Phase Analysis of Sulfides of Rare Earth Elements in Steel*

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Synopsis

The chemical behavior of various compounds of rare earths, both synthesized and isolated from steels, were investigated in order to establish a method for phase analysis of rare earth elements in hot-rolled steels.

The chemical behavior of various compounds of rare earths from steels was carried out by the electrolytic solution method in nonaqueous solvent. The residues examined by X-ray diffraclometry contained sulfide, oxysulfide $R_2O_S$ (R means a rare earth element), and/or oxide of rare earths.

The procedure for phase analysis of rare earths in steel is as follows:

1. The difference in the amount between total rare earths and combined rare earths gives the amount of metallic rare earths.
2. The isolated residue was treated with $30\text{ ml}$ of methanol containing $5\%$ triethanolamine and $1\%$ tetramethylammonium chloride at a current density of $50\text{ mA/cm}^2$ under nitrogen atmosphere, and then, the isolated residue was filtered. (Separation of combined rare earth elements.)
3. The amount of rare earths as sulfides can be calculated by subtracting the amount of rare earths as oxysulfide and oxide from that of combined rare earths. The method for phase analysis was applied to several hot-rolled steels containing various amounts of rare earths and sulfur.
4. The anisotropy (C/L) of impact values is considerably affected by the ratio (r) of sulfur as rare earth sulfides, defined by

$$r = \frac{S_{\text{RE}}}{S_{\text{RE}} + S_{\text{RS}}}$$

The relation was expressed by an equation and discussed.

I. Introduction

Recently, various effects of rare earth elements on steel have attracted attention and in particular, the effect of sulfide shape control on the improvement in toughness and workability of steels has been once again highly evaluated.

Though rare earths are effective for improvement in toughness and workability of steels, the mechanism of the effects on other properties of steel is almost never distinct. Thus, it is necessary to establish a method for phase analysis of rare earths in steels. Then, the behavior on precipitation of rare earth precipitates can be clarified and the significance of rare earth elements can be more clearly known in steelmaking.

In the present study, rare earth precipitate was isolated from hot-rolled steels by electrolytic solution method in nonaqueous solvent, and their chemical behavior were investigated on various reagents. Consequently, a method for phase analysis of rare earth elements was established, in which sulfide was well separated from oxysulfide and oxide. The relation between analytical results for sulfide of rare earths and anisotropy of impact values at low temperature was clarified, and the effect of rare earth element addition on impact characteristics was understood quantitatively.

II. Experimental

1. Steel Samples Examined

Chemical composition of hot-rolled steels examined are summarized in Table 1. A bottom poured ingot of about $26\text{ t}$ was slabbled into three slabs, such as, top, middle and bottom in the direction of height and hot-rolled in plate. Sample series A and B were obtained from each slabs of ingot, so as to correspond to edge, $1/4$ depth and center from the surface. Sample C was melted in a $10\text{ kg}$ vacuum melting furnace, to which addition of manganese was decreased to make more sulfides of rare earth precipitate. Sample D was melted by $10\text{ kg}$ melting furnace in an

<table>
<thead>
<tr>
<th>Sample</th>
<th>R*</th>
<th>S</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>0.04</td>
<td>0.005</td>
<td>0.12</td>
<td>0.25</td>
<td>1.5</td>
<td>0.017</td>
<td>0.006</td>
</tr>
<tr>
<td>A-2</td>
<td>0.03</td>
<td>0.013</td>
<td>0.05</td>
<td>0.25</td>
<td>1.5</td>
<td>0.017</td>
<td>0.006</td>
</tr>
<tr>
<td>B</td>
<td>0.01</td>
<td>0.008</td>
<td>0.16</td>
<td>0.26</td>
<td>1.3</td>
<td>0.018</td>
<td>0.003</td>
</tr>
<tr>
<td>C</td>
<td>0.06</td>
<td>0.013</td>
<td>0.06</td>
<td>0.20</td>
<td>0.2</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>D</td>
<td>0.15</td>
<td>0.015</td>
<td>0.11</td>
<td>0.20</td>
<td>0.9</td>
<td>0.004</td>
<td>0.006</td>
</tr>
</tbody>
</table>

* Samples A-1, A-2 and D: mischmetal added
Samples B and C: metallic Ce added
R: rare earth elements

*** Product R & D Laboratories, Nippon Steel Corp., Fuchinobe, Sagamihara 229.
atmosphere, to which addition of rare earth elements was increased to use as a sample for determination of rare earths in solid solution. Mischmetal, used in samples A and D to add rare earths, had the following composition: Ce; 48%, La; 30%, Nd; 15% and Pr; 4%. High Ce-alloy used in samples B and C had the composition; 98.5% rare earth elements (Ce: 94.2%) and 0.7% Fe.

