Long ball-milling of bcc-FeCr at different injected powers: amorphization and partial crystallization

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Abstract. The structural changes induced by long ball-milling of the α-FeCr bcc phase in vacuum in a vibratory Fritsch P0 mill at two different amplitudes, were studied by Mössbauer spectroscopy and X-ray diffraction. In previous studies we showed that amorphization is an intrinsic phenomenon which occurs when grinding alpha and sigma phases of near-equatomic FeCr alloys. With long periods of milling at different injected powers, we observe a phenomenon of amorphization-partial crystallization-amorphization which is reminiscent of the cyclic amorphization-crystallization phenomenon that takes place in various ball-milled alloys.

1. Introduction

The importance of Fe–Cr alloys is known both in science and industry. Fe–Cr binary alloys are important from both applied and fundamental points of view. Among the various applications, we can select for instance their use in advanced nuclear reactor applications, due to their corrosion resistance combined with good mechanical properties. Indeed, these alloys are a base for low activated ferritic-martensitic steels widely used as structural materials for fission reactors and being now considered as candidate materials for future fusion reactors. Ferritic-martensitic steels provide an attractive alternative to austenitic stainless steels because they demonstrate a very high resistance to swelling up to neutron irradiation damage doses of 200 displacements per atoms [1].

In previous studies, we showed that amorphization is an intrinsic phenomenon which is observed when grinding alpha and sigma phases of near-equatomic FeCr alloys. Indeed, amorphization occurs even in presence of low to very low levels of oxygen, a gas which is known to favour it in concentrated Fe–Cr alloys [2]. In the following, we report on the structural changes, as evidenced by Mössbauer spectroscopy and X-ray diffraction, which occur when ball-milling the α-FeCr bcc phase in vacuum in a vibratory Fritsch P0 mill at two different injected powers. A phenomenon of amorphization-partial crystallization-amorphization behaviour that occurs when milling the α-FeCr bcc phase for long periods is described.

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2. Experimental

A bcc Fe\textsubscript{42.9}Cr\textsubscript{56.9} at% alloy was prepared by melting together appropriate amounts of Fe and Cr in an induction furnace. Ball-milling of this alpha phase was performed in vacuum in a vibratory Fritsch P0 mill. 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 [2]. Tiny amounts of powders were removed at different milling times to be characterized. In this way two series of samples were obtained, depending on the amplitude of vibration of the mill (maximum: $A \sim 3$ in scale; and medium: $A \sim 2$–2.5 in scale). Milling times up to 1500 h and 2500 h were applied to series 1 and 2, respectively.

X-ray diffraction (XRD) was performed at room temperature (RT) using Cu K\textsubscript{α} radiation ($\lambda = 0.154184$ nm) to characterize the microstructural changes. \textsuperscript{57}Fe Mössbauer spectra were recorded at RT in a transmission geometry using a standard constant acceleration spectrometer. A \textsuperscript{57}Co source in Rh matrix with strength of $\sim 20$ mCi was used. The spectra were analyzed by a constrained Hesse-Rübartesc method [3] which yields a hyperfine magnetic field distribution, $P(B)$. The \textsuperscript{57}Fe isomer shifts are given with respect to $\alpha$-Fe at RT.

3. Results and Discussion

The composition of the alpha phase (series 1; $A \sim 3$) milled for 100 h, 400 h, 750 h and 1500 h was obtained to be Fe\textsubscript{55.7}Cr\textsubscript{44.3} at%, Fe\textsubscript{55.3}Cr\textsubscript{44.1} at%, Fe\textsubscript{56.0}Cr\textsubscript{44.0} at% and Fe\textsubscript{56.9}Cr\textsubscript{33.1} at%, respectively. The oxygen content was equal to 0.2 at%, 0.7 at%, 0.8 at% and 1.0 at%, respectively. For series 2 ($A \sim 2.0$ to 2.5), the composition of the alpha phase is Fe\textsubscript{57.1}Cr\textsubscript{42.9} at% and Fe\textsubscript{58.9}Cr\textsubscript{42.0} at%, after 960 h and 2430 h of milling, respectively. These compositions were estimated from the hyperfine magnetic field values [4,5] and are close to those obtained from microprobe analysis of some samples. The iron content increases due to contamination by the milling tools, but the oxygen, despite its increase, remains small even after 1500 h hours of milling.

