



Orientation dependence of nitrogen supersaturation in austenitic stainless steel during low-temperature gas-phase nitriding

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Abstract

A hardened surface layer was produced on 316L austenitic stainless steel via low-temperature gas-phase nitriding. The effects of nitriding temperature, nitrogen activity and processing time were systematically studied. Concentration–depth profiling by Auger electron spectroscopy revealed very high levels (up to 25 at.%) of interstitial nitrogen in solid solution. This causes a lattice parameter expansion of up to 10% at the alloy surface. X-ray diffractometry revealed that the expansion – and thus the level of nitrogen supersaturation – strongly depends on the crystallographic orientation. We attribute this effect to the elastic anisotropy of austenite, exacerbated by a nitrogen-induced paramagnetic-to-ferromagnetic transition.

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1. Introduction

Diffusing interstitial solutes (such as nitrogen or carbon) into the surface of austenitic stainless steel at low temperature can generate a precipitate-free hardened surface layer (“case”) with a “colossal” supersaturation of the solutes, causing a significant expansion of the lattice parameter. The nature of the resulting, so-called “expanded” austenite has been of interest since its discovery in the mid-1980s [1,2]. Three common techniques to produce nitrogen-supersaturated expanded austenite are plasma nitriding [3], ion implantation [4] and gas-phase nitriding [5,6]. Gas-phase nitriding, in particular, has a ready control of the nitriding activity [1,5,6], which enables systematic studies of the underlying thermodynamics and kinetics. The non-equilibrium conditions under which a colossal nitrogen

supersaturation can be accomplished have been denoted as nitrogen “paraequilibrium” [7–9].

Christiansen et al. [10] compared the dilatation per atom of nitrogen and carbon interstitials in austenite and found that they are equally strong dilators. The maximum non-equilibrium concentration of nitrogen in low-temperature-nitrided austenitic stainless steel can reach 38 at.% [10,11]. With low-temperature carburization, carbon concentrations of up to ≈ 15 at.% have been realized [10,12]. Owing to the larger concentration, the corresponding lattice parameter expansion accomplished by low-temperature nitriding can be as large as 10% [10,11,13], compared to $\approx 3\%$ in low-temperature-carburized austenite [10,12]. It has been known for over a decade [12,14,15] that the lattice parameter expansion caused by such high concentrations of interstitial nitrogen is apparently anisotropic, e.g. after carburizing $d_{111} < d_{200}$, where d_{hkl} denotes the spacing of the $\{hkl\}$ lattice planes. This has been explained in terms of a crystallographically anisotropic, i.e. orientation-dependent Poisson effect in response to the (large) residual biaxial stresses generated by the interstitials [12].

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In the present study, we report the effects of nitriding temperature, nitrogen activity in the gas phase and nitriding duration. We also investigate the paraequilibrium nitrogen solubility predicted by CALPHAD modeling and compare it to the experimentally observed surface concentrations of nitrogen. The results lead to a new model explaining the effect of grain orientation on the nitrogen supersaturation and corresponding lattice parameter expansion.

2. Experimental methods

All gas-phase nitriding experiments were performed employing a customized nitriding furnace (CVD Equipment Corporation, Ronkonkoma, NY). The process begins with a “surface activation” step in which gaseous HCl [16] ($325\text{ }^{\circ}\text{C}$ (598 K) in 0.21 min^{-1} ($3.3\text{ mm}^3\text{ s}^{-1}$) HCl and 1.8 l min^{-1} ($30\text{ cm}^3\text{ s}^{-1}$) N_2) removes the passivating surface oxide. The nitriding is subsequently carried out by providing a gas mixture containing NH_3 , H_2 and N_2 . At any given temperature, the activity of nitrogen a_{N_2} is determined by the partial pressures of NH_3 and H_2 gases according to

$$a_{\text{N}_2} = \left(K \times \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \right)^2 \quad (1)$$

where K is the equilibrium constant for the dissociation reaction of NH_3 and P_{NH_3} and P_{H_2} are the partial pressures of NH_3 and H_2 , respectively. The individual effects of temperature, nitriding activity and duration on low-temperature gas-phase nitriding of the 316L alloy were quantitatively investigated. (Values of K were obtained from FactSage thermochemical software.)

