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Experimental Evidences of New Nitrogen-Containing Phases in Nitrided Steels

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The properties of a material depend very often on the presence of a minor component forming nanosized domains. Knowing the structure of these domains is crucial for modifying the properties and/or the reactivity of the material. Nevertheless, this information is usually of involved access due to the lack of crystallinity of the domains. Moreover, for covering materials the specimen of interest appears in a significant concentration only in surface layers.[1] This is the case of nitrided materials in which N atoms are introduced into the outermost layers to modify surface properties.[2,3] Although nitriding is a very common step in materials processing, the identification of the species responsible for the changes in the properties has not been fully ascertained.[4] Here, we report the existence of new nitrogen-containing phases of nanometer-scale size in a steel submitted to ammonia gas nitriding, which drastically enhances it surface hardness (by a factor of 4). Since the new phases are not crystalline and are located in the surface layers, X-ray absorption fine structure (EXAFS)[5] and X-ray photoelectron (XPS)[6] spectroscopies have been used to characterize them. Our results suggest that these new phases, closely related to interstitial nitrides of the alloyed elements, are responsible for the increase in hardness.

A sample of ferritic commercial steel—3% Cr, 0.8% Mo, 0.5% Mn, 0.3% V, 0.3% C, Fe[7]—was submitted to a gas nitriding treatment, which consists of heating the steel under flowing 70% NH_3/N_2 for 35 h at 550 °C.[8] The hardness of the steel, measured with a Matsuzawa Seiki Co. microhardness tester at loads of 300 g, before and after the nitriding process was 280 and 700 Vickers (HV), equivalent to 4 and 8 in the Mohs scale, respectively.[9] The sample submitted to the nitriding treatment will be referred to as nitrided or N and the control sample un-nitrided or UN.

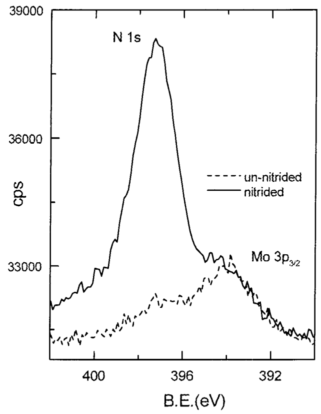

Figure 1. X-ray photoelectron spectra corresponding to the N 1s signal from the nitrided (solid line) and control (dotted line) samples. N 1s: 397.1 eV; Mo $3p_{3/2}$: 394.1 eV.

Glancing angle-X-ray diffraction[10] showed that α-Fe, ferrite (with body-centered cubic structure), was the only crystalline phase before and after the nitriding process. XPS is a surface-sensitive technique[3] that has been useful in the analysis of related systems.[11] It informed us about the content and oxidation state of O, N, Fe, Cr, Mo, and Mn from the outermost surface layers of the sample.[12] As shown in Figure 1, the main difference observed with this technique between the control and the nitrided sample was the appearance of a well-resolved peak at 397.1 eV, corresponding to the N 1s level, overlapping with that of the Mo $3p_{3/2}$ level, and similar to that observed in the XPS spectra of CrN and TiN[13] and of ϵ-Fe_2N_{1-x}.[14]

Since neither new crystalline phases nor substantial changes in chemical composition were detected in the nitrided steel, techniques that do not rely on long-range order had to be used, such as EXAFS. This technique provided us with access to chemically specific information on the average local structure around the alloyed

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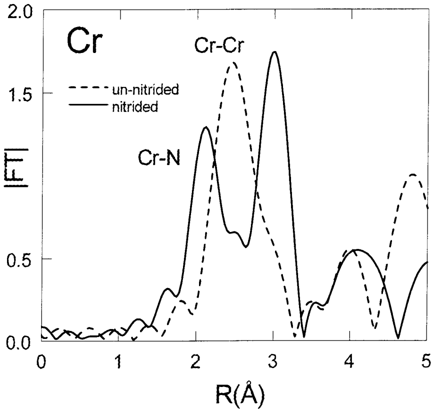

Figure 2. Magnitude of the phase-corrected Fourier transform of the EXAFS spectra of the Cr K-edge of the nitrided (solid line) and un-nitrided (dashed line) sample.

elements located in the zone extending from the surface to a depth of approximately 50 μm. This is a technique that has provided useful information in the study of pure nitrided titanium.[15] The raw spectra, collected in fluorescence detection mode,[16] have been included in Figure 1S of the Supporting Information. As seen there, the signal-to-noise ratio is worse for Mn and V K-edges than for a Cr K-edge since their concentrations were extremely low (0.5% and 0.3% for Mn and V, respectively, and 3% for Cr). The results presented here show that in the three studied elements the local atomic environments were drastically altered by the nitriding process. As an example, Figure 2 includes the Fourier transform (FT, showing the radial distribution around the absorbing atom site) of the EXAFS spectra of the Cr K-edge recorded before and after the nitriding process. As can be seen, the un-nitrided sample is characterized by a first peak at around 2.5 Å, typical of the bcc structure of this metal.[17] This peak does not appear in the nitrided sample, which instead shows two new peaks at around 2.0 and 3.0 Å. Similar changes were observed in the FT of Mn and V (see Figure 2S of the Supporting Information). They strongly resemble the corresponding FT of the pure TiN[15] spectrum. In contrast, no changes were observed in the EXAFS spectra of the major component of the steel, iron, as previously observed by Kizler et al.[18] in the study of ferritic and austenitic nitrided steels. To the best of our knowledge, detection of noncrystalline domains involving nitrogen atoms in commercial steels has not been reported previously. Nevertheless, Bor et al. have reported the formation of a VN phase in an Fe−2 at. % V alloy submitted to gas nitriding at 913 K, by using transmission electron microscopy and electron diffraction.[19]

