Isolation and Determination of Sulfides in Ti-bearing Ultra Low Carbon Steels

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(Received on April 30, 1993; accepted in final form on July 15, 1993)

Bake hardening properties of Ti-bearing ultra low carbon steels are affected by the precipitation behavior of TiN, MnS, TiS and $Ti_4C_2S_2$. Thus the methods of isolation and determination of these precipitates have been developed and applied to the study on the precipitate change with reheating of the steels.

All precipitates, TiN, MnS, TiS and $Ti_4C_2S_2$ were extracted by MS electrolysis. TiN was extracted by 10% (v/v) bromine-methanol. MnS was isolated from the residues (extracted by MS electrolysis) by 50°C HCl treatment. TiS in the 50°C HCl treated residues was decomposed by 10% (m/v) iodine-methylacetate and $Ti_4C_2S_2$ remained. Mn, Ti and S in the residues were determined directly by X-ray fluorescence method. N was determined by neutral titration method. The determined compositions of precipitates except TiS almost corresponded with their stoichiometries. TiS was determined to $TiS_{1.3}$.

Whole nitrogen precipitated as TiN and the amount did not change with reheating temperatures between 950 and 1 250°C. Total amount of the sulfides such as MnS, TiS and $Ti_4C_2S_2$ changed scarcely with reheating temperatures, but the amount of each sulfide changed largely. Precipitates in the steels reheated below 1 050°C were mainly $Ti_4C_2S_2$. It decomposed and transformed into TiS and MnS with raising the reheating temperature, and decreased drastically at 1 150°C. The precipitates above 1 150°C were mainly MnS and TiS, and the fraction depended on the ratio of Ti to Mn concentration in the steels.

KEY WORDS: isolation; extraction; sulfide; carbosulfide; ultra low carbon steel; bake hardenable steel.

1. Introduction

Recently a Ti-bearing ultra low carbon steel has been developed and widely used for an automobile steel sheet as a bake hardenable steel sheet (BH-steel) because of its good cold formability and high strength. Generally a BH-steel has a small amount of carbon and nitrogen (a few ten ppm), and is controlled to retain a few ppm carbon in a soluble state by adding a suitable amount of Ti and by annealing at a suitable temperature. However the control of precipitation is not easy, because BH-steels have only small amount of C, N and Ti and their precipitates are largely affected by heat treatment processes.

In a Ti-bearing ultra low carbon steel some sulfides such as MnS, TiS and $Ti_4C_2S_2$ precipitate in addition to TiC and TiN. Especially Ti carbosulfide, $Ti_4C_2S_2$ precipitating during reheating of slabs plays an important role to control the solute carbon atoms. The crystalline structure of $Ti_4C_2S_2$ was studied first by Kudielka and Rohde.¹⁾ Liu *et al.*²⁾ identified a sulfide precipitating in Ti microalloyed steels to $Ti_4C_2S_2$ not Ti_2S , by analytical electron microscopy, although both the diffraction patterns are nearly identical. Kawasaki *et al.*³⁾ studied the effect of $Ti_4C_2S_2$ on the bake hardening properties in Ti-bearing ultra low carbon steels. Sulfides in the steels

have been reported to precipitate as Ti_xS_y ($x < y$) in a higher temperature region of austenite and as $Ti_4C_2S_2$ in a lower temperature region.^{4,5)}

The previous studies have been done by using electron microscope or analytical electron microscope with emphasis on the thermodynamical stability of sulfides.⁶⁾ However the amount of each sulfide has not been studied. The amount of each sulfide including $Ti_4C_2S_2$ is necessary to be examined in order to control the solute carbon atoms in BH-steels.

The Nonmetallic Inclusion Analysis Subcommittee of the Iron and Steel Analysis Committee of the Iron and Steel Institute of Japan has reported some recommended methods for the isolation and determination of sulfides in several steels after the joint research.⁷⁾ However the report does not present a method which shows the way to isolate Ti sulfides including $Ti_4C_2S_2$ and to determine their amounts.

Thus in the present study, we have investigated potentiostatic electrolysis methods and the subsequent chemical treatments to isolate each sulfide and to determine the composition and amount. The developed method was applied to the study on the sulfides precipitating in a series of Ti-bearing ultra low carbon steels.