Plate thickness of sample A was 16 mm and the remainder, 10 mm.

2. Identification of Precipitates of Rare Earth Elements

Precipitates of rare earth elements in hot-rolled steels listed in Table 1 was observed by both optical microscope and electron microprobe X-ray microanalyzer. The electrolytically isolated residue was investigated by X-ray diffractometry for the identification of the precipitate. Some representative examples of the precipitate of rare earth elements observed by optical microscope are shown in Photo. 1. Photograph 1 (a) is a micrograph of spherical cerium sulfide precipitated in sample C, which never elongates in the direction of rolling as manganese sulfide. Photograph 1 (b) shows clustered oxysulfide precipitated in sample A-1, which is often observed in such steel plate as taken from center portion of ingot, but this tendency gradually disappears with decrease in the amount of rare earth elements added. In Photo. 1 (c), the angular precipitate marked with arrow is oxide, which almost always contains Al₂O₃. Photograph 2 shows the results of electron microprobe X-ray microanalysis on these precipitates. Photograph 2 (a) is some characteristic X-ray scanning images of spherical cerium sulfide in sample B and the angular oxide containing Al₂O₃ can be observed below. Photograph 2 (b) is that of clustered oxysulfide in sample A-1. In this analysis, the ratio of each rare earth content, such as Ce, La, Nd and Pr, in the precipitate of steel added with the mischmetal was almost equal to that in mischmetal itself. Photograph 2 (c) is the image of angular oxide in sample A-2, which contains Al₂O₃.

The precipitates of rare earths were isolated from samples shown in Table 1 by electrolytic solution method in nonaqueous solvent containing triethanolamine, and then, the residues were investigated by X-ray diffractometry. Precipitates of rare earths were not detected in sample B, which is low in amount of rare earths added. R₂O₃S, in which R means a rare earth element, was detected as oxysulfide from samples A and D, and Ce₂O₃S from sample C. In the present study, however, oxysulfide having a formula R₂O₃S₂ could not be detected at all. RAIO₃ was detected as oxide from sample D, but no oxide was found from other samples. Sulfide was observed only from sample C. Though diffraction lines were so weak and not definite, they almost coincided with that of CeS listed in ASTM cards.

3. Determination of Rare Earth Elements

Photometric method with arsenazo I⁴ was used for determination of rare earth elements in steel. This method was adopted as one of the analytical methods of Japan Society for the Promotion of Science in July, 1971. Sample was dissolved in sulfuric acid (1+5) with heating, then rare earths were precipitated with hydrofluoric acid as fluoride, and filtered. The precipitate was decomposed with sulfuric acid and nitric acid, and the color reaction with arsenazo I was used for determination of rare earth elements.

The isolated residue was melted with potassium disulfate and the melt was dissolved with warm sulfuric acid (1+5). Rare earths were separated as fluoride, and the determination was completed by the arsenazo I method as described above.

4. The Method for Isolation of Rare Earth Element Precipitate

Rare earths in steels are usually precipitated as sulfide, oxysulfide and oxide. Methods of the isolation of precipitates are as follows: acid dissolution methods with hydrochloric acid (1+1), sulfuric acid (1+5), and cold nitric acid,²⁵ halogen-organic solvent method with 10% iodine solution in methanol; electrolytic solution method with electrolyte consisting of 15% sodium citrate, 30% citric acid and 1.2% potassium bromide at pH3;⁴⁶ electrolytic solution method with electrolyte consisting of 5% sodium citrate, 2% potassium bromide and 1% potassium thiocyanate at pH8;⁷¹ electrolytic solution method with nonaqueous...
electrolyte consisting of 5% triethanolamine and 1% tetramethylammonium chloride in methanol, which is hereinafter abbreviated as electrolytic solution method in nonaqueous solvent.

