Torsion and Tensile Properties of Thin Wires of Nickel-Free Stainless Steel with Nitrogen Absorption Treatment

Daisuke Kuroda¹, Takao Hanawa¹, Takaaki Hibaru², Syuji Kuroda² and Masaki Kobayashi²

¹Biomaterials Center, National Institute for Materials Science, Tsukuba 305-0047, Japan
²Steel Research Center, National Institute for Materials Science, Tsukuba 305-0047, Japan

A new manufacturing process for nickel-free austenitic stainless steel has been developed by authors. In combination with machining and a nitrogen absorption treatment, this process makes it possible to form small precise devices with a maximum thickness or diameter of 4 mm. The refinement of grains of Fe-24Cr-2Mo in mass% was attempted by thermo-mechanical treatment before nitrogen absorption treatment in order to increase the mechanical properties after nitrogen absorption treatment. Torsion and tensile properties and microstructures of Fe-24Cr-2Mo before and after nitrogen absorption treatment were evaluated to understand the effects of grain refinement on nitrogen absorption. The thin wire of the alloy is completely austenitized with nitrogen absorption at 1473 K for over 7.2ks. The mean grain size of the alloy with nitrogen absorption decrease with the grain refinement process attempted in this study. The values of ultimate tensile strength and elongation in the alloy with and without nitrogen absorption increase with the grain refinement process. The torsional stress and rotation angle to fracture of the alloy increase with the grain refinement process and nitrogen absorption. According to the results of the torsion and tensile tests, the thin wire of the alloy with nitrogen absorption is expected to have good mechanical properties than conventional austenitic stainless steels.

1. Introduction

A new manufacturing process for nickel-free austenitic stainless steel has been developed by authors.¹ In combination with machining and a nitrogen absorption treatment, this process makes it possible to form small precise devices with a maximum thickness or diameter of 4 mm. Ingot of ferritic stainless steel, Fe-24Cr-2Mo in mass%, is worked to various dimensions such as round bar, thin plate, and thin wire.¹ The balance between strength and elongation in each test specimen with nitrogen absorption is the same as that in conventional austenitic stainless steel such as 316L.

However, the temperature for nitrogen absorption, 1473 K, is sufficiently high for grain growth, and the coarsening is observed after nitrogen absorption.¹ The grain growth and coarsening causes decrease in the mechanical properties. Therefore, a nitrogen absorption treatment that allows the retention of strength and ductility is performed with a grain refinement process before nitrogen absorption treatment.

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 torsion and tensile properties and microstructures of Fe-24Cr-2Mo in mass% 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. The results were compared to those of the alloy in the previous study¹ and conventional austenitic stainless steel.

2. Experimental Procedure

2.1 Specimen preparation

Ingot with 20 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 alloy. The ingot was then cut into three equal parts. Figure 1 shows a schematic diagram of the forging process. Hot radial forging, followed by 99% cold radial forging, was conducted in the previous study.³ In this study, 84% hot radial forging and 99.99% cold radial forging were conducted to obtain finer grains than in the previous study.³ Thin wires (1.0 mm in diameter) were obtained through hot and cold radial forging. Specimens for the torsion and tensile tests (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 to the radial forging direction in specimens for the tensile test.

![Schematic diagram of the forging process of a thin wire](image)

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

<p>| Table 1 Chemical composition of Fe-24Cr-2Mo (mass%). |</p>
<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>O</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>&lt;0.01</td>
<td>&lt;0.002</td>
<td>0.0002</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>25.80</td>
<td>2.04</td>
<td>0.016</td>
<td>&lt;0.001</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
2.2 Nitrogen absorption

Specimens for the torsion, tensile, and hardness tests of the alloy 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.1–3) The pressure of the inside of the furnace was reduced to 2 Pa, and nitrogen gas (99.999%) 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\(^{-1}\). The pressure of nitrogen absorption for 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 each specimen was removed with #600 SiC paper in water after nitrogen absorption.

