Supersaturated solid solution obtained by mechanical alloying of 75 % Fe, 20 % Ge and 5 % Nb mixture at different milling intensities

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Abstract

Mechanical alloying process of $Fe_{75}Ge_{20}Nb_5$ composition has been studied at different milling frequencies from initial pure powder mixture to the development of a single bcc phase (supersaturated solid solution). As an intermediate state, an intermetallic phase is formed, which disappears after further milling or after thermal treatment (ascribed to an endothermic process at 700-800 K). A preferential partition of Nb and Ge to the boundaries between nanocrystals of bcc Fe-Ge-Nb supersaturated solid solution is observed from XRD and Mössbauer results.

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1.   Introduction

Ball milling has been shown as a very versatile technique for production of
metastable systems: nanocrystalline, amorphous, supersaturated solid solutions,
quasicrystals, etc [1]. Although similar final products can be obtained by ultra fast
cooling techniques [2,3], the mechanisms involved in the production of metastable
phases are quite different. In ultra fast cooling techniques, the atoms have no time to
diffuse in order to form the corresponding stable structure and high temperature
structures can be frozen at temperatures much lower than their stability range in
equilibrium conditions. As a limit, amorphous solid structures are obtained by freezing
the disordered structure of the liquid melt. Mechanical evolution induced by ball milling
is due to the energy transferred from the milling media to powder particles,
continuously submitted to fracture and cold welding processes which will define their
final morphology.

Ball milling is especially suitable to form supersaturated solid solutions allowing
some immiscible elements to alloy out of the compositional range of equilibrium [1,4].
Nanocrystalline state is easily obtained by ball milling [1] and is considered an
intermediate state previous to the development of supersaturated solid solutions or
amorphous phases [4]. On the other hand, in Fe-based systems, nanocrystalline
microstructure is interesting from the point of view of magnetic properties as averaging
out of magnetocrystalline anisotropy is expected [5].

In this work, the mechanical alloying process of $Fe_{75}Ge_{20}Nb_5$ system is studied
from an initial mixture of pure powders to the development of a bcc supersaturated solid
solution. The use of different milling frequencies allows studying the mechanical
process at different milling rates as the time evolution of the different parameters can be
rescaled using an equivalent time $t_{eq}=t\cdot(\Omega/\Omega_0)^3$, where Ω_0 is a reference frequency [6].

2.   Experimental

$Fe_{75}Nb_5Ge_{20}$ composition was produced from pure powders (purity≥99 %) by ball milling in a Fritsch Pulverisette 5 planetary ball mill using hardened steel balls (10 mm diameter) and vials. The initial powder mass was 5 g and the ball to powder ratio 10:1. Three different values of the rotational speed of the main disk, Ω, were used: 150, 250 and 350 rpm. Some powder was taken out after selected times (from 1 h to 150 h), opening and closing the vials in argon atmosphere to avoid oxygen and humidity contamination.

Size and morphology of the powder particles were studied by scanning electron microscopy (SEM) in a Jeol JSM-6460 LV and energy dispersive X-ray (EDX) analyses were performed using an Incax-sight of Oxford Instruments. The crystalline structure was studied by X-ray diffraction (XRD) using Cu-Kα radiation in a Bruker D8I diffractometer and the local environment of Fe atoms was analyzed by Mössbauer spectrometry (MS). Mössbauer spectra were recorded at room temperature in a transmission geometry using a ^{57}Co(Rh) source. The values of the hyperfine parameters were obtained by fitting with NORMOS program [7]. Thermal stability of the samples was studied by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 under argon flow. Specific saturation magnetization, σ_S was measured in a Lakeshore 7407 vibrating sample magnetometer (VSM), applying a maximum field of 1.5 T.

3.   Results and discussion

3.1   Scanning electron microscopy and Energy dispersive X-ray spectroscopy:

Morphology and composition evolution.

