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Nitrogen Permeation Treatment of Duplex and Austenitic Stainless Steels

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Abstract The 22%Cr-5%Ni-3%Mo duplex and 18%Cr-8%Ni austenitic stainless steels have been nitrogen permeated under the 1 Kg/cm^2 nitrogen gas atmosphere at the temperature range of 1050°C~1150°C. The nitrogen-permeated duplex and austenitic stainless steels showed the gradual decrease in hardness with increasing depth below surface. The duplex stainless steel showed nitrogen pearlite at the outmost surface and austenite single phase in the center after nitrogen permeation treatment, while the obvious microstructural change was not observed for the nitrogen-permeated austenitic stainless steel. After solution annealing the nitrogen-permeated stainless steels(NPSA treatment) at 1200°C for 10 hours, the hardness of the duplex and austenitic stainless steels was constant through the 2 mm thickness of the specimen, and the $\alpha+\gamma$ phase of duplex stainless steel changed to austenite single phase. Tensile strengths and elongations of the NPSA-treated duplex stainless steel remarkably increased compared to those of solution annealed (SA) duplex stainless steel due to the solution strengthening effect of nitrogen and the phase change from a mixture of ferrite and austenite to austenite single phase, while the NP-treated austenitic stainless steel displayed the lowest value in elongation due to inhomogeneous deformation by the hardness difference between surface and interior.

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***Key words**: Nitrogen Permeation Treatment, Solution Nitriding, Duplex Stainless Steel, Austenitic Stainless Steel, Nitrogen Pearlite, Phase Change, Tensile Property, Hardness*

1. Introduction

It has been known that nitrogen greatly increases the corrosion resistance and mechanical properties of stainless steel[1~4]. Thus many researches on nitrogen-alloyed stainless steel have been mainly focused on the effect of nitrogen addition on corrosion and mechanical properties.

The method of nitrogen addition in stainless steel has been divided into two main production routes, pressure metallurgy and powder metallurgy[2]. Recently, solution nitriding is also introduced to the addition method of nitrogen in stainless steel[3, 5~7]. This new nitrogen addition method is to heat treating the stainless steel in the nitrogen atmosphere at the temperature ranges between 1050°C and 1150°C. The solution nitriding treatment changes the microstructure and phase near the surface of stainless steels, which results in the improvement of mechanical properties and corrosion resistance. Thus, the solution nitriding treated duplex and austenitic stainless steels are expected to use in the corrosive environments such as pumps in the corrosive fluid, pipelines in the oil well and chemical containers[8].

It has been generally known that the phase near the surface of solution nitriding treated duplex($\alpha+\gamma$) stainless steel has been austenite due to the presence of nitrogen which is strong austenite-forming element, while the phase of solution nitriding treated austenitic stainless steel has remained in austenitic phase without phase change[3,7]. However, when the permeated nitrogen content is over the equilibrium solubility limit, nitrides are precipitated, and thus the microstructure can be changed to austenite or a mixture of ferrite(martensite) and nitrides. Therefore, the process accompanying the formation of nitrides is also expected to affect the microstructure and the mechanical properties of alloys, but a few studies have been performed to investigate the effect of solution nitriding in terms of hardness and tensile properties.

The objectives of the study are to investigate the surface phase changes, nitride precipitation, hardness and tensile properties of duplex and austenitic stainless steels after nitrogen permeation heat treatment at the temperatures range of 1050~1150°C.

2. Materials and Experimental Procedure

The duplex stainless steel was melted by a vacuum induction-melting furnace. The ingot (20 kg) was hot rolled to 12 mm thick plate and cold rolled to 2 mm thickness. The commercial austenitic stainless steel of AISI 304 type was also cold rolled to plates having 2 mm thickness. Table 1 shows chemical composition of the two stainless steels.

The two kinds of stainless steel was grinded to #1500 with emery paper and heat treated in the 1 kg/cm^2 nitrogen gas atmosphere at temperatures range from 1050°C to 1150°C for 10 hours (NP treatment) using a pressure changeable furnace and subsequently quenched in water. To investigate the effect of nitrogen addition on hardness and tensile properties, some of the nitrogen-permeated specimens were solution annealed at 1200°C for 5 hours (NPSA treatment), and the cold rolled specimens without nitrogen permeation treatment were solution annealed at 1200°C for 5 hours(SA treatment).

