Strengthening and Toughening of Hot-direct-rolled Steels by Addition of a Small Amount of Titanium

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A laboratory study has been made on the mechanical properties of hot-direct-rolled steels containing a small amount of titanium.

In the steels processed by hot-direct-rolling, even a small amount of titanium content (0.005–0.02 wt%) which has little effect on the strengthening of the steels processed by conventional reheat-rolling was found to be very effective both in the strengthening and in the low temperature toughening. Chemical analyses and electron microscopy confirmed that in the hot-direct-rolling process, most of titanium is in super-saturated solid-solution during cooling after solidification down to the temperature at the start of hot rolling. The titanium in solution precipitates as very fine particles of titanium nitride during the hot rolling.

From a further detailed study of the change in mechanical properties with nitrogen content for the direct-rolled low-titanium steels, it was concluded that the higher nitrogen content steels (more than 40 ppm) are strengthened mainly by TiN particles of non-embrittling type which precipitate during hot rolling. For the lower nitrogen content steels (less than 20 ppm), the main strengthening is caused by TiC particles of embrittling type which precipitate after hot rolling.

KEY WORDS: hot-direct-rolling; low titanium steels; tensile strength; toughness; microhardness; grain size; precipitation hardening by TiN and TiC.

1. Introduction

A hot-direct-rolling (HDR) process¹⁾ is one of the current interests in the steel industry because it provides a great potential to reduce energy and labour costs. However, this new process is supposed to cause a change in mechanical properties because steels are subjected to heat cycles different from those of conventional reheating process. Matsumura *et al.*^{2,3)} reported that the ferrite grain size of the final products is apt to become coarser as a result of the prior austenite grain size being larger (sometimes up to several millimeters). They also reported an increased precipitation-hardening by HDR processing. The present authors were particularly interested in the test result obtained by Sato and Matsukura⁴⁾ that in titanium steels, the strength obtained by HDR process is much higher than that obtained by conventional reheat-rolling (Conv.) process.

It is well known⁵⁻⁷⁾ that in order to obtain a higher strength in titanium steels by Conv. processing, the nitrogen content should be reduced as low as possible and also a 600°C coiling practice should be adopted. Such proposals are based on an idea that the fine TiC particles precipitated during the slow cooling after coiling at 600°C contribute to the strengthening. However, the coarse TiN particles present after soaking do not contribute to the strengthening. In the HDR process, however, the strengthening effect by the TiC and/or TiN precipitation may be much en-

hanced by its unique heat-cycle.

The present study covers the following subjects:

- 1) Comparison of the mechanical properties obtained by HDR process with those obtained by Conv. for niobium-, vanadium-, and titanium-steels, and, in particular, for the steels containing a small amount of titanium (below 0.02 wt%).
- 2) Effects of nitrogen content on the mechanical properties in the low titanium steels processed by HDR.

2. Experimental Procedures

The chemical compositions of the steels used are given in Tables 1 and 2. The three typical precipitation-hardened steels listed in Table 1 were used to investigate the difference in mechanical property and microstructure between the steels processed by HDR and by Conv. As shown in Table 2, the contents of titanium in another series of steels cover a range from 0.002 to 0.015 % in order to investigate the effect of nitrogen on the mechanical properties in the low titanium steels processed by HDR. The steels containing three levels of nitrogen content (*ca.*, 20, 45 and 70 ppm) were provided. All the steels were vacuum-induction melted, and then cast into 50×180×150 mm slabs.

Fig. 1 shows a schematic diagram representing the processing adopted in the present study to simulate the HDR and Conv. processes in practice. In HDR

Table 1. Chemical compositions of precipitation-hardened steels. (wt%)

Steel	C	Si	Mn	P	S	Al	N	Others
A	0.07	0.19	1.06	0.003	0.004	0.046	0.0041	0.04 Nb
B	0.07	0.19	1.04	0.003	0.005	0.051	0.0051	0.09 V
C	0.07	0.17	0.99	0.003	0.005	0.043	0.0048	0.02 Ti

Table 2. Chemical compositions of low-titanium steels. (wt%)

Process	C	Si	Mn	P	S	Al	N	Ti	Note
Conv.	0.06-0.07	0.16-0.18	0.92-0.99	<0.003	0.003-0.006	0.012-0.045	0.0047-0.0051	0.004-0.016	Middle N
	0.06-0.07	0.14-0.21	0.88-1.01	<0.003	0.004-0.005	0.016-0.027	0.0016-0.0022	0.005-0.015	Low N
HDR	0.06-0.07	0.15-0.20	0.91-0.99	<0.003	0.004-0.005	0.012-0.018	0.0039-0.0052	0.002-0.013	Middle N
	0.06	0.18-0.20	0.98-0.99	<0.003	0.005	0.011-0.012	0.0065-0.0071	0.007-0.015	High N

Fig. 1.

