On the Behaviours of the Precipitated Sulphide Inclusions in Solid Steel*

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Synopsis

In order to make a systematic survey on the behaviour of sulphur in solid steel, precipitated sulphide inclusions in solid steel, were studied microscopically through heat treatment of steels and the electrolytically isolated sulphide inclusions were investigated by electron diffraction technique and the electron probe method. Moreover, experiments were conducted to the effect of carbon and manganese contents in steel on the precipitation and solution temperatures of the inclusions.

I. Introduction

It is well known that sulphur has great effect on the quality of a steel. Few studies, however, have been made concerning the detail of the composition of sulphide in steel, because in most cases it is generally very fine. Since the equilibrium diagrams of Fe-FeS, Fe-S-Mn give only an outline of sulphide in solid steel, the details still depend on future studies. A recent work by Kaneko, et al.¹⁾ on the sulphurization of the elements in steel is an important contribution to the study of sulphide. But any systematic general survey of the behaviour of sulphur or sulphide in solid steel has not been made yet, fundamental studies of this aspect being needed.

In a steel cooled from a high temperature the following sulphides are found: sulphide already suspended in the molten steel; sulphide segregated and precipitated during solidification of the steel; and solid sulphide precipitated in austenite grains and along grain boundaries by a decrease in solid solubility of sulphur in the steel with lowering the temperature of

the solidified steel, which is termed “precipitated sulphide in solid steel” in this work. Studies²⁾⁻⁵⁾ on this kind of sulphide inclusion have been carried out to some extent, but the characteristics and behaviour are not well known. For example, among this type of sulphide inclusions, the plate-like sulphide precipitated in a Widmanstätten structure is frequently found in commercial steel ingots (25 kg–75 tons), and this sulphide with its characteristic shape presumably affects the quality of steel. The composition and behaviour of this sulphide, however, have been seldom studied.

The present work is to make a systematic survey of the changes in the morphology and composition of the precipitated sulphide inclusions. In this paper are included the studies of the plate-like inclusions which were already published^{6),11),18)} as well as the studies of other precipitated sulphide inclusions observed during the investigations.

II. Behaviour of Precipitated Sulphide Inclusions during Cooling and High Temperature Brittleness of Steel

1. Behaviour of Precipitation

In order to determine the precipitation temperature and critical cooling velocity and to examine the morphology of precipitated sulphide inclusions, the following experiments were conducted.

Ni-Cr steel ingot of 500 g (Nos. 1–4 in Table 1) was melted in a Tammann furnace, slowly cooled down to

Table 1. Chemical composition of specimens (%)

No.	Specimens	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	Remark
1	Ni-Cr steel	0.25	1.20	0.33	0.011	0.040		1.53	0.79			500 g ingot
2	„	0.23	1.23	0.32	0.009	0.034		1.52	0.80			„
3	„	0.24	1.06	0.32	0.011	0.035		1.55	0.80			„
4	„	0.17	0.17	0.33	0.012	0.031		1.55	0.80			„
5	„	0.28	0.56	0.22	0.013	0.055		1.50	1.00			
6	„	0.21	1.16	0.17	0.021	0.046		1.33	0.75			
7	C steel	0.08	0.24	0.20	0.011	0.055						
8	Ni-Cr steel	0.23	1.05	0.18	0.021	0.042		1.33	0.76			
9	C steel	0.08	0.21	0.20	0.011	0.055						
10	„	0.16	0.15	0.16	0.012	0.033						
11	HS	0.28	0.30	0.56	0.016	0.057	0.15	2.96	0.07	0.49	0.09	
12	LS	0.28	0.29	0.50	0.016	0.005	0.15	2.90	0.07	0.48	0.10	

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various temperatures, and water-quenched. In other series, a specimen of 15 mm in diameter and 15 mm in length cut out from forgings of Ni-Cr steel and C steel, shown by Nos. 5-7 in Table 1, was inserted in a Tammann tube with alumina powder (mixed with 0.3% charcoal powder). After heating the specimen in a SiC furnace for 20 min. in the range of 1 450°-1 500°C, it was cooled to various temperatures at a certain given rate and was kept for 30 min. at that temperature, followed by water-quenching. For identification of sulphide in the specimen, silver nitrate⁷⁾ and chromic acid⁸⁾ were used as reagents.