2.3 Examination of microstructure and mechanical properties

Gripped parts of torsion test specimens were employed for microstructural observation. 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 torsion test with and without nitrogen absorption were identified using X-ray diffractometry (XRD) with CuK\(\alpha\) radiation (40 kV and 300 mA). The hardness test was performed using a micro Vickers hardness tester. The torsion test was performed in air using a torsion testing machine with a capacity of 0.2 N as shown in Fig. 2. The rotation speed of gripped part was 0.1 Hz. Torque and rotation angle to fracture were estimated throughout the torsion test. The torsional stress, \(\tau\) was calculated by the following equation:

\[
\tau (N/m^2 = Pa) = T (N-m)/Z_p (m^3)
\]

where \(T\) is the torque and \(Z_p\) is the polar modulus of section. The polar modulus of section, \(Z_p\), was calculated by the following equation:

\[
Z_p (m^3) = \pi d^3 / 16
\]

where \(d\) is the diameter of the specimen for torsion test.

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 \times 10^{-6} \text{ 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) after torsion and tensile tests.

For comparison, changes in phases, hardness and torsion 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

XRD profiles of Fe-24Cr-2Mo with and without nitrogen absorption and Fe-24Cr-2Mo heated at 1473 K in an argon atmosphere are shown in Fig. 3. Only diffraction pattern of ferrite (\(\alpha\) phase) was observed from Fe-24Cr-2Mo without nitrogen absorption and Fe-24Cr-2Mo heated at 1473 K in an argon atmosphere (Figs. 3(a) and (b)), indicating that phase transformation from \(\alpha\) phase to austenite (\(\gamma\) phase) does not occur in an argon atmosphere. On the other hand, only peaks originating from \(\gamma\) phase were observed from the alloy with nitrogen absorption for over 7.2 ks, indicating that the thin wire of the alloy is completely austenitized with nitrogen absorption treatment for 7.2 ks (Fig. 3(a)). Using XRD, neither CrN nor Cr\(_2\)N was identified in any specimen with nitrogen absorption, indicating that precipitation of nitride
does not occur in Fe-24Cr-2Mo with nitrogen absorption. The result of XRD in this study is in good agreement with that in the previous study.1–3)

The microstructures of Fe-24Cr-2Mo with nitrogen absorption and Fe-24Cr-2Mo heated in an argon atmosphere are shown in Fig. 4. The microstructures of the alloy before nitrogen absorption and heat treatment in an argon atmosphere were a fine α phase expanded along the radial forging direction. The α phase was only observed in Fe-24Cr-2Mo heated in an argon atmosphere (Figs. 4(a) and (b)). Fine grains in Fe-24Cr-2Mo were grown and coarsened with the nitrogen absorption treatment and heat treatment in an argon atmosphere. The mean grain size of the alloy after heated for 21.6 ks in an argon atmosphere was 433 µm. The grains were the largest with 21.6-ks nitrogen absorption (Fig. 4(e)). The mean grain size of the alloy after 21.6-ks nitrogen absorption was 126 µm. The mean grain size of the alloy slightly increased with increasing nitrogen absorption time. 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 coarsening. In addition, that of the alloy after 21.6-ks nitrogen absorption and heated for 21.6 ks in an argon atmosphere in the previous study was 132 µm and 527 µm, respectively.3) The grain size of the alloy in this study was smaller than that in the previous study,3) 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

The changes in micro Vickers hardness of Fe-24Cr-2Mo with and without nitrogen absorption treatment and the alloy heated in an argon atmosphere are shown in Fig. 5. For comparison, that of the alloy with and without nitrogen absorption treatment and heated in an argon atmosphere in the previous study3) is also shown.

---

D. Kuroda, T. Hanawa, T. Hibaru, S. Kuroda and M. Kobayashi

---

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.

