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Investigation of nitrided 304L stainless-steel coatings by positron annihilation spectroscopy

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Abstract

Nitrided 304L stainless-steel coatings were deposited on low carbon steel substrates by dc-magnetron sputtering in a reactive atmosphere of argon and nitrogen. The nitrogen partial mass flow (pN_2) was varied linearly from 0% to 100% resulting in a nitriding of the stainless-steel coatings with nitrogen concentrations up to 46 at%. Positron annihilation spectroscopy is used to characterize the defect structure of the coatings. The remarkable evolution of the defect structure with increasing pN_2 is discussed.

Keywords: Positron annihilation; Steel; Nitriding; Magnetron sputtering

1. Introduction

The understanding of the addition of nitrogen to iron to improve the surface hardness and tribological properties, goes back to early 1900s (Fry, 1923). Nitriding of stainless steels is an excellent method to improve their wear resistance without compromising their well-known corrosion resistance performance. Several modern techniques are used for nitriding such as conventional ion implantation, pulsed plasma nitriding, plasma immersion ion implantation (PI^3), laser nitriding and reactive magnetron sputtering. Sputter-deposited films typically exhibit a wide range of defects. The purpose of this work is to investigate the microstructure and in particular to characterize the evolution of the defect structure of these sputtered films and how this could be influenced by the nitriding process.

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2. Experimental details

2.1. Sample preparation

Samples of a low carbon steel sheet with a thickness of 0.5 mm were cut into $20 \times 20\,mm^2$ squares. The samples were mechanically polished with sandpapers of different grain sizes and finally to a mirror finish with diamond paste down to 1 μm. Prior to deposition they were cleaned with pentane. The coatings were deposited using an unbalanced dc-magnetron sputtering system. A 50-mm diameter AISI-304L stainless steel (composition in wt%: Fe 70%, Cr 18%, Ni 10%, Mn 2%) disk target was placed just above the magnets with a good thermal contact and was cooled during deposition. A chimney was placed between the target and the sample holder to avoid contamination of the sputter chamber. The magnetron power was set to 200 W during deposition of the samples. Although the substrate was heated by electron and ion bombardment, the temperature was below 373 K during deposition. The coatings were reactively deposited for 20 min with various Ar/N_2 gas mixtures up to a thickness of 325 nm. During deposition the total gas flow rate remained constant at 35 sccm.

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2.2. Experimental techniques

The defect structure of the layers was investigated by positron annihilation spectroscopy. The Ghent variable energy positron beam was used to perform depth selective analysis of the Doppler broadening of the annihilation radiation (DBAR). The energy of the magnetically guided positron beam is variable between 0.1 and 30 keV. The annihilation radiation is detected by an HPGe detector with a 25% efficiency and a resolution of 1.17 keV at 514 keV. Using a 15 mCi ^{22}Na source moderated by a 1 μm tungsten single crystalline moderator we measure a count rate of $10^3\,s^{-1}$ in the photo-peak at 1 cm behind the sample. For each measurement there were at least 10^6 counts recorded in the photo-peak. The Doppler broadened 511 keV annihilation line is commonly characterized by the well-known "Shape" parameter S and a "Wing" parameter W. These parameters represent, respectively, the fraction of the surface of a central part and the fraction of the surface of the outer parts under the annihilation line to the total surface under the annihilation line. From the definition of the S and W parameter it is clear that S is dominated by the annihilation of positrons with low energetic electrons as valence electrons and W by the annihilation with higher energetic core electrons. A raising of the S and lowering of the W parameter measured for a same type of material could therefore indicate the presence of (bigger) open volume defects because a reduced fraction of the positrons trapped in the defects will annihilate with core electrons in favor of the annihilation with valence electrons. The areas used for the characterization were chosen in order to give $S = 0.5$ $(511 \pm 0.72\,\text{keV})$ and $W = 0.05$ $(2.1\,\text{keV} < |E_\gamma - 511\,\text{keV}| < 6.4\,\text{keV})$ for a p-type Si (1 0 0) wafer.

The characterization of the layers was performed at LARN by nuclear elemental analyses with the ALTAÏS 2 MV Tandetron accelerator. The thickness and elemental composition of the coatings were measured by Rutherford backscattering spectroscopy (RBS) and particle induced X-ray emission (PIXE). Nuclear reaction analysis (NRA) was used to measure the nitrogen concentration using $^{14}N(\alpha,p)^{17}O$ at 5.3 MeV.

3. Results and discussion

The results of the NRA and RBS measurements are summarized in Table 1. The total amount of nitrogen incorporated in the film was found to be proportional to the nitrogen flow up to a partial nitrogen flow (pN_2) of 55%. For higher partial flows of nitrogen a saturation of the concentration of the nitrogen in the film is reached with a mean concentration of 46 at%. The PIXE measurements confirmed that the relative amount of Fe, Cr, Ni and Mn in the nitrogen-containing coatings stays within the specifications of the AISI 304L sputter target. For $pN_2 > 20\%$ the deposition rate decreased linearly which is reflected in the thickness of the coatings.

Table 1
Characteristics of the reactive sputter deposited 304L coatings as measured with NRA, RBS and DBAR

pN_2 (%)	[N] (at%)	Thickness (nm)	(S, W)
0	0	325	(0.457, 0.095)
9	9.0	325	(0.432, 0.110)
11	11.2	325	(0.426, 0.114)
15	13.5	325	(0.423, 0.116)
35	30.4	290	(0.419, 0.117)
50	42.3	265	(0.420, 0.116)
90	55.3	190	(0.423, 0.112)
100	35.7	305	(0.436, 0.098)

Conversion electron Mössbauer spectroscopy (CEMS) and grazing incidence X-ray diffraction (GXRD) measurements (Colaux, 2002) showed that for nitrogen concentrations up to 17 at% (pN_2 20%) the nitrogen atoms are in solid solution in the iron matrix. It is well known from literature that this nitrogen-supersaturated or expanded fcc phase has an improved wear resistance and a higher corrosion resistance (Dahm, 2000). For higher nitrogen flows the nitrogen forms both iron and chromium nitrides which typically induce wear resistance.

