Precipitation of Copper Sulfide in Ultra Low Carbon Steel Containing Residual Level of Copper

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The influence of residual copper (≤0.01 mass%) on sulfide precipitation in ultra low carbon steel was studied with microanalysis using Field Emission-Transmission Electron Microscopy (FE-TEM), X-Ray Diffraction (XRD) of the extracted precipitates and quantitative chemical analysis of extraction residue.

A small amount of copper (≤0.01 mass%) plays an important role in sulfide formation in steel, as does manganese. Two types of sulfides were found in ultra low carbon steel with residual copper: (1) MnS covered with copper sulfide (Cu–S) and (2) “free-standing” Cu–S, with sizes of φ100~300 nm and less than about 640 nm, respectively. The atomic ratio of Cu/S was determined to be 1.8 ± 0.3 by Energy Dispersive X-ray spectroscopy (EDX), and the phase was determined to be Cu5S4 from XRD of the extracted precipitates.

Quantitative chemical analysis revealed that almost all sulfur (71 mass ppm) was precipitated as sulfides in steel containing 73 ppm of sulfur. The concentration of sulfur as Cu5S4 was 24 ppm, which accounts for about 35% of the total quantity of sulfur. This indicates that the formation of copper sulfide has to be taken into account in precise analysis of sulfides in low Mn and S systems (Mn ≈ 0.20%, S ≈ 0.007%).

The precipitation of Cu–S in water-quenched (WQ) samples and the morphologies of MnS-cored BN & Cu–S-covered MnS in hot-rolled and WQ samples suggest that Cu–S is formed at temperatures between “below 750°C” and 620°C and is also precipitated even during a short time in water-quenching.

Keywords: copper sulfide, manganese sulfide, boron nitride, precipitate, ultra low carbon steel, transmission electron microscopy, X-ray diffraction, quantitative chemical analysis, extracted residue, residual element, tramp element

1. Introduction

With the improvement of steelmaking technology, impurities in mild steel, especially IF steel, have been removed to the greatest extent possible in order to increase its elongation and r-value (Lankford value). Recently, the carbon, nitrogen and sulfur contents have been lowered to single-digit ppm levels in some cases. However, it is not practical to completely eliminate all these elements from steel. Sulfur, carbon, and nitrogen are often stabilized as precipitates.

Sulfur is related to hot-shortness. S is known to segregate to grain boundaries in the austenite phase. If S and iron react to form FeS, the FeS will lead to intergranular fracture in hot-rolling. Therefore, in practice a considerable amount of Mn is added to steel to prevent hot-shortness.

Previous studies1–4) have reported the Mn/S ratio and also the content of Mn and S required to prevent hot-shortness from the viewpoint of “reduction of area”. Their data are shown as lines and hatched areas in Fig. 1. Each definition was slightly different, but the investigators reported the same concept: S was precipitated as MnS or (Mn,Fe)S.

The precipitation of sulfur has also been investigated with chemical analysis. The Non-metallic inclusions analysis subcommittee, supported by The Iron and Steel Institute of Japan (ISIJ), carried out quantitative analyses of sulfur precipitation.5) The S content in steel, the S content as sulfides and the S content calculated by using the Mn content in extracted residue were determined by chemical analysis and then compared with each other. Solid circles in Fig. 1 are the samples in which more than 95% of the S content is precipitated as sulfide. Figure 2 shows the case that is indicated by the solid circle with a white arrow in Fig. 1. From the viewpoint of chemical analysis, the graph also supports the concepts of earlier studies.1–4) The addition of Mn is effective in stabilizing almost all the sulfur as MnS.
However, we found that sulfide precipitation is different when both Mn and S are present at very low levels. Figure 3 is an example of the sample used in this paper (cf. Table 1). The content of S in the steel is 73 ppm and the S precipitated as sulfides is 71 ppm. However, the calculated S content is only 47 ppm when calculated using the Mn and Fe content in the extracted residue on the assumption that the atomic ratios of MnS and (Mn,Fe)S are Mn:S = 1:1 and (Mn+Fe):S = 1:1. The S content as sulfides calculated from the amount of Mn and Fe is always much smaller than the S content directly analyzed as sulfides.