Fig. 5 Comparison of the micro Vickers hardness of Fe-24Cr-2Mo with and without nitrogen absorption and Fe-24Cr-2Mo heated at 1473 K in an argon atmosphere. For comparison, that of the alloy with and without nitrogen absorption treatment and heated in an argon atmosphere in the previous study3) is also shown.
previous study. However, the hardness of the alloy with nitrogen absorption in this study was smaller than that in the previous study. On the other hand, the hardness of the alloy heated in an argon atmosphere in this study was the same as that in the previous study. The hardness of Fe-24Cr-2Mo increased with 7.2-ks nitrogen absorption, and the value was maintained when the duration of the nitrogen absorption was extended. The hardness of the alloy showed the maximum value (HV=337) at 21.6-ks nitrogen absorption. On the other hand, the hardness decreased in an argon atmosphere with heating for 7.2 ks. This indicates that the release of residual stress by heat treatment in an argon atmosphere.

3.3 Changes in tensile properties by nitrogen absorption

Figure 6 shows the ultimate tensile strength, 0.2% proof stress, elongation to fracture, and reduction of area of Fe-24Cr-2Mo with and without nitrogen absorption treatment and Fe-24Cr-2Mo heated in an argon atmosphere. The tensile strength, 0.2% proof stress, and reduction of area of the alloy decreased with nitrogen absorption, while elongation to fracture of the alloy increased with nitrogen absorption. Elongation to fracture of the alloy increased with increasing nitrogen absorption time. The value of tensile strength of the alloy with nitrogen absorption is much larger than that of 0.2% proof stress of the alloy with nitrogen absorption, indicating that magnitude of work-hardening increased with solid-solution strengthening of nitrogen. Fe-24Cr-2Mo with nitrogen absorption for 14.4 ks showed maximum ultimate tensile strength (1033 MPa). Elongation to fracture of the alloy showed the maximum value (65%) at 21.6-ks nitrogen absorption. The maximum values of tensile strength and elongation obtained from the alloy with nitrogen absorption in this study are larger than those of the alloy with nitrogen absorption in the previous study (985 MPa and 41%). In this study, the amounts of nitrogen in the thin wires of Fe-24Cr-2Mo at 7.2-ks and 21.6-ks absorption were 0.92 mass% and 0.95 mass%, respectively. The amount of nitrogen in the thin wire of the alloy increased with 7.2-ks nitrogen absorption, and the amount was maintained when the duration of the nitrogen absorption was extended. On the other hand, the amounts of nitrogen of the thin wires of Fe-24Cr-2Mo at 7.2-ks and 21.6-ks absorption were 0.92 mass% and 0.93 mass% in the previous study. The amount of nitrogen of the alloy with nitrogen absorption in this study was the same as that in the previous study. Therefore, tensile properties of the alloy with nitrogen absorption in this study improved with the grain refinement process attempted in this study. The tensile strength and 0.2% proof stress decreased and elongation to fracture and reduction of area 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 21.6 ks in an argon atmosphere showed maximum ultimate tensile strength and elongation to fracture, 310 MPa and 19%, respectively. The tensile strength and elongation to fracture obtained from the alloy heated in an argon atmosphere in this study are the same as those of the alloy heated in an argon atmosphere in the previous study. The tensile strength,
0.2% proof stress, and elongation to fracture of the alloy with nitrogen absorption were larger than those of the alloy heated in an argon atmosphere.

The relation between ultimate tensile strength and elongation to fracture of Fe-24Cr-2Mo with and without nitrogen absorption is shown in Fig. 7. The figure also contains the data on a round bar, thin plate, and thin wire of Fe-24Cr-2Mo with nitrogen absorption and 316L steel previously reported.1–3) The best balance between strength and elongation was given by 21.6-ks nitrogen absorption in Fe-24Cr-2Mo, and the balance was larger than that in the thin wire in the previous study3) and conventional austenitic stainless steel.1) However, the balance between strength and elongation of thin wire of the alloy with nitrogen absorption was lower than that of the thin plate in the previous study.2)

