MAGNETIC AND MÖSSBAUER SPECTROSCOPY STUDY OF Fe-Cr-Al THIN FILMS SPUTTERED ON Si SUBSTRATES

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Abstract. Fe and Fe-Cr-Al thin films, both as sputtered on Si substrates as well as after subsequent annealing treatments in hydrogen atmosphere, have been investigated by means of X-ray reflectometry, magneto-optic Kerr effect and Mössbauer spectroscopy with respect to structural and related magnetic characteristics. The as deposited films are showing chemically disordered bcc structures, assigned to Fe-Si and Fe-Cr-Al-Si phases, respectively, with soft magnetism and magnetic texture, both influenced by the presence of Si, Cr and Al atoms. The softness of the films as well as the magnetic texture are strongly modified via hydrogenation treatments. In addition, such treatments induce the expulsion of Si, Cr and Al atoms from the as deposited phases, providing almost pure Fe films of much well crystallized bcc structure.

Key words: Fe and Fe-Cr-Al thin films, XRR, vectorial-MOKE, CEMS.

1. INTRODUCTION

Fe-Cr-Al alloys are part of the so called complex metallic alloys (CMAs) [1], characterized by large unit cells, inherent disorder and a large number of point defects. It was shown that the mechanical parameters such as the ductility, yield stress and workability, as well as the corrosion resistance [2] of Fe-Al bulk alloys can be improved by substitution with an additional element, through the so-called third element effect (TEE) [3, 4]. A viable approach was proven to be the addition of Cr atoms in the $\text{Fe}_2\text{Al DO}_3$ structure, with Cr occupying preferentially either next nearest neighbors of Al sites [5] or iron vacancies [6]. At relatively low concentrations, Cr and Al atoms show a high solubility in the bcc Fe structure. Of a significant interest is also the study of Fe-Cr and Fe-Cr-Al alloys and thin films with compositions approaching the one of special steels proposed to support plasma facing components in the next generation of tokamak torus for nuclear fusion reactions [7]. Given the dependence of most mechanical parameters and of the corrosion resistance to the local structure and metallurgic phase composition of
such special steels, the interest is also focused on the changes induced in the local structure by penetration of light atoms (e.g., hydrogen, helium or deuterium) escaping from the confined hot plasma.

In our parallel studies on Fe-Cr thin films sputtered on Si substrates [8], it was observed that the presence of Cr atoms in the bcc $\alpha$-Fe structure changes drastically the Fe local configuration, by increasing the structural and chemical disorder with direct influence on the values of the average hyperfine magnetic field (a decrease by 0.15 T for each 1 at. % of Cr was evidenced). On the other side, previous studies on Fe-Cr-Al thin films or multilayers containing such elements were also reported in the literature. It was shown that the thickness of the film and the temperature of the substrate during deposition have a considerable influence on the degree of crystallinity in the case of Al-rich Al-Cr-Fe thin films (10–30 nm thickness) prepared by flash evaporation [9]. Diffusion aspects induced by annealing were also studied on bi- and tri-layers of Al/Cr, Al/Fe, Cr/Fe, Cr/Al/Fe with thickness of 200 nm, indicating that Al is expected to distort the bcc $\alpha$-Fe structure in a more pronounced way, relative to Cr addition [10].

In addition to previous studies, this work concerns a comparative study of Fe and Fe-Cr-Al thin films sputtered on Si substrates and subsequently subjected to a hydrogenation treatment. Low Cr content approaching the content specific to the special steel supporting plasma facing components as well as low Al content has been chosen in order to assure their complete solubility in the bcc Fe structure. The Fe local configuration, magnetic properties and interfacial intermixing processes have been analyzed via X-ray reflectometry (XRR), magneto-optic Kerr effect (MOKE) vector-magnetometry and $^{57}$Fe conversion electron Mössbauer spectroscopy (CEMS).

