Nitriding of steel in potassium nitrate salt bath

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Abstract

A potassium nitrate salt bath has been used for nitriding of interstitial-free steel. The nitriding behavior can be reasonably well described by nitrogen diffusion in iron. Most nitrogen is dissolved interstitially. During nitriding, a slight oxidation of the steel surface also takes place. The nitried specimen achieves a pronounced solid-solution strengthening.

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1. Introduction

Nitriding is a surface treatment technique used to introduce nitrogen into metallic materials to improve their surface hardness, mechanical properties, wear and corrosion resistance, as well as fatigue life. Established nitriding methods include gas nitriding, plasma nitriding, laser nitriding, reactive magnetron sputtering and nitrogen implantation, and plasma immersion ion implantation [1]. Although the above methods are well established, some of them have disadvantages from an engineering viewpoint, for example, they may require the use of rather complicated and/or expensive apparatus. One of the traditional and most commonly applied nitriding methods for steel parts is salt bath nitriding by means of liquid salts containing cyanide and cyanate. In fact, this process is actually a nitrocarburizing process [2], since the environment of molten salt contains both carbon and nitrogen and the two elements generally diffuse into the surface of steel parts, simultaneously. To our knowledge, up to the present no nitriding process for steel without simultaneous carburization has been realized with salt baths.

The reported decomposition temperatures of potassium nitrate (KNO₃) are about 527–567 °C [3] and 628 °C [4] obtained by differential scanning calorimetry and differential thermal analysis techniques, respectively, and potassium nitrate may directly decompose to oxide (K₂O) [5–7] according to the following reactions (1) or (2).

$$2\text{KNO}_3 \rightarrow \text{K}_2\text{O} + 2\text{NO}_2 + 1/2\text{O}_2 \tag{1}$$

$$2\text{KNO}_3 \rightarrow \text{K}_2\text{O} + 5/2\text{O}_2 + \text{N}_2 \tag{2}$$

Therefore, the thermal decomposition of KNO₃ on heating may liberate nascent nitrogen before the formation of molecular nitrogen (N₂). The nascent nitrogen can diffuse into the steel coupon.

The objective of this study was to investigate the possibility of nitriding steel in a KNO₃ salt bath.

2. Experimental procedure

A 4 mm thick hot-rolled interstitial-free (IF) steel provided by POSCO, Korea was used in this study. Its chemical composition is given in Table 1. Vickers hardness test specimens of 2.8 mm thickness produced from IF steel sheets cold rolled to a thickness reduction of 30% were annealed for 1–300 min at 650 °C in two kinds of salt baths, the KNO₃ bath (the nitrate bath) and the 67% CaCl₂–33% NaCl bath (the chloride bath), to provide two different atmospheres, namely a possibly nitriding atmosphere and an inert atmosphere. After annealing, the specimens were...
The 2.8 mm thick sheet was further rolled to about 1 mm thickness and then subjected to X-ray diffraction (XRD) to identify their structures. Sheet specimens were polished before carrying out the XRD scan. XRD measurements were performed using a MAC Science Co. M18XHF-SRA diffractometer with Cu Kα radiation (λ = 0.154056 nm). The instrument was set up for Bragg–Brentano geometry with a line focus and a graphite monochromator in diffracted beam arm. The slit configuration was as follows: divergence slit = 1°; receiving slit = 0.3 mm; scatter slit = 1°. XRD patterns were scanned in steps of 0.02° (2θ), in the 2θ range from 20 to 119°. Silicon (α-Si) was used as an external standard. Optical micrographs were taken from 3% nital-etched samples using an Olympus PMG3 microscope.

The nitrogen and oxygen concentrations in a 0.4 mm thick surface-layer and a 0.5 mm thick center-layer of the sample taken from the hot-rolled sheet after annealing for 3 h in the KNO3 bath at 650 °C were measured using a LECO TCH 600 Nitrogen/Oxygen/Hydrogen Determinator (with an experimental error of less than 0.1 ppm).

The 2.8 mm thick sheet was further rolled to about 1 mm thickness to make tensile specimens with gauge dimensions of 1 × 6 × 25 mm, in accordance with ASTM E8M-99, with the tension axis parallel to the rolling direction. One specimen was heated in the nitrate bath and another one was heated in the chloride bath at 650 °C for 3 h. They were subjected to tensile tests on an Instron-5582 at an initial strain rate of 4.23 × 10⁻⁵ s⁻¹ at 70 °C.

