Nitriding of stainless steel in an rf plasma

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Treatment of stainless steels in an rf-powered nitrogen plasma achieves a much increased rate of nitriding, as well as higher hardness and corrosion resistance than traditional nitriding. Small amounts of adsorbed hydrogen are found to be necessary initially, and the process of nitriding is modeled on the basis of this hydrogen increasing the surface sticking coefficient for nitrogen, which is followed by nitrogen diffusion into bulk in the form of nitrogen-vacancy (weakly bound) pairs. The detailed microstructural role of chromium in the process is also discussed.

INTRODUCTION

Interest in nitriding of metal surfaces has been rapidly growing. Applications range from improvement of corrosion and wear-resistance to modification of electronic properties. Industrial methods, which include traditional gas and liquid nitriding, have more recently moved in the direction of ion implantation and plasma treatments using dc,[1] rf,[2] or microwave[3] discharges. Plasma and ion nitriding have a number of advantages over gas nitriding, especially in the treatment of stainless steels which are generally considered difficult to nitride. At the temperatures attained in plasma treatment, nitrided stainless steels retain well their hardness and corrosion resistance.

Despite the recent commercial applications of both ion and plasma nitriding, little is known of the microstructural effects of these processes. Thus choice of optimum parameters for nitriding has almost always been made by trial and error. Moreover, explanations given for the microscopic processes involved in rf-plasma nitriding are full of contradictions.

General questions arise that are both microstructural and plasma diagnostic in origin. For example, why is ion nitriding, in which a component is exposed to a much smaller density of nitrogen-containing species, more effective than conventional ammonia-gas or salt-bath processing? And why does plasma nitriding require much shorter times and give less distortion and yet better wear resistance and fatigue strength than traditional methods?

Other questions appear to be solely diagnostic; for example, why is an rf plasma much more effective than a dc plasma for nitriding,[4] and what is the role of hydrogen in the plasma gas mixture which, for nitriding of steels, is never optimum without the presence of some hydrogen?[5] We believe that even the latter questions may have their answers embodied in surface microstructural effects. For example, the rate of nitriding—once an equilibrium surface concentration has been established—should be controlled by diffusion, but our results with rf nitrogen plasmas[4] indicate rates of nitriding far in excess of the limit expected thermodynamically.

We propose in this paper a mechanism in which the diffusion involves nitrogen-vacancy pairs, whose formation is catalyzed by hydrogen adsorption and the initial creation of hydrogen-vacancy (excitoniclike) pairs at the surface. The model is supported by the fact that the surface nitride configuration closely relates to that of nitrogen atoms in low-index planes of Fe_4N. This helps to promote formation of the nitrogen-vacancy pairs.

PLASMA-NITRIDING MECHANISMS

Gas adsorption followed by interstitial diffusion of nitrogen is not sufficient alone to explain the rates and depths of nitriding achieved by plasma treatment. Two essentially opposed models have hitherto been proposed for the microscopic processes involved. These are the ionic model[5] and the atomic model.[6]

According to the former, the nitriding is caused by bombardment and adsorption of nitrogen ions from the plasma. It has been demonstrated, for example, that with dc plasmas a cathode current is required. The ionic mechanism requires diffusion of so-called ion-vacancy pairs in the nitriding process,[6] following combination of N ions with vacancy states at the surface. The most tightly bound pairs would be composed of vacancy-ion interstitials. Electrostatic forces would dominate,[7] and it has been calculated that a local effective coefficient of diffusion, for the vacancy-ion pairs, would be proportional to the current density of ions in the plasma.[8]

Evidence for the ionic model is found in the sensitivity of nitriding to a magnetic field[9]; i.e., a lower gas pressure in the discharge can be used when a magnetic field is applied and a diffuse nitride layer still obtained. The ionic model also explains the faster nitriding obtained in a dc plasma on the basis of ion-induced radiation damage. However, a strong electric field should affect the process, which is contrary to experimental observation. Additional objections to the ionic model have also been raised.[5]

The atomic mechanism for plasma nitriding is essential-

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ly the opposite. It has been deduced experimentally[6] that the nitriding is caused principally by neutral species, and the conclusion reached is that atomic nitrogen is the active species. The role of the plasma in this model is to produce nitrogen atoms by dissociation of the N_2 molecules. The diffusion is principally of nitrogen atoms. Support is provided by the observation that an electrically screened sample, protected from nitrogen ions by a biased grid, can be nitrided with the same plasma parameters as used for a nonscreened target. Similarly, it has been observed[10] that the nitriding is unaffected, or even slightly improved, when an ion-repelling dc bias is applied to the sample itself. Other experimental observations[11] support the atomic model, while objections include the magnetic field effect which can only be explained in terms of the ionic model.

