Effect of Nb on the Proof Strength of Ferritic Stainless Steels at Elevated Temperatures

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The effect of Nb on the high temperature proof strength of 0.46% Nb-added ferritic stainless steel was studied from the viewpoints of solid solution strengthening, precipitation strengthening, and precipitation strengthening during tensile test and/or preceding hold time. The results obtained were as follows.

(1) The increase in high temperature proof strength in Nb-added ferritic stainless steel is particularly remarkable at around 700°C in comparison with that in Ti-added steels.

(2) After aging treatment for 2 h at 700°C, in addition to the approximately 0.14% content of coarse Nb carbides and nitrides which had precipitated before this aging treatment, fine Fe_2Nb Laves phase particles with a size of 0.02 μm precipitated out in an amount of approximately 0.3%, and virtually no solid solution Nb existed in the steel. The 700°C proof strength in this condition showed a value near the 700°C proof strength before the aging treatment, that is, when approximately 0.3% solid solution Nb was present.

(3) When aging treatment is performed at 700°C for 2 h or more, virtually all the added Nb precipitates out. The coarsening of the Fe_2Nb Laves phase particles within the range of 0.02–0.05 μm during aging at 700°C greatly decreases the high temperature proof strength at 700°C.

(4) Cold rolled steel sheets of Nb-added ferritic stainless steel are normally manufactured by annealing at a temperature of 900°C or higher in order to cause recrystallization. Accordingly, before measurement of the proof strength at 700°C, the steel contains a large quantity of solid solution Nb. The phenomenon of particularly high strength at 700°C is considered to be attributable to the precipitation of this solid solution Nb as a fine Fe_2Nb Laves phase during the tensile test and/or preceding hold time.

KEY WORDS: stainless steel; Laves phase; proof strength at elevated temperatures.

1. Introduction

Purification of automotive exhaust gas has been a subject of intense study in recent years due to public concern about global environmental problems. Increasing the temperature of the exhaust gas tends to activate the catalyst and is therefore considered an effective means of improving the gas purification ratio.¹⁾ At present, many automotive exhaust system parts such as the exhaust manifold, front pipe, and converter shell are produced from SUH409L (11%Cr–Ti) or SUS410L (12% Cr) with a sheet thickness of 1–2 mm. However, from the viewpoint of preventing buckling and improving high temperature fatigue properties, there has been a growing need for a material with improved proof strength at elevated temperatures.^{2,3)} For this reason, Nb-added ferritic stainless steels have been developed,^{4–7)} as these steels possess excellent high temperature proof strength and oxidation resistance. It has been reported^{5,6,8)} that the proof strength of Nb-added stainless steels is higher than that of SUH409L and SUS410L in the temperature region of 600–900°C. In particular, it should be noted that the proof strength of Nb-added steels is exceptionally high at temperatures around 700°C. However, the strengthening mechanism at temperatures around 700°C, where this unique high strength phenomena is observed, has not been

elucidated.

In this paper, the authors studied the effect of Nb on high temperature proof strength, particularly at 700°C, with special attention to the Nb precipitates, including Nb precipitation during tensile test and/or preceding hold at 700°C and solid solution Nb.

2. Test Specimens and Experimental Procedure

2.1. Test Specimens

The test materials were 15% Cr ferritic stainless steels with Nb addition in the range of 0–0.7%. The same base steel with 0.21% and 0.37% Ti addition was used for comparison. Test specimens were prepared by vacuum melting to 50 kg ingots. The chemistry of the materials tested is shown in **Table 1**. Because the C and N contents were reduced while the Si content was increased, the materials consisted of a ferritic single phase regardless of the heat treatment conditions applied in these experiments. The microstructures were confirmed with an optical microscope. The ingots were hot forged to a sheet thickness of 27 mm, and after holding at 1150°C for 1 h, were hot rolled to a thickness of 5 mm and water cooled. The annealing temperatures were 1000°C and 900°C for the Nb-added steels and the other steels, respectively in order to produce fully re-

crystallized grain structure. After holding for 5 min to recrystallize the steels, the sheets were air cooled. These hot rolled sheets were then cold rolled to a sheet thickness of 2 mm. After cold rolling, recrystallization annealing was performed by holding the Ti-added steel and Nb- and Ti-free steels at 900°C for 60 sec, holding the 0.3% Nb-added steel at 950°C for 60 sec, and holding the 0.5% Nb-added steel and 0.7% Nb-added steel at 1 000°C for 60 sec in order to produce fully recrystallized grain structure with the same grain size. Test materials were also prepared by performing additional aging treatment of the cold rolled and annealed sheets at 700°C for times ranging from 2 h to 10 h in order to investigate the Nb precipitation behavior.

