Fabrication of Fine-grained High Nitrogen Austenitic Steels through Mechanical Alloying Treatment

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Mechanical alloying (MA) treatment was applied for the fabrication of fine-grained high nitrogen stainless steels. Chromium nitride (Cr$_2$N) powder was mixed with Fe–Cr binary alloy powder to control its mean chemical composition to be Fe–23mass%Cr–1mass%N which is enough to stabilize austenitic structure at room temperature. The powder mixture was mechanically alloyed up to 360 ks in an argon gas atmosphere (MA powder). The MA powder was packed in a stainless steel tube in a vacuum and consolidated by warm rolling at 1 073 K. The consolidated materials were finally heated to various temperatures (1 173–1 473 K) for austenitizing and then quenched without holding at the temperatures. Although the materials heat-treated below 1 323 K had bcc (martensitic) matrix, those heat-treated above 1 373 K had stable austenitic structure with a small amount of Cr$_2$N. The grain size of matrix was maintained to be fine due to dispersed oxide particles within matrix in all steels. For example, the materials heat-treated at 1 473 K had fine austenitic structure in which the grain size was 2.2 µm and the solute nitrogen concentration was 0.86 mass%. The steel had very high yield strength of 1.1 GPa and moderate elongation of 30%. Such a high strength of the steel was explained by the combined strengthening mechanism of nitrogen solid solution strengthening and grain refining strengthening.

KEY WORDS: high nitrogen steels; austenite; mechanical alloying; yield strength; solid solution strengthening; grain refining strengthening; Hall–Petch relationship.

1. Introduction

Solid solutioning of nitrogen is very effective for improving not only strength but also corrosion resistance of austenitic steels,$^{1,2}$ thus, many kinds of high nitrogen austenitic stainless steels have been developed for the last decade.$^{3-6}$ However, it has been also pointed out that the high nitrogen austenitic steels exhibit ductile–brittle transition behavior as in ferritic steels, and the ductility of the steels is significantly lowered at low temperature.$^{7,8}$ Therefore, strengthening due to nitrogen seems to be limited in terms of application for structural use at low temperature.

On the other hand, grain refining is well known to be effective for strengthening steel without losing toughness.$^9$ With decreasing grain size, strength of steels is increased yielding to Hall–Petch relationship, while ductile–brittle transition temperature is shifted to lower temperature. Considering these facts, if the nitrogen solid solution strengthening and grain refining strengthening could be used simultaneously, the strength of the steels would be further increased with sufficient ductility and corrosion resistance.

In order to develop such a high strength austenitic stainless steel, we used mechanical alloying (MA) technique which enables not only alloying with variable chemical composition but also refining of grains. In this study, microstructure and tensile properties were investigated for the high nitrogen stainless steels with fine-grained structure fabricated with the MA technique. The strengthening mechanism of the developed steels was also discussed in terms of contribution of the solid solutioning of nitrogen and the grain refining to the strength.

2. Experimental Procedure

Fe–Cr alloy powders (Fe–16 or 20mass%Cr powder) and Cr$_2$N powder were mixed to control its mean chemical composition to be Fe–23mass%Cr–1mass%N which is enough to stabilize austenitic single structure at room temperature.$^{10}$ The powder mixture was put into a stainless steel pot with steel balls (SUJ2, 15 mm in diameter), and then sealed under argon gas atmosphere. MA treatment was carried out with a planetary ball mill up to 360 ks. The powder with the particle size under 45 µm (~350 mesh) was separated from the as-MA powder, and it was packed in a stainless steel tube (SUS304, 16 mm in diameter) in a vacuum. The sealed tube was warm-rolled to the thickness of 1.5 mm at 1 073 K for consolidation of the MA powder. The consolidated materials were finally heated to various temperatures (1 173–1 473 K), followed by water quenching
without holding at the temperature to avoid coarsening of grains. The specimen was subjected to microstructural observation with optical and electron microscopes, and tensile testing. The specimens for optical and scanning electron microscopies were polished and chemically etched with concentrated hydrochloric acid, and the thin foil specimens for transmission electron microscopy were prepared by electrolytic polishing using solution of 10% perchloric acid and 90% acetic acid.

