Patterning of magnetic structures on austenitic stainless steel by local ion beam nitriding

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Abstract

Periodic arrays of ferromagnetic structures with micrometer and submicrometer lateral sizes have been prepared at the surface of a paramagnetic austenitic stainless steel by means of ion beam nitriding through different types of shadow masks (such as transmission electron microscopy grids or self-assembled porous alumina membranes). This method takes advantage of the formation of the ferromagnetic supersaturated nitrogen solid solution γN phase (i.e., expanded austenite) upon nitriding at moderate temperatures. The local character of the induced ferromagnetism is confirmed by magneto-optical Kerr effect measurements together with magnetic force microscopy imaging. Furthermore, the influence of the nitriding temperature and time on the induced ferromagnetic and structural properties has been analyzed.

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1. Introduction

Owing to their good ductility, weldability and outstanding resistance to corrosion and oxidation [1], austenitic stainless steels (ASSs) are extensively used in numerous industrial and technological domains, such as nuclear power stations or biomedical applications. However, these materials are rather soft, resulting in poor wear resistance. Therefore, the possible hardening of these steels could significantly enlarge their fields of application. In fact, nitriding of ASSs at moderate temperatures (~400 °C) has established itself as an appealing route to improve both hardness and wear resistance without loss of corrosion resistance. Among a variety of nitriding techniques, such as DC plasma nitriding [2], low-pressure plasma-assisted methods [3–6] or plasma immersion ion implantation [7,8], low-energy high-current-density nitrogen ion implantation (referred to hereafter as ion beam nitriding) is particularly suitable, because of its high efficiency in the production of nitrided layers [9–12]. Despite its line-of-sight limitation, this technique provides an independent control of the process parameters such as ion energy, flux or temperature.

Nitriding of ASSs at moderate temperatures leads to the formation of a supersaturated nitrogen solid solution, often called in the literature “expanded austenite” or γN phase [13,14], which is responsible for both microhardness and wear resistance without loss of corrosion resistance. Among a variety of nitriding techniques, such as DC plasma nitriding [2], low-pressure plasma-assisted methods [3–6] or plasma immersion ion implantation [7,8], low-energy high-current-density nitrogen ion implantation (referred to hereafter as ion beam nitriding) is particularly suitable, because of its high efficiency in the production of nitrided layers [9–12]. Despite its line-of-sight limitation, this technique provides an independent control of the process parameters such as ion energy, flux or temperature.

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and enhanced wear resistance without loss of corrosion resistance. Remarkably, this phase shows ferromagnetic behavior, whose origin is linked to the expansion of the austenite (γ) lattice due to the incorporation of nitrogen atoms into interstitial positions [15]. Nitrogen depth profiles in this type of treatments consist of a quasilinear decrease from the near-surface nitrogen concentration followed by a sharp leading edge [14]. Since the threshold for ferromagnetism requires nitrogen concentrations of ∼10–15 at.% [13,15], not the whole nitried layer is ferromagnetic, thus rendering two magnetically dissimilar parts (one ferromagnetic and the other paramagnetic) depending on the nitrogen concentration along the depth. Interestingly, it has been reported that ferromagnetic iron nitrides, such as ε-Fe3N1+x-type, can be also formed within the nitried layer [15–19].

It is noteworthy that the majority of studies involving magnetic measurements in ASS are related to stress-induced martensite formation (ferromagnetic at room temperature) [20–23], and are aimed at the detection of this phase as a non-destructive method for structural damage assessment. Nevertheless, an interesting local approach has been recently presented by Sort et al. [24], where nanoindentation has been used to produce ordered arrays of ferromagnetic structures, taking advantage of the phase transformation (from non-magnetic face-centered cubic (fcc) austenite to ferromagnetic body-centered cubic martensite) which occurs upon plastic deformation. However, magnetic patterning attempts on non-magnetic steels are rather scarce (and are usually based on stress-induced patterning [21,24]) although interest in patterned thin films has been sparked by magnetic recording [25,26].

In this paper, we report on the influence of irradiation temperature and time on the magnetic and structural properties of AISI 304L ASS after ion beam nitriding. Moreover, periodic arrays of ferromagnetic structures in the micrometer and submicrometer scale have been prepared at the surface of these steels by direct magnetic patterning using shadow masks. In fact, this patterning technique could be suitable for a range of applications, including recording media, magnetic sensors or magnetic separators.

2. Materials and methods

Disk-shaped samples (10 mm diameter and 2 mm thickness) were cut from commercial AISI 304L ASS polycrystalline bars and then polished to a mirror-like appearance using diamond paste and, as a final step, SiO2 particles. It is worth mentioning that no traces of stress-induced martensite were found after this pretreatment step, resulting in the surface being non-ferromagnetic.