The subject of this paper is to explain this difference, as shown in Fig. 3, together with sulfide precipitation in ultra low carbon, nitrogen and sulfur steel (0.17%Mn–0.0073%S/Table 1). In addition to Mn, we pay attention to the residual level of another sulfide-forming element that has not previously been mentioned in such an ultra low carbon steel (see Section 4.3).

We provide new evidence to explain the above discrepancy and discuss the temperature at which sulfides are formed.

2. Experimental Procedure and Samples

Both physical and chemical analyses were performed. The sample was an ultra low carbon steel. Its chemical composition is shown in Table 1. This steel is a boron-added steel with 0.17% Mn and 0.01% Cu, without any carbide-, sulfide- and nitride-formers except for boron as a nitride-former and Mn as a sulfide-former. Hot-rolled sheet steel was used in this study. The sample was commercial steel sheet from a blast furnace-LD converter. The sample was processed under the following heat conditions: slab reheating temperature (SRT) = 1220°C, hot-rolling final temperature (FT) = 900°C, and hot-rolling coiling temperature (CT) = 620°C.

Microanalysis was performed using Field Emission-Transmission Electron Microscopy (FE-TEM) to determine the composition of the precipitates by conventional Energy Dispersive X-ray spectroscopy (EDX/with Be window) and Electron Energy Loss Spectroscopy (EELS). An elemental mapping was carried out with postcolumn-type imaging EELS (Gatan 678 Imaging EELS). Carbon extraction replica samples were used in FE-TEM analysis, prepared by potentiostatic etching using 4% Methyl Salicylate–1% salicylic acid–1% tetramethyl ammonium chloride–methanol (4% MS) electrolyte. Since copper-containing phases were investigated, we used Al-grids or Ti-grids as supporting meshes.

By using extracted residues, all precipitates in the steel were also qualitatively measured with XRD using a Cu Kα X-ray tube. The precipitates were chemically extracted with 10% AcetylAcetone–tetramethyl ammonium chloride–ethanol (10% AA) electrolysis, collected on a filter and then examined with low-angle (1 deg.) XRD to determine the phases of the precipitates.

The total amount of each type of sulfide was measured by quantitative chemical analysis, as shown in Fig. 4. All the precipitates were extracted by potentiostatic extraction using 4% MS electrolyte. The Mn, Fe and Cu content were determined by Ion-Coupled Plasma atomic emission spectroscopy (ICP), while the S content in the extract was quantified by infrared absorption after the extract was dissolved with a mix of HNO₃, H₂SO₄ and HClO₄. The S content corresponding to each type of sulfide was calculated on the basis of the atomic ratios, using the quantities of the metallic elements (see Section 3.1).

Two kinds of electrolyte were used in this experiment: 4% MS for TEM preparation & chemical analysis and 10% AA for XRD preparation, because 4% MS is very effective for sulfide extraction, but the time for extraction is much longer than with 10% AA. Since XRD requires a large amount of extracted residue, 10% AA was used for this.

In addition, the precipitation of sulfides was investigated, using Water-Quenched (WQ) samples whose cooling rate

![Fig. 2 Example of chemical analysis of sulfur precipitates, adapted from K. Narita’s data (solid circle with white arrow in Fig. 1).](image1)

![Fig. 3 Analytical mystery of sulfide precipitation — an example in ultra low carbon steel (0.17%Mn–0.0073%S/Table 1).](image2)

<table>
<thead>
<tr>
<th>Table 1 Chemical composition (mass%).</th>
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![Graph](image3)
was faster than 500°C/s. The samples were 4 mm thick. They were processed with salt baths in three heat patterns: (a) 1220°C for 20 min → WQ, (b) 1220°C for 20 min → 900°C for 20 min → WQ and (c) 1220°C for 20 min → 750°C for 20 min → WQ.

Precipitates were examined by TEM with an ultrathin window-type EDX (to detect lighter elements such as B, C and N).

