On a PH Type Stainless Steel Containing High Nitrogen and High Silicon*

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A metallographical study has been carried out on the steel melted and cast under the 10 atmospheric pressure of nitrogen. The chemical composition of this steel is 16% Cr-3% Si-4% Ni-4% Cu-0.44% N-Bal Fe. Various factors have been clarified to obtain a high strength PH type stainless steel. The results may be summarized as follows:

(1) Thorough soaking at about 1100°C and repeated light deformations at the temperature in the initial stage of forging are necessary to hot-work without forming cracks in the cast ingot.

(2) The microstructure of the steel water-quenched from 1100°C after held for 10 min consists of austenite having a small amount of insoluble nitride particles. The austenite is still stable even after cooled down to -180°C. The higher the solution-quenching temperature, the less the amount of the insoluble nitride becomes.

(3) On tempering of the solution-quenched steel, the yield strength increases remarkably, and the ductility decreases. To make the steel strong and tough, it is adequate to hot-cold work during the tempering at 700°C of the steel water-quenched from 1100°C and subsequently reheat at 450°C for 60 min to relieve the internal stress. When 33% hot-cold rolled by the above treatment, the steel shows such an excellent final tensile properties as $\sigma_B=129\sim121$ kg/mm², $\sigma_S=109\sim116$ kg/mm² and $\delta=22\sim23\%$.

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I. Introduction

The effect of silicon addition to the 17-4 PH type stainless steel had been clarified by one of the authors in a previous paper⁽¹⁾ from the metallographic point of view. The present paper deals with the phase changes and improvement of mechanical properties in one of the Si-containing 17-4 PH type stainless steel by heat-treat-

ment and hot-cold working. This steel was melted and cast at a 10-atmospheric pressure of nitrogen and had the chemical composition of 16% Cr-3% Si-4% Ni-4% Cu-0.44% N-Bal Fe.

II. Preparation of the Specimen

The high-pressure melting furnace used for melting and casting of the steel was a 15 kVA high-frequency induction furnace having a structure similar to that of the common inside heating type vacuum-melting furnace, except that the vacuum tank body and multiple vacuum-sealing parts were so designed as to stand an inner pressure up to 15 atm. The vacuum tank

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was of a horizontal cylinder type of about 800 mm in both diameter and length and equipped with a 1,500 l/min rotary oil pump, a 380 l/sec oil diffusion ejector pump and a 1900 l/sec oil diffusion pump so as to replace the air in the tank with nitrogen. The melting capacity per charge was 5 kg and a crucible of fused magnesia with an inside diameter of 85 mm was used. The depth of the 5 kg molten steel was about 100 mm.

Chemical elements for melting such as Fe, Cr, Ni and Cu were all electrolytic high-purity elements, while Si was added as the simple metal. Fe, Cr and Ni were previously charged into the crucible, melted in a vacuum of 1×10^{-3} mm Hg and heated to about 1500°C. Then high-purity nitrogen was introduced to make 1 atm. Next, Mn, Si and Cu were added and again nitrogen gas was introduced. When the gas reached the 10 atmospheric pressure, the metal was kept for 30 min and then cast into a mould in the atmosphere of the same pressure. The mould, made of copper, was of the square type with the dimension of 62 mm in the upper side, 54 mm in the lower side, 180 mm in height and 45 mm in wall-thickness. The total time required for melting and casting was about 55 min.

After thorough soaking at 1100°C~1000°C, the cast ingot was forged into a 15 mm square billet (forging ratio : 16) and subsequently hot-rolled to the thickness of 7.2 mm at about 1100°C~1000°C. Hot-working of the cast ingot was not easy and therefore both thorough soaking at about 1100°C and repeated light deformations at the temperature in the initial stage of forging were necessary to hot-work without forming cracks in the cast ingot. The chemical composition of the steel melted is shown in Table 1.

Table 1 Chemical composition (%) of the alloy.

