ON MANUFACTURE OF HEAT-RESISTING STEEL CONTAINING HIGH CONCENTRATION OF NITROGEN AND ITS HIGH TEMPERATURE PROPERTIES

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Abstract

To utilize nitrogen as an alloying element in heat-resisting steels, an experimental study was made on the fundamental phenomena occurring in melting and casting of various high-chromium steels under high-pressure nitrogen atmosphere. By this technique, sound ingots containing high concentration of nitrogen could practically be obtained, and the new high strength heat-resisting steel could be developed, some of which have the creep-rupture strength at $700°C$ -10^3 hr far exceed 20 kg/mm^2 with an excellent high-temperature ductility.

Introduction

It has been known for many years that nitrogen has an excellent potential as an alloying element in austenitic stainless steels and heat-resisting steels [1 ~ 4]. However, in the ordinary method of melting and casting, it is seldom that the stably alloyable nitrogen content surpasses 0.2% in the austenitic steels, except for such high-manganese steel as a 21-4N valve steel. Even if the nitrogen above this value were added in the melt, a sound ingot could not be obtained, because of blowholes on solidification. On the other hand, it is stated that the nitrogen solubility in molten and solidified iron is nearly proportional to the square root of the partial pressure of the nitrogen gas in the atmosphere [5]. Subsequently, it is expected that if the pressure of nitrogen gas in the melting atmosphere is enhanced, the stably alloyable nitrogen content will be increased.

From this view point, one of the authors have projected a research on melting in nitrogen under high pressure. By developing melting and casting method in nitrogen atmosphere under high pressure up to 10 atm [6] [7], the basic conditions for the stable and sure melting of some stainless and heat-resisting steel have been established. Some of the steels produced by this method contained such high concentrations of nitrogen that they previously could not be expected to be melted properly under the ordinary method. There was found only a few examples of the melting in nitrogen atmosphere under high pressure [3, 8, 9], so that the potential of this method has not been properly recognized. The present paper gives a summary of the research on

melting in high-pressure nitrogen performed previously by the authors including a part of the results of the study on heat-resisting properties of steel products containing nitrogen up to about 0.6% or 0.7%.

High-Pressure Melting Furnace and Melting Procedure

The high-pressure melting furnace used in this experiment is a 15 kVA high-frequency induction furnace that has a structure similar to that of the common inside-heating type vacuum-melting furnace, but both vacuum tank body and many vacuum sealing parts are designed and manufactured so as to stand an inner pressure of 15 atm max. Figure 1 shows an apparence of this tank which is of a horizontal cylinder type with a diameter of about 800 mm and a length of about 800 mm and additionally equipped with vacuum pump in order to replace the air in the tank with nitrogen. The melting quantity per charge is 5 kg and a crucible of fused magnesia with an inside diameter of 85 mm is used. The depth of the 5 kg molten steel is about 100 mm.

Base materials, consisting of electrolytic iron, chromium and nickel, were previously charged into the crucible, melted down in a vacuum and heated to about 1550°C. Then a high-purity nitrogen was introduced to make 1 atm. Then manganese, silicon, molybdenum, tungsten and boron were added and again nitrogen gas was introduced. When the gas reached the required pressure, the metal was kept for the required time and then cast into the mold in the atmosphere under the same pressure. The mold, made of copper was of the square or round type with the dimension of about 180 mm in
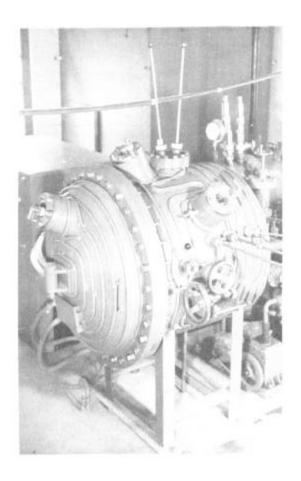
Figure 1.   The main part of the high-pressure melting furnace.

height, and 45 mm in wall thickness.

