

Nitrogen uptake by an Fe–V alloy: Quantitative analysis of excess nitrogen

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Received 4 November 2005; received in revised form 1 February 2006; accepted 13 February 2006

Available online 17 April 2006

Abstract

Nitrogen absorption isotherms of Fe–2 wt.% V alloys were determined experimentally to study the differences in chemical bonding for various types of absorbed nitrogen. It was observed that the nitrogen uptake was larger than necessary for precipitation of all vanadium as nitride and for equilibrium dissolution of nitrogen in the ferrite matrix: uptake of excess nitrogen. Three types of absorbed nitrogen could be distinguished: (i) nitrogen in the stoichiometric vanadium nitride; (ii) nitrogen adsorbed at the vanadium nitride precipitate/ α -Fe matrix interface; (iii) nitrogen dissolved interstitially in the ferrite matrix. Quantitative analysis of the nitrogen absorption isotherms was possible by adopting a model that incorporates (immobile) excess nitrogen, identical to nitrogen adsorbed at the nitride/matrix interface, and (mobile) excess nitrogen, identical to the surplus nitrogen solubility of the ferrite matrix due to the misfit stress field surrounding the nitride precipitates.

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Keywords: Iron alloys; Precipitation; Nitrides; Residual stresses; Absorption isotherm

1. Introduction

Nitriding is a thermochemical surface engineering process by which nitrogen is introduced into the surface region of ferritic iron-based (steel) workpieces at temperatures in the range 500–580 °C. The industrial importance of nitriding is great because it improves fatigue strength, tribological properties and/or corrosion resistance. These properties result from the development of an outer (compound) layer composed of (largely) iron nitrides and a diffusion zone underneath where alloying element nitrides can occur.

There are several nitriding methods, e.g., plasma nitriding, salt bath nitriding and gaseous nitriding. The most well-known method for introducing nitrogen into a (ferritic) workpiece is gaseous nitriding. Nitriding in

NH₃/H₂ gas mixtures is equivalent to nitriding in N₂ at a pressure of several thousand atmospheres (thermodynamic argument [1]) and is possible due to the slow thermal decomposition of NH₃ (kinetic argument [2]).

During internal nitriding, if the iron matrix (substrate) contains alloying elements with a relatively high affinity for nitrogen, like titanium, aluminium, vanadium and chromium, alloying element nitride precipitates can develop (in the “diffusion zone”), which leads to a pronounced increase of hardness. A number of studies have been devoted to the nitriding of binary iron-based alloys: Fe–Ti [3–5], Fe–Al [6–11], Fe–V [12–20] and Fe–Cr [21–25]. The increase in hardness or fatigue resistance depends on the chemical composition of the precipitates, their coherency with the matrix, their size and their morphology.

Results from previous work on the nitriding of Fe–V alloys [12–20], of relevance to the present work, can be summarized as follows. Nitriding of low-vanadium-content Fe–V alloy (say, 2 wt.% V (or below) [20]) leads to the formation of finely distributed, plate-like precipitates of

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vanadium nitride (VN; typically about 40 Å long with a thickness of about 10 Å, precipitated along {001}_α matrix planes [12,17]). The coherent VN precipitates induce strain fields in the surrounding ferrite matrix and thereby influence the nitrogen solubility of the ferrite matrix. It appears that nitrated Fe–V alloys have a considerable capacity for the uptake of so-called excess nitrogen (i.e., more nitrogen than necessary for: (i) precipitation of all vanadium as nitride and (ii) equilibrium saturation of the ferrite matrix; e.g., see Refs. [19,20]). The total amount of excess nitrogen can be divided into two types: mobile and immobile excess nitrogen (for a detailed discussion, see Refs. [20,24,25]).

The analysis of nitrogen absorption isotherms¹ allows a distinction to be made between the various kinds of differently (chemically) bonded nitrogen, as has been shown by applying this technique to nitrated Fe–Al alloys [7]. Nitrogen absorption isotherms were first determined in detail for pure iron by Lehrer [26] and for Fe–Al alloy by Podgurski et al. [6].

Until now the direct compositional analysis of the coherent, extremely tiny, thin nitride precipitate platelets (see above) has appeared impossible. Doubts have been raised that the composition of the nitrides would not be purely MN (here VN) but rather (M,Fe)N, which would simply explain the observation of excess nitrogen [27,28].

Possibly similar to the occurrence of excess nitrogen in Fe–M alloys, excess oxygen can be taken up in internally oxidized metal alloys (see Section 4.3.1): During internal oxidation of copper, silver and lead alloys uptake of excess oxygen occurred and was ascribed to oxygen segregated at oxide/matrix interfaces [29–34].