2. EXPERIMENTAL DETAILS

Thin Fe and Fe-Cr-Al films, enriched in the $^{57}$Fe Mössbauer isotope, have been deposited on Si(001) substrates with native oxide layers. The base pressure in the deposition chamber has been of about 5·$10^{-6}$ Torr (enough to expect a weak oxidation of the metallic films), while the working pressure of Ar has been close to a value of 5·$10^{-2}$ Torr. The sputtering power has been 100 W and the substrate has not been heated during deposition. No chemical treatments have been applied to the Si substrate containing a native Si oxide with the intention to avoid a considerably increase of roughness. The target surface has been cleaned by an initial “at site” sputtering at 100 W for 15 minutes. The relative content of the Cr and Al atoms in the intermetallic film has been deduced from the relative evaporation rates in corroboration with the relative areas of small Cr and Al plackets fixed on the main Fe target.
The thicknesses of the Fe and Fe-Cr-Al layers have been estimated via a previous calibration versus the deposition time and further checked on the Fe-Cr-Al layer via X-ray reflectometry (XRR). The XRR measurements have been performed with a Bruker type (AD 8 ADVANCED) diffractometer working with Cu(Kα) radiation of 0.154 nm wavelength. The LAPTOP program has been used for fitting the XRR spectra. The sample codes, the geometrical structures, the deposition time and the expected thickness of the as deposited thin films are listed in Table 1.

Table 1
Sample codes, geometrical structure, deposition time and expected thickness of the Fe and Fe-Cr-Al films

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Geometrical structure</th>
<th>Deposition time (minutes)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Fe</td>
<td>Si[Fe+(^{57})Fe]</td>
<td>5</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>Si/Fe-Cr-Al</td>
<td>Si[Fe+Cr(11%)+Al(5,5%)+(^{57})Fe]</td>
<td>3</td>
<td>10 ± 1</td>
</tr>
</tbody>
</table>

Subsequent annealing treatments have been performed at 300 °C for 90 min under 10 bars of H₂ pressure, after 20 cycles of vacuum/purging of hydrogen, at 150 °C.

Surface sensitive \(^{57}\)Fe Conversion Electron Mössbauer Spectroscopy (CEMS) measurements have been used in order to study the phase composition and the local structure of the Fe and Fe-Cr-Al films. The spectra have been acquired at room temperature, in perpendicular geometry (with the gamma radiation perpendicular to the sample plane) with the sample placed in a home-made gas flow proportional counter. A \(^{57}\)Co source (Rh matrix) of 15 mCi activity and a spectrometer working with sinusoidal waveform were employed. The NORMOS computer program by Brand [11] has been used for the least-squares fitting of the CEM spectra. The isomer shifts are reported relative to \(\alpha\)-Fe at room temperature.

Magneto-optical Kerr effect (MOKE) magnetometry measurements have been performed using a miniMOKE (AMACC Anderberg & Modéer Accelerator AB) with a standard laser diode source (\(\lambda = 640 \text{ nm}\)) and a photodiode detector. The polarizer and analyzer are of Glan-Thompson type. A Lock-in amplifier collects the signals from the photodiode, as modulated via a Faraday rod placed in the detection chain, under a 1000 Hz sinusoidal current commanded by the amplifier. The sample holder allows the rotation of the sample in its own plane, at different azimuthal angles \(\theta\) between a reference in-plane direction and the direction of the hyperfine field.
3. RESULTS AND DISCUSSIONS

The thickness, density and roughness of the Fe-Cr-Al thin film have been checked via X-ray reflectometry technique based on reflection of X-rays from surfaces and interfaces. A structural model consisting of the silicon substrate (a), an interfacial SiO\textsubscript{2} oxide layer (b) and the Fe-Cr-Al alloy layer (c), was used for the calculation of the reflectometry curves. The thickness, density, and interfacial roughness of the Fe-Cr-Al layer and SiO\textsubscript{2} layer were varied according to LEPTOS algorithm in order to minimize the difference between the XRR scans and the fitting curves. The mass density profile of sample Fe-Cr-Al obtained via XRR patterns is presented in Fig. 1, and the comparison of experimental and calculated XRR profiles is presented in the inset. The specific parameters of the structural model leading to the best fit of the XRR experimental data are presented in Table 2. Mostly a metallic Fe based component film of about 10 nm thickness and with high roughness at surface and a SiO\textsubscript{2} oxide layer of about 2 nm at the interface with the Si substrate were observed. However, the unexpected low value of the mass density for the main layer gives a first hint about its possible oxidation and in correlation with the high density of the SiO\textsubscript{2} layer suggests also a strong atomic intermixing process between the as deposited film and the Si substrate.

![Mass density profile of the sample Si/Fe-Cr-Al](image)

Fig. 1 – Mass density profile of the sample Si/Fe-Cr-Al, as obtained from the fitting of the XRR data (shown in the inset).

