Mössbauer spectroscopy and X-ray diffraction studies of ball-milling-induced transformations of a near-equiatomic FeV sigma phase: Influence of oxygen

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Abstract

^{57}Fe Mössbauer spectroscopy and X-ray diffraction were used to study the structural changes induced by ball milling a coarse-grained $Fe_{48.1}V_{51.9}$ at% sigma phase in a vibratory mill in argon with a frequent gas renewal. The sigma phase transforms into a bcc alpha phase till 140 h of milling. Mössbauer spectroscopy also shows the presence of an amorphous phase. Further, X-ray diffraction and Mössbauer spectroscopy reveals the presence of a corundum type oxide $(V_{1-x}Fe_x)_2O_3$ and of a spinel FeV_2O_4 in samples milled for 140 h and longer. Mössbauer spectroscopy clearly shows that the spinel phase starts to form after 140 h of milling. Oxidation is progressive and occurs first via an unmixing process which deprives the Fe–V bcc matrix of vanadium atoms.
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1. Introduction

According to the Fe–V phase diagram, a disordered bcc solid solution (alpha phase) is formed over a broad concentration range at high temperature but is interrupted at temperatures below 1525 K by the presence of the sigma phase which is tetragonal, for near equiatomic compositions [1]. A similar brittle phase, also formed in Fe–Cr alloys, is for instance detrimental to their mechanical behavior. A metastable ordered compound FeV with a structure of the B2 type (CsCl) is rather easily formed [1–3].

In nanocrystalline materials, phase transformations may differ from those of classical materials (transformation kinetics, metastable phases, etc.). Differences were reported, for instance, for Fe–Cr and Fe–Cr–Sn alloys [4,5] and for nearly equiatomic Fe–V alloys for which the formation of a metastable B2 alloy competes with that of a sigma phase [2].

Phase transformations driven by plastic deformation (ball milling, severe plastic deformation, cold rolling, etc.) are both of fundamental and applied interest [6–13].

Mechanical alloying of concentrated blends of Fe and V powders in a conventional ball mill, in argon atmosphere, yields a bcc alpha phase instead of sigma although it is stable at 300 K [14,15]. Further, an amorphous Fe–V alloy [16] or a mixture of an alpha phase and of an amorphous phase [17] were also reported to form by mechanically alloying. Ball milling of the alpha FeV phase transforms it into an alpha phase, in argon [13,14] or in vacuum [7,8].

However, a contamination of the ground powders by residual gases or by the materials constituting the milling tools, may drive the transformation to a final state which differs from the one that would be reached by the sole action of shearing.

In the present paper, we describe the influence of oxygen on the evolution of a nearly equiatomic Fe–V alpha phase when it is ground in a vibratory mill in argon with a frequent gas replacement.

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2. Experimental

A sigma phase $Fe_{48.1}V_{51.9}$ at% alloy was ball milled in a Fritsch P0 vibratory mill. The starting alloy was prepared by melting together, in argon, appropriate amounts of Fe and V in an induction furnace. The composition is close to that studied by Bakker et al. [7,8]. The as-cast alloy consists of a bcc phase. The sigma phase was then formed by annealing the as-cast alloy in vacuum at 1000 °C for 100 h. The brittle sigma phase was finally powdered with a pestle in an agate mortar. A mass of about 5 g of alpha-FeV was ball milled in accumulated milling times under argon atmosphere in a Fritsch P0 mill working at its maximum amplitude of vibration (3 in. scale).

X-ray diffraction (XRD) was performed at room temperature (RT) using CuKα radiation ($\lambda = 0.15406$ nm) to characterize the microstructural changes induced by ball milling.

Mössbauer spectroscopy was also used to follow the phase evolution. ^{57}Fe spectra were recorded at RT in a transmission geometry using a standard constant acceleration spectrometer. A ^{57}Co source in Rh matrix with a strength of ≈ 25 mCi was used. The spectra were analyzed by a constrained Hesse–Rübartsch method [18], which yields a hyperfine magnetic field distribution. Lorentzian line-shapes were employed in this procedure. The ^{57}Fe isomer shifts are given with respect to α-Fe at RT.