The phase change and precipitates of nitrogen-permeated specimens were investigated using optical microscopy, SEM(scanning electron microscopy)/EDX (energy-dispersive x-ray spectrometer) and EPMA (electron prove x-ray microanalysis), and hardness variations were measured by a microvickers hardness tester(200 g load). The tensile specimens having 2 mm thickness and gauge length of 50 mm were prepared for the NP-treated, NPSA-treated and SA-treated specimens. Tensile properties were investigated by Instron type tensile testing machine with a crosshead speed of 1 mm/min.

3. Results and Discussion

3.1. Microstructual Changes after Nitrogen Permeation Treatment

Fig. 1 shows optical micrographs of the duplex stainless steel after nitrogen permeation treatment for 10 hours. The strong nitride-forming element, chromium, facilitates permeating the nitrogen into austenite, leading to the phase changes from duplex ($\alpha+\gamma$) phase to nitrogen pearlite like lamella precipitate at the outmost surface[6]. Also it was observed to be the presences of the austenite single phase in the middle region and a mixture of austenite and ferrite(duplex) in right side. The austenitic phase formed in the center was the widest at 1150°C as shown in Fig. 1. The fact indicates that nitrogen, austenite-forming element, the most deeply penetrates into the surface at 1150°C. To investigate the nitrogen pearlite formed near surface, EDX analysis was performed as shown in Fig. 2. The precipitates show the higher Cr peaks and lower Fe peaks ((a) and (b)) than those observed on matrix ((c)). On considering the EDX-spectra and phase diagram in Fig. 3, it is supposed that the precipitates are Cr_2N. It is interesting to note that the permeation depth of

Table 1. Chemical composion of stainless steels. (wt.%)

Specimens	C	Si	Mn	P	S	Cr	Ni	Mo	N	Fe
Austenitic Stainless steel	0.04	0.45	1.04	0.023	0.002	18.38	8.2	-	-	Bal
Duplex Stainless steel	0.03	0.08	0.24	0.02	-	21.53	7.52	2.96	0.03	Bal

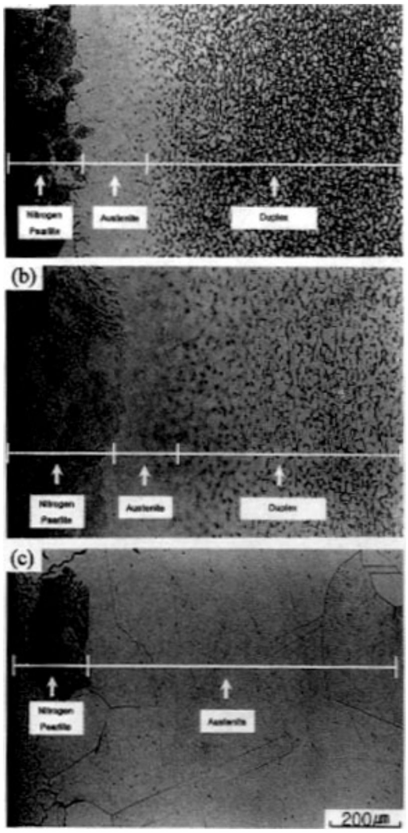

Fig. 1. Optical micrographs showing the cross-sectional microstucture of duplex stainless steel after heat treating for 10 hrs in the 1kg/cm^2 nitrogen atmosphere:(a) 1050°C, (b) 1100°C and (c) 1150°C

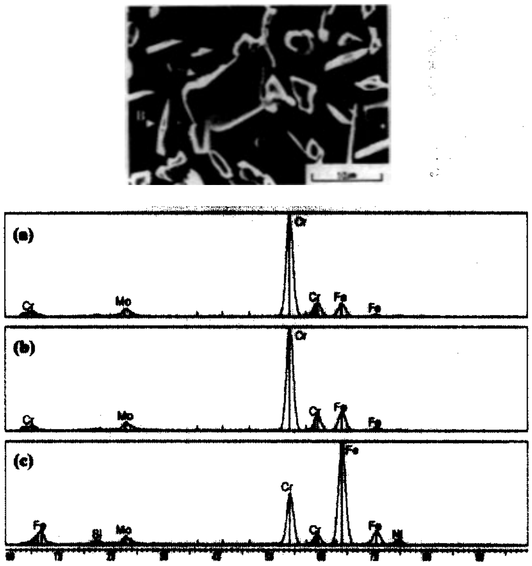

Fig. 2. DEX analysis for precipitates and γ phase formed near the surface of the duplex stainless steel after heat treating for 10 hrs in the 1kg/cm^2 nitrogen gas atmosphere:(a) blocky precipitate, (b) needle like precipitate and (c) γ phase.