2. Experimental Procedures

2.1. Experimental Materials

Four Ti-bearing ultra low carbon steels were prepared by vacuum induction melting. After heating the ingots at 1200°C, they were forged above 900°C. Then they were heated up to 1250°C for a half hour and hot rolled into 6 mm thick plates at temperatures between 900 and 1000°C being followed by air cooling. The chemical compositions are listed in **Table 1**. Mn content was only varied in four levels. To simulate the reheating process of slabs, the plates were annealed at 1250, 1150, 1050 and 950°C for one hour in Ar gas atmosphere, and quenched into water. Some plates were annealed at 1050°C after annealing at 1250°C.

2.2. Potentiostatic Electrolysis Method

Extraction of the whole precipitates from the steel matrices was employed by means of potentiostatic electrolysis in which methanol containing 1% (m/v) salicylic acid, 4% (v/v) methyl salicylate and 1% (m/v) tetramethylammonium chloride was used as an electrolyte (denoted as MS electrolysis below).⁸⁾ A sample with the surface area of 0.0012 m² was immersed into the MS electrolyte bubbled by Ar gas flow and was dissolved electrochemically at the current density of 200 A/m² until the weight loss of 0.5 g. After the end of electrolysis the samples were ultrasonically vibrated in the electrolyte in order to strip the precipitates from the sample surfaces. The precipitates were collected by filtration using Nucleopore Filter of 25 mm diameter with pore size of 0.2 µm.

2.3. Compositional Analysis of Precipitates

Determination of S in the sulfides is generally employed by infrared absorption method after combustion in an induction (IR method) or by H₂S evolution-methylene blue spectrophotometric method.⁷⁾

Because handling of the above methods is complicated, we have tried a X-ray fluorescence (XRF) method to determine S directly using the precipitates collected on a filter. Since relationship between S-K α intensities and S amounts obtained by H₂S evolution-ethylene blue spectrophotometric method (H₂S evolution method) shows good linearity as shown in **Fig. 1**, the XRF method is capable to determine S directly. Metallic elements in the precipitates can be determined simultaneously by the XRF method. The XRF analysis was performed by Simultix 3530 (Rigaku) with Rh-target for fixed time of 20 sec.

2.4. Grazing Incidence X-ray Diffraction

A grazing incidence X-ray diffraction method was used

for the identification of precipitates, because the amount of collected precipitates on the filter was very small. The filter with the precipitates was stuck on a glass plate and X-ray of Co-K α was irradiated at an incident angle of 1.0 degree.

3. Procedures of Isolation and Determination

3.1. Determination of Total S and Un-extracted S

Total S in the steels was determined by the IR method. S in the precipitates extracted by MS electrolysis was determined by XRF method. Un-extracted S was defined as the difference between total S and S in the extracted precipitates.

3.2. Isolation and Determination of TiN

Steel chips of 5 g were dissolved by 10% (v/v) bromine-methanol of 200 ml and the residues were filtrated on a membrane filter with 0.2 µm pores. After the residues were decomposed by 20 ml H₂SO₄ with 1 g copper sulfate (5-hydrate) and 10 g potassium sulfate, N was determined by neutral titration method following steam evaporation as ammonia.⁹⁾ Ti in the residues was determined by XRF method.

3.3. Isolation and Determination of Sulfides

3.3.1. H₂S Evolution Method

An apparatus for H₂S evolution method is shown in **Fig. 2**. The precipitates extracted by MS electrolysis were transferred together with a Nucleopore filter to a decomposition flask in **Fig. 2**. 50 ml washing solution prepared by mixing three volumes of HCl(1+60) with one volume of hydrazine dihydrochloride solution (5 g/l) was transferred to a washing bottle. 50 ml absorbing solution was transferred to an absorption flask. The absorbing solution was prepared by diluting 55 g zinc acetate (dihydrate) and 14 g sodium acetate (trihydrate) together with water until whole volume of 1000 ml.

Fig. 1. Analytical curve for the determination of sulfur by X-ray fluorescence method.

Table 1. Chemical compositions of steels examined. (mass%)

Steel	C	S	Si	Mn	P	Ti	sol.Al	N	O
Q1	0.0024	0.0065	0.001	0.06	0.008	0.045	0.041	0.0007	0.002
Q2	0.0023	0.0067	0.002	0.18	0.008	0.044	0.041	0.0009	0.003
Q3	0.0027	0.0067	0.002	0.34	0.008	0.046	0.039	0.0008	0.002
Q4	0.0030	0.0064	0.003	0.72	0.007	0.044	0.042	0.0017	0.001

 Fig. 2. Apparatus of H_2S evolution method.

