Mechanical Properties of Thin Wires of Nickel-Free Austenitic Stainless Steel with Nitrogen Absorption Treatment

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We have developed a new manufacturing process for nickel-free austenitic stainless steel. In combination with machining and a nitrogen absorption treatment, this process makes it possible to form small precise devices. The new manufacturing process can be used to manufacture small devices with a great deal of precision and parts with a maximum thickness or diameter of 4 mm. However, the temperature for the nitrogen absorption, 1473 K, was sufficiently high for grain growth, and coarsening was observed after nitrogen absorption. Therefore, a nitrogen absorption treatment that allows the retention of strength and ductility is performed with a grain refinement process before nitrogen absorption. In this study, we attempted the refinement of grains by thermo-mechanical treatment before nitrogen absorption treatment in order to increase the mechanical properties after nitrogen absorption treatment. The mechanical properties and microstructures of Fe–24Cr–2Mo with fine grains before and after nitrogen absorption treatment were evaluated to understand the effects of grain refinement on nitrogen absorption. The austenitic phase was obtained only from the surface to a 0.5-mm depth in the alloy with nitrogen absorption at 1473 K for 7.2 ks. The balance between strength and elongation in the alloy with nitrogen absorption at 1473 K for over 10.8 ks was the same as that in conventional austenitic stainless steel. The value of ultimate tensile strength in the alloy with nitrogen absorption increased with the grain refinement process attempted in this study. The elongation in the alloy with nitrogen absorption over 18.0 ks decreased because of grain growth. Therefore, grain refinement before nitrogen absorption treatment can increase the mechanical properties of nickel-free austenitic stainless steel.

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1. Introduction

Nickel-free austenitic stainless steels, such as Fe–(19–23)Cr–(21–24)Mn–(0.5–1.5)Mo–(0.85–1.1)N (Bio-Dure\textsuperscript{1})\textsuperscript{10}, Fe–15Cr–(10–15)Mn–4Mo–0.9N, Fe–18Cr–18Mn–2Mo–0.9N, and Fe–(15–18)Cr–(10–12)Mn–(3–6)Mo–0.9N in mass\% that have a high concentration of nitrogen and no nickel and show high strength and corrosion resistance, have been developed because nitrogen is an austenite former, as is nickel.\textsuperscript{1,4} A nickel- and manganese-free austenitic stainless steel, Fe–23Cr–2Mo–1.5N in mass\%, is also developed.\textsuperscript{5–7} However, nickel-free austenitic stainless steels are generally difficult to work with for the production of thin plates, wires, and small precise devices because the work hardening is large and the thermal conductivity is small in austenitic stainless steels.\textsuperscript{8} In addition, the addition of nitrogen reduces the formability because it increases the brittleness of the austenitic phase.\textsuperscript{5} Therefore, the production of small precise devices with austenitic stainless steel is expensive, and the dimensions of commercial products are limited.

Therefore, we have developed a new manufacturing process for nickel-free austenitic stainless steel. In combination with machining and a nitrogen absorption treatment, this process makes it possible to form small precise devices. Ingot of ferritic stainless steel, Fe–24Cr–2Mo in mass\%, was worked to test specimens with various dimensions. Nitrogen was absorbed by the specimens in a furnace filled with nitrogen gas with a pressure of 101.3 kPa at 1473 K to develop a simple and convenient manufacturing process of nickel-free austenitic stainless steels. Changes in the mechanical properties of the alloy with nitrogen absorption treatment are discussed on the basis of the resultant microstructure. Ferritic Fe–24Cr–2Mo is austenitized with nitrogen absorption to a 2-mm depth from the surface. The hardness, ultimate tensile strength, 0.2\% proof stress, and elongation to fracture increased, and the reduction of area decrease in Fe–24Cr–2Mo by austenitization due to nitrogen absorption. The ultimate tensile strength and 0.2\% proof stress of the alloy with nitrogen absorption for 129.6 ks is much larger than those of 316L steel, while the elongation to fracture and reduction of area are smaller than those of 316L steel. Therefore, small devices and parts with a maximum thickness or diameter of 4 mm can be manufactured with this process in the previous study.\textsuperscript{10}

However, the temperature for nitrogen absorption, 1473 K, is sufficiently high for grain growth, and the coarsening is observed after nitrogen absorption. Nitrogen absorption is performed with a diffusion of nitrogen through the grain boundary, that is, a diffusion from the surface to the grain boundary and from the grain boundary to the inside grain, indicating that coarsening decreases the rate of nitrogen absorption.\textsuperscript{11,12} In addition, the coarsening causes a decrease in the ultimate tensile strength and elongation to fracture. Therefore, a nitrogen absorption treatment that allows the retention of strength and ductility is performed with a grain refinement process before nitrogen absorption treatment.

