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Low Temperature Tensile Properties of High Temperature Gas-nitrided Duplex Stainless Steel

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Abstract This investigation was focused on the low temperature tensile properties, phase change, changes in nitrogen content and corrosion resistance in the 22Cr-5Ni-3Mo duplex stainless steel after high temperature gas nitriding and solution annealing (HTGN-SA). From the HTGN-SA treatment, the duplex (ferrite + austenite) phase changed into austenite single phase. The nitrogen content of austenite single-phase steel showed a value of ~0.54%. For the HTGN-SA treated austenitic steel, tensile strength increased with lowering test temperature, on the other hand elongation showed the maximum value of 28.2% at -100^{o}C. The strain-induced martensitic transformation gave rise to lead the maximum elongation. After HTGN-SA treatment, corrosion resistance of the austenite single-phase steel increased remarkably compared with HTGN- treated steel.

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Key words : *HTGN treatment, duplex stainless steel, low temperature tensile test, strain-induced martensite*

1. Introduction

Generally, duplex stainless steels (DSS) have been used as oil pipeline and sea water pump in deep sea due to good corrosion resistance and high tensile strength. They are also applied for severe environment, like pole area, thus this steels have been continuously developed [1, 2]. And also it is true that DSS has lower workability than ferritic and austenitic single phase stainless steels. However, according to addition of nitrogen, the microstructure of DSS may be changed from duplex to austenite single phase due to a strong austenite forming effect of nitrogen. Therefore the workability will be increased [3].

Recently, high temperature gas nitriding (HTGN) was introduced as a method for adding nitrogen to the surface of stainless steels. This method involves a diffusion process for nitrogen to permeate the surface of stainless steels through heat treatment in an atmosphere containing nitrogen gas at high temperature [3~6]. When nitrogen, a strong austenite forming element, permeate from the surface into the interior of stainless steels, the surface microstructure changes into austenite depending on the amount of permeated nitrogen and the process temperature. As a result, HTGN treatment increases the corrosion resistance and mechanical properties [3, 7].

This study aimed to understand the characteristics of HTGN treatment and the effect of mechanical properties at low temperature in DSS steel after changing the microstructure from ferrite plus austenite (duplex) to austenite single phase. The investigation was focused on the phase changes from duplex phase to austenitic single phase and low temperature mechanical properties.

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Table 1. Chemical composition of the 2205 duplex stainless steel (wt. %)

Specimen	C	Si	Mn	P	S	Cr	Ni	Mo	N	Fe
Duplex 2205	0.030	0.397	1.49	0.018	0.013	22.07	5.77	3.16	0.267	Bal.

2. Experimental Procedure

The steel used in this investigation was cold rolled plate of 22Cr-5Ni-3Mo duplex stainless steel (DSS). Table 1 shows the chemical composition of the steel. The plate was machined to dimensions of 20 mm × 100 mm × 1.5 mm. Specimens for tensile testing were machined in accordance with ASTM-8 standard, paralleled to the rolling direction. After grinding with emery paper, the steel was HTGN-treated in a pressure changeable furnace in a gaseous atmosphere containing 1 kg/cm^2 nitrogen at 1200°C for 3 hrs, followed by water quenched. Subsequently, solution annealing (SA) was introduced at 1150°C for 3 hrs in flowing Ar gas.

Optical microscope (OM) was used to observe the phase transforming from duplex to austenitic. The phase formed after HTGN treatment was identified by an X-ray diffractometer (XRD) using Cu-Ká radiation. Micro-Vickers hardness was measured under a load of 300 g from the surface to the interior. The changes in nitrogen content were analyzed at the perpendicular cross-section of the steel from the surface to a depth of 50 μm using a Glow Discharge Spectrometer (GDA). Tensile test was carried for the steel of austenite single phase with the cross head speed of 1mm/min. The test temperature was adjusted to −196°C, −100°C, −50°C, −25°C, 0°C and 25°C by using liquid nitrogen, alcohol and ice water. The corrosion resistance of the HTGN and HTGN-SA treated steel was evaluated using a potentiodynamic polarization method in an aqueous solution of 1 N H_2SO_4.