After Ar gas purging, 50 ml/ HCl was transferred to the decomposition flask through a funnel in a current of Ar gas of 100 ml/min and the decomposition done for 30 min. The decomposition behavior of MnS, TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ was investigated by heating HCl solution at 50°C and the boiling point. H_2S evolved by the decomposition of sulfides was absorbed by the absorbing solution and S in the solution was determined by ethylene blue spectrophotometric method.¹⁰⁾

3.3.2. Halogen-Ester Method

Isolation of Ti sulfides, TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ was examined by using 10% (m/v) iodine-methylacetate, 10% (m/v) iodine-methanol or 10% (v/v) bromine-methanol.

Filters collecting the precipitates were mounted again in a filtration apparatus and the halogen solution of 100 ml/ warmed at 60°C was poured slowly into the apparatus with taking 10 min. After washing enough with methanol, S and Ti in the residues on the filter were determined by XRF method.

4. Results and Discussion

4.1. Characterization of Precipitates by X-Ray Diffraction

The precipitates extracted by MS electrolysis were identified by grazing incidence X-ray diffraction. TiN was identified for whole samples. Peak intensities of TiS, MnS and $\text{Ti}_4\text{C}_2\text{S}_2$ changed with annealing temperatures and with steel compositions. The amounts of the sulfides were quasi-quantified by their peak intensities normalized by the peak intensity of TiN, because the amount of TiN did not change with annealing temperatures as discussed below.

The obtained fractions of sulfides changing with annealing temperatures are shown in Fig. 3 for steels Q1 (0.06 mass% Mn) and Q4 (0.72 mass% Mn). The sulfide precipitating in steel Q1 annealed at 950°C was only $\text{Ti}_4\text{C}_2\text{S}_2$ and the fraction decreased with rising of annealing temperature. The fraction of TiS increased with annealing temperature and only TiS was detected in steel Q1 annealed at 1250°C . MnS was not detected in steel Q1. On the other hand, both $\text{Ti}_4\text{C}_2\text{S}_2$ and MnS were detected in steel Q4 annealed at 950 and 1050°C . Annealing the steel Q4 at 1150 and 1250°C , only MnS

Fig. 3. Approximate fraction of sulfides determined by grazing incidence X-ray diffraction.

 Fig. 4. Stoichiometric relationship between Ti and N in the precipitates extracted by 10% (v/v) bromine-method.
○: Q1, ●: Q2, □: Q3, ■: Q4

was detected.

4.2. Isolation and Determination of TiN

Ti and N in the residues extracted by bromine-methanol method were determined by the procedures described in Sec. 3.2. The amounts of N in the residues approximately corresponded to total N in the steels and free N did not exist. The determined values of Ti and N in the residues are plotted in Fig. 4. Since they distributed nearly on the stoichiometric line of TiN, the residues were found to be TiN particles. The result was confirmed by the fact that S was not detected in the residues by XRF method. The amount of TiN changed scarcely with annealing temperatures as shown in Fig. 4.

4.3. Determination of Precipitated S

S in the residues extracted by MS electrolysis was determined by XRF method for all steels annealed between 950 and 1250°C . The result is shown as open circles in Fig. 5. The obtained values are slightly lower than total S in the steels determined by IR method as described in Sec. 3.1. Defining the differences between S determined in the residues and total S as un-extracted S,

Fig. 5. Annealing temperature variation of S amounts in sulfides extracted by MS electrolysis.

○: S in extracted sulfides,
●: un-extracted S (Total S - S in extracted sulfides)

Fig. 6. Effect of HCl temperature on S amounts evolving as H_2S .

○: evolution at 50°C, ●: evolution at boiling temperature

the values are plotted as solid circles in Fig. 5. The values of un-extracted S increase with annealing temperatures for all steels and are especially larger in steel Q4. Although the un-extracted S could be caused by leaking of tinny sulfide particles through the $0.2\mu m$ pores of Nucleopore filters, this cannot explain the behavior of un-extracted S with annealing temperatures. Considering that Liu and Jonas⁶⁾ have reported the presence of solute sulphur of 7.5 ppm(m/m) in a 0.05 mass% Ti low alloy steel annealed at 1260°C, large fraction of the un-extracted S is thought to be solute sulphur. However it was expressed as un-extracted S, because solute sulphur was not examined.