The conversion electron Mössbauer (CEM) spectra of the as prepared Si/Fe and Si/Fe-Cr-Al samples are shown in Fig. 2 a and b, respectively. Both spectra are characterized by a main broad sextet pattern fitted via distributed hyperfine magnetic fields, and a central doublet component of much lower intensity. The probability distribution of the hyperfine magnetic fields is shown on the right side
of each corresponding spectrum. Accordingly, the magnetic component in the CEM spectrum of the Si/Fe sample (Fig. 2a) is characterized by an average isomer shift (IS) of 0.12 mm/s, a very low quadrupole splitting (QS) of −0.07 mm/s and an average magnetic hyperfine field of $B_{hf}$ of 23.6 T, being therefore assigned to a disordered Fe-Si phase. The Mössbauer spectra of Fe$_3$Si phase with ideal DO3 structure [12, 13] present a distribution of magnetic hyperfine fields with two maxima at 20 T and 31 T, corresponding to A and B sites. These values are different from the ones corresponding to the two local maxima in the probability distribution of the present Si/Fe sample, observed at about 16 T and 25 T, respectively. Having in mind also the much larger distribution probability, an even increased average Si content is expected in the Fe film, most probable with also a concentration gradient along the film thickness. The secondary paramagnetic doublet with relative spectral area of 11% is assigned to a superparamagnetic Fe$^{3+}$ based oxide phase, proving clearly the partial local oxidation of the Fe film over the whole depth.

The CEM spectrum of the Si/Fe-Cr-Al sample, shown in Fig. 2b, was also fitted via distributed hyperfine magnetic fields responsible for the broad sextet pattern and a secondary paramagnetic doublet. The broad sextet provides an average isomer shift (IS) of 0.21 mm/s, quadrupole splitting (QS) of 0.01 mm/s and average hyperfine magnetic field ($B_{hf}$) of 20.2 T. A high penetration of the Si atoms in the deposited film is expected also in this case and the mentioned sextet has to be assigned to a Fe-Cr-Al-Si film with disordered bcc structure. However, the comparatively rather reduced value of the average hyperfine magnetic field (20.2 T for sample Si/Fe-Cr-Al as compared to 23.6 T for sample Si/Fe) has to be strictly related to the presence of Cr and Al atoms in this sample. This interpretation is supported by [8], where it was shown that Cr addition decreases the hyperfine magnetic field by 0.2 T per at. % Cr. However, according to the above presented data of this study, the presence of Al atoms decreases additionally the hyperfine magnetic field by about 0.2 T per at. % Al. The central doublet component with a relative spectral area of 22% is again assigned, via its hyperfine parameters IS of 0.34 mm/s and QS of 1.15 mm/s, to a super-paramagnetic Fe$^{3+}$ oxide in a distorted configuration.

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Fe-Cr-Al</td>
<td>Fe-Cr-Al</td>
<td>10.2</td>
<td>1.5</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>2.3</td>
<td>0.4</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>--</td>
<td>--</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Fig. 2 – CEM spectra collected at room temperature on the as obtained sputtered films, as follows: a) Si/Fe; b) Si/Fe-Cr-Al.

Fig. 3 – CEM spectra collected at room temperature on the hydrogenated films, as follows: a) Si/Fe; b) Si/Fe-Cr-Al.
The CEM spectra of the Si/Fe and Si/Fe-Cr-Al samples, after the hydrogenation treatment are shown in Fig. 3 a and b, respectively. The spectra are characterized by much narrower lines of the sextet (with line widths of 0.31 mm/s and 0.46 mm/s in case of Si/Fe and Si/Fe-Cr-Al samples, respectively) with almost zero IS and QS values. A specific hyperfine magnetic field of 33.14 (2) is observed, proving clearly the formation, in both cases, of clean and well crystallized bcc Fe films. The reduction of the Cr content after hydrogenation treatments was also evidenced by X-ray photoelectron spectroscopy in one of our previous studies on binary Fe_{0.89}Cr_{0.11} thin films [8]. The weak central doublet assigned to a superparamagnetic Fe oxide decreases its relative contribution to only 14% in the case of the Si/Fe hydrogenated sample and 7% in the Si/Fe-Cr-Al sample. Correspondingly, one can conclude on the double effect of the hydrogenation treatment which expels the Si, Cr and Al atoms from the metallic films but also improves the bcc crystalline structure, via a reduction and homogenization process.