3. Results

3.1 Characterization and quantitative analysis of sulfides observed in hot-rolled ultra low carbon steel

Figures 5–9 show that there are three kinds of precipitate in the ultra low carbon steel: (a) manganese sulfide (MnS), (b) copper sulfide (Cu–S) and (c) boron nitride (BN), and these precipitates are seen in the following three different shapes, in combination and/or free-standing:

1. Every surface of MnS is covered with either Cu–S (Fig. 6) or BN (Fig. 7). As for the size of these complex precipitates, the former is 100~300 nm in diameter and the latter is 100~200 nm in diameter.

2. Small “free-standing Cu–S” (Fig. 5) are present as well as “Cu–S coating on MnS” (Figs. 5 and 6). The former is below 40 nm in diameter, and the latter is a thin layer of 40~50 nm. Complex precipitates of MnS and Cu–S are round. The presence of two types of Cu–S is also demonstrated by elemental mappings with imaging EELS in Figs. 8(a)–(c) which are zero loss image (≈5–5 eV), Mn-L image (630~660 eV) and Cu-L image (925~975 eV), respectively.

3. In most cases, BN has MnS (~φ20 nm) as a central nucleus (Figs. 5 and 7). The important point is that the MnS in the core of BN does not include copper. The MnS in the core will also be mentioned in Section 4.2 to explain the temperature at which Cu–S is formed.

4. As determined from low-magnification TEM micrographs of Fig. 9, the size of all precipitates is schematized in Fig. 10. The important point is that the size distribution of MnS is not gaussian. The precipitates are divided into two groups: BN-covered MnS and CuS-covering MnS. The former is about 20 nm and the latter is 100~300 nm. Please note that Figs. 9(b) and (c) are the same view with different tilt angles, which confirms that all BN forms on a core of MnS.

The atomic ratios of MnS and Cu–S were quantitatively analyzed from the EDX spectrum. Figure 11 shows the atomic ratio of Cu/(Cu+Mn) from EDX analysis when an electron beam strikes the entire area of a sulfide. As the sulfides become smaller, the Cu content gets higher (solid...
Fig. 6  Detailed analysis of MnS: (a) TEM micrograph and (b) atomic ratio by EDX.

Fig. 7  Detailed analysis of BN: (a) TEM micrograph, (b) EELS spectrum (1) and (c) EDX spectrum (2).

Fig. 8  Elemental mappings of MnS by imaging EELS: (a) zero loss (elastic) image, (b) Mn–L edge map and (c) Cu–L edge map.
circles in Fig. 11). Sulfides smaller than 40 nm are composed solely of Cu and S. The exception (open circles in Fig. 11) is that a small size of sulfide at the center of BN is "pure" MnS (without "coating" Cu–S). By EDX analysis, the atomic ratio of free-standing Cu–S was determined to be 1.8 ± 0.3.

Also, the atomic ratio of the coating Cu–S was estimated with EDX at 1.6~1.8 by the following procedure: (1) Since the Cu content near the center of an MnS is quite small, as shown in Fig. 6(b)−②, the atomic ratio of MnS can be regarded as M_{n_{1,0}}S_{1,0}. (2) The EDX spectrum at the edge of a large MnS is used for the estimation of the atomic ratio of Cu/S in the coating Cu–S, as shown in Fig. 6(b)−①−③. (3) On the assumption that the atomic ratio of Mn:S is 1:1, the amounts of Mn and S from MnS are subtracted from "②" and the atomic ratio of the coating Cu–S is calculated. In this way the coating Cu–S was estimated to be CuS_{1.6−1.8}. Therefore, these two types of Cu–S (free-standing and coating) can be regarded as having the same composition.

XRD was used to determine the crystal structure of Cu–S. Figure 12 shows that there are three kinds of precipitates in the sample: MnS, Cu–S and BN. The peaks of Cu–S are broad, which suggests that both free-standing Cu–S and coating Cu–S are small in size. The Cu–S is presumed to be Cu_{0.5}S_{0.5}: geerite (JCPDS: 33-491).