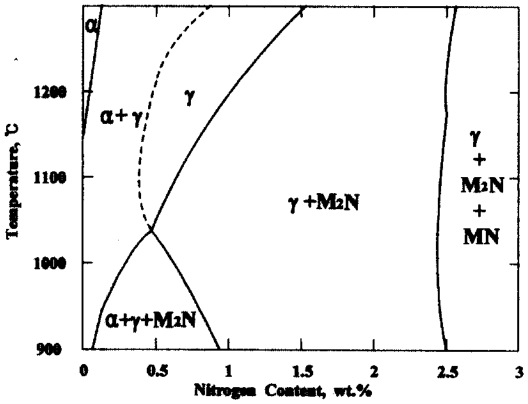

Fig. 3. Phase stability diagram with temperature and nitrogen content on the austenite domains of 22% Cr-5%Ni-3%Mo duplex stainless steels.[6]

nitrogen pearlite is the deepest at 1100 °C as shown in Fig. 1. This fact can be deduced from the Fig. 3, pseudo-phase diagram[6] of 22% Cr-5%Ni-3%Mo which is the similar chemical composition as the duplex stainless steel used in this study. To facilitate the formation of the nitrogen pearlite near the surface, the amount of nitrogen needed to form Cr_2N must be small, and the diffusion rate of nitrogen must be high. Fig. 3 shows the relation between temperature and nitrogen content needed to form M_2N [6]. Nitrogen content needed to form M_2N is approximately 0.5%N at 1050°C and 0.8% at 1150°C, implying that the formation of M_2N at 1150°C is more difficult. However, the diffusion rate of nitrogen at 1150°C is higher than that at 1050°C. Accordingly, the formation of nitrogen perarlite may be facilitated at 1100°C between 1050 and 1150°C .

The optical micrographs of austenitic stainless steel after heat treatment in the 1 kg/cm^2 nitrogen gas atmosphere for 10 hours are shown in Fig. 4. The microstructural changes and any precipitates

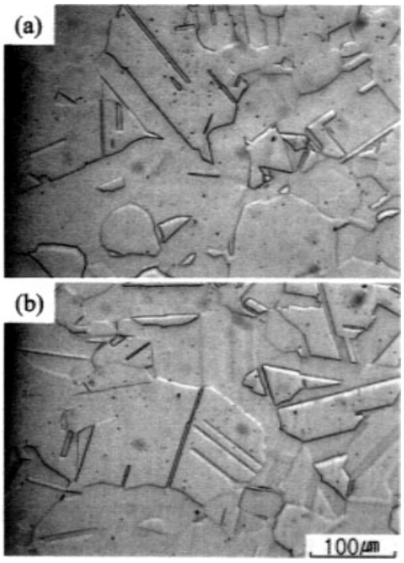

Fig. 4. Optical micrographs showing the cross-sectional microstructure of austenitic stainless steel after heat treating for 10 hrs in the 1kg/cm^2 nitrogen gas atmosphere: (a) 1100°C and (b) 1150°C.

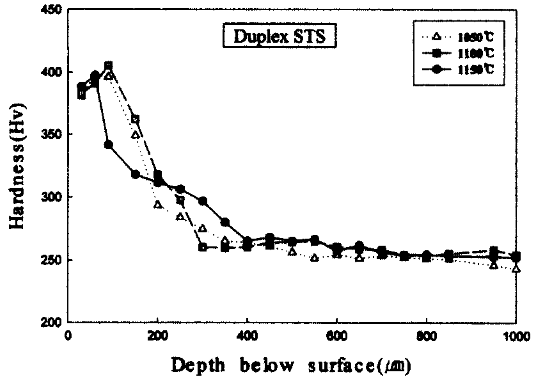

Fig. 5. Variation of hardness with depth below the surface after nitrogen permeation treatment of duplex stainless steel.

were not observed.