4.4. Isolation and Determination of MnS

As MnS is known to be decomposed with H_2S evolution by HCl, the decomposition temperature was examined with HCl temperature of 50°C and the boiling point in order to isolate MnS from Ti-sulfides. Sulphur evolving as H_2S was determined by H_2S evolution method as described in Sec. 3.3.1.

The results examined at HCl temperatures of 50°C and boiling point are shown in Fig. 6. The determined values of S by H_2S evolution method with 50°C HCl were zero for the steels Q1, Q2 and Q3 annealed at all temperatures

Fig. 7. Stoichiometric relationship between S and Mn in the residues treated by 50°C HCl determined by H_2S evolution and XRF method.

○: H_2S evolution method, ●: XRF method

Fig. 8. Variation of S and Ti in the residues with the fraction of HCl to water in the HCl treatment (100 ml) at 50°C for the steel Q4 annealed at 1250°C (open) and 950°C (solid).

○: S, △: Mn, □: Ti

except for the steel Q3 annealed at 950°C. This implies that Ti sulfides could not be decomposed by 50°C HCl, with considering the results by X-ray diffraction in Fig. 3. While, certain values of S were determined by boiled HCl for the steel Q1 which contained Ti sulfides at all annealing temperatures. Thus some fraction of Ti sulfides is thought to be decomposed by boiled HCl. The determined values of S by H_2S evolution method with boiled HCl are nearly same with those determined by 50°C HCl for the steel Q4 containing large amount of MnS. These results suggest that only MnS is decomposed by 50°C HCl and that Ti sulfides such as TiS and $Ti_4C_2S_2$ are not decomposed by 50°C HCl.

Figure 7 shows the relationship between S determined by H_2S evolution method with 50°C HCl and Mn determined by XRF method in the precipitates extracted by MS electrolysis for all the samples. Since these values distribute nearly on a stoichiometric line of MnS as shown in Fig. 7, it is confirmed that MnS can be isolated from TiS and $Ti_4C_2S_2$ by the treatment using 50°C HCl.

Because the procedure of H_2S evolution method is complicated, the determination of S in MnS by XRF method was tried. At first S and Mn in the residues extracted by MS electrolysis were determined by XRF method. The filter with the residues was mounted in the filtration apparatus and HCl solution of 100 ml at 50°C was poured slowly. Then S, Mn and Ti in the residues

were determined again by XRF method. At the same time the effect of HCl concentration on the decomposition of MnS and Ti sulfides was examined. The aqueous solution of HCl was changed from (1+1) to (1+10) fraction.

The result was shown in Fig. 8. In both the samples of steel Q4 annealed at 950 and 1250°C, Mn was detected in the residues treated by dilute HCl solution below (1+3) fraction. This implies that dilute solution of HCl cannot decompose MnS. While S in the residues is almost constant for HCl treatment with the higher fraction than (1+3). The determined values of Ti in the residues are almost constant as shown in Fig. 8. These results suggest that HCl solution with (1+3) fraction decomposes MnS enough and does not decompose TiS, $Ti_4C_2S_2$ and TiN. Therefore, when S and Mn in the residues are determined by XRF method before and after HCl (1+3) treatment at 50°C, the differences for S and Mn should correspond to the stoichiometric values of MnS. In fact, these values distribute near the stoichiometric line as shown in Fig. 7 (solid circles).

4.5. Isolation of TiS and $Ti_4C_2S_2$

Whole sulfides precipitating in the steels were decomposed by bromine-methanol. As $Ti_4C_2S_2$ was thought to be chemically stabler than TiS and MnS, $Ti_4C_2S_2$ was tried to be isolated from TiS and MnS by using chemically weaker solutions than bromine-methanol.

The precipitates extracted by MS electrolysis were treated by various halogen-methanol or halogen-ester solutions at 60°C. Then Ti and S in the residues were determined by XRF method. The result for steel Q1 is shown in Fig. 9. The determined values of Ti in the residues without the treatment decreased with raising annealing temperature and corresponded to the change of TiS fraction with annealing temperature, because stoichiometric value of Ti against S in TiS is half of that in $Ti_4C_2S_2$.