Differential scanning calorimetry was used to study the transformations of the samples milled for 140 and 200 h which occur during heating in an argon flow from RT to 900 °C with a heating rate of 40 °C/min.

3. Results and discussion

Chemical compositions were determined by microprobe analysis. They are $Fe_{48.1}V_{51.9}$ at% and $Fe_{52.3}V_{47.7}$ at% for the starting sigma phase and for the final sample milled for 200 h, respectively. The oxygen content of the latter sample is at least 6 wt%. Contamination by steel and by oxygen is thus evidenced.

Fig. 1 shows the XRD patterns of FeV after different milling periods. After 5 h of milling, the main effect is the broadening of the XRD peaks of the starting sigma phase which reveals a refinement of the mean crystallite size. After 30 h, a pattern of the bcc phase is already observed. Ground samples remain bcc for longer milling times but the peaks are broadened due to a reduction of crystallite size and to the effect of strain. The formation of the bcc phase by milling a near-equiatomic sigma FeV phase was already reported by Bakker et al. [7,8]. For prolonged milling, from 160 to 200 h, we observe that a corundum-type oxide $(V_{1-x}Fe_x)_2O_3$ and a spinel FeV_2O_4 form.

Fig. 2 shows RT ^{57}Fe Mössbauer spectra for samples milled for the indicated periods. The starting sigma phase is paramagnetic at RT with a mean isomer shift $\langle IS\& \rangle = -0.20$ mm/s. With increasing milling time, a magnetic component appears. It represents 72% of the spectral area at 140 h of milling. Its mean hyperfine field, $\langle B \rangle$, first
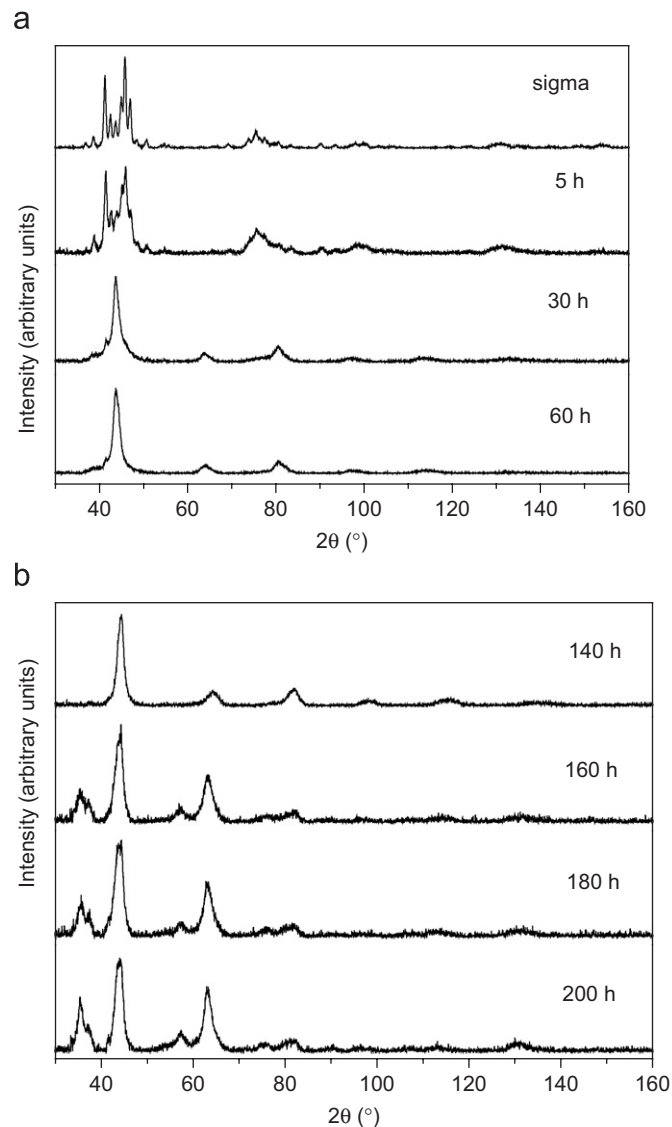

