Calculation of Nitrogen Absorption into Austenitic Stainless Steel Plate and Wire

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1. Introduction

The nitrogen absorption into austenitic solid solution (solution nitriding)1–3) is a kind of heat treatment to add a large amount of nitrogen into stainless steel. This treatment is recently focused as a new method to improve mechanical properties and corrosion resistance of structural materials for biomedical uses. In particular, the solution nitriding is suitable for small precise devices such as thin plate and wire4) because the time required for full nitrogen absorption to the center of materials is not so long. However, the treatment time has not been strictly determined taking account of the material size but empirically set at an enough time for completing the nitrogen absorption. It is important to estimate the minimum treatment time for the materials with different size in order to promote the production efficiency and control the austenite grain size.

The behavior of nitrogen absorption depends on the treatment temperature (diffusivity of nitrogen) and nitrogen potential on the surface of materials, and it can be estimated by solving Fick’s second law for nitrogen diffusion in austenite phase. Besides, some correction is needed for the nitrogen absorption in wire because the behavior of nitrogen absorption from round surface is different from that from flat surface.

In this paper, the behavior of nitrogen absorption into plate and wire was theoretically analyzed for an austenitic stainless steel, and then the time required for full nitrogen absorption to the center was quantitatively evaluated as a function of the thickness of plate and the diameter of wire.

2. Experimental Procedure

Figure 1 schematically shows the profile of nitrogen concentration which will be formed by nitrogen absorption from the surface of plate (a) and wire (b). If the diffusion of nitrogen atoms is uni-dimensional to the x (or r)-axis, the nitrogen concentration is given as a function of distance and time at a given temperature, by solving the following diffusion equation.

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{(plate)} \quad \text{(1)}
\]

\[
\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial C}{\partial r} \right) \quad \text{(wire)} \quad \text{(2)}
\]

C is the nitrogen concentration and D is the diffusion coefficient. A numerical method was devised to integrate the Eqs. (1) and (2), and this enables to compute the value of C for the following boundary and initial conditions.

\[
C = 0 \quad \text{at} \quad 0 < x < d \quad \text{or} \quad 0 < r < \frac{d}{2}, \quad t = 0 \quad \text{(3)}
\]

\[
C = C_0 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = d \quad \text{or} \quad r = \frac{d}{2}, \quad t > 0 \quad \text{(4)}
\]

\[
\frac{\partial C}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad \text{(5)}
\]

d is the thickness of plate or the diameter of wire. Since the concentration at surface \( C_0 \) was fixed to be \( C_0 = 1 \) in the computation, the C means so-called ‘normalized nitrogen concentration’.

To demonstrate the validity of calculation, the behavior of nitrogen absorption was experimentally investigated by using commercial stainless steel wire and plate (SUS304). Chemical compositions of the materials are shown in Table 1. The wire of 1 mm in diameter and the plate of 1 mm thick were subjected to the solution treatment at 1473 K for 1.8 ks in a vacuum, followed by air cooling to ambient temperature. The grain sizes of the solution-treated materials were confirmed to be around 90 μm in both materials. Subsequently, these materials were electrically etched with a solution of phosphoric acid and chromic acid, and then subjected to solution nitriding of 1473 K–(0.6 to 16.2 ks) in a nitrogen gas atmosphere of 0.1 MPa (1 atm), followed by...
3. Results and Discussion

Figure 2 represents the experimentally measured hardness (plots) and the theoretically calculated nitrogen concentration (lines) in 304 stainless steel plate of 1 mm thick (a) and wire of 1 mm in diameter (b) which were subjected to solution nitriding at 1 473 K for various times. The diffusion coefficient for the calculation was sought so as to fit to solution nitriding at 1 473 K for various times. The diffusion coefficient of 2.4 m²/s was obtained for the optimal calculation. According to the review by Gavriljuk and Berns, the diffusion coefficient of nitrogen in austenitic stainless steel is in the range from 1.2×10⁻¹¹ to 4.5×10⁻¹³ m²/s.* The change in hardness and normalized nitrogen concentration successfully coincide at any solution nitriding time in both of the plate and the wire materials. Since the hardness of austenite matrix is proportional to the solute nitrogen concentration up to 0.7% in nitrogen-bearing austenitic stainless steels,** this result indicates the validity of the profile of normalized nitrogen concentration which has been calculated.