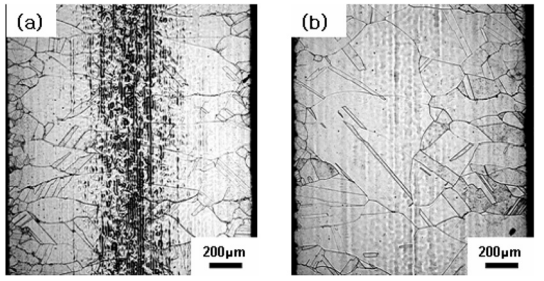


Fig. 1. Optical micrographs of duplex stainless steels. (× 50).
(a) HTGN treatment at 1200°C for 3 hrs
(b) SA treatment at 1150°C for 3hrs after HTGN treatment.

3. Result and Discussion

The microstructure of DSS after HTGN treatment at 1200°C for 3 hrs and followed by SA treatment at 1150°C for 3 hrs (HTGN-SA) is shown in Fig. 1. Large austenite grains appeared after HTGN treatment, and duplex microstructure (ferrite + austenite) was shown in the center region (Fig. 1(a)). However, after HTGN-SA treatment, austenite single phase appeared without ferrite phase (Fig. 1(b)). In this figure, the small austenite grains were observed at the near surface.

Fig. 2 shows pseudo-phase diagram of 2205 (22Cr-5Ni-3Mo) DSS [8]. This diagram shows the phase change with increasing nitrogen content. The nitrogen content of austenite single phase region at 1150°C (SA treatment temperature) appeared the values between ~0.41%N and ~0.69 %N.

Fig. 3. shows the variation of nitrogen content with depth below the surface after HTGN-SA treatment. For HTGN-treated steel without SA treatment, the nitrogen content showed the high value at near surface, however the content

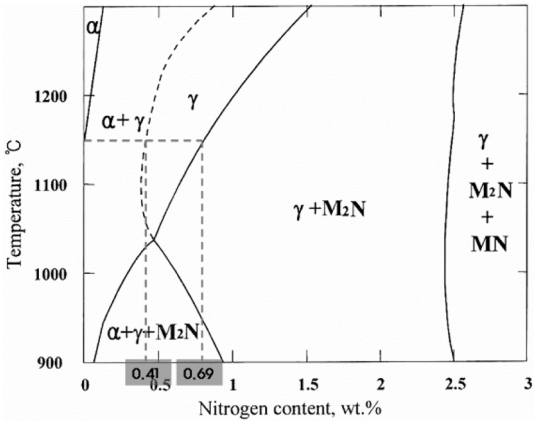


Fig. 2. Phase stability diagram of 22%Cr-5%Ni-3%Mo duplex stainless steels with temperature and nitrogen content showing the austenite domains at 1150°C[8].

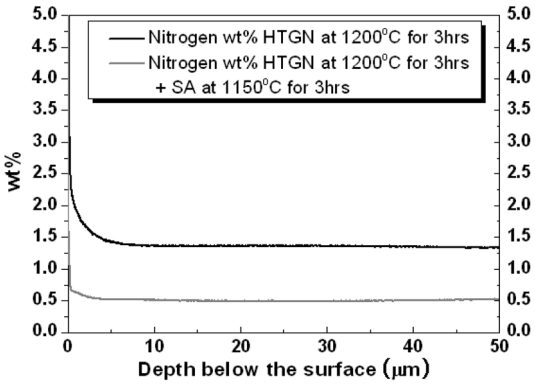


Fig. 3. Changes in nitrogen content of duplex steel with depth below the surface after HTGN and HTGN-SA treatment.

nearly unchanged with the value of ~1.34% from 7 μm to 50 μm. After HTGN-SA treatment, the highest value of 0.8%N was shown at the outmost surface, and the content dropped steeply down to 3 μm from the surface. Above 3 μm from the surface, the content showed nearly constant value of 0.54% with increasing depth below the surface. Thus, after HTGN-SA treatment, the austenite single phase was formed except the near surface.

