Mechanical Properties and Microstructures of a Thin Plate of Nickel-Free 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. 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 which allows the retention of strength and ductility was 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. The mechanical properties and microstructures of Fe–24Cr and 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 only obtained from the surface to a 0.1-mm depth in Fe–24Cr and Fe–24Cr–2Mo with nitrogen absorption at 1473 K for 2.7 ks. The balance between strength and elongation in Fe–24Cr and Fe–24Cr–2Mo with nitrogen absorption at 1473 K for 2.7 ks was better than that in conventional austenitic stainless steel. The values of ultimate tensile strength in both alloys with nitrogen absorption increased with the grain refinement process attempted in this study. The balance between strength and elongation in both alloys with nitrogen absorption over 2.7 ks decreased because of grain growth. Therefore, the process described in this study can be used to manufacture small devices with a great deal of precision and parts with a maximum thickness or diameter of 0.2 mm in a short time. Grain refinement in a nickel-free austenitic stainless steel can increase the balance between the strength and elongation.

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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 (BioDure[®] 108), 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.^{1–4)} Nickel- and manganese-free austenitic stainless steel, Fe–23Cr–2Mo–1.5N in mass%, is also developed.^{5–7)} However, nickel-free austenitic stainless steels are difficult to work with for the production of small precise devices because the work hardening is large and the thermal conductivity is small in austenitic stainless steels.⁸⁾ In addition, the addition of nitrogen reduces the formability because it increases the brittleness of the austenitic phase.⁹⁾ Therefore, the production of small precise devices with nickel-free 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. Ingots of ferritic stainless steels, Fe–24Cr and Fe–24Cr–2Mo in mass%, were worked to various dimensions for test specimens. 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 both alloys with nitrogen absorption treatment are discussed on the basis of the resultant microstructure. Ferritic Fe–24Cr and Fe–24Cr–2Mo were 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 decreased in Fe–24Cr and Fe–24Cr–2Mo by austenitization due to nitrogen absorption. The ultimate tensile strength and 0.2% proof stress of these alloys with nitrogen absorption for 129.6 ks were much larger than those of 316L steel, while the elongation to fracture and reduction of area were much smaller than those of 316L steel. Therefore, small devices and parts with a maximum thickness or diameter of 4 mm were manufactured with this process in this study.

However, the temperature for nitrogen absorption, 1473 K, is sufficiently high for grain growth, and 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. 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.

Grain refinement is a fundamental technique to control the microstructure of metallic materials, and a fine grain generates 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.¹⁰⁾ Among the above processes, thermo-mechanical treatment is the most popular because it is applied to various shapes and dimensions. To obtain fine grains with recrystallization, as many crystal nuclei as possible must be generated during forging. This is achieved by the increase of nucleation sites and the

generation of many dislocations under a cold forging process.

In this study, we attempted the refinement of grains by thermo-mechanical treatment before nitrogen absorption treatment. The mechanical properties and microstructures of Fe–24Cr and Fe–24Cr–2Mo with fine grains generated by hot forging and cold forging before and after nitrogen absorption treatment were evaluated to understand the effects of grain refinement on nitrogen absorption.

2. Experimental Procedure

2.1 Specimen preparation

Ingots with 3.5 kg of Fe–24Cr and Fe–24Cr–2Mo in mass% were prepared by a vacuum high-frequency induction melting process. Table 1 shows the chemical compositions of the ingots of Fe–24Cr and Fe–24Cr–2Mo. The ingots were then cut into two 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.¹¹⁾ In this study, 95% cold forging was conducted after hot forging to obtain finer grains than in the previous study.¹¹⁾ A thin plate (0.2 mm in thickness) was obtained through hot and cold forging. Specimens for the tensile test (0.2 mm in thickness, 5 mm in width, and 10 mm in gage length) were prepared from the thin plates of Fe–24Cr and Fe–24Cr–2Mo with machining using a milling machine. The tensile axis was the same as the rolling direction in specimens for the tensile test.