Grain refinement is a fundamental technique to control the microstructure of metallic materials, and fine grains generate high strength and ductility. Thermo-mechanical treatments utilizing phase transformation and recrystallization, rapid cooling solidification, and mechanical alloying are effective techniques to obtain fine grains.\textsuperscript{13} Among the above processes, thermo-mechanical treatment is the most popular because it can be applied to various shapes and dimensions. To obtain fine grains with recrystallization, crystal nuclei as many as possible must be generated during forging. This is achieved by the increase of nucleation sites and the
In this study, we attempted the refinement of grains by thermo-mechanical treatment before nitrogen absorption treatment in order to increase the mechanical properties after nitrogen absorption treatment. The mechanical properties and microstructures of Fe–24Cr–2Mo with fine grains generated by hot forging and cold forging were evaluated both before and after nitrogen absorption treatment to understand the effects of grain refinement on nitrogen absorption.

2. Experimental Procedure

2.1 Specimen preparation

Ingot with 3.5 kg of Fe–24Cr–2Mo in mass% was prepared by a vacuum high-frequency induction melting process. Table 1 shows the chemical composition of the ingot of Fe–24Cr–2Mo. The ingot was then cut into four equal parts. A schematic diagram of the forging process is shown in Fig. 1. Hot forging, followed by 25% cold forging, was conducted in the previous study.10 In this study, 84% hot forging and 99% cold forging were conducted to obtain finer grains than in the previous study.10 Thin wires (1.0 mm in diameter) were obtained through hot and cold forging. Specimens for the tensile test (1.0 mm in diameter and 10 mm in gage length) and hardness test (1.0 mm in diameter and 10 mm in length) were prepared from the thin wires. The tensile axis was along the drawing direction in specimens for the tensile test.

2.2 Nitrogen absorption

Specimens for the tensile test and hardness test of Fe–24Cr–2Mo were polished with #600 SiC paper in water and then ultrasonically rinsed in acetone for 300 s. After rinsing, the specimens were separately located to a 304 steel reticular stage. The area for nitrogen absorption in the specimens did not contact the stage. The stage with the specimens was inserted into the nitrogen absorption furnace as shown in Fig. 2. The pressure of the inside of the furnace was reduced to 2 Pa, and nitrogen gas (<99.99%) was introduced and continuously flew into the furnace to maintain a pressure of 101.3 kPa. The temperature of the furnace was increased from ambient to 1473 K at a rate of 0.08 K s⁻¹ and kept for 7.2 ks, 10.8 ks, 14.4 ks, 18.0 ks, and 21.6 ks. Immediately after heating, the specimens were quenched into a water bath. The scale generated on tensile test specimen and hardness test specimen was removed with #600 SiC paper after nitrogen absorption.

2.3 Examination of microstructure and mechanical properties

Gripped parts of tensile test specimens were employed for microstructural observation with an optical microscope. Specimens for microstructural examination and hardness test were finally polished with #600 SiC paper and buffed. After etching with a Villela reagent, the microstructure was observed with an optical microscope. Phases of specimens for the tensile test with and without nitrogen absorption were identified using X-ray diffractometry (XRD) with CuKα radiation (40 kV and 300 mA).

The hardness test was performed using a micro Vickers hardness tester to estimate the changes in hardness with nitrogen absorption. Tensile tests were performed in air using an Instron-type tensile testing machine with a capacity of 10 kN. The crosshead speed was 8.33 × 10⁻⁶ m s⁻¹. Ultimate tensile strength, 0.2% proof stress, and elongation to fracture were estimated throughout the tensile test. At least, three measurements were carried out under the same conditions, and the mean values were calculated. The fractured surfaces were observed with a scanning electron microscope (SEM).

For comparison, changes in phases, hardness, and tensile properties that were the result of heating without nitrogen absorption were investigated by heating under the same temperature and time as the nitrogen absorption treatment in an argon atmosphere.

3. Results and Discussion

3.1 Changes in microstructures by nitrogen absorption

Figure 3 shows the XRD profiles of Fe–24Cr–2Mo with and without nitrogen absorption and Fe–24Cr–2Mo heated at 1473 K in an argon atmosphere. Only diffraction pattern of ferrite (α phase) was observed from Fe–24Cr–2Mo without nitrogen absorption, indicating that the structure consisted of only α phase (Fig. 3(a)). On the other hand, those for 7.2 ks showed only peaks originating from the austenite (γ phase), indicating that the structure was completely transformed to a γ phase. Therefore, the thin wire of Fe–24Cr–2Mo with a diameter of 1.0 mm is completely austenitized with nitrogen.
absorption treatment over 7.2 ks (Fig. 3(a)). On the other hand, only a diffraction pattern of \( \gamma/C11 \) phase was observed from Fe–24Cr–2Mo heated at 1473 K in an argon atmosphere, indicating that phase transformation from \( \alpha/C11 \) phase to \( \gamma/C13 \) phase does not occur in an argon atmosphere (Fig. 3(b)).