Experimental Results

Nitrogen Solubility in Steels with High Chromium Concentration and Effect of High-Pressure of Nitrogen

It has been known that, in Fe-Cr alloys, the nitrogen solubility is remarkably increased with increase of Cr concentration in every phase of γ, δ and the molten state [10 ~ 12]. The temperature coefficient of nitrogen solubility in both the γ-phase and the molten state proved to be negative. And the nitrogen solubility was somewhat less in the δ-phase that has been primarily crystallized on solidification from the molten state than in both liquid phase and γ-phase. This is one of the reason why a sound steel ingot of high nitrogen concentration is difficult to be obtained by the ordinary method. On the other hand, when melting and casting are performed under high-pressure nitrogen, the nitrogen solubility in the molten state is remarkably increased; at the same time, the nitrogen, being a γ-forming element, makes easy a primary crystallization of γ-phase on solidification; and a casting and melting under suppression of gas evolving under high-pressure expectedly should facilitate the obtaining of a sound steel ingot. Moreover, the nitrogen solubility in γ-phase is remarkably enhanced with decreasing of temperature. It is thus supposed that the steel with high nitrogen concentration solidified without once generating blowholes presents no opportunity for nitrogen to evolve from the inside to the outside of the steel even if it is subjected to forging or heat treatment after heating to high temperature under atmospheric pressure. Herein lies the significance of a high-pressure melting.

By the way, with respect to the relations between the nitrogen solubility (% N) in molten iron and the nitrogen partial pressure (p_{N_2}) in the atmosphere, Sieverts gave the following formula [5]:

$$\% N = K(p_{N_2})^{1/2}, \text{ where } K = \text{constant.}$$

Kasamatsu and Matoba [13] stated that the nitrogen solubility in molten pure iron will not follow the Sieverts' law when the p_{N_2} is below 2.3 atm and Humbert and Elliot [11] reported that this law will hold true with the pure iron and Fe-Cr alloys with chromium content up to 57% in the range of 0.5 - 1.1 atm nitrogen. Moreover, Kurochklin [14] described that the n in the undermentioned formula will be increased from 0.5 in the pure iron to 1.02 in 50% Cr-Fe alloy:

$$\% N = K(p_{N_2})^n.$$

As stated above there are diverse opinions in accordance with different research even under a low pressure of $p_{N_2} \leqslant 2.3$ atm in respect to whether the nitrogen

solubility in molten iron shall follow the Sieverts' law. Moreover, nothing has been made clear with regard to the nitrogen solubility under a high pressure in the range of 10 atm. Therefore, the authors investigated the effect of p_{N_2} on nitrogen solubility in the range from a low pressure to 10 atm with 316 L type steels.

From the experimental results, it has been found that the total % N was increased as the molten metal holding time during melting was prolonged, while the % N nearly reached an equilibrium value at the holding time of about 1 h. The total % N value in the case of 1 h holding at about 1550°C under respective pressure of p_{N_2} being 1, 4, 7 and 10 atm is plotted against $\sqrt{p_{N_2}}$ in Figure 2. It is known from this figure that % N and $\sqrt{p_{N_2}}$ stand in a linear relationship and follow Sievers' law. In other words, in the formula:

$$\% N = K(p_{N_2})^{1/2},$$

the value of K is obtained from each observed value by the method of least squares as follows:

$$K = 0.183.$$

From these results, it is supposed that Sieverts' law almost applies between the saturated nitrogen solubility at about 1550°C and the atmospheric nitrogen pressure with 316L type molten steel within the range up to about 10 atm in the present experiment.

Soundness of Steel Ingots

In the aforementioned high-pressure melting of 316L type steels, sound ingots always free from blowholes were obtained under every melting condition. As stated before, generally in the case of solidification on primary crystallization of δ-phase, and if the N concentration in molten steel is larger than the saturated nitrogen solubility in δ-phase, the nitrogen is evolved in the form of gas on solidification and unsound steel ingots with blow holes are obtained. Besides, even in the case of a solidification in the form of primary crystallization of γ-phase and if the saturated nitrogen solubility is less than the nitrogen concentration in molten steel, unsound ingots also would be produced. Moreover, the nitrogen solubility in steel much depends on the alloy composition and the solidification process of molten steel also is different in accordance with the composition of alloys including nitrogen. Thus, whether the steel ingot becomes sound or unsound will be decided delicately by various complex conditions.

In order to make clear the basic relationship with respect to these facts, at first some Cr in a range of 10 – 25% was added to 20% Ni-Fe alloys that were held for 20 min in 4 atm nitrogen and cast into ingots, of which the relation between chromium and nitrogen concentration versus the soundness was examined. In melting of
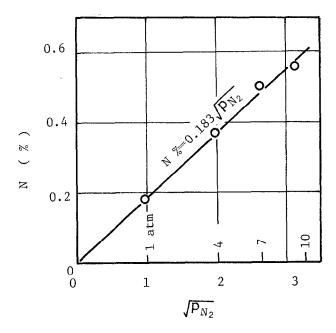
Figure 2. Relation between N_2-pressure and nitrogen content of type 316L steels melted at about 1,550°C for 1 hr.

