Sulfide Precipitation in Titanium-Added Steel with Residual Level of Copper (3) —Decrease of Copper Sulfide by Long-Time-Annealing in Ferrite Region—

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This report corresponds to the third paper in three consecutive papers to know the whole sulfide precipitation in Ti-added steel by adding a new knowledge that even a trace level of copper (0.01%Cu) acts as a sulfide-former. The authors show the strange phenomenon of copper sulfide in Ti-added steel in long-time-annealing in ferrite region. When annealed for short time (ex. 90 s), much of Cu-S is precipitated, but the amount of Cu-S is small at longer-time-annealing, while TiS reduces and $\text{Ti}_4\text{C}_2\text{S}_2$ increases monotonically. This phenomenon does not mean that Cu-S is initially formed and then dissolved away, but the Cu-S precipitation should be interpreted as causal evidence of “(re-)solute sulfur and its re-precipitation” along the same concept in the first and the second papers. Long-time-annealing means that our proposed reaction “ $4\text{TiS} + 2[\text{C}] \rightarrow \text{Ti}_4\text{C}_2\text{S}_2 + 2[\text{S}]$ ” proceeds rightward and the re-solute sulfur is re-precipitated as $\text{Ti}_4\text{C}_2\text{S}_2$ (and MnS). Consequently, the amount of Cu-S is small. In contrast, short-time-annealing is not long enough to stabilize re-solute sulfur as $\text{Ti}_4\text{C}_2\text{S}_2$ (and MnS) and much of sulfur still remains solute. Therefore the amount of Cu-S is increased.

Furthermore, the phenomena in three consecutive papers is organized into an integrated concept to understand the whole sulfide precipitation in Ti-added steel in both austenite and ferrite region. [doi:10.2320/matertrans.MRA2008300]

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1. Introduction

In the third report of three consecutive papers,^{1,2)} the authors show the strange transitional change of copper sulfide precipitation in Ti-added steel in accordance with annealing-time in ferrite region. Through the analysis, our proposed theory of Cu-S precipitation is reinforced and also the whole phenomenon of sulfide precipitations in Ti-added steel is clearly shown in relation with Cu-S precipitation induced by a trace level of Cu, which has been regarded as solute in steel. In addition, the sulfide phenomena through three consecutive papers are organized into an integrated mechanism to explain the whole sulfide precipitation in both austenite and ferrite regions in Ti-added steel and also to cover the phenomenon in non-Ti-added steel.

Our proposed mechanism has a common root through three consecutive papers,^{1,2)} which can apply to ferrite region and austenite region in both Ti-added and non-Ti-added steel. The concept is based on three things: (1) (re-)solute sulfur exists and it is re-precipitated along the estimated reaction “ $4\text{TiS} + 2[\text{C}] \rightarrow \text{Ti}_4\text{C}_2\text{S}_2 + 2[\text{S}(\text{re-solute})]$ ”, (2) $\text{Ti}_4\text{C}_2\text{S}_2$, MnS and Cu-S are formed in ferrite region (3) the Cu-S precipitation occurs at low temperature in ferrite region, even during WQ.

Our standpoint^{3–20)} and reviews of past studies have already been mentioned in details in the first report.¹⁾ In addition, the sulfide precipitation in ferrite region in Ti-added steel has been already reviewed again in the second paper.²⁾

In this third paper, the past studies on solute carbon in steel are mentioned below. It is related to the above mechanism “ $4\text{TiS} + 2[\text{C}] \rightarrow \text{Ti}_4\text{C}_2\text{S}_2 + 2[\text{S}]$ ”, in which solute carbon is a required condition.

Most of steel products include solute carbon which is not precipitated as carbide and stays as solid solution in steel. Those steel products usually occurs age-hardening (or strain aging), which means that yielding stress (YS) gets high after holding for long hours and/or at high temperature, because solute carbon diffuses into energetic-unstable strained area near dislocation even at near room temperature and interferes with the mobility of dislocations. A majority of steel products are age-hardenable steel.

Although it had been exceptional, non-age-hardenable steel “IF steel” has been commonly produced through the current steelmaking technology. The sample used here is Ti-IF steel which stands for Ti-stabilized Interstitial-Free steel. Carbon and nitrogen are removed up to near technological limits (below 30 ppm: often referred as to ultra low carbon and/or ultra low nitrogen) and they are fully stabilized by carbide-former and nitride-former as carbide and nitride into IF steel, respectively.

