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Comment on ''Grain-boundary structure and magnetic behavior in nanocrystalline ball-milled iron''

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Del Bianco, Hernando, Bonetti, and Navarro [Phys. Rev. B **56**, 8894 (1997)] published Mössbauer spectroscopy and magnetization measurements on ball-milled iron. The observed changes were attributed to the increased grain-boundary fraction and this was supported by measurements on heat treated samples. The recovery of the physical properties of bulk iron after the heat treatments was attributed to grain growth and atomic rearrangement at the grain boundaries. The effect of possible impurities (e.g., Cr originating from the milling tools) was not considered in any respect. We show that the results on the heat treated samples do not exclude the possibility of explaining some features of the Mössbauer hyperfine field distribution by impurities instead of a reduced hyperfine field of the grain-boundary atoms. Heat treatments of small grain size $Fe_{95}Cr_5$ samples were performed under argon and in a vacuum of 10^{-7} Pa. Significant reduction of the Cr content of the alloy phase can be observed at elevated temperatures, which is explained by Cr_2O_3 formation in the surface region. [S0163-1829(99)04821-3]

Del Bianco *et al.*[1] reported experimental results on iron powders mechanically ground for different times in a hardened tool steel vial. The observed changes in the Mössbauer spectra and in the bulk magnetic properties were interpreted as being due to changes in the grain size and in the grain-boundary structure. Besides reducing the grain size and creating several kind of defects in the material, mechanical grinding also incorporates impurities. It is well known that the amount of the impurities can be as much as a few atomic percent during a one day milling[2] depending on the milling intensity and the hardness of the milling tools and the milled material. Separating the effect of the impurities is a basic requirement when nanocrystalline properties are discussed, however, in the paper of Del Bianco *et al.* no reference is made to any impurity analysis. In fact, the Mössbauer spectroscopy results reported for 32 h milled powder appear to show the presence of a Cr impurity. While the results for heat treatment of the 32 h powder can be interpreted as showing that there was no significant level of impurities, since the properties of pure Fe were recovered, we can demonstrate that this behavior is not inconsistent with their samples containing a small amount of Cr.

The use of steel milling tools can introduce significant levels of Cr impurity into the milled material, as is obvious from previous reports[3–5] on ball-milled iron. The hyperfine field distributions[1] determined for the 32 h powder both in the as received state and in the early stage of the heat treatments (at 695 K and 770 K) contain a peak at around 30 T, which is not discussed in the paper, but it is certainly attributable[6] to the presence of a significant Cr impurity. It is also important to recognize that the 30 T peak appears in the hyperfine field distribution at that stage when the resonant area of the distribution attributed to grain boundaries is doubled, though the change of the average grain size is minimal and does not exceed the experimental error. This component is either not detectable or quite insignificant in samples milled for shorter times. It supports, as well, that the 30 T peak belongs to Cr impurities. If one analyzes the results this way it turns out that the Cr content of the 32 h sample can be in the 0.3–0.5 at. % range. (The component fitted by the hyperfine field distribution is 17.4% of the total spectrum. It is estimated from Fig. 1 of Ref. 1, that the peak around 30 T makes it about 20–25% of this distribution and it should be further divided by the bcc coordination number.)

We also performed a set of milling of pure iron in a low energy impact tube mill.[5] Impurity analysis was performed by energy dispersive x-ray spectroscopy (EDX) and x-ray fluorescent analysis. The average grain size determined by x-ray diffraction was below 10 nm after 160 h of milling. Mössbauer spectrum of the sample ball milled for 470 h is shown in Fig. 1(a). It was fitted by a binomial distribution allowing first and second neighbors according to the bcc structure, and in accordance with the impurity analysis 2 at. % Cr content was calculated. The small peak in the center of the spectrum which was not fitted by the binomial distribution most probably belongs to a high Cr content alloy