3.2 Effect of Nitrogen Permeation and Solution Annealing in Microstructure and Hardness.

Fig. 5 shows the hardness variation of the NP-treated duplex stainless steel with depth below surface at three temperatures. The hardness is the highest at the outmost surface, steeply decrease to ~400 μm, and nearly constant or slowly decrease over ~400 μm. To obtain constant nitrogen content through the 2mm thickness of duplex and austenitic stainless steels, the NP-treated specimens were solution annealed at 1200°C for 5 hours and quenched in water, which were designated by NPSA-treated specimen. The microstructural changes of NPSA-treated duplex stainless steel with temperature are shown in Fig. 6. The nitrogen pearlite existed near the surface disappears, and austenite single phase with some precipitates along grain boundaries and

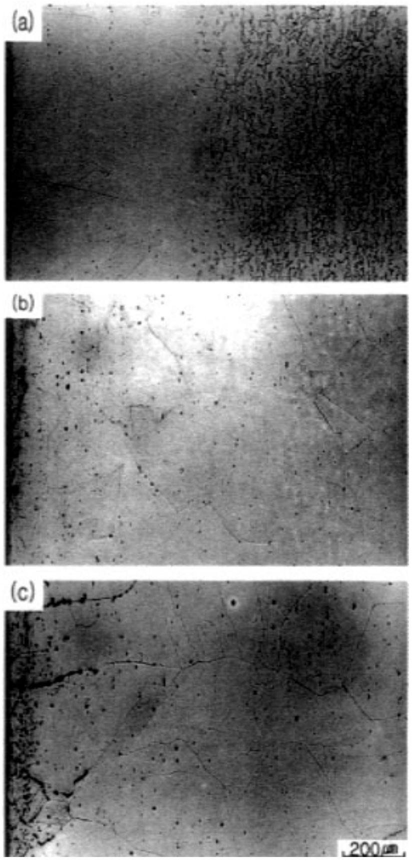

Fig. 6. Optical micrographs showing the cross-sectional micrographs of the solution-annealed duplex stainless steel at 1200°C for 5 hrs after nitrogen permeation treatment at various temperature: (a) 1050°C, (b) 1100°C and (c) 1150°C

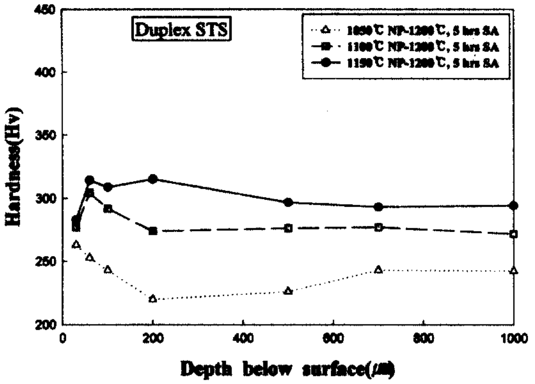

Fig. 7. Variation of hardness with depth below the surface of solution-annealed duplex stainless steel at 1200°C for 5 hrs after nitrogen permeation treatment.

in interiors is observed as shown in Fig. 6(b) and (c). However the duplex microstructure composed of ferrite and austenite is still existed in the right region of the NPSA-treated specimen at 1050°C as shown in Fig. 6(a). The duplex stainless steels treated by the NPSA exhibits relatively constant hardness through the specimens(Fig. 7) compared to the duplex stainless treated by the NP(Fig. 5). To investigate the effects of NP and NPSA treatments in hardness, the content of nitrogen and chromium was analyzed using a EPMA in the NP- and NPSA-treated duplex stainless steels as shown in Fig. 8. In the case of the duplex stainless steel treated by the NP, the higher hardness was observed near the surface where the higher nitrogen and chromium contents was detect-ed as shown Fig. 8(a). On the other hand, the duplex stainless steel treated by the NPSA exhibits nearly constant hardness through the specimen where the nitrogen and chromium contents are constant as shown in Fig. 8(b). The fact indicates that the higher hardness near the outmost surface of the duplex stainless steel treated by the NP is mainly caused by the formation of nitrogen pearlite. The hardness variation in austenitic stainless steel is shown in Fig. 9. The hardness observed at three temperatures gradually decreases with increasing

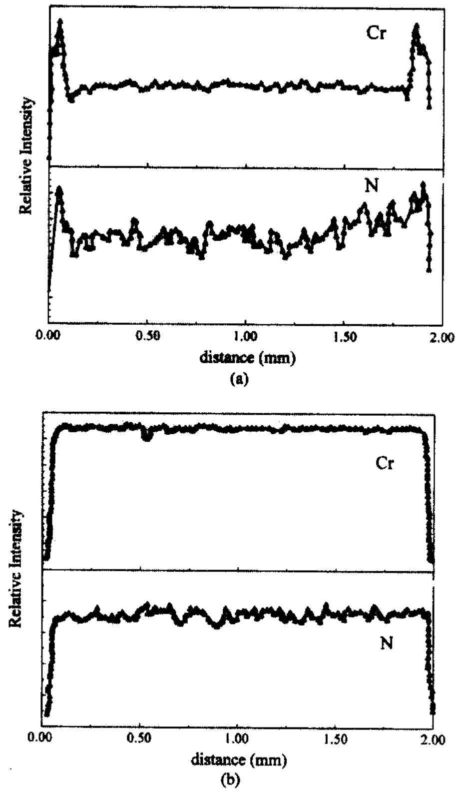

Fig. 8. EPAM analyses for chromium and nitrogen in the (a) NP-and (b) NPSA-treated duplex stainless steels.