Fig. 1. X-ray diffraction patterns of an FeV sample milled for the indicated periods. The top pattern is that of the starting tetragonal sigma phase.

increases, up to 26.8 T for 180 h of milling. Then, it decreases to 18.7 T in a sample milled for 200 h. Between ~30 and 120 h of milling, the hyperfine magnetic field distribution (HFMD) of that component shows a narrow peak at a field which is identical with or close to the field of alpha-Fe at RT and a broad and almost featureless band from ~10 to ~30 T (Fig. 2) as seen also for HMFDs of binary mixtures of elemental powders of Fe and of various T elements during the early steps of the mechanically alloying process [19,20]. The fact that HMFDs with such features are observed here is somewhat surprising as Fe and V atoms are already chemically combined at the atomic scale in the starting sigma phase while they are unmixed in the starting elemental powder blends of the aforementioned $Fe_{1-x}T_x$ systems [19,20]. The latter results were consistent with nanometer sized Fe-rich regions separated from either T-rich zones or other phases already
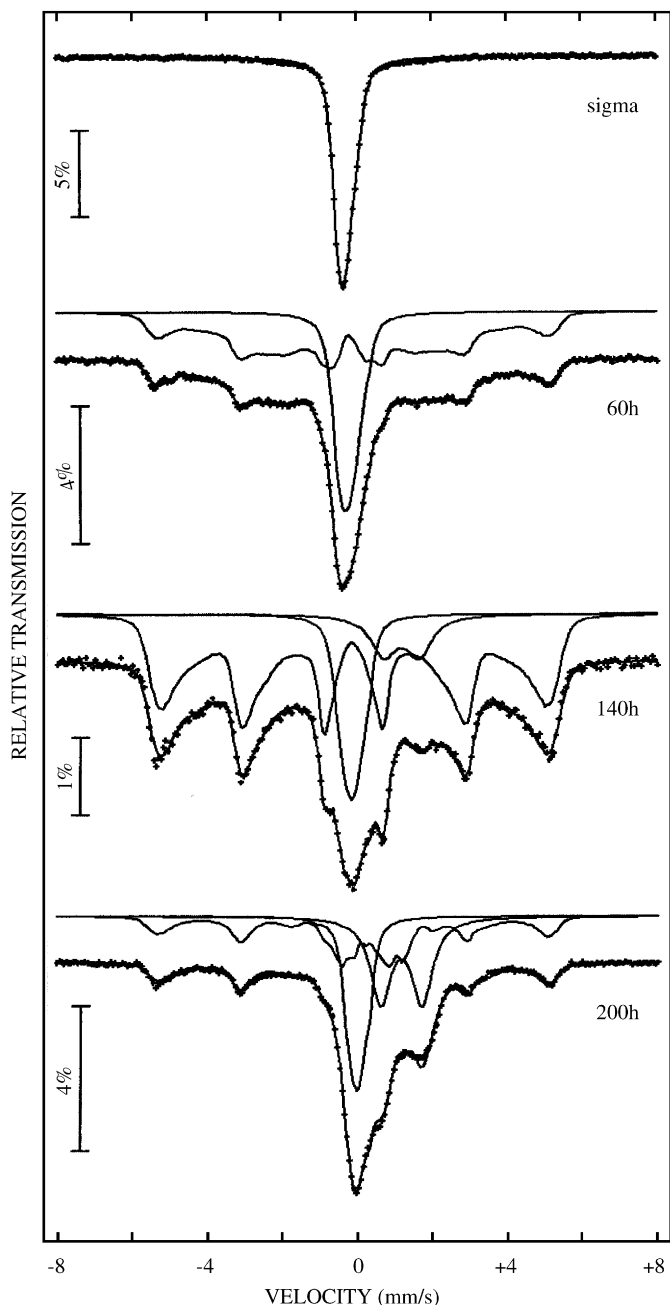
Fig. 2. ^{57}Fe Mössbauer spectra of the FeV sigma phase milled for the indicated periods.