By using the atomic ratios of (Mn,Fe)S_{1.0} and Cu_{0.5}S_{0.5}, the amounts of each sulfide can be quantitatively determined, based on the chemical extraction and isolation method (Fig. 4). Figure 13 shows that the difference in Fig. 3 corresponds to the sulfur as Cu_{0.5}S_{0.5} (24 ppm), and this accounts for about 35%, although Cu is only present in the steel at a residual level (≤0.01%).
3.2 Characterization of sulfides appearing in water-quenched samples

Figures 14–17 are TEM micrographs of precipitates in sheet steel treated by (a) 1220 °C for 20 min → WQ, (b) 1220 °C for 20 min → 900 °C for 20 min → WQ and (c) 1220 °C for 20 min → 750 °C for 20 min → WQ, respectively.

First we note the general characteristics of Cu–S in WQ samples. As in the hot-rolled sample, its morphology is categorized into two styles: a coating type and a free-standing type. Although both of them surely exist, the quantity is minute. Also, it should be noted that free-standing Cu–S is not shown in Figs. 14–17, because its precipitates are very small and not numerous.

Next, each style of Cu–S is examined in detail. The layer of coating Cu–S in all WQ samples is so thin that it cannot be identified solely by its contrast in TEM micrographs (Figs. 14, 15 and 17), and its existence can be confirmed only by the Cu-Kα peak in EDX spectra, as shown in Figs. 14-(4), 15-(4) and 17-(4). It should be noted that the Cu-Kα peak is from coating-type Cu–S, because the atomic ratios at the edge of Figs. 14-(4) and 17-(4) are found to be S:Mn:Cu = 52:36:12 and S:Mn:Cu = 50:40:10, respectively. If the Cu-Kα peak were from pure Cu on MnS, the atomic ratio of Mn:S would be about 1:1. Since S-rich MnS cannot exist stoichiometrically, Cu-Kα peaks in the EDX spectra in Figs. 14, 15 and 17 imply the existence of coating-type Cu–S, and also that the coating of Cu–S on MnS in WQ samples is very thin. The thickness seems to be about a single nm, judging by EDX analyses that Cu-Kα peak is always found more or less when the electron beam is converged to the edge of precipitates (mainly composed of MnS).

The free-standing Cu–S is not shown in the TEM micrographs. The size is single-digit nm ~10 nm, judging from a few examples observed with TEM. Also, EDX spectra prove the precipitate is composed of Cu and S. The quantity of both types of Cu–S is too small to permit distinguishing one from the other in the Cu–S precipitate in each WQ sample.

Finally, the precipitate in each WQ sample can be described as follows. In sample (a), although the quantity is small, most of the precipitates are MnS (about 100 nm) whose surface is covered with a very thin layer of Cu–S, as shown in Fig. 14-(1). Free-standing Cu–S also exists, but the number of such precipitates is minuscule. BN does not exist. In sample (b), the size of MnS (about 200–500 nm) is larger than in sample (a), as shown in Fig. 15-(1). As in sample (a), BN is not observed and only a few examples of free-standing Cu–S are seen, although sample (b) was processed at 900 °C for 20 minutes.

In sample (c), BN (φ200–500 nm) is seen widely in addition to the sulfides, as shown in Fig. 16-(1). In all cases, BN has a small kernel of MnS (not covered with Cu–S) in the center, as shown in Fig. 16-(3). In addition, Cu–S–covered MnS shows the same tendency in sample (a), as shown in...
Fig. 17-(1). As for free-standing Cu–S, there are only a few, and the situation is the same as in samples (a) and (b).

The precipitates in three WQ samples are schematized in Fig. 18, together with the hot-rolled sample. The above investigation is summarized as follows:

1. Cu–S exists in every WQ heating pattern. It is seen as a coating rather than in a free-standing form.
2. The thickness of the Cu–S coating is presumed to be a single nm in three WQ samples and the size of free-standing Cu–S also ranges from single-digit nm to 10 nm.
3. The Cu–S precipitate does not look different in any WQ samples.
4. MnS at the core of BN is not covered with Cu–S.
5. The size of MnS in the 900°C-C-WQ sample (1) is larger than in the 1200°C-C-WQ and 750°C-C-WQ (2) samples.