Specimen obtained from the core portion of ingot in sample A-1, and from the edge portion of ingot in sample A-2 were used for experiments. Sample C with much sulfide precipitate and sample D with rare earth elements in solid solution were also used. The results are shown in Table 2.
All other isolation methods give lower results than the electrolytic solution method in nonaqueous solvent, so that this method can be applied as the most effective isolation method for precipitates of rare earth elements. Apparently from the result on sample D, the electrolytic solution method in electrolyte of citrate may be applicable to the samples rich in oxysulfide and oxide, but gives somewhat lower results.

The electrolytic solution method in nonaqueous solvent was studied on constant current densities in the range 20 ~ 100 mA/cm². The results were always the same under any condition studied, and thus, the method is applicable to quantitative isolation of sulfide, which is chemically unstable. Under the electrolysis condition at a current density of 100 mA/cm², generation of heat in the electrolyte was observed and so the electrolyzer was cooled with water during electrolysis.

Sulfur content in the residue obtained by this method was determined by the combustion para-rrosanine photometric method. The result was found same as total sulfur content. Therefore not only sulfides of rare earth elements, but also other sulfides were isolated quantitatively.

Based on the above-mentioned preliminary experiment, the electrolytic solution method was used with constant current density of 50 mA/cm² in nonaqueous solvent as the isolation method for precipitates of rare earth elements in steels.

From the results obtained by the electrolytic solution method in nonaqueous solvent, almost all rare earth elements added were found as precipitates. Evidently, total amounts of rare earth elements in steels are equal to precipitated ones as far as this range of rare earth addition is concerned. However, about 0.010% of rare earths was found in the solid solution by the electrolytic solution method in nonaqueous solvent on sample D which was melted for determination of rare earths in solid solution. Rare earth elements in solid solution, which exist in such a steel as sample D, were determined by the following method. The method consists of determining total precipitates of rare earth elements by the electrolytic solution method in nonaqueous solvent, and subtracting the amount of rare earths in the precipitate from total rare earths in steel.

5. Separation and Determination of Rare Earth Sulfides

The chemical behavior of various synthesized compounds of rare earths was studied as a preliminary experiment in order to establish a method for separation and determination of rare earth sulfides from the residue obtained by the electrolytic solution method in nonaqueous solvent. The reagent used for decomposition of sulfide were 50 to 100 ml of methanol containing 10% iodine, 10% bromine, 3% mercury (II) chloride, 3% mercury (II) iodide, 10% mercury (II) nitrate, 0.2% silver sulfate, or 1% silver nitrate, respectively. About 20 mg of synthesized sample was added to each reagent solution, and each mixture was stirred for 40 min. The residue was filtered through a Nuclepore filter (0.2 μ), and the content of rare earths were determined on the filtrate and the residue, respectively. The results are shown in Table 3.

Sulfide is almost dissolved, while oxysulfide and oxide remain unaffected by treatment with 10% iodine solution in methanol and 1 or 3% silver nitrate solution in methanol. Because treatment with silver nitrate solution in methanol often gives abnormal results in the succeeding separation as fluoride and determination of rare earths, the treatment is unsuitable for separation of sulfide. Thus, the residue obtained by the electrolytic solution method in nonaqueous solvent was treated with 10% iodine solution in methanol, to dissolve sulfide and leave oxysulfide and oxide as residues. The residues obtained by the electrolytic solution method in nonaqueous solvent on samples C and D were treated with 10% iodine solution in methanol. After filtration, insoluble residues were examined by X-ray diffractometry. As shown in Photos. 3 (a) and (b), Ce₂O₃S was found in sample C; R₂O₃S and AI₂O₃ were found in sample D; however, no sulfide was detected both in sample C and D at all. This fact also confirms the complete dissolution of sulfide by the treatment above-mentioned.

6. Method for Phase Analysis of Rare Earth Elements in Steel

From results of above experiments, following method was established as a phase analysis of rare earth elements in steel.

