NIOBIUM IN FERRITIC AND MARTENSITIC STAINLESS STEELS

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Abstract

A review has been presented of the effects of niobium in ferritic and martensitic stainless steels, introducing some new stainless steels containing niobium. An addition of niobium to the steel has a beneficial effect on improving the corrosion resistance of ferritic stainless steel, since niobium reacts with carbon to form stable carbides, consequently, resulting in keeping effective content of chromium in the matrix. Niobium added 22% chromium-1.2% molybdenum ferritic stainless steel shows remarkable environmental corrosion resistance in comparison with Type 304 and 316. An addition of niobium is one of the most effective ways to give a ferritic stainless steel a good deep drawability. An amount of niobium, which is necessary to improve this property, is related to a content of carbon and nitrogen. Ferritic stainless steels containing an appropriate amount of niobium exhibit good mean r-value. Soluted niobium and molybdenum are effective in improving the high temperature strength. An amount of soluted niobium depends on the annealing temperature, and niobium precipitates rapidly when the steel is annealed at the lower temperature. Therefore, this behavior of niobium affects complicatedly on mechanism of the influences of this alloying element on the high temperature strength. Niobium added martensitic stainless steel shows very good tempering resistance, since niobium is beneficial to inhibit forming chromium carbides. Consequently, martensitic stainless steel is able to keep effective content of chromium in the matrix, which causes for the steel to improve corrosion resistance, as same as ferritic stainless steel.

Introduction

Stainless steel has been used variously nowadays owing to its many superior properties such as formability, strength, and corrosion resistance. History of stainless steels is just about 100 years, which means very short term in comparison with other steels and metals. In addition, it has been as short as approximately 50 years since stainless steels commenced to be manufactured commercially and used for materials of many types of applications.

Type 304 and Type 430 are well known as the most popular stainless steels and presumably dominate more than half of all products of stainless steels. However, demands for stainless steel has grown markedly in this decade, consequently, various types of stainless steels with significantly good properties have been developed and used for many applications.

In recent years, one of the applications for stainless steels has been markedly growing, that is, materials of an exhaust gas emission control system for vehicle has been changed from carbon steel to stainless steel (1, 2). In this application, heat resistance, i.e. high temperature strength and thermal fatigue resistance is required for the stainless steel, and niobium has been studied as a very effective alloying element to improve those properties.

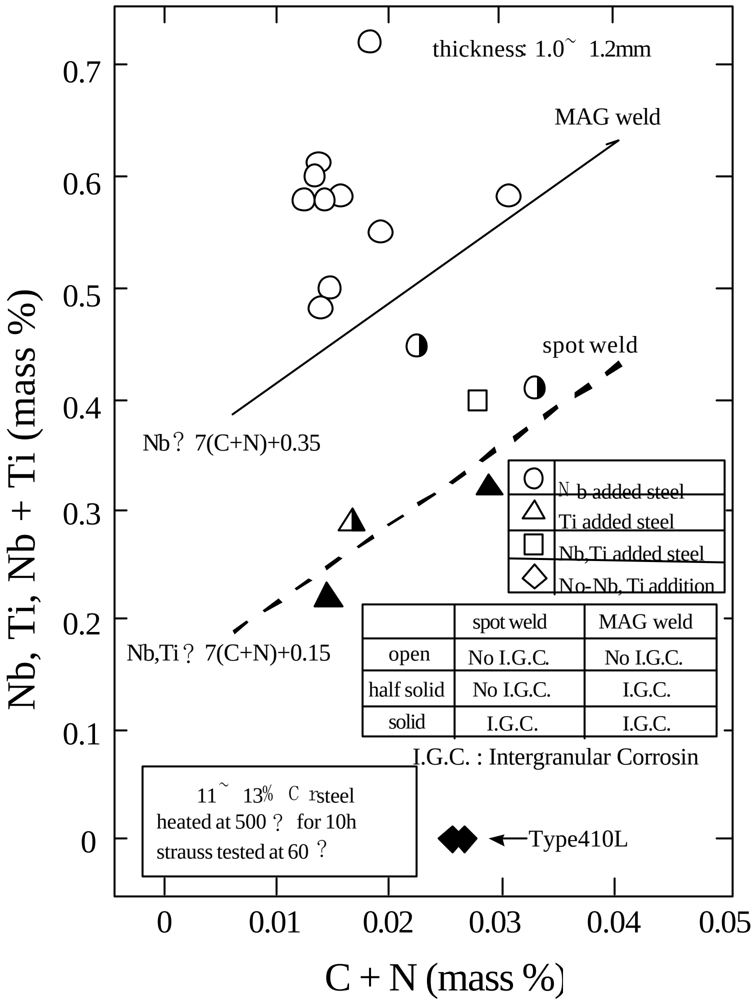
In another applications of exhaust gas emission control system, stainless steels are used as material for a muffler because of its good corrosion resistance (3). The most important and necessary property for the steel used for this application is intergranular corrosion resistance against exhaust emission gas environment. Particularly, the intergranular corrosion takes place in welded area due to a sensitization of the material. Since niobium is quite effective to improve intergranular corrosion resistance, 11mass% chromium based stainless steel containing niobium has been studied for this application.

