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On the hyperfine field of bcc 304 L stainless steel films

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Abstract

We show that by ion-beam sputtering of a 304 L stainless steel target under ultra high vacuum, it is possible to elaborate thin films exhibiting both a bcc single phase and a strongly ferromagnetic structure at 293 K. The hyperfine field measured at the ^{57}Fe nucleus using the Mössbauer effect is studied in details as a function of sample thickness. The field value is close to that of bulk α -iron while the direction of the magnetization lies in the film plane when the thickness of the sample is $\sim 0.4\ \mu\text{m}$. Experimental values are compared with data available in the literature. The possible role of chromium atoms is also discussed.

1. Introduction

Ordinary 304 stainless steel (SS) appears in the fcc γ -phase which is non-magnetic at room temperature. Such a structural state can be obtained by annealing and quenching from about 1050°C. Ferrite (the bcc α -phase) normally does not form without subzero temperature treatment or severe deformation below about 80°C. Concerning the modification of 304 SS, it was also found that the austenitic γ -phase transforms into the martensitic α -phase due to the stress induced by ion-implantation. The magnetic properties of the SS surface can then be modified by the phase transformation because the martensite is ferromagnetic and the austenite is not magnetic. The ion-implantation induced transformations were studied by Hayashi et al. [1] who reported the observation of an α -phase in helium implanted austenitic 304 SS. Much work was also published by the Copenhagen group [2] who measured the percentage of transformed α -phase as a function of ion fluence and species. Finally Sandra et al. [3] have shown that the ion-beam induced local modification in 304 SS was applicable to permanent recording using changes in magnetic properties.

The occurrence of the above $\gamma \rightarrow \alpha$ transformations is connected to the low austenite stability due to the low position of 304 SS in the Schaeffler diagram. Another way to obtain 304 SS in the ferromagnetic α -phase is to use sputter-deposition techniques. In this field, let us mention the pioneer work by Dahlgren [4] in which the deposits were produced by the triode sputtering method. More recently Childress et al. [5] have obtained single-phase bcc thin films of 304 SS by DC magnetron sputtering. We have also mentioned similar results using an ion-beam sputtering system [6]. It is the purpose of the present paper to analyse the local magnetic properties of ferromagnetic bcc 304 SS thin films elaborated using the later technique. We have mainly investigated the hyperfine field at the ^{57}Fe nucleus using the Mössbauer effect working either in transmission or scattering mode (conversion electron Mössbauer spectroscopy -CEMS-). Both the field modulus and orientation were determined and the results compared with those available in the literature.

2 - Experimental

About 0.4 μm thick 304 SS films were prepared on kapton substrates by an ion-beam sputtering equipment, as described in a previous paper [6]. The chemical composition of the sputter deposited alloys was determined by an electron probe micro-analysis, indicating that the deposited alloys are homogeneous within an error limit of $\sim 1\%$. The results are indicated in table 1 and can be compared to those obtained with the target material which was a commercial grade 304 L SS sheet.

Table 1

Concentration of 304 SS alloys (target metal and sputter deposited films).

Alloys	Concentration [at. %]					Structure
	Fe	Cr	Ni	Si	Mn	
Target	72.1	18.7	6.7	0.8	1.4	fcc
Films	73.7	15.3	8.6	1.1	0.7	bcc

Mössbauer spectra were recorded at both 293 and 77 K in a standard constant acceleration spectrometer with a 50 m Ci ^{57}Co source in a Rh matrix. For CEMS experiments, the back-scattered electrons were detected by a gas flow proportional counter [7].

3 - Results and discussion

Figure 1 shows the transmission Mössbauer spectrum at 293 K for 10 superposed films of bcc 304 L stainless steel, indicating a clear ferromagnetic sextet whose wide linewidth may be ascribed to the distribution of hyperfine field caused by a random atomic distribution at near neighbour sites of ^{57}Fe nuclei. The spectrum was fitted by a superimposition of several six lorentzian line patterns with different isomer shifts and magnetic splittings. The full width at half maximum was about 0.26 mm/s and the relative intensity of the second and fifth peaks were adjusted to get the best fit ; the contribution of the electric field gradient was neglected. As shown in figure 2a, the smoothed distribution curve of H_{hf} at 293 K, $P(H_{\text{hf}})$, reveals a broad peak whose halfwidth is about 95 kOe. The

average hyperfine field $\bar{H}_{\text{hf}}$ is found to be 308 kOe. We have also obtained the intensity ratio of the sextet as 3 : 4 : 1 : 1 : 4 : 3 ; this result indicates that the magnetic hyperfine field aligns parallel to the sample plane, being consistent with the magnetization measurements. Another transmission experiment performed at 77 K has not shown any notable change in Mössbauer spectrum shape ; one can only observe an increase in average hyperfine field as expected. The corresponding field distribution presented in figure 2b has allowed to calculate $\bar{H}_{\text{hf}} = 326$ kOe instead of 308 kOe at 293 K. Finally the upper part of a single film was also analysed using the CEMS technique at 293 K ; the corresponding spectrum shown in figure 3 is typical for a thickness of $\sim 200 - 250$ nm. The average hyperfine field is then deduced as