Sulphides were observed within grains and along grain boundaries in the specimen water-quenched from a temperature above 1 400°C. Along grain boundaries were detected blue sulphides (Fe-Mn-S with a comparatively low Mn content) with a small dihedral angle,⁹⁾ which showed an evidence of previous melting (Photo 1 (a)); while in grains were observed two-phase sulphides consisting of black globular sulphide (Mn-Fe-S with a comparatively high Mn content) and tan-purple sulphide (Fe-Mn-S with a low Mn content) (Photo 1 (b)); light blue sulphide (Fe-Mn-S with a low Mn content) (Photo 1 (c)); and light yellow steel matrix (with an evidence of previous melting) surrounded by a circular group of two-phase sulphides (Photo 1 (d)).

(a) Sulphide inclusions at grain boundary
(b) Globular sulphide inclusions in grain
(c) Two-phase sulphide inclusions in grain
(d) Ring structure of sulphide inclusions in grain

Photo 1. Sulphide inclusions in the steel water-quenched from 1 405°C ($\times 600$) ($\frac{2}{5}$)

These sulphides are termed "precipitated sulphides in liquid steel", in order to distinguish them from "precipitated sulphides in solid steel". The sulphides of the former type are mostly produced at the temperature at which steel is solidified and the continuous cooling results in practically no additional generation of them. But during the cooling Mn, Cr, V and others were transferred to sulphides from steel matrix and the compositions of sulphides were changed¹⁰⁾.

In the steel, slowly cooled from a high temperature to below 1 200°C, it was observed that plate-like sulphides shown in Photo 2 (a) were precipitated in a Widmanstätten structure on the {100} plane of austenite grains, and at the same time, very fine particles were precipitated along grain boundaries. Precipita-

(a) Plate-like sulphide inclusions precipitated on plane {100} of austenite: slowly cooled from 1 405°C to 1 000°C. ($\times 550$)
(b) Very small plate-like sulphide inclusions and very fine particles of sulphide inclusion: rapidly cooled from 1 405°C to 900°C. ($\times 540$)

Photo 2. Precipitated sulphides in solid steel ($\frac{1}{2}$)

tion of plate-like sulphide suddenly took place at the almost same temperature, i.e., at about 1 200°C, regardless of the kind of steel used, and the critical rate of cooling at the precipitation temperature was approximately 60°C/min.¹¹⁾ Many thin plate-like sulphides and very fine particles (Photo 2 (b)) were observed in the specimens, which were rapidly cooled to 950°-900°C from a high temperature at a higher rate than the critical cooling rate, kept for 10-25 min. at that temperature and water-quenched. On the other hand, only precipitated sulphides in liquid steel which had already existed at a high temperature, were observed in the specimens rapidly cooled to 800°C from a high temperature and kept for four hours at the temperature. Compared with the slowly cooled steel, the rapidly cooled steel was clean. Precipitation of sulphur in solid steel may have been suppressed.

In the specimen slowly cooled to 900°C from a high temperature and kept for 1/2 to eight hours at the temperature, plate-like sulphides of the usual shape and size were detected, but no evidence of their growth and aggregation was observed. This indicates that plate-like shape is stable and that the precipitation of this type of sulphide is completed in a comparatively short period, over the range of 1 200°-1 000°C.

2. Impact Test at High Temperatures

A general study of the effect of sulphur on the toughness of steel at high temperatures has been performed by Niedenthal.¹²⁾ In the study, he has conducted an impact test by directly heating specimens at temperatures higher than various testing temperatures. Josefsson¹³⁾ has recently reported the effect of heating up to 1 300°C on an impact test at 950°C. But as explained in the subsequent sections, the present work proved that the behaviour of precipitation of sulphide in steel was completely dependent upon the heat treatment after heating to about 1 400°C or after solidifying

into an ingot. Therefore, the conventional method, in which specimens were heated directly from room temperature to testing temperatures, is not suitable to measure high-temperature embrittlement of steel ingots, steel forgings and steel weldings during cooling, and for testing forginability of burnt and overheated steels. From the above standpoint, a high-temperature impact test was conducted, after heating two types of steel—with high and low sulphur contents—at 1 400°C and slow cooling to various testing temperatures.

Two 1.5 ton Ni-Mo-V steel ingots (with 0.057 and 0.005% of sulphur, shown respectively in Nos. 11, 12 in Table 1) were forged into 210×210 mm square billets. Then, 10×10×55 mm unnotched specimens for impact test were cut out in parallel with the direction of forging. To prevent oxidation, the specimens were placed in a Tammann tube with alumina powder (mixed with 0.3% charcoal powder) and were heated in a SiC furnace. Analysis of the central region of the specimen prior to and after the heat treatment revealed a decrease of about 7% in a carbon content. The specimens, after heating for 30 min. at 1 405°C, were slowly cooled to the testing temperature and kept for 30 min. at the temperature. Then, the Tammann tube was taken out of the furnace and the test piece was ruptured by a 30 kg-m Charpy impact machine. The time taken from taking-out to rupturing was 10 sec. The dropping in temperature during that period was within 20°C at 1 200°C.