When steel chips were directly treated by 10% (v/v) bromine-methanol, the determined Ti values became small and S was not detected in all annealing temperature as shown in Fig. 9. The determined Ti values corresponded to those of TiN. While, when the residues

Fig. 9. Ti and S determined in the residues treated by various halogen-solution.

○: without treatment, ●: 10% iodine-methylacetate
□: 10% iodine-methanol, ■: 10% bromine-methanol

were treated by 10% (m/v) iodine-methylacetate or by 10% (m/v) iodine-methanol, both the determined Ti and S decreased with raising annealing temperature. Especially, when the residues treated by 10% (m/v) iodine-methylacetate, the determined Ti value approached to that in the residues without the treatment at 950°C annealing and to that in the residues with bromine-methanol treatment at 1250°C annealing. The steel Q1 contained mainly $Ti_4C_2S_2$ at the annealing temperature of 950°C and mainly TiS at the annealing temperature of 1250°C as shown in Fig. 2. Therefore TiS in the residues extracted by MS electrolysis could be almost decomposed by 10% (m/v) iodine-methylacetate, and both TiN and $Ti_4C_2S_2$ could be remained without decomposition.

On the other hand, S was determined to relatively large values even in the residues treated by 10% (m/v) iodine-methylacetate at 1250°C annealing as shown in Fig. 9. The S value was larger than that estimated by the Ti value. When sulfides such as TiS and Ti_2S_3 are decomposed by HNO_3 , free S is known to form.¹¹⁾ Thus in the treatment of 10% (m/v) iodine-methylacetate, free S is thought to form. In fact the determined values of S in the residues by XRF method decreased with repeating of the measurement, because free S is thought to sublime in the vacuum of XRF instrument.

The remaining of free S on the filter was suppressed by increasing the volume of 10% (m/v) iodine-methylacetate as shown in Fig. 10. That is, the determined S value in the steel Q1 annealed at 1250°C was still large with the solution of 50 ml and it decreased to small amount with the solution above 100 ml. While the S values in the steel Q1 annealed at 950°C did not change with the amount of the solution. Thus $Ti_4C_2S_2$ was not decomposed by the increase of solution. Therefore the isolation of TiS from $Ti_4C_2S_2$ was done by using 10% (m/v) iodine-methylacetate of 100 ml at 60°C. Large amount of free S formed even by the treatment for the residues containing large amount of MnS. Thus such residues were treated by 10% (m/v) iodine-methylacetate after 50°C HCl(1+3) treatment.

Moreover, the decomposition of TiS by 10% (m/v) iodine-methylacetate was confirmed by X-ray diffraction for the residues before and after the treatment as shown in Fig. 11. The diffraction peaks of TiS disappeared by

Fig. 10. Variation of S and Ti with volume in 10% iodine-methylacetate treatment for the steel Q1 annealed at 1250°C (○) and 950°C (●).

Fig. 11. X-ray diffraction patterns of extracted precipitates in the steel Q1 before and after 10% iodine-methylacetate.
(a), (c), (e): before treatment and (b), (d), (f): after treatment
(a), (b): annealed at 950°C, (c), (d): annealed at 1050°C, (e), (f): annealed at 1150°C

Fig. 12. Stoichiometric relationship between S and Ti both in decomposition and in residues after 10% iodine-methylacetate treatment.
●, ▲, ■, ◆: decomposition for steels, Q1, Q2, Q3 and Q4 respectively, ○, △, □, ◇: residues for steels, Q1, Q2, Q3 and Q4 respectively

the treatment of 10% (m/v) iodine-methylacetate. However the intensities of $Ti_4C_2S_2$ changed scarcely with the treatment.

4.6. Determination of TiS and $Ti_4C_2S_2$

The values of S and Ti in TiS which was isolated by 10% (m/v) iodine-methylacetate are plotted in Fig. 12. They distribute rather near the stoichiometric line of Ti_2S_3 than that of TiS. The average ratio of S to Ti was 1.3. Sanagi *et al.*⁴⁾ have reported that Ti_xS_y ($x < y$) precipitates at the annealing temperature 1250°C. Okamoto and Mizui⁵⁾ have also reported that the ratio of Ti to S in Ti sulfide precipitating in low Mn steels was 45/55. Although our result was in agreement with their reports, X-ray diffraction or electron diffraction could not identify those sulfides.

