Factors Inducing Intergranular Fracture in Nickel-free High Nitrogen Austenitic Stainless Steel Produced by Solution Nitriding

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Fe–25mass%Cr–1.1mass%N alloys with different impurity content were produced by solution nitriding and then subjected to tensile tests at ambient temperature. Yield strength and tensile strength of the alloys are much higher than those of conventional austenitic stainless steels, but the brittle intergranular fracture is caused during uniform deformation without local elongation. It was confirmed that the intergranular fracture takes place at high angle random boundary and that the grain boundary segregation of impurities significantly promotes intergranular fracture. Deformation-induced martensite did not concern the intergranular fracture. In addition, it was suggested that marked stress concentration is caused at grain boundary by the piled-up dislocations in planar array and it would be one of the important factors inducing intergranular fracture.

KEY WORDS: high nitrogen steel; austenite; intergranular fracture; grain boundary segregation; impurity; deformation-induced martensite; planar dislocation array; dislocation pile-up; stress concentration.

1. Introduction

Nickel-free high nitrogen austenitic stainless steel is recently focused as a material used for medical metallic instruments in terms of the prevention of skin allergy caused by nickel.^{1,2)} In addition, since the strength property and corrosion resistance of stainless steel is greatly improved by the addition of nitrogen, it is also expected high nitrogen austenitic steel could be applied to osteosynthesis implants for internal fixation (e.g. bone plate, intramedullary nail) in fractures.³⁾ Some kinds of nickel-free austenitic stainless steels have been already standardized as medical materials; however, more information on the manufacturing process and properties should be necessary for the high nitrogen nickel-free austenitic stainless steel to be widely applied to biomaterials.

Authors have been studying the manufacturing process of high nitrogen steels by means of solution nitriding. The solution nitriding is one of chemical heat treatments to add a large amount of nitrogen to stainless steel through the nitrogen absorption from the material surface, which is performed by holding the material in a high temperature N₂ gas.^{4–6)} This is a simple and powerful method to obtain high nitrogen austenitic stainless steel plates or wires without the special equipment for pressurized melting.^{2,7–9)} The amount

of nitrogen to be absorbed by solution nitriding is increased with increasing chromium content of the base steel (the material prepared for solution nitriding). For example, when Fe–25Cr[†] binary alloy is subjected to solution nitriding in an N₂ gas of 0.1 MPa–1 473 K, nitrogen can be absorbed up to approximately 1 mass%.⁶⁾ As a result, austenite phase is formed at solution nitriding temperature, and besides, the Ms temperature is lowered below ambient temperature, leading to the stabilization of austenitic structure even without nickel.

The Fe–25Cr–1N alloy produced by solution nitriding exhibited not only high tensile strength of more than 700 MPa owing to its high yield stress but also moderate elongation of several tens percent due to large work hardening rate.¹⁰⁾ However, it was also found that the Fe–25Cr–1N alloy causes brittle fracture, despite austenitic steel, during uniform deformation without local elongation on tensile testing. We have also confirmed the brittle fracture in the Fe–25Cr–1N alloy is attributed to intergranular fracture.¹⁰⁾ Such a brittle fracture during plastic deformation is a serious problem for structural materials in terms of the deformability and the safety of built-up structure. In order to modify the brittleness, it is important to find the factors inducing brittle fracture, and then some prevention against the brittle fracture has to be considered. On the other hand,

[†] Throughout this article, the chemical composition is expressed in mass percent, unless otherwise stated.

Table 1. Chemical compositions of ferritic steels prepared as the base materials for solution nitriding (mass%).

	Cr	Mo	C	N	Si	Mn	P	S	O	Fe
Fe-25Cr-LP	25.02	-	0.012	0.0012	0.16	0.15	0.027	0.0032	0.0048	bal.
Fe-25Cr-HP	25.11	-	0.002	<0.0010	<0.01	<0.01	<0.005	0.0004	0.0104	bal.

Fig. 1. Optical micrographs showing ferrite to austenite phase transformation behavior during solution nitriding in Fe-25Cr-HP alloy. The solution nitriding was performed at 1 473 K for 3.6 ks (b), 10.8 ks (c) and 43.2 ks (d).

it was reported that a Fe–Cr–Mn–N system austenitic stainless steels produced by the high-pressurized melting exhibit a sufficient ductility with local elongation.¹¹⁾ Although the difference between both cases has not been clarified yet, it is possible that the fracture mode might depend on the susceptibility of deformation-induced martensitic transformation, marked grain coarsening and grain boundary segregation of impurities in the case of solution-nitrided austenitic steels.