	C	Si	Mn	P	S	Ni	Cu	Cr	Ntotal
30S-10	0.004	2.80	0.47	0.011	0.010	4.35	4.01	15.94	0.44

III. Experimental Results and Discussion

1. Change in the nitrogen concentration of steel by high-temperature heating

The behavior of nitrogen in the steel during heating to a high-temperature in various atmospheres was investigated using a thermobalance. Scraps (about 100~200 mesh) of the forged billet granulated by filing were used as the specimens. The curve of weight change during heating of the specimen in vacuum is shown in Fig. 1. The weight decrease which indicates denitrogenization was found to begin from around 200°C during heating in vacuum. The amount of denitrogenization increased with increasing temperature, until a subsequent holding up to 30 min at 1100°C.

The ratio in weight change due to the heating was calculated from equation $n = [(W - W') / W] \cdot 100$, where W and W' were weights of the specimen before and after the heating. The n value calculated from data shown in Fig. 1 was -0.32% , which indicated that about 73

% ($= 0.32 / 0.44 \cdot 100$) of nitrogen initially contained in the specimen was removed during heating in vacuum at 1100°C for 60 min. During heating in the 1 atmospheric pressure of nitrogen, however, as shown in Fig. 2, a rapid increase in weight was found to begin in the vi-

Fig. 1 Weight change during heating in vacuum of the granular specimen as forged.

Fig. 2 Weight change during heating in 1 atm-N₂ of the granular specimen as forged.

cinity of 950°C, and after holding for 120 min at 1100°C, the ratio in weight change, n , was calculated to be $+0.58\%$; that is, the granular specimens were found to absorb nitrogen at temperatures higher than 950°C under the 1 atmospheric pressure of nitrogen. The curve of weight change during heating in air is shown in Fig. 3. The weight increase with temperature was

Fig. 3 Weight change during heating in air of the granular specimen as forged.

thought to be due to the nitrogen-absorption and oxidation which occurred almost simultaneously. It was found

that the nitrogen-absorption and oxidation of the bulk specimens were not so strong as those of the granular specimens.

2. Microstructure and hardness of solution treated specimens

Photo. 1 shows a microstructure of the specimen

× 400

Photo. 1 Microstructure of alloy slow cooled from 700°C after held for 30 min. Etched electrolytically by 10% oxalic acid.

which was slow cooled after being held at 700°C for 30 min, in which many precipitation particles embedded in the α iron matrix could be observed. Due to heating at 950°C for 10 min, the greater part of the matrix converted into austenite as shown in Photo. 2, but many of the precipitation particles remained unchanged. At the temperature of 1100°C, the structure of the steel came to consist only of almost single austenite as shown in Photo. 3.

× 400

Photo. 2 Microstructure of alloy water quenched from 950°C after held for 10 min. Etched electrolytically by 10% oxalic acid.

× 400

Photo. 3 Microstructure of alloy water quenched from 1100°C after held for 10 min. Etched electrolytically by 10% oxalic acid.

Fig. 4 is an illustration of the relationship between the solution treatment temperatures and the Vickers hardness of the specimen water-quenched from that temperature. The hardness after solution quenching decreased with increasing temperature because of the

Fig. 4 Vickers hardness of the specimen water quenched from various temperatures.

dissolution of nitride particles into the matrix, and the austenite became more stable with increasing temperature.

3. Phase change by heat-treatment

Fig. 5 shows a differential dilatation curve of the specimen which was slow cooled after being held at 700

Fig. 5 Differential dilatation curve of the specimen during slow heating, air cooling and subzero cooling.

°C for 30 min. On the heating curve, a remarkable contraction which occurs at a temperature above 500°C seems to be due to the precipitation of nitride and the $\alpha \rightarrow \gamma$ transformation, and the A_3 ending temperature where the α phase is completely transformed into the γ

phase can be found at about 820°C. Above the temperature of 820°C, a conspicuous expansion is observed due to the dissolution of nitride particles into the austenite matrix. Austenite thus formed is so stable that it does not transform into martensite even if cooled down to -195°C after water-quenched from 1050°C. Fig. 6

Fig. 6 Differential dilatation curve during slow heating and air cooling of the specimen water quenched from 1050°C after held for 10 minutes.