3. Results and discussion

Fig. 1 shows the XRD spectrum of a powder sample of the surface scale removed from the surface of the 2.8 mm thick IF steel annealed for 3 h at 650 °C in the nitrate bath. The XRD result indicates that the powder sample consisted of magnetite (Fe3O4), hematite (Fe2O3), and wustite (FeO). Therefore, oxygen must have been generated in the nitrate bath during annealing by decomposition of KNO3 according to the reactions (1) and/or (2). The sample underwent a loss of about 0.05 mm in thickness on each side due to the surface oxidation upon annealing in the nitrate bath for 3 h at 650 °C.

Fig. 2 shows the Vickers hardness of the surface of the 2.8 mm thick IF steel as a function of annealing time at 650 °C in the nitrate and chloride baths. The surface scales of the specimens annealed in the nitrate bath were removed before hardness testing. For the sample annealed in the nitrate bath, the hardness drops a little due to recovery and then increases with increasing time. On the other hand, for the chloride-bath-annealed (CBA) sample, the hardness first decreases to a minimum value due to recovery and slightly increases again to a maximum peak, followed by a decrease with increasing time as expected when recrystallization and subsequent grain growth take place (Fig. 3). The weak hardness peak in the CBA sample may be an experimental error or due to strain aging (not dynamic strain aging). This needs further study. However, the two different hardness evolutions at the later stage of annealing suggest that different reactions take place in the nitrate and chloride-bath-annealed samples.

The unusual increase in the hardness of the nitrate-bath-annealed (NBA) sample was supposed to be related to diffusion of nitrogen into the steel sample. If the nitrogen diffusion occurred in the sample, a hardness gradient is to be expected. The hardness distribution of the NBA sample is shown in Fig. 4. Indeed, the hardness decreases with
increasing distance from the surface. In order to prove the presence of nitrogen in the sample, a chemical analysis was performed. The results in Table 2 indicate that the nitrogen concentration of the surface layer is almost 10 times higher than that of the center layer. The oxygen concentration varies little with depth, indicating that most oxygen is consumed to form oxides at the surface. It is quite clear that nitriding took place in the sample.

In order to investigate the state of nitrogen in the sample, XRD analyses of samples were performed before and after annealing in the nitrate bath at 650 °C for 3 h. The results are shown in Fig. 5. The lattice parameters calculated from the XRD data are given in Table 3. The diffraction pattern (Fig. 5) does not contain reflections of iron nitrides. However, as the nitrogen concentration is rather small (cf. Table 2), and thus, if nitrides had been formed, the volume fraction of nitrides would therefore also be small, X-ray diffraction phase analysis may not be sensitive enough to detect the presence of iron nitrides. On the other hand, the values in Table 3 indicate that the lattice parameter of the annealed sample is slightly higher than that of the unannealed sample. This finding suggests that most nitrogen occupies interstitial sites in the annealed sample. The differences in peak intensities of the sample before and after annealing are due to a texture change after annealing.

We estimate the nitrogen concentration at the surface of the NBA sample using the lattice parameter data in Table 3. According to Wriedt and Zwell [8], the unit cell parameter of α iron increases linearly by 3.2 × 10⁻³ nm per wt.% N dissolved. If the lattice-parameter expansion after nitriding (2.3 × 10⁻⁴ nm from Table 3) is assumed to be caused by the nitrogen intrusion, then the nitrogen concentration of the surface of the NBA sample is estimated to be about 0.072 wt.%. The concentration determination via the lattice expansion measured by X-ray diffraction implies that residual stresses do not significantly affect measured diffraction line positions. Though nitrogen up-take generally leads to the generation of stresses, it is likely that no significant residual stresses are present in the investigated specimens, as the concentration of 0.072 wt.% determined from the measured lattice expansion is compatible with the surface concentration estimated from the average concentration in a surface layer (as determined by chemical analysis) on the basis of nitrogen diffusion (see below).

Next, we want to check if the measured nitrogen concentration in Table 2 is reasonable in terms of diffusion. Assuming that the diffusion behavior of nitrogen in the nitrate-nitriding of the IF steel sample is the same as that for the nitrogen diffusion in α-Fe, the diffusion coefficient at 650 °C can be calculated to be 2.605 × 10⁻¹¹ m² s⁻¹ from the following equation [9]:

$$D_N = 6.6 \times 10^{-7} \exp \left( \frac{-Q}{RT} \right) \text{ (m}^2\text{ s}^{-1})$$ (3)

where $D_N$ is the diffusion coefficient of nitrogen in α-Fe, $Q = 77.8$ kJ mole⁻¹ the activation energy for nitrogen
diffusion, \( R = 8.3143 \) (J mol\(^{-1}\) K\(^{-1}\)) the ideal gas constant, and \( T \) the absolute temperature (K).