Figure 1 shows SEM images of samples after selected milling times along with the corresponding powder particle size distribution. Mean powder particle size, $<d>$ was obtained as an average over 100-200 particles per sample. Lower panel of figure 2 shows the evolution of $<d>$ as a function of the milling time for the three milling frequencies studied in this work. As observed, the evolution is similar for samples milled at 150 and 250 rpm; at low milling times $<d>$~15 μm and decreases down to ~5 μm for longer times. The stable value is achieved at shorter times milling at 250 rpm than at 150 rpm, in agreement with a higher power supplied by milling as the angular speed increases. On the other hand, $<d>$ values at 350 rpm, ~10 μm, are almost independent of the milling time. Although the reduction of the powder size could occur at shorter milling times than the explored for 350 rpm samples (t<2 h), the stable value is clearly larger than 5 μm obtained for samples at 150 and 250 rpm. This could be ascribed to the expected higher temperature inside the vial when milling at 350 rpm (the frequency and duration of pause intervals were the same, independently of the milling rate), which could enhance the coalescence among the small powder particles. A more energetic milling at 350 rpm implies larger forces during the process, which could enhance sticking the powder onto the vial wall, preventing further refinement of the powder size. However, the evolution of different properties of this composition is found to appropriately rescale using an equivalent time proportional to Ω^3 [6], indicating that the possible differences in the global milling process are not relevant enough.

The trend towards compositional homogenization and Cr contamination from the milling media were studied by EDX. Fe and Ge are the more abundant elements in the composition studied and thus the homogenization of the powder particle composition could be followed from the ratio between Ge and Fe+Ge content of each particle. The minimum dispersion found for this parameter (calculated as the difference between the

maximum and minimum Ge/[Fe+Ge] content ratio measuring a set of 20 particles) is

$\Delta \sim 0.04$. This value is obtained, at 150 rpm, only after 150 h, being $\Delta = 0.11$ after 100 h

milling. At 250 rpm, $\Delta \sim 0.04$ after 20 h milling and, at 350 rpm, this value is already

achieved after 10 h milling, being $\Delta = 0.09$ just after 2 h milling. This minimum

dispersion in the relative content of Ge implies the existence of a certain compositional

range of the final powder mixture: from 18 to 22 at. % Ge, assuming an average Ge

concentration of 20 at. %. A similar effect could be observed for Nb content of the

powder particles, but its low concentration prevents a detailed discussion similar to that

done for Ge.

Average values of Ge and Fe content are the nominal ones for 150 and 250 rpm,

at any milling time, and for 350 rpm at milling times below 50 h. However, for 350 rpm

and milling times above 50 h, a relative enrichment in Fe as well as a relative

impoverishment in Ge are found. This can be ascribed to contamination from the

milling media. However, instead of measuring Fe enrichment in such Fe rich

composition, contamination can be better estimated from the increase in Cr, as this

element is not present in the initial composition and very small amounts can be easily

identified by EDX. Figure 2 (upper panel) shows the average Cr content of a powder

particle as a function of the milling time. A small linear increase of the Cr content ($<$ 1

at. %) is only evident for 350 rpm at long milling times ($t \geq 50$ h), being negligible for

the other two angular speeds used up to 150 h milling. This small Cr contamination

might imply a small Fe contamination [8].

3.2   X-ray diffraction: Structural evolution.

The phase evolution detected by XRD is common for the three studied

frequencies, following a recently proposed Ω^3 law [6]: At the beginning, the bcc Fe, bcc

Nb and fcc Ge are the only phases detected. As mechanical alloying progresses, bcc Fe

maxima become more intense and broader, whereas those of bcc Nb and fcc Ge are

reduced and a new phase appears, characterized by a diffraction peak at ~37 ° (possibly

hexagonal Fe_3Ge_2 intermetallic). This intermetallic phase disappears for longer milling

times. Finally, bcc supersaturated solid solution is the only phase detected in the XRD

patterns. Figure 3 shows the XRD patterns of samples milled 150 h at the three studied

frequencies. No big differences can be observed between the XRD patterns of samples

milled at 250 and 350 rpm for 150 h, where the bcc Fe-Ge-Nb supersaturated solid

solution is the only phase detected. Similar XRD patterns were already found after 50

and 10 h milling at 250 and 350 rpm, respectively. In the case of 150 rpm sample, the

peak at ~37 ° ascribed to the intermetallic compound is also observed and the shape of

the (110) peak of the α-Fe type phase is asymmetric as it was also shown for other ball

milled compositions [9]. This asymmetry, observed in the XRD patterns of samples for

which the intermetallic compound is formed, might indicate the existence of α-Fe

crystallites with different composition. The simplest way to fit such diffraction maxima

preserving the asymmetric character is by using two theoretical curves (Lorentzian in

the studied case). In some cases (shortest milling times), a third peak was used to fit the