$\bar{H}_{\text{hf}} = 311$ kOe, which is somewhat higher than in transmission geometry at the same temperature. The field also aligns parallel to the surface of the sample.

The results of the magnetic investigations performed using a vibrating sample magnetometer were already published [8] so that they will be only shortly reported here. They were obtained at 293 K with a 0.35 μm thick sample. The magnetization easily

Fig. 1. - Transmission Mössbauer fitted spectrum at 293 K

Fig. 2. - Smoothed hyperfine field distributions $P(H_{hf})$ at (a) 293 K and (b) 77 K

Fig. 3. - Conversion electron Mössbauer spectrum at 293 K.

saturates in the in-plane direction, but it does not in the direction perpendicular to the sample plane due to the demagnetization effect. The former case shows saturation at fields on the order of 0.5 kOe and the coercivity is 55 Oe. The perpendicular loop reaches saturation at 13.5 kOe. The saturation magnetization is 140 emu/g. The material is found to be magnetically soft and the easy axis lies in the film plane which is consistent with the Mössbauer measurements.

The value of the hyperfine field $\bar{H}_{\text{hf}} = 308$ kOe determined in transmission geometry appears to be slightly lower than that of bulk α -iron (330 kOe). In the absence of chromium the material under study can be regarded as a binary $\text{Fe}_{100-x}\text{Ni}_x$ alloy with $x \sim 10$ for which the hyperfine field is ~ 338 kOe according to reference [9]. The drop in field from 338 to 308 kOe may be explained by the presence of Cr atoms in 304 SS films though, as discussed in what follows, they are not probably randomly distributed. The effect of Cr is to significantly reduce the average moment of Fe atoms since, in Fe rich alloys, Cr atom moments are known to be negative [10]. Similar comments could be also done concerning the magnetization of the films which is less than that of bulk $\text{Fe}_{90}\text{Ni}_{10}$ ($\sim 1,35 \mu_B$ instead of $2,3 \mu_B$).

The discussion will now concern the 293 K hyperfine field values of the α -phase of 304 SS as a function of the preparation mode. The data available in the literature are presented in table 2.

Table 2

Hyperfine field ($\bar{H}_{\text{hf}}$) as a function of the preparation mode for bcc 304 SS.

Preparation mode	Thickness (nm)	$\bar{H}_{\text{hf}}$ (kOe)	Reference
ion-implantation	-	240 - 270	2
magnetron sputtering	> 1000	255	5
ion-beam sputtering	100 - 200	266 - 271	6
ion-beam sputtering	400	308	this work

From the above table, it appears that the $\bar{H}_{\text{hf}}$ value determined in the present study is higher than the other ones which appear to be in good agreement ; the total Cr content is nearly the same in all cases. The results also show that, using the ion-beam sputtering technique, the hyperfine field value of the 304 SS films deposited onto a kapton substrate increases with increasing thickness. This trend is also supported by the CEM spectrum presented in figure 3 which was taken from the upper part of the sample. This phenomenon is attributable to the segregation of Cr atoms which is promoted by a probable increase in temperature during the film growth since the substrate is not watercooled. The segregation of Cr is assumed to take place towards the grain boundaries ; hence the neighbourhood of Fe atoms located in the host is depleted in Cr which leads to an increase in hyperfine field. The precipitation of Cr atoms has been already reported in Co-Cr films [11].

It is known that morphology of sputter deposited alloys influences their magnetic properties. In the present study, the films display an in-plane magnetic anisotropy since the intensity ratio of the ferromagnetic sextet is 3 : 4 : 1 : 1 : 4 : 3 in the Mössbauer spectrum. This feature is probably attributable to a high density stacking but further investigations are still necessary to determine the actual film microstructure.

As a conclusion, we have prepared 0.4 μm thick films of bcc 304 SS which exhibit an internal field at the iron nucleus of 308 kOe at 293 K and an in-plane magnetic anisotropy. It is also shown that the field increases with increasing thickness due to the probable segregation of Cr atoms during the film growth.

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