Thermal and rolling conditions for hot-direct-rolling (HDR) and conventional reheat-rolling (Conv.) processes.

process, the cast slabs were put into a furnace kept at 1150°C before the surface temperatures of the slabs cooled down to 1000°C, soaked for 20 min and then hot-rolled to 7 mm thick plates. In both HDR and Conv. processes, the hot-rolled plates were water-sprayed to 600°C and then furnace-cooled to room temperature at a rate of 20°C per hour to simulate a 600°C coiling practice. From the middle-thickness portions of the plates, 2 mm thick tensile test specimens with a 50 mm gauge length (JIS-13B) and 5 mm thick standard Charpy V-notched impact test specimens were machined in the rolling direction. Samples for metallurgical examination were quenched from various stages of the HDR and Conv. processes. The chemical analyses were made by a method modified from that given in a literature⁹⁾: Ti-compounds were extracted by potentiostatic electrolysis in an electrolyte of methylalcohol containing 10 %-acetyl-acetone and 1 %-methylammoniumchloride, and nitrides were extracted by chemical dissolution in a bromine-ester solution.

Precipitates extracted by replicas from the final products were also observed by electron microscopy to investigate the difference in precipitation between the steels processed by HDR and by Conv.

3. Results and Discussion

3.1. Niobium-, Vanadium-, and Titanium-steels Produced by HDR and Conv. Processes

Fig. 2 shows the tensile and yield strengths obtained by HDR and Conv. processes for niobium-, vanadium-, and titanium-steels. All the three steels from the HDR process exhibited a higher strength than those from the Conv. process. It is noted here that the ultimate-tensile strength (TS) of the titanium steel from HDR process is approximately 6 kgf/mm² higher than that from Conv. process. This result agrees quite well with the strengths of 5 to 7 kgf/mm² reported by Sato and Matsukura,⁴⁾ although the titanium contents of their steels (more than 0.02 %) were higher than that of the steel used in present study.

The optical micrographs are shown in Fig. 3. In the niobium steel, there was not a marked difference in grain size between the steels processed by HDR and by Conv. The grain size of the vanadium steel was larger for HDR process than for Conv. process but an opposite tendency was observed in the titanium steel. This peculiarity in the vanadium steel is due to the prior coarse grain size of austenite in HDR process. In the niobium steel, the thermomechanical effect by niobium appears to have minimized the difference in grain size between the steels processed by

Fig. 2. Tensile and yield strengths obtained by HDR and Conv. processes in precipitation-hardened steels.

HDR and by Conv. In the case of HDR process, an addition of small amount of titanium exerts, however, a beneficial effect on the grain size, and also on the tensile strength. A further detailed investigation was undertaken to clarify this preferable tendency in the low titanium steel.

3.2. Effects of an Addition of a Small Amount of Titanium on the Mechanical Properties and Microstructure of HDR and Conv. Processed Steels

Fig. 4 shows the tensile and yield strengths of both HDR and Conv. processed steels as a function of titanium content, where the nitrogen level was fixed to 50 ppm. As shown by previous studies,⁵⁻⁷⁾ the strength of Conv. processed steel was not changed by such a small addition of titanium. However, the TS and YS of HDR processed steel were significantly increased respectively by 5 and 6 kgf/mm² even by a small titanium addition of 0.006 %.

Fig. 5 shows microstructural changes produced by titanium addition and by processing condition. The ferrite grain size in Conv. processed steels was about 8 μm , irrespective of titanium content. However in HDR processed steels, the grain size of an 0.002 % titanium steel (showing no increase in strength) was large, i.e., 12 μm , whereas the grain size of the 0.008 % titanium steel (undergoing an increase in strength) was reduced to the same order as that observed in Conv. processed steels. A discussion for this result will be given later.

The electron micrographs of the 0.008 % titanium steel are presented in Fig. 6. A marked difference in the type of precipitates between the steels processed by HDR and by Conv. was clearly observed. In the matrix of the Conv. steel, three types of precipitates were observed. Those are spherical MnS particles with a size of approximately 0.1 μm , rectangular TiN particles of 250 to 500 $\text{\AA}$ in size and coarse TiN particles of 0.1 μm in size in contact with MnS. On the other hand, in the HDR steel, two types of pre-

Fig. 3. Microstructures of precipitation-hardened steels processed by HDR or Conv.