Table 1. Results of the high-pressure melting in
nitrogen atmosphere of 20% Ni-Cr-Fe alloys

Alloy No.	Amount of Cr added (%)	Melting conditions	Chemical composition (%)						Soundness of ingots
			C	Si	Mn	Cr	Ni	Total N	
30	10		0.006	0.28	0.94	9.77	19.79	0.153	Porous
32	15	a)	0.003	0.38	0.97	14.47	20.11	0.230	Sound
33	20		0.003	0.33	0.98	19.90	19.94	0.355	Sound
34	25		0.003	0.32	0.99	24.40	20.00	0.486	Sound
31	10	b)	0.003	0.28	0.96	9.82	20.01	0.186	Sound

a) Held at 1,550°C in 4 atm nitrogen atmosphere for 30 min. followed by casting under the same pressure of nitrogen

b) Held at 1,550°C in 4 atm nitrogen atmosphere for 25 min. followed by casting in 10 atm nitrogen atmosphere

Table 2. Results of the high-pressure melting
of 10% Cr-20% Ni-Fe alloys

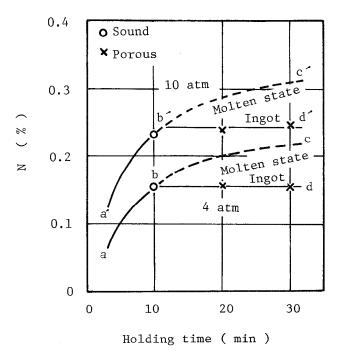| Melting conditions		Chemical composition (%)						Soundness of ingots
N_2 pressure (atm)	Holding time (min.)	C	Si	Mn	Cr	Ni	Total N	
4	10	0.003	0.31	0.97	9.89	19.20	0.155	Sound
	20	0.002	0.38	0.99	9.89	20.02	0.156	Porous
	30	0.006	0.28	0.94	9.77	19.79	0.153	Porous
10	10	0.001	0.09	0.79	12.55	19.08	0.233	Sound
	20	0.003	0.33	0.98	9.98	19.84	0.240	Porous
	30	0.009	0.24	0.93	10.66	19.81	0.268	Porous

Figure 3.   Effect of holding time of molten 10%Cr—20%Ni—Fe alloys under high-pressure nitrogen atmosphere on nitrogen content of alloys and on ingot soundness.
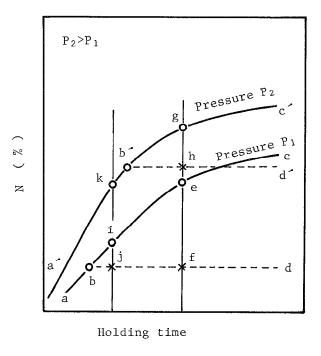

Figure 4.   Schematic diagram illustrating the correlation between the nitrogen content of a steel in molten state, that in cast state and the holding time of the melt under the nitrogen atmosphere.

such alloys 0.5% Si and 1.0% Mn were added as deoxidizers besides Cr and Ni. Chemical analyses of these steel ingots are shown in Table 1.

Within the range of 15-25% Cr, the N % was remarkably increased in parallel with the increase of Cr% and sound ingots were always obtained, while 10% Cr addition caused blow holes and also the N concentration of steel ingots was no more than 0.153%. However, when the similar 10% Cr alloy which had been held for 25 min at 4 atm, had come in contact with more nitrogen introduced and pressurized up to 10 atm for about 3 min and immediately was cast (No. 31 alloy), it showed a sound ingot containing 0.186% N. In other words, even in the case of 10% Cr, a sound ingot might be obtained if the N_2 pressure in atmospheres had been sufficiently great in contrast with the N concentration in molten steel.

Then, with such 10% Cr—20% Ni-Fe alloys, the holding time was changed in nitrogen at 4 atm and 10 atm and, after casting under such pressures as they were, the soundness of ingots was examined. The results are summarized in Table 2. The relationship between the holding time and the N% in ingots is shown in Figure 3.

Sound ingots were obtained by holding for 10 min both at 4 atm and 10 atm, while unsound ingots with many pores were obtained by holding for 20 min and 30 min. As shown in Figure 3, the N concentration in molten steel was presumed to be increased along a tendency of a-b-c at 4 atm, and a'-b'-c' at 10 atm. However, when the concentration was increased above b or b', the nitrogen would be issued in gas form on solidification and the N concentration in steel ingots would show a fixed value to be decided by the nitrogen pressure in atmosphere such as bd and b'd' regardless of the N concentration in molten steel.