2.2 Nitrogen absorption

Specimens for the tensile test of Fe–24Cr and Fe–24Cr–2Mo were polished with #600 SiC paper in water and then ultrasonically rinsed in acetone for 300 s. After polishing, the specimens were separately fixed to a 304 steel reticular stage. The area for nitrogen absorption in the specimens did not contact the stage. The stage with the specimen 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 blown 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 a specific time for 1.8 ks, 2.7 ks, 3.6 ks, 4.5 ks, and 5.4 ks. Immediately after heating, the specimen was quenched into a water bath. The scale on tensile test specimens generated was not removed after nitrogen absorption.

2.3 Microstructural examination

Gripped parts of tensile test specimens were employed for microstructural observation with an optical microscope. Specimens for microstructural examination were finally polished with #600 SiC paper and buffed. After etching with a Vilella 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 diffraction analysis (XRD) with $\text{CuK}\alpha$ radiation (40 kV and 300 mA).

2.4 Hardness test

Gripped parts of tensile test specimens with and without nitrogen absorption were employed for a hardness test with a micro Vickers hardness tester to estimate the changes in hardness with nitrogen absorption. Specimens for the hardness test were finally polished with #600 SiC paper and buffed. In addition, changes in hardness that were the result of heating and not nitrogen absorption were investigated by heating under the same temperature and time as the nitrogen absorption treatment in an argon atmosphere. At least, three measurements were carried out under the same conditions, and the mean values were calculated.

2.5 Tensile test

The tensile test was performed in air using an Instron-type tensile test machine with a capacity of 10 kN. The crosshead

Table 1 Chemical compositions of Fe–24Cr and Fe–24Cr–2Mo (mass%).

	C	Mn	P	S	Ni	Cr	Mo	O	N	Fe
Fe–24Cr	0.002	—	<0.002	0.0002	<0.01	25.70	—	0.018	<0.001	Bal.
Fe–24Cr–2Mo	0.002	—	<0.002	0.0002	<0.01	25.80	2.04	0.016	<0.001	Bal.

Fig. 1 Schematic diagram of the forging process of a thin plate. H.F.: hot forging, C.F.: cold forging, R.A.: reduction of area, t : thickness, w : width, and l : length.

Fig. 2 Schematic diagram of the nitrogen absorption system.

speed was $8.33 \times 10^{-6} \text{ m s}^{-1}$. Ultimate tensile strength, 0.2% proof stress, elongation to fracture, and reduction of area were estimated throughout the tensile test. At least, five measurements were carried out under the same conditions, and the mean values were calculated. The fractured surfaces of Fe-24Cr and Fe-24Cr-2Mo specimens were observed with a scanning electron microscope (SEM).

3. Results and Discussion

3.1 Changes in microstructures by nitrogen absorption

Figure 3 shows the XRD profiles of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption. Only the diffraction pattern of ferrite (α phase) was observed from both Fe-24Cr and Fe-24Cr-2Mo without nitrogen absorption, indicating that the structure consisted of only α phase. XRD profiles from Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption for 1.8 ks showed peaks originating from both α phase and austenite (γ phase), indicating that the structure consisted of both α and γ phases. On the other hand, those for 2.7 ks showed only peaks originating from the γ phase, indicating that the structure was completely transformed to the γ phase. Therefore, thin plates of Fe-24Cr and Fe-24Cr-2Mo with a thickness of 0.2 mm are completely austenitized with nitrogen absorption treatment over 2.7 ks. On the other hand, round bars of both alloys with a diameter of 4 mm were completely austenitized with nitrogen absorption treatment over 43.2 ks.¹¹⁾ Nitrogen absorption in stainless steel proceeds with diffusion through the grain boundary and diffusion from the grain boundary to the inside of the

grain.¹²⁾ However, nitrogen absorption in stainless steel with a coarse grain mainly proceeds by the lattice diffusion. The thickness of the specimens in this study (0.2 mm) was smaller than that in the previous study (4 mm).¹¹⁾ Therefore, thin plates of both alloys in this study were completely austenitized with nitrogen absorption in short time.

Using XRD, neither CrN nor Cr₂N was identified in any specimen with nitrogen absorption, indicating that no nitride was formed in Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption.