As niobium is very useful for improving various properties of stainless steel, influences of niobium of stainless steel have been widely studied. In this report, emphasis is placed on the effects of niobium on various properties such as high temperature, corrosion resistance, formability, and tempering resistance of ferritic or martensitic stainless steels. Furthermore, remarkable properties of new developed stainless steels containing niobium are introduced to show the effects of this alloying element.

Effect of Niobium on Corrosion Resistance of Ferritic Stainless Steel

Effects of Niobium on Intergranular Corrosion of 12% Chromium Based Ferritic Stainless Steel

Type 410L or Type 409 has been used for material for the exhaust gas emission system of a vehicle because of their good corrosion resistance, formability, and heat resistance (4). However, in recent years, temperature of exhaust gas has been designed higher, since the higher temperature of exhaust gas contributes for a catalytic converter to reduce the amount of harmful gasses, such as NOx, SOx, and HC (5). On the contrary, the higher temperature possibly results in more corrosive environment for the material. For instance, a precipitation of chromium-carbide takes place at the temperature of exhaust gas in a muffler, i.e. 400-500? , which results in depletion of chromium in grain boundaries followed by intergranular corrosion. Since weld area is particularly susceptible to the intergranular corrosion, it is necessary to improve the corrosion resistance of the 12% chromium based steel or develop a new steel which shows good property against this type of corrosion.



	spot weld	MAG weld
open	No I.G.C.	No I.G.C.
half solid	No I.G.C.	I.G.C.
solid	I.G.C.	I.G.C.

I.G.C. : Intergranular Corrosin

Figure 1: Effects of niobium and titanium and carbon + nitrogen content on intergranular corrosion of welds for 12mass% chromium ferritic stainless steel.

The effects of niobium and titanium on improving the intergranular corrosion resistance of 12% chromium weld steel were studied (Figure 1) (3). Lowering carbon and nitrogen content in the steel is quite effective to inhibit intergranular corrosion, as studied before (6). Then, an addition of niobium and titanium to the steel has a furthermore beneficial effect on improving the corrosion resistance. Precipitation of chromium carbide in MAG weld area tends to take place much more than in spot type weld, since a rate of cooling after MAG weld is rather low in comparison with a spot type weld. Therefore, amount of niobium and titanium, which is necessary for the steel to inhibit the corrosion in MAG weld, is higher than in spot type weld. It is concluded with this figure that more than 7(C+N)+0.35 mass% niobium content is necessary to inhibit intergranular corrosion in case of MAG weld area. Meanwhile, more than 7(C+N)+0.15 mass% niobium is necessary in case of spot type weld. Substantial intergranular corrosion takes place at the interface between the heat affected zone and base metal in MAG weld area of Type 410L (Figure 2). Type409L aged at 500? for 10h shows intergranular corrosion in base metal in adjacent to the weld metal, while 12Cr-0.6Nb steel aged at 500? for 10h exhibits good corrosion resistance.

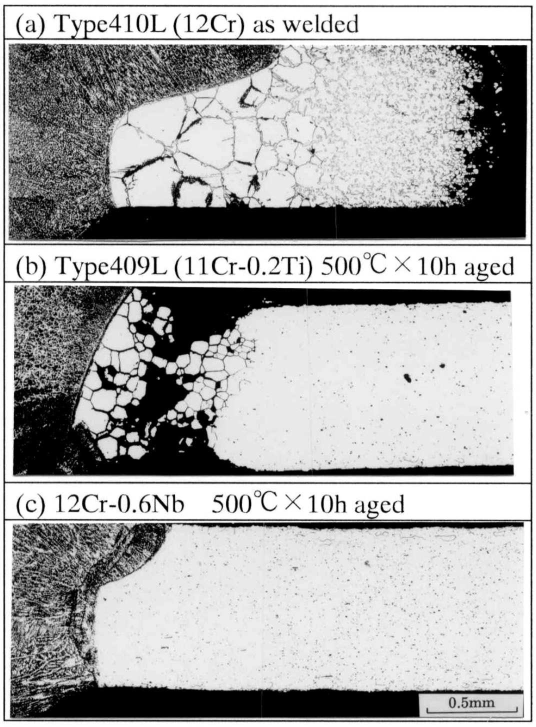


Figure 2: Microstructures of cross section of MAG weld after corrosion test.

Effects of Niobium on Atmospheric Corrosion For 22% Chromium Based Ferritic Stainless Steel

Since ferritic stainless steel has good atmospheric corrosion resistance, this type of stainless steel has been used for roofs and curtain walls recently (7). However, atmospheric condition is especially hard to the material for roofs with respect to corrosion in some area where sea is in relatively short distance, because particulate coming from sea water is quite corrosive substance. Considering these conditions for atmospheric corrosion, rather high chromium contained ferritic stainless steel has been examined for this applications. Furthermore, effects of niobium on atmospheric corrosion resistance of ferritic stainless steel were investigated, and a new ferritic stainless steel containing small amount of niobium was developed (7).