(200) fcc Ge diffraction maximum. Once this is done, the lattice parameter of the

thinnest contribution (width ~0.45±0.10 °) is close to that of pure α-Fe and the lattice

parameter of the broadest one (width ~1.12±0.05 °) is ~2.89 Å, close to that of the final

bcc supersaturated solid solution (see below). As milling time increases, the relative

area of the broadest contribution increases. Once the supersaturated solution is formed,

the (110) α-Fe type diffraction maximum becomes symmetric. This indicates that the

transition of the α-Fe crystallites to the bcc supersaturated solution is progressive and

crystallites with different composition coexist in a certain range of milling times.

Several effects can affect the broadening of the diffraction maxima peaks: small

crystal size, microstrain and, as it was pointed above, the non existence of a single

composition but a compositional range, which would lead to a distribution of lattice

parameters. In order to overcome the difficulties arising from individualizing each

contribution to broadening, some limit values have been calculated, as a first approach,

from the (110) maximum of the bcc Fe-type phase. Therefore, a minimum value of the

crystallite size, D_{min}, has been obtained considering that the small crystallite size is the

only effect responsible for the broadening of the diffraction peak. Also, a maximum

value for the microstrains, ε_{max}, has been estimated considering microstrains as the only

effect responsible for the peak broadening. Neglecting the expected distribution of

lattice parameters, an average value, a, has been obtained from the 2θ position of the

diffraction peak after applying Scherrer formula. The obtained results are shown in

figure 4 as a function of the milling time for the three studied frequencies. Values of

D_{min} are refined (faster as the frequency increases) down to ~5 nm and ε_{max} increases up

to ~6 %. It is worth mentioning that these values are only lower/upper limits for the

actual ones and, therefore, $D>5$ nm and ε<6 %. The D_{min} values are of the order of those

reported for similar compositions. However, these ε_{max} values are too high (generally,

microstrain values achieved during milling are ~1.5 %) [1]. This indicates that

crystallite size is a more relevant contribution to the broadening than that of

microstrains. Saturation behavior is observed for 250 rpm and 350 rpm after 50 and 10

h milling, respectively, coinciding with the formation of the supersaturated solid

solution. Average lattice parameter shows an abrupt jump from 2.860±0.005 Å

(approximately that of pure α-Fe) to 2.895±0.005 Å when the supersaturated solid

solution is formed. The expansion of the crystalline cell, ~4 %, is due to the presence of

both, Ge and Nb, in bcc Fe as their addition yields an increase of the lattice parameter.

In the case of Ge, which is soluble in α-Fe up to ~10 at.%, the increase of the lattice

parameter is $1.7 \cdot 10^{-3}$ Å per at.% Ge [10]. In the case of Nb, although this element, in

equilibrium conditions, is practically insoluble in the α-Fe phase, we can assume as a

rough working hypothesis a linear dependence of the lattice parameter of the bcc phase

with the Nb content, using the values of the Fe and Nb pure phases (a=2.8664 [11] and

3.30660 Å [12], respectively). As a consequence, a rate of ~$4.4 \cdot 10^{-3}$ Å per at.% Nb is

derived. Considering $Fe_{75}Ge_{20}Nb_5$ bcc supersaturated solid solution as the final product

of milling, the expected lattice parameter would be 2.92 Å, larger than the measured

value (2.895±0.005 Å). In fact, it is reasonable that elements other than to Fe

preferentially partition to the boundaries between crystallites. This must affect mainly

Nb atoms, due to its very low solubility in bcc-Fe. Therefore the final microstructure

would be small crystallites of bcc $Fe_X Ge_Y Nb_Z$ solid solution (X>75, Y≤20 and Z<5)

coated by Nb enriched boundary layers. These layers should be responsible for the

thermal stability of the nanocrystalline microstructure observed for this composition

[13].