The above experimental facts will be used in the discussion in the following Section 4.2 of the temperature at which Cu–S is formed.

4. Discussion

4.1 Precise quantification of sulfides in low Mn and S system

The main subject of this paper is to explain the difference that is shown in Fig. 3. The unsolved problem is that the S content in sulfides in the residue is not equal to the S content calculated from the Mn and the Fe contents in the residue. The latter is always smaller than the former.

As shown in Fig. 13, the difference corresponds to the S that is present as CuS₅, although the Cu content is a residual level (~0.01 mass%). Copper sulfide has to be considered for a precise analysis of sulfide precipitation in ultra low carbon steel. In the sample, one-third of the total sulfide is accounted for by CuS₅.

4.2 Temperature to form Cu–S

In this section, we discuss the temperature at which Cu–S is formed, based on the data in Section 3.1 and 3.2.

One of the important clues is the morphology of MnS. As shown in Figs. 5–9, MnS is covered with either BN or Cu–S, and “double-layered” MnS does not exist (for example, neither surface-coat Cu–S & under-coat BN nor surface-coat BN & under-coat Cu–S is observed). Since MnS is located in the center of both precipitates, MnS is formed at a higher temperature than BN and Cu–S.

The morphology of the precipitates also gives us a hint about whether BN or Cu–S is formed at a higher temperature. If Cu–S were precipitated at a higher temperature than BN, the core of BN would be MnS, with a covering of Cu–S. Even if BN is formed at a higher temperature than Cu–S, it has only to finish precipitating before Cu–S starts to be formed. Therefore, BN is presumed to be formed at a higher temperature than Cu–S.
The solubility product of BN suggests that it begins to be formed at about 1000°C, but the precipitation in WQ samples (Figs. 14–18) says that BN in the hot-rolled sample begins to precipitate somewhere between “below 900°C” and “down to 750°C”, because BN is seen only in sample (c), treated thus: 1220°C for 20 min → 750°C for 20 min → WQ, and not observed in sample (b), produced by treatment at 1220°C for 20 min → 900°C for 20 min → WQ. Therefore, Cu–S is presumed to be formed at a lower temperature than BN starts to be precipitated, between “below 900°C” and 750°C.

The second clue is that the thickness of Cu–S is below 40~50 nm in the hot-rolled sample (Figs. 6 and 8) and is presumed to be about single-nm size in three WQ samples (Figs. 14–17).

When a sample is quenched from a certain temperature, the precipitate is often regarded as fixed at that moment (temperature). However, the concept cannot be applied to the phenomena in our samples.

If Cu–S is interpreted to be formed at temperatures above 1220°C from the data on the 1220°C-WQ sample in Fig. 14, the experimental facts are inconsistent with each other. In such a case, the core of BN would be MnS with a coating of Cu–S, and also the amount of Cu–S in all WQ samples would be equal to that of the hot-rolled sample in which Cu–S accounts for about one-third of all precipitated sulfur, as shown in Fig. 13. Actually, these three WQ samples have a very small quantity of Cu–S (in precipitate number and layer thickness), as shown in Figs. 14–17. Therefore, the low content of Cu–S in WQ samples suggests that Cu has such a strong affinity to sulfur that it can make Cu–S even in the short time available during quenching, despite the rapid cooling at over 500°C/s.

According to the second clue above, it is natural that Cu–S should be formed near a cooling temperature of 620°C. Since the Cu–S in the 750°C-WQ sample is probably based on the precipitation during quenching, the temperature to form as much Cu–S as in the hot-rolled sample is estimated to be below 750°C. Therefore, we presume that Cu–S is precipitated at a temperature between “below 750°C” and 620°C.

Finally, the whole precipitation (Figs. 5, 10 and 13) in our samples is discussed. The sizes of precipitates should theoretically fall on a gaussian distribution in the hot-rolled sample, in which the precipitation can be regarded as an equilibrium process. As shown in Fig. 10, however, the size distribution of MnS has two peaks for BN-cored MnS (~φ20 nm) and MnS with a coating of Cu–S (φ100~300 nm), although each peak itself is gaussian.

