# Mechanosynthesis of supersaturated ternary solid solutions $(FeCo)_{100-x}Sn_x$ and their ordering by annealing at low temperature

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## Abstract

Iron-cobalt alloys have exceptional magnetic properties and are mechanically relatively strong [1]. Near-equiatomic FeCo alloys are bcc (A2) below ~1250K [1]. They order to a CsCl type structure (B2) at temperatures below ~1000K. A possible way to study alloys which tend to order is to prepare them by high-energy ball-milling HEBM from mixtures of elemental powders [2]. The as-milled alloys are generally in a metastable disordered state and may be ordered by annealing at well-chosen temperatures. We investigated recently the synthesis of metastable ternary alloys $(FeCo)_{100-x}Sn_x$ (x~ 0-33 at%) by HEBM [3, 4, 5]. The ternary system Fe-Co-Sn is essentially uninvestigated. The equilibrium solubility of Sn in FeCo (A2 or B2) is ~ 1 at% [6].

Milling of powder mixtures of Fe, Co and Sn was performed in argon atmosphere using a planetary Fritsch Pulverisette P6 mill. Alloys were annealed at 673K for 15h in quartz tubes sealed under vacuum. The evolution of the alloying process and the annealed alloys were characterized by X-ray and neutron diffraction and by $^{57}$Fe and $^{119}$Sn Mössbauer spectroscopy.

X-ray diffraction patterns of ground powders show the presence of nanocrystalline disordered bcc phases (grain size ~4-8 nm). The lattice parameter a(x) increases steadily with Sn content till x ≤ 25 in a way fully consistent with the dissolution of Sn in FeCo as discussed in [3, 4, 5]. For alloys with Sn contents of 25 and 33 at% bcc Fe-Co-Sn alloys coexist with nanocrystalline hexagonal $Co_3Sn_2$ (see too figure 1). The maximum solubility of Sn in near-equiatomic Fe-Co is thus less than 25 at% Sn in our milling conditions, being of the order of 20 at% Sn.

Figures 1 and 2 present room temperature (RT) $^{57}$Fe and $^{119}$Sn Mössbauer spectra of as-milled alloys (FeCo)Snx (10h milling) and those of as-milled alloys annealed at 673K for 15h. Figure 3 shows the RT hyperfine magnetic field distributions (HMFD), P(H), of $Fe_{44}Co_{44}Sn_{12}$ milled for 10h and then annealed at 673K for 15h. Neutron diffraction patterns are displayed in Figure 4 for $(FeCo)_{100-x}Sn_x$ (6 ≤ x ≤ 25) alloys milled during 10h and then annealed at 673K for 15h.

The average $^{57}$Fe HMF decreases when the Sn content increases in the as-milled state (fig. 1 left). The decrease is much less for annealed alloys (4≤x≤20) and the widths of the HMFD's are smaller for the annealed alloys (fig. 1 right). For x=12 (fig. 3 right) the average $^{57}$Fe HMF's are 31.7 T and 32.7 T in the as-milled and annealed alloy respectively. The $^{57}$Fe HMF's are not very sensitive to chemical order in these alloys. By contrast, the $^{119}$Sn HMF's show a strong sensitivity to chemical order when dissolved in B2 FeCo (~0.3 at.%Sn) [6]. The HMF is about 25 T for Sn atoms which sit on the Co sublattice while it is as small as ~0.7 T for those which sit on the Fe sublattice [6]. Figures 2 and 3 show that the $^{119}$Sn spectra vary strongly when the as-milled alloys are annealed at 673K. For x=12 (fig. 3 left) the average $^{119}$Sn HMF increases from 9.8 T to 16.3 T between the as-milled and the annealed states. The maximum $^{119}$Sn HMF (fig. 3), 24.5 T, is close to the value measured for Sn dissolved in perfectly ordered FeCo [6]. The ordering by annealing shown by $^{119}$Sn Mössbauer spectra is confirmed by neutron diffraction patterns (fig. 4) which evidence clearly the presence of (100) and (111) superlattice lines.

In summary, the maximum solubility of Sn in FeCo is considerably increased by HEBM. In our milling conditions the latter increases from ~1 at.% at thermal equilibrium to ~20 at. %. The metastable as-milled alloys are bcc and disordered. They order by annealing at moderate temperatures (here 673K) for any Sn content less than 20 at.%.