The present study was performed to investigate in detail the various types and amounts of absorbed nitrogen, and thereby also to determine the nature of the excess nitrogen (see above), at least for the Fe–V alloys considered here.

2. Theoretical background

2.1. Nitrogen uptake in Fe–V alloys

If an Fe–V alloy is nitrated such that no iron nitrides can be formed at the surface (i.e., the nitriding potential is sufficiently low [1,2]; see Section 2.2), only a diffusion zone containing VN precipitates develops (“internal nitriding”). The total nitrogen uptake, c_N , of internally nitrated Fe–V alloys can be given as

$$c_N = [N]_{\alpha}^0 + [N]_{VN} + [N]_{\text{strain}} + [N]_{\text{dislocation}} + [N]_{\text{interface}} \quad (1)$$

where $[N]_{\alpha}^0$ is the equilibrium solubility of nitrogen in unstrained α -Fe corresponding to the temperature T and the applied nitriding potential $r_n = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$ (see Ref. [1] and Section 2.2), $[N]_{VN}$ is the amount of nitrogen incorpo-

rated in the equilibrium VN, $[N]_{\text{strain}}$ is the additional (excess) nitrogen dissolved due to the misfit stress field in the iron matrix lattice, $[N]_{\text{dislocation}}$ is the (excess) nitrogen trapped at dislocations and $[N]_{\text{interface}}$ is the (excess) nitrogen adsorbed at the precipitate/matrix interface.

In Eq. (1), $([N]_{\alpha}^0 + [N]_{VN})$ represents the “normal” capacity of nitrogen uptake and $([N]_{\text{strain}} + [N]_{\text{dislocation}} + [N]_{\text{interface}})$ is the total amount of “excess” nitrogen. The total amount of excess nitrogen can be divided into two types: mobile excess nitrogen, i.e., $[N]_{\text{strain}}$, and immobile excess nitrogen, i.e. $[N]_{\text{dislocation}}$ and $[N]_{\text{interface}}$. Due to the relatively low dislocation densities in recrystallized samples (which pertains to the current experiments) $[N]_{\text{dislocation}}$ can be neglected here.

2.1.1. Nitrogen adsorbed at the precipitate/matrix interfaces

It has been suggested [3–5,7,35] that a significant part of the excess nitrogen in nitrated binary iron-based alloys is adsorbed at the nitride/matrix interfaces, $[N]_{\text{interface}}$. The amount of interfacial nitrogen depends not only on the total precipitate/matrix interfacial area but also on the interface structure (for VN in α -Fe the nitride platelet faces have the orientation $(001)_{\alpha\text{-Fe}}// (001)_{VN}$, which is compatible with the Bain orientation relationship [17]). A VN precipitate with excess nitrogen adsorbed at the interface with the matrix can be regarded as a VN_X compound, i.e. $(X - 1)$ nitrogen atoms per VN_X molecule are bonded/adsorbed to the coherent faces of the particle/platelet (see Fig. 1(b)), i.e.

$$X = \frac{[N]_{VN} + [N]_{\text{interface}}}{[N]_{VN}} \quad (2)$$

The magnitude of X depends on the thickness of the platelets assuming that at every octahedral interstice adjacent to the $(001)_{\alpha\text{-Fe}}// (001)_{VN}$ interface (see above) one excess nitrogen atom is trapped; the maximum value of X equals 3 and occurs for a monolayer of VN.

2.1.2. Nitrogen dissolved in the strained iron lattice

Due to elastic accommodation of the misfit between a (coherent) nitride particle and the iron matrix, a dilatation of the lattice of the matrix occurs [4,35]. Straining of the matrix influences the solubility of nitrogen in the ferrite matrix. A model predicting the amount of nitrogen dissolved in ferrite containing misfitting nitride particles has been described in Ref. [35]. The essence of that model is summarized briefly below.

A VN precipitate developing in the ferrite matrix experiences a positive volume misfit. Then, supposing fully elastic accommodation, the treatment by Eshelby [36] for a finite matrix shows that a positive dilation of the matrix occurs. The matrix lattice dilation generated by the misfitting nitrides, induced by the hydrostatic component of the image stress field of finite bodies, provides a geometrical understanding for the occurrence of enhanced solubility of nitrogen. This dilation is not a direct function of temperature. The actually occurring temperature-dependent amount of

¹ A nitrogen absorption isotherm shows the dependence of the amount of nitrogen taken up by a (homogeneously) nitrated specimen as a function of the nitriding potential (directly related to the chemical potential of the nitriding atmosphere).

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