Based on the bimodal (two-peak) size distribution of MnS, we discuss below the precipitation of Cu–S, by examining the WQ samples. Although only a few MnS exist and their size is about 100 nm in both 1220°C-WQ and 750°C-WQ samples, the MnS in the 900°C-WQ sample ranges in size to about 200 nm. This suggests that MnS in both 1220°C-WQ and 750°C-WQ specimens remains undissolved when the sample is reheated to 1220°C, and also that MnS cannot grow in size at either 1220°C or 750°C. Therefore, the temperature required to form MnS is presumed to be between “below 1220°C” and “over 750°C”, if the diffusion of Mn and S is not considered. As mentioned in the first clue above (the morphology of MnS), BN is presumed to be precipitated below 900°C, because BN does not exist in the 900°C-WQ sample. The overlap region of 750~900°C is an important temperature range to explain why MnS has a bimodal size distribution.

Figure 19 shows the estimated precipitation of MnS in the hot-rolling process to explain why MnS has a bimodal size distribution:

1. At 900°C, (a) some of the MnS is being precipitated or (b) all of the MnS has already been nucleated.
2. At “below 900°C”, BN is formed on (a) all of the MnS already precipitated or (b) some part of the MnS that has finished nucleation, when MnS is about 20 nm and before Cu–S is precipitated on MnS (the smaller peak in Fig. 10).
begin to precipitate below 900°C mechanism (a) or (b) is correct. Related to the bimodal size distribution of MnS, whether formed by different mechanisms. Therefore, we presume that MnS at BN’s core and MnS with a coating Cu–S should be intensely in a certain temperature range. It is strange that formed.

Theoretically, precipitation should occur continuously and intensively in a certain temperature range. It is strange that MnS at BN’s core and MnS with a coating Cu–S should be formed by different mechanisms. Therefore, we presume that the interruption of the growth of MnS by BN is strongly related to the bimodal size distribution of MnS, whether mechanism (a) or (b) is correct.

As for the temperature to form precipitates, BN is likely to begin to precipitate below 900°C and then the MnS at the core (for the smaller peak in Fig. 10) stops growing. Also, the MnS (for the larger peak in Fig. 10) is likely to grow at a somewhat lower temperature than BN starts to be formed. If BN is formed at a temperature much lower than 900°C, MnS will not be able to grow to a size of 100~300 nm, because MnS is thought to grow in the austenite phase. As for Cu–S, as indicated in the second clue (size of Cu–S), it is presumed to be precipitated at temperatures between “below 750°C” and 620°C. Coating Cu–S is seen in the WQ samples rather than free-standing Cu–S. This fact is reinforced by the TEM micrographs (Figs. 14, 15 and 17) to show that the former makes use of MnS as a nucleus. Therefore, we estimate that the former is formed at higher temperature than the latter.

Interestingly, although Cu is present only at a very low level (≈0.01%), one-third of the sulfur in ultra low carbon steel can be precipitated as Cu–S. In addition, Cu apparently has such a strong affinity for sulfur that it can form a sulfide even during the short time available during quenching, despite the rapid cooling at over 500°C/s.

Such an interesting Cu–S precipitation pattern makes a remarkable contrast with the other Cu-related precipitate “ε-Cu”, which cannot be formed without an isothermal process at 500 to 600°C lasting longer than 10 min. Therefore, we presume that the precipitation of Cu–S is not effected by Cu alone, but that both S and Cu collaborate in the precipitation of Cu–S.

### 4.3 Comparison of copper sulfide precipitation: our data and past studies

As mentioned in Section 4.2, Cu–S is presumed to be formed at temperatures between “below 750°C” and 620°C and is able to precipitate even during quenching. An interesting point is that Cu has such a strong affinity for sulfur that a small amount of Cu–S can be precipitated even during quenching. However, Cu–S is not thermodynamically predicted to precipitate. Only MnS is expected to be formed, according to the latest thermodynamic data.