depth below surface, and the NP-treated specimen at 1150°C displayed the highest hardness. Since the NP treatment in the austenitic stainless steel did not cause any obvious microstructural change which may affect the hardness of the austenitic stainless steel, the change of hardness in the austenitic stainless steel seems to be closely related to the amount of nitrogen permeated during the NP treatment. Accordingly, the hardness display the highest value at 1150°C. The hardness difference between surface and interior in the duplex stainless steel is greater than that in the austenitic stainless steel. This is considered to be cause by the nitrogen pearlite formed near the surface of the duplex stainless steel as already mentioned above.

Comparing with the NP-treated austenitic stainless steel, the microstructures of the NPSA-treated aus-

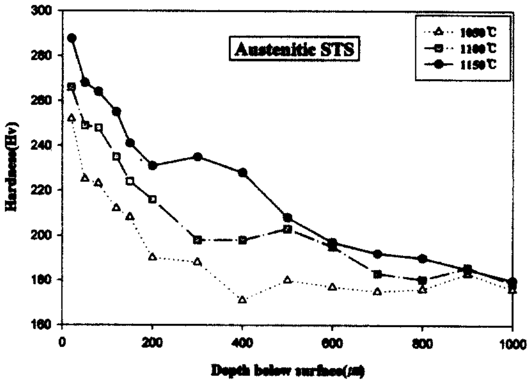

Fig. 9. Variation of hardness with depth below the surface after nitrogen permeation treatment of austenitic stainless steel.

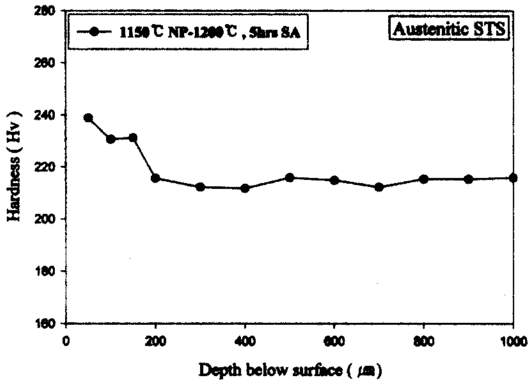

Fig. 10. Variation of hardness with depth below the surface of solution-annealed austenitic stainless steel at 1200°C for 5 hrs after nitrogen permeation treatment.

tenitic stainless steel were nearly unchanged except grain coarsening is observed. However, the trend of the change of hardness with depth at 1150 °C was different as shown in Fig. 9 and Fig. 10. This is attributed to the distribution of nitrogen. In other words, during the solution annealing, the nitrogen existed near the surface of the austenitic stainless steel is uniformly distributed through the specimen, which cause nearly constant hardness for the NPSA-treated specimen.

3.3 Effect of Nitrogen Permeation in Tensile Strength and Elongation

Fig. 11 shows the changes of tensile properties

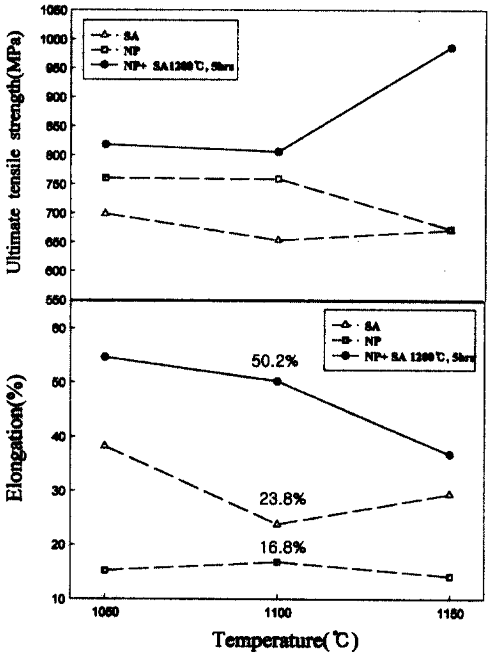

Fig. 11. Tensile properties of SA-, NP- and NPSA-treated duplex stainless steel at the temperature range of 1050~1150°C

