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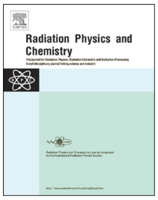

Generation of superparamagnetism in metallic α-iron by swift heavy ion irradiation

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HIGHLIGHTS

- Superparamagnetic iron was prepared by swift heavy ion irradiation.
- Superparamagnetic iron occurs together with amorphous iron.
- Occurrence of superparamagnetic iron was shown by 57Fe Mössbauer spectroscopy.

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ABSTRACT

^{57}Fe conversion electron Mössbauer spectroscopy was used to study the effect of swift heavy ion irradiation on electrochemically deposited metallic pure α-iron. We succeeded in preparing superparamagnetic iron by irradiating the electrochemically prepared thin α-iron films using 247 MeV Kr ions with a fluence of 1×10^{13} ion cm^{-2} which converted 50% of crystalline α-iron into amorphous and superparamagnetic phases, the latter being $>20\%$. The results are discussed in terms of the thermal spike model for the formation of the amorphous phase which could be essential for the formation of superparamagnetic iron.

1. Introduction

In our previous works we performed Mössbauer spectroscopic and XRD studies on the radiation effect of 246 MeV Kr, 470 MeV Xe and 710 MeV Bi ions on electrochemically deposited iron thin films (Kuzmann et al., 2006; Stichleutner et al., 2011). It was found that as a result of irradiation partial amorphisation of iron took place in the electrochemically deposited crystalline ferromagnetic α-iron coatings. The relative amount of the ferromagnetic amorphous phase increased with both ion energy and ion mass as well as with the fluence of irradiation. Besides ferromagnetic amorphous iron, another iron phase was also identified in the room temperature Mössbauer spectra of the swift heavy ion irradiated samples and was associated with superparamagnetic iron.

Superparamagnetism (Bean and Livingston, 1959; Guimarães, 2009; Coey, 2010) is a relaxation phenomenon observed below the Curie temperature in single domain ferromagnetic or ferrimagnetic nanoparticles/nanograins (Bødker et al., 1992; Pankhurst and Pollard, 1993; Brahma et al., 2002; Wilks et al., 2005; Fernández et al., 2008; Jafari et al., 2010; Sakamoto et al., 2010; Nomura and Reuther, 2011) (1–10 nm) where magnetisation can randomly flip between the opposite directions of the easy axis, provided that the thermal energy is sufficient to overcome the corresponding energy barrier. The mean time between flips is known as the Néel

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relaxation time (Néel, 1949; Brown, 1963; Knobel et al., 2008; Bedanta and Kleemann, 2009; Morup et al., 2010; Kolhatkar et al., 2013). Smaller nanoparticles/nanograins can be expected to exhibit a larger frequency of superparamagnetic relaxation. When the time window of the experimental method used to determine the magnetisation of superparamagnetic nanoparticle/nanograin ensembles is significantly longer than the Néel relaxation time, the detected magnetisation tends to average to zero, which is a typical characteristic of the superparamagnetic state (Lopez-Diaz et al., 2002). Superparamagnetic iron was originally found to form under natural circumstances in samples from the moon surface (Hafner, 1975; Housley et al., 1973; Housley et al., 1974). Superparamagnetic inclusions of metallic iron, some tens of nm in size, were formed in the amorphous rims of lunar regolith grains from solar-wind-reduced indigenous iron silicates by either radiation-induced lattice rearrangement, or micrometeorite-induced vaporisation and recondensation, or both (Kerridge, 1994).

However, a process to obtain superparamagnetism in metallic pure α-iron is still unknown. In this work we extended our study on the radiation effect of swift heavy ions on electrochemically deposited iron thin films by conversion electron Mössbauer measurements carried out at low temperature, in order to confirm the presence of superparamagnetic iron in our irradiated samples.

2. Experimental

The α-iron coatings were prepared using a constant current technique with a continuous flow electrodeposition cell plating system. The thin films were deposited on electro-polished pure copper substrates using the following electrolyte composition: $FeSO_4$ 0.2 mol dm^{-3}, Na-gluconate 120 g dm^{-3} and peptone 0.1 g dm^{-3}. The electrolyte was operated at 60 °C with a pH=7.0 and plating times of 20 min were used.

The swift heavy ion irradiation of electroplated α-iron was carried out with 246 MeV energy $^{86}Kr^{8+}$ ions with a fluence of 1×10^{13} ion cm^{-2} at room temperature, at a current density of 0.5 μA cm^{-2} and at a pressure of about 10^{-3} Pa, at the U-400 cyclotron of the Flerov Laboratory of Nuclear Reactions, JINR, Dubna, Russia.