The results of the experiment are shown in Fig. 1. The pieces with bending angle of less than 128° were not fractured. Low sulphur steel (LS steel) did not fracture in all the range of 1 350° to 800°C, and its

Fig. 1. Impact value and bending angle versus testing temperature for high and low sulphur steels

absorbed energy curve rose up linearly as the temperature lowered. At 850°C the rate of the increase became higher and then decreased, due to Ar_3 transformation. The discontinuity in the curve between 950°–850°C can be regarded as an indication of minor red shortness even in a low sulphur steel, but the curve can be deemed to indicate the resistance to plastic deformation of austenite. On the other hand, high sulphur steel (HS steel) fractured along grain boundaries at 1 350°C, its absorbed energy, being about 70% of that of LS steel, with high-temperature embrittlement. When the testing temperature was lowered to 1 200°C, some specimens did not fracture; nevertheless, the energy curve rose up in parallel with that of LS steel. But at 1150°C, the absorbed energy fell down abruptly, and the specimens showed severe embrittlement and appreciable intergranular fractures. This embrittlement was the greatest at 1 050°C. As the temperature was lowered, the energy curve rose up linearly again parallel with the broken line which was an extension of the energy curve between 1 350°C and 1 200°C to lower temperatures. A slight decrease in the rising rate of the absorbed energy curve between 850°–800°C can be attributed to Ar_3 transformation. All the specimens fractured in the range of 1 150°–800°C. The absorbed energy value of HS steel at 950°C was 42% of that of LS steel, and 54% compared with that of the broken line. This shows that HS steel yields extreme embrittlement.

From the foregoing experiments, the following conclusions are obtained: the low sulphur steel with 0.005% S rarely yields embrittlement, but the steel with 0.057% S, though containing 0.5% Mn, shows high-temperature embrittlement at the temperature above 1 200°C, and also produces excessive red shortness at the temperature below 1 200°C, the embrittlement remaining even below the austenitizing temperature. The temperature around 1 200°C, at which the toughness is abruptly decreased, corresponds to the temperature at which precipitated sulphide in solid steel begins to be formed. Microscopic examination confirms that the sulphide has been precipitated in grains and along grain boundaries. Generation of cracks and ruptures along weakened grain boundary by the propagation of cracks may be attributed to reduction in the cohesion of grain boundary, and to grain hardening.

The observed energy curve for a high sulphur steel showed a similar tendency to the Niedenthal's experiment¹²⁾ (No. 17 steel, C 0.03%, Si tr., Mn 0.10%, P < 0.01%, S 0.022%, O 0.092%). The relation between the abrupt change of brittleness at 1 200°C reported in his experiment, and the precipitation of sulphide in solid steel will be discussed in another report¹⁴⁾.

III. Behaviour of Precipitated Sulphide Inclusions during Heating

1. Heating from Room Temperature

The steel, which had sulphides precipitated in molten state together with precipitated sulphides in solid state, was rapidly heated from room temperature to 1 400°C, kept for one min. to ten hrs. at the

temperature, and water-quenched, followed by microscopic examination.

Specimens 25 and 25 mm in diameter and in length were cut out from forgings of C steel and Ni-Cr-Mo steels (Nos. 8–10 in Table I). After heating at 1 340°C for 20 min. in argon atmosphere in a SiC furnace, they were cooled in the furnace to 1 000°C, kept for 30 min. at the temperature to have sulphide in solid steel completely precipitated, and water-quenched or cooled to room temperature. These specimens were, then, heated rapidly at various temperatures in the range of 650°–1 400°C in a salt bath or a SiC furnace (in argon gas), and kept at the temperature, followed by water-quenching.

Since there was no discernible difference in the composition of the specimens which may have given any effect on the behaviour of sulphur, the following description was made without reference to the kind of steel.

When the specimens were heated at 650°C, the shape and constituents of plate-like sulphide did not change from those prior to heating. Some of the plate-like sulphides changed into dot-like ones after 800°C for one min. but all of them after 800°C for one hour took the dot-like shape (Photo 3 (a)). In the specimens heated at 900°C for three hours, the original

shape of plate-like sulphides was hardly observable, and changed into very fine particles, through the stage of the dot-like shape (Photo 3 (b)). The very fine sulphide particles, which had existed along grain boundaries were observed to have grown larger than those prior to heating. The reaction of the remaining few plate-like sulphides with chromic acid revealed that the sulphides after heating, tended to be enriched in manganese, compared with those prior to heating.

