

Nanocrystalline α -Fe Layer Examined by Mössbauer Spectrometry

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A few micrometers thick nanocrystalline α -Fe layer with the mean crystallite size $d_{XRD} = 14$ nm was deposited in low-pressure microwave plasma, using $\text{Fe}(\text{CO})_5$ vapour. Its nanocrystalline character was proved on its surface under SEM (surface was formed of deposited nanoparticles) and in its volume using TEM (deposited nanoparticles were stacked up, creating columns). No significant iron oxide phases were observed in the transmission ^{57}Fe Mössbauer spectrum measured at 5 K nor in the surface-sensitive ^{57}Fe conversion electron Mössbauer spectrum measured at 293 K.

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1. Introduction

Microwave-plasma-assisted chemical vapour deposition (MPCVD) is a well-established method for the synthesis of nanocrystalline films [1, 2]. As a fundamental material, the nanograined α -Fe layer is a desirable topic for investigation. Nevertheless, the studies of nanocrystalline α -Fe layers deposited by a MPCVD method are rare.

In this paper we present results obtained by the study of a few micrometers thick nanocrystalline α -Fe layer deposited in low-pressure microwave plasma.

2. Experimental methods

Our experimental setup was straightforward and similar to the one used in our previous work [3]. Operating conditions were as follows: gas pressure of 2 kPa, microwave power of 250 W, Ar flow of 280 sccm, and $\text{Fe}(\text{CO})_5$ flow of 1.75 g/min. The $\text{Fe}(\text{CO})_5$ injection point (quartz tube with 6 mm inner diameter) was situated 15 cm downstream from the launcher (surfaguide). Deposition time was 60 seconds. α -Fe thin films were deposited on the reactor inner wall of 45 mm quartz tube close to the launcher and also on the inner wall of the most upper part of injection tube.

X-ray diffraction (XRD) pattern was measured on a PANalytical X'Pert Pro MPD device and pattern fitting was done using X'Pert High Score Plus 2.0a and ICSD database and it yielded mean crystallite size d_{XRD} . Scanning electron microscopy (SEM) was done on a JEOL JSM 6700F. Transmission electron microscopy (TEM) was performed on a Philips microscope CM12. The foil for TEM observations was prepared by applying ion machining to the original sample. Transmission ^{57}Fe Mössbauer spectrum (TMS) was obtained at standard transmission geometry with ^{57}Co in Rh matrix source. As a result of the fitting procedure, performed with CONFIT

software package, we obtained relative spectrum area A for a given component and spectral component parameters: hyperfine magnetic induction B_{HF} , width of hyperfine Gaussian distribution ΔB_{HF} , quadrupole shift ε_Q , quadrupole splitting ΔE_Q , isomer shift δ (against α -Fe), and line intensity I . A CCS-800 Mössbauer closed-cycle refrigerator system from Janis was used for low temperature measurement. Conversion electron Mössbauer spectrum (CEMS) was measured at room temperature using a gas flow (90 vol.% He, 10 vol.% CH_4) electron detector.

3. Results

Under a conventional light microscope the pieces of the deposited layer exhibited generally metallic shine, but on some places of the surface also macroscopic reddish-brown areas (about 20% of the whole surface) were observed, indicating possible oxidation of the surface.

The XRD pattern of the as-synthesized pieces of the layer exhibited only α -Fe diffraction lines (ICSD #53451, $R_{wp} = 5.41$, GOF = 24.7) with the mean crystallite size $d_{XRD} = 14$ nm. No other significant peaks were observed.

The morphology of the broken piece of the layer was examined under SEM (Fig. 1a) and it revealed that the surface of the layer consisted of deposited nanoparticles with the diameter of about 20 nm (Fig. 1b). The shape of the fracture surface of the layer exhibited such a structure as if the volume of the layer contained columns, which could be formed of nanoparticles. TEM confirmed this assumption (Fig. 2): the grains had the tendency to be stacked up in columns oriented nearly perpendicularly to the surface.

To suppress superparamagnetism in small particles/grains and so being able to observe the spectral components (esp. those with $B_{HF} > \alpha$ -Fe) belonging to possible iron oxide compounds with magnetic ordering, the TMS for the sample was measured at 5 K (Fig. 3). However, it was not significantly different from the room-temperature TMS. The low-temperature TMS was fitted with α -Fe sextet ($B_{HF} = 33.9$ T, $2\varepsilon_Q = 0.00$ mm/s,

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$\delta = 0.14$ mm/s, $A = 0.78$, $I_2/I_1 = 0.65$, full line), Gaussian distribution ($B_{HF} = 31.9$ T, $\Delta B_{HF} = 13.1$ T, $2\varepsilon_Q = 0.00$ mm/s, $\delta = 0.20$ mm/s, $A = 0.19$, dashed line), and a doublet ($\Delta E_Q = 0.36$ mm/s, $\delta = 0.26$ mm/s, $A = 0.03$, full line). The spectrum fit is shown with bold full line. The distribution was assigned to Fe atoms at the interfaces of the grains [4]. No components characteristic for iron oxides were found [5].