shows a differential dilatation curve during slow heating and air cooling of the specimen which was water-quenched from 1050°C after being held for 10 min. A considerable contraction can be seen in the temperature range from 550° to 630°C on the heating curve. This contraction is obviously caused by the nitride precipitation from the austenite matrix. Austenite formed by holding at 1050°C for 5 min does not transform into martensite by air cooling from that temperature as shown in Fig. 5. When a bulk specimen was subzero-cooled into a liquid-nitrogen bath after water-quenched from 1100°C, austenite remained unchanged without decomposing into martensite. When a specimen was subjected to plastic deformation by rolling at room temperature, a part of the austenite transformed into martensite and the specimen showed a strong ferro-magnetic property. From the above results, it can be concluded that the Md point of austenite in the steel after solution-quenched from 1100°C lies above room temperature. Differential dilatation curves of the specimen air cooled or subzero-cooled after tempering at 500°C, 550°C and 700°C for various periods of time are shown in Fig. 7. The contraction of the specimens, caused by precipitation from austenite, during holding at 500°C and 550°C increased with the increasing temperature and tempering time. However, during the 700°C tempering, as shown in the figure, the dilatation curve on heating indicates a slight contraction at 500°~650°C, and subsequently changes again into expansion above 650°C, followed by a contraction during holding at 700°C. At the temperature of 500°~550°C, the precipitation from austenite seemed to occur easily, but above that temperature the amount of precipitation decreases. On further heating alloying elements were depleted in the austenite by precipitation and the austenite began to decompose into ferrite, resulting in an expansion. A small and gradual

contraction which occurred during a subsequent holding at 700°C, was considered due to a competition of the expansion caused by the $\gamma \rightarrow \alpha$ transformation and the contraction by the precipitation. One can confirm the formation of the ferrite as shown in Photo. 4 and Photo. 5. The amount of the ferrite increased with the holding time.

Fig. 7 Differential dilatation curves of specimens air- or subzero-cooled from various temperatures after held for various times.

×400

Photo. 4 Microstructure of alloy air cooled from 700°C after held for 3 hr. Etched electrolytically by 10% oxalic acid.

×400

Photo. 5 Microstructure of alloy air cooled from 700°C after held for 6 hr. Etched electrolytically by 10% oxalic acid.

The precipitant was supposed to be Cr_2N and a Cu-rich solid solution. By subzero-cooling of the specimens which were air cooled after being held for 8 hr

at 500°C, the austenite began to transform into martensite at -160°C. When the specimen was held for 8 hr at 550°C, the martensitic transformation began at -120°C by subsequent subzero-cooling. By air-cooling after holding for 3 and 6 hr at 700°C, the remaining austenite began to transform into martensite at 160°C and 170°C, being considerably higher than room temperature. Although the difference in M_s points of the specimens air-cooled after holding for 3 and 6 hr was very small, it was confirmed that the specimen held for 6 hr contained a considerably larger amount of martensite than that held for 3 hr after air-cooling to room temperature.

4. Improvement in mechanical properties by heat treatment with hot-cold working

Fig. 8 shows hardness changes of specimens by tempering times at 450°, 500°, 550° and 700°C after

Fig. 8 Vickers hardness of specimens air cooled from various temperatures after held for various hours.

1050°C solution treatment. The hardening by tempering below 550°C was simply caused by the precipitation, whereas a remarkable hardening by tempering at a temperature as high as 700°C would be attributed to both the precipitation and the martensite transformation during air-cooling. The cause of the above transformation was due to the depletion of alloying elements in the retained austenite as a result of the increasing amount of the precipitant by high-temperature aging. Due to the aging at 700°C, the hardness of the specimen increased and attained a maximum with the tempering time up to 4 hr, and then decreased with the aging time. The reason why the hardness curve at 700°C showed the maximums may be considered as follows; one

is the growth of the precipitant, the other is the amount of martensite decreased by the $\gamma \rightarrow \alpha$ transformation at the tempering of 700°C.

Tensile properties of the plate-form specimens were investigated by aging at 700°C for 2, 3, or 4 hr and reheating to 450°C for 1, 4 or 6 hr after the solution treatment at 1100°C for 10 min. The reheating treatment at 450°C was added to the heat treatment process in order to relieve the stress caused by the newly formed martensite during air cooling from 700°C. The size of the specimens used was 3 mm in thickness, 5 mm in width and 30 mm in length. Tensile properties of the alloy are shown in Table 2. Comparing the values

Table 2 Tensile properties of the alloy air cooled from 700°C after held for various times and subsequently reheated at 450°C for various times.