Figure 4 is an illustration of these relationships. In the figure, the relationship between abc, a'b'c' and bd, b'd' are similar to the case in Figure 3. When the N% in molten steel is increased to above b in the case of low pressure P_1 or above b' in the case of high pressure P_2 blow holes occur on solidification and the N% in steel ingots is decreased respectively down to bd and b'd'. For example, a molten steel with an N concentration of "e" is cast under a pressure as it is, the N% in ingots is reduced to "f" and "g" is decreased to "h". However, when a molten steel with N concentration of "i" is directly cast under a pressure P_1, blow holes occur and the N% in steel ingots becomes "j". However, when the pressure of the atmosphere has been increased to the pressure P_2 in a short time and the steel has been immediately cast, a sound ingot may be obtained because the N% is lower than the limit b' between soundness and unsoundness at the pressure P_2. It is based on this reason why a sound ingot has been obtained by holding the 10%Cr—20%Ni-Fe alloy (as shown in the preceding Table 1) for

25 min at 4 atm and then increasing the pressure up to 10 atm followed by casting.

Table 3 shows the results of high-pressure melting of 17-4 PH steel and 13% Cr heat-resisting steel.

In the case of 17-4 PH steel with 3% Si, and when the steel has been held for 30 min at 4 atm and directly cast, the unsound steel ingot is obtained even if the N concentration in ingots is 0.27%. On the contrary, when the steel has been held for 25 min at 4 atm, then pressurized up to 10 atm and immediately cast, a sound ingot even with 0.35% N is obtained. The results of this case corresponds to the aforementioned results. Besides, as shown in Table 3, the steel with 3% Si added to 17-4 PH steel becomes unsound after holding for 30 min at 4 atm before casting, while it becomes sound after holding 30 min at 10 atm before casting. In the latter case, it is presumably because the N% in molten steel has been increased and much γ-phase has been crystallized out during solidification.

Moreover, the steel with 0.5% Si added and cast after holding for 30 min at 4 atm can give a sound ingot even if it contains more N% than in the case of 3% Si. The reason is because Si is a ferrite-forming element as well as an element reducing the N solubility in molten steel [12], and because the less Si the more the N% in molten steel even under the same melting conditions thus facilitating the development of γ-phase during solidification.

Table 4 shows the results of high-pressure melting of some high Cr-Fe alloys all giving sound ingots. As shown in this Table, even under the same melting conditions, 18% Cr—10% Mn steel contained more N% than 18%Cr—4%Ni steel, and 22%Cr—2%Ni steel included more N% than 22%Cr steel. Besides, with 20%Cr—20%Ni-Fe alloy as the basic series of LCN-155, it is known that the more Co added in the same 10 atm - 10 min-melting, the less the N% becomes. Besides, in the case when an alloy charge of 60%Cr-40%Fe had been cast after holding for 30 min at 10 atm, the N on solidification reached 2.79% at the Cr content of 51.74%.

Plastic Workability, Machinability and Weldability of Steel Melted and Cast under High-Pressure Nitrogen

The aforementioned various steel ingots melted under high pressure showed a bit more difficulty generally in forging as the N concentration was increased. Nevertheless, they proved the full possibility of being extended from a 60 mm square ingot into a 15 mm square billet as well as the possibility of hot and cold workability into far smaller sections.

In addition, with respective steel types no particular difficulty was observed in machining operations such as turning, sawing, shaping and milling.

Table 3. Results of high-pressure melting in nitrogen atmosphere of 17-4 PH and 13% Cr steels

| No. | Steel type | Melting conditions | | Pressure of nitrogen in casting (atm) | Chemical composition (%) | | | | | | | Soundness of ingots |
		Pressure of nitrogen (atm)	Holding time (min)		C	Si	Mn	Cr	Ni	Cu	Total N	
49	17-4 PH type with 3% Si	4	10	4	0.005	2.92	0.57	17.42	4.07	3.60	0.22	Sound
22		4	30	4	0.009	3.07	0.48	16.85	4.06	4.00	0.27	Porous
29		4	25	10	0.016	2.85	0.48	16.74	4.45	4.00	0.35	Sound
21		30	30	10	0.004	2.80	0.47	15.84	4.35	4.01	0.44	Sound
28	17-4 PH type with 0.5% Si	4	30	4	0.015	0.40	0.47	16.76	4.43	3.96	0.37	Sound
05N		1	30	1	0.01	0.20	0.74	12.95	-	-	0.054	Sound
25N		4	30	4	0.01	0.43	0.97	12.67	-	-	0.246	Porous
35N	13 Cr	4	30	10	0.01	0.45	0.92	12.73	-	-	0.346	Porous
26N		4	5	10	0.01	0.33	0.75	12.90	-	-	0.263	Sound
38N		10	30	10	0.01	0.38	0.89	12.87	-	-	0.380	Porous