Since solute carbon in IF steel does not exist by definition and IF steel is alloy-designed to stabilize all of carbon and nitrogen, it has been accepted as a common concept that age-hardening does not occurs in IF steel. Also, the precipitation in Ti-IF steel has been traditionally interpreted to finish only in austenite region and not to occur in ferrite region, except for some limited papers.^{10–24)} In other words, carbon in Ti-IF steel has been regarded as completely stabilized as carbide. Therefore, it has to be made clear whether solute carbon

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Table 1 Chemical compositions of Ti-added steel (mass%).

sample	Heat Treatment	C	Si	Mn	S	Cu	Ti
0.04%Ti-IF	(iii) Long minute-Annealing	0.0018	0.01	0.15	0.0074	0.010	0.040
0.06%Ti-IF	range (α)	0.0017	0.01	0.16	0.0062	0.008	0.064

really exists in as-hot-rolled IF steel to prove that sulfide precipitation occurs along our proposed theory.¹⁻²⁰⁾

Please note that the terminology is very confusing in this scientific field. There have been some reports to mention the correlation between age-hardening and solute carbon in “Ti-stabilized Ultra Low Carbon Bake-Hardenable steel (Ti-ULC-BH)”^{25,26)} whose chemical compositions are designed to be lower sulfur (<20 ppm) and/or higher Mn (>1%) to obtain BH properties so that carbon is partially and/or weakly stabilized into TiC by inhibiting the precipitation of $\text{Ti}_4\text{C}_2\text{S}_2$.²⁷⁻³⁰⁾

It should be noted that BH steel, ULC steel, IF-BH steel can be regarded as the same category of age-hardenable steel, but these steels are not IF steel. They include solute carbon and are designed to expect strain-age-hardening-based YS up. Strictly speaking, IF-BH steel is an inconsistent term. IF and BH are opposing definitions to each other, but “IF-BH steel” is regularly used for the name to mean ULC-based BH steel. The sample used here is “Ti-IF steel” and it has been believed that solute carbon does not exist. Our proposed mechanism is required for solute carbon in as-hot-rolled IF steel and therefore the existence has to be proven experimentally.

In the following section, the whole sulfide precipitation is explained by using long-annealing samples, together with the Cu-S precipitation. The mechanism is not only derived by experimental facts but also proven conclusively.

2. Samples and Experimental Procedure

In understanding sulfide precipitation in Ti-added steel, the authors selected Ti-stabilized Interstitial-Free (Ti-IF) steel, because it is so simple a system that we are able to obtain a precise result of sulfide characterization.

The main characteristic is that all Ti-added samples include 0.01%Cu, which is inevitably present even if scraps are not used for steelmaking. The samples are from commercial-based as-hot-rolled steel which was produced through a trial operation from blast-furnace & LD-converter-based steelmaking and continuous-casting, and then hot-rolled.

As shown in Table 1, the samples of (iii) with two levels of Ti addition (0.04%Ti and 0.06%Ti) were prepared to carry out research on the transitional change on sulfide precipitation in ferrite region in accordance with annealing time. They are referred to as “0.04%Ti-IF” and “0.06%Ti-IF”, by using the Ti content. Note that the numbering intentionally starts with (iii) and the following numbering starts with (10). They are consecutive numbers from the first paper.¹⁾

As shown in Fig. 1, samples of 0.04%Ti-IF and 0.06%Ti-IF are prepared (10) as-hot and then annealed at 850°C for (11) 90 s → AC (Air Cooling), (12) 5 min → AC and (13) 30 min → AC. It should be noted that AC in sheet steel is as rapid as 200 to 500°C/s.

Fig. 1 Schematic diagram of heat treatment of (iii).

Fig. 2 Schematic procedure of Aging Index (AI) measurement.

Please note that both “0.04%Ti-IF” and “0.06%Ti-IF” in this paper do not correspond to “0.04%Ti-IF” in the first and second papers^{1,2)} and “0.07%Ti-IF” in the first papers,¹⁾ respectively. Each element slightly differs, but they are referred to as “0.04%Ti-IF” and “0.06%Ti-IF”, because steel product has an allowable range of chemical compositions in real production and can be regarded as same steel sheets within an allowance.

Experiments were carried out mainly through two methods: (a) microanalysis with the use of a Transmission Electron Microscope (TEM) and its analytical spectrometric gears and (b) quantitative chemical analysis of each sulfide (“*Tai-Betsu* analysis” in a Japanese technical term) with the application of extracted residue and its dissolution technique. These two methods are shown in detail in the first report¹⁾ of three consecutive papers.^{1,2)}

In addition, the (iii) as-hot samples were evaluated by (c) Aging Index (AI) through a mechanical evaluation technique to estimate the existence of solute carbon. This experiment is required for the discussion of the estimated mechanism of the first reaction in our proposed mechanism.²⁾ The AI procedure is based on a conventional method as shown in Fig. 2: (1) 8%-pre-strain is applied in a tensile test and (2) then tension is unloaded, (3) the sample is kept at 100°C for 1 h and (4) the tensile test is performed again. (5) The increase in stress corresponds to “AI”. “AI > 0” indicates that the sample contains solute carbon, while “AI = 0” indicates that the carbon and/or nitrogen are fully stabilized as carbide and nitride.