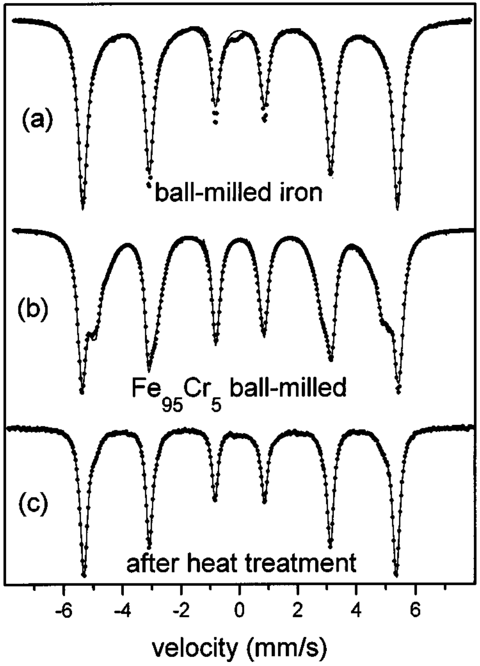

FIG. 1. Mössbauer spectra of (a) Fe powder ball milled for 470 h, (b) $Fe_{95}Cr_5$ sample prepared by ball milling a mixture of the elemental powders for 94 h, and (c) the $Fe_{95}Cr_5$ sample after heat treatment under argon at 970 K for 20 h. The spectra were fitted by binomial distributions allowing first and second neighbors according to the bcc coordination.

phase.[7] Recrystallization heat treatments were performed in a vacuum of 10^{-4} Pa, and similar to the results of Del Bianco *et al.*,[1] the Mössbauer spectra of the heat treated samples agreed well with those of unmilled iron in spite of the measured Cr content. It is well known[8] from corrosion studies that Cr has a very high affinity to oxygen and heat treatment at low oxygen pressure is used to form a protective Cr_2O_3 layer on the surface. Cr diffuses from the bulk to the surface and Cr_2O_3 is formed even in a vacuum of 10^{-7} Pa. In case of a small grain-size powder of Fe-Cr alloy this process might easily produce a complete depletion of Cr inside the grains. To check the significance of this process in our recrystallization heat treatment, a $Fe_{98}Cr_2$ alloy was annealed under identical conditions and the x-ray photoelectron spectroscopy spectra [ESA-31 Debrecen (Ref. 9)] was measured on the surface before and after annealing. The spectra showed that even in 70 nm depth from the free surface (70 minutes Ar^+ sputtering with 2 keV, 20 $\mu A/cm^2$) about 60% of the Cr atoms changed from metallic to oxide during our heat treatment. For a further check, Fe and Cr powder mixture and an Fe-Cr alloy ingot were ball milled in a tube mill working under vacuum for 94 h to produce small grain-size powder samples with $Fe_{95}Cr_5$ composition. The two kinds of samples showed identical Mössbauer spectra and that of the sample prepared from the powder mixture is shown in Fig. 1(b). Mössbauer spectra of this sample after a heat treatment under argon at 970 K for 20 h (similar to the annealing applied by Del Bianco *et al.*[1]) can be seen in Fig. 1(c). Both spectra were fitted by binomial distribution. This evaluation showed that the Cr content of the ball-milled sample agrees with the nominal concentration and has changed from 5 to 1 at. % during the heat treatment. The ball-milled sample was also heat treated in a high-vacuum (10^{-7} Pa) furnace at 870 K for 4 days. Reduction of the Cr content (to about 3 at. %) can be observed even in this case. It seems, however, that this reduction of the Cr content of the bcc phase does not occur under ball milling conditions. The Cr content determined from the Mössbauer spectra agreed well with the nominal one when $Fe_{100-x}Cr_x$ samples $(0.3<x<5)$ were prepared[10] by ball milling the elemental powders. Probably the effective temperature of the milling process is not high enough for the reaction to occur.

It is clear that there is a possibility of impurities contributing significantly to the changes in Mössbauer spectra arising from ball milling of Fe. Our results show that the recovery of bulk iron properties after heat treatment is not an unambiguous indication that differences observed in the Mössbauer spectra of coarse grain and ball-milled iron powders are merely caused by the enhanced grain-boundary contribution. Due to the small grain size, surface chemical reactions can play an important role during the heat treatment. Mössbauer spectroscopy is a very sensitive tool to detect impurities in the order of 0.1 at. % in bulk amounts of samples and without any special sample preparation method which could modify the sample. Under such circumstances the documentation of a careful analysis of all the possible impurities cannot be neglected when the Mössbauer spectra of such samples are discussed.

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