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Nitriding of Fe–Cr–Ni films by low energy ion implantation

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Abstract

Nitrogen low energy implantation was carried out simultaneously into thin austenitic stainless steel films, deposited by ion-beam sputtering, and bulk samples with the aim to investigate the influence of the grain size and microstructure on diffusion and phase formation. Nitrogen uptake, diffusion and phase formation were investigated using SIMS, XRD and TEM. The diffusion itself is very similar in bulk material and thin films, indicating that the grain size differing by close to a factor of 1000 is not the dominating factor. In contrast, the transition towards CrN precipitates within a martensitic host was only found for the thin films implanted at 360 °C.

Keywords: PIII; steel; diffusion; TEM; XRD

1. Introduction

Austenitic stainless steel, well known for its outstanding corrosion resistance, can be nitrided using energetic ion for improving the hardness and wear resistance [1]. Typically, a modified layer thickness up to 10–15 μm can be obtained with a fast nitrogen diffusion observed in the temperature window of 300–400 °C [2]. At lower temperatures, ε-nitride is formed, whereas CrN precipitation and a reversion of the remaining matrix into ferrite is observed at higher temperatures. A competition of oxygen and nitrogen for the surface adsorption sites requires an oxygen partial pressure of 10^{-5} mbar or better, depending on the ion current density [3]. At the same time, the diffusion rate is observed to be correlated with the grain size [4,5]. However, the transport along grain boundaries is not the dominating mechanism [6,7].

Formation of expanded austenite using direct PVD methods has not been reported until now, which could be related with intrinsic stress inside the expanded austenite layers of up to 1.5 GPa [8]. However, there is abundant information on α''-$Fe_{16}N_2$, ε-Fe_3N and related nitrides obtained at varying temperatures and gas flows using vacuum arc [9] and magnetron sputtering [10,11]. Nevertheless, laser nitriding in nitrogen atmosphere can lead to the expanded phase [12].

In a previous work [13], plasma immersion ion implantation (PIII) of nitrogen into Fe–Cr–Ni films, deposited with ion-beam sputtering from an austenitic stainless steel target was reported. In this work, these experiments are extended to low energy implantation (LEI) of nitrogen in the range of 800 to 1500 eV, where additional preheating is possible and the initial phase of the nitriding process can be investigated.

2. Experiment

Thin Fe–Cr–Ni films were deposited on Si (111) substrate by ion-beam sputtering (IBS) of austenitic stainless steel target (AISI 304, respective DIN 1.4301/X5CrNi18.10). The ion-beam sputtering experiments were performed in a UHV chamber (base pressure 10^{-8} mbar, deposition pressure 10^{-4} mbar) using accelerated Argon ions [14]. The process times were adjusted for a final layer thickness of 500–1500 nm at a deposition rate of about 0.4 nm/s. The growing film was bombarded by high energy backscattered Ar ions, together with sputtered atoms at a kinetic energy ranging from 1 to 5 eV. The geometrical setup and further details can be found in Ref. [15].

Subsequently, these deposited Fe–Cr–Ni layers, together with coupons from the same steel grade as the original sputter target, were implanted with nitrogen using low energy ion implantation. The experiments were performed in a different vacuum chamber at a base pressure of better than 10^{-8} mbar, using an ECR broad beam ion source operating at 2.54 GHz

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with a diameter of 125 mm. In this report, a fixed acceleration voltage and temperature of 1 kV and 360 °C were respectively used. The implantation time was varied between 1 and 15 min, corresponding to an incident flux of about $0.2–3.2\times10^{17}$ nitrogen atoms/cm^2 [16]. For the initial heating of the samples, the substrate holder was rotated by 180° and the backside was heated by the ion beam for 60 min to obtain an equilibrium distribution across the whole substrate holder.

The samples were characterised by secondary ion mass spectroscopy (SIMS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy. SIMS was employed to obtain qualitative and quantitative information on the nitrogen depth distribution as well as on the composition of the films and the bulk material. X-ray diffraction (XRD) measurements were carried out to identify the phase components, while morphology in plan-views and cross section was analysed by SEM.

The nanostructure of the nitrogen-implanted coating was imaged in a 400 kV JEM 4010 transmission electron microscope (TEM, point resolution 0.155 nm). Cross-sectional TEM samples were obtained by face-to-face gluing, embedding into alumina tubes [17], slicing, mechanically grinding, one-sided dimpling, polishing and Ar^+ ion-beam etching at a glancing angle of 5° and an acceleration voltage of 2.5 keV. Micrographs recorded onto plane film were digitised using a Nikon CoolScan 9000 ED scanner camera capable of a true resolution of 4000 dpi.