Since the nitriding thickness of IF steel sample nitrided at 650 °C for 3 h can be estimated as \( x = 0.53 \) mm according to the equation \( x = \sqrt{\frac{D_N}{T}} \) [10] with effective diffusion coefficient of nitrogen \( D_N = 2.605 \times 10^{-11} \) m\(^2\) s\(^{-1}\) and nitriding time \( t = 3 \) h, which is obviously smaller than the half of thickness of IF steel sample, and the quantity of KNO\(_3\) in the nitrate bath is high enough for the generated nitrogen concentration to be constant on the surface of the sample, the nitrogen diffusion during nitriding can be described by the following equation [10]:

\[
C(x, t) = C_s \left[ 1 - \text{erf} \left( \frac{x}{2 \sqrt{D_N t}} \right) \right] \quad (4)
\]

where \( C(x, t) \) and \( C_s \) represent the concentrations of diffusion species at depth \( x \) after time \( t \) and at \( x = 0 \), respectively, and \( D \) is the diffusion coefficient. The expression erf\((x/2\sqrt{Dt})\) is the Gaussian error function.

We calculate the surface concentration \( C_s \) from the measured average nitrogen concentration \( C(= 0.0556 \text{ wt.\%}) \) of the 0.4 mm surface layer and \( C(x, t) \) calculated using Eq. (4). The expression for \( \overline{C} \) can be obtained by the trapezoidal rule [11].

\[
\overline{C} = \frac{1}{n} \int_{x_0}^{x_n} c(x, t) \, dx
\]

with the depth interval \( \Delta x = 0.01 \) mm, the number of intervals \( n = 40 \), \( x_0 = 0 \), \( x_n = 0.4 \) mm, \( D = 2.605 \times 10^{-11} \) m\(^2\) s\(^{-1}\), and \( t = 3 \) h. Then, we obtain \( C_s = 0.070 \text{ wt.\%} \) for \( \overline{C} = 0.0556\% \). The \( C_s \) value is very close to the 0.072 wt.\% obtained from XRD measurements.

Abe [12] has reported that the substitutional–interstitial dipoles are formed in the alpha solid solution of iron if the first-order interaction coefficient between a substitutional solute and an interstitial solute is a negative value, and suggested that Mn–N dipoles form in the alpha solid solution of iron, due to a negative interaction coefficient of N with Mn. Therefore, the formation of Mn–N dipoles may affect the result for the determination of the nitrogen content. However, the good agreement between the \( C_s \) value and the surface concentration estimated by the XRD measurements suggests that, if the formation of Mn–N dipoles occurs, it does not significantly affect either the amount of interstitially dissolved nitrogen or its diffusion behavior. The good agreement thus also confirms that the concentration of interstitially dissolved nitrogen determined via the lattice expansion measured by XRD is not significantly affected by the presence of a state of residual stress.

Tensile testing results of the CBA and NBA specimens reveal a pronounced difference in the deformation behavior as shown in Fig. 6. The flow stress of NBA specimen is more than two times higher than that of the CBA specimen. Furthermore, severe serration (with an average stress-drop of 18.5 MPa and a maximum stress-drop of 50.45 MPa) occurs in the NBA specimen, whereas very fine serrations (with an average stress-drop of 1.05 MPa and a maximum stress-drop of 2.3 MPa) are observed in the CBA specimen. The severe serration implies dynamic strain aging due to nitrogen in solid solution in the NBA specimen. These results suggest that a KNO\(_3\) bath can be used for nitriding of steel to achieve solid–solution strengthening of steel.

4. Conclusions

The study of nitriding of IF steel specimens in a KNO\(_3\) salt bath for 3 h at 650 °C led to the following conclusions.
The nitriding behavior of IF steel in the KNO₃ bath can be reasonably well described by nitrogen diffusion in iron, with the surface concentration of nitrogen being about 0.07 wt.% at 650 °C. Most nitrogen atoms occupy interstitial sites. The 1 mm thick nitrided specimen shows a tensile strength of 890 MPa and an elongation to fracture of 15% at 70 °C. The KNO₃ bath can thus be used for nitriding of steel to achieve solid-solution strengthening of steel.

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References