An additional controversy centers on the role of hydrogen in the plasma gas. One proposal is that the hydrogen simply reduces surface oxides, without participating in the nitriding process. This is supported by the claim that nitriding can be achieved in a pure nitrogen-argon plasma,[2,5,12] but is not consistent with the finding that efficacy of nitriding of steel is increased in the presence of hydrogen.[2] This contradiction led to a proposed "active hydrogen" mechanism[5] in which nitrogen-hydrogen molecular ions are formed and dissociate at the cathode, producing active nitrogen which penetrates the surface barrier. This proposal is supported by the fact that the addition of only 1% hydrogen (insufficient to be effective in deoxidizing the surface or to produce a significant increase in ion flux) has a large effect on the rate of ion nitriding.

To explain the effect of hydrogen, Edenhofer[11] proposed a mechanism in which the nitride is formed in the gaseous interphase, between the solid and the gas, after the Fe ions are sputtered from the cathode. This mechanism we regard as unlikely, and our proposed model, in which an excitoniclike hydrogen-vacancy pair is formed, involves three stages: (1) surface sticking, (2) adsorption and nitrogen-vacancy pair creation, and (3) diffusion of nitrogen-vacancy pairs.

SURFACE STICKING

The sticking coefficient on iron for the dissociative adsorption of N_2 molecules is extremely low. Depending on the surface structure, it lies in the range of 10^{-7}–10^{-6} s.[13]

The dissociative chemisorption of N_2 molecules can be formulated in two steps: $N_2 \rightarrow N_2(ad) \rightarrow 2N(ad)$; i.e., molecularly adsorbed $N_2(ad)$ is the precursor for the dissociative adsorption.[14] Direct dissociation, $N_2 \rightarrow 2N(ad)$, is discounted, first, because $N_2(ad)$ is known slowly to convert to $N(ad)$ with or without the presence of N_2 in the gas phase,[15] and second, because the sticking coefficient for dissociative adsorption in iron is several orders smaller than is the coefficient for trapping in the molecular state. Also there is no evidence for an increase of overall sticking coefficient with increasing translational energy for N_2 molecules; so the activation barrier cannot be directly overcome by increase of temperature.

A possible intermediate step, in dissociative adsorption, is observed in vibrational states of N_2 molecules.[16] X-ray and UV photoelectron studies, plus HREELS measurements,[14] show that the precursor state is a nitrogen molecule aligned with its axis parallel to the surface. This alignment causes an increase of the N—N bond length in the molecule and considerable weakening of the bond, resulting from partial occupation of the antibonding molecular levels by charge transfer from the iron atoms, with consequent reduction in the activation energy for dissociation. Transitions from the N_2 molecular gamma state (N—N bond perpendicular to the surface) to the molecular alpha state (N—N bond parallel to the surface) have an activation energy that depends on the degree of gamma and alpha coverage of the surface.[15]

The observed increase in the work function of iron with nitrogen adsorption[17] supports the view that charge transfer occurs into the antibonding σg^* levels, indicating the alpha state to be an electron acceptor. Decreases of work function of iron[13] have been observed in the presence of small amounts of coadsorbed hydrogen, while similar decreases in work function have been reported for adsorbed nitrogen.[18] Initially, an activation barrier (E_a in Fig. 1) separates the precursor state from the chemisorbed state, determining the probability of chemisorption.[18,19] Thus coadsorbed hydrogen plays a crucial role in decreasing the work function of the metal and through this directly influences the nitriding process.

ADSORPTION AND NITROGEN-VACANCY PAIR CREATION

For transition metals with high densities of 3*d* electrons, adsorption of even small amounts of hydrogen in the pres-