Fig. 4 shows hardness variation with depth below the surface after HTGN and HTGN-SA treatment. Hardness of HTGN-treated steel

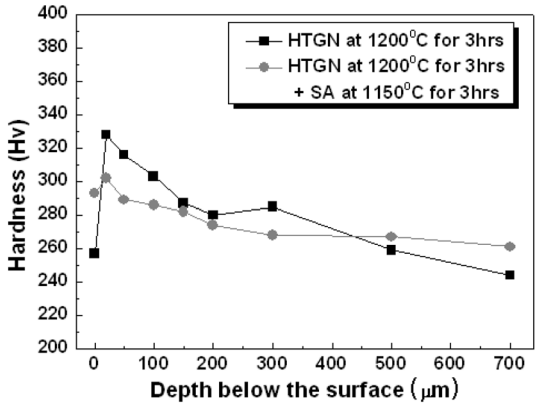
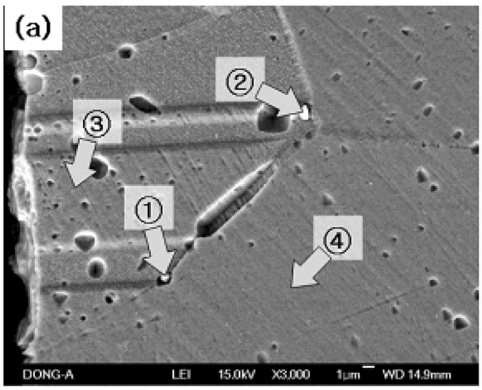


Fig. 4. Hardness as a function of depth below the surface after HTGN and HTGN-SA treatment.

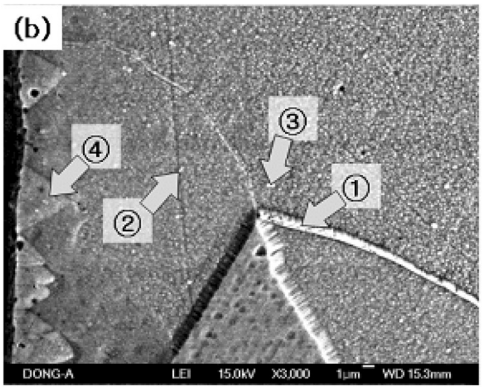
appeared as 304 Hv and 250 Hv at the surface and the interior respectively. After HTGN-SA treatment, hardness appeared 285 Hv and 232 Hv at the surface and the interior, individually. That is, the hardness decreased at the near surface and increased in the interior region after HTGN-SA treatment. Although the hardness of HTGN-SA treated steel at the near surface was still higher than that of HTGN-treated steel, the hardness was flattened by the diffusion of nitrogen from the surface to the interior. This high hardness at the surface region may be caused from the relatively fine grain size and fine undissolved precipitate.

Fig. 5 shows SEM micrograph and EDX analysis results of the surface region after HTGN and HTGN-SA treatment. For HTGN-treated steel, fine precipitates were observed, which are considered precipitates as chromium nitride and carbo-nitride for HTGN-treated steel. After HTGN-SA treatment, very fine precipitates appeared in the matrix of austenite. However, it is not clear that this precipitate is chromium nitride or not. Also, at the surface region, small austenite grains that were not coarsened by HTGN-SA treatment were shown, probably the segregation of nitrogen at the grain boundaries inhibited the grain growth.