Figure 8 shows the scanning electron micrographs of fractured surfaces of Fe-24Cr-2Mo with and without nitrogen absorption treatment. Specimen without nitrogen absorption shows a ductile fracture surface (Fig. 8(a)). Fe-24Cr-2Mo with nitrogen absorption specimens 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.4) In addition, the grain boundary cracks generate during cold rolling in a highly nitrogen contained (0.9 mass%) Fe-Cr-Mn-N steel.5) Over 0.9 mass% nitrogen can be absorbed by Fe-24Cr-2Mo with nitrogen absorption treatment.1) Therefore, the brittle fractures observed in the alloy with nitrogen absorption were caused by brittleness of the \(\gamma\) phase.

The tensile 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.

3.4 Changes in torsion properties by nitrogen absorption

Figure 9 shows the torsional stress and rotation angle to...
fracture of Fe-24Cr-2Mo with and without nitrogen absorption and Fe-24Cr-2Mo heated in an argon atmosphere. The torsional stress and rotation angle to fracture of the alloy increased with nitrogen absorption. Fe-24Cr-2Mo with nitrogen absorption for 14.4 ks showed maximum torsional stress (1258 Pa). Rotation angle to fracture of the alloy showed the maximum value (3094 °C14) at 7.2-ks nitrogen absorption. On the other hand, the torsional stress of the alloy decreased and rotation angle to fracture increased with a heat treatment in an argon atmosphere. Fe-24Cr-2Mo with heated for 21.6 ks showed maximum torsional stress (465 Pa). Rotation angle to fracture of the alloy showed the maximum value (2964 °C14) at 7.2-ks heat treatment in an argon atmosphere. The torsional stress and rotation angle to fracture of the alloy with nitrogen absorption were larger than those of the alloy with heating in an argon atmosphere. Therefore, torsion properties of the alloy increased with nitrogen absorption.

Figure 10 shows the relation between torsional stress and rotation angle to fracture of the alloy with and without nitrogen absorption and that of the thin wire of 316L steel in annealed condition. The balance between torsional stress and rotation angle to fracture of the alloy increased with nitrogen absorption. The balance between torsional stress and rotation angle to fracture of the alloy with nitrogen absorption was larger than that of the annealed 316L steel, while that of the alloy with a heating in an argon atmosphere as smaller than that of 316L steel. The best balance between torsional stress and rotation angle to fracture was given by 18.0-ks nitrogen absorption in Fe-24Cr-2Mo, and the balance was larger than that in 316L.

4. Conclusions

The refinement of grains of Fe-24Cr-2Mo in mass% was attempted by thermo-mechanical treatment before nitrogen absorption treatment in order to increase the mechanical properties after nitrogen absorption treatment. Torsion and tensile properties and microstructures of Fe-24Cr-2Mo before and after nitrogen absorption treatment were evaluated to understand the effects of grain refinement on nitrogen absorption. The results obtained are as follows:

(1) The mean grain size of Fe-24Cr-2Mo with nitrogen absorption decrease with the grain refinement process attempted in this study.

(2) The tensile properties of the alloy with nitrogen absorption in this study improved with the grain refinement process attempted in this study. The best balance between strength and elongation is given by 21.6-ks nitrogen absorption in Fe-24Cr-2Mo, and the balance was larger than that in conventional austenitic stainless steel.

(3) The torsion properties of the alloy increase with the grain refinement process and nitrogen absorption. The balance between torsional stress and rotation angle to fracture in Fe-24Cr-2Mo with nitrogen absorption at 1473 K for over 7.2 ks is larger than that in conventional austenitic stainless steel.

(4) The thin wire of the alloy with nitrogen absorption is expected to have good mechanical properties than conventional austenitic stainless steels.

Acknowledgements

We would like to thank Mr. Kenshi Morita, Mr. Hironori Kawasaki and Mr. Morihide Makino for their valuable support during the experiments.
REFERENCES