1. Determination of rare earth elements in precipitate: Transfer 600 ml of methanol containing

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Table 2. Analytical results of rare earth elements in isolated residues by various methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
<th>A-1</th>
<th>A-2</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (1 + 1)</td>
<td>0.042</td>
<td>0.032</td>
<td>0.060</td>
<td>0.153</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ (1 + 5)</td>
<td>0.012</td>
<td>0.018</td>
<td>0.002</td>
<td>0.060</td>
<td></td>
</tr>
<tr>
<td>cold HNO₃ (1 + 4), −5°C</td>
<td>0.026</td>
<td>0.012</td>
<td>0.004</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td>1% CH₃OH (10%)</td>
<td>0.036</td>
<td>0.012</td>
<td>0.030</td>
<td>0.130</td>
<td></td>
</tr>
<tr>
<td>5% Na-citrate, 2% KBr, 1% KCNS electrolysis (pH 8) −300 mV vs. SCE</td>
<td>0.030</td>
<td>0.016</td>
<td>0.035</td>
<td>0.130</td>
<td></td>
</tr>
<tr>
<td>15% Na-citrate, 30% citrate, 1% KBr electrolysis (pH 3) −300 mV vs. SCE</td>
<td>0.034</td>
<td>0.017</td>
<td>0.040</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>5% (CH₃CH₂OH)₃N, 1% (CH₃)₄NCl, CH₃OH electrolysis +100 mV vs. SCE</td>
<td>0.042</td>
<td>0.030</td>
<td>0.060</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>5% (CH₃CH₂OH)₃N, 1% (CH₃)₄NCl, CH₃OH electrolysis 50 mA/cm²</td>
<td>0.042</td>
<td>0.031</td>
<td>0.061</td>
<td>0.140</td>
<td></td>
</tr>
</tbody>
</table>

* R: rare earth elements
Table 3. Chemical behavior of rare earth compounds synthesized

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Dissolved fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeS Ce₃S</td>
<td>La₂S₃ Ce₂O₂S La₂O₂S₃</td>
</tr>
<tr>
<td>I₂·CH₂OH (10%)</td>
<td>87 100 0 0 0 90 0 0</td>
</tr>
<tr>
<td>I₂·CH₂OH (10%)·60°C</td>
<td>95 100 0 0 1 100 21 31</td>
</tr>
<tr>
<td>I₂·CH₂OH (1%)</td>
<td>71 90 0 0 0 80 0 0</td>
</tr>
<tr>
<td>Br₂·CH₂OH (10%)</td>
<td>100 100 40 0 96 100 96 87</td>
</tr>
<tr>
<td>Br₂·CH₂OH (10%)·60°C</td>
<td>100 100 88 0 100 100 100 100</td>
</tr>
<tr>
<td>HgCl₂·CH₃OH (3%)</td>
<td>19 0 0 0 0 100 0 0</td>
</tr>
<tr>
<td>Ag₂SO₄·CH₃OH (0.2%)</td>
<td>33 8 0 0 0 28 0 0</td>
</tr>
<tr>
<td>AgNO₃·CH₃OH (3%)</td>
<td>100 100 0 0 0 100 0 0</td>
</tr>
<tr>
<td>AgNO₃·CH₃OH (1%)</td>
<td>100 100 0 0 0 100 0 0</td>
</tr>
<tr>
<td>AgNO₃·CH₃OH (0.5%)</td>
<td>86 73 0 0 0 59 0 0</td>
</tr>
</tbody>
</table>

(a) Cu target  
(b) Co target

Photo 3. Results of X-ray diffraction of the residue separated by dissolution with I₂·methanol (10%)

5% triethanolamine and 1% tetramethylammonium chloride to an electrolytic cell as the electrolyte. Bubble nitrogen through the solution to remove oxygen under water-cooling, and set a polished sample for electrolysis. Electrolyze 0.5 to 2 g of sample according to the content of rare earths, at a current density of 50 mA/cm². When the electrolysis is complete, strip the residue from sample by ultrasonic washing in methanol. Filter both electrolyte and washing solution of methanol through a Nuclepore filter (0.2 μ) under suction, and wash with methanol. With the residue obtained, complete the determination as described in II. 3.

(2) Determination of rare earth elements as oxy-sulfide and oxide: Transfer the residue obtained in (1) on the other portion of sample, to a 100 ml Erlenmeyer flask. Add 50 ml of 10% iodine solution in methanol, and stir the mixture for 30 min with bubbling nitrogen at room temperature. Filter the mixture through a Nuclepore filter (0.2 μ) under suction, and wash with methanol. With the residue obtained, complete the determination as described in II. 3.

(3) Determination of manganese sulfide: Add 5 ml of sulfuric acid (1+1) and 10 ml of nitric acid to the filtrate obtained in (2) evaporate to dense white fumes, and cool. Complete the determination of manganese with the solution by a proper method.

(4) Calculate the amount of metallic rare earth elements by subtracting that of rare earths in precipitate obtained in the procedure (1) from total rare earths obtained on another portion of sample.