with temperatures in the duplex stainless steel. The specimen which was treated by the NPSA displays the highest values in tensile strength and in elongation, while the SA-treated and NP-treated specimens represent the lowest values in ultimate tensile strength and in elongation. The improvement in ultimate tensile strength of the specimens treated by NP or NPSA is caused by the solution strengthening effect. Nitrogen permeated into the surface of the duplex stainless steel is expected to strengthen it due to the solution strengthening effect, resulting in an increase of ultimate tensile strength. In Fig. 11, it is interesting to note that the NPSA-treated specimen shows the highest elongation, while the NP treated specimen show the lowest elongation. The lower elongation observed in the NP-treated specimen is considered to be caused by big hardness difference between the surface and interior due to the formation of nitrogen pearlite at the outmost surface. Also, phase change

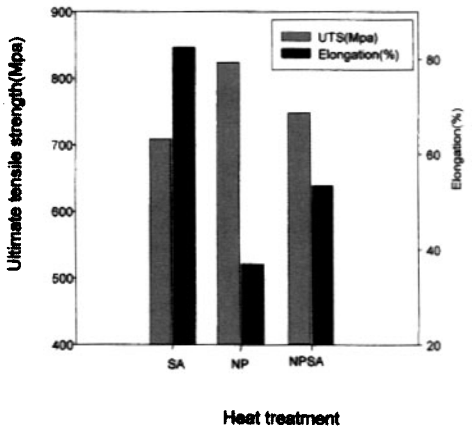

Fig. 12. Tensile properties of SA-, NP- and NPSA-treated austenitic stainless steel at 1150°C

due to the permeation of nitrogen may affect the elongation. The specimen treated by the NPSA was found to mainly form austenic single phase as shown in Fig. 6. The γ single phase relatively displays uniform deformation, which leads to an increase of the elongation. Although the NPSA-treated specimen at 1050°C shows the α+γ phases in the interiors as shown in Fig. 6(a), a decrease of ferrite phase(black area) in NPSA-treated specimen compared to NP treated specimen(Fig. 1(a)) cause an increase of the elongation.

The remarkable increase of the elongation in the NPSA-treated specimen compared to SA-treated specimen results from the fact that the α+γ duplex microstructure changes to γ single phase. The difference in deformation mode between α and γ phase[10,11] causes a decrease of the elongation in the SA-treated specimen, but the γ single phase in the NPSA-trated specimen relatively displays uniform deformation, which leads to an increase of the elongation.

Fig. 12 shows the tensile properties of the austenitic stainless steels. The SA-treated specimen shows the lowest tensile strength and the highest elongation, while the NP- or NPSA-treated specimens shows an increase in the tensile strengths and a decrease in the elongation compared to SA-treated specimen. An increase of tensile strength in NP- or NPSA-treated austenitic stainless steels is attributed to solid solution strengthening effect by nitrogen dissolved into austenitic stainless steel. In Fig. 12, the NP-treated specimen represents the lowest elongation. This is considered to be caused by inhomogeneous deformation due to the hardness difference between surface and interior. Thus the specimen treated by the NPSA displays the higher elongation compared to that treated by the NP due to uniform hardness through the specimen.

4. Conclusions

The 22%Cr-5%Ni-3%Mo duplex and 18%Cr-8%Ni austenitic stainless steels have been nitrogen permeated under the 1 Kg/cm^2 nitrogen atmosphere at the temperature between 1050°C and 1150°C. The obtained results are summarized as follows:

1. The nitrogen-permeated austenitic and duplex stainless steels show the gradual decrease in hardness with increasing depth below surface. The duplex stainless steel shows nitrogen pearlite at the outmost surface and austenite single phase in the middle after nitrogen permeation treatment, while the obvious microstructural change is not observed for the nitrogen permeated austenitic stainless steel.

2. After solution annealing the nitrogen-permeated stainless steels at 1200°C for 10 hours, the hardness of the duplex and austenitic stainless steels is constant through the 2mm thickness of the specimen, and the α+γ phase of duplex stainless steel changes to austenite single phase.

3. Tensile strengths and elongations of the NPSA-treated duplex stainless steel remarkably increase compared to those of solution annealed duplex stainless steel due to phase change from a mixture of ferrite and austenite to austenite single phase and solution strengthening effect of nitrogen, while

the NPSA-treated austenitic stainless steel displays a decrease in elongations and a slight increase in tensile strength compared to the SA-treated austenitic stainless steel.

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