XRD patterns of the alpha phase as a function of milling time only show the broadening of the bcc peaks (not shown). Figure 1 shows RT \textsuperscript{57}Fe Mössbauer spectra for different times of milling of the alpha phase, of series 1 and 2. A paramagnetic contribution, with an isomer shift $\langle IS \rangle = -0.078(1)$ mm/s (series 1) and $\langle IS \rangle = -0.098(1)$ mm/s (series 2), consistent with that reported for clean co-evaporated Fe–Cr amorphous phases [6], arises in the middle of the spectra. For the magnetic part, the mean hyperfine magnetic field $\langle B \rangle$ is almost constant during milling with $\langle B \rangle \sim 17.6$ T, $\langle IS \rangle = -0.096$ mm/s and $\langle B \rangle = 18.2$ T, $\langle IS \rangle = -0.082$ mm/s, for series 1 and 2, respectively. The calculated field is 17.5 T for the starting alloy and 20.0 T of the composition of alloys milled for 500 h and longer. As milling decreases the field by about $\sim 2$ T [5], the expected field of $\sim 18$ T agrees with experiment.

Figure 2 shows the paramagnetic area fraction $A_p(t)$, as obtained from Mössbauer spectra, as a function of milling time for the alpha phase for both series. The fraction $A_p(t)$ represents essentially the fraction of Fe atoms in the amorphous phase. It is close to the fraction of amorphous phase as that phase and the bcc phases have similar compositions. That fraction is in very good agreement with that we deduced from magnetization measurements.

When milling at the maximum amplitude of vibration ($A \sim 3$ in scale), we observe that the steady increase of the amorphous phase fraction is interrupted at about 750 h of milling (figure 2) where a partial crystallization of the amorphous phase takes place as evidenced by Mössbauer spectra. Then, amorphization starts again but at a slower rate. Cyclic amorphization-crystallization behaviour takes place in various alloys when subject to ball-milling (for instance Al-Zr, Co-Ti [7]) or to e.g. accumulative roll-bonding (for instance Zr based intermetallic alloys [8]). Although, we don’t observe here a full cycle, because of the very long milling times needed at the injected power level at which the mill works, the amorphization-partial crystallization-amorphization behaviour that we observe is reminiscent of that cyclic phenomenon.

When the $\alpha$-FeCr phase is milled with an amplitude of vibration smaller than the previous one ($A \sim 2$–2.5 in scale), the area fraction of the Mössbauer spectra associated with Fe in the amorphous phase
increases monotonically (figure 2). In contrast to the previous experiment, the amorphous phase does not crystallize. Except for the amorphization-partial crystallization-amorphization behaviour, figures 1 and 2 show that milling times scale approximately as $A^2$.

**Figure 1.** RT $^{57}$Fe Mössbauer spectra for different times of milling of the alpha phase: (a) $A = 3$ and (b) $A = 2$ to 2.5.
Figure 2. Evolution of the amorphous paramagnetic fraction obtained from Mössbauer spectra with grinding time: (a) $A = 3$ and (b) $A = 2$ to 2.5.

That experiment confirms that eventual detrimental contaminations by steel or by residual gases do not play an essential role in the phenomenon that we observe, as also predicted before [9]. Oscillatory phenomena were reported to occur during ball-milling. For instance, the nanocrystalline fraction in cryomilled zinc, the fraction of bcc and hcp phases in ball-milled Co (see [10] and references therein). The existence of cyclic amorphization is predicted theoretically by Johnson et al. [10] as a function of the materials parameters and of the input power.

In conclusion, the transformations of alpha FeCr with long ball-milling times at two different injected powers were followed by Mössbauer spectroscopy and X-ray diffraction. An amorphization-partial crystallization-amorphization behaviour is reported for the higher injected power. Experiments at still higher injected powers to shorten the milling times are worth being performed to know if that phenomenon is indeed cyclic. The injected power must however be not too high because of the risk to bypass the formation of the amorphous phase.

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