Table I Chemical compositions of ferritic stainless steel for atmospheric corrosion.
(mass%)

C	Si	Mn	Cr	Mo	Nb	Ti	Al	N
0.01	0.21	0.20	22.1	1.23	0.25	0.19	0.08	0.01

Representative stainless steel for atmospheric corrosion contains high chromium and molybdenum with small addition of niobium and titanium (Table 1). 22 mass% chromium-1.2 mass% molybdenum steel was determined as basic metal on the basis that sufficient amount of chromium and molybdenum is indispensable to improve a pitting potential of the stainless steel. According to the results of the experiment of the pitting potential, niobium is considered effective on improving pitting corrosion resistance (Figure 3). In this figure, pitting potential experiment was done with condition of 20%NaCl at 80? . Since there is a tendency that pitting potential decreases with increasing niobium content, 0.25mass% niobium is added to the developed steel. Rust area of such austenitic stainless steels as Type 304, 316 increases significantly with increasing cycle number (Figure 4). Meanwhile, the rust area curves of ferritic stainless steels, such as Type444 and the developed steel, are characterized by a slight increase in the first 600 cycles followed by a rather flattering of the curve at longer cycles. The developed steel shows the lowest rust area in all tested steels at any cycles.

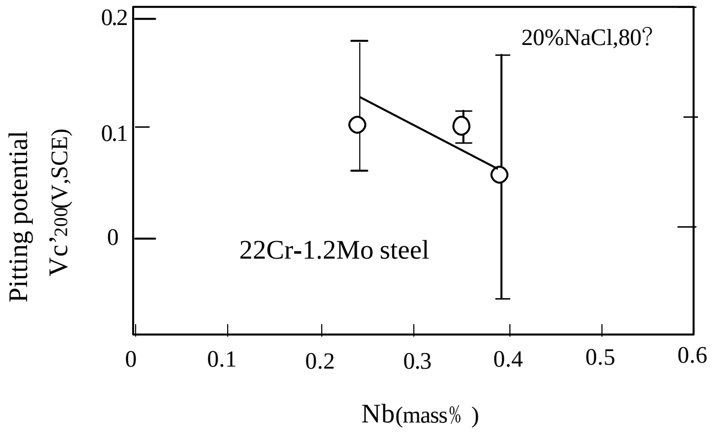


Figure: 3 Effect of niobium on pitting potential of 22mass%Cr-1.2mass%molybdenum.

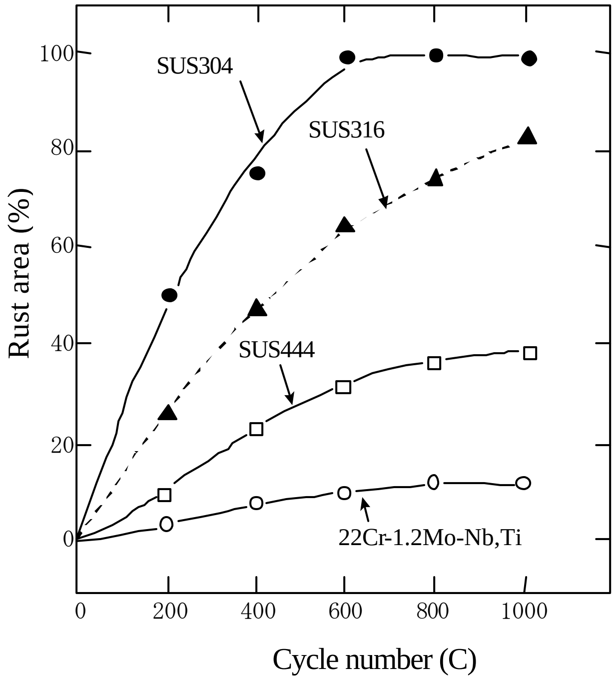


Figure 4: Rust area of specimens after cyclic corrosion test.

Effect of Niobium on Formability of Ferritic Stainless Steel

Cost of the ferritic stainless steel is relatively lower than austenitic stainless steel, consequently, a product of ferritic stainless steel represented by Type 430, has been growing nowadays. An application of the ferritic stainless steel is so various that required properties for each application change respectively. However, formability of ferritic stainless steels is inferior to that of austenitic stainless steel like Type 304. Accordingly, many investigations have been carried out on the formability of ferritic stainless steel, especially, deep drawability has been the most significant concern. As described before, corrosion resistance of ferritic stainless steel is improved by an addition of small amount of such alloying elements as niobium. Similarly, an effect of niobium has been studied with respect to the formability of ferritic stainless steels, which leads to the conclusion that an addition of niobium is one of the most effective way to give a ferritic stainless steel a good deep drawability (8, 9). An amount of niobium, which is necessary to improve this property, is associated with a content of carbon and nitrogen. An appropriate amount of niobium gives ferritic stainless steel good mean r-value (Figure 5) (8). The excellent deep drawability of the niobium-stabilized sheet is strongly related to the texture component of matrix, which is affected by cold rolling reduction and annealing temperature (9).