Figures 4 and 5 show the microstructures of Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption treatment for each time. Fe-24Cr and Fe-24Cr-2Mo before nitrogen absorption consisted of a fine α phase expanded along the rolling direction. The α phase was completely transformed to a γ phase after 1.8-ks nitrogen absorption. Fine grains in Fe-24Cr and Fe-24Cr-2Mo were grown and coarsened with the nitrogen absorption treatment. The grains were the largest with 5.4-ks nitrogen absorption (Figs. 4(f) and 5(f)). The mean grain sizes of both alloys after 5.4-ks nitrogen absorption were 125 μm and 80 μm , respectively. On the other hand, those of both alloys after 129.6-ks nitrogen absorption in the previous study were 750 μm and 604 μm , respectively.¹¹⁾ The grain size in this study was smaller than that in the previous study,¹¹⁾ indicating that grains in both alloys were refined with the grain refinement process attempted in this study. The grains in Fe-24Cr-2Mo were smaller than those in Fe-24Cr independently of the nitrogen absorption time.

Fig. 3 X-ray diffraction patterns of (a) Fe-24Cr and (b) Fe-24Cr-2Mo with and without nitrogen absorption.

Fig. 4 Optical microstructures of Fe-24Cr with nitrogen absorption treatment.

Fig. 5 Optical microstructures of Fe-24Cr-2Mo with nitrogen absorption treatment.

3.2 Changes in micro Vickers hardness by nitrogen absorption

Figure 6 shows the changes in micro Vickers hardness of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption treatment. For comparison, those with heating in an argon atmosphere are also shown. Although the micro Vickers hardness of these alloys after annealing was 140–150, that of thin plates of alloys after 95% cold forging was

Fig. 6 Comparison of the micro Vickers hardness of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption and Fe-24Cr and Fe-24Cr-2Mo heated at 1473 K in an argon atmosphere.

360 in Fe-24Cr and 390 in Fe-24Cr-2Mo because of work hardening. The hardness of these alloys decreased after 1.8-ks nitrogen absorption because of the release of residual stress. The hardness of Fe-24Cr was almost constant after a longer treatment, while that of Fe-24Cr-2Mo showed the maximum value ($Hv = 388$) at 2.7-ks nitrogen absorption and decreased after 2.7 ks. The hardness of thin plates of Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption for over 2.7 ks was the same as that of a round bar of either alloy with nitrogen absorption for 126.9 ks. The microstructures of both alloys with nitrogen absorption for 129.6 ks showed only a γ phase. Therefore, the γ phase was also obtained by nitrogen absorption for 2.7 ks in thin plates of both alloys. On the other hand, the hardness decreased in an argon atmosphere with heating for 1.8 ks, and the value was maintained when the duration of the heating was extended. The hardness of Fe-24Cr-2Mo was larger than that of Fe-24Cr with nitrogen absorption treatment over 2.7 ks. The magnitude of solid-solution strengthening by nitrogen in Fe-24Cr-2Mo was larger than that in Fe-24Cr because nitrogen solubility in γ phase increased with increasing chromium and molybdenum contents.¹³⁾ In addition, the difference in hardness between these alloys is also caused by the difference in microstructure, which is shown in Figs. 4 and 5.

According to the results on hardness and microstructure, the mechanical strength of the thin plate in this study is expected to be larger than that of the round bar previously studied.¹¹⁾

3.3 Changes in mechanical properties by nitrogen absorption

Ultimate tensile strength, 0.2% proof stress, elongation to fracture, and reduction of area of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption treatment are shown in Fig. 7. Figure 7 contains the results in 316L steel for comparison. The tensile strength and elongation to fracture of Fe-24Cr-2Mo (969 MPa and 5%, respectively) were larger than those of Fe-24Cr (797 MPa and 3%, respectively) before nitrogen absorption. The tensile strength and 0.2% proof stress of both alloys with nitrogen absorption were larger than those of 316L steel, while the elongation to fracture and reduction of area in both alloys were smaller than those of 316L steel. Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption for 2.7 ks showed maximum ultimate tensile strength, 1032 MPa and 1167 MPa, respectively. On the other hand, Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption for 129.6 ks in the previous study¹¹⁾ showed maximum ultimate tensile strength, 823 MPa and 982 MPa, respectively.¹¹⁾ The values of ultimate tensile strength in both alloys with nitrogen absorption increased with the grain refinement process attempted in this study. The tensile strength of these alloys decreased with nitrogen absorption over 2.7 ks, a phenomenon caused by grain growth with the treatment times shown in Figs. 4 and 5. This indicates that the gage region of the tensile test specimen is deformed uniformly rather than locally. This uniform deformation under a large stress is caused by a significant magnitude of work hardening. The gradient of plastic deformation on the stress-strain curves is calculated as follows:

Fig. 7 (a) Ultimate tensile strength and 0.2% proof stress and (b) elongation to fracture and reduction of area of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption.

$$((\text{Ultimate tensile strength}) - (0.2\% \text{ proof stress}))/\text{strain}$$

The calculated values for Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption for 2.7 ks are 1.2 GPa and 1.5 GPa, respectively. The value in 316L steel obtained in the previous study¹¹⁾ is 0.5 GPa, and the values in Fe-24Cr and Fe-24Cr-2Mo were twice larger than the value in 316L steel.

Therefore, the work hardening in nitrogen-absorbed alloys is accelerated with a solution of nitrogen, which caused high ductility. No martensite (α' phase) was observed at the fractured surface nor was it identified using XRD, indicating that no stress-induced martensitic transformation in specimens with nitrogen absorption occurred.

Figure 8 shows the relation between ultimate tensile strength and elongation to fracture of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption. The figure also contains the data on a round bar of each alloy with nitrogen absorption for 129.6 ks and 316L steel previously reported.¹¹⁾ The best balance between strength and elongation was given by 2.7-ks nitrogen absorption in both Fe-24Cr and Fe-24Cr-2Mo, and the balance was better than that in the round bar specimens and 316L steel shown in the previous study.¹¹⁾

Scanning microphotographs of fractured surfaces of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorp-

Fig. 8 Ultimate tensile strength and elongation to fracture of Fe-24Cr and Fe-24Cr-2Mo with and without nitrogen absorption and of conventional austenitic stainless steels.

tion treatment are shown in Figs. 9 and 10. Specimens without nitrogen absorption show a ductile fracture surface containing dimples (Figs. 9(a) and 10(a)). Fe-24Cr and Fe-24Cr-2Mo after 2.7-ks nitrogen absorption specimens show good ductility (Fig. 7(b)), while specimens with nitrogen absorption show a brittle fracture surface containing both intergranular and transgranular fracture surfaces. In each alloy, the roughness and intergranular-fractured surface area on the fracture surface increased with nitrogen absorption treatment time. The addition of nitrogen reduces the formability because it increases the brittleness of the γ 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 and Fe-24Cr-2Mo with nitrogen absorption treatment.¹¹⁾ Therefore, the brittle fractures observed in both alloys with nitrogen absorption were caused by brittleness of the γ phase. In both cases, coarsening with treatment time was observed. The grains in Fe-24Cr-2Mo with nitrogen absorption were finer than those in Fe-24Cr. This is in good agreement with the results of microstructural observation as shown in Figs. 4 and 5. The decreases in the ultimate tensile strength and elongation to fracture of the alloys with 5.4-ks nitrogen absorption were caused by coarsening.

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

4. Conclusions

The γ phase was only obtained from the surface to a 0.1-mm depth in Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption at 1473 K for 2.7 ks. The balance between strength and elongation in Fe-24Cr and Fe-24Cr-2Mo with nitrogen absorption at 1473 K for 2.7 ks was better than that in conventional austenitic stainless steel. The values of ultimate

Fig. 9 Scanning electron micrographs of fractured surfaces of Fe-24Cr with nitrogen absorption for (a) 0 ks, (b) 1.8 ks, (c) 2.7 ks, (d) 3.6 ks, (e) 4.5 ks, and (f) 5.4 ks.

Fig. 10 Scanning electron micrographs of fractured surfaces of Fe-24Cr-2Mo with nitrogen absorption for (a) 0 ks, (b) 1.8 ks, (c) 2.7 ks, (d) 3.6 ks, (e) 4.5 ks, and (f) 5.4 ks.

tensile strength in both alloys with nitrogen absorption increased with the grain refinement process attempted in this study. The balance between strength and elongation in the both alloys with nitrogen absorption over 2.7 ks decreased because of grain growth. Therefore, the process described in this study can be used to manufacture small precise devices and parts with a maximum thickness or diameter of 0.2 mm in a short time. Grain refinement in a nickel-free austenitic stainless steel can increase the balance between the strength and elongation.

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