On the other hand, the determined values of S and Ti in $Ti_4C_2S_2$ distribute almost near the stoichiometric line of $Ti_4C_2S_2$ as shown in Fig. 12. However the values of S distribute somewhat higher than the line for the samples

Fig. 13. Effect of annealing temperature on the amounts of $Ti_4C_2S_2$, TiS, MnS and un-extracted S in the steels examined.
○: Q1, ●: Q2, □: Q3, ■: Q4

containing larger amount of $Ti_4C_2S_2$. It was thought to be caused by the co-precipitation of $Ti_4C_2S_2$ with TiS,^{12,13)} the presence was not examined.

4.7. Precipitation Behavior of Sulfides

The above developed methods for the isolation and determination of sulfides were applied to the study on the precipitate change with reheating of Ti-bearing ultra low carbon steels.

The obtained amount of each sulfide, MnS, $TiS[Ti_xS_y$ ($x < y$)] or $Ti_4C_2S_2$ was expressed by S concentration in the steels as shown in Fig. 13. The precipitation behavior of sulfides with annealing temperatures was almost similar in the steels Q1, Q2 and Q3 of which Mn concentrations were from 0.06 to 0.34 mass%. The sulfides precipitating in those steels were mainly $Ti_4C_2S_2$ and TiS. The amount of $Ti_4C_2S_2$ decreased and that of TiS increased drastically at 1150°C as shown in Fig. 13. This implies that $Ti_4C_2S_2$ transforms into TiS at the temperature between 1050 and 1150°C, because the total amount of sulfides remained almost constant at whole annealing temperatures.

On the other hand, the sulfides precipitating in the steel Q4 containing higher Mn concentration (0.72 mass%) were mainly MnS and $Ti_4C_2S_2$ as shown in Fig. 13. In the steel $Ti_4C_2S_2$ transformed into MnS with the decomposition at the annealing temperature between 1050 and 1150°C.

The precipitation behaviors of $Ti_4C_2S_2$ and MnS are in good agreement with the thermodynamical calculation by Liu and Jonas.⁶⁾ The slight increase of un-extracted S with raising annealing temperature implies that small amounts of solute S form at the higher annealing temperatures of whole steels examined.

Fig. 14.
Flow chart of developed methods for isolation and determination of sulfides.

In Fig. 13, it is noted that the sulfide precipitations in the steels annealed at 1050°C after 1250°C annealing do not show any change comparing with those annealed at 1250°C. Because the sample was re-annealed at lower temperature than that of drastic transformation of $\text{Ti}_4\text{C}_2\text{S}_2$ to TiS or MnS, $\text{Ti}_4\text{C}_2\text{S}_2$ is thought not to precipitate in the short annealing time of 1 h.

5. Conclusion

The methods of isolation and determination of TiN, MnS, TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ precipitating in Ti-bearing ultra low carbon steels have been developed and applied to the study on the precipitation behavior in reheating process of the steels. The results obtained are as follows:

(1) The procedures of developed methods are summarized in Fig. 14. All precipitates, TiN, MnS, TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ were extracted by MS electrolysis. TiN was extracted by 10% (v/v) bromine-methanol. MnS was isolated from the residues (extracted by MS electrolysis) by 50°C HCl treatment, because only MnS was decomposed with H_2S evolution. TiS was isolated from the 50°C HCl treated residues by 10% (m/v) iodine-methylacetate, because TiS was decomposed by the solution and $\text{Ti}_4\text{C}_2\text{S}_2$ remained.

(2) Mn, Ti and S in the residues on extraction filters were determined directly by X-ray fluorescence method. N was determined by neutral titration method. The determined compositions of precipitates except TiS almost corresponded with their stoichiometries. TiS was determined to $\text{TiS}_{1.3}$.

(3) Whole nitrogen precipitated as TiN and the amount did not change with reheating temperatures between 950 and 1250°C. Total amount of the sulfides such as MnS, TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ changed scarcely with reheating temperatures, but the amount of each sulfide changed largely. The precipitates in the steels reheated below 1050°C were mainly $\text{Ti}_4\text{C}_2\text{S}_2$. It decomposed and transformed into TiS and MnS with raising the temperature, and decreased drastically at 1150°C. The precipitates in the steels reheated above 1150°C were mainly MnS and TiS, and the fraction depended on the ratio of Ti to Mn concentration in the steels.

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