Ion beam nitriding processes (i.e., ion irradiation using nitrogen ions) were carried out with a Kaufman-type ion source in the temperature range 300–400 °C. The ion energy and the ion current density were ∼1 keV and 0.5 mA cm⁻², respectively. The ratio of the charged species in the ion beam was estimated to be 55% N⁺ and 45% N⁺ [27], corresponding to a flux of ∼3 × 10¹⁵ ions cm⁻² s⁻¹. The processing times were 5, 7 or 30 min. For the patterning process, a 2000 mesh Cu transmission electron microscopy (TEM) grid (with a mesh size of 7.5 × 7.5 µm², 12.5 µm pitch, 20 µm thickness and 3.05 mm diameter) placed on the surface of the ASS samples was employed as a shadow mask in the nitriding processes to fabricate arrays of ordered ferromagnetic entities in the micrometer scale. In addition, alumina membranes (5 µm thickness with pseudo-ordered 300–350 nm diameter pores, self-organized in hexagonal arrays) prepared by means of anodization procedures [28] were used in order to obtain magnetic patterns in the submicrometer range. This type of membrane has already been used as irradiation masks to produce magnetic nanopatterning on Co/Pt multilayer films [29] and in TiO2 single crystals [30].

Quantitative nitrogen depth profiles were determined by nuclear reaction analysis (NRA) using the 14N(d,α)12C nuclear reaction at an incident deuterium energy of 1.4 MeV. The structure of the modified surface layer was also investigated by X-ray diffraction (XRD) using a Siemens D5005 diffractometer with Cu Kα1 (λ = 0.15406 nm) radiation at a fixed incident angle of 1° (i.e., glancing incidence mode). The magnetic properties of either the homogeneously nitried areas or the patterned regions were determined by magneto-optic Kerr effect (MOKE) magnetometry (Durham Magneto-optics, maximum in-plane applied field of 70 mT). Note that the MOKE signal represents the change in the angle of polarization of light as a function of the applied magnetic field and is proportional to the magnetization of the sample, although quantitative determination of the sample magnetization is not possible by MOKE. Finally, atomic/magnetic force microscopy (AFM/MFM, Veeco/DI Multimode) imaging was used to examine the surface topography and the local magnetic domain structure of the produced patterns, respectively.

3. Results and discussion

3.1. Structural and magnetic characterization of homogeneously nitried ASS

The structure of the virgin ASS sample is consistent with the fcc lattice structure (i.e., austenite phase, γ). Conversely, as can be seen in Fig. 1, for the nitried samples, each austenite peak exhibits a satellite peak, located at lower diffraction angles (i.e., lattice expansion), which are related to the formation of the “expanded austenite”. The amount of the γN phase increases with the processing temperature, as is evidenced by the increase in the intensity of the γN XRD peaks at the expense of the γ ones. It is noteworthy that after nitriding at 300 °C for 5 min the austenite peaks are already slightly asymmetric (see Fig. 1) due to the existence of tiny tails located on the left-hand side of the austenite XRD peaks. This indicates the incipient formation of the “expanded austenite” phase even for rather mild conditions. Interestingly, peaks located around 38.8° might
be attributed to hexagonal iron nitrides (ε-Fe₃N₁₋ₓ-type) (see Fig. 1).

The above structural results are consistent with NRA observations (see Fig. 2). Actually, for higher processing temperatures and/or longer treatments, the retained fluence and maximal nitrogen concentration are larger and the nitrogen penetration is deeper. For instance, the depth of the nitrogen-rich layers corresponding to the 400 °C/5 min and 400 °C/30 min nitrided samples is around 0.6 and 1.2 μm, respectively (see Table 1) [31]. As expected, the implanted fluences, obtained by multiplying the ion flux and the processing time (i.e., 5 or 30 min), are larger than the retained ones, obtained from the integration of the curves in Fig. 2, since both backscattering and sputtering processes take place during nitriding. Moreover, whereas the maximal nitrogen concentration corresponding to the 350 °C/5 min and 400 °C/5 min samples is rather similar, the retained fluence of the 400 °C/5 min sample is almost twice the value of the 350 °C/5 min specimen, demonstrating the role of temperature in promoting nitrogen interstitial diffusion and, therefore, in achieving larger nitrogen penetration depths.