Table 4. Results of the high-pressure melting in nitrogen
atmosphere of some stainless and heat-resisting steels

Types of steel	Melting conditions		Chemical composition (%)							
	N_2 pressure (atm)	Holding time (min.)	C	Si	Mn	Cr	Ni	Co	Others	Total N
18 Cr-4 Ni	1	10	0.006	0.37	0.92	18.15	3.95	-	-	0.090
	10	10	0.005	0.38	0.97	18.17	4.13	-	-	0.592
18 Cr-10 Mn	1	10	0.005	0.38	10.45	17.89	-	-	-	0.136
	4	10	0.003	0.36	10.70	17.96	-	-	-	0.459
	7	10	0.004	0.35	10.50	18.04	-	-	-	0.656
	7	30	0.005	0.41	10.55	18.14	-	-	-	0.772
	10	30	0.005	0.41	10.60	17.22	0.01	-	-	0.959
22 Cr	10	10	0.004	0.33	0.90	22.16	-	-	-	0.485
22 Cr-2 Ni	10	10	0.003	0.32	0.90	21.98	2.00	-	-	0.561
LCN-155	10	10	-	-	1.05	19.29	19.17	-	-	0.355
	10	10	-	-	0.96	19.21	19.53	9.10	-	0.338
	10	10	-	-	0.92	19.17	18.62	19.62	-	0.280
	4	30	0.006	0.09	1.14	19.72	19.93	19.69	Mo 3.00 W 2.45 Nb 0.96	0.269
60 Cr-Fe	10	30	0.078	0.054	0.057	51.74	-	-	-	2.79

Spot weldability and arc weldability have also been investigated with an 18%Cr—10%Mn type steel containing high concentration of nitrogen up to about 0.8%. Both of welding methods gave a very good and sound weld, if ordinary welding conditions recommended for welding of commercial austenitic stainless steels are adopted. The spot weldability of the steels scarcely depended upon nitrogen concentration, and was about the same as that of commercial austenitic stainless steels. But, in the steel containing higher concentration of nitrogen, i.e., more than 0.5%, a small number of expulsions and blowholes in the weld nugget could be detected. Therefore, in case of welding such a steel, better properties of the nugget will be obtained by adjusting welding condition to prevent them. The nitrogen in base metals scarcely diffused out of the nugget even in the steel containing about 0.8% nitrogen. Consequently, the spot weld shear strength rose in proportion to the increase in nitrogen content and any decrease of it did not occur on account of nitrogen diffusion.

In the arc welding, a part of nitrogen, which had been contained in base metal, evolved into atmosphere and also a part of that diffused out to the weld deposit. The decrease of the nitrogen concentration in base metal, however, is considered to be not so much. And hardness and tensile strength of the weld increased with increasing nitrogen content in base metals. As the nitrogen content of the base metals, increased, and as power input for the arc welding increased, some blowholes tend to be included in the deposit metal, and the density of them became considerable when the nitrogen content of the base metals exceeds 0.65%, so that, it has been concluded that a reliability of the weld bond in such higher nitrogen steels are somewhat decreased and the bead apparences are deteriorated.

Investigation on the weldability of Cr-Ni austenitic heat-resisting steels containing high concentration of nitrogen has today been continued.

Change of Nitrogen Concentration by High-Temperature Heating with a Steel Melted and Cast in High-Pressure Nitrogen

Even a steel with high-N concentration that had been obtained by high-pressure melting presumably would not be worthy of the significance of high-pressure melting if the N was diffused and evolved from steel. In order to make clear this point experimentally, with 316L type steel containing 0.450%N, the weight change during heating to 1,100°C in air and in a vacuum was traced, using a thermo-balance, and the change of N% before and after heating was obtained by chemical analysis. The specimen had a dimension of 8 x 55 x 0.6 mm and a weight of about 2g. While heating in vacuum to 1,100°C for about 45 mm, it experienced a weight decrease from around 600°C. This continued even during holding at 1,100°C. The chemical

analysis of the specimen after heating for 3 h at 1,100°C indicated that the N concentration was decreased from 0.450% to 0.292%. The value nearly corresponded with the weight decrease measured by the thermo-balance. After heating in air, however, a remarkable increase in the weight was noted. Most of such an increase presumably was due to oxidation of the specimens. However, in accordance with the results of chemical analysis, the N concentration was slightly increased from 0.450% to 0.477%. These results indicate that the steel melted under high pressure showed remarkable denitriding after heating at a high temperature in high vacuum, while no denitriding occurred when it was heated in air, but rather there was a slight tendency to absorb nitrogen.