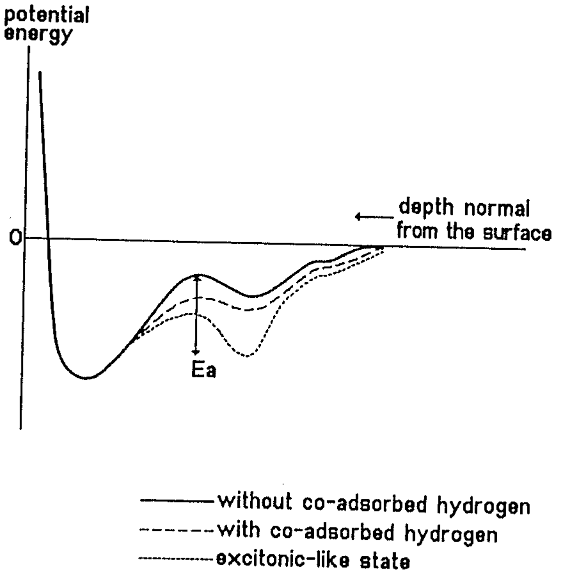

FIG. 1. Schematic energy diagram for proposed nitriding model. E_a is the activation barrier between chemisorbed N atom and physisorbed N atom. Both this energy barrier and the potential of the intermediate state of physisorbed nitrogen are lowered (dashed curve) in the presence of coadsorbed hydrogen, while the formation of an excitoniclike subsurface hydrogen state produces (dotted curve) an intermediate metastable state of even lower potential. The shallower minimum, close to the surface, represents the adsorbed N_2 precursor state.

ence of a large concentration of vacancies at the surface causes the formation of hydrogen-vacancy (excitoniclike) surface states.[20,21] These are acceptorlike levels[22] with large correlation lengths that can assist in the capture of nitrogen species from the gas phase into an adsorbed state.

We propose their formation to be the first step in the plasma nitriding of stainless steels. Figure 1 shows schematically an energy diagram for the absorbed species in the nitriding process. The molecular bond of the adsorbed N_2 is weakened by charge transfer into the excitoniclike hydrogen state, and the nitrogen atomic p states then interact with metallic iron s and d states. These hybridized states at the top of the iron d band cause new pd bonding and pd antibonding states to occur, respectively, below and above the Fermi level, stabilizing the precursor state (dotted curve, Fig. 1). Thus the nitrogen and hydrogen electronically exchange, producing nascent adsorbed hydrogen atoms and nitrogen-vacancy pairs. The latter diffuse into the bulk material, while the former can cause formation of new excitoniclike states. Only very little hydrogen is needed (less than the 1% found to be effective[5,13]). In our work residual hydrogen, from hydrocarbon background gases, has been found to be sufficient. We find that when UHV conditions are established, prior to attempts to nitride in a pure nitrogen plasma, that no surface hardening occurs, and that little nitrogen (or hydrogen) pickup is detected on investigation of the treated surface by secondary-ion mass spectrometry (SIMS).

The surface nitride formed in plasma-nitrided samples has been shown by x-ray diffraction studies[4] to be $\gamma' Fe_4N$, which is isomorphous with γ iron. The vacancy concentration is highest in the low-index planes, assisting in the formation of excitoniclike states.[21,23] Thus the nitride precipitation in this form assists nitrogen absorption by the proposed mechanism. The high energy of excitation of gaseous species in the plasma helps to promote both the necessary H-ion trapping at the surface and the N—N bond dissociation. With rf-powered discharges, the excitation can be specific to a molecular bond, and the excitoniclike states effectively form "hot spots" on the surface, similar to those claimed for methane plasmas.[24]

A nitrogen-vacancy (weakly bonded) pair could be created from either the ionic or atomic state of nitrogen. Formation from N ions is not favored, in our view, because the high energy of N ions can easily cause impact desorption of the hydrogen (bound at the surface in hydrogen-vacancy excitoniclike states). Ion damage and implantation could be a direct mechanism for creation of nitrogen-vacancy pairs, but chemical exchange of hydrogen-nitrogen species at the surface would—we believe—be far more effective for their creation. Their formation, depending on the initial creation of a hydrogen-vacancy surface state and not on ion damage at the surface, can also explain contradictions in reports of the effect of operating the sample, in rf plasma nitriding, at a floating potential. It is not of direct consequence whether the sample is "floating." Although the latter may prevent excessive ion damage, and thus allow subsurface excitoniclike hydrogen states to form, the presence of at least residual hydrogen is also essential.

DIFFUSION

The local diffusion coefficient for all species in the damaged region is large,[8] while thermodynamically "nonrequired" oxygen species and other impurities are removed from the surface by the plasma so that the critical surface regions consist of only the reagent species. The proposed hydrogen-nitrogen exchange thus results in neutral nitrogen-vacancy (weakly bonded) pairs, which migrate into the bulk by fast substitutional diffusion. This contrasts with the interstitial mechanism required for N-ion diffusion and invokes no electrostatic forces as needed for charged N-ion vacancy pairs.[8]

The diffusion is assisted by the atomic configuration of dissolved nitrogen atoms in iron. These exist in octahedral interstitial sites.[25] When a vacancy occurs at an iron site in a neighboring octahedron, the potential field can cause an interstitial nitrogen atom to move easily to the interstitial site of this neighboring octahedron, by coupling with the iron vacancy. An iron vacancy migrates rapidly; thus a weakly bonded vacancy-nitrogen pair when formed will move quickly into the bulk from the plasma-damaged region. The potential barrier for migration of the nitrogen atom into a neighboring octahedral cluster that shares an iron vacancy is much smaller than to an octahedron that has no vacancy. The iron vacancy is a lattice defect to which the diffusing nitrogen atom couples itself weakly.