(5) Calculate the amount of rare earths as sulfide by subtracting that of rare earths as oxysulfide and oxide obtained in the procedure (2) from rare earths in precipitate obtained in the procedure (1).

(6) If no rare earth elements in solid solution is found in a sample, rare earth elements as sulfide are also determined with following procedure.

Dissolve 1 to 2 g of sample with 10% iodine solution in methanol with stirring at room temperature, and filter the mixture through a Nuclepore filter (0.2 μ) under suction. With the residue obtained, complete the determination of rare earth elements as oxysulfide and oxide. Calculate the amount of rare earths as sulfide by subtracting that of rare earths as oxysulfide and oxide from total rare earths.

7. Analytical Results

Table 4 shows the results of phase analysis for the precipitate of rare earth elements in rare earth bearing steels, by the above-mentioned method.
Analytical results on rare earth elements in solid solution, precipitate, sulfide and oxysulfide-oxide showed satisfactory precision.

Phase analysis was also carried out on four heat-treated samples, that is, normalized at 900°C for 1 hr; quenched and tempered at 1 000°C for 1 hr and at 600°C for 1 hr; quenched at 1 300°C for 2 hr, to investigate the thermal behavior of rare earth element precipitates. All heat-treated samples showed approximately the same value of rare earth element precipitate with as-rolled one. Rare earth element precipitates, which are generally high in melting point, are hardly affected by such a heat treatment. For example, melting point of cerium sulfide (which is not always agreed by observers) is such high as 2 450°C. Although the same shape of precipitates was observed with optical microscope before and after the heat treatment, quenching from 1 300°C made the shape of oxide precipitate irregular to some extent and smaller in tendency.

8. Relation between Anisotropy of Impact Values and Amount of Rare Earth Sulfides

Based on the above-mentioned results, phase analysis of sulfides was carried out on hot-rolled steel plate manufactured from a large ingot. A method was used to combine the amount of precipitated rare earth elements and the anisotropy (C/L) of impact values was studied. The anisotropy is a ratio of impact value normal to rolling direction (C direction) and that parallel to it (L direction). The impact values were measured on samples A and B. The impact value, normal to rolling direction, of steel plate obtained from the edge portion of ingot was higher than that of steel plate obtained from the core portion. Thus anisotropy of impact values is also improved. (See Table 5.) Because contents of rare earth elements and oxygen increase toward bottom side of the ingot, and are also higher in the core portion than in the edge portion, more oxysulfide and oxide are precipitated in the core portion than in the edge. This fact has a bad effect on impact properties.

Table 5 shows the results of phase analysis of sulfide and impact values measured at −20°C on some representative steel plates of samples A and B. Analysis of rare earth element sulfides were made 3 to 6 times and the average value is given in the table. Besides sulfide, oxysulfide also has the effect on impact properties. Apparently, when the amount of oxysulfide precipitate is increased, impact value is decreased. The amount of sulfur as oxysulfide was determined by the following method.

Dissolve 2 g of sample with 150 ml of 10% iodine solution in methanol at 60°C to decompose sulfides of manganese and rare earth elements. When the dissolution of sample is complete by confirming with a magnet, filter the mixture through Nuclepore filter (0.2 μ) under suction, and wash well with methanol. With the residue, complete the determination of sulfur as oxysulfide by the combustion pararosaniline photometric method.

From the results obtained on samples A and B by the above mentioned method, about 80 to 90% of total sulfur is combined as manganese sulfide and rare earth sulfides. Especially, there is a tendency of more sulfur as manganese sulfide. The amount of sulfur combined with rare earths is only about 5.5% at most of total sulfur. Increase in rare earth sulfides improves the impact characteristics. The amount of sulfur combined as oxysulfide is about 25% at most of total sulfur and about 10% in average. Oxysulfide is not elongated by rolling for lack of plasticity and precipitated in a shape of cluster. If the amount of rare earth elements added is decreased to 0.01%,
then the clustered oxy sulfide precipitated in the core portion of ingot of sample A-1 is not found at all. The amount of sulfur combined as oxy sulfide is also a little. The effect of oxy sulfide on impact properties is thought to be less than sulfide.

In sample A-1, less precipitate of rare earth sulfides is found for more addition of them. Analytical results show much precipitate of oxide group, which agree with such precipitation of oxy sulfide as in Photo. (b).