Creep and Creep-Rupture Properties of Austenitic Heat-Resisting Steels Melted and Cast under High-Pressure Nitrogen

Creep-rupture tests were made at 700°C on the 316L steel containing various amounts of nitrogen. Results are shown in Figure 5. The 1,000 hr rupture strength of the steel increases markedly with increasing nitrogen content and is almost doubled at 0.33%N, while the strength decreases with further increasing nitrogen content. The later decrease in the strength is attributable to a rapid precipitation of supersaturated nitrogen from the austenite matrix. It has been reported that nitrogen, unlike carbon, is one order higher in its solubility in the base austenite [15]. Fiture 6 shows steady state creep rate-stress data at 700°C for 18Cr—14Ni austenitic steels with or without Mo and N. From this results, a relation between creep strength at the strain rate of 0.1%/hr and nitrogen content in the steel are obtained as shown in Figure, and a power law dependence n [16] for creep are as follows:

| Mark | Composition | | | Power law |
	C%	Total N%	Mo%	dependence n
N1	0.015	0.017	0.01	5.8
N2	0.004	0.264	0.01	5.5
NM1	0.012	0.039	2.04	8.5
NM2	0.002	0.277	2.10	8.0

It is quite clear that nitrogen, dissolved as an interstitial solute in the austenite together with Cr and Mo, may considerably increase the creep resistance. If, then, nitrogen in excess of about 0.3%, combined with Cr, Mo, and other elements, can be retained as dissolved for a long time at high temperature for use, it can be anticipated that the strength will be further increased.

Thus, 25%Cr—28%Ni was chosen for the base composition of the steel to be developed. 28%Ni content was selected in this steel to secure the austenitic phase even when a certain amount of ferrite- or σ-forming elements such as Mo and W are added. 25%Cr content was selected
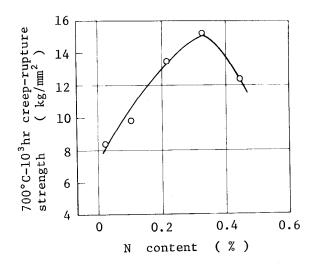
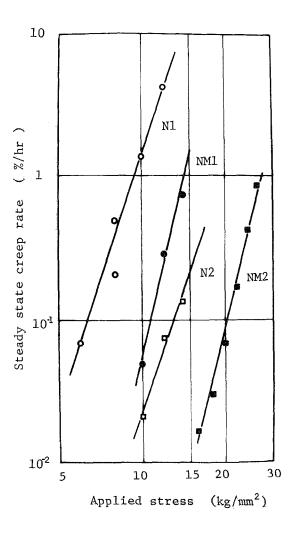Figure 5. Effect of nitrogen on creep-rupture strength of the type 316L steel at 700°C.

Figure 6.   Influence of Mo and N on stress-creep rate curve of 18%Cr—14%Ni austenitic steel.

Steel	C %	Ni %	Cr %	Mo %	Total N %
N1	0.015	13.36	17.08	0.01	0.017
N2	0.004	14.08	17.94	0.01	0.264
NM1	0.012	13.77	17.94	2.04	0.039
NM2	0.002	14.08	17.89	2.10	0.277
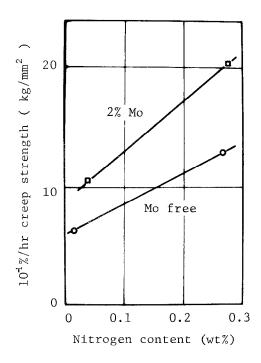
Figure 7.   Relation between 10^{-1}%/hr creep strength and nitrogen content of 18%Cr—14%Ni austenitic steel with or without Mo.

to promote oxidation resistance at high temperatures such as 700°C or above and to secure a high concentration of nitrogen in the steel which is melted and cast under a high-pressure nitrogen atmosphere.

High-pressure melting technique was applied to this 25%Cr—28%Ni steel so that nitrogen of up to about 0.54% could be alloyed. The effects of Mo and N on the creep rupture strength at 700°C are summarized in Figure 8.

In Figure 8(a), the effects of Mo are classified by low nitrogen steel (less than 0.10%N), medium nitrogen steel (0.15—0.20%N) and high nitrogen steel. In the case of low nitrogen and medium nitrogen steels, the increase in strength due to the addition of Mo follows a similar trend. The increment of strength at 6% Mo is 5—6 kg/mm^2. However, the effect of Mo in high nitrogen steel shows a different tendency. The strength increases markedly by more than 10 kg/mm^2 with the addition of 2% Mo. This can be more clearly observed in Figure 8(b). The effect of nitrogen in about 0.2% is almost the same, whether Mo is added or not; however, at levels higher than 0.2%, the strength drops sharply in the absence of Mo, while in a steel containing this element the strength increases almost linearly with increasing nitrogen. It is interesting to note here that when Mo is added to a high nitrogen steel, a special effect on strength is observed due to the coexistence of Mo and N [17, 18].