2.2. Experimental Procedure

A high temperature tensile test was performed in the temperature range from 200°C to 900°C. After heating to the specified temperature, the test pieces were held for 20 min, and 0.2% proof strength was measured at a strain rate of 0.3%/min. The configuration of the test pieces is shown in **Fig. 1**. In order to study the effect of precipitates on high temperature proof strength, precipitates were identified by observation with a transmission electron microscope (TEM) equipped with an energy dispersion X-ray (EDX) spectroscope. Identification was also performed by quantitative chemical analysis of the residue after electrolytic extraction using an acetyl-acetone type solution and by X-ray diffraction analysis.

3. Experimental Results

3.1. Effect of Nb on High Temperature Proof Strength

The 0.2% proof strength of the 15%Cr–0.5%Nb steel and 15%Cr–0.4%Ti steel at temperatures from Room Temperature(RT) to 900°C is shown in **Fig. 2**. At all temperatures, 0.2% proof strength is improved by Nb addition. **Figure 3** shows the 0.2% proof strength ratio of the 15%Cr–0.5%Nb steel to the 15%Cr–0.4%Ti material for estimating the degree of improvement at each temperature.

Table 1. Chemical compositions of specimens (mass%).

Steel	C	Si	Cr	Nb	Ti	N
15Cr	0.004	0.81	15.0	—	—	0.009
15Cr–0.3Nb	0.006	0.82	14.9	0.27	—	0.008
15Cr–0.5Nb	0.008	0.84	15.1	0.46	—	0.007
15Cr–0.7Nb	0.007	0.83	14.9	0.69	—	0.008
15Cr–0.2Ti	0.006	0.81	15.0	—	0.21	0.009
15Cr–0.4Ti	0.007	0.82	15.1	—	0.37	0.007

Fig. 1. Dimension of specimens (mm). (thickness: 2 mm)

The test results by Utsunomiya⁵⁾ *et al.* were plotted in **Fig. 3**, together with the results of this work. The 0.2% proof strength ratio of Nb-added stainless steels is extremely high at temperatures around 700°C. **Figure 4** shows the effect of Nb addition on the 0.2% proof strength of the 15% Cr steels at 700°C. For comparison, the values for Ti-added steels are also shown. The effect of Nb addition on 0.2% proof strength at 700°C is also remarkable in comparison with that of Ti addition. Based on these findings, the strengthening mechanism was studied as described in the following using the 15%Cr–0.5%Nb steel.

Fig. 2. 0.2% proof strength of ferritic stainless steels at temperatures from RT to 900°C.

Fig. 3. 0.2% proof strength ratio of the 15Cr–0.5Nb and 12Cr–0.6Nb⁵⁾ steels to the 15Cr–0.4Ti steel at temperatures from RT to 900°C.

Fig. 4. Effects of Nb and Ti contents on 0.2% proof strength at 700°C.

Fig. 5. Transmission electron micrographs of 15Cr-0.5Nb steel; (a) before tensile test and (b) after tensile test with 0.2% strain at 700°C.

Fig. 6. Influence of aging time at 700°C on contents of insol. Nb and insol. Fe.

3.2. Precipitates and TEM Microstructure before and after Tensile Test

Figure 5 shows the TEM microstructures of a cold rolled and annealed sheet of 15%Cr-0.5%Nb steel and the same steel after applying 0.2% nominal strain at 700°C, followed by air cooling. Before the tensile test, mainly coarse precipitates in the size range of 0.1–0.3 μm were observed. On the other hand, in the microstructure after 0.2% nominal strain at 700°C, in addition to the coarse precipitates that were present before tensioning, a large quantity of fine precipitates with a size on the order of 0.03 μm were also observed. Nb and Fe peaks were observed for fine precipitates in EDX analysis. On the other hand, Nb peak was observed and Fe peak was not observed for the coarse precipitates in EDX analysis. The fine precipitates seem to have an effect on 0.2% proof strength at 700°C. However, the fine precipitates could not be identified by the electron diffraction pattern due to their fine sizes.