Fig. 3 Typical images of transitional morphological change of multi-precipitate-combined sulfide by long-time-annealing in Ti-added steel.

3. Results

3.1 Transitional change of sulfide precipitation in long-time-ferrite-annealed 0.04%Ti-IF and 0.06%Ti-IF samples

In this section, a transitional change of sulfide at 850°C is discussed. The transition of sulfide precipitation in 0.04%Ti-IF and 0.06%Ti-IF is studied by using (10) as-hot samples and annealed samples at 850°C for (11) 90 s → AC (Air Cooling), (12) 5 min → AC and (13) 30 min → AC. It should be noted that AC in sheet steel results in cooling as rapid as 200 to 500°C/s.

First of all, a typical example of transitional change is shown in Fig. 3 to provide a simple overview of transitional morphological appearances. Detailed morphological changes in 0.04%Ti-IF and 0.06%Ti-IF samples are shown in Figs. 5 and 6, respectively.

In studying a series of TEM micrographs in Fig. 3, the authors have to call attention to a few special points in advance. It should be noted that examples in Fig. 3 are composed of picked-up “typical sulfides” from Ti-stabilized IF steel with various Ti additions and annealing temperatures, which are not limited in 0.04%Ti-IF nor 0.06%Ti-IF in this third paper. In addition, each sulfide dares to be adjusted to almost the same size and the magnification is different in each image. The real size is approximately 150 to 400 nm. Therefore, Fig. 3 shows how the sulfide in Ti-added steel changes morphologically and compositionally as the annealing is done for longer time.

In as-hot sample, TiS is the main sulfide and its morphology is round-shaped or oval-shaped. The surface layer is not smooth and TiS sometimes accompanies a partially-attached tiny-sized precipitate or a thinly-coated frilled structure. By annealing for a short time, for example, for 90 s, the sulfide is changed into a multi-precipitate-combined sulfide: TiS is located in the center, $\text{Ti}_4\text{C}_2\text{S}_2$ are formed as a bulge-shaped precipitate partially attaching on TiS, and Cu-S is observed on some of the overlapped areas

between TiS and $\text{Ti}_4\text{C}_2\text{S}_2$. Through long-time-annealing, the sulfide eventually changes to “donut-shaped” and/or “croissant-shaped (crescent-roll-shaped)”. TiS, which used to exist at the center of a multi-precipitate-combined sulfide in the 90 s-annealed sample, disappears or gets small and thin, finally leaving a hole. Each bulge-shaped $\text{Ti}_4\text{C}_2\text{S}_2$ precipitate grows larger and is mutually combined together. Interestingly, Cu-S is hardly confirmed in 30 min-annealed samples, especially in 0.06%Ti-IF.

Although shown as typical examples in Fig. 3, all long-time-annealed sulfides are not always observed as “donut-shaped” nor “croissant-shaped (crescent-roll-shaped)” and some of them are somewhat deformed. As explained in Fig. 4 by using a donut, such a complex-shaped multi-precipitate-combined sulfide has a 3-dimensional configuration and it is often observed as a different shape (2-dimensional-projected image) in accordance with the viewing angle. Therefore, the shape cannot be defined by a few TEM micrographs and it should be judged in a comprehensive manner by using many data. For the same reason, the size of these sulfides cannot be defined by a few TEM micrographs, either.

Detailed TEM micrographs of 0.04%Ti-IF and 0.06%Ti-IF samples are shown in Figs. 5 and 6, respectively. Basically, the similar transitional change occurs and the strange phenomenon of Cu-S is also confirmed. The only difference is the sulfide in the as-hot sample. The sulfide in 0.04%Ti-IF sample is composed mainly of TiS, while the sulfide in 0.06%Ti-IF sample has thinly-coated frilled other sulfides and/or partially-attached tiny-sized other sulfides on TiS.

From a chemical analytical point of view, *Tai-Betsu* analysis of each sulfide is shown in Fig. 7. Basically, the tendency reflects the TEM observations of Figs. 3, 5 and 6. As mentioned in TEM micrographs, the interesting thing is the Cu-S precipitation phenomenon. Cu-S is rarely confirmed in as-hot sample, and the amount of Cu-S is considerably precipitated at short-annealing (850°C for 90 s), but it decreases at long-annealing (850°C for 30 min).