In sample A-2, much precipitate of rare earth sulfides is observed, which correspond to more than half of the amount of their addition. Precipitated manganese sulfide is relatively decreased in spite of such a high total sulfur as 0.013%, because of the consumption of sulfur in the form of rare earth sulfides, and thus impact characteristics are improved.

In sample B, large amount of precipitated cerium sulfide is found and much sulfur is used to form them. Because the precipitation of granular sulfide is caused by the addition of other rare earth elements such as La, Nd, Pr, etc., as well as Ce, the same effect on impact properties is expected.

III. Discussion

The anisotropy \((C/L)\) of impact values varies with sulfur content and microstructure of steel, state of inclusion, rolling condition, etc., but in particular with manganese sulfide.

Because the manganese sulfide makes impact characteristics deteriorate, it is necessary to know the amount and its shape. The more the sulfide is precipitated, the more the probability of crack generation is increased. At the same time, propagation of crack is promoted, which results in the deterioration of steels. A remarkable stress concentration would be caused at the tips of inclusions by the action of stress at right angles with the inclusion of manganese sulfide elongated long in the direction of rolling. Thus, manganese sulfide usually behaves as a source of crack generation, and properties of steels are deteriorated. The number and length of manganese sulfide elongated in the direction of rolling are usually measured with microscope, and the results are compared with the impact value at right angles with rolling direction.\(^3\text{,}^{10}\) However, in the present paper, sulfides of rare earths and manganese were determined by the method for phase analysis to obtain the amount of precipitates of sulfide forming elements. The amount of precipitate was compared with the impact values. The amount of sulfur combined as sulfides of manganese and rare earths was calculated. The relation between the amount of sulfur as sulfides and the anisotropy of impact values at \(-20^\circ\text{C}\) was used as a way to evaluate the effect of rare earth addition. The ratio between the amount of sulfur as rare earth sulfides and that of total sulfur as sulfides is obtained from the following equation:

\[
r = \frac{S_{RS}}{S_{RS} + S_{MRS}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

where, \(S_{RS}\): amount of sulfur as rare earth sulfide

\(S_{MRS}\): amount of sulfur as manganese sulfide

Figures 1 and 2 show the relation between anisotropy of impact values and the characteristic value \(r\) which corresponds to the ratio of sulfur as rare earth sulfides. Figure 1 shows the result on sample A of plate thickness 16 mm, and Fig. 2, on sample B of 10 mm. \(r=0\) means that all sulfur is contained as manganese sulfide and no precipitation of rare earth sulfides is found. To the contrary, \(r=1\) means that all sulfur is contained as rare earth sulfides and no precipitation of manganese sulfide is found. By the addition of rare earth elements, the anisotropy of impact values is improved in comparison to steels of no addition \((r=0)\), and thus the effect of rare earth addition is recognized. Production of steels with \(r\) value of more than 0.6 is thought impossible by any conventional process because \(r\) is varied between 0.13 and 0.58 and is never exceeded 0.58 in the rare earths bearing steel.

The above-mentioned results certainly indicate a close relation between \(r\) and the anisotropy \((C/L)\) of impact values. The more \(r\) approaches to 1, the more \(C/L\) is improved, approaching to 1. Because \(C/L\) depends on sulfur content, microstructure, state of inclusion, plate thickness and rolling condition, etc., the improvement of \(C/L\) up to 1 is impossible only by means of rare earth addition.

As mentioned above, the addition of rare earths decreases in the amount of manganese sulfide formed, which is elongated long by rolling and causes severe

\[\text{Fig. 1. Relation between anisotropy (C/L) of impact value and yielding coefficient (r) of rare earth elements sulfide on sample A}\]

\[\text{Fig. 2. Relation between anisotropy (C/L) of impact value and yielding coefficient (r) of rare earth elements sulfide on sample B}\]
stress concentration. More sulfur is combined as rare earth sulfides, and consequently the impact value is improved at right angles with direction of rolling.

The relation between the ratio \( r \) of sulfur as rare earth sulfides and the anisotropy \( C/L \) of impact values is expressed by the following equation.

\[
C/L = (1-E_s) \frac{b(1-r)}{ar+b(1-r)} \cdot E_b \quad \text{(2)}
\]

where, \( E_b \): the effect of sulfide shape on anisotropy
\( E_s \): the effect of other factors on anisotropy
\( a, b \): constants.