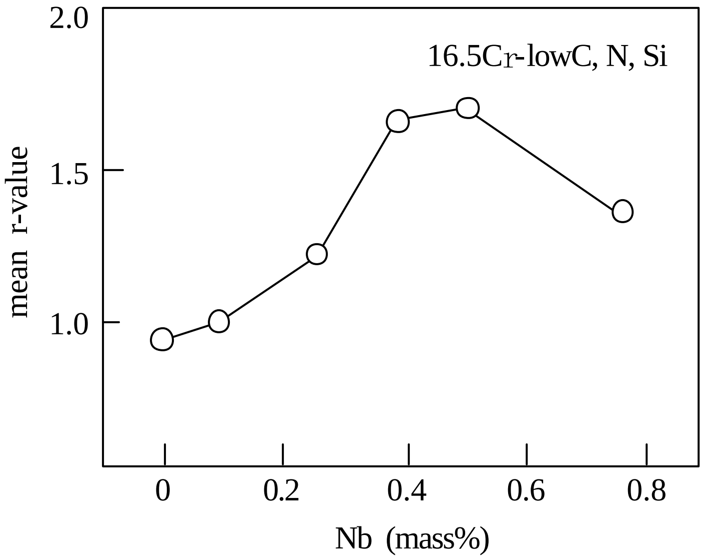


Figure 5: Effect of niobium on mean r-value of 16.5mass%Cr stainless steel.

Many studies have been done about an effect of titanium and niobium on press formability, represented by mean r-value, concluding that appropriate amounts of those elements are effective. However, a deleterious factor is also present in case of an excessive addition of those elements (10, 11). For example, a transition temperature of a longitudinal crack increases with increasing of titanium content (Figure 6) (10). Although, niobium raises the transition temperature as well, the gradient of the curve versus niobium content is rather lower in comparison with the effect of titanium. Even though a ferritic stainless steel has good mean r-value, making a deformation is possibly difficult in case of the higher transition temperature, since this transition temperature is one of the decisive factor for formability.

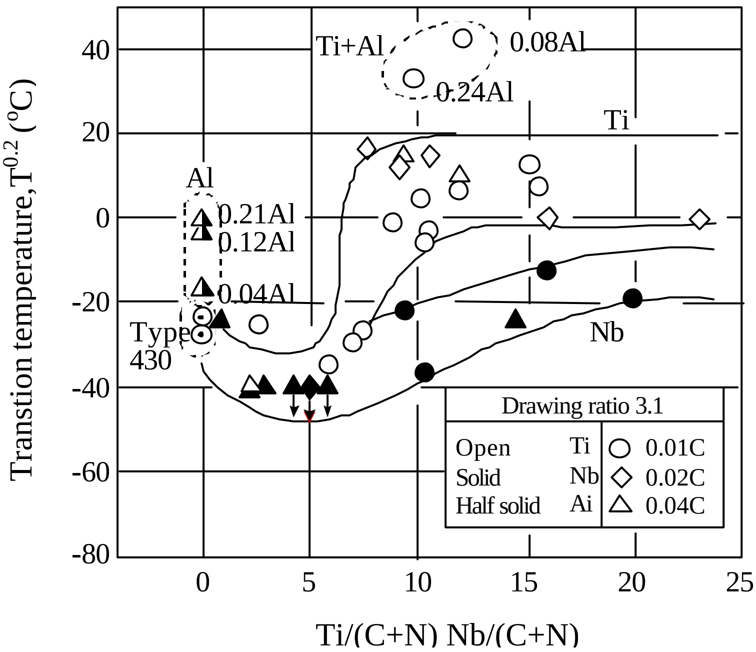


Figure 6: Effect of Ti/(C+N) and Nb/(C+N) on transition temperature.

Type 430LX, basic chemical composition of which is shown in Table 2, is the representative ferritic stainless steel containing small amount of niobium. Since this steel has both better formability (Table3) and superior corrosion resistance in comparison with Type 430, number of applications has been growing remarkably.

Table II Chemical compositions of Type430LX ferritic stainless steel (mass%)

C	Si	Mn	Cr	Nb	N
0.01	0.23	0.20	17.2	0.40	0.01

Table III Mechanical properties of Type430LX and Type430

	Proof stress (N/mm^2)	**Tensile stress (N/mm^2)**	**Erichsen -value (mm)**	**Elongation (%)**	**Hardness (HV)**	**mean r-vaule**
Type430LX	290	510	9.9	30	151	1.75
Type430	340	520	9.1	30	160	1.11

Precipitate of niobium appears in ferritic stainless steel containing niobium depending on the annealing temperature. Recrystallization does not take place sufficiently if NbC is existent in the matrix, in other words, having NbC soluted in matrix is indispensable for recrystallization. Accordingly, increasing content of niobium and carbon leads for the steel to raise the recrystallization temperature. Recrystallization is considered the one of the most decisive factor for ridging (roping) property, which is due to an unfavorable texture formed during hot rolling, of a ferritic stainless steel. Recrystallization temperature of titanium added ferritic stainless steel is not so high in comparison with niobium added ferritic stainless steel, consequently, when both steels are annealed at the same temperature, recrystallization occurs more rapidly in titanium added steel. This behavior enables titanium added steel to show better ridging property than niobium added steel in case of annealing at the same temperature.