Fig. 4 2-dimensional projected images of 3-dimensional configuration from different angles, by using a “donut”.

Fig. 5 Transitional morphological change in accordance of annealing time in 0.04%Ti-IF.

The following explanation is general description of the whole sulfide precipitations.

In both 0.04%Ti-IF and 0.06%Ti-IF, as-hot samples are composed mainly of TiS. Through following 90 s-annealing, TiS “decreases”, and $Ti_4C_2S_2$, MnS and Cu-S “increase” in both steels. The distinction in the 90 s-annealed samples of both steels is the content of “S as Cu-S”; 0.04%Ti-IF sample has more Cu-S than 0.06%Ti-IF sample. When annealed for longer minutes (5 to 30 min), TiS decreases, $Ti_4C_2S_2$ and MnS increase, but conversely Cu-S “decreases” in the 0.04%Ti-IF sample, and, in contrast, TiS, MnS and Cu-S “decrease”, and $Ti_4C_2S_2$ increases in the 0.06%Ti-IF sample.

It should be noted that the above parenthetical description of “Cu-S decreases” is not a proper expression, because it may probably make us misunderstood that Cu-S is initially formed and then it is dissolved and reduced. If it really occurred, it would not be possible to explain the phenomenon

from the thermodynamical viewpoint. In our opinion, the Cu-S phenomenon should be regarded as the consequence that Cu-S can be precipitated when the preceding sulfide reactions are completed and then re-solute sulfur still exists.

The above results in Figs. 3, 5, 6 and 7 implies that Cu-S is formed during WQ if re-solute sulfur still remains in steel, after the preceding sulfide precipitation is finished at 850°C. That is to say, the sulfide precipitation can be interpreted along the same mechanism in the first and the second papers that (re-)solute sulfur exists and it is re-precipitated at low temperature in ferrite region.^{1,2)}

3.2 Aging Index of as-hot-rolled 0.04Ti-IF and 0.06Ti-IF steel

As mentioned in the second paper,²⁾ the authors has explained the sulfide precipitation in ferrite region in Ti-added steel by using the chemical reaction “ $4TiS + 2[solute$

Fig. 6 Transitional morphological change in accordance of annealing time in 0.07%Ti-IF.

Fig. 7 Annealing-time-dependent change of sulfide precipitation in Tai-Betsu analysis in 0.04%Ti-IF and 0.06%Ti-IF.

$C] \rightarrow Ti_4C_2S_2 + 2[solute\ S]$. However, this chemical reaction is required for “solute carbon” in Ti-added steel when the reaction occurs.

Through three consecutive papers, Ti-stabilized IF steels are used for a series of experiments. Judging from the name “IF steel”, or Interstitial-atom-Free steel, all interstitial elements, such as carbon and nitrogen, have to be stabilized as precipitates. In reality, however, solute carbon exists in the as-hot sample of recently-produced Ti-stabilized IF steel.

Figure 8 shows strain-stress curves of Aging Index (AI) measurements in both 0.04%Ti-IF and 0.06%Ti-IF, which are evaluated as a lower-yielding-strength-based strength increase through a subtraction of “8% pre-strained strength” from “yielding strength in tensile test of a heat-treated sample at 100°C for 1 h after 8% pre-strained”. The Aging Index (AI) of 0.04%Ti-IF and 0.06%Ti-IF are the same values of 33 MPa.

“IF steel” is alloy-designed to stabilize all of the interstitial elements as precipitates, for example, it has been controlled, for example, by using the parameters of “ $C(at\%) / Ti(at\%) < 1$ ”, “ $[Ti - N/14 \times 48(\text{used for } TiN) - S/32 \times 48(\text{used for } TiS)]/48 \times 12 - C > 0(\text{mass}\%)$ (enough to stabilize carbon)” and so on. Figure 8 means that as-hot sample in Ti-IF contains solute carbon, and strictly speaking, as-hot steel sheets of 0.04%Ti-IF and 0.06%Ti-IF in this paper can be regarded literally as “non-IF steel”. In other words, the data in Fig. 8 proves the existence of “solute carbon” in as-hot Ti-IF steel which is regarded as the required condition in our proposed mechanism “ $4TiS + 2[solute\ C] \rightarrow Ti_4C_2S_2 + 2[solute\ S]$ ”.

4. Discussions

4.1 Mechanism of sulfide precipitation at long-annealing of ferrite region in Ti-added steel and interpretation of Cu-S precipitation

The same mechanism in the first¹⁾ and the second papers²⁾ is applied to these phenomena. The concept is based on the idea that (re-)solute sulfur comes out in the first reaction and it is re-precipitated in the second reaction.