316L samples were nitrided in 11 separate treatments. Six treatments were performed at 713 K ($440\text{ }^{\circ}\text{C}$) for 20 h, with a_{N_2} equal to 1, 200, 1700, 7400, 1.8×10^5 and 4×10^9 . For the last activity, only NH_3 and N_2 were used but we assumed that 1% H_2 was produced by the dissociation of NH_3 . (Other researchers [6] considered this condition as infinite activity.) For $a_{\text{N}_2} = 7400$, nitriding treatments were performed at three other temperatures for 20 h: 623 K, 693 K and 723 K ($350\text{ }^{\circ}\text{C}$, $420\text{ }^{\circ}\text{C}$ and $450\text{ }^{\circ}\text{C}$). At 713 K and $a_{\text{N}_2} = 7400$, nitriding was also performed for 5 h and for 80 h. After each treatment, the sample was furnace-cooled in a N_2/H_2 atmosphere.

Auger electron spectroscopy (AES) cross-sectional line scans were used to determine composition–depth profiles, using a PHI-680 scanning Auger microprobe (Physical Electronics, Chanhassen, MN). Before the acquisition of each AES line scan, $\approx 50\text{ nm}$ of material was sputtered off the cross-sectional sample by an Ar^+ plasma to remove hydrocarbon contaminants and native oxide. During acquisition of the AES line scans, dynamic Ar^+ sputtering was carried out to avoid oxygen accumulation from the chamber. This was needed because the overlap of oxygen and Cr peaks [17] could induce uncertainty on the absolute

Cr content. A calibration procedure was performed on two steel standards (B.S.81 N and MBH NSC4) with certified nitrogen contents. By comparing the certified composition of those two samples and quantification results observed from AES analysis, the analytical uncertainty was estimated to be $<1\%$ in absolute nitrogen concentration.

A cross-sectional specimen was prepared from the specimen nitrided for 80 h by cutting the specimen perpendicular to the nitrided surface, mechanically polishing the exposed cross-section and lightly etching in an Ar plasma to reveal the grain structure. The cross-section was examined by scanning electron microscopy (SEM) using an xT Nova Nanolab 200 (FEI, Eindhoven, Netherlands), and the orientations of several grains adjacent to the nitrided surface were determined by electron backscatter diffraction (EBSD).

X-ray diffractometry (XRD) with Cu K_α radiation was employed for phase identification and lattice parameter measurements, using a Scintag (Cupertino, CA) X-1 diffractometer. Grazing incidence XRD (GI-XRD) with an incidence angle of 1° was employed to study lattice spacings at the surface. XRD was also used to estimate the residual stresses, using the sample tilting $\sin^2\psi$ method [18]. A $\{311\}$ reflection was used for this measurement, and the X-ray elastic constants were determined using the published elastic constants for a Fe–18 wt.% Cr–12 wt.% Ni alloy [19] and the approximations proposed by DeWit [20].

One sample was also examined with synchrotron X-rays at the Advanced Photon Source facility at Argonne National Laboratory. This apparatus uses a $\sim 300\text{ nm}$ diameter incident X-ray beam in order to investigate single grains. A two-dimensional X-ray detector was used to determine the individual grain orientations and lattice spacings, and a differential aperture enabled depth-dependent diffraction data. More information on the technique can be found in Ref. [21].

3. Results

3.1. Nitrogen concentration–depth profiles

The effects of nitriding duration, activity and temperature on the nitrogen concentration–depth profiles are shown in Fig. 1a–c, respectively. All profiles demonstrate a concave shape with sharply decreasing diffusion tails. This profile is typical for low-temperature nitriding of austenitic stainless steels and other face-centered-cubic (fcc) metals, but very different from standard complementary-error-function-like diffusion profiles. Two different models have been employed to explain these diffusion profiles: the trapping–detrapping model [22,23] and the concentration-dependent diffusivity model [24,25]. Though they assume different microscopic mechanisms, both models can fit the shape of the experimental profiles in Fig. 1 (see Appendix A). The determination of the more appropriate model is not within the scope of this paper.

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