In other words, ridging property degrades in order of niobium and carbon content due to the precipitation of NbC, which enhance recrystallization temperature (Figure 7) (12).

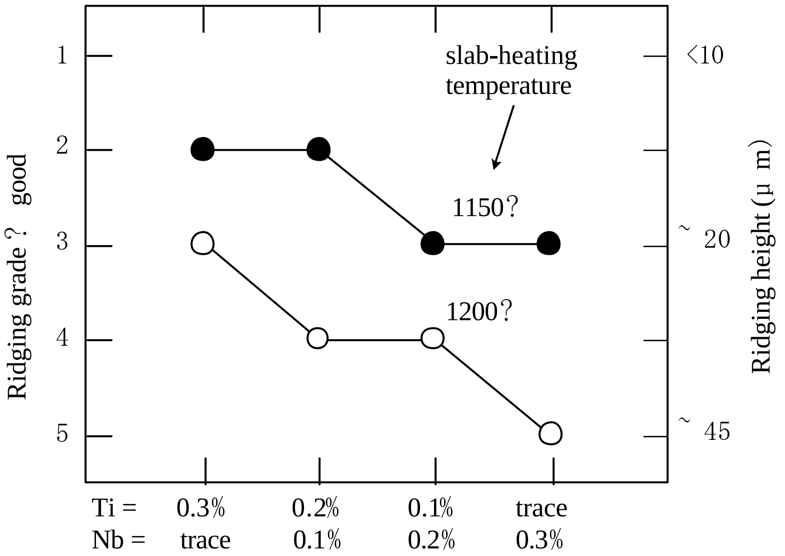


Figure 7: Comparison in the ridging property of 16mass%Cr ferritic stainless steel containing various titanium and niobium.

Effects of Niobium on High Temperature Strength of Ferritic Stainless Steel

Type 409L (11Cr-Ti) is used as material for an exhaust manifold of a vehicle designed for exhaust gas at temperature of about 800? and Type 430J1L(18Cr-0.4Nb-0.5Cu) is used for about 900? . However, the exhaust gas temperature is still designed higher, which result in shift of the material toward the higher quality of stainless steel. However, the heat resistance of a conventional high-chromium contained ferritic stainless steel is not satisfactory for the manifold. Therefore, there has been a strong demand for a heat resistant ferritic stainless steel having a competitive cost. Considering this demand into account, the effect of niobium and molybdenum on high-temperature properties have been investigated on the base of Type 430LX (18Cr-Nb) in order to improve the heat resistance of the ferritic stainless steels used for exhaust manifold (1). 18Cr-Nb ferritic stainless steel was the basic tested alloy, and effects of niobium and molybdenum on high temperature strength were investigated. Molybdenum is considered effective on improving the high temperature strengthening, since proof stress increases linearly with increase of molybdenum content at both temperature of 900? and 1000? (Figure 8 and 9). It is found that a similar tendency is observed in niobium effect. The proof stress increases linearly as a function of niobium content up to 0.8mass% followed by rather flattered curve at more than 0.8mass% niobium. Compared these figures, niobium is considered more effective on improving the high temperature strength in case that the same amount of these elements are added to the steel. The high temperature strength is largely dependent on an amount of solid solution and precipitation as well as grain size. In this study, solid solution and precipitation is considered decisive factors, since the grain size of all the tested specimens were almost same, i.e. the grain size number of the specimens is between four and five. Considering these facts, the annealing temperature was changed to clarify the effects of the amount of solid solution and precipitates on the high temperature strength of 18Cr-2.0Mo-0.5Nb steel and 18Cr-2.2Mo-1.0Nb steel at 1000? (Figure 10). The proof stress in 18Cr-2.0Mo-0.5Nb steel rises slightly at the temperature from 1000? to 1050? followed by nearly constant value at over 1050? . As for 18Cr-2.2Mo-1.0Nb steel, the curve is quite different from 18Cr-2.0Mo-0.5Nb steel, that is, the proof stress increases remarkably with increasing the annealing at the temperature of over 1050? . It is considered that all amount of molybdenum for both steels is soluted in matrix annealed at the temperatures between 1000 and 1200? , since an amount of molybdenum in solid solution is nearly constant at every annealing temperatures, and also very close to the contained quantity (Figure 11). On the contrary, the amount of niobium in solid solution for 1.0mass%Nb steel increases as the annealing temperature rises. However, the amount of niobium in solid solution for 0.5mass%Nb steel is not significantly affected by the annealing temperature. These behavior is well corresponding to the change in 0.2% proof stress shown in Figure 9. It is suggested that soluted niobium and soluted molybdenum are effective in improving the high temperature proof strength.