In this study, two kinds of nickel-free high nitrogen austenitic stainless steel (Fe–25Cr–1N alloy) with different impurity content were produced by solution nitriding, and then the mechanical properties were investigated by means of tensile testing. The contribution of deformation-induced martensite, stress concentration at grain boundary caused by the piled-up dislocations in planar array and grain boundary segregation of impurity was then discussed for clarifying the mechanism of the occurrence of intergranular fracture.

2. Experimental Procedure

As the base materials for solution nitriding, two kinds of ferritic stainless steel (Fe–25Cr alloy) with different impurity content were prepared in this study. The chemical compositions of these steels are listed in **Table 1**. The low purity steel, Fe–25Cr-LP, contains phosphorus of 270 ppm and sulfur of 32 ppm, while the high purity steel, Fe–25Cr-HP, contains less phosphorus and sulfur contents, which are below 50 ppm and 4 ppm, respectively. The ingots (50 kg) were produced by induction melting in a vacuum and then casting into metallic molds. The ingots were homogenized by annealing at 1 473 K and then followed by hot forging to make bars of 50 mm in diameter. The specimens cut from the hot-forged bars (40 mm×15 mm×1 mm) were wet-polished and then electrically polished with a solution of phosphoric acid and chromic oxide ($\text{H}_3\text{PO}_4 : \text{CrO}_3 = 2 : 1$). Solution nitriding was performed to specimen at 1 473 K up to 72.0 ks in nitrogen gas under 0.1 MPa pressure. After the solution nitriding, the specimens were water-cooled so as not to cause austenite decomposition and nitride precipita-

tion upon cooling.

Tensile tests were carried out with an Instron-type testing machine at the initial strain rate of 5.5×10^{-4} /s for the plate specimens (gage: 3 mm width×6 mm length×1 mm thickness). The microstructure and fracture surface were observed with an optical microscope and a scanning electron microscope (SEM). The grain boundary segregation was detected by Auger electron spectroscopy (AES) for the specimens fractured in the vacuum chamber. Crystallographic characterization was also carried out by means of the electron backscattering pattern (EBSP) method using a FE-SEM. The data obtained by EBSP method were analyzed by orientation imaging microscopy (OIMTM). Phase identification was carried out by microfocus X-ray diffraction.

3. Results and Discussion

3.1. Microstructure Formed by Solution Nitriding

The base materials, Fe–25Cr-LP and -HP alloys, originally possess stable ferritic structure because they contains little austenite stabilizing elements. However, the ferrite phase transforms to austenite phase during solution nitriding at elevated temperature with absorbing a strong austenite stabilizer; nitrogen. **Figure 1** represents the optical micrographs showing the behavior of ferrite to austenite phase transformation in Fe–25Cr-HP alloy during solution nitriding at 1 473 K. The original ferritic structure (a) starts the phase transformation from the specimen surface where the nitrogen concentration is increased, as shown in (b). The austenite layer gradually grows (c), and finally, the whole of specimen is covered with austenite (d). The grain size of the austenite is several hundred microns (300–500 μm). **Figure 2** shows X-ray diffraction patterns for the specimens before and after the solution nitriding. It is confirmed that the specimen has fully transformed to austenite after the solution nitriding treatment. In addition, the hardness profile in **Fig. 3** indicates the uniform distribution of nitrogen within the specimens. The chemical analysis of these specimens shows that the nitrogen concentration has reached 1.1 mass% which is the equilibrium value obtained under

Fig. 2. X-ray diffraction patterns of Fe-25Cr-LP alloy prepared as the base material (a) and Fe-25Cr-1.1N-LP alloy produced by solution nitriding at 1473 K for 43.2 ks (b).