Defects such as vacancies, dislocations or impurity atoms introduced during the growth of a film can reduce dislocation mobility and can in this way also increase hardness. Magnetron sputtered films typically have a very high dislocation density. Positron annihilation spectroscopy is an excellent probe of vacancy-type defects. Only a small selection of the total amount of samples was investigated with depth selective DBAR. The results of the S parameter analyses are shown in Fig. 1. The surfaces of the samples show the highest S parameters. For incident positron energies from 2 keV the influence of the surfaces on the S becomes negligible and the S parameters observed up to 7.5 keV (depending on the thickness of the coating) are dominated by the S parameters of the stainless-steel coatings. For higher energies the S parameters evolve to the value of the low carbon steel substrate reaching this value from 25 keV. These spectra were analyzed using VEPFIT (Schut, 1990). The results are summarized in Table 1. It is clear that as soon as nitrogen is added to the sputter atmosphere a drastic reduction of the S parameter is observed compared to coatings sputtered under pure Ar. This reduction in S parameter continues up to a pN_2 of 50%, for higher pN_2 the S parameter increases again but never reaching the high value of the Ar sputtered

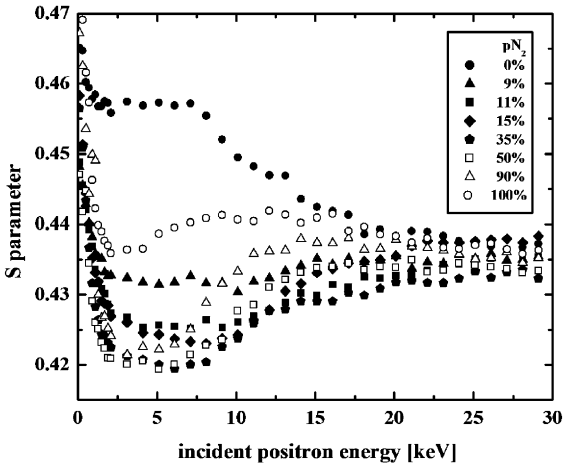

Fig. 1. S parameter plotted as a function of incident positron energy of 304L coatings reactively sputtered in Ar/N_2 atmospheres with different partial pressures of nitrogen (pN_2).

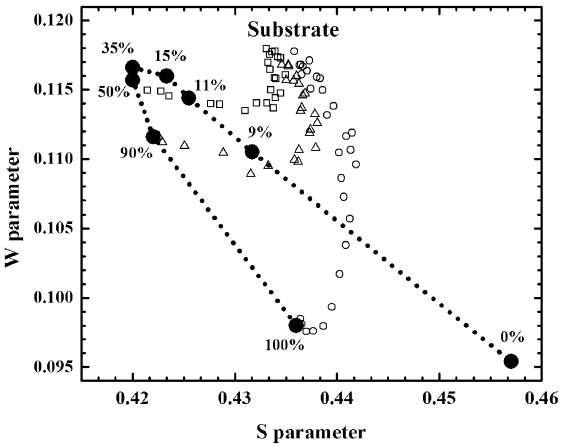

Fig. 2. $S-W$ plot of the cluster points of 304L coatings reactively sputtered in Ar/N_2 atmospheres with different partial pressures of nitrogen. For $pN_2 > 35\%$ the evolution from the cluster point of the coating to the substrate is shown.

coating. Additional information can be gained if we map the depth selective DBAR measurements in an $S-W$ plot (Mantl, 1978; Liszkay, 1994) because every kind of positron annihilation site is characterized by a typical (S, W) couple. The results are presented in Fig. 2. For clarity only the cluster points for most of the different coatings and for the substrate are presented. These cluster points represent successive energies for which constant (S, W) coordinates are measured implying a distinct characteristic (S, W) for the layer or substrate.

From Fig. 2 it is clear that the cluster points for coatings sputtered with pN_2 up to 15% are laying on a strait line. Because of the linearity property of S and W this implies that the observed evolution can be effectively described as trapping of the positrons taking place at two distinct annihilation sites. These annihilation sites are characterized as one having a high S and low W value and another with a low S and high W value. This behavior could indicate that with increasing nitrogen introduction the fraction of relatively big open volume defects decreases in favor of relatively small open volume defects. It is also worth stating that the line shape parameters evolve in a strait line from the cluster point of the coating to the substrate.

For the coatings sputtered with $pN_2 > 15\%$ an evolution to another not yet identified defect site is observed. Also the cluster points of these coatings do not evolve linearly to the substrate but seem to pass through an interface zone. These effects could be correlated on the one hand to the reduced deposition rate which is a consequence of a different sputter deposition mode or on the other hand to the formation of the nitrides which are observed by CEMS and GXRD.

4. Conclusions

Reactively sputtered nitrided coatings were investigated using depth selective DBAR. The coatings showed an interesting evolution of the defect structure. Future investigations as depth selective positron annihilation lifetime spectroscopy should be performed in order to quantify the defect structures of the reactively sputtered nitrided coatings and to try to determine whether the improved wear resistance of those coatings is solely due to the formation of interstitial nitrogen and nitrides or due to the combination with the observed defect modification.

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