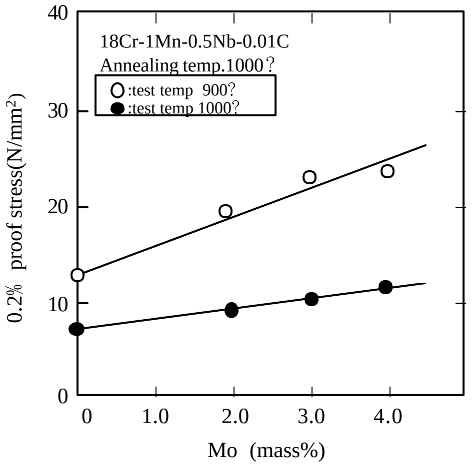


Fig. 8. Effect of molybdenum on proof stress of ferritic stainless steel at 900 and 1000? .

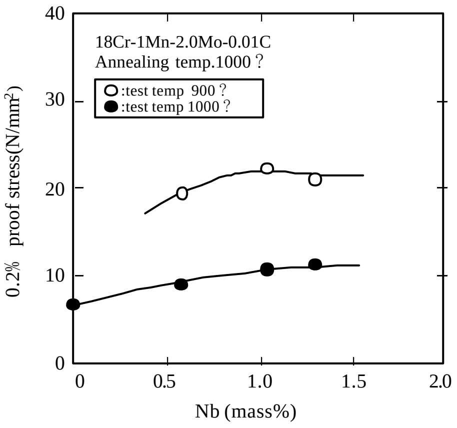


Fig. 9. Effect of niobium on proof stress of ferritic stainless at 900 and 1000? .

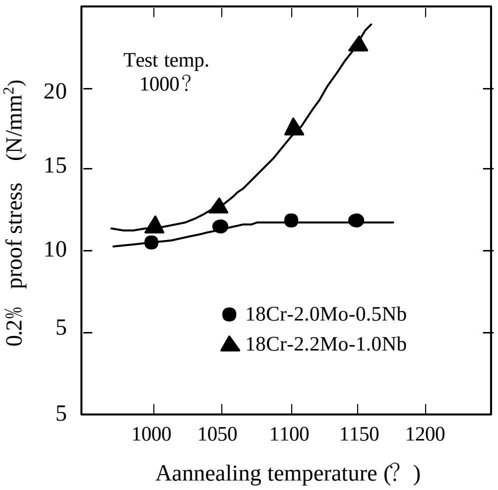


Figure 10: Effect of annealing temperature on proof stress of ferritic stainless steel at 1000? .

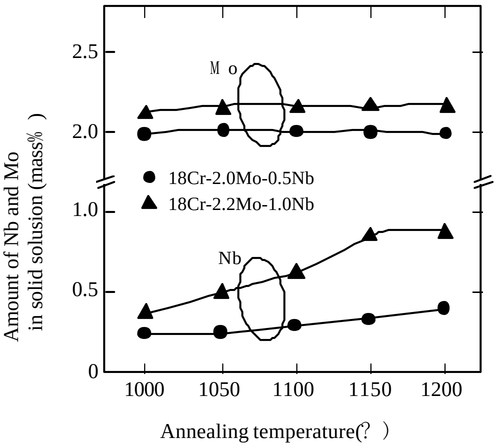
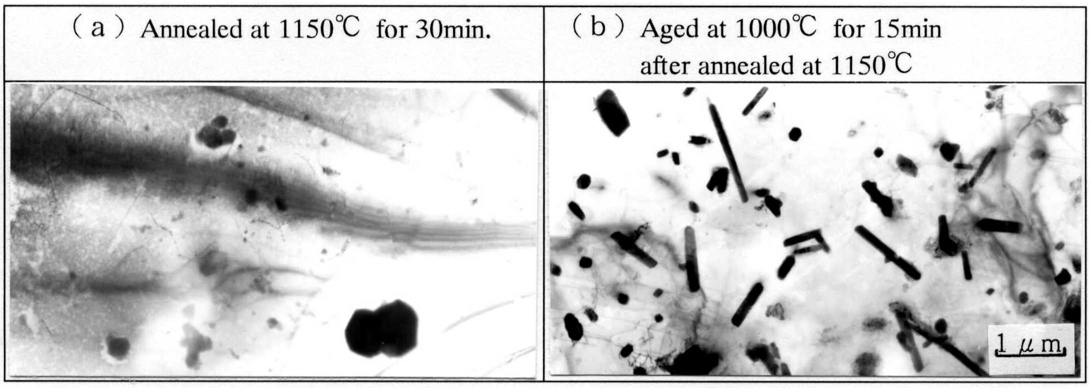


Figure 11: Effect of annealing temperature on amount of niobium and molybdenum in solid solution.