In order to obtain some information on the strengthening mechanism in these high nitrogen steels, metallographic and X-ray diffraction studies were made. Variation in lattice parameter of austenite matrix due to aging at 700°C was measured on two kinds of steels, whose chemical compositions are as follows:

Mark	C	Cr	Ni	Mo	N
22N	0.011	26.28	27.81	1.21	0.221
31N	0.009	24.49	27.84	2.11	0.311

In the 22N steel having 0.22%N and 1.21%Mo, no parameter change of austenite, that is, no precipitation of nitride, occurs during aging at 700°C up to 3,000 hr, whereas in 31N steel having 0.31%N and 2.11%Mo, a marked decrease in the parameter occurs. From metallographical examinations, a precipitation of σ-phase, instead of Cr$_2$N, is observed in aged specimens of 21N steel, whereas in 31N steel a precipitation of Cr$_2$N and π-phase (β-Mn structure [19]) is observed both within grains and on grain boundaries or twin boundaries.

It was concluded from these results that, in the high nitrogen steels with Mo, about 0.2%N is retained as dissolved in the austenite matrix for a long period of creep rupture testing even at such high temperatures as

700°C and contributes together with Mo to creep rupture strength through the solid solution strengthening mechanism.

In most of the heat-resistant steels, carbon is used as an alloying element for high temperature strengthening. For purposes of comparison, effects of carbon on 25%Cr—28%Ni—2%Mo steel were investigated. In the case of the specimen solution treated at 1,250°C, the 700°C—1,000 hr rupture strength rises almost linearly in proportion to the carbon content, reaching 15.5 kg/mm^2 at 0.35% carbon. This strength is about 2 kg/mm^2 less than when the same weight percent nitrogen is added. In addition, rupture elongation is always greater than 20% when nitrogen is added, but in the 0.35% carbon steel solution quenched from 1,250°C, the elongation is less than 10%.

Experiments were also made in which carbon and nitrogen were added. The 700°C—1,000 hr rupture strength of a steel containing 0.17% carbon and 0.27% nitrogen was obtained, and it is noted that the strength at the same level of Mo and N is smaller than that of the steels containing less carbon.

It can be said from these results that, in the high nitrogen steel, the addition of carbon is not required and should be avoided.

In further investigation, a large amount of nitrogen was added in combination with V, W and B to 25%Cr—28%Ni—2%Mo steel, then the steel was tested for creep rupture strength at 700°C. Some of the test results are shown in Figure 9. Steel 31N22W shows an almost linear stress-rupture curve even after the test period of 20,000 hr at 700°C and possesses rupture strengths of 23.0 kg/mm^2 in 1,000 hr and 14 kg/mm^2 in 10,000 hr. The strengths of steel 31N22W are greater than those of steel 48N09V and 42N03B, although nitrogen content in that steel is relatively low. This shows that coexistence of W and N together with Mo contributes remarkably to strengthening. Steel 42N03B has an excellent high temperature ductility. It contains about 0.03%B and has a rupture elongation of more than 60%, which increases with increasing rupture time.

In view of the above facts, combinations of B, W and N were added to 25%Cr—28%Ni—2%Mo steel which was then tested. W content was fixed in the range of 5.1—5.7% to examine the effect of nitrogen. In Figure 10 (a), the rupture strength of 700°C—1,000 hr rises sharply with the addition of nitrogen, reaching a high level of more than 26 kg/mm^2 at a N level of about 0.67%. Compared with other steels not containing W and B (shown by dotted line), a marked strengthening effect due to the simultaneous addition of B and W is observed in the low concentration range of nitrogen. The rupture strength (700°C—1,000 hr) of steel 42N03B is also shown in the figure. It is noted that the strength increment due to 5%W
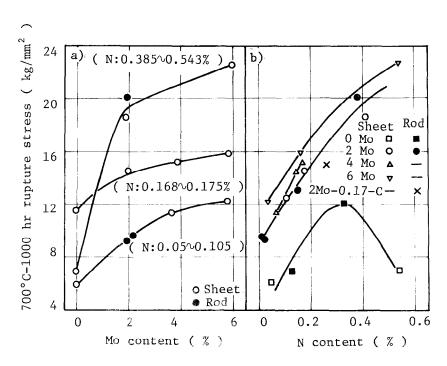
Figure 8. Effect of Mo and N on 700°C—1,000 hr creep-rupture strength of the 25%Cr—28%Ni austenitic steels (solution treatment : 1,200°C)
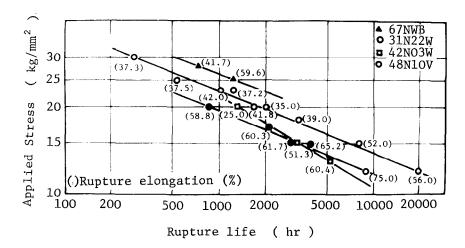