3. Results and Discussion

3.1. Microstructural Change of Powders during MA Treatment

Figure 1 represents optical micrographs showing change in structure of the powder mixture of Fe–Cr alloy and Cr$_2$N during MA treatment. The powders are crashed and stuck together repeatedly, and then the layered structure is formed within the powders in the early stage of MA treatment (10.8 ks). The structure is refined with treatment time (36, 108 ks), and finally (360 ks), homogenized in the optical micro-scale. The microstructural change with MA treatment was examined by means of X-ray diffraction analysis. The obtained diffraction patterns are shown in Fig. 2. The peaks of bcc (ferrite) and Cr$_2$N are clearly detected in the as-mixed powder, but the Cr$_2$N peaks gradually shrink with MA treatment and then fully disappear after the MA of 36 ks. This means that alloying has completed in the powders by the MA treatment and its microstructure has become ferritic single-phase structure. Figure 3 shows the results of TEM observation for the microstructural change. Judging from the Debye rings in the diffraction patterns and the dark field images, the ferrite grains have already refined to several hundred nm even in the 36 ks MA powder although the grains have elongated shape. With increasing MA treatment time, the grains becomes smaller and equiaxed shape. After 360 ks MA treatment, the ferrite grain size was estimated at 35 nm by X-ray diffraction analysis. It is also confirmed that no Cr$_2$N exists in these MA powders.

3.2. Microstructure of Consolidated Bulk Material

Figure 4 represents an optical micrograph and a diffraction pattern of the specimen which was consolidated at 1 073 K for the 360 ks MA powder (consolidated material). The consolidated material has a homogeneous and fine microstructure with full density. The X-ray diffraction pattern
reveals that the microstructure consists of ferrite matrix and a small amount of Cr$_2$N which precipitated on the warm rolling for consolidation. For the consolidated material, the heat treatment was carried out to austenitize. Figure 5 shows X-ray diffraction patterns of the heat-treated materials (1 173–1 473 K). The specimen heat-treated below 1 273 K has a microstructure composed of bcc (martensite) and Cr$_2$N, while the specimens heat-treated above 1 373 K have an austenite matrix. The amount of Cr$_2$N decreases with increasing heat treatment temperature because the solubility of Cr$_2$N in austenite is enlarged at high temperature.11) The results suggest that solutioning at high temperature is required for dissolving sufficient amount of nitrogen into matrix to stabilize austenitic structure at room temperature.
under 2.2 μm in each steel. This is mainly due to the grain boundary pinning effect by fine oxide particles which have been introduced from the surface oxidized layer of as-received powders and dispersed on the MA treatment. The black spots in the pictures are thought to be traces of the oxide particles fallen away from the specimen surface or etch-pits generated at the particles because they could not be observed before the etching. Chemical analysis demonstrated that the amount of solute nitrogen in the matrix increases with raising heating temperature. The nitrogen concentrations of the heat-treated materials are 0.53 % N, 0.68 % N and 0.86 % N for the specimen (a), (b) and (c), respectively.

3.3. Mechanical Properties of Fine-grained High Nitrogen Austenitic Steels

Figure 7 represents nominal stress–strain curves of the developed fine-grained high nitrogen austenitic steels. The curve of a conventional austenitic steel (SUS304L) is also shown for a reference. Yield strength of the developed materials is markedly increased through solid solution strengthening due to nitrogen and grain refining strengthening. Especially the 1 423 K heat-treated material has the yield strength of 1.1 GPa which is about four times higher than that of SUS304L. The peculiar deformation behavior in the 1 373 K heat-treated material was confirmed to be due to a strain-induced martensitic transformation on the tensile testing. It should be also noted that the 1 423 K heat-treated material has uniform elongation of 30 % in spite of the high strength. This is derived from the high work-hardening rate which is characteristic of high nitrogen austenitic steels. Figure 8 shows true stress and work-hardening rate as a function of true strain in the developed steel (1 423 K heat-treated material) and SUS304 shown in Fig. 7. The developed steel has not only higher strength but also higher work-hardening rate compared with SUS304L. As a result, plastic stability is kept to high strain region, and this leads to the large uniform elongation of 30 % as pointed by the arrow (a). If the work-hardening rate of the developed steel was the same as that of SUS304L, uniform elongation would be given at the point shown by the arrow (b) and its value was 15% at the most.

3.4. Strengthening Mechanism of Fine-grained High Nitrogen Austenitic Steels

The fine-grained high nitrogen austenitic steels are strengthened by both solid solution strengthening and grain refining strengthening. Contribution of each strengthening mechanism was evaluated with the knowledge that has been obtained from previous study. Figure 9 shows the relation between yield strength and solute nitrogen concentration in austenitic steels with various base compositions. The yield strength has the linear relationship with $\left(\text{atomic fraction of nitrogen}\right)^{2/3}$ as explained by Labusch’s theory.