When the slowly cooled steel was heated at 1 000°C for 2 hrs., plate-like sulphides in the steel were completely decomposed into very fine particles. At 1 100°C these particles were aggregated to small ones, which, heated at a higher temperature, were coalesced into large ones. But they decreased in number and the austenite grains became cleaner. In the steel heated at 1 405°C for 1 hr. the coalesced particles disappeared and only sulphides precipitated in liquid state remained in grains and along grain boundaries, the steel being cleanest. These remaining sulphides with a low Mn content were numerous, but in some cases, even black globular sulphides with a higher Mn content were accompanied by those with the low Mn content. This indicates that at a higher temperature, sulphides with a lower Mn content are stable.

2. Successive Heating after Precipitation of Sulphide

In the previous paragraph, it was observed that when the steel cooled from a high temperature in order to have sulphides precipitated in solid state was reheated from room temperature, plate-like sulphides were rapidly decomposed at a higher temperature than the austenitizing temperature (800°C). In section II, it was stated that plate-like sulphides in the steel slowly cooled from a high temperature to 900°C were stable, when they were kept even for eight hrs. at the temperature.

In relation to the latter case, the behaviour of plate-like sulphides at higher temperatures was investigated.

The similar specimens and experimental apparatus were used with the following procedure: the specimens, after heating at 1 405°C for 20 min., was cooled in the furnace to 1 000°C. While they were kept at 1 000°C for 20 min. plate-like sulphides were completely precipitated and they were heated up again for 30 min. at various temperatures in the range of 1 100°–1 400°C, followed by water-quenching. With raising the third heating temperatures, the number of plate-like sulphides decreased, but the plate-like shape remained. At 1 350°C, both ends of a plate-like sulphide were rounded and plate-like sulphides became seldom in number, but their plate-like shape remained unchanged to some extent. This indicates that the shape is stable. At 1 400°C, plate-like sulphides were not detected, which showed that they were completely soluble in solid steel.

IV. Effect of Carbon and Manganese

It was reported¹⁵⁾ that the solubility of sulphur in solid steel considerably decreased with the increasing Mn content, but the experiments on the effect of carbon have not been reported yet. Even though they

(a) Decomposed plate-like sulphides in the steel reheated to 800°C ($\times 1\,550$)
(b) Fine sulphide particles in the steel reheated to 900°C ($\times 530$)
(c) Plate-like sulphides in the steel subsequently reheated to 1 350°C, after cooling to 1 000°C ($\times 2\,400$)

Photo 3. Change of plate-like sulphide in the steels reheated to various temperatures ($1/2$).

contain a considerable amount of manganese, precipitated sulphides in solid steel are detected in commercial steels. Here, a study was conducted on the effect of carbon and manganese in solid steel upon precipitation and solution temperatures.

Ten steels (C 0.1–0.9%, Mn 0.1–1.4%, S 0.02–0.5%) were first melted in an induction furnace, cast in a 5 kg-ingot mould, forged into a rod of 12 mm in diameter and cut into specimens 15 mm in length (Table 2). To measure the precipitation temperature, the specimens were first heated in a SiC furnace at 1 430°C for 30 min., slowly cooled down to various temperatures at a slower rate than the critical cooling rate of the precipitation, and kept for one hr. at the temperature, followed by water-quenching. Then, the presence of plate-like sulphides was examined microscopically. For the solution temperatures, following the measurement of solution temperature described in section III. 2, the specimens were heated at 1 430°C for 30 min., slowly cooled to 1 000°C and kept for 30 min., so as to have plate-like sulphides adequately precipitated. After successive heating (without cooling the specimens) to various temperatures, they were kept for one hr. at the temperatures and water-quenched. Then the presence of plate-like sulphides was examined.

The results of the experiments are as follows:

In H4, and M4 steels with 1.4%Mn, plate-like sulphides were not detected. Therefore, the temperature of their precipitation and solution could not be measured. But in the steel with Mn less than 0.4%, plate-like sulphides were always found.

Their precipitation occurred at a constant temperature, 1 180°–1 200°C, regardless of the contents of Mn and C. These results coincide with those obtained with C steel and Ni-Cr steels described in section II. 1. On the other hand, various solution temperatures were obtained: in H1 and M1 steels with 0.09%Mn, it was about 1 290°C which was the lowest temperature observed, regardless of carbon contents; in the steels with 0.25–0.41%Mn, 1 320°C in a high

carbon content and 1 400°C in a low carbon content, respectively. This shows that the higher the carbon content in steel, the lower the solution temperature.