Fig. 3. Hardness profile of Fe-25Cr-1.1N alloys produced by solution nitriding (1473 K-43.2 ks).

the solution nitriding condition of 1473 K-0.1 MPa. Besides, there was no large difference between both specimens in the kinetics of nitrogen absorption and grain size of austenite obtained. In order to demonstrate that nitrogen is absorbed in solid solution without precipitation of nitrides, the microstructure near grain boundary was observed with TEM. **Figure 4** represents the TEM image of Fe-25Cr-LP alloy solution-nitrided at 1473 K for 72.0 ks (Fe-25Cr-1.1N-LP alloy). Austenitic single structure is observed, and no precipitate exists at the grain boundary of austenite. In general, it is known that the thermal stability of nickel-free austenite is much lower than conventional austenite containing nickel, and thus, nickel-free or low-nickel austenitic steel sometimes causes grain boundary precipitation of nitride during isothermal holding¹²⁾ or cooling after welding.¹³⁾ Also in the Fe-25Cr-1.1N steel, it was reported that cellular nitrides are formed through the decomposition of austenite at around 1200 K.¹⁰⁾ However, this specimen was quenched into water from the austenite single phase region at 1473 K, thus fully austenitic structure with super-saturated nitrogen was kept at ambient temperature. Specimens with such a austenitic single-structure were provided to the following experiments.

3.2. Behavior of Tensile Deformation and Fracture in Solution-nitrided Austenitic Steel

Figure 5 shows nominal stress-strain curves of the Fe-25Cr-1.1N-LP and -HP alloys produced by solution nitriding. The result of an annealed low nitrogen austenitic

Fig. 4. TEM image around austenite grain boundaries in Fe-25Cr-1.1N-LP alloy.

Fig. 5. Nominal stress-strain curves of Fe-25Cr-1.1N-LP alloy (a), Fe-25Cr-1.1N-HP alloy (b) and SUS316L (c).

stainless steel, SUS316L, is also shown for reference. Both of nickel-free high nitrogen steels exhibit very high yield strength above 600 MPa, which is approximately three times higher than that of SUS16L. In addition, the tensile strength also reaches an extremely high level owing to markedly large work hardening rate which is characteristic of high nitrogen austenitic steels.¹⁴⁾ However, these steels fractures abruptly on uniform deformation without local elongation. Besides, it should be noted that the elongation is significantly smaller in the LP alloy than in the HP alloy. This result indicates that both steels cause brittle fracture during tensile deformation, but the LP alloy is more susceptible to it than HP alloy. **Figure 6** shows macroscopic fracture surfaces of the tensile-deformed LP (a) and HP (b) alloys observed with SEM. It is found that typical intergranular fracture surface appears on the whole fracture surface in the LP alloy. On the other hand, the HP alloy exhibits the different types of fracture surface which are caused through transgranularly, although intergranular fracture surface still appears. The magnified picture of the transgranular fracture surface is shown in **Fig. 7**. It is found that ductile fracture characterized by dimples takes place. Tomota *et al.*^{14,15)} investigated the mechanism of low temperature brittle fracture in various kinds of high nitrogen austenitic steels, and reported that cleavage-like fracture is caused by slipping-off on an active slip plane with a high density of dislocations. However, such a cleavage-like fracture was not observed in this study though the typical pla-

nar dislocation arrays were observed similarly as Tomota's results (mentioned in Sec. 3.4.3). It seems that the cleavage like-fracture takes place in the case of deformation at low temperature or high strain rate.

3.3. Crystallographic Character of the Intergranularly Fractured Grain Boundary

Figure 8 represents crystallographic orientation map obtained by EBSD analysis for the cross section near the fracture surface of Fe-25Cr-1.1N-LP alloy. A pair of fractured test pieces was set together face to face to obtain the information on the crystallographic character of intergranularly fractured grain boundaries. The misorientation angle and the grain boundary character of the grain boundaries are indi-

cated for each boundary ($\Sigma 3$: twin boundary, R: random boundary). It is found that most of intergranularly fractured grain boundaries are high angle random boundaries with the misorientation more than 15 degrees. Although some straight $\Sigma 3$ boundaries (annealing twin boundaries) exist close to the fracture surface, they remain without causing intergranular fracture. However, it is also true that intergranular fracture along $\Sigma 3$ boundary takes place as shown by the yellow arrow. Considering that the boundary is curved irregularly, it is probably that the boundary is an asymmetric $\Sigma 3$ boundary which has been accidentally formed as one of austenite grain boundaries. Since such an asymmetric $\Sigma 3$ boundary is known to have high grain boundary energy,¹⁶⁾ it is not strange that such a boundary causes intergranular fracture.