Conversion electron Mössbauer measurements of as-deposited and irradiated α-iron samples were performed by conventional Mössbauer spectrometers (WISSEL) with flowing gas (96% He, 4% CH_4 at 293 K and purified helium at 15 K) proportional counters and ^{57}Co(Rh) sources of 1.85 GBq activity, at room temperature and at 15 K. For the 15 K CEMS measurement a cryostat (IwataniCryoMini D310) and counter assembly was used (Fukumura et al., 1991a; Fukumura et al., 1991b). The information can be obtained mainly from sample depths less than 100 nm (Kobayashi et al., 1993; Yonekura et al., 1983). Isomer shifts are given relative to α-iron. The evaluation of Mössbauer spectra was performed by least-square fitting of the lines using the MOSSWINN code (Klencsár et al., 1996). During the fitting procedure the amplitudes of 2nd and 5th lines of sextets were set to be independent, while independent linewidths for 1st and 6th, 2nd and 5th, 3rd and 4th line pairs were constrained.

3. Results and discussion

^{57}Fe conversion electron Mössbauer spectra of electrodeposited α-iron samples: (a) spectrum for as-deposited sample recorded at 293 K, (b) spectrum for sample irradiated with 246 MeV energy Kr ions with a fluence of 1×10^{13} ion cm^{-2} recorded at 293 K, (c) spectrum for irradiated sample recorded at 15 K are shown in Fig. 1. The Mössbauer parameters are shown in Table 1. The presented numerical results derived from Fig. 1a,b slightly deviate from those published in Ref. (Kuzmann et al., 2006) since we applied a different model for the evaluation of the spectra, resulting in a better quality of the fits in the present cases.

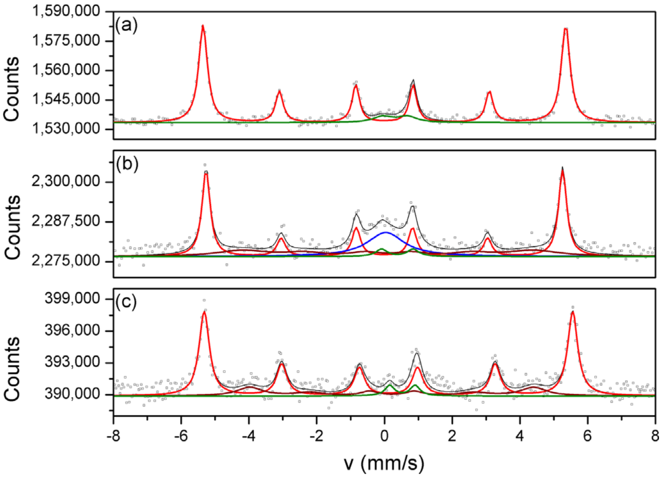

Fig. 1. ^{57}Fe conversion electron Mössbauer spectra of electrodeposited α-iron samples: (a) spectrum for as-deposited sample recorded at 293 K, (b) spectrum for sample irradiated with 246 MeV energy Kr ions with a fluence of 1×10^{13} ion cm^{-2} recorded at 293 K, (c) spectrum for irradiated sample recorded at 15 K.

We investigated metallic pure α-iron in the form of thin electrodeposited films. The room temperature spectrum of the non-irradiated, as-deposited sample shown in Fig. 1(a) consists of a dominating sextet (S1) with narrow spectral lines and a small intensity doublet (D1). Sextet S1 is the fingerprint of the crystalline α-iron which has a bcc structure (Stevens and Stevens, 1965). This was also confirmed by XRD measurements which revealed solely the presence of the crystalline α-iron phase in the electrodeposited sample. This result is consistent with the type of structure to be expected from the electrodeposition of iron. Doublet D1 can be attributed to an iron oxy-hydroxide phase based on its characteristic Mössbauer parameters (Stevens and Stevens, 1965). As X-ray diffractograms did not exhibit the existence of this phase it can be interpreted to be a thin layer (circa 10 nm) which has formed on the surface of the electrodeposited α-iron. This phase can be explained by the corrosion of the surface of the electrodeposited α-iron by air after electrodeposition.

Fig. 1(b) shows the room temperature spectrum of the irradiated sample, which is decomposed into two sextets (S1 and S2), a doublet (D1) and a singlet (P1). The corresponding Mössbauer parameters are shown in Table 1. This decomposition was found to be the optimal for the spectrum fitting at minimal number of components, which is consistent with those obtained previously on swift heavy ion irradiated α-iron thin films (Kuzmann et al., 2006; Stichleutner et al., 2011). We used a broad singlet instead of a doublet in (Kuzmann et al., 2006) for component P1 based on the works of (Afanas'ev and Chuev, 2001; Afanas'ev and Chuev, 2003). Sextet S1 again relates to the crystalline α-iron phase. Sextet S2 has very broad spectral lines which are typical of amorphous phases. This component can be considered as a superposition of a number of magnetically split sub-spectra belonging to iron atoms being in slightly different microenvironments. The Mössbauer parameters of sextet S2 are an excellent match for those of amorphous iron phase (Suslick et al., 1991; Long et al., 1998) and thus sextet S2 was assigned to amorphous iron phase (Kuzmann et al., 2006; Stichleutner et al., 2011). Doublet D1 again corresponds to the iron-oxy-hydroxide phase. Singlet P1 exhibits a very broad line and the value of the isomer shift of singlet P1 shown in Table 1 is characteristic of metallic bcc iron. Taking into consideration the phase composition of the electrodeposited sample,