3.3   Differential scanning calorimetry: Thermal evolution.

DSC plots of samples milled 150 h at different frequencies are shown in figure

5. No big differences were observed between samples milled at 250 and 350 rpm,

except for a larger enthalpy of the broad exothermic peak after milling at 250 rpm (68

J/g) than at 350 rpm (60 J/g). This exothermic peak, extended from 400 to 800 K, can

be ascribed to structural and strain relaxation phenomena of powder particles. In the

case of the sample milled 150 h at 150 rpm, besides the broad exothermic peak, DSC

plot exhibits an endothermic process from 650 to 800 K. Similar endothermic processes

have been reported in the literature [14,15], although no satisfactory explanation could

be found to be applicable to the studied case. As it will be shown below, tendency to

homogenization could explain the presence of this endothermic process.

The irreversible character of both exothermic and endothermic processes is

demonstrated in figure 6, which shows several DSC scans performed on a sample

preheated to the indicated temperatures. The DSC scan of the as-milled sample is also

shown for comparison. After the sample is preheated up to a certain temperature, the

transformation disappears in a second scan up to the maximum temperature reached in

the previous treatment, without affecting the rest of the peak at higher temperatures.

The existence of an endothermic process in the DSC scans is linked with the

microstructure developed for milling as it can be observed in figure 7. This figure shows

the DSC scans for the different samples milled at 250 rpm along with their

corresponding XRD patterns. It can be observed that the DSC endotherm is only

observed when the intermetallic compound is detected in the XRD patterns but neither

at the very beginning of the milling process (when only initial phases are detected) nor

at the final stages (when the supersaturated solid solution is formed). The absolute

values of the measured enthalpy of both the exothermic and the endothermic processes,

as a function of the milling time, are shown in figure 8 for the sample milled at 250

rpm. It can be observed an increase of the exothermic process enthalpy ascribed to

relaxation phenomena (stored enthalpy) with the increase of the milling time from 0 to 3

h, followed by a continuous decrease for t>3 h until a saturation value is achieved when

the supersaturated solid solution is formed. Similar behavior was observed for the

enthalpy stored during milling single element powders [16,17].The endothermic process

enthalpy could be related to the amount of intermetallic compound in as-milled samples,

being maximum when the ratio between the area of the intermetallic diffraction line

peaked at ~37 ° and that of the (110) of the α-Fe type phase is maximum.

In order to confirm the relationship between the DSC endotherm and the

intermetallic compound, XRD spectra were recorded on the sample milled 10 h at 250

rpm and heated up to two different temperatures: 573 K and 873 K (below the onset and

above the completion of the endothermic process, respectively, see figure 6). The room

temperature XRD spectra of the corresponding samples are shown in figure 9 along

with the XRD pattern of the as-milled sample. Heating up to 573 K does not yield

changes in the phases detected by XRD. However, heating up to 873 K implies that the

peak at ~37 ° disappears as well as other peak at ~54 °, which could be ascribed to fcc

Ge. However, the peak at ~38 °, which corresponds to bcc Nb does not disappear but

becomes sharper (indicating crystal coarsening and/or microstrain release). These

results indicates that the endothermic peak observed is linked with the homogenization

of the system by solving the intermetallic compound (and probably residual fcc Ge too)

into the bcc supersaturated solid solution. More detailed information can be extracted

from the analysis of the (110) peak of the bcc Fe phase. Figure 9 (right) shows

enlargements of the relevant 2θ range, where experimental data (circles) are plotted

along with fitting curves (lines). Heating up to 573 K yields only a slight shift of the

(110) maximum to lower values of 2θ but its asymmetry is preserved and two

Lorentzian peaks are needed to fit the maximum (individual contributions are also

shown in the figure). However, heating up to 853 K, the (110) peak clearly shifts to

lower values of 2θ and becomes symmetric (fitted is done using a single Lorentzian

peak). These features evidence the relationship between the endothermic DSC process

and the homogenization of the samples. It is worth noticing that this homogenization is

expected to occur into each powder particle but the dispersion in composition between

independent powder particles and observed by EDX might not be affected by the

thermal treatments performed in this study.

3.4   *Mössbauer spectrometry: Local Fe environment evolution.*

Figure 10 shows the MS spectra of samples milled 150 h. A general description

of the MS spectra evolution with milling time can be given. For short milling times, MS

spectra can be fitted using a single sextet characteristic of pure α-Fe, with a hyperfine

magnetic field, HF=33 T. As milling progresses, new contributions appear at high

hyperfine fields but smaller than 33 T, due to both impurities into the lattice (Ge and

Nb) and to refinement of crystallite size, which would yield the existence of a non

negligible interface contribution. Small contributions present at low fields are ascribed

to Fe atoms out of the α-Fe crystallites. Therefore, these spectra were fitted using a

sextet with HF=33 T and two hyperfine field distributions in order to preserve the

different nature of high and low field contributions. Finally, once the supersaturated

solid solution is formed, a single hyperfine field distribution is enough to fit the spectra.