3.3. Precipitates and TEM Microstructure after Aging

Figure 6 shows the effect of aging time at 700°C on the contents of precipitated Nb and Fe, which were measured by electrolytic extraction from cold rolled and annealed sheets of 15%Cr-0.5%Nb steel. Precipitation of both Nb and Fe reached saturation after aging treatment for 2 h. As shown in Fig. 6, the increased content of precipitates attributable to aging was 0.29 mass% in the case of Nb and 0.28 mass% in the case of Fe. Figure 7 shows the results of X-ray diffraction analysis. The X-ray diffraction analysis of the electrolytic extraction residue showed only an extremely

Fig. 7. X-ray diffraction pattern of residues extracted from 15Cr-0.5Nb steel; (a) annealed at 1000°C for 60 s and (b) aged at 700°C for 2 h after annealing at 1000°C for 60 s.

Fig. 8. Transmission electron micrographs; (a) annealed at 1000°C for 60 s, (b) aged at 700°C for 2 h after annealing at 1000°C for 60 s, and (c) aged at 700°C for 10 h after annealing at 1000°C for 60 s.

strong diffraction peak for Nb(C, N) and a weak diffraction peak for M₆C in the cold rolled and annealed steel that was not given aging treatment. On the other hand, when aging was performed at 700°C for 2 h or more, a strong diffraction peak for Fe₂Nb Laves phase was also observed in addition to the above-mentioned precipitates. The effect of Fe₂Nb Laves phase on the proof strength was discussed in Sec. 4.

Figure 8 shows the TEM microstructure of cold rolled and annealed steels before and after aging at 700°C. In the cold rolled and annealed steel before aging, mainly coarse precipitates in the size range of 0.1–0.3 μm were observed as described in Sec. 3.2. It was concluded that these precip-

Fig. 9. Influence of aging time at 700°C prior to tensile test on 0.2% proof strength at (a) 700°C and (b) RT.

itates were Nb(C, N) by EDX analysis and X-ray diffraction analysis of the electrolytic extraction residue shown in Figs. 7(a) and 8(a). The TEM microstructures of the cold rolled and annealed steels that were aged at 700°C for 2 h and for 10 h are shown in Figs. 8(b) and 8(c), respectively. In the material that was aged for 2 h, in addition to the coarse precipitates with sizes of approximately 0.1 μm , which existed in the non-aged material, a large quantity of fine precipitates in the size range of 0.02 μm or smaller were also observed. Coarsening of the size of these precipitates to 0.05 μm was observed in the material that was aged for 10 h.

3.4. Effect of Aging Time on 0.2% Proof Strength at 700°C and Room Temperature (RT)

Figure 9 shows the effect of aging time at 700°C on the 0.2% proof strength at 700°C and RT. Aging for 10 h reduced the proof strength at 700°C by approximately 60 MPa, to a value about half that before aging. In contrast, aging for 10 h reduced the proof strength at RT by only approximately 40 MPa.

3.5. Effect of Reheating after Aging

If the Nb-precipitates which formed during aging treatment at 700°C are again heated to a higher temperature, it is conceivable that the Nb-precipitates will dissolve back into the matrix in the form of solid solution Nb. Figure 10 shows the effect of the time of additional reheating treatment at 900°C after aging at 700°C for 10 h on the 0.2% proof strength at 700°C and solid solution Nb. As the reheating treatment time at 900°C increased, both the proof strength at 700°C and the content of solid solution Nb increased.

4. Discussion

4.1. Effect of Nb on 0.2% Proof Strength at 700°C

Using the results in Fig. 6 and Fig. 9(a), Figure 11 shows the effect of the content of solid solution Nb on the 0.2% proof strength at 700°C. The content of solid solution Nb is the value obtained by subtracting the amount of precipitated Nb, as determined by analysis, from the total content of Nb.