Fig. 8 Aging Index of as-hot-rolled 0.04%Ti-IF and 0.06%Ti-IF steel.

The following mechanism needs the existence of already-precipitated TiS and solute carbon, both of which have been proved experimentally. For the sake of simplicity, the mechanism is divided into two reactions and the following “re-solute sulfur” is assumed as virtual existence.

The first reaction is a trigger to reconfigure sulfide precipitation, in which already-precipitated TiS is reacted into “first $\text{Ti}_4\text{C}_2\text{S}_2$ ” and simultaneously “re-solute sulfur” comes out. In the second reaction, the “re-solute sulfur” is re-precipitated as one of three candidates: “second $\text{Ti}_4\text{C}_2\text{S}_2$ ”, MnS and Cu-S.

[First reaction]

[Second reaction] (three possible candidates)

In our opinion, the first reaction and the second reaction are basically one-way continuous precipitations. Since solute sulfur cannot be found experimentally, it is thought that re-solute sulfur is quickly re-precipitated as other sulfides, as soon as it appears along the first reaction. Probably, these two reactions is correlated through Le Chatelier’s law.

The parameters for the first reaction are the amount of solute carbon and temperature and time in heat-treatment. The ones for the second reaction are the amount of solute sulfur, temperature and time in heat-treatment, the amount of solute carbon and the amount of each sulfide-former element. The mechanism to reconfigure sulfide precipitation is dependent on many mutually-related factors. Since it has been proven in Fig. 7 in 3.2 section that solute carbon exists in the Ti-IF steel used here, our mechanism does not have any obstacles to explain the phenomena.

By applying the above mechanism, we can interpret a strange phenomenon on the Cu-S precipitation in *Tai-Betsu* analysis in Fig. 7 that the Cu-S content is large in 90 s-annealed sample but it is “reduced (hard to observe)” in 30 min-annealed sample. The important point is how far rightward the first reaction proceeds during heat treatment and then what stabilizes the “re-solute sulfur” along the second reaction according to thermodynamics.

At short-annealing, the (1st) reaction proceeds rightward and simultaneously “re-solute sulfur” comes out. The

annealing time is so short that the (2nd-1) and (2nd-2) reactions cannot stabilize all of the “re-solute sulfur”. The remaining “re-solute sulfur” is stabilized as Cu-S in ferrite region during WQ. In contrast, at long-annealing, the (1st) reaction proceeds further rightward and simultaneously more “re-solute sulfur” comes out. The annealing time is so long that the (2nd-1) and (2nd-2) reactions can stabilize much of the “re-solute sulfur”. The remaining “re-solute sulfur” gets lower and therefore the amount of Cu-S is reduced. The Cu-S phenomenon should be regarded as a consequence that (re-)solute sulfur is reduced by stabilizing with various sulfide-former through the thermodynamics and the remaining solute sulfur is precipitated by a small amount of Cu at the end of a series of sulfide precipitations. It is not thermodynamically possible to interpret literally that Cu-S is initially precipitated at short-annealing and dissolved away at long-annealing.

At the (1st) reaction of the change from TiS to $\text{Ti}_4\text{C}_2\text{S}_2$, precipitated sulfur is reduced by half in quantity. By using this knowledge, sulfide precipitation can be understood more precisely. The method for interpretation has mentioned in Fig. 11 in the second paper.²⁾

As shown in Fig. 9, through the comparison between 90 s-annealed and 30 min-annealed 0.04%Ti-IF, it is concluded that the longer-annealed sample has both “first” and “second $\text{Ti}_4\text{C}_2\text{S}_2$ ”. In contrast, it can be estimated that the shorter-annealed sample has only “first $\text{Ti}_4\text{C}_2\text{S}_2$ ” and “re-solute sulfur” is stabilized as mainly Cu-S during WQ.

The above mechanism has a broad range of applications to explain the whole sulfide precipitation in ferrite region in Ti-added steel and to interpret the role of Cu-S precipitation. As compared to the past studies,^{21–24)} our viewpoint can be regarded as innovative and comprehensive. As mentioned in “Purpose of our studies and reviews of past reports” in the first paper¹⁾ and in “Introduction” in the second paper,²⁾ the sulfide precipitation in ferrite region has been exceptionally reported only by K. Yamada *et al.*^{21,23)} and H. Murakami *et al.*,^{22,24)} but their mechanisms are mutually contradictory and can be restrictedly used only for their reporting phenomena. In contrast, our mechanism has a wide application to explain the whole sulfide precipitation phenomena in ferrite region in Ti-added steel and their reported phenomena can be also interpreted logically.