From these results, it is generally suggested that the existence of high angle random grain boundaries is essential condition for the occurrence of intergranular fracture. Recently, Kokawa *et al.*^{13,17)} reported the thermomechanical treatment technique, so-called "grain boundary engineering", to increase the ratio of low energy coincident boundaries and decrease high angle random boundaries. This technique will be expected as one of effective methods for suppressing intergranular fracture.

3.4. Factors Inducing Intergranular Fracture

3.4.1. Possibility of Intergranular Fracture Promotion by Deformation-induced Martensitic Transformation

Formation of deformation-induced martensite sometimes leads to a brittle fracture especially in high strength metastable austenitic steels. For example, Shimada¹⁸⁾ investigated the fracture behavior of 18Cr stainless steel in which the microstructure is controlled to be austenite by adding 0.6 mass% of carbon, and reported that brittle intergranular fracture had occurred with the formation of deformation-induced martensite along austenite grain boundaries. He suggested that the plate-like martensite is brittle at ambient temperature and it provides nucleation sites or propagation routes of cracks. Also in the Fe-25Cr-1.1N alloys, if the deformation-induced martensitic transformation has occurred during the tensile deformation, this might be the main reason for the occurrence of brittle intergranular fracture because the martensite containing 1.1 mass% N should be very hard and brittle. However, no bcc phase was found in the orientation map of the Fig. 8 and also, as can be seen in the diffraction pattern in Fig. 9, no bcc phase was detected by the microfocus X-ray diffraction analysis

Fig. 6. SEM images showing fracture surfaces of tensile-tested Fe-25Cr-1.1N-LP (a) and Fe-25Cr-1.1N-HP (b) alloys.

Fig. 7. Magnified SEM image of fracture surface of tensile-tested Fe-25Cr-1.1N-HP alloy.

Fig. 8. Crystallographic orientation map of the cross section in Fe-25Cr-1.1N-LP alloy fractured by tensile testing. The numbers indicate the misorientation angles of grain boundaries. The symbols of $\Sigma 3$ and R denote coincident twin boundary and random boundary, respectively.

Fig. 9. X-ray diffraction patterns of tensile-tested Fe-25Cr-1.1N-LP (a) and Fe-25Cr-1.1N-HP (b) alloys obtained on the fracture surfaces.

carried out just on the fracture surface of tensile-tested Fe-25Cr-1.1N-LP alloy. Thus, it is concluded that the intergranular fracture in the Fe-25Cr-1.1N alloys is not due to the deformation-induced martensitic transformation but due to the characteristics of the grain boundary itself.

3.4.2. Effect of Grain Boundary Segregation of Impurities on the Intergranular Fracture

Since the intergranular fracture is more apparent in Fe-25Cr-1.1N-LP alloy with higher impurity content, it is expected that the grain boundary segregation of impurity atoms weakens the atomic bonding at grain boundary and results in the promotion of intergranular fracture. This idea agrees well with the result of the Fig. 8, that is, the intergranular fracture has occurred at high angle random boundaries where grain boundary segregation or adsorption tends to be easily caused compared to at coincident special boundary.¹⁹⁾ **Figure 10** shows AES spectra obtained on the intergranular fracture surface of Fe-25Cr-1.1N-LP and -HP alloys and on the transgranular fracture surface of the HP alloy. The concentrations of elements estimated by the analysis of the spectra are listed in **Table 2**. In the Fe-25Cr-1.1N-LP alloy, the concentrations of P and S at intergranular fracture surface reach 2–3 at% and 1–2 at%, respectively. These concentrations of impurities at grain boundary are two orders of magnitude higher than the average one, and this means that marked grain boundary segregation occurred during solution nitriding. On the other hand, in the HP alloy, the impurity concentration is less than the detection limit of the analysis for both intergranular and transgranular fracture surface. In the LP alloy prepared in this study, the long-time holding at high temperature during solution nitriding have inevitably caused the marked grain boundary segregation of impurities, and thus, the intergranular fracture must have occurred more easily compared with conventional high nitrogen austenitic steels produced through the high-pressurized melting. However, the intergranular fracture was not completely suppressed even in the HP alloy with extra low impurity content. Therefore, not only the weakening of grain boundary by the segregation of impurities but also another factor such as a marked stress concentration at grain boundary should be also considered to understand the phenomenon of intergranular fracture in solution-nitrided nickel-free austenitic

Fig. 10. AES spectra obtained on intergranular fracture surface of Fe-25Cr-1.1N-LP (a) and -HP (b) alloys and on transgranular fracture surface of the HP alloy (c).