Remarkably, as can be seen in Fig. 3a–c, MOKE measurements of the nitrided samples exhibit a clear ferromagnetic behavior. Moreover, since the average grain size of the ASS samples is about 30 μm and the employed laser spot of the MOKE apparatus was focused down up to 3 μm in diameter, changes in the remnant magnetization, Mᵢ, and coercivity, Hᵧ, are observed when varying the in-plane angle of measurement (Fig. 3b) due to the crystallographic orientation of the measured grain with respect to the applied field (i.e., magnetocrystalline anisotropy). Note that both the remnant magnetization and the coercivity, Hᵧ, decrease when increasing the in-plane angle of measurement (i.e., from 0° (easy axes) to 90° (hard axes)). Measurements carried out in other regions (i.e., other grains) often lead to different magnetization reversal curves due to the different orientations of the various grains with respect to the applied field direction. In addition, measurements using a completely defocused laser spot ~100 μm in diameter were also performed, resulting mainly in hysteresis loops comprising all in-plane contributions due to the random grain orientation (see Fig. 3c). Comparing the hysteresis loops of the different samples (Fig. 3a–c), it can be seen that the induced coercivity is comparable for all samples since the nature of the generated phase is similar in all cases. Interestingly, taking into account that MOKE is a surface-sensitive technique (~20–50 nm penetration depth), this implies that all the nitriding treatments induce sufficient nitrogen content at the surface of the patterned areas to induce a ferromagnetic phase. Note that the virgin ASS samples exhibit no MOKE signal (i.e., non-hysteretic behavior) (see Fig. 3d). However, as can be seen

![Graph](image1.png)

**Fig. 1. X-ray diffraction patterns of nitrided ASS samples (nitriding duration 5 min for 300 and 350 °C and 5 and 30 min for 400 °C). The stars correspond to the γₜ phase and the plus symbols to the ε-Fe₃N₁₋ₓ-type phase.**

![Graph](image2.png)

**Fig. 2. NRA nitrogen distribution profiles of the nitrided A304L ASS specimens. The lines are visual guides.**

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>300 °C/5 min</th>
<th>350 °C/5 min</th>
<th>400 °C/5 min</th>
<th>400 °C/30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Implanted nitrogen fluence (atoms cm⁻²) × 10¹⁷</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>54</td>
</tr>
<tr>
<td>Retained nitrogen fluence (atoms cm⁻²) × 10¹⁷</td>
<td>0.66</td>
<td>2.4</td>
<td>4.3</td>
<td>11</td>
</tr>
<tr>
<td>Maximal nitrogen concentration (at.%)</td>
<td>8.1</td>
<td>17.2</td>
<td>17.7</td>
<td>22.7</td>
</tr>
<tr>
<td>Sputtered depth (nm)</td>
<td>85</td>
<td>82</td>
<td>152</td>
<td>240</td>
</tr>
<tr>
<td>Standard deviation (nm)</td>
<td>10</td>
<td>12</td>
<td>20</td>
<td>23</td>
</tr>
</tbody>
</table>

in Fig. 3a, short-term irradiation at 300 °C already yields an easily measurable ferromagnetic response. This is consistent with glancing incidence XRD, which shows that, even for the mildest conditions, expanded austenite is formed. However, this may appear to be at variance with the NRA results, although one has to bear in mind that the depth resolution of NRA is around 150 nm near the surface [14]. Thus this technique would not be able to determine the nitrogen concentration of the sample nitrided at 300 °C for 5 min, since its nitrogen penetration depth (see Fig. 2) is almost the depth resolution of NRA at the surface. Nevertheless, the presence of ferromagnetic hexagonal iron nitrides (\(\varepsilon\)-Fe\(_2\)N\(_{1+x}\)-type [16,17]) within the nitrided layer may also explain, to some extent, the ferromagnetic character of the sample nitrided at 300 °C for 5 min.

3.2. Micrometer-scaled magnetic patterning

As can be seen from the MFM image of the sample nitrided at 400 °C for 5 min through a TEM grid (Fig. 4a), magnetic patterns of a few microns in size are indeed formed at the surface of the sample. Fig. 4a is the corresponding MFM image of Fig. 4b (topographic image) taken in an applied magnetic field of ~70 mT, where a magnetic dipolar contrast can be clearly seen in each entity, confirming the feasibility of the production of periodic arrays of isolated ferromagnetic structures (i.e., dark and bright areas due to magnetic stray fields are only observed inside the patterns, while no contrast is visualized outside the structures).

The AFM image of the patterned area (Fig. 4b) shows that a sputtering process of the surface took place during nitriding (see also Table 1), resulting in the formation of a periodic array of squared pits. Since the sputtering depends on crystalline orientation and the samples are polycrystalline, an average value of the sputtered depth is given in Table 1. Note that the aforementioned corrugation process of the diverse surfaces is more pronounced for longer irradiation times and/or higher temperatures. The hysteresis loop of the patterned area obtained by MOKE is shown in Fig. 4c. The hysteresis behavior of the homogeneously nitrided areas and the patterned ones are quite similar due to the fact that the induced ferromagnetic structures are relatively large (micrometer range), leading to entities with magnetic multidomain configurations [32].