Fig. 9 Mechanism “ $4\text{TiS} + 2[\text{C}] \rightarrow \text{Ti}_4\text{C}_2\text{S}_2 + 2[\text{S}]$ ”-based interpretation of sulfide precipitations to (a) as-hot & 850°C for 90 s and (b) as-hot & 850°C for 30 min.

4.2 Integrated mechanism of sulfide precipitation in steel

The authors have already shown the mechanism of Ti-added steel in austenite region with the subsequent cooling in the first paper¹⁾ and the theory in ferrite region in the second²⁾ and this third papers. In this section, these proposed mechanisms are integrated into a unified concept to explain all the sulfide precipitation phenomena in steel.

First of all, the mechanism in Ti-added steel is mentioned. Figure 10 is a schematic diagram to explain sulfide precipitation in Ti-added steel. The unified mechanism is based on the newly-added concept of (#3) for ferrite region and (#2-2) for austenite region, in addition to the traditional concept of (#1) and (#2-1). Of particular note is newly-pointed (α -1st) and (γ -1st) of TiS-based reconfiguration and (α -2nd-3) of Cu-S precipitation in ferrite region.

The fundamental of this integrated theory is based on the combination phenomenon of (re-)solute sulfur and its re-precipitation. As mentioned through three consecutive papers,^{1,2)} “re-solute sulfur” is from TiS-based reaction which is “ $4\text{TiS} + 2[\text{C}] \rightarrow \text{Ti}_4\text{C}_2\text{S}_2 + 2[\text{S (re-solute)}]$ ”. It should be noted that “re-solute sulfur” is virtual existence for explanation. When “re-solute sulfur” comes out to matrix, it will be quickly re-precipitated by one of sulfide-

former elements into sulfide. When re-solute sulfur still remains after the preceding precipitations are completed, it is re-stabilized as Cu-S even during WQ. Therefore, it is thought that re-solute sulfur cannot be confirmed when observed a sample at room temperature. In contrast, “solute sulfur (in narrow meaning)” is based on the remaining free sulfur which cannot be stabilized beyond precipitable sulfur limit, when heat-treated at high temperature.

Our group points out that the reactions of (#1) to (#3) are important chemical reactions to deepen understanding of sulfide precipitation in Ti-added steel, especially (#3) in ferrite region. In addition, the reaction of (α -2nd-3) in (#3), the Cu-S precipitation, should be understood as one of the important reactions among mutually-related sulfide precipitations, especially as the final sulfide precipitation to stabilize both “solute sulfur” and “re-solute sulfur”. It can be interpreted that Cu acts as a strong sulfide-former to stabilize (re-)solute sulfur along the mechanism of (α -2nd-3) in (#3) even if Cu is at a trace level of 0.01%.

It has been proven experimentally through three consecutive papers that the (#1) reaction and the (#3) reaction really occur in austenite and ferrite region, respectively.^{1,2)}

The traditional concept in Ti-added steel is also shown in both the (#1) and the (#2-1) of the schematic diagram in

Fig. 10 Integrated mechanism of sulfide precipitation in Ti-added steel.

Fig. 10. In the past studies, the focus of attention has been targeted to only the three sulfide precipitations of $(\gamma-1)\text{TiS}$ in (#1), $(\gamma-2)\text{Ti}_4\text{C}_2\text{S}_2$ in (#2-1) and $(\gamma-3)\text{MnS}$ in (#2-1). Three candidates of sulfide precipitation in austenite region are competitive reactions to stabilize solute sulfur at high temperature. Which precipitate is formed most predominantly is dependent on temperature and time in heat-treatment and the amounts of sulfide-formers (Ti and Mn). It has been still believed that this scientific field has been regarded as investigated thoroughly, and that these phenomena can be predicted through equilibrium thermodynamical calculation in austenite region.

Although the conventional theory is well established, the authors present another estimated reaction in austenite region. There seems to be no direct evidence to prove whether either reaction of (#2-1) or (#2-2) occurs in austenite region or whether both precipitations proceed, but we think that the (#2-2) reaction really occurs. Judging from TEM micrographs of as-cast and its austenite-heat-treated Ti-IF in Fig. 6 in the first paper,¹⁾ it is microscopically evident that rod-like-structured $\text{TiS-Ti}_4\text{C}_2\text{S}_2$ -combined sulfides in as-cast sample always have overlapping points or TiS in austenite-heat-treated sample is uniformly covered with $\text{Ti}_4\text{C}_2\text{S}_2$. If only the $(\gamma-2)$ reaction in (#2-1) occurs along the traditional concept, it will be difficult to explain why any free-standing $\text{Ti}_4\text{C}_2\text{S}_2$ does not exist in as-cast and austenite-heat-treated Ti-added steel in the first paper.¹⁾ Therefore, the traditional phenomenon may be also interpreted through the (#2-2) reaction, which means the (#3) reaction can be extended to the precipitation in austenite region.