The foregoing results suggest that in a low manganese or a high carbon steels, when they are slowly cooled even from the forging temperature, sulphides precipitate in solid state. A good example is found in Brammar's report⁵⁾, in which rectangular precipitates (α -MnS) were observed in burnt En 42, En 111 steels. It probably corresponds to the plate-like sulphide as precipitated sulphide in solid steel. As mentioned in the previous section, no precipitation of sulphides in solid steel was detected in a steel with 1.4%Mn. Therefore, a further experiment was conducted with a C steel, 500 g (L4 in Table 2) with a lower Mn content. The specimen was melted in a Tammann furnace, after solidification, cooled slowly at the rate of 5°C/min. Also prepared were the similarly treated steel ingots (L5 and L6 in Table 2), in order to find out the behaviour of precipitated sulphides in the steel with an excessively low Mn content.

The experiments revealed that L4 steel with 0.90%Mn did not produce plate-like sulphides, except precipitated sulphides in liquid state. Considering the report¹⁶⁾ that plate-like sulphide is present in the test pieces (25 kg) of SC49 (JIS) cast steel with about 0.7%Mn, it may be concluded that approximately 0.7%Mn is the maximum amount for precipitation of sulphide in solid steel. The experiment also revealed that in L5 and L6 steels with extremely low Mn contents, only precipitated sulphides in liquid state were observed, but no plate-like sulphides were detected. This indicates that sulphur precipitated from steel matrix during cooling is in the form of FeS, which, in turn, is migrated to grain boundaries, instead of forming plate-like sulphides, because it is in liquid state at the temperature.¹⁷⁾

V. Irreversibility of Plate-like Sulphide¹⁸⁾

As stated previously, when a steel was cooled from high temperatures, plate-like sulphides were precipi-

Table 2. Chemical composition of specimens and temperatures of precipitation and solution

Specimen	C (%)	Si (%)	Mn (%)	P (%)	S (%)	Temperature of precipitation (°C)	Temperature of solution (°C)
H 1	0.77	0.39	0.09	0.005	0.022	1 190	1 290
H 2	0.73	0.38	0.28	0.005	0.037	1 180	1 320
H 3	0.78	0.41	0.41	0.005	0.085	1 180	1 330
H 4	0.89	0.39	1.36	0.005	0.446		
M 1	0.29	0.37	0.09	0.005	0.020	1 200	1 285
M 2	0.36	0.38	0.32	0.005	0.048	1 180	1 370
M 3	0.31	0.42	0.35	0.005	0.098	1 190	1 370
M 4	0.49	0.39	0.36	0.005	0.466		
L 2	0.14	0.33	0.29	0.009	0.030	1 200	1 370
L 3	0.20	0.32	0.25	0.009	0.071	1 180	1 400
L 4	0.10	0.25	0.90	0.011	0.038		
L 5	0.11	0.34	0.03	0.009	0.062		
L 6	0.06	0.36	tr.	0.007	0.056		

pitated between 1 200°–1 000°C. Further, when they were kept for several hours below the temperature, they neither grew nor coalesced; and even when heated as high as 1 350°C, they were so stable as to keep the plate-like shape. However, plate-like sulphides in steels, reheated from room temperature to the austenitizing temperature, were rapidly decomposed into very fine particles. To investigate such irreversibility of the behaviour of plate-like sulphide during heating and cooling, electrolytically isolated plate-like sulphides were examined by a microscope, electron diffraction technique and the electron probe method.

First, two Ni-Mo-V steels which contained high sulphur and low sulphur respectively, as shown in Nos. 11 and 12 in Table I, were prepared. On applying the same heat treatment, in the high sulphur steel (HS steel) precipitated a large amount of plate-like sulphides, while the low sulphur steel (LS steel) contained so small an amount of sulphur that the precipitation of sulphides was almost impossible. Microscopic comparison of the electrolytically isolated residues of the two was made to recognize plate-like sulphides. These steels were melted in a 6-ton basic arc furnace, cast in a 1.5-ton mould, and forged into a 210 mm square billet, from which the specimens, 14×14×65 mm, for heat treatment tests were cut out in parallel to forging direction. They were then heat-treated in a SiC furnace (in argon atmosphere) and a lead bath, and water-quenched from the austenitizing temperature, in order to prevent precipitation of carbide, and machined into probes, 10×10×60 mm, for electrolysis.

The procedure of electrolytic extraction, analogous to the method of Kaneko¹⁹⁾ was employed here and the following conditions were applied: electrolyte (15% sodium citrate+1% potassium bromide), a 15×70 mm copper electrode, a 44 φ×150 mm porous-alumina diaphragm, current density of 10 mA/cm², current of 200–300 mA, time of electrolysis of 80–100 hrs. deposit of about 20 g, maintenance of neutrality in an anodic chamber by dropping sodium hydrate, and maintenance of acidity in a cathodic chamber by circulating the buffer solution (electrolyte+6% sodium citrate at pH 4.4). The difficulty of keeping the anodic chamber neutral during a longer period of electrolysis resulted in marked separation of crystal grains from specimens, which was attributed to preferential corrosion along grain boundaries. The electrolytically isolated residues were suspended in distilled water for several times in order to remove electrolyte.