The use of a hyperfine magnetic field distribution instead of a discrete number of sextets

is justified by the huge number of different Fe neighborhoods. In fact, considering the 8

nearest neighbors (NN) in the first shell and the 6 next nearest neighbors (NNN) in the

second shell, there are a total of 1260 possible configurations. Figure 11 shows the

hyperfine field distribution for the different samples studied in this work. It can be

observed that the single sextet spectrum is observed only for 2 h at 250 rpm and up to

10 h for 150 rpm. It is worth noting that small contributions in the low field region,

below 5 T (which could be a paramagnetic contribution due to ambiguity of fitting

procedure for such complex systems), increase for samples where the intermetallic

compound was detected by XRD. These low field contributions become negligible once

the supersaturated solid solution is formed and a smooth broad maximum extended

from 10 to 35 T is observed.

Table 1 summarizes the main results obtained from the fitting of the different

MS spectra. Once the supersaturated solid solution is formed (t≥50 h for 250 rpm and

t≥10 h for 350 rpm), there are no significant changes between the spectra. As milling

time increases, average hyperfine field, $<HF>$, decreases from 33 T down to ~26 T due

to the presence of Nb and Ge atoms into the bcc lattice. The average value of the isomer

shift, $<IS>$, also increases from that of the pure Fe to ~0.19 mm/s but, at 350 rpm, for

long milling times, it decreases again, which could be ascribed to the effect of Fe and Cr

contamination.

Abovementioned results on the lattice parameter of the bcc supersaturated solid

solution indicated that the average composition of this phase might be poorer in Nb and

Ge than the global composition of the powder studied. In fact, previous studies on

binary Fe-Nb milled powders indicated that the supersaturated solid solution saturates at

a Nb content <2.5 at. % [18]. Assuming this value as a maximum for the Nb content in

our ternary system, it would be possible to extract some information about the Ge

content from Mössbauer results. From literature data on binary Fe-Ge [19] and Fe-Nb

[18] alloys, the effect of the number of NN and NNN neighbors of Ge and Nb on the

hyperfine magnetic field of a probed Fe atom can be expressed as:

Ge: $HF = 34.54 - 2.36\, n^{1.5} - 1.67\, m$ [19]   (1)

Nb: $HF = 33.0 - 3.55\, p - 2.30\, q$ [18]   (2)

where n and m are the number of Ge atoms as NN and NNN, respectively; p and q are

the number of Nb atoms as NN and NNN, respectively. Two features of Fe-Ge system

are worth mentioning: there is a non linear relationship between HF and n, as it occurs

for Fe-Ga [20] and Fe-Si [21]; and the value of HF for a Fe atom completely

surrounded by Fe atoms in the first and second shell (*HF*=34.54 T) is different to that of

pure Fe (*HF*=33.0 T), which could be ascribed to the increase of the lattice parameter as

Ge is incorporated into the lattice. Expression concerning Nb effect on *HF* is linear with

p and *q* but it must be taken into account that this expression was found only for a Nb

content into the bcc Fe-Nb lattice <2.5 at.%. In such a case, configurations with *p*+*q*>2

are negligible. On the other hand, configurations with more than 4 Ge as NN are

paramagnetic [19] and therefore a *HF*=0 might be assigned for these contributions.

Theoretically, it could be possible to calculate the *HF* value ascribed to each

individual (*n,m,p,q*) configuration but using such huge number of different

configurations is senseless. However, some simplifications can be done if some average

values are calculated. First, the low Nb content allows considering Nb as a perturbation

on the binary Fe-Ge system. Therefore the average reduction of *HF* due to the presence

of Nb as NN and NNN is obtained depending on the Nb content and incorporated to

expression (1). Moreover, the effect of Ge as NNN is also averaged. Therefore, only the

contributions characterized by the number of Ge atoms in the first shell, *n*, are

considered reducing expression (1) and (2) to:

$$HF(n) = \frac{\sum\limits_{m,p,q} HF(n,m,p,q)\, P_{nmpq}}{\sum\limits_{m,p,q} P_{nmpq}} = 34.54 - 2.36\, n^{1.5} - <\Delta HF_{pq}> - <\Delta HF_m> \quad (3)$$

where <*ΔHF$_{pq}$*> is the global reduction in *HF* due to the presence of Nb atoms as NN

and NNN, and <*ΔHF$_m$*> is the global reduction due to Ge atoms as NNN. These

average reductions depend on Ge and Nb content. Table 2 shows the calculated values

for several proposed compositions.

