Magnetic study of amorphization of ball-milled FeCr alloys

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Abstract. The magnetization of sigma and alpha FeCr samples ball-milled in vacuum is reported as a function of milling time. The change of the saturation magnetization with milling time is non-monotonic in the sigma series: after an initial increase due to the transformation to the magnetic alpha phase, then it decreases as in the alpha phase. The results are fully consistent with our previous results from Mössbauer spectroscopy that established the formation of an amorphous phase.

1. Introduction

Ferritic steels with high Cr concentration are commonly used in industry due to their good corrosion resistance, their mechanical properties and their relatively low cost. FeCr alloys are used for instance in advanced applications, for instance in oil refineries and in power plants [1].

The sigma phase of these alloys (near-equiaxial compositions) drastically deteriorates their properties. This phase is formed from the bcc α-phase at temperatures between 800K and 1100K, for equiaxial compositions. The behaviour under ball-milling of a sigma Fe-Cr phase was studied earlier by Bakker [2, 3]. The sigma phase is not stable and was concluded to transform solely into a bcc nanostructured phase from X-ray diffraction patterns. However, this interpretation does not account for the variation of the low-temperature magnetisation with milling time. The magnetisation expected for a coarse-grained bcc Fe-Cr alloy with the same composition is about 2 μB/at. Fe, which it is not expected to deviate much from that value in nanostructured alloys, differs strongly from the reported value of 1.2 μB/at. Fe [2, 3]. In our previous studies, besides the α-phase, an amorphous phase was shown to form when milling in vacuum a FeCr σ-phase for periods longer than 20h. An amorphous phase, evidenced by Mössbauer spectroscopy, forms too, but at a much slower rate than the latter, when milling the α-phase, instead of the σ-phase, in vacuum [4]. This amorphization, which is favored by residual gases, is however an intrinsic phenomenon, as reported before [5].

We have performed a magnetization study on samples milled for different periods starting from sigma and alpha FeCr structures. In this work we present the analysis of the change of the saturation magnetization and we analyze the consistency with our previous Mössbauer results.

2. Experimental

A Fe51.8Cr48.2 at% alloy was prepared by melting together appropriate amounts of Fe and Cr in an induction furnace. Then the sigma phase was obtained by annealing the as-cast bcc alloy in vacuum at 700°C for 100 h [4, 6]. Another bcc Fe49.7Cr50.3 at% sample was prepared similarly in an induction
furnace. Ball-milling of both phases (sigma and alpha) was performed in vacuum in a vibratory Fritsch P0 mill working at its maximum amplitude of vibration (3 in scale). The mill consists of a hardened steel vial with a hardened steel ball whose diameter is 5 cm and whose mass is 500 g. A mass of about 5 g of FeCr was ball-milled in accumulated times in the same conditions as those reported previously [4]. In this way two series of samples were obtained, in the following referred as sigma or alpha (milling time), according to the initial state. Milling times up to 200h and 1500 h were applied to the sigma and alpha phase series, respectively.

X-ray diffraction (XRD) was performed at room temperature (RT) using Cu K\textsubscript{$\alpha$} radiation ($\lambda$ = 0.154184 nm) to characterize the microstructural changes. $^{57}$Fe Mössbauer 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 \approx 20 mCi was used. The spectra were analysed by a constrained Hesse-Rübertsch method [7] which yields a hyperfine magnetic field distribution, $P(B)$. The $^{57}$Fe isomer shifts are given with respect to $\alpha$-Fe at RT.

Magnetization measurements were carried out in a cryogen-free vibrating sample magnetometer (VSM) of CRYOGENIC Instruments with magnetic field up to 10 Tesla and temperature in the range 1.7K up to 320K. The saturation magnetizations were measured at T=5K.

3. Results and Discussion
The main transformation evidenced by XRD was that of the sigma to the alpha phase, as seen in previous works done in milling the sigma phase [6, 8]. The modifications of the alpha phase diffractograms consist merely of an increase of the peak widths, as also seen previously [6, 9]. By contrast, the substantial difference between the magnetic behaviors of the alpha and sigma phase allows to evidence an evolution of the ground materials. Figure 1 shows the isothermal magnetization curves at 5K for the samples of both sigma and alpha series as a function of milling time.

![Figure 1](image-url)
The major initial transformation of the sigma into the alpha phase can be readily observed in the figure, with the increase of the magnetization values with milling time up to a maximum of about 1.8 $\mu_B$/Fe atom. For times longer than about 60 h, the magnetization decreases. On the other hand, for the alpha phase series, the tendency is a progressive decrease of the magnetization values.

To extract quantitative information on the magnetic phases the magnetic field dependence of the approach to magnetization saturation has been modelled by including the combination of a linear term in the field (arising from paramagnetic susceptibility) and a reciprocal field dependence, associated to an inhomogeneous contribution [10]. Other contributions associated with anisotropy [11] were not considered. The milling time dependence of the saturation magnetization $M_S(t)$ thus obtained for the two series is presented in Figure 2.

![Figure 2](image_url)

**Figure 2.** Milling time dependence of the saturation magnetization for the sigma (left) and alpha (right) series. Open triangle symbols represent the annealed samples.

The decrease of the saturation magnetization can be associated with the formation of the amorphous phase which was evidenced by Mössbauer spectroscopy as an intrinsic phenomenon [4,5,6]. A direct comparison of the results from the two techniques is shown in figure 3. The insets show the ferromagnetic area fraction $A_F(t)$, as obtained from Mössbauer spectra taken at RT, as a function of milling time for the same samples of the sigma and alpha phase series [4,5,6]. The fraction $A_F(t)$ represents essentially the fraction of Fe atoms in the magnetically ordered alpha phase. In the Mössbauer spectra fits it has been assumed that the Lamb- Mössbauer factor was the same in the sigma, alpha and amorphous phases. A fraction of about 50% is reached in both cases. It approaches a constant for the bcc phase milled during long times. A dynamical equilibrium state is reached: in our milling conditions, it consists in a mixture of an alpha phase and of an amorphous phase [5].

The linear relations between the magnetic saturation $M_S(t_m)$ and the Mössbauer area $A_F(t_m)$ are clearly seen for both series in the main plots of figure 3. The slopes of the lines are 2.06 and 2.14 $\mu_B$/Fe for the sigma and alpha series, respectively. These values correspond basically to the ones obtained in the annealed samples, for which $A_F=1$. They confirm that the Fe moment of the alpha phase does not depend in an essential way on the crystallite size. It should also be noted that the correlation encompasses the non-monotonous behavior of the sigma series. The deviations observed at lower magnetizations (and fractions) for the sigma phase series are due to the additional contribution of the sigma phase, since the magnetic measurements were taken at 5K, below the ordering temperature of the sigma phase (~20K for this composition [12]), while the Mössbauer spectra were taken at RT, at which only the alpha phase is ordered. The severe reduction of the saturation magnetization to about half the maximum value after long milling times, which is accompanied by quantitatively the same
reduction of $A_F$ (with the increase of the paramagnetic peak) cannot be simply associated to a reduction of the crystallite size of the alpha phase, which would maintain higher magnetization values, but instead to the formation of an amorphous phase.

In conclusion, the transformations of the sigma and alpha FeCr phases with long ball-milling times were followed by magnetization measurements. A good agreement was found with the Mössbauer spectroscopy study, which established the formation of an amorphous phase.

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