Using XRD, neither CrN nor \( \text{Cr}_2\text{N} \) was identified in any specimen with nitrogen absorption, indicating that no nitride was formed in Fe–24Cr–2Mo with nitrogen absorption. This is in good agreement with the results of XRD in the previous study.\(^{10}\)

Figure 4 shows the microstructures of Fe–24Cr–2Mo with nitrogen absorption treatment and Fe–24Cr–2Mo heated in an argon atmosphere. The microstructures of Fe–24Cr–2Mo before nitrogen absorption and heat treatment in an argon atmosphere were a fine \( \alpha \) phase expanded along the rolling direction, while the \( \alpha \) phase was completely transformed to a \( \gamma \) phase after 7.2-ks nitrogen absorption (Fig. 4(c)). Fine grains in Fe–24Cr–2Mo were grown and coarsened with the nitrogen absorption treatment. The grains were the largest with 21.6-ks nitrogen absorption (Fig. 4(e)). On the other hand, the \( \alpha \) phase was only observed in Fe–24Cr–2Mo heated in an argon atmosphere (Figs. 4(a) and (b)). The mean grain size of the alloy after 21.6-ks nitrogen absorption was 132 µm. On the other hand, that of the alloy after heated in an argon atmosphere was 527 µm. The grain size of Fe–24Cr–2Mo heated in an argon atmosphere was much larger than that of the alloy with nitrogen absorption, indicating that nitrogen works as a strong inhibitor against the grain coarsening. In addition, that of the alloy after 129.6-ks nitrogen absorption in the previous study was 604 µm.\(^{10}\) The grain size of the alloy after nitrogen absorption in this study was smaller than that in the previous study,\(^{10}\) indicating that the resultant grain in the alloy was refined with the grain refinement process attempted in this study.

### 3.2 Changes in hardness by nitrogen absorption

Figure 5 shows the changes in micro Vickers hardness of Fe–24Cr–2Mo with and without nitrogen absorption treatment. For comparison, that with heating in an argon atmosphere is also shown. Although the micro Vickers hardness of the alloy after annealing was 150, that of thin alloy wire after 99% cold forging was 285 because of work

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\( \text{CuK}_\alpha \)

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300 µm

(c) \( \text{N}_2 \) 7.2 ks

(d) \( \text{N}_2 \) 10.8 ks

(e) \( \text{N}_2 \) 21.6 ks

Fig. 4 Optical microstructure of Fe–24Cr–2Mo in each treatment. (a) and (b) heated at 1473 K in an argon atmosphere, and (c), (d), and (e) heated at 1473 K in a nitrogen atmosphere.
hardening. The hardness of Fe–24Cr–2Mo increased after 7.2-ks nitrogen absorption. The hardness of Fe–24Cr–2Mo showed the maximum value (Hv = 394) at 7.2-ks nitrogen absorption and decreased after 7.2 ks. The hardness of Fe–24Cr–2Mo heated in an argon atmosphere was almost constant after 7.2 ks. The hardness of the thin wires of Fe–24Cr–2Mo with nitrogen absorption for over 7.2 ks was the same as that of a round bar of the alloy with 129.6-ks nitrogen absorption. In addition, the microstructures of the alloy with nitrogen absorption showed only a \(/ C13\) phase (Figs. 3 and 4). On the other hand, the hardness decreased in an argon atmosphere with heating for 7.2 ks, and the value was maintained when the duration of the heating was extended.