formed by very rough interfaces, characterized at the atomic scale by distributions of lengths of flat regions and of step heights [19,20]. In any case, the transformation by milling of the FeV sigma phase into a bcc phase in the present conditions is not polymorphic. In the case of a transformation without composition change, we would expect to observe a spectrum similar to the one shown by Fig. 6 of [21] for an as-milled bcc $Fe_{53}V_{47}$ alloy for which the mean field of the sole magnetic part is 14.3 T at RT [21]. Its HMFD consists essentially of a narrow peak at ∼1 T, which accounts actually for the intense central peak of the spectrum, and of a broad Gaussian-like peak centered on a

field of 14.3 T. The bcc phase which forms here is clearly heterogeneous. The large value of the magnetic fraction (72% of the total area for 140 h of milling) rules out the hypothesis that a significant role might be played by iron contamination in the observed evolution.

The relative area of the paramagnetic component decreases with milling time and its mean isomer shift ⟨IS⟩ changes, being already −0.039 mm/s for 140 h of milling (18% of the spectrum), suggesting that it is no longer related to the sole sigma phase but also to an additional amorphous phase [17]. The spectrum of the sample milled for 140 h was fitted with a supplementary doublet with a quadrupole splitting QS = 0.96 mm/s and an isomer shift IS = 1.3 mm/s. This doublet represents 10% of the spectral area and is attributed to the presence of a ternary oxide. For longer milling times, the relative area of the paramagnetic subspectrum and the mean ⟨IS⟩ increase, being 29% and 0.10 mm/s, respectively, for 200 h of milling. For this sample the doublet represents 33% of the area and has QS = 1.11 mm/s and IS = 1.29 mm/s. These values are consistent with the presence of a spinel FeV_2O_4 as deduced from the XRD pattern. The formation of such an oxide is consistent with the large amount of oxygen present in the sample. The progressive increase of the isomer shift of the paramagnetic component may be attributed to the formation of a corundum-type oxide, as deduced from XRD, $(V_{1-x}Fe_x)_2O_3$ whose IS at RT are 0.38 and 0.51 mm/s for $x = 1$ and for $x = 0.3$, respectively [22]. Differential scanning c alorimetry traces obtained for the samples milled for 140 and 200 h show a peak at around 600 °C. We have annealed the samples milled for 140 and 200 h isothermally at 600 °C. After 6 min of annealing, Mössbauer results show that the amorphous phase in the sample milled for 140 h crystallizes as the area of the central single line is drastically reduced.

From XRD patterns and RT Mössbauer spectra, we conclude that the sample milled for 200 h and annealed at 600 °C is composed of four phases, namely bcc-Fe, fcc-Fe, a corundum type oxide, $(V_{1-x}Fe_x)_2O_3$ with x of the order of 0.3, and a spinel FeV_2O_4. These results will be described in more detail in a forthcoming paper.

4. Conclusions

A near-equiatomic FeV sigma phase transforms by milling in our conditions first into a bcc alpha phase, which is magnetic at RT. RT Mössbauer spectra show not only the appearance of a magnetic heterogeneous bcc phase but also reveal the presence of a single line due to a non-magnetic phase which differs from the sigma phase. The latter component is due to an amorphous phase until 140 h of milling, but beyond, it can no longer be attributed solely to an amorphous phase as it does not disappear at the crystallization temperature revealed by calorimetry. Ternary oxides with corundum and spinel-type structures start to form after 160 h of milling as evidenced by XRD. An Fe doublet corresponding to Fe^{2+} in a ternary oxide is indeed concomitantly observed in Mössbauer spectra.

Their formation is due to the high oxygen contents accumulated in the samples milled for very long times because of periodic vial openings for argon replacement. Further studies are underway to characterize the behavior of a near equiatomic Fe–V sigma phase when milled in vacuum.

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