Table 2. Concentration of elements (at%) estimated from AES spectra shown in Fig. 10. The estimation was carried out two times for each fracture surface.

	Fe	Cr	P	S	N	C	O
Fe-25Cr-1.1N-LP Intergranular	62	28	2	1	7	—	—
	59	29	3	2	7	—	—
Fe-25Cr-1.1N-HP Intergranular	59	30	—	tr	11	—	—
	65	27	—	tr	8	—	—
Fe-25Cr-1.1N-HP Transgranular	67	27	—	—	6	—	—
	66	27	—	—	7	—	—

tr: <1%, —: undetected

steel.

3.4.3. Stress Concentration at Grain Boundary by Piled-up Dislocations in Planar Array

The formation of planar dislocation arrays, one of characteristic structures of high nitrogen austenitic steels,^{14,15)} seems to be also related with the occurrence of intergranular fracture in the Fe-25Cr-1.1N alloys. **Figure 11** is a schematic illustration showing the difference in dislocation structure developed during tensile deformation in conventional steel (a) and high nitrogen austenitic steel (b). In the conventional polycrystalline steel, different slip systems work simultaneously and cross-slip also occurs easily during deformation when the stacking fault energy is not too low, and this leads to a cell-type dislocation arrangement. Since the formation of dislocation cells is a kind of relaxation process of internal stress caused by dislocation pile-up, this reduces the work hardening of the material during tensile deformation. However, it is known that polycrys-

talline austenitic stainless steel tends to form planar dislocation arrays with increasing nitrogen concentration through the significant reduction of the ability to cross-slip. As a result, work hardening is markedly enhanced through slip band formation and deformation twinning in certain cases.²⁰⁾ The planarly piled-up dislocations should cause a marked stress concentration at grain boundary because of the lack of stress relaxation process. **Figure 12** represents a transmission electron micrograph showing the dislocation structure developed near a grain boundary in Fe-25Cr-1.1N-HP alloy tensile-deformed to the yielding point. It is confirmed that planar dislocation arrays are formed within the austenite grain and the dislocations are piled-up at the grain boundary. Due to the marked stress concentration caused by the piled-up dislocations, another slip system is activated from the grain boundary to the adjacent grain, as shown by the arrows. Although the introduction of another slip system is one of the stress relaxation processes at grain boundary, the stress concentration caused by the piled-up dislocations could not be sufficiently relaxed in the material because of the reduced ability of cross-slip. Consequently, the stress concentration at grain boundary should be gradually enlarged with increasing strain, and finally, reaches a critical value to cause intergranular fracture.

It should be considered here that the grain size is so large that the stress concentration at grain boundary must be magnified in the solution-nitrided steel compared to the other materials with normal grain size of several tens microns. In the engineering point of view, some method to refine the grain size has to be applied to solution-nitrided steels for obtaining sufficient ductility and deformability.

Fig. 11. Schematic illustration showing dislocation structure development in conventional steel and high nitrogen austenitic steel.

Fig. 12. TEM image showing dislocation structure developed at or around a grain boundary in Fe-25Cr-1.1N-HP alloy tensile-deformed to its yield point.

For example, authors have proposed some methods for grain refinement of solution-nitrided steels by using nitride precipitation²¹⁾ and two-step phase transformation.²²⁾ The effect of grain refinement on the tensile deformation behavior is a next subject to be investigated for further improvement of the mechanical properties in high nitrogen nickel-free austenitic steels.

4. Conclusions

(1) The high nitrogen nickel-free austenitic stainless steel, Fe-25mass%Cr-1.1mass%N alloy produced by solution nitriding, causes intergranular fracture during tensile deformation at ambient temperature after the uniform elongation of several tens percent.

(2) The intergranularly fractured grain boundary is characterized by high angle random boundary.

(3) The intergranular fracture is promoted by grain boundary segregation of impurities such as phosphorus and sulfur. However, even in the high purity alloy with extra-low phosphorus and sulfur contents, the intergranular fracture is not completely suppressed because of the intrinsically-weak grain boundary of this steel.

(4) The stress concentration at grain boundary caused by the piled-up dislocations in planar array seems to be one of the important factors inducing intergranular fracture. To improve the ductility and deformability of the solution-nitrided steel, grain refinement would be required to reduce the stress concentration at grain boundary.

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