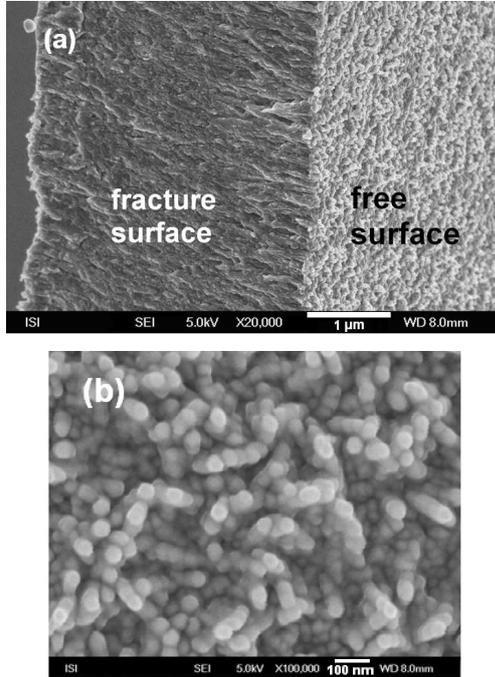


Fig. 1. SEM images for (a) the edge of a piece of α -Fe layer and (b) its free surface viewed from above.

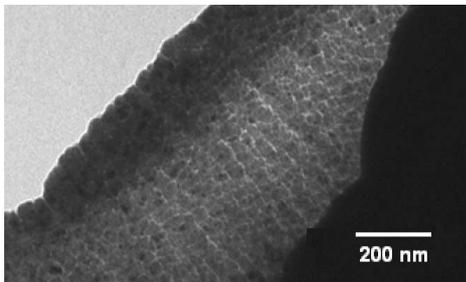


Fig. 2. TEM image for the thin foil prepared from a piece of α -Fe layer.

CEMS served to investigate the surface layer with the thickness of about 300 nm (the approximate escape depth of conversion electrons). The CEMS spectrum was fitted with α -Fe sextet ($B_{HF} = 32.9$ T, $2\varepsilon_Q = 0.00$ mm/s, $\delta = 0.02$ mm/s, $A = 0.85$, $I_2/I_1 = 0.79$, full line), Gaussian distribution ($B_{HF} = 31.3$ T, $\Delta B_{HF} = 28.5$ T, $2\varepsilon_Q = 0.00$ mm/s, $\delta = 0.00$ mm/s, $A = 0.14$, dashed line), and a singlet ($\delta = 0.09$ mm/s, $A = 0.01$, full line).

The spectrum fit is shown with bold full line. No clearly assignable iron oxide components were observed.

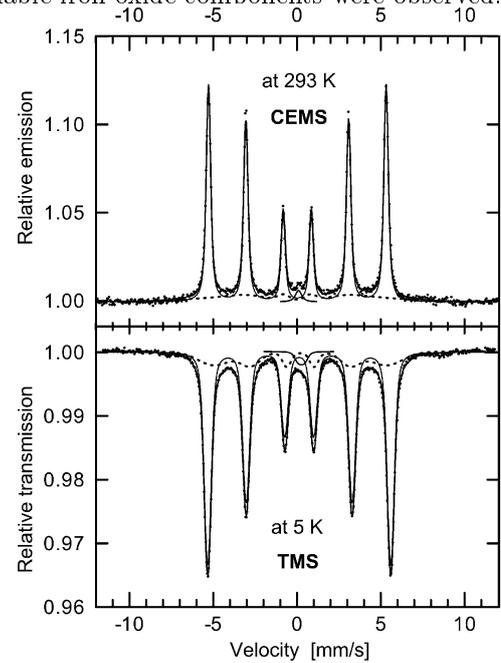


Fig. 3. MS spectra for a few pieces of α -Fe layer.

4. Conclusions

Although the layers had macroscopic reddish-brown areas on their surfaces, which might be iron oxides, no iron oxide phases in significant amounts were identified in TMS spectrum nor CEMS spectrum. Hence, the reddish-brown areas on the surfaces could be some byproducts of the decomposition of $\text{Fe}(\text{CO})_5$ [6], exhibiting themselves in the middle part of the Mössbauer spectra.

Acknowledgments

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