3.3 Changes in mechanical properties by nitrogen absorption

According to the results on hardness and microstructure, the mechanical strength of the thin wire in this study is expected to be larger than that of the round bar previously studied. Ultimate tensile strength, 0.2% proof stress, and elongation to fracture increased and 0.2% proof stress decreased with nitrogen absorption, indicating that magnitude of work-hardening and ductility increased with solid-solution strengthening of nitrogen. Fe–24Cr–2Mo with nitrogen absorption for 21.6 ks showed maximum ultimate tensile strength (985 MPa) and 0.2% proof stress (727 MPa). On the other hand, elongation to fracture of Fe–24Cr–2Mo with and without nitrogen absorption treatment and Fe–24Cr–2Mo heated in an argon atmosphere are shown in Fig. 6. The tensile strength and elongation to fracture increased and 0.2% proof stress decreased with nitrogen absorption, indicating that magnitude of work-hardening and ductility increased with solid-solution strengthening of nitrogen. Fe–24Cr–2Mo with nitrogen absorption for 21.6 ks showed maximum ultimate tensile strength (985 MPa) and 0.2% proof stress (727 MPa). On the other hand, elongation to fracture of Fe–24Cr–2Mo showed the maximum value (41%) at 18.0-ks nitrogen absorption and decreased after 18.0 ks. The tensile strength and 0.2% proof stress decreased and elongation to fracture increased with a heat treatment in an argon atmosphere. The hardness of the cold-forged Fe–24Cr–2Mo was also decreased with the heat treatment (Fig. 5). These results suggest the residual stress was released by the heat treatment. Fe–24Cr–2Mo heated at 1473 K for 14.4 ks in an argon atmosphere showed maximum ultimate tensile strength (331 MPa), 0.2% proof stress (245 MPa), and the elongation to fracture (17%). The tensile strength, 0.2% proof stress, and elongation to fracture of Fe–24Cr–2Mo with nitrogen absorption were larger than those of Fe–24Cr–2Mo heated in an argon atmosphere. Therefore, the tensile properties of thin wires of Fe–24Cr–2Mo were improved by nitrogen absorption treatment. No martensite (\(/ \gamma'\) phase) was observed at the fractured surface nor identified using XRD, indicating that no stress-induced martensitic transformation in specimens with nitrogen absorption occurred.

Figure 7 shows the relation between ultimate tensile strength and elongation to fracture of Fe–24Cr–2Mo with and without nitrogen absorption. The figure also contains the data on a round bar of Fe–24Cr–2Mo with nitrogen absorption and 316L steel previously reported. The best balance between strength and elongation was given by 18.0-ks nitrogen absorption in Fe–24Cr–2Mo, and the balance was the same as that in conventional austenitic stainless steel. However, the balance between strength and elongation of thin wire of the alloy with nitrogen absorption was lower than that of the round bar in the previous study.

Scanning electron micrographs of fractured surfaces of Fe–24Cr–2Mo with and without nitrogen absorption treatment are shown in Fig. 8. Specimen without nitrogen absorption show a ductile fracture surface containing dimples (Fig. 8(a)). Fe–24Cr–2Mo with nitrogen absorption speci-
mens showed good elongation (Fig. 6(b)), whereas the fractured surface of specimens with nitrogen absorption showed a brittle fracture surface. The addition of nitrogen reduces the formability because it increases the brittleness of the \(\gamma\) phases.\(^9\) In addition, the grain boundary cracks generate during cold rolling in a highly nitrogen contained (0.9 mass%) Fe–Cr–Mn–N steel.\(^{14}\) Over 0.9 mass% nitrogen can be absorbed by Fe–24Cr–2Mo with nitrogen absorption treatment.\(^{10}\) Therefore, the brittle fractures observed in the alloy with nitrogen absorption were caused by brittleness of the \(\gamma\) phase. The coarsening with treatment time was observed. This is in good agreement with the result of microstructural observation as shown in Fig. 4. The decrease in the elongation to fracture of the alloy with 21.6-ks nitrogen absorption was caused by coarsening.

The mechanical strength of Fe–24Cr–2Mo is governed by the refinement of grains, according to the results of microstructural observations, tensile test, and observation of fractured surface.

![Graph](image)

**Fig. 7** Ultimate tensile strength and elongation to fracture of Fe–24Cr–2Mo with and without nitrogen absorption and of conventional austenitic stainless steels.

![Scanning electron micrographs](image)

**Fig. 8** Scanning electron micrographs of fractured surfaces of Fe–24Cr–2Mo with nitrogen absorption for (a) 0 ks, (b) 7.2 ks, (c) 10.8 ks, (d) 14.4 ks, (e) 18.0 ks, and (f) 21.6 ks.
4. Conclusions

The γ phase was obtained only from the surface to a 0.5-mm depth in Fe–24Cr–2Mo with nitrogen absorption at 1473 K for 7.2 ks. The balance between strength and elongation in Fe–24Cr–2Mo with nitrogen absorption at 1473 K for over 10.8 ks was the same as that in conventional austenitic stainless steel. The value of ultimate tensile strength in the alloy with nitrogen absorption increased with the grain refinement process attempted in this study. The elongation in the alloy with nitrogen absorption over 18.0 ks decreased because of grain growth. Therefore, grain refinement before nitrogen absorption treatment is effective to increase the mechanical properties of nickel-free austenitic stainless steel.

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