MFM and MOKE measurements confirm that the ferromagnetic entities are surrounded by a paramagnetic matrix, as expected, since the distance between the structures is in the micrometer range and nitrogen lateral diffusion is far less than 1 \(\mu\)m (in fact, the penetration depth for the most nitrided sample is about 1.2 \(\mu\)m).

As in the continuous approach, changes in \(H_C\) are also observed when varying the in-plane angle of measurement (not shown) due to magnetocrystalline anisotropy, since the corresponding MOKE measurements were performed using a focused laser spot. As expected, after defocusing the laser spot (i.e., several grains measured), hysteresis

Fig. 3. (a) Focused MOKE loop of the sample nitrided at 300 °C for 5 min. (b) Focused MOKE measurements of the 350 °C/5 min sample along the hard axes (90°), 45° and the easy axes (0°). (c) Focused and defocused MOKE loops of the 400 °C/5 min sample. The inset in (c) shows an enlarged image of the MOKE loops. (d) MOKE measurements of the non-nitrided specimen. Measurements in panels (a), (b) and (c) correspond to homogeneously nitrided samples.
loops composed of both easy and hard axis contributions were again obtained.

3.3. Submicrometer-scaled magnetic patterning

As a proof of principle, periodic arrays of ferromagnetic structures in the submicrometer range have also been directly prepared at the surface of the paramagnetic ASS by nitriding through alumina templates (see Fig. 5a (AFM) and Fig. 5b (MFM in an applied magnetic field of ~70 mT)). In this case, the ion beam nitriding process was performed at 400 °C for 7 min in order to minimize the lateral diffusion of nitrogen. Hence, the obtained ferromagnetic structures are surrounded by a paramagnetic matrix (i.e., non-nitrided areas). Nevertheless, although some areas show clear isolated magnetic entities, other areas appear to be magnetically interconnected. This arises from the pseudo-ordered nature of the alumina templates, where, in some areas, the separation walls between pores may not be thick enough (see Fig. 5a) to avoid lateral nitrogen diffusion through these isolation regions. In spite of the existing non-homogeneity in this patterned media, coerciv-
ities, $H_C$, of around 9 mT are typically obtained (see Fig. 5c), whereas $H_C \sim 2-4$ mT are measured in the microscaled patterned areas (see Fig. 4). Since the laser spot of the MOKE system was focused down to a diameter of 3 μm (i.e., large enough to measure several structures), interconnected structures and isolated ones are susceptible to being measured simultaneously. Note, however, that if the laser spot of the MOKE system is varied between 3 and 20 μm within one grain, the resulting hysteresis loops are virtually identical. The enhanced $H_C$ may be ascribed to both the physical constraints that the reduced sizes of the nanoscaled structures impose on the propagation of magnetic domains [33] and the existence of single-domain entities [33]. Furthermore, as occurs for the homogeneously irradiated samples, changes in $H_C$ are also observed when varying the in-plane angle of measurement due to the specific crystallographic orientation of the measured grain.

It should be pointed out that conventional methods for magnetic dot fabrication, such as electron beam lithography, nano-imprinting onto capping resist layers, chemical routes or scanning probe lithography, are rather complex and usually involve multiple processing steps [33]. Conversely, the employed method yields large patterned areas in a single and direct step (i.e., ion beam nitriding through shadow masks to generate local ferromagnetism) that typically takes just a few minutes. It is notable that this approach uses ion irradiation in a “constructive” way (i.e., to generate magnetism) rather than in a “destructive” way as it is usually used (i.e., to destroy magnetism) [34]. Nevertheless, it should be mentioned that periodic arrays of magnetic structures have occasionally been produced via creation of ferromagnetism using other approaches, e.g., laser patterning [35]. The main drawback of using ion beam nitriding for magnetic patterning is the observed sputtering due to extensive energetic ion irradiation which results in surface roughening (see Table 1). For some possible applications, where the surface roughness plays a crucial role, this can be overcome by minimizing physical damage effects (e.g., shorter processing times) or by employing other nitriding techniques such as plasma or gas nitriding [36,37]. However, the obtained topographic structure can be favorable for other applications such as magnetic separators.

4. Conclusions

In summary, we have demonstrated that it is possible to fabricate, in a controlled manner, periodic arrays of micron and submicron magnetic structures at the surface of nonmagnetic austenitic stainless steels by means of ion beam nitriding. This method is based on the expansion of the austenite lattice due to the incorporation of nitrogen atoms that occurs during irradiation of ASSs. In principle, this process of selectively and locally inducing ferromagnetism could also be performed by means of other nitriding processes such as gas or plasma nitriding. Hence, this patterning technique could have a wide range of applications, including recording media or magnetic sensors. Moreover, other types of applications, such as magnetic separators (e.g., localized zones to trap magnetic particles), could be envisaged for the generated structures.

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