Fig. 10. Effect of reheating time at 900°C after aging at 700°C for 10 h on content of sol.Nb and 0.2% proof strength at 700°C. Arrows indicate the values before aging at 700°C.

Fig. 11. Influence of solute Nb after aging at 700°C on 0.2% proof strength at 700°C. * Total Nb(0.46%)—insol.Nb.

In a condition in which it may be thought that substantially no solid solution Nb exists in the steel after aging at 700°C for 2 h or more, for example, at a solid solution Nb content level of approximately 0.03%, the 0.2% proof strength varied greatly, over a range of 85–42 MPa. Therefore, it is considered that the content of solid solution Nb is not the main factor which influences the 0.2% proof strength at 700°C. In the steels shown in Fig. 6, Figs. 8(b) and 8(c), a precipitated Nb content of approximately 0.43% was identified. In other words, substantially all of the added Nb had precipitated out, and virtually no solid solution Nb was present. Considering these results, it is clear that the size and/or inter - particle distance of the fine precipitates of Nb shown in Figs. 8(b) and 8(c) is the main factor which influences the changes in 0.2% proof strength at 700°C by aging.

As shown in Figs. 9 and 11, the 0.2% proof strength of the cold rolled and annealed steel that was not given aging treatment was the highest of those in this study. The solid solution Nb content of this steel is approximately 0.3%. Because the fine Nb precipitates were not observed before the tensile test in this cold rolled and annealed steel, the possibility that an increase in proof strength was realized as a result⁹⁾ of the solid solution Nb content of approximately 0.3% is conceivable. However, the following results which

were obtained in this work must also be considered:

(1) After the tensile test at 700°C in the cold rolled and annealed steel that was not aged, the fine Nb precipitates which had not been observed before the tensile test were observed in large quantity (Fig. 5).

(2) Even in a condition in which it is considered that virtually no solid solution Nb exists in the steel after aging at 700°C for 2 h, the 0.2% proof strength at 700°C was high, showing a similar value to that of the cold rolled and annealed steel that was not aged (Figs. 6 and 11).

Based on these results, it is considered that the fine precipitates that formed during tensile test at 700°C and/or preceding hold for 20 min increased the 0.2% proof strength of the cold rolled and annealed steel, which was higher than that of the steels aged for more than 2 h, in addition to the strengthening by solid solution Nb.

4.2. Identification of Fine Nb Precipitates after Tensile Test

It was difficult to identify the fine Nb precipitates shown in Fig. 5(b) by the electron diffraction pattern because of their fine size. However, as shown in Fig. 6, the mass ratio of the Nb and Fe that were newly precipitated as a result of aging at 700°C was 1 : 1. Considering the facts that this is near the weight ratio of Nb and Fe in the Fe₂Nb Laves phase, which is 1 : 1.2, and a strong diffraction peak for the Fe₂Nb Laves phase shown in Fig. 7(b) was also observed in the steels aged for more than 2 h, it may be concluded that the fine Nb precipitates when cold rolled and annealed steels are given aging treatment at 700°C consists mainly of the Fe₂Nb Laves phase.

In the tensile test of the cold rolled and annealed steel that was not aged, the specimen was held at 700°C for 20 min before applying strain, and strain was then applied. Therefore, in explaining the existence of the Fe₂Nb Laves phase shown in Fig. 8(b), it is considered that the applied

strain and/or preceding hold for 20 min was conducive to precipitation of the above-mentioned Fe₂Nb Laves phase. From this, it might be concluded that the high 0.2% proof strength of the Nb-added stainless steel at 700°C was attributable to the precipitation of the fine Fe₂Nb Laves phase.

5. Conclusion

The effect of Nb on 0.2% proof strength at 700°C in Nb-added ferritic stainless steels was studied. The following results were obtained.

In the sheet of 15%Cr–0.46%Nb steel annealed at 1000°C, solid solution Nb exists in large quantity. The proof strength of this material at 700°C was approximately two times higher than that of the sheet of 15%Cr–0.37%Ti steel.

It is considered that one of the reasons for above - mentioned phenomena is fine Fe₂Nb Laves phase that precipitated during tensile test and/or preceding hold at 700°C.

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