 T being in good agreement with the dependence found for Fe-Ge system [3] and supporting the deconvolution performed. The value at $n = 0$ is bigger than for crystalline Fe-Ge [3] and could be ascribed to the nanometric size of the crystals and to the presence of Cr from contamination [1].

From $HF(0,0) - HF(0) = 2.4 \pm 0.1$ T, the average number of Ge atoms in the second coordination shell is 1.44 atoms. Assuming a maximum ordered DO₃ phase, the concentration of Ge in the solid solution would be $C_{Ge} \sim 25(1.44/6) = 6$ at.%. However, considering a totally disordered phase, the presence of 1.44 atoms in the set of 14 atoms surrounding a central Fe, $C_{Ge} \sim 10$ at.%, which agrees with the solubility limit of Ge into bcc Fe in thermodynamic equilibrium [7]. The latter result is also in better agreement than the former one with the lattice parameter derived from XRD, $a = 2.888 \pm 0.003$ Å, which implies a concentration of 13.2 at% Ge in bcc crystals.

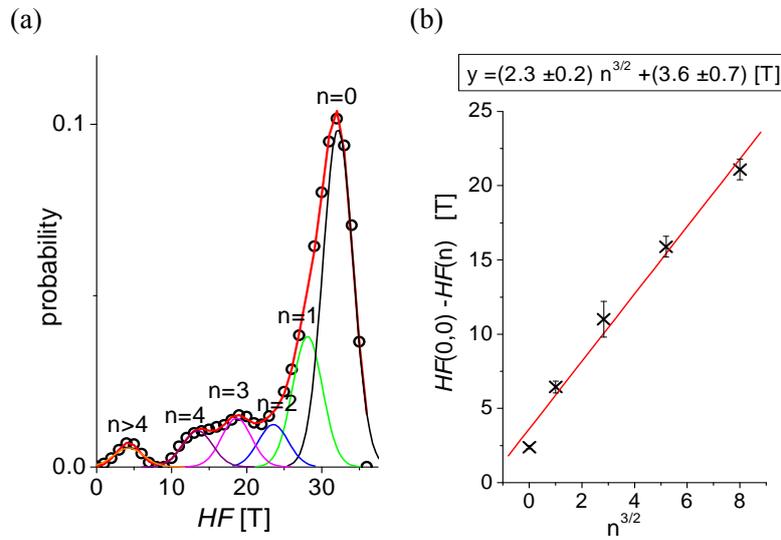


Figure 3. (a) deconvolution of HF distribution at 723 K; (b) HF reduction as a function of number of Ge atoms as near neighbour.

4. Conclusions

Thermal evolution of Fe environments of the supersaturated bcc Fe(Ge,Nb) solid solution produced by mechanical alloying of Fe₇₅Ge₂₀Nb₅ was studied. Sample heated up to 473 K shows no evolution and a Fe_{73.5}Ge₁₅Nb_{1.5} composition can be estimated but after heated up to 723 K, the composition is Fe₉₀Ge₁₀, close to the limit of thermodynamical equilibrium.

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