The above mechanism can also cover the phenomena in non-Ti-added steel. If Ti-related matters are removed from proposed reactions in Fig. 10, the sulfide precipitation in non-Ti-added steel can be interpreted. As mentioned in our paper in non-Ti-added steel,^{3,9-15)} when sulfur and Mn are low in content, especially in recent-produced steel, Mn can no longer stabilize all of sulfur and therefore Cu-S should be interpreted to stabilize such remaining solute sulfur.

The authors think that the whole sulfide precipitation can be understood more precisely through this integrated mechanism, especially the phenomenon in ferrite region. The key point for interpretation is that Cu-S precipitation occurs at low temperature in ferrite region, even during WQ. In other

words, WQ technique has been regarded as a convenient method to freeze precipitation just before WQ, but exceptionally Cu-S precipitation cannot be stopped by WQ, although it may be difficult to accept such a challenging phenomenon intuitively.

4.3 Expected matters derived by integrated mechanism

The following five things can be expected or still remain mysterious in the above integrated concept.

- (1) A small amount of Cu in steel is expected to diffuse faster than published data.³¹⁾
- (2) What temperature is Cu-S formed at?
- (3) Cu-S is independently formed and separation-based precipitation does not occur from complete-solid-solution-typed precipitate, for example, $(\text{Mn,Cu})\text{S}$, $(\text{Mn,Cu})(\text{O,S})$. Cu-S is precipitated as free-standing-typed and/or coating-typed in non-Ti-added steel and at some of overlapping area between TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ in $\text{TiS-Ti}_4\text{C}_2\text{S}_2$ -combined sulfide in Ti-added steel.
- (4) Our mechanism is completely different from any other published data. Why did the past studies conclude that Cu-S is formed at temperatures as high as steel is melted? Or is it possible to describe Cu-S phenomenon thermodynamically?
- (5) All precipitates should be crystallographically energetic-stable form in shape, for example, round-shaped, oval-shaped, cubic, polygonal-shaped, or habit-plane-surrounding-shaped. Why does multi-precipitate-combined sulfide, mainly $\text{TiS-Ti}_4\text{C}_2\text{S}_2$ -combined sulfide, have a strange irregular shape? Why does such an energetic-unstable shape exist?

In regard to (1), although mentioned in the second paper,²⁾ our experimental results lead to the conclusion that a small amount of Cu in steel can diffuse very fast. The prediction goes against the established concept that the diffusion of substitutional element is almost the same to Fe-self-diffusion,³¹⁾ but our observing phenomena can be regarded as one of proofs to support that Cu can diffuse faster. It can be thought that re-solute sulfur comes out along our proposed reaction " $4\text{TiS} + 2[\text{C}] \rightarrow \text{Ti}_4\text{C}_2\text{S}_2 + 2[\text{S (re-solute)}]$ " and it is often re-precipitated as Cu-S at some of overlapping area in $\text{TiS-Ti}_4\text{C}_2\text{S}_2$ -combined sulfide. The question is why sulfur stay there and Cu comes there and stabilizes the sulfur as Cu-

S, although sulfur is an interstitial element to diffuse faster and Cu is a substitutional element to diffuse at the level of Fe-self-diffusion according to the conventional concept. We have not had a clear answer for it. Our prediction that Cu can diffuse very fast is inductively deduced.

Interestingly, there have been some reports in the field of irradiation-induced embrittlement in material for atomic reactors,^{32–36} which mention that Cu diffusion is about two orders of magnitude faster than Fe self-diffusion and is interpreted through Self-Interstitial-Atom (SIA) mechanism, although these experiments are carried out by using Fe-1%Cu or Fe/Cu/Fe diffusion pairs heat-treated at over 1000°C. In our opinion, these phenomena have the same origin to our reports^{1–20} and each Cu-related or Cu-S-related phenomenon is viewed from a different angle.

In regard to (2), it is true that Cu-S is formed as the final sulfide precipitation after the all preceding reaction are completed and it can be precipitated in ferrite region during WQ, but the precise temperature has not been clear yet. The precipitation of Cu-S surely occurs during WQ. Therefore, unfortunately, it means that there are no experimental techniques to freeze the Cu-S precipitation.