The magnetic texture of the Fe and Fe-Cr-Al films (both as deposited and after hydrogenation treatments) has been investigated also by means of magneto-optic Kerr effect (MOKE) vectorial magnetometry at room temperature. Figure 4 presents the MOKE hysteresis loops of the Si/Fe sample, before hydrogenation (a–c) and after hydrogenation (d–f), measured in longitudinal configuration and at different azimuthal angles \( \theta \) (with \( \theta \) the angle between the field direction and Si[1 1 0] direction). A strong dependence of the MOKE signal with the azimuthal angle is observed for the as deposited film, proving its magnetic texture. According to a simple Stoner-Wohlfarth model extended to the case of an island type growing of the film, it can be shown that the most rectangular shape of loop indicates the case of a field pointing along the most probable direction of distributed easy axis (called EA in the following) corresponding to magnetic mono-domains, whereas the texture degree is related to the squares of the loop along this peculiar direction [14].

From the physical point of view, such type of growing is giving rise to a so called Fe nanoparticule film [15]) with a narrow angular distribution of the easy axis and might be achieved by very energetic deposition methods, in condition of an uniaxial stress induced during the deposition process. Excepting such magnetic texture effects, the fact that our deposition method is very energetic is also supported by the strong diffusion of the Si atoms from the substrate into the Fe film.

Whereas the as deposited Si/Fe film has an average EA oriented along the Si[1 1 0] (Fig. 4c), the hydrogenated Si/Fe film has almost no magnetic texture (the squares of the loops does not significantly change with angle \( \theta \) (Fig. 4 d–f).
An additional effect of the hydrogenation is the much increased coercive field observed in the hydrogenated sample ($\mu_0H$ is between 0.01 and 0.02 T) as compared to the as deposited one ($\mu_0H$ is less than 0.001 T). While an additional oxidation can be not a possible explanation of the increased coercivity, being excluded by the CEM spectra, the only explanation seems to be rather related to the improved crystallinity and uniformity of the film, imposing a different mechanism for the magnetic loop (e.g. related to moving domain walls).

The longitudinal MOKE hysteresis loops of sample Si/Fe-Cr-Al, before hydrogenation and after hydrogenation, at different azimuthal angles $\theta$, are presented in Fig. 5 a–c and d–f, respectively.

Similar to the Si/Fe system, a strong magnetic texture is clearly evidenced in case of the as prepared sample, but with the EA oriented at 45 degree versus the Si [1 1 0]. The coercive field, $\mu_0H_C$ of only 0.001 T, indicates again a very soft magnetic character, but the presence of Cr and Al atoms modifies the direction of the magnetic texture. After the hydrogenation treatment, the initial texture is partially destroyed and the coercive field increases at a value $\mu_0H_C$ of 0.003 T, however lower than in the case of the hydrogenated Si/Fe sample. Having in mind that the linewidth of the sextet pattern in the CEM spectrum of the hydrogenated Si/Fe-Cr-Al sample is larger (0.46 mm/s) than in case of the hydrogenated Si/Fe
sample (0.31 mm/s), indicating a weaker crystallinity (or a more defected bcc structure), in direct relation to a softer magnetic character and just a partial loose of the magnetic texture, the Mössbauer spectroscopy gives support for the assumed relationship between the magnetic behavior and the peculiar structural aspects of the films, induced either by the presence of the Al and Cr atoms or by subsequent hydrogenation treatments.

4. CONCLUSIONS

Thin Fe and Fe-Cr-Al films have been sputtered on Si(0 0 1) substrates and subsequently annealed in hydrogen atmosphere. The as prepared films are mainly metallic, consisting of distorted bcc Fe-Si and Fe-Cr-Al-Si phases, respectively. The presence of Cr and Al atoms decreases slightly the average hyperfine field at the Fe nucleus, but also influences the softness and the direction of the magnetic texture in the as deposited films. The hydrogenation treatment increases considerably the coercive field and removes the magnetic texture in relation to a
higher degree of crystallinity and homogeneity of the metallic films. Of highest practical relevance, also with respect to the behavior of plasma facing components under irradiation with light elements, is the expelling of the Cr and Al atoms from the surface of Fe-Cr and Fe-Cr-Al alloys, induced by the penetration of hydrogen atoms in the structure.

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REFERENCES