Fig. 4. Effects of titanium content on the tensile and yield strengths of HDR and Conv. processed steels.

cipitates were observed. The one was large (approximately 0.1 μm) MnS. The other was that observed as numerous and fine (100 $\text{\AA}$) particles. These fine precipitates were too small to be identified by electron microscopy, but were estimated as TiN based on the chemical analysis described later.

3.3. Effects of Nitrogen on the Tensile and Yield Strengths of Low Titanium Steels Processed by HDR

Fig. 7 shows the tensile and yield strengths of tita-

(a), (b) 0.002 % Ti steel (c), (d) 0.008 % Ti steel
Fig. 5. Microstructural changes by titanium content and by processing condition.

Fig. 6.
Electron micrographs of 0.008%Ti-0.0047%N steels.

nium steels as a function of titanium content for the three nitrogen levels; *ca.* 20, 45 and 70 ppm. At the 45 ppm nitrogen level, the highest tensile strength was attained in the whole titanium range investigated. This finding is in contrast to the result⁵⁻⁷⁾ obtained by the Conv. process for which the nitrogen content should be reduced as low as possible to obtain a higher strength. Fig. 8 shows the strength *vs.* ductile-brittle transition temperature (*vTs*) plot for the HDR processed titanium steels. The higher nitrogen steels possessed lower transition temperatures than the lower nitrogen steels at any given strength level.

3.4. Precipitation of Titanium-compound in HDR Processed Steels

A steel containing 0.08 % C, 1.0 % Mn, 0.02 % Al, 0.011 % Ti, and 0.0033 % N was prepared. In the steel, the contents of nitrogen and titanium are stoichiometrically the same approximately. The steel was processed in accordance with the HDR schedule given in Fig. 1. The amounts of insoluble titanium and nitride were analysed for the samples quenched from various stages of the process, *i.e.*, after soaking at 1150°C for 20 min, after finished rolling at 850°C and after simulated coiling at 600°C. The results are given in Table 3.

In the Conv. process, approximately 80 % of the total titanium was in precipitation after soaking at 1 150°C. The insoluble titanium is considered to have existed in titanium-nitride from the fact that the ratio of the amount of insoluble titanium to that of insoluble nitrogen is approximately equal to that of

TiN. This conclusion seems to be also supported by the calculation based on the equation of equilibrium solubility product of TiN derived by Sawamura and Mori⁹⁾ where 93 % of the total titanium could be combined with nitrogen at the soaking temperature of 1 150°C. Therefore, the coarse TiN particles as observed in Fig. 6(c) is concluded to have precipitated after the soaking.

In the HDR process, however, only about 20 % of the total titanium was present even after keeping the slabs at 1 150°C for 20 min. This titanium is also considered to have existed in titanium-nitride from the ratio of the amount of insoluble titanium to that of insoluble nitrogen. In the sample water-quenched just after the finish-rolling, the amount of insoluble titanium increased up to approximately 73 % of the total titanium. This amount was almost the same as that of the final product. From these results, it was also concluded that the titanium in solution at the soaking stage precipitates as TiN during the hot rolling. These precipitates are believed to be quite numerous and fine as shown in Fig. 6(d).

Oda and Amano¹⁰⁾ studied the precipitation of titanium-nitride in a low titanium steel during cooling after soaking at 1 320°C. According to their study, TiN precipitation could not be observed at a high cooling rate of 36°C per minute or more, but could be observed at slower cooling rates. Sato and Matsuura⁴⁾ also reported that the strength of an 0.02 % titanium steel obtained by HDR process was decreased by keeping the slab at 1 250°C for more than 60 min. The present study of HDR process, however, employed a relatively fast cooling rate of about 60°C per minutes between solidification and 1 200°C, and also employed a relatively short soaking time of 20 min at 1 150°C. Therefore, it appears reasonable that about 80 % of the total titanium remained in solution after the soaking.

3.5. Strengthening of HDR Steels by an Addition of a Small Amount of Titanium

The micro-hardness of the ferrite matrix was measured for an 0.008 % titanium steel to examine the reason of the difference between the strengths obtained by HDR and by Conv. processes.

Fig. 9 shows that the matrix of the Conv. steel has 145 in H_v , while that of the HDR steel has 182 H_v . This difference ($\Delta H_v=37$) corresponds to a TS of 12 kgf/mm^2 . This value may be large compared to that given in Fig. 4. Considering the scatter of the micro-hardness data, however, the authors concluded that the HDR processed steel is strengthened basically by the precipitation-hardening of the ferrite matrix due

Fig. 7. Effects of titanium content on the tensile and yield strengths in HDR processed steels for three levels of nitrogen content.