1. Morphological Observation

In order to examine the stereographic shape of plate-like sulphide and to distinguish it from the other residues, comparison was made under the microscope on the electrolytically isolated residues, taken from HS steel and LS steel subjected to heat treatment (1 405°C for 30 min.—furnace cool—1 000°C for two hrs.—water-quench) to make plate-like sulphides precipitate.

In the residue of HS steel, numerous rectangular plates of various size were observed. Under incident light, they exhibited bright yellow or light greyish white colour, (Photo 4(a)), which made it easier to distinguish them from other elements of the residue. But in that of LS steel, the presence of such plates was not detected. As the dimension of plate-like sulphides usually detected on the polished surface of metallographic specimens was 5–30 microns in length and about one micron in width, it corresponded to that of rectangular plates in the electrolytically isolated residues and therefore, it could be concluded that these plates were plate-like sulphides. Rectangular plates, extracted from the steel kept just below the precipitation temperature of plate-like sulphide (1 180°C), decreased in number but became comparatively larger in size. Plate-like sulphides, extracted from the steel slowly cooled from a high temperature and kept at 900°C for 6 hrs. were found to have no tendency of growth or coalescence, which coincided with the results of the observation on metallographic specimens described in section II.

It was also described in section III that upon rapid heating of a steel to a high temperature after full precipitation of plate-like sulphides during slow cooling from about 1 400° to 1 000°C, the plate-like sulphides kept their plate-like shape even at a higher temperature than the precipitation temperature of

(a) Original shape
(b) Reheated to 1 370°C without cooling below 1 000°C
(c) Reheated to 870°C after cooling to room temperature from 1 405°C

Photo 4. Isolated plate-like sulphide inclusion (×1 300) (1/2)

plate-like sulphides, and they decreased in number and began to lose their shape, at 1 350°C, close to the solution temperature. Plate-like sulphides, extracted from the steel in this state, that is, 1 405°C for 30 min.—furnace cool—1 000°C for 30 min.—1 370°C for 1 hr.—water-quench, as shown in Photo 4(b), presented thinned rectangular edges and round corners, and under incident light, they turned yellow. Compared with those in Photo 4(a), it was recognized that they generally became thinner.

It was stated in section II that as soon as a steel containing plate-like sulphides was reheated from room temperature to the austenitizing temperature, plate-like sulphides changed into randomly oriented very fine particles, through the stage of dot-like shape. Photo 4(c) shows the plate-like sulphides which were extracted from the steel in the above-mentioned state (1 405°C for 30 min.—furnace cool—1 000°C for 30 min.—water-quench). It is seen that, being different from the shape and colour in Photo 4(b), the rectangular plates have openings in the centre and with opaque light blue colour at their edges change into thicker strings. It can be assumed here that the dot-like sulphides observed on the polished specimen coincide with the section of these strings.

Plate-like sulphides, isolated from the steel reheated to a higher temperature (900°C for 30 min.), lost their previous rectangular shape and changed into opaque light blue strings, 1–2 μ in width. The sulphides in this state, when observed microscopically on the polished surface, are recognized as very fine sulphide particles randomly distributed. Observation of the extracted plate-like sulphides revealed that the plate-like sulphides after reheating, behaved in different ways, depending on the initial temperature.

2. Analyses by Electron Diffraction and Electron Microprobe

Plate-like sulphides, precipitated on the plane {100} of austenite grains during cooling, have a Widmanstätten structure and would, therefore, match with the lattice of austenite. To examine the condition of their matching, the electrolytically isolated plate-like sulphides were investigated by an electron diffraction technique. In order to have precipitated plate-like sulphides, HS steel was first cooled in a furnace from a high temperature to 1 000°C. The residues electrolytically extracted from the steel, were dried on a collodion film over copper mesh with holes 15 μ in diameter. Thinner plate-like sulphides were selected as the specimens for an electron microscope (50 kV) under the microscope in transmitted light. The result is shown in Table 3. The pattern (Photo 5(a)) is a grid pattern, corresponding to a structure of a single crystal, and was very similar to that of α -MnS (cubic NaCl type). According to the identification¹¹⁾ by chemical reagent of plate-like sulphides they are composed not only of MnS, but of FeS. To clarify this point, the extracted plate-like sulphides were examined by an electron probe microanalyser, “Tronalyser”, made by Akashi Works, Ltd. with the following conditions; accelerating voltage: 20 kV,