Holding time at 450°C (hr)	kg/mm ² , %	1	4	6
Holding time at 700°C (hr)				
2	σ_B	—	—	94.5
	σ_S	—	—	74.5
	δ	—	—	24.0
3	σ_B	93.0	96.5	—
	σ_S	80.0	75.5	—
	δ	18.5	15.4	—
4	σ_B	87.0	85.5	—
	σ_S	75.4	75.0	—
	δ	10.8	10.1	—

shown in Table 2 with those in the solution-quenched state, it is evident that by the tempering, the strength increases and the elongation decreases. Both the strength and the elongation increased with decreasing holding time at 700°C. On the other hand, when the formation of α from γ by a diffusion transformation proceeded with a prolonged holding at 700°C, not only the decrease in tensile strength but also a remarkable elongation decrease were observed. It may be concluded from these results that by a simple combination of solution quenching and tempering, it is impossible to produce a sufficiently strong and tough stainless steel. Then, it was examined to apply a 33% hot-cold rolling during tempering at the temperatures of 550°, 600°, 650° or 700°C to the steel solution treated from 1100°C. A technique used in this examination was as follows: The solution-quenched specimens were dipped into a lead bath held at the various temperatures stated above, and then rolled at these temperatures. In all the cases, the rolling carried out so as to complete for 10 min and by 6 passes. When rolling was carried out, two different combinations were examined of the rolling with aging at these temperatures; one was the rolling after dipping in a lead bath for 3 min (namely, the earlier stage rolling) and subsequent aging for 50 min, the other was the rolling after prior aging for 50 min (the later stage rolling). Finally, all the specimens were air-cooled from each temperature.

Hardness and tensile tests and measurements of $\alpha\%$ by a ferrite indicator were conducted on the specimens hot-cold worked. The results are given in Fig. 9. When the specimen rolled in the earlier stage, the diffusion and

precipitation of solute atoms in the aging were promoted by the residual strain resulting from the rolling, and thus the concentration of the alloying elements in austenite became low. As a result, more austenite decomposed into martensite by air-cooling after the aging.

Fig. 9 Some mechanical properties of specimens hot-cold rolled 33% in the earlier stage or in the later stage during holding 60 min at various rolling temperatures and subsequently reheated at 450°C for 60 min.

Therefore, the specimen hot-cold rolled in the earlier stage showed a stronger magnetism than the hot-cold rolled one in the later stage of rolling, and this tendency became remarkable with rise in the temperature of rolling. The hardness of the specimens also increased with increasing temperature of hot-cold working in the earlier stage. This might be attributed to the martensitization caused by the increasing precipitation. That is, the hardening trend by hot-cold rolling, becomes small due to stress relief during aging. However, the hardness of the specimen could from aging temperature increased with the amount of martensite due to the reduced concentration of alloying elements in austenite, because the formation of precipitation from austenite is larger than softening due to stress relief during aging after rolling. On the other hand, by the later stage rolling, the hardness of the specimens did not change appreciably with the rolling temperature: It was probable that with the increasing temperature of rolling, the precipitation and martensitization were promoted only slightly because of the lack

of the earlier stage rolling, and that the work-hardening decreased with increasing temperature. In general, the tensile properties of the steel hot-cold worked were superior to that without hot-cold working. The specimens rolled in the earlier stage had a higher tensile

Fig. 10 Some mechanical properties of specimens rolled 33% at 700°C in the earlier stage during the holdings and subsequently reheated at 450°C for 60 min.