The spectra of bcc supersaturated solid solution were fitted in this work using a

single hyperfine magnetic field distribution, and thus paramagnetic contributions are not

only those at *HF*=0 as the fitting procedure cannot distinguish paramagnetic

contribution from low field ones (≤5 T). Fortunately, there is no ambiguity in the

interpretation of the obtained *HF* distribution. As it is shown in table 2, the lowest

physically meaningful value of *HF*, corresponding to *n*=4, is clearly larger than 5 T.

Therefore, the peak in the HF distribution at ~4 T can be ascribed to paramagnetic

configurations, i.e. *n*>4. After these considerations, the *HF* distributions were fitted

using 5 Gaussian functions with the same width, whose center positions were fixed

equal to the calculated values for *n*=0 to 4, respectively, using expression (3). Another

Gaussian function was used to fit the peak ascribed to paramagnetic contributions, *n*>4.

As an example, figure 12 shows the fit of the *HF* distribution obtained for the sample

milled at 250 rpm for 100 h for two different compositions of the bcc supersaturated

solid solution, indicating the corresponding value of *n* for each individual contribution.

From such fittings, the area of each individual contribution is measured and can be

compared with the theoretical probabilities calculated for a fully disordered bcc Fe-Ge-

Nb system. Figure 13 shows, for different proposed $Fe_X Ge_Y Nb_Z$ compositions, a

comparison between these theoretical and experimental values. As for samples milled at

250 rpm for 50, 100 and 150 h, supersaturated solid solution was the unique phase

detected by XRD and contamination was negligible, experimental values were obtained

from the average of the areas obtained from fitting their *HF* distribution. This allows an

estimation of the error bars, also indicated in figure 13. A fairly good agreement is

found for Y=15 and Z=2.5 at.% (root mean square deviation between experimental and

calculated area fractions, σ=±0.02) and for Y=15 or 20 and Z=1 at.% (σ=±0.05 and

±0.04, respectively). It is worth noting that the lattice parameter obtained for these

compositions are 2.896<*a*<2.899 Å, in agreement with the value measured by XRD.

Average hyperfine magnetic field is represented in figure 14 along with room

temperature specific saturation magnetization, σ_S, as a function of the milling time.

Both magnitudes might be linked and thus follow a similar trend: when milling at 150

and 250 rpm an initial decrease of $<HF>$ and σ_S is observed down to a value of ~27 T

for $<HF>$ and ~1.7 T m^{3}kg^{-1} for σ_S. In the case of samples milled at 350 rpm, $<HF>$ is

lower than for the other two milling frequencies at short milling times but there are no

significant differences in σ_S. Moreover, an increasing trend can be observed milling at

350 rpm for long milling times due to Fe contamination from the milling media.

5.   Conclusions

Mechanical alloying process of $Fe_{75}Ge_{20}Nb_5$ alloy has been studied at different

milling frequencies from initial pure powder mixture to the development of a single bcc

phase (supersaturated solid solution). Several conclusions can be drawn from the

present paper:

- A bigger final powder particle size is observed for the sample milled at the

  highest frequency, possibly ascribed to a higher temperature inside the vial,

  which might favor the coalescence of powder particles against fracture.

- Contamination was negligible in all the studied samples, except for the sample

  milled at the highest frequency for milling times t>50 h (Cr content < 1 at. %).

- The mechanical transformation can be simplified in three steps: Initially, there is

  a mixture of pure bcc Fe, fcc Ge and bcc Nb phases. Progressively, Nb and Ge

  phases disappear, whereas an intermetallic compound is formed and the lattice

  parameter ascribed to α-Fe type phase increases. Finally, a supersaturated solid

  solution bcc Fe-Ge-Nb phase is formed.