Table 3. Lattice spacings measured from the electron diffraction pattern of isolated plate-like inclusion

Observed value		From A.S.T.M. data		
Specimen		α -MnS		
d (Å)	Intensity	d (Å)	I/I_0	hkl
3.04	VS	3.015	13	111
2.67	S	2.612	100	200
1.89	VS	1.847	48	220
1.73	M			
1.58	W	1.575	6	311
		1.509	19	222
1.33	M	1.306	8	400
1.28	M			
1.23	W			
1.19	VW	1.168	19	420

(a) Electron diffraction pattern of plate-like sulphide
(b) Mn $K\alpha$ radiation scanning image of plate-like sulphide
(c) Fe $K\alpha$ radiation scanning image of plate-like sulphide

Photo 5. Electron diffraction pattern and scanning images of plate-like sulphide ($1/2$)

probe current: 0.11 μ A, crystal: LiF (vacuum), detector: scintillation counter, standard specimen: pure iron and pure manganese.

A part of the electrolytically extracted residue used in the electron diffraction technique, was dried on a mount of pure aluminium. Photo 5(b) and (c) show the scanning images of a plate-like sulphide. Distribution of manganese all over the sulphide and decrease in iron on the circumference were observed. As the result, it is confirmed that iron is present in the plate-like sulphide as a single crystal of MnS.

Spot analysis of manganese and iron in the central region of plate-like sulphides reveals that the primary values are calculated at 34.5wt%Mn and 10.2wt%Fe. Since plate-like sulphides are single crystals of MnS containing iron in solid solution, the composition of plate-like sulphides on binary system of FeS-MnS is: FeS is 23.0wt% and MnS is 77.0wt%, and it would be assumed that plate-like sulphides are MnS which is almost saturated with FeS at room temperature. In the above calculation, the absorption and excitation of X-ray were disregarded.

3. Cause of the Irreversibility

Provided that the lattice constant of plate-like sulphides is almost the same as that of α -MnS ($a=5.224 \text{ \AA}$ at room temperature, sodium chloride structure of cubic crystal)²⁰⁾, and the lattice constant of steel is almost the same as that of γ -iron ($a=3.656 \text{ \AA}$ at 950°C , face-centred cubic structure)²⁰⁾, the base plane of sodium chloride structure with the side of $5.17 \text{ \AA}$, which is close to the lattice constant of α -MnS, would be formed as in Fig. 2, and plate-like sulphides would be precipitated in steel under this condition of matching. When iron which has a smaller atomic radius ($1.27 \text{ \AA}$)²⁰⁾ than that of manganese ($1.30 \text{ \AA}$)²⁰⁾

is contained as solid solution in manganese sulphide, it would be assumed, according to Vegard's law, that the lattice constant of MnS solid solution could be decreased, and further, that growth of plate-like sulphides would be expected to give a less extensive strain to the lattice of austenite.

But this condition of matching can not be satisfied if the allotropic transformations of either matrix (austenite) or precipitates (MnS solid solution) occur. There are three allotropic transformations in MnS²⁰⁾: $\alpha \rightleftharpoons \beta (727^\circ\text{C})$, $\beta \rightleftharpoons \gamma (1100^\circ\text{C})$, $\gamma \rightleftharpoons \delta (1380^\circ\text{C})$. However, when the steel, which contains precipitated plate-like sulphides formed during slow cooling from a high temperature, is kept for a long time at 900°C , plate-like sulphides are stable, and keep their original shape, upon continued heating to 1350°C . This indicates that the allotropic transformations of MnS have little effect on them. Therefore, the allotropic transformations (Ar_3 , Ar' , Ar'') of austenite must be a cause for dissatisfying the condition of matching. Then, if the transformed steel is heated to a lower temperature, the plate-like sulphides, which did become incoherent, would not change their shape, because of difficulty in migration of sulphur atoms at that temperature. But if the steel is heated to such a temperature as produces refreshed austenite, the migration of sulphur atoms would become easier, and the incoherent plate-like sulphides would tend to reduce as much of their surface energy as possible, so that they would change into a globular shape. On the other hand, if the steel which has precipitated sulphides and is subsequently heated at high temperatures, the plate-like sulphides would keep the most stable plate-like shape at a temperature close to the solution temperature, because they maintain coherent relationship with austenite.