Figure 9. Typical stress-rupture curves at 700°C of 25%Cr—28%Ni—2%Mo austenitic heat-resisting steel (solution treatment : 1,200°C)

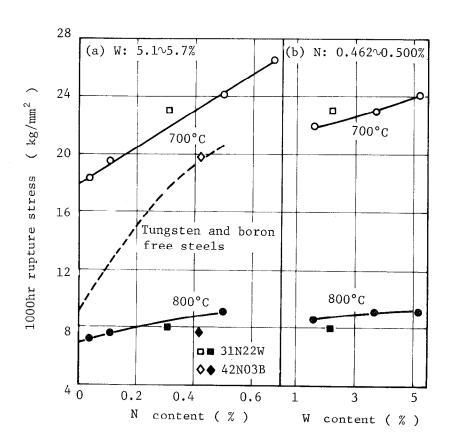| Steel	C %	Cr %	Ni %	Mo %	W %	V %	B %	Total N %
31N22W	0.028	23.53	26.46	1.55	2.19	—	—	0.307
42N03B	0.005	24.16	27.78	1.80	—	—	0.027	0.420
48N09V	0.028	24.45	27.65	1.55	—	0.95	—	0.483
67NWB	0.020	24.62	27.12	1.90	5.70	—	0.050	0.668

Figure 10. Effect of N and W on 1,000 hr creep-rupture strength at 700°C and 800°C of the 25% Cr—28%Ni—2%Mo—0.05%B steels (solution treatment : 1,200°C)

is about 3.5 kg/mm^2 in the neighborhood of 0.42%N. Also indicated in the figure is the strength of steel 31N22W. Here, at 700°C, steel containing low W (steel 31N22W) shows a slightly higher strength than that containing high W, while the reverse is true for 800°C—1,000 hr. At 800°C, as at 700°C, the strength of a steel in which W and B coexist is improved by the addition of nitrogen. An increment of about 2 kg/mm^2 is brought about by the addition of 0.5% nitrogen. As shown in Figure 10(b), at a fixed level of nitrogen, the rupture strength increases almost linearly with the addition of W, both at 700°C and 800°C, but this effect is not as pronounced as is observed in Figure 10(a) when the nitrogen content is changed.

The minimum value of creep rupture elongation encountered in these experiments was not less than 20%, showing that these steels generally have a good high temperature ductility. Steels containing B particularly have an excellent ductility.

When, as described above, Mo, W, V and B are added in various combinations, with 25%Cr—28%Ni steel as the base, and with the use of the high-pressure melting technique, the 700°C—1,000 hr creep rupture strength far exceeds 20 kg/mm^2, and the high temperature ductility is also greatly improved. Of the 25%Cr—28%Ni steels tested, those which have 700°C—1,000 hr rupture strength far stronger than 20 kg/mm^2 are 1.9%Mo—5.7%W—0.67%N—0.05%B steel, 2.1%Mo—5.2%W—0.50%N—0.05%B steel and 1.6%Mo—2.2%W—0.31%N steel, whose rupture strengths are 26.5, 24.1 and 23.0 kg/mm^2, respectively.

Summary and Conclusion

In the article above, the basic conditions were determined for safely and surely melting high—Cr steels with a remarkably high nitrogen concentration by employing a new melting and casting method under high-pressure nitrogen. Almost all kind of steel, manufactured by application of this method of melting, shows a good ability for forging, machining, and welding, even when it contains high concentration of nitrogen.

And high strengh heat-resisting steels were developed which contains such elements as N, Mo, W, V, and B with 25%Cr—28%Ni as the base composition. Particularly, to utilize remarkable strengthening effect of high concentration of nitrogen, some of the steels tested were prepared using the aforementioned melting method. It was presumed from metallographic and X-ray studies that, in the high nitrogen materials with Mo, about 0.2% nitrogen is retained as dissolved in austenite matrix for long period of testing even at such high temperature as 700°C, and contributes together with Mo to creep-rupture strength through the so-called solution strengthening mechanism.

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