strength, lower yield strength and smaller elongation than that rolled in the later stage. Moreover, the maximum value of the yield strength was obtained by the rolling in the later stage at 600°C, and in this rolling condition of the specimen showed such tensile properties as $\sigma_B = 121 \text{ kg/mm}^2$, $\sigma_S = 116 \text{ kg/mm}^2$ and $\delta = 22\%$. In Fig. 10 are shown changes in mechanical and magnetic properties of the steel with increasing holding time at 700°C after the 33% rolling in the earlier stage of the tempering at the same temperature. It is obvious from the figure that both the amount of ferrite and the hardness of the steel increase with increasing holding time. But the tensile strength of the steel attained a maximum at the holding time of 60 to 90 min at 700°C, and thereafter decreased with prolonged holding. It was interesting that the elongation of the steel showed a similar behavior as the tensile strength. The relation between the yield strength and the holding time at 700°C was not clear. Photo. 6 shows a microstructure of the alloy air cooled from 450°C after a 33% hot-cold rolling in the earlier stage during holding for 60 min at 700°C. It was apparent that a greater part of the austenite in this specimen transformed into martensite, because the specimen showed a considerably larger amount of precipitation, a higher hardness and a stronger magnetism than that in the solution quenched state. The

existence of the martensite, however, was difficult to be confirmed microscopically. It can be concluded from the above results that an adequate treatment to give strength and toughness to this steel will be as follows : Water-quenching from 1100°C after holding for 10min,

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Photo. 6 Microstructure of the alloy air cooled from 450°C after hot-cold rolled 33% in the earlier stage during holding for 60 min at 700°C. Etched electrolytically by 10% oxalic acid.

→ hot-cold working in the earlier stage during holding for 60 min at 700°C → air cooling, → stress-relief tempering at 450°C for 60 min → air cooling. It was also made clear that the hot-cold working in the later stage was more desirable to obtain a particularly high yield strength.

As already noted, the application of the heat-treatment with the hot-cold working would enable to produce a steel with excellent mechanical properties, (tensile strength ; 140 kg/mm², yield strength ; 108 kg/mm² elongation ; 27% and Vickers hardness ; 415). The microstructure of the steel in this condition consists of a small amount of tempered martensite, a great deal of austenite, and dispersed precipitants of Cr₂N and the Cu-rich phase.

IV. Summary

A metallographic study has been carried out on the steel of 16%Cr-3%Si-4%Ni-4%Cu-0.44%N-Bal Fe which had been melted and cast under the 10 atmospheric pressure of nitrogen, and various factors have

been clarified to obtain a high strength PH type stainless steel. The results are summarized as follows :

(1) Thorough soaking at about 1100°C and repeated light deformations at the temperature in the initial stage of the forging are necessary to hot-work without forming cracks in the cast ingot.

(2) The variation in the nitrogen concentration occurs on the surface of the steel due to heating atmospheres ; in the heating in vacuum and in argon-the denitrogenization, and in the heating in one atmospheric pressure of nitrogen-the nitrogen absorption. The weight increase due to the heating in air arises from both the oxidation and the nitrogen absorption on the surface of the steel.

(3) The microstructure of the steel water-quenched from 1100°C after held for 10 min consists of austenite having a small amount of insoluble nitride particles. The austenite is still stable even when cooled down to -180°C. The higher the solution-quenching temperature, the less the amount of the insoluble nitride becomes.

(4) precipitants, probably Cr₂N and a Cu-rich solid solution are formed in the austenite by the tempering at 500°~550°C after the solution-quenching. If the tempering at 500°~550°C is prolonged, a small amount of martensite is formed below -100°C by the subsequent subzero-cooling after the tempering. Both the precipitation and the ferrite formation from the austenite are found to proceed simultaneously during the tempering at 700°C. By the subsequent cooling from the tempering temperature, the remaining austenite transforms into martensite at temperatures considerably higher than room temperature.

(5) On tempering of the solution-quenched steel, the yield strength increases remarkably, while the ductility decreases. To make the steel strong and tough, it is adequate to hot-cold work during the tempering at 600°C of the steel water-quenched from 1100°C and subsequently to reheat at 450°C for 60 min so as to relieve the internal stress. When 33% hot-cold rolled in the above treatment, the final tensile properties are found to be $\sigma_B = 129 \sim 121$ kg/mm², $\sigma_S = 109 \sim 116$ kg/mm² and $\delta = 22 \sim 23$ %. Stronger magnetism and lower σ_S are obtained by the hot-cold working in the earlier stage of tempering.