It is thought that Cu-S is formed at a certain temperature in ferrite region during WQ. According the experimental data in non-Ti-added steel,^{3,9–15} Cu-S is precipitated at below 750°C during WQ and free-standing Cu-S is observed easily in as-hot non-Ti-added steel with CT: 620°C. From the data in Ti-added steel, Cu-S is formed in ferrite region during WQ. However, the authors know that Cu-S is precipitated to some extent whatever heat treatment is done, although the data are not shown here. Therefore, we want to point out the possibility that Cu-S is formed at quite low temperature near room temperature, such as a similar case in aging phenomena of carbon. As another similar example, it has been widely known that brass(Cu-Zn-alloy)-coating on steel code and vulcanized rubber (sulfur) for tire are easily combined into Cu-S at low temperature (below 100 to 200°C),^{37–40} although the contents of sulfur and Cu are so high.

In regard to (3), it is microscopically evident that Cu-S is independently formed through three consecutive papers.^{1,2} The precipitation is not based on the separation from complete-solid-solution-typed sulfide and oxy-sulfide.

The topic of (4) is related to either the above (1) or the second reactions in our proposed mechanism in Fig. 10. Although some groups have reported the solubility product of Cu-S⁴¹ and thermodynamical data,^{42,43} these data are based on WQ-method-based Cu-S phenomenon by using intentionally-Cu-added steel. Therefore, one possibility is that Cu-S precipitation might be misinterpreted as formed at temperature just before WQ, or the other possibility is that Cu-S is really formed at temperatures as high as these papers are saying, because the second reaction in our mechanism is a competitive precipitation among three candidates. When Cu is intentionally added, the reaction of Cu-S may be selected to occur at high temperature.

In our opinion, it is difficult to describe the Cu-S precipitation thermodynamically when Cu is at trace level. Cu-S is formed at low temperature in ferrite region even during WQ. Therefore it means that there are no proper experimental techniques to freeze the precipitation. Addi-

tionally, especially in Ti-added steel, the Cu-S precipitation is not in equilibrium. It is influenced by the preceding sulfide precipitations and can be regarded as a time-dependent phenomenon.

In regard to (5), the strange morphology of precipitate is based on the sulfide precipitation that does not reach equilibrium in usual heat treatment. If the precipitation occurs along the first reaction in our proposed mechanism “4TiS + 2[C] → Ti₄C₂S₂ + 2[S]”, the equilibrium state means that the reaction will continue until TiS is used up. However, in most cases, TiS still remains in a multi-precipitate-combined precipitate, which means it does not reach equilibrium, that is, precipitations can be regarded as intermediate state. Therefore, it is thought that energetic-unstable-irregular-shaped precipitates can exist.

5. Summary

The authors provide the following new concepts of sulfide precipitation in Ti-added steel, especially Ti-stabilized IF steel by using long-annealed samples, and give the integrated mechanism to interpret all the sulfide phenomena through three consecutive papers.^{1,2}

(1) Even a trace level of 0.01%Cu can act as a sulfide-former in Ti-added steel, and Cu-S is formed during WQ.

(2) The sulfide precipitation in both austenite and ferrite regions can be interpreted through the integrated mechanism in Fig. 10. The fundamentals of this mechanism are based on the combination effect of (re-)solute sulfur and its re-precipitation.

(3) In ferrite region, already-precipitated TiS is changed into Ti₄C₂S₂ and re-solute sulfur comes out, and then it is re-precipitated as three candidates of sulfides: Ti₄C₂S₂, MnS and Cu-S. The Cu-S precipitation occurs only when re-solute sulfur still remains after the preceding reactions are completed. The strange phenomenon that Cu-S disappears in long-annealed Ti-IF steel can be explained along the mechanism below, that is, much of re-solute sulfur is stabilized as Ti₄C₂S₂ and/or MnS, and re-solute sulfur cannot be stabilized by Cu.

[Our proposed mechanism in ferrite region]

[First reaction]

[Second reaction]

(4) In austenite region, it is thought that both or either of two possible reactions occurs. The one is the conventional reaction and the other reaction is the above-mentioned (3) mechanism. If the sample is cooled slowly, the precipitation also occurs in ferrite region along the above-mentioned (3) reactions

[Conventional reaction in austenite region]

[Another reaction] (extension of the mechanism in ferrite region)

[First reaction]

[Second reaction]

(5) In non-Ti-added steel, the sulfide precipitation should be interpreted along Ti-related-phenomena-exclusive above-mentioned (3) and (4) mechanisms. The solute sulfur is based on the phenomenon that Mn cannot stabilize all of sulfur in steel. When sulfur and Mn are low in content, Mn can no longer stabilize all of sulfur and remaining sulfur is precipitated as Cu-S by small amount of Cu.

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