In this study Cu–S is found in both hot-rolled and WQ samples. Generally speaking, the cooling process after cooling at hot-rolling can be regarded as equilibrium, and most precipitates are formed as stable phases. If Cu–S is also a stable phase, thermodynamic data must be revised. Or if Cu–S is a metastable phase, the kinetics of the reaction of Mn and S must be considered.

The role and effects of a residual level of copper have not been reported in the past. However copper sulfide in steels with higher Cu content has been reported. Since the precipitation of copper sulfide should be governed by just one theory rather than being differently explained in each steel with a different chemical composition, we compare our results to the past studies.

Past studies are related to hot-shortness, weldment, HSLA steel, soft-magnetic steel and others. The interesting points are that (1) these reports say that Cu–S is formed at over 1000°C and (2) both coating and free-standing Cu–S are not mentioned together in any reports. For example, the following three chemical reactions are proposed in Refs. 14, 17 and 23.

For coating:
\[
2\text{MnS} + 4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{S} + 2\text{MnO} \quad \text{(Ref. 14)}
\]

For free-standing:
\[
2\text{FeS} + 4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{S} + 2\text{FeO} \quad \text{(Ref. 17)}
\]

For free-standing:
\[
2\text{Cu} + \text{FeS} \rightarrow \text{Cu}_2\text{S} + \text{Fe} \quad \text{(Ref. 23)}
\]

The reactions in Refs. 14 and 17 suggest that Cu–S is formed at such a high temperature that steel is melted. It is reported that the reaction proceeds at 1100°C, judging from the free energy.
In Electric-Resistance-Welded (ERW) steel pipe, a sulfur-enriched phase on the surface of MnS has been reported in relation to grooving corrosion, although more than 0.1% Cu is added. These investigators have not identified its phase crystallographically and stoichiometrically, but we surmise that it could be Cu–S.

As mentioned above, there have been no reports that Cu–S is formed in steel with only residual levels of copper, and even in a system with higher levels of Cu, Cu–S precipitation has been differently interpreted. The reason seems mainly that only a few Cu–S are observed even in WQ samples, so we imagine that they have been judged to be formed at high temperature. As mentioned in Section 4.2, Cu–S can be presumed to be formed at between “below 750 °C” and 620 °C, and even in the very short duration of the WQ process. We would like to emphasize that this temperature is much lower than that required by conventional concepts.

5. Conclusions

We studied Cu–S precipitation in an ultra low carbon steel (0.17%Mn–0.0073%S–0.01%Cu) and the following results were obtained.

(1) A residual Cu (≥0.01%) forms copper sulfide in ultra low carbon steel.

(2) The Cu–S has two forms: a “free-standing” type and a “coating” type on the surface of MnS and/or (Mn,Fe)S. Their composition and crystal structure appear the same by EDX and the precipitate is estimated to be CuSs from XRD applied to extracted residue.

(3) Coating Cu–S is presumed to be formed at between “below 750 °C” and 620 °C, and the free-standing type is estimated to be formed at a lower temperature than the coating type. In addition, Cu apparently has such a strong affinity for sulfur that it can make Cu–S even in the short time available during quenching, despite rapid cooling at over 500 °C/s.

(4) The amount of sulfur present as Cu–S, stabilized with a residual level of copper, accounts for as much as 35% of the entire amount of sulfur.

(5) Thin-layered Cu–S (~single nm) is observed on the surface of MnS even in WQ samples. If Cu–S is a stable phase, its thermodynamic data should be revised. If it is a metastable phase, its precipitation may be explained by kinetics.

Consequently, in any precise quantitative analysis of sulfides, Cu–S must be taken into account. The precipitation of sulfide by a small amount of Cu (≥0.01 mass%) cannot be ignored.

Acknowledgments

The authors are grateful to Dr. K. Yamada, Dr. A. Chino, Dr. Y. Hosoya and Dr. T. Inazumi at JFE Steel Corporation and Dr. K. Araki, formerly at NKK Corporation for their valuable discussions. Also, we would like to thank Dr. C. Trevor at Gatan Inc. for technical support and helpful discussions on imaging EELS.

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