In Eq. (2), the anisotropy in case of \( r=0 \), that is, no addition of rare earth elements, is given by \( 1-E_s-E_b \). On the other hand, when all sulfides are changed into rare earth sulfides by the addition of rare earth elements, that is \( r=1 \), the anisotropy is given by \( 1=E_b \). In Figs. 1 and 2, consequently, \( C/L \) is expressed with a curve connecting \( 1-E_s-E_b \) and \( 1-E_s \), and the curvature of this curve is determined by the constants \( a \) and \( b \), which express the respective effect of rare earth sulfide and manganese sulfide on the anisotropy of impact values. The ratio \( a/b \) is approximately equal to 2 according to the analytical results obtained so far, and in other words, the effect of rare earth sulfides is about twice as much as that of manganese sulfide on improvement of the anisotropy of impact values. \( 1-E_s-E_b \) shows the value of \( C/L \) at \( r=0 \), and is equal to 0.43 in the present experiments both on samples A and B.

Since both \( E_b \) and \( E_s \) are unknown, and the ratio \( a/b \) is about 2 and is not definite, the ratio is assumed to be 2.0 for approximate calculation. Three most probable measured values (\( \pm \)) in both figures were selected. These values were substituted in Eq. (2) to set up simultaneous equations. Each \( E_b \) was obtained to calculate the average value by elimination of \( E_s \). \( E_b \) is found to be 0.54 and 0.49 on samples A and B, respectively, while \( E_s \) 0.03 and 0.08. Since in these series of experiments approximately similar values for \( E_s \) (\( E_s \): 0.09 to 0.11) are obtained on other samples, \( E_b \) can be estimated to be about 0.1. This fact means that \( C/L \) can be improved up to 0.90, if \( r \) attains 1, and that \( C/L \) can be improved by \( E_s = 0.47 \) with addition of rare earth elements, from 0.43 at \( r=0 \).

\( E_s = 0.47 \) and \( E_b = 0.10 \) were substituted in Eq. (2), and the relation between \( C/L \) and \( r \) on various steels was obtained. The relation is drawn with solid line in Figs. 1 and 2 as an approximate curve. If this figure is prepared in advance, the approximate value of anisotropy \( (C/L) \) of impact values of steels can be estimated from \( r \) obtained by phase analysis, because measured values on each steel are distributed near the curve.

**IV. Conclusions**

The method for phase analysis of rare earth elements in steel was studied, and the following conclusions were obtained:

1. Granular sulfide, clustered oxysulfide \( (R_3O_S) \) and oxide containing \( Al_2O_3 \) were identified as precipitates of rare earths in steels.

2. Method for phase analysis of rare earths was established as follows: Total precipitate is isolated by the electrolytic solution method with a electrolyte consisting of 5% triethanolamine and 1% tetramethylammonium chloride in methanol, at a current density of 50 mA/cm². Sulfide is dissolved with 10% iodine solution in methanol and separated from oxysulfide and oxide. When rare earth elements are present in solid solution, rare earths in precipitates are determined by the above-mentioned electrolysis. The difference in the amount between total rare earths in steel and that in precipitate gives the amount of rare earth elements in solid solution.

3. In hot-rolled plate of rare earth bearing steel, less manganese sulfide is present, which is elongated by rolling, and causes stress concentration and crack generation. When non-plastic and spherical sulfides of rare earths are precipitated, the impact characteristics is improved. The impact characteristics at the edge of ingot is more improved than that in the center part. Because oxygen content is higher in the center part, oxide as well as oxysulfide are easy to precipitate, and in addition the cooling velocity is higher at the edge to make the precipitate smaller.

4. Almost all sulfur is combined as sulfides, which tends to form manganese sulfide rather than rare earth sulfides. The fraction of sulfur fixed as rare earth sulfides is at most about 55% of total sulfur content and the more the fraction of rare earth sulfides is increased, the more the impact characteristics is improved. About 10% of total sulfur content is combined as oxysulfide, which does not affect the impact characteristics so remarkably as sulfide.

5. Although heat treatment contributes to the uniform and fine grain size with improved impact values, the anisotropy \( (C/L) \) of impact values does not almost change. Perhaps because the shape and amount of rare earth element precipitates are kept unchanged due to its high melting point.

6. The relation between anisotropy \( (C/L) \) of impact values and the ratio \( r \) of sulfur as rare earth sulfides is determined to estimate quantitatively the effect of addition of rare earth element on the impact characteristics.

**REFERENCES**

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