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1 Plastic deformation stably occurs on condition that the work-hardening rate is larger than the true stress. Because the true stress required for plastic deformation is increased by the work-hardening at a locally deformed region, this leads to the interruption of necking deformation. When the values of work-hardening rate and true stress are reversed, the plasticity is unstabilized and a macroscopic necking deformation begins.
found that solid solution strengthening by other alloying elements such as Cr, Ni and Mn is small enough to be negligible for discussing the strength of high nitrogen steels. With this figure, we can estimate the increment of strength by the solid solution strengthening due to nitrogen in the developed steels. For example, the 1473 K heat-treated material contains 0.86 % nitrogen in the austenite solution, therefore, the increment of the yield strength by the solid solution strengthening should be around 490 MPa. On the other hand, the grain refining strengthening can be estimated from Hall–Petch relationship ($\Delta \sigma = 0.82 d^{-1/2}$) in austenitic steels. For example, $\Delta \sigma = 0.1 + 0.6d^{-1/2}$ (GPa) was proposed for Fe–12.4%Cr–9.4%Ni–2.0%Mo–0.083%N alloy. However, the slope of Hall–Petch relation (Hall–Petch coefficient); $k$ is known to be varied depending on the nitrogen concentration. In order to find the correspondent $k$ values for the developed high nitrogen steels, the nitrogen concentration dependence of $k$ value was examined by means of tensile tests using some nitrogen-bearing austenitic steels with various grain sizes. Figure 10 shows the relation between Hall–Petch coefficient $k$ and nitrogen concentration in the austenitic steels. The $k$ value increases with increasing nitrogen concentration in the low nitrogen region, but the increment tends to level off in the high nitrogen region over 1 mass%. From this result, the $k$ value for the 1473 K heat-treated material containing 0.86% solute nitrogen is estimated at 0.82. The Hall–Petch relationship rewritten with the $k$ value of 0.82 is shown in Fig. 11. This relationship reveals that the grain refining from 100 to 2.2 $\mu$m in the 1473 K heat-treated material results in the increment of yield strength by 470 MPa.

It is generally accepted that the yield strength of materials ($\sigma_y$) consists of two components; thermal stress ($\sigma_t$) and athermal stress ($\sigma_a$). The relation among them is expressed as follows:

$$\sigma_y = \sigma_t + \sigma_a$$

In the case of the fine-grained high nitrogen steels, the thermal stress corresponds to the strength of base austenite matrix including solid solution strengthening due to nitrogen, and the athermal stress does to the grain refining strengthening. Since the base strength of nitrogen-free austenite is about 150 MPa, yield strength of the developed austenitic steel is roughly estimated at 1110 MPa by the addition of $\sigma_t$ (150 MPa+490 MPa) and $\sigma_a$ (470 MPa). This value well corresponds to the experimental value of 1100 MPa. Therefore, we can conclude that the strengthening mechanism of the developed fine-grained high nitrogen steels can be explained by combining grain refining strengthening and nitrogen solid solution strengthening.

4. Conclusions

Mechanical alloying (MA) treatment was applied for fabricating fine-grained high nitrogen stainless steels, and the microstructure and tensile properties were investigated for the developed steels. The conclusions obtained are summarized as follows.

(1) Powder mixture of Fe–Cr binary alloy powder and chromium nitride (Cr$_3$N) powder is completely alloyed and homogenized by the MA treatment for 360 ks. The MA powder has a ferritic single structure with ultra fine grains of 35 nm in diameter.

(2) The MA powder can be consolidated to a bulk material with full density by warm rolling. Microstructure of
the consolidated material is of (ferrite+Cr$_2$N) two-phase structure.

(3) Heat treatment above 1373 K makes the microstructure of consolidated bulk materials austenitic through solid-solutioning of nitrogen into matrix. The grain size is kept at around several microns owing to the pinning effect of fine oxide particles.

(4) The material heat-treated at 1473 K had fine austenitic structure in which the grain size is 2.2 \( \mu \text{m} \) and the solute nitrogen concentration is 0.86 mass\%. The yield strength and elongation of the material are 1.1 GPa and 30\%, respectively. Such a high strength of the steel was explained by the combined strengthening mechanism of nitrogen solid solution strengthening and grain refining strengthening.

REFERENCES