Nitriding of Nanocrystalline Iron in the Atmospheres with Variable Nitriding Potential

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Supporting Information

The present XRD data was acquired at elevated temperature. Moreover, a variable concentration of nitrogen in iron was supposed. The goal is to evaluate the nitrogen concentration in a particular phase utilizing the knowledge about its lattice parameters. To achieve this goal a procedure was designed for each phase: α – Fe, γ' – Fe_4N and ε – Fe_xN, separately.

α – Fe

The lattice parameter of α – Fe was studied extensively in the past and its magnitude is well known. Its value under atmospheric pressure and at room temperature is given as a_a = 0.28864 nm[1]. The influence of temperature[2] and pressure[3] on the lattice parameter of α – Fe was also established. The former one can be expressed by Eq. (1)[1]

$$a_\alpha(T) = 0.285449 + 3.973 \cdot 10^{-6} \cdot T \ \ [\text{nm}] \quad (1)$$

At 400 ^{o}C the Eq. (1) gives the value a_α(400 ^{o}C) = 0.28814 nm.

The influence of nitrogen atoms dissolved in α – Fe on the respective lattice parameter is also known. It is given for iron samples at room temperature by Eq. (2)[1]

$$a_\alpha(x_N) = 0.28664 + 0.079 \cdot x_N \quad (2)$$

where x_N is a molar fraction of N atoms in the sample. No dependence of $a_\alpha(x_N)$ regarding the temperature influence was found. It is assumed that the slope of the Eq.(2) is not dependent on the temperature. The intercept of the Eq. (2) was recalculated for 400 ^{o}C and a result is shown as Eq. (3) given below

$$a_\alpha(x_N, 400^{o}C) = 0.28814 + 0.079 \cdot x_N \quad (3)$$

The nitrogen concentration in α – Fe at 400 ^{o}C was calculated utilizing the lattice parameter a_α evaluated from the Rietveld refinement of XRD data.

γ' – Fe_4N

The iron nitride γ' – Fe_4N can be conceived as close-packed iron sublattice of fcc type containing nitrogen at octahedral interstices. The homogeneity range of γ' is narrow, but the effect of small compositional variation on the lattice parameter is relatively strong[4]. The lattice parameter $a_{\gamma'}$ for room temperature is about 0.379 nm with a small variation coming from uncertainty of nitrogen contents[5]. In this study this parameter is taken as $a_{\gamma'}$ = 0.37988 nm. The linear thermal expansion coefficient α of γ' phase obtained for the studies at temperatures between 20 and 500 ^{o}C[4] is described by Eq. (4)

$$\alpha = (7.62 \pm 0.75) \cdot 10^{-6} \ \ [K^{-1}] \quad (4)$$

Applying the Eq. (5) given below

$$\frac{\Delta a}{a_0} = \alpha \cdot \Delta T \tag{5}$$

where ΔT is a temperature change and a_0 is the lattice parameter for $\Delta T = 0$, the change of the lattice parameter Δa can be calculated. As a result at 400 ^{o}C $a_{\gamma'}$ = 0.38115 nm. The relation between the lattice parameter $a_{\gamma'}$ of γ' phase and its nitrogen content c_N is also known[4]. With nitrogen concentration expressed in atomic percent the relation is given by Eq. (6)

$$a_{\gamma'}(c_N) = 0.37988 + 14.82 \cdot 10^{-4} \cdot (c_N - 20) \ \ [\text{nm} \tag{6}$$

Eq. (6) disregards the influence of the temperature. Therefore, correspondingly to the procedure applied for α – Fe it is assumed that the slope of Eq. (6) is not changed at elevated temperature and only the intercept is calculated for 400 ^{o}C from Eq. (6). Thus the Eq. (7)

$$a_{\gamma'}(c_N) = 0.38115 + 14.82 \cdot 10^{-4} \cdot (c_N - 20) \ \ [\text{nm} \tag{7}$$

is utilized to calculate the nitrogen concentration in γ' – Fe_4N phase at 400 ^{o}C employing the lattice parameter evaluated from the Rietveld refinement of XRD data.

ε - Fe_xN

The iron nitride ε – Fe_xN can be conceived as close-packed iron sublattice of hcp type containing nitrogen at octahedral interstices. The ε phase has a wide homogeneity range. The corresponding dependencies of the two lattice parameters, a_ε and c_ε characterizing the hcp iron sublattice of ε on nitrogen content are reasonably well known[6, 7]. These parameters can be calculated for room temperature according to Eq. (8) and Eq. (9)

$$a_{\varepsilon}(y_N) = 0.44652 + 0.06851 \cdot y_N \ \ [\text{nm}] \tag{8}$$

and

$$c_{\varepsilon}(y_N) = 0.42433 + 0.03903 \cdot y_N \quad [\text{nm}] \tag{9}$$

where y_N is the fraction of interstitial sites occupied by nitrogen atoms[7].

The literature dealing with the temperature dependence of these parameters is scarce. Only few papers mention study of the lattice parameters of ε phase at temperatures different than room temperature[8-11]. The most comprehensive study is presented by Leineweber et al.[10] where a detailed temperature dependence of a_ε and c_ε in the range between room temperature and 440 ^oC is shown. However the data are given only for two samples differing in composition. At 400 ^oC the sample denoted as ε - $Fe_3N_{1.10}$ is characterized by the parameter c_ε = 0.44238 nm. At 410 ^oC the sample denoted as ε - $Fe_3N_{1.22}$ is characterized by the parameter c_ε = 0.44311 nm.

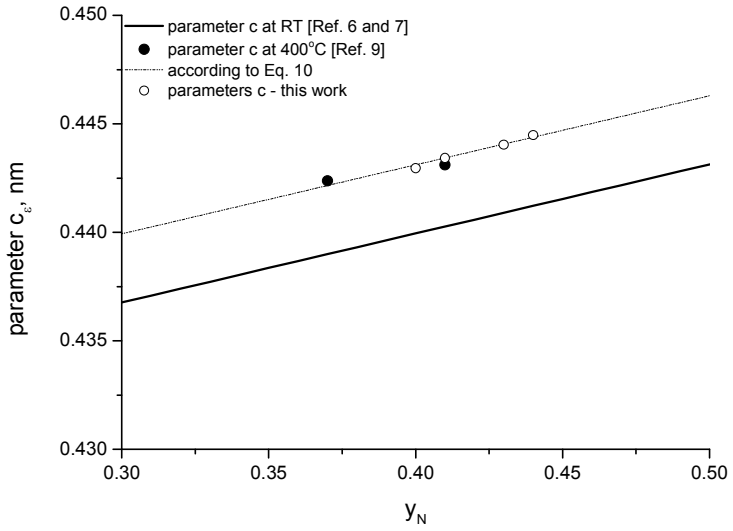

Fig. 1. Dependence of lattice parameter c_ε of ε phase on the site occupancy y_N.

These two experimental points were applied to construct the general dependence $c_\varepsilon = f(y_N)$ at 400 ^oC. In Fig. 1. the dependence of parameter c_ε on the fraction of sites occupied by nitrogen atoms is shown. The thick line represents the values according to Eq. (9) corresponding to room

temperature experiments. Black dots are data taken from Ref. [10] acquired at approx. 400 °C. It was assumed that the slope of the dependence $c_\varepsilon = f(y_N)$ at 400 °C is identical as at room temperature. A respective linear regression line is shown as dotted line. It is described by the Eq. (10)

$$c_\varepsilon(y_N) = 0.43099 + 0.03903 \cdot y_N \quad [\text{nm}] \tag{10}$$

which was next used to calculate the site occupancy y_N in ε phase in the present study.

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