In this high temperature strength test, specimens are heated from the room temperature to the test temperature in 15 minutes followed by keeping at the test temperature for 15 minutes before the tensile test starts. It is necessary to take the effects of these procedures on microstructures into consideration, therefore, precipitation behaviors of molybdenum and niobium in those procedures were studied. The microstructures of 18Cr-2.2Mo-1.0Nb steel annealed at 1150? for 30 minutes (annealed specimen; Figure 12a) and aged at 1000? for 15 minutes after annealing treatment (specimen before the tensile test starts; Figure 12b) were observed as follows. In the annealed specimen (Figure 12a), the precipitates of approximate 1.0μ m in diameter are present. From the result of diffraction patterns of the precipitates, it is confirmed that the spherical precipitates are identified as M_6X and MX carbonitride. Finely dispersed rod-shaped precipitates, which appear during the procedure of heating specimen or keeping the tested temperature, are identified as Fe_2Nb Laves phase (Fig.12b).


（a） Annealed at 1150℃ for 30min.

（b） Aged at 1000℃ for 15min after annealed at 1150℃

Figure 12: TEM observation for precipitates of 18Cr-2.2Mo-1Nb.

Mass ratio of precipitates to matrix for each elements of 18Cr-2.2Mo-1.0Nb steel were measured so as to study the mechanism of the improving high temperature strengthening (Table 4). Molybdenum does not exist as precipitate even though various heat treatments are done. All amount of molybdenum solute in the matrix at the temperature above 1000? , which makes it clear that the increase in 0.2% proof stress with increasing molybdenum content is due to the solution strengthening of this element. Both ratios of niobium and iron in specimen (a) are relatively small. However, both ratio of those elements in specimen (b) are larger than specimen (a), which means the amount of precipitates increase significantly during aging at 1000? . The ratios is close between specimen (b) and specimen (c) , which means that the amount of precipitates depend largely on the annealing temperature. It is thought that soluted niobium in matrix after annealing at 1150? precipitates as Laves phase during the heating before the tensile test. Therefore, it can not be clearly concluded that the increase in 0.2% proof stress at high temperature (Figure 10) is attributable to solid solution strengthening.

Table IV Ratio of precipitates to matrix for each elements of 18Cr-2.2Mo-1.0Nb steel. (Mass%)

heat treatment	Fe	Cr	Nb	Mo
(a) annealed at 1150? for 30min.	0.11	0.04	0.14	0.02
(b) aged at 1000? for 15 min. after annealed at 1150? for 30min.	0.87	0.17	0.62	0.02
(c) annealed at 1000? for 30min.	0.91	0.16	0.61	0.02

Since Laves phase (in Figure 12b) precipitates at an interval of about 1µ m in length before the tensile test starts, it is suggested that the increase of 0.2% proof stress with increasing of annealing temperature in 18Cr-2.2Mo-1.0Nb steel shown in Figure 10 is due to the precipitation strengthening of niobium. Dependence of high temperature strength of 0.5mass%Nb steel on annealing temperature is smaller than that of 1.0mass%Nb steel, because the Laves phase precipitated is few in 0.5mass%Nb steel. It is inferred from the result of Figure 11 and Table 4 that the amount of about 0.3mass% niobium is effective in solution strengthening.

Effect of Niobium on the Properties of Martensitic Stainless Steel

Martensitic stainless steel has characteristically high hardness. Especially, precipitation hardening type of the martensitic stainless steel has the hardest phase in all type of stainless steels, therefore, this type of stainless steel is used for various applications. Precipitation hardening type of martensitic stainless steel has Ms (Temperature for martensite transformation start on cooling) above room temperature, therefore, it shows martensitic substrate by solution heat treatment. For the purpose of increasing hardness, additional alloying elements such as copper, titanium, aluminum, and niobium are contained in this type of stainless steel. These alloying elements are effective to increase hardness by aging at the temperature of 300~500? , because of precipitates of these alloying elements. Accordingly, this stainless steel does not need quenching to achieve maximum hardness unlike the martensitic stainless steel of Type 420. The process of the aging treatment seems easier than quenching for manufacturers or customers for these stainless steels. Additionally, relatively low carbon content gives this type of stainless steel good corrosion resistance. Hence, it is likely that applications of the precipitation type of martensitic stainless steels are growing nowadays.

Niobium is added to several precipitation hardening type of martensitic stainless steels (Table 5). 17-4PH was developed by Armco Steel Corp. It contains carbon content lower than 0.07mass% for the purpose of improving formability by decreasing hardness of solution treated steel. Aging gives this steel very high hardness, since fine Cu-rich phase precipitates at the aging temperature. In this steel, niobium is added to the steel to stabilize carbon by forming niobium carbide, which results in inhibiting to form chromium carbides. Additionally, niobium added steel shows good tempering resistance, that is, the decrease in hardness versus tempering temperatures lowers with increasing niobium content (Figure 13) (13).