(wt%)

	Fe	N	C	Cr	Mn	Ni	Mo
①	28.69	18.26	-	41.25	6.30	1.77	3.72
②	24.16	13.24	4.69	50.61	0.97	1.27	-
③	63.15	1.77	2.83	20.98	1.23	5.94	3.51
④	65.45	1.13	-	22.88	1.61	5.10	3.83



(wt%)

	Fe	N	O	Cr	Mn	Ni	Mo
①	63.64	0.67	-	21.99	1.55	5.49	4.12
②	66.06	2.89	-	21.80	1.26	5.13	2.52
③	64.00	0.66	-	22.90	1.44	6.15	4.27
④	66.66	-	2.76	20.99	1.74	5.30	2.09

Fig. 5. SEM micrograph and EDX analysis results of duplex stainless steel.
(a) HTGN-treated steel (b) HTGN-SA treated steel

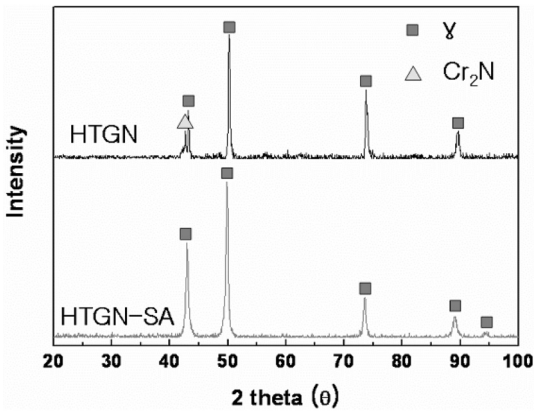


Fig. 6. X-ray diffraction patterns after HTGN and HTGN-SA treatments.

Fig. 6 shows X-ray diffraction patterns of HTGN and HTGN-SA treated steels. For HTGN-treated steel, weak Cr_2N peak was detected in the matrix of austenite (γ). However, austenite peak were observed for HTGN-SA treated steel. That is, the precipitates appeared in Fig. 5(a) was Cr_2N and the most of precipitates was dissolved by HTGN-SA treatment.

Generally, when metastable austenite phase deformed at low temperature, the deformation induced plasticity of austenite developed continuously. Consequently, the tensile strength and elongation have increased due to the deformation induced martensite[9].

Fig. 7 shows the relation between tensile properties and test temperature. The results showed the increase of tensile strength with lowering test temperature. Value of elongation showed the maximum of 28.2% at −100°C. This maximum elongation was found to the austenitic and duplex stainless steels [9]. The maximum elongation is related with transformation induced

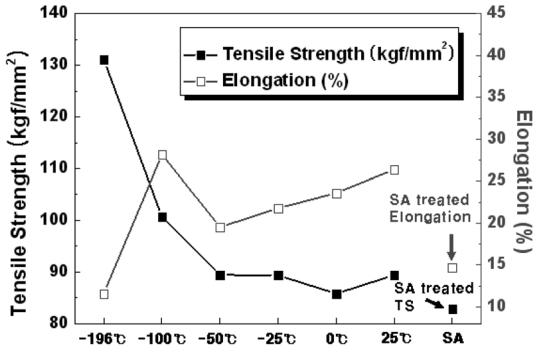
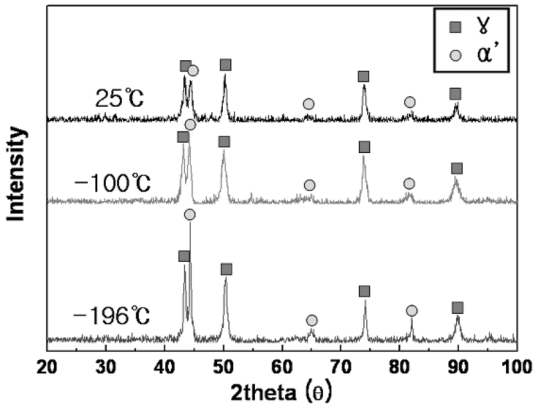


Fig. 7. Tensile strength and elongation as a function of test temperature for HTGN-SA treated steel.

plasticity, that is, transformation of austenite to martensite by plastic deformation (deformation-induced martensite). It has been known that the deformation -induced martensite at the hardened neck region is prohibited further necking during tensile test, thus the progressive propagation of deformation -induced martensite through tensile specimen increases elongation [9].