To confirm this view, the following experiment was conducted. A carbon steel (C 0.20%, Si 0.32%, Mn 0.25%, P 0.009%, S 0.071%) was heated at 1430°C for 20 min., slowly cooled to 1000°C and kept for 20 min. at the temperature. This treatment aimed at having plate-like sulphides fully precipitated. One of the specimens was further cooled in a furnace to 610°C and held for 30 min. to make the transformation of $\gamma \rightarrow \alpha$ complete. The another specimen was subsequently furnace-cooled to 850°C and held for 30 min. to preserve it in the state of γ . Both specimens were then heated to 1000°C and held for 30 min., followed by water-quenching.

The results⁶⁾ showed, as expected, that no plate-like sulphide was present at all in the specimen which had been transformed from γ to α , and that very fine sulphide particles were only detected. In the specimen, in which the state of γ had been kept, only perfect plate-like sulphides were observed.

The view was further confirmed with another experiment. If a steel is fully saturated with sulphur in solid solution by heating to 1430°C , water-quenched to prevent the precipitation of plate-like sulphides, and then rapidly heated to the range of austenite, the plate-like sulphides must be precipitated from supersaturated austenite with sulphur. In the speci-

Fig. 2. Relation between the crystal structures of plate-like sulphide inclusion and austenite

men so treated and further heated at 850°C for 8 hr., imperfect plate-like sulphides and very fine sulphide particles were observed all over the examined surface of the specimens, as shown in Photo 6. In the specimen heated at 1 000°C for 1 hr., very fine particles were still detected, but the degree of imperfection of the plate-like shape decreased. The appearance of the very fine particles would probably be attributed to a great number of nucleations and the slow rate of growth of plate-like sulphides at lower temperatures.

The case, in which precipitates with a Widmanstätten structure change their shape by the transformation of matrix, has not been reported of any precipitates in other metals. It is interesting to note that by heat treatment of steel ingot or steel casting, the transformation of γ - α causes spheroidization of plate-like sulphides as well as refinement of steel grains and evacuation of excess hydrogen in steel.

Photo 6. Imperfect plate-like sulphides and very fine sulphide particles in the steel reheated to 850°C after water quenching from 1 430°C ($\times 630$) ($1/3$)

VI. Conclusions

In order to make a systematic survey on the behaviour of sulphur in solid steel, precipitated sulphide inclusions in solid steel were studied microscopically through heat treatment of steels and the electrolytically isolated sulphide inclusions were investigated by electron diffraction technique and the electron probe method.

It was shown that sulphide inclusions precipitated in a solid steel below 1 200°C, when the steel was cooled from the temperature above the solution temperature of the precipitated sulphide at a slower rate than 60°C/min. The precipitated sulphide inclusions had two forms: a plate-like inclusion which had a Widmanstätten structure and precipitated on {100} plane of the austenite structure and a very fine particle inclusion which precipitated along the grain boundary of austenite. As the result of the impact test in the temperature range of 800° to 1 350°C of steels which were slowly cooled from 1 405°C, it was found that the embrittlement of steels below 1 200°C was induced by precipitation hardening of austenite grains and reduction of grain boundary cohesion, and it did not vanish even at the temperature below A_{r3} .

When the steel in which the precipitation of sulphide inclusions had been suppressed by rapid cooling from a high temperature was reheated at austenitizing temperature, imperfect plate-like inclusions in grains and very fine particle inclusions along grain boundaries precipitated.

When the steel in which precipitation of sulphide inclusion had occurred through slow cooling from a high temperature to room temperature was reheated at austenitizing temperature, the plate-like inclusions in it were decomposed rapidly to very fine particle inclusions.

But when the steel which had been slowly cooled to a lower temperature or austenite region from a high temperature was reheated to higher temperature, the plate-like inclusions in it were not decomposed and kept their shapes up to the solution temperature.

The results of electron diffraction analysis and electron probe microanalysis on electrolytically isolated plate-like inclusions showed that the plate-like inclusion was composed of a single crystal of α -MnS solid solution containing 23wt% FeS and coherently matched the lattice of austenite on {100} plane, and the phenomena of decomposition of the plate-like inclusion in reheated steel occurred due to lack of cohesion between lattices of the plate-like inclusion and refreshed austenite.

In steels containing up to about 0.7%Mn, precipitated sulphide inclusions were observed, but in steels with 0.03%Mn they were in molten state at the precipitating temperature and migrated into the grain boundary of austenite.

The solution temperature of precipitated sulphides was affected by contents of manganese and carbon in steel. In low manganese steels (0.1%) the solution temperature was 1 200°C independently of carbon content, and in steels containing 0.2%–0.4%Mn the higher the carbon content (0.1%–0.8%) of steel the lower the solution temperature was (1 400–1 320°C). But, the precipitation temperature of the sulphide was almost constant (1 180°–1 200°C, independently of contents of manganese and carbon in steels.

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