3. Results

Fig. 1 shows a cross section of a Fe–Cr–Ni thin film deposited onto Si with a thickness of 1260 nm before the subsequent nitrogen implantation. A fine and dense columnar structure with diameter of 25–100 nm, corresponding to the deposition regime at ambient temperature with ion bombardment is visible. The corresponding XRD data, depicted in Fig. 2 prove that the austenitic fcc structure is retained after the sputter deposition process, albeit with the orientation distribution slightly deviating from a random one, tending towards the (311) direction being preferentially oriented normal to the surface.

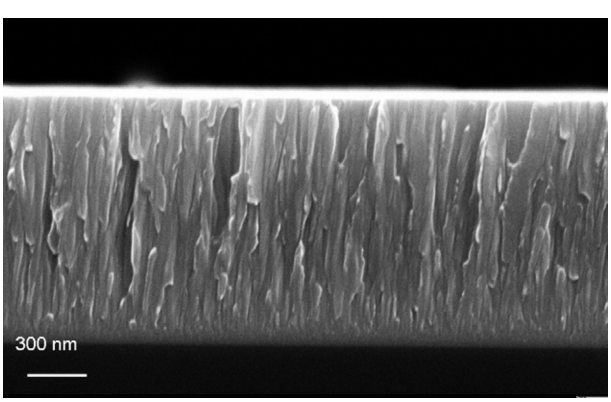

Fig. 1. SEM image of cross section of Fe–Cr–Ni film as deposited on Si.

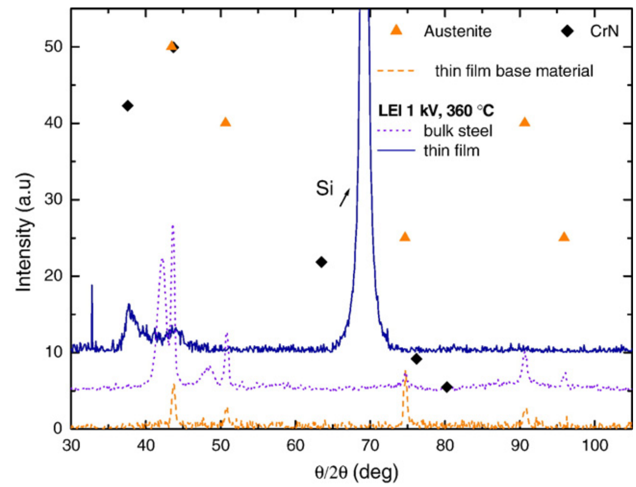

Fig. 2. XRD spectrum of as deposited Fe–Cr–Ni thin film, in comparison with bulk and thin film after LEI for 6 min.

The chemical composition of these films is deviating less than 10% from the original material, as checked by secondary ion mass spectroscopy (SIMS). No enrichment with carbon or oxygen was found, while the nitrogen content is increased by a factor of 2–5 compared to the base material. The contamination with argon from the sputter ion beam is less than 2 at.%. One major difference between PIII and LEI, besides the possibility of preheating in the latter case, is the highly different current density as PIII at 10 keV necessitates an ion flux reduced by

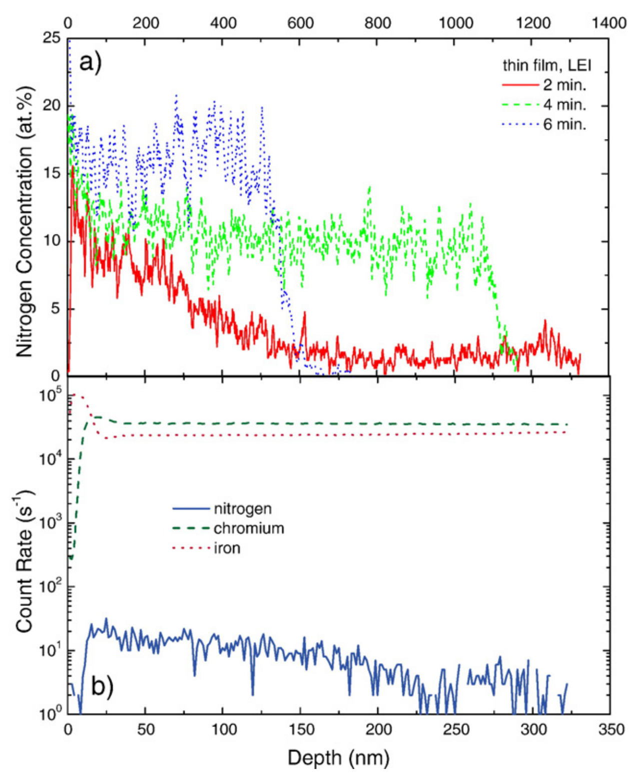

Fig. 3. a) SIMS nitrogen depth profiles of thin films implanted with nitrogen at three different times, b) SIMS count rates as a function of depth for a bulk sample nitrided for 2 min. Please note the different depth scale for panels a and b.