In this Figure, the strength and the elongation increased and decreased, respectively, with increasing test temperature. Generally, the reason to increase the strength and to decrease the elongation at low temperature is that the deformation-induced martensite controls the strength and the elongation. And the reason to decrease the strength and the elongation at high temperature is that the most plastic deformation induces by slip due to the high stability of austenite and also the quantity of induced-martensite is small. Thus, during tensile testing, austenite couldn't overcome initial necking at high temperature [10, 11].

Fig. 8 shows X-ray diffraction patterns after tensile testing the HTGN-SA treated steel. With test temperature getting lower, the intensity of α' (martensite) peaks increased. Reports on the low temperature tensile strength of metastable austenitic steel said that the phase transformation by plastic deformation induced in sequence of



2Θ / Temp(℃)	43	44 (α')	50	65 (α')	74	82 (α')	90
25℃ (Intensity)	96	86	99	13	76	20	40
-100℃ (Intensity)	79	114	110	18	99	20	49
-196℃ (Intensity)	161	250	136	28	87	51	57

Fig. 8. X-ray diffraction patterns after low temperature and room temperature tensile testing the HTGN-SA treated steel.

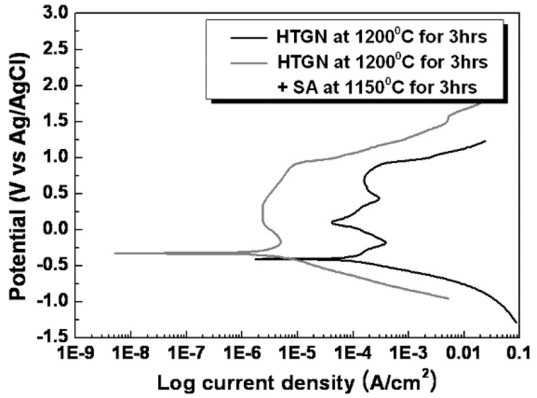


Fig. 9. Potentiodynamic polarization curves of HTGN and HTGN-SA treated steels.

γ → ε-martensite → α'-martensite [12, 13]. That is, α'-martensite was changed from å-martensite [9]. However, in this experiment, the peak of ε-martensite did not detect, and thus direct transformation of γ → α' was shown.

Fig. 9 shows potentiodynamic polarization curves of HTGN and HTGN-SA treated steels. Considering the passivity behavior, the corrosion resistance increased by HTGN-SA treatment. It is

supposed that SA treatment decreased the density of precipitate, and consequently increased the corrosion resistance.

4. Conclusions

After HTGN-SA treatment of the 22Cr-5Ni-3Mo duplex stainless steel, the low temperature tensile properties, phase change, changes in nitrogen content and corrosion resistance were experimentally investigated. The following conclusions were made.

1. The HTGN treatment of duplex stainless steel changed the surface microstructure to austenite single phase, however the interior region remained ferrite plus austenite phase. After HTGN-SA treatment, the microstructure appeared to austenite single phase through all thickness of the specimen. However, the fine grains were observed at the surface region.

2. Although the nitrogen content showed the constant value of 0.53% through the thickness of the specimen after HTGN-SA treatment, hardness decreased gradually with depth due to the relatively fine grain size and un-dissolved precipitate at the surface region.

3. Tensile strength increased with lowering test temperature, on the other hand elongation showed the maximum value of 28.2% at -100^{o}C. The deformation- induced martensitic transformation gave rise to lead the maximum elongation

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