Based on Fick’s second law, we can theoretically estimate the nitrogen absorption behavior in the same way for any plate and wire with different size. However, in order to use this calculation practically, the normalized nitrogen concentration should be converted into actual nitrogen concentration expressed in mass%. The actual nitrogen concentration is obtained by multiplying the normalized nitrogen concentration by the equilibrium nitrogen concentration at the solution nitriding temperature. This operation means that the nitrogen concentration at specimen surface is fixed at the equilibrium concentration during the solution nitriding. In the previous paper, the equilibrium nitrogen concentration at 1 473 K is given by the following equation for Fe–Cr–Mn ternary system alloy.

\[
\%N = 5.11 \text{product log} \left\{ 0.196 \times 10^{1.15 + 9.0 \times 10^{-3} \%Cr} - 7.6 \times 10^{-10} \%Cr^2 + 3.4 \times 10^{-10} \%Mn \%Mn - 2.59 \times 10^{-7} \%Mn^2 \%Cr^2 - 5.0 \times 10^{-10} \%Cr \%Mn^2 \right\} 
\text{(at 1 473 K)} 
\]  

The Eq. (6)** could be also applied to the present 304 steel because the nickel contained in the steel gives little influence on the nitrogen absorption phenomenon. Putting chromium and manganese contents shown in the Table 1 (17.8 and 1.3) into \[\%Cr\] and \[\%Mn\] in the Eq. (5), respectively, the value of 0.50 mass% is obtained as the equilibrium nitrogen content. This value is almost same as the experimentally measured nitrogen content in a 304 specimen with full nitrogen absorption (treated for 36 ks); 0.48 mass%.

As an example of calculation, Figure 3 shows the profiles of nitrogen concentration in 304 steel plates of 0.1 mm (a) or 1 mm thick (b) and wires of 0.1 mm (c) or 1 mm in diameter (d), which have been subjected to the solution nitriding at 1 473 K. As is easily expected, the increase in nitrogen concentration is faster in the wires than in the plates when the materials have same dimension in thickness and diameter. Figure 4 shows the time for the full nitrogen absorption as a function of material size in 304 stainless steel plate and wire. Here, we thought as the full nitrogen absorption is when the nitrogen concentration reaches 95% of equilibrium nitrogen content in the center of the material. From this figure, we can estimate the minimum time required for solution nitriding in the materials with any size.

* Since the diffusion coefficient is varied depending on the chemical composition of steel, it should be obtained for each material to make a strict estimation when this calculation is applied to other kinds of austenitic stainless steel.
** This equation is expressed by an unfamiliar function of ‘product log’, but in the case of low or medium nitrogen steel (N%<0.8%) in which the N-N interaction is not required to be considered, another usable equation can be applied:  

\[
\%N = 10^{1.15 + 6.0 \times 10^{-9} \%Cr} - 7.6 \times 10^{-10} \%Cr^2 + 3.4 \times 10^{-10} \%Mn \%Mn - 2.59 \times 10^{-7} \%Mn^2 \%Cr^2 - 5.0 \times 10^{-10} \%Cr \%Mn^2 \]  

(at 1 473 K)
4. Conclusions

The nitrogen absorption behavior into 304 austenitic stainless steel can be successfully estimated by the numerical method using the diffusion equation for the solution nitriding in plate and wire materials. The value of $2.4 \times 10^{-10}$ m$^2$/s was used for the calculation as the diffusion coefficient of nitrogen in austenite at 1473 K. The boundary condition on nitrogen concentration at specimen surface is given by the equilibrium nitrogen concentration as a function of the chemical composition of the steel. The time required for full nitrogen absorption can be also estimated by this calculation in both of plate and wire materials as a function of thickness and diameter, respectively.

REFERENCES


Fig. 3. Profiles of nitrogen concentration in 304 stainless steel plates of 0.1 mm (a) or 1 mm thick (b) and wires of 0.1 mm (c) or 1 mm in diameter (d), which have been subjected to the solution nitriding at 1473 K.

Fig. 4. Relation between the time for full nitrogen absorption and material size in 304 stainless steel plate and wire.