Fig. 8. The strength vs. transition temperature plot for 0.002 to 0.015 % Ti steels processed by HDR.

Table 3. Results of chemical analyses. (wt%)

Steel used: 0.08C-1.0Mn-0.02Al-0.011Ti-0.0033N

Process	After soaking		After rolling		After coiling	
	Insol. Ti	N as nitride	Insol. Ti	N as nitride	Insol. Ti	N as nitride
HDR	0.002	0.0008	0.008	0.0022	0.009	0.0023
Conv.	0.009	0.0027	—	—	0.010	0.0029

Fig. 9. Optical micrographs showing the difference in indentation hardness (10 gf-load) of the ferrite matrix between HDR and Conv. processed 0.008%Ti-0.0047%N steels.

to the numerous and fine precipitates as observed in Fig. 6(d). The data for the HDR processed steel plotted in Fig. 4 show that with titanium addition the YS increases more than the TS and thereby the ratio of YS to TS approaches the values (0.8~0.9) usually observed in precipitation hardened steels. This fact also seems to support the above explanation in terms of the ferrite matrix strengthening by precipitation.

The amounts of insoluble titanium in HDR processed steels containing various amounts of nitrogen and titanium were examined in order to clarify the effect of precipitation on the low temperature toughness shown in Fig. 8. Fig. 10 shows the results which indicate a combination of a low nitrogen content with a high titanium content resulting in the precipitation of TiC besides that of TiN. This is because the amount of insoluble titanium is in excess of that required for TiN formation. When the nitrogen content is higher than 40 ppm, all the precipitates in the steels used in the present study seem to be TiN as explained before.

Suppose that for lower nitrogen content steels, the main strengthening factor is the TiC precipitation during slow coil cooling, while for higher nitrogen content steels, the strengthening factor is the strain-induced TiN precipitation in non-recrystallized austenite region during hot rolling, then the results of Fig. 8 are well explained as follows; an embrittlement associated with an increase in strength for lower nitrogen steels is caused by the TiC precipitates which are coherent to the ferrite matrix—this corresponds to the precipitation hardening in non-controlled or normalized steels as described by Irvine *et al.*,⁽¹¹⁾ while for higher nitrogen steels a superior low temperature toughness results from the dispersion hardening^(12,13) by fine TiN particles which precipitate on a high density of dislocations introduced by rolling in the austenite region and consequently are incoherent to the ferrite matrix—this corresponds to the precipitation hardening observed in high grade controlled Nb and/or V steels.⁽¹⁴⁾

Another preferable effect of a small titanium addition for HDR processed steels is to reduce the ferrite grain size as shown in Fig. 3(e). This effect can be recognized as a thermomechanical effect caused by the fine TiN precipitates induced by hot rolling.

Fig. 10. Chemical analysis of insoluble Ti for steels containing various amounts of nitrogen and titanium after processing by HDR.

4. Conclusions

A laboratory simulation of the HDR process was applied to the steels containing a small amount of titanium less than 0.02 %. The mechanical properties and microstructure of the HDR processed steels have been examined compared to those of Conv. processed steels. The titanium precipitation behaviour in the HDR process has also been clarified.

The main results are as follows:

(1) By the HDR process, even an addition of a small amount of titanium (0.005~0.02 wt%) which has little effect on the strengthening by the Conv. process is very effective both in strengthening and in improving the low temperature toughness.

(2) Judging from chemistry of precipitation before and after hot rolling and electron microscopic observation of the final products, it was concluded that in Conv. processed steels, most of titanium exists in coarse TiN particles after the soaking process, being ineffective in the strengthening. In the HDR processed steels, however, most of titanium remains in super-saturated solid-solution after the soaking process and the titanium precipitates during hot rolling as very fine particles of titanium nitride which contribute to the strengthening.

(3) In the low titanium steels (less than 0.015 % Ti) processed by HDR, the steels containing more than 40 ppm nitrogen are strengthened mainly by the non-embrittling type TiN which precipitates during hot rolling. When the nitrogen content is less than 20 ppm, however, the embrittling type TiC which precipitates after hot rolling becomes the dominant factor in the strengthening.

(4) In HDR processed steels, an addition of a small amount of titanium resulted in a grain size which is almost equal to or smaller than that of Conv. processed steels. This is a thermomechanical effect due to the fine TiN particles which precipitate during hot rolling.

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