For diffusion into the nondamaged bulk material, a plentiful source of nitrogen atoms and unpaired vacancies exist on the damaged surface layer. The nitrogen atoms originate as trapped N ions, immediately screened by the metal valence-band electrons. Their migration lowers the local density of electronic states by rearrangement of the d electrons in a manner well known[26] for antibonding surface-state interactions.

In the absence of hydrogen (and hydrogen-nitrogen exchange), the sticking coefficient is much less, and the nitriding depth and hardness achieved are much smaller.[5] On the other hand, addition of hydrogen to the nitrogen plasma, reducing the formation of stoichiometric iron nitrides, results in increased hardness,[2] which indicates that the surface hardening is due to formation of a homogeneously nitrided (clustered) matrix rather than simply to a precipitated iron nitride phase. We discuss this further below.

MICROSTRUCTURAL STUDIES

Microstructural aspects of the nitriding of steels are dominated by the role of chromium, which is often added as an alloying element to steels that are to be nitrided because of its affinity for nitrogen. It has the effect of increasing the hardness of the steel[27] by formation of chromium nitride particles. The strong nitrogen-chromium interaction results in all of the chromium in the matrix-forming nitride. The chromium nitride particles are randomly distributed, when the precipitation is homogeneous, and the large internal stress introduced[28] can cause high microhardness. The microstructural origin of the high stresses is, however, complex. First, the iron nitride phases produced by nitriding (ϵ

and/or γ' phases) have larger specific volumes than the steel from which they form and thus grow in a state of compressive stress. At greater depths, where the nitrogen potential becomes insufficient to form iron nitrides, solid solution hardening is caused by the tetragonal distortion of the matrix by nitrogen in the octahedral interstices. However, the largest microstress, in both iron nitride and steel matrices, is due to Cr and N solute-atom clustering (which we believe in stainless steels to be a GP-zone-type clustering[29]) and precipitation of stoichiometric CrN.

It has been shown[25] that homogeneous precipitation in nitrided alloys is preceded by a stage of coherent clustering, in which substitutional-interstitial atom clusters are formed. On aging, these eventually transform to an incoherent equilibrium precipitate. This has been demonstrated for chromium steels by Rozendaal, Colijn, and Mitemeijer[28] and Mortimer, Grievenson, and Jack[30] and has been shown by Hendry, Mazur, and Jack[31] to be the cause of embrittlement in ferritic stainless steels. Precipitation of extremely fine chromium nitride has also been shown to occur in the γ'-Fe_4N layer of austenitic stainless steels in previous work by Billon and Hendry[27]; it may be inferred to follow from preprecipitation clusters. A detailed discussion of the large specific strengthening effect of clustering has been given by Rickerby and Hendry[32] who describe a model for the mechanical effect.

A mechanism proposed by Mittemeijer and co-workers,[28] for the way in which stresses arise on nitriding, differs in detail from the clustering mechanism proposed by Rickerby *et al.*[29,32] Mittemeijer and co-workers identify a macrostress due to growth (a specific-volume effect) and a microstress due to precipitation, without invoking preprecipitation clusters. The macroscopic effect overall is, however, the same.

CONCLUSIONS

Small (residual) amounts of hydrogen are found to be needed in the rf-plasma nitriding of stainless steels. The mechanism proposed for the nitriding process involves initial formation at the surface of hydrogen-vacancy excitoniclike pairs, with which nitrogen atoms exchange to form nitrogen-vacancy pairs, releasing hydrogen for further generation of the excitoniclike pairs. Fast diffusion of nitrogen-vacancy (weakly bonded) pairs can occur by a mechanism that involves nitrogen atoms in octahedral interstitial sites coupling to an iron vacancy in a neighboring octahedron.

The microstructures produced in plasma-nitrided stainless steel are similar in phase distribution[4] to those produced by conventional nitriding. However, the microstructure is much finer in scale, as a result of the increased nitrogen solubility and diffusivity produced by the plasma process, and produces higher values of hardness.

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