## References

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## Figures

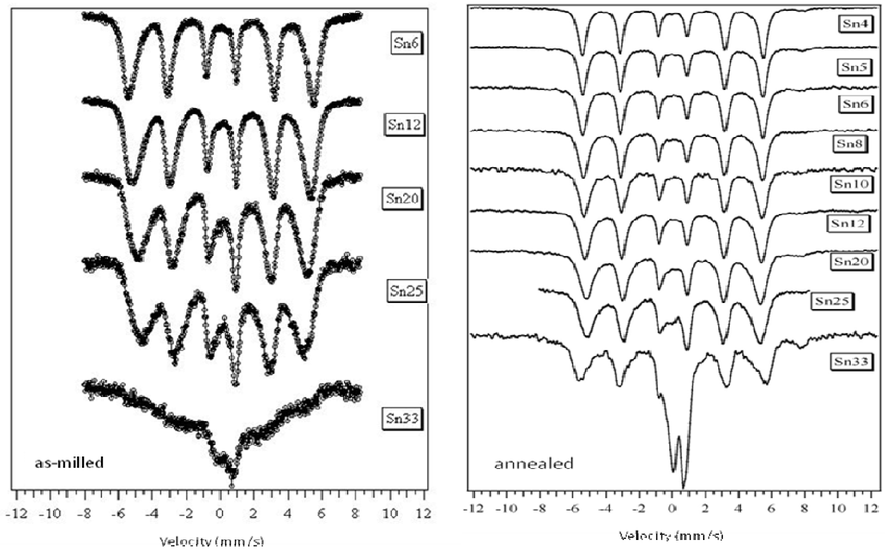


**Figure 1**- RT $^{57}Fe$ Mössbauer spectra of mechanically alloyed (FeCo)Snx: as-milled (left) and annealed at 673K (right)

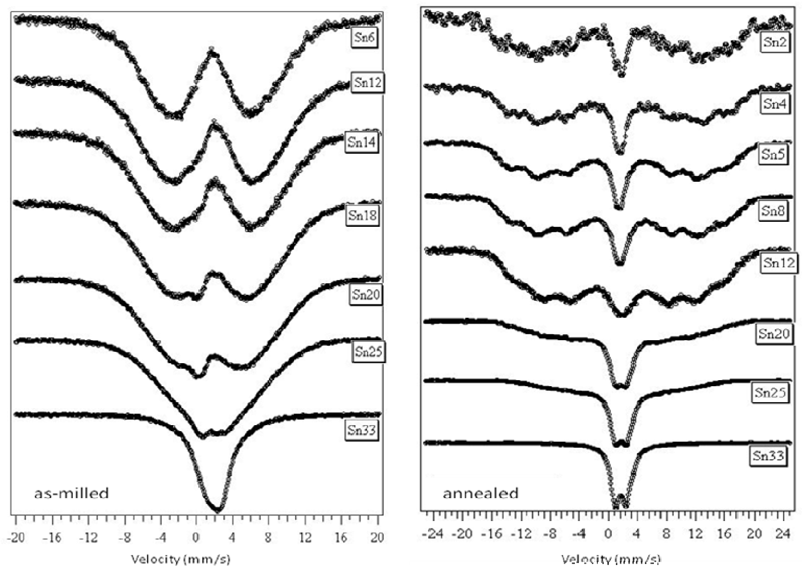


**Figure 2**- RT $^{119}Sn$ Mössbauer spectra of mechanically alloyed (FeCo)Snx: as-milled (left) and annealed at 673K (right)

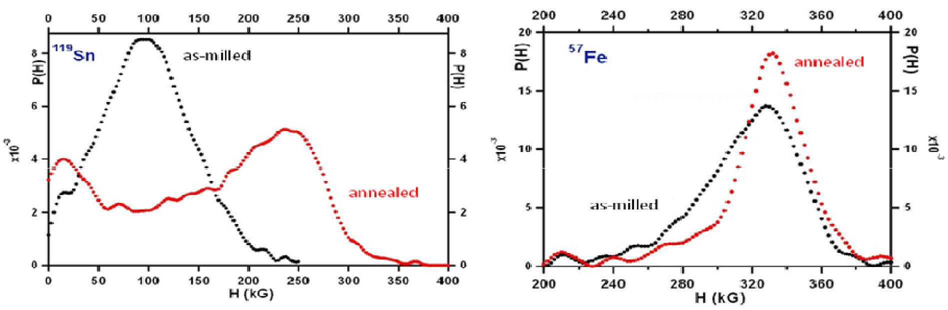


**Figure 3**- RT hyperfine magnetic field distributions ($^{119}Sn$: left, and $^{57}Fe$: right) of $(FeCo)_{88}Sn_{12}$ alloy, as-milled and annealed

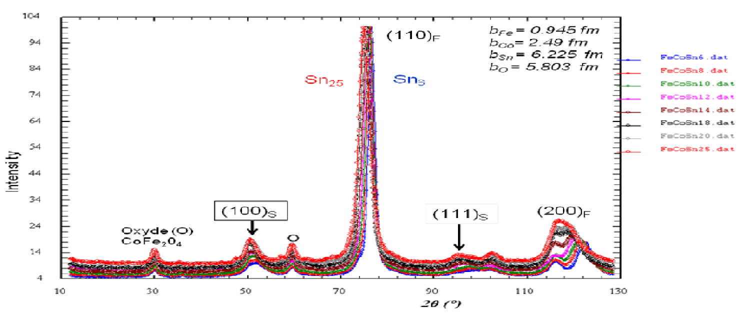


**Figure 4**- Neutron diffraction patterns of $(FeCo)_{100-x}Sn_x$ ($6 \le x \le 25$) alloys milled during 10h and then annealed at 673K for 15h.