Table V Chemical compositions of representative precipitation type of martensitic stainless steels (mass%)

	C	Si	Ni	Cr	Cu	Ti	others
SUS630	0.05	0.3	4	17	4		Nb+Ta:0.3
ASTM XM-12	0.04	0.3	4.5	15	3		Nb+Ta:0.3
ASTM XM-16	0.03	0.3	8.5	11.8	2.25	1.2	Nb+Ta:0.3
ASTM XM-25	0.03	0.25	6.5	14.9	1.5		Nb:0.75

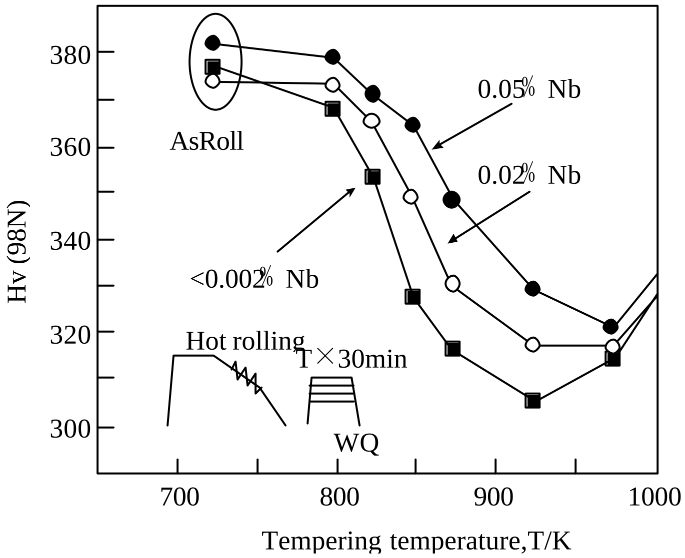


Figure 13: Effect of niobium on hardness in tempered martensitic stainless steel.

With the same reason, this steel maintains the effective content of chromium, which enables the steel to improve corrosion resistance (Figure 14) (13). It is apparent that niobium is effective in enhancing pitting potential as shown in this figure.

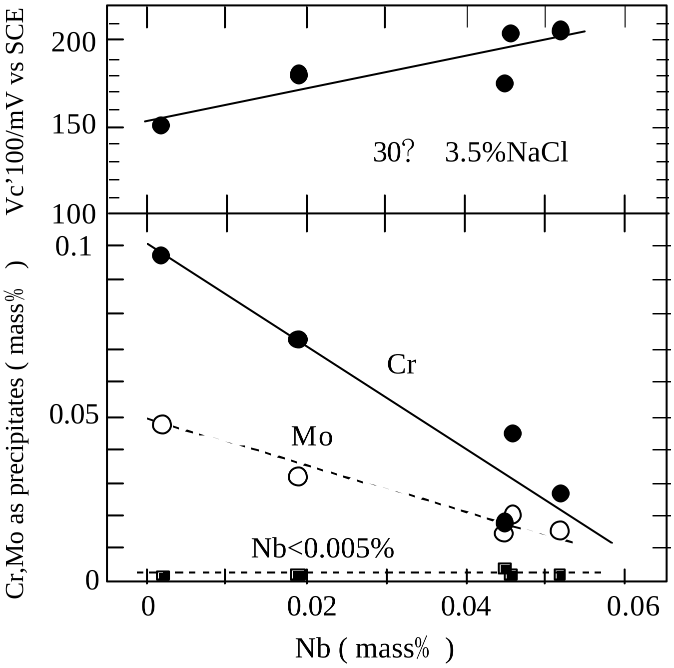


Figure 14: Effect of niobium on Vc'100 and chromium, molybdenum content of precipitate.

Summary

A review has been presented of the effects of niobium in ferritic and martensitic stainless steels, introducing some new stainless steels containing niobium.

An addition of niobium to the steel has a beneficial effect on improving the corrosion resistance of ferritic stainless steel, since niobium reacts with carbon to form stable carbides, consequently, resulting in keeping effective content of chromium in the matrix. It is concluded that more than 7(C+N)+0.35 mass% niobium content is necessary to inhibit intergranular corrosion in case of MAG weld area. On the other hand, more than 7(C+N)+0.15 mass% niobium is necessary in case of spot type weld.

Pitting potential decreases with increasing niobium content. Niobium added 22% chromium-1.2% molybdenum ferritic stainless steel shows remarkable environmental corrosion resistance. While rust area of Type 304 and 316 increases significantly with increasing cycle number of atmospheric corrosion test, the rust area of this ferritic stainless steel is characterized by a slight increase in the first 600 cycles followed by a rather flattering of the curve at longer cycles.

An addition of niobium is one of the most effective ways to give a ferritic stainless steel a good deep drawability. An amount of niobium, which is necessary to improve this property, is related to a content of carbon and nitrogen. Ferritic stainless steels containing an appropriate amount of niobium exhibit good mean r-value.

Soluted niobium and molybdenum are effective in improving the high temperature strength. An amount of soluted niobium depends on the annealing temperature. Precipitation takes place rapidly when the steel is annealed at the lower temperature. Therefore, this behavior of niobium affects complicatedly on mechanism of the influences of this alloying element on the high temperature strength.

Niobium is added to several precipitation types of martensitic stainless steels. Niobium added martensitic stainless steel shows very good tempering resistance, since niobium is beneficial to inhibit forming chromium carbides. Consequently, martensitic stainless steel is able to keep effective content of chromium in the matrix, which causes for the steel to improve corrosion resistance, as same as ferritic stainless steel.

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