Table 1. Coordination Distances in Å Obtained from the Analysis of the K-Edges EXAFS Spectra of the Indicated Elements in the Nitrided Sample[a]

	V	Cr	Mn		V	Cr	Mn
6 × M−N	2.05	2.04	2.09	8 × M−N	3.64	3.60	3.66
12 × M−M	2.92	2.93	2.90	6 × M−M	4.15	4.13	4.12

[a] Estimated errors. *R*: first shell, 0.01 Å; higher shells, 0.01−0.03 Å.

Taking into account these facts, the EXAFS spectra of the three elements were analyzed using the FEFF 8.00[20] and FEFFIT 2.54 codes,[21] including the first four coordination shells of MN nitrides, which have the rock-salt structure. Single scattering contributions and selected multiple scattering ones were taken into account, following a procedure similar to that described elsewhere.[22a,b] $S_0{}^2$ was set equal to 0.81, the optimized value obtained as described elsewhere.[22c] The optimized coordination distances have been included in Table 1. MN nitrides were initially described as interstitial nitrides and their structures were thus defined alternatively as a face-centered cubic, fcc, metal network with N atoms in the octahedral holes.[17] Those of Groups 3−7 are characterized by their extreme hardness.[23] The quantitative analysis of these spectra showed that the majority of the V, Mn, and Cr atoms form interstitial nitrides in which nitrogen is located in octahedral holes. These results are consistent with those of Bor et al.,[19] who find that VN particles in the Fe−2 at. % V system nitrided at 793 K are smaller than 2.5 nm and for this reason are not visible by TEM.

In addition to the existence of nitrided phases, a fraction of the metal centers, around $^1/_4$ of Mn and V and $^1/_3$ of Cr, retain the bcc-type structure, characterized by a M−M coordination shell at 2.5−2.7 Å. Several trials were made including other occupation factors for each metal ($^2/_3$, $^2/_4$), but no good fit was attained. Those centers should correspond to the remaining un-nitrided metal sites. Similarly, Palshin et al. observe that around $^1/_5$ of titanium centers remained as Ti^0 in a plasma nitrided pure titanium sample.[15] Comparative plots of the best fit, including the above-described contributions, and the experimental spectra of the three elements are included as Supporting Information (Figures 3S−5S). We would like to emphasize the sensitivity of the technique, which has provided detailed information about the local structure of elements in extremely low concentrations (0.3% for V).

The novelty of the results presented here is that we have been able to detect significant changes in the local structure around the minor components of a commercial steel and that those changes can be related to the increase in the surface hardness. We envisage the

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hardening process being induced by ammonia gas nitriding as follows. The presence of the alloyed elements with strong affinity for N facilitates the incorporation of nitrogen into the α-Fe matrix. Nevertheless, the increase in hardness in the nitrided systems cannot be ascribed either to the N-saturated Fe matrix or to iron nitrides such as ϵ-Fe_3N and γ'-Fe_4N since their hardness[11] is lower than that observed in the nitrided sample. The new hard phases must necessarily involve the alloyed elements and can be described as interstitial nitrides with rock-salt structures. Furthermore, the EXAFS results strongly suggest the presence of iron atoms in the new N-containing phases, which would explain the role of iron in the increase of hardness. Thus, although N is a light element and in small concentration, it is the driving force of a drastic structural change when reacting with V, Cr, and Mn, which, in turn, causes the increase in hardness. The EXAFS results combined with those from XPS, which unambiguously confirm the presence of nitrogen, provide direct evidence for the existence of new nanostructured phases that very likely play a relevant role in the enhancement of the hardness.

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Supporting Information Available: (Figure 1S) EXAFS raw data of the alloyed elements in the nitrided sample: V K-edge, Mn K-edge, and Cr K-edge. (Figure 2S) Magnitude of FT of the EXAFS spectra in the nitrided sample: V K-edge (dashed line), Mn K-edge (dotted line), and Cr K-edge (solid line). (Figures 3S−5S) Comparative plots of the experimental EXAFS spectra (solid lines) of Cr, V, and Mn K-edges in the nitrided sample and computed EXAFS spectra (dashed lines). (a) k^1-weighted EXAFS spectra in k space. (b) Magnitude and imaginary part of the phase-corrected FT (k^2-weighted) of the EXAFS spectra included in part (a) of each figure. Fourier filtered spectra ($\Delta R = 0.5-4.5$ Å) have been fitted (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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