- Thermal evolution of some ball milled samples exhibits an endothermic peak

  besides the exothermic one related to the stored energy. This endothermic peak

is ascribed to the process of solution of minority intermetallic compound on the

majority bcc phase.

- Mössbauer studies and lattice parameter results on the supersaturated solid

   solution yield the qualitative result of a preferential partition of Nb and maybe

   Ge to the boundaries between nanocrystals which are enriched in Fe with respect

   to the nominal composition. Nevertheless, the estimated amount of Nb and Ge

   inside the nanocrystals is clearly beyond the maximum solubility of these

   elements on the α-Fe phase.

Acknowledgments

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Figure captions

Figure 1: SEM images and powder particle distribution histograms of samples milled at

different intensities for selected milling times.

Figure 2: Cr content (above) and average powder particle size (below) as a function of

milling time.

Figure 3: XRD patterns of samples after 150 h milling at different rotational speeds.

Figure 4: Average lattice parameter, minimum limit for crystal size and maximum limit

for microstrains.

Figure 5: DSC scans for samples milled 150 h at different rotational speeds.

Figure 6. Heating DSC scans at 40 K/min for a sample milled 10 h at 250 rpm after

heating up to the indicated temperatures at 40 K/min. The dotted line shows the DSC

plot for the as-milled sample.

Figure 7: DSC scans and XRD patterns for samples milled at 250 rpm for different

times.

Figure 8: Enthalpy released during the exothermic relaxation process (hollow circles)

and enthalpy absorbed during the endothermic process (solid squares) as a function of

the milling time for samples milled at 250 rpm.

Figure 9: XRD patterns of a sample milled 10 h at 250 rpm in the as-milled state and

after heating up to the indicated temperatures at 40 K/min. Insets are enlargements of

the interested 2θ ranges.

Figure 10: Mössbauer spectra of powder milled at different intensities for selected

milling times.

Figure 11: Hyperfine field distribution probabilities of powder milled at different

intensities for the different studied milling times.

Figure 12: Fitting of hyperfine field distribution of the sample milled at 250 rpm for 100

h fixing the HF values calculated from equation (3) for two different proposed

compositions.

Figure 13. Comparison between experimental (average over samples milled at 250 rpm

for 50, 100 and 150 h) and calculated probabilities of the different configurations

characterized by the number of Ge atoms as near neighbors. The x value n=5

corresponds to the sum of all configuration with n>4.

Figure 14: Average hyperfine magnetic field (above) and specific saturation

magnetization (below) as a function of the milling time for different milling

frequencies.

Table 1. Hyperfine parameters obtained from Mössbauer spectra.

Ω	Time	A [33 T]	A [imp]	A [Int]	<HF>	<IS>
rpm	h	%	%	%	T	mm/s
150	5	100	0	0	33.00	0.000
	10	100	0	0	33.00	0.000
	20	74.7	20.5	4.8	30.46	0.061
	50	51.7	41.2	7.1	28.16	0.116
	100	48.7	44.9	6.4	27.91	0.112
	150	33.5	61.6	4.9	27.22	0.135
250	5	76.8	17.1	6.1	30.35	0.036
	10	58.8	33.8	7.4	28.60	0.088
	20	26.9	68.1	5.0	26.92	0.142
	50	0	100	0	26.02	0.197
	100	0	100	0	26.46	0.193
	150	0	100	0	26.81	0.192
350	5	9.7	83	7.3	26.16	0.248
	10	0	100	0	24.89	0.187
	20	0	100	0	25.13	0.184
	50	0	100	0	25.34	0.180
	100	0	100	0	26.23	0.158
	150	0	100	0	27.52	0.149

Table 2. Average reduction due to Nb neighbors as NN and NNN and due to Ge atoms

as NNN and HF value of the average configuration with 4 Ge as NN for several

compositions of bcc-$Fe_{100-Y-Z}Ge_YNb_Z$ (Y=10, 15, 20 at.% and Z=1 and 2.5 at.%).

at.% Nb	1			2.5			5		
$<\Delta HF_{pq}>$ (T)	0.45			1.13			2.26		
at.% Ge	10	15	20	10	15	20	10	15	20
$<\Delta HF_m>$ (T)	1.07	1.61	2.15	1.07	1.61	2.15	1.07	1.61	2.15
HF(n=4)	14.14	13.60	13.06	13.46	12.92	12.38	12.33	11.79	11.25