Technology of Evaluating Minute TiN Inclusions in High-carbon Steel Wire Rod for Advanced Applications

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Abstract

In high-carbon steel wire rod to be drawn into fine diameters, it is necessary to suppress breakage caused by inclusions during the wire drawing process. In the past, breakage in high carbon steel wires was mainly due to alumina inclusions. However, with the higher reduction in the diameter of wires, breakage started from titanium nitride (hereinafter referred to as TiN), which is more minute than alumina, has become remarkable. To study the means for suppressing TiN and to verify their effects, it is necessary to establish both a technique to analyze the ultra-low concentration of Ti dissolved in steel and a technique to evaluate the number of TiN inclusions. This paper describes a method for quantifying concentration of dissolved Ti using a secondary ion mass spectrometer owned by the Kobe Steel group and a technique for evaluating the number of TiN particles, which has been newly developed by applying a chemical extraction method. This paper also describes how the correlation between the number of TiN particles and the frequency of wire breakage has made it possible to predict the quality of extra fine wires.

Introduction

High-carbon steel wires can be strengthened with appropriate heat treatment and cold wire drawing. Hence, they are used as materials that support social infrastructures, such as galvanized steel wires for bridges, steel wires for prestressed concrete (PC), and wire ropes, as well as tire reinforcement materials such as steel cords and bead wires. The application has recently expanded to the material for cutting out silicon wafers from silicon ingots.

With such an expansion of applications, the diameters of product wires are being reduced more and more. In particular, for the cutting of silicon ingots, an extra-fine wire of 50 to 130 μm in diameter is required in order to minimize the cutting allowance. It is known that, in wire drawing, the final process of manufacturing, the presence of non-metallic inclusions (hereinafter referred to as "inclusions") such as alumina (Al_2O_3) sized 30
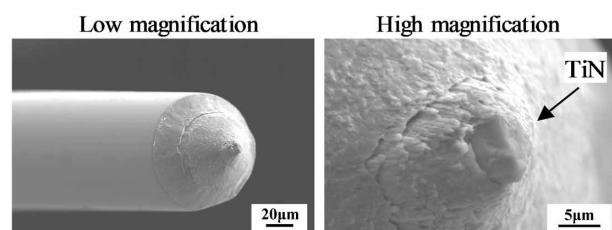

Fig. 1 Fracture surface of extra-fine wire starting from TiN

to 50 μm in the extra-fine wire induces breakage originating in the inclusions.[1] However, recent advances in wire-diameter reduction have revealed that breakage occurs with a titanium nitride (hereinafter referred to as "TiN") sized 5 to 20 μm as the origin (**Fig. 1**), which hitherto has not been the case. As with alumina-based inclusions, breakage originated from TiN also decreases the productivity of wire drawing. Therefore, it is necessary to suppress the formation of TiN in steel as much as possible.

Studying the generation conditions and means of suppressing TiN requires quantitative analysis of the concentration of dissolved Ti and the number of TiN particles in the steel. In particular, ensuring quantitative accuracy becomes challenging when the concentration of dissolved Ti is a trace amount. Hence this paper describes the estimation results for the critical Ti concentration for suppressing the formation of TiN, the origin of breakage. This paper also introduces quantitative analysis means with high precision, including a method for quantifying the concentration of dissolved Ti using a secondary-ion mass spectroscope owned by the Kobe Steel group and a newly developed evaluation technology for quantifying the trace number of TiN particles. Also reported is a breakage test conducted on the high-carbon steel wire manufactured by an actual machine. The results have enabled predicting the rate of breakage from TiN on the basis of the correlation with the number of TiN particles.

1. Generation mechanism of TiN in steel and estimation of critical Ti concentration

Inclusions in steel products are roughly classified into exogenous types mixed from refractory and slag in contact with the molten steel and endogenous types formed by the chemical reaction of components dissolved in the steel. Due to their generation mechanism, the exogenous inclusions are mainly oxide and are relatively coarse. Meanwhile, TiN, which becomes the breakage origin, is considered endogenous, and its suppression requires the elucidation of the generation mechanism.

Hence, a study has been conducted first on the possibility that Ti and N dissolved in molten steel will react to form TiN crystals during the steelmaking process. The solubility product of TiN when TiN is formed by the reaction of dissolved Ti and N is expressed by Eq. (1):[2]

$$\log[Ti]_L\,[N]_L = -14{,}000/T + 4.70 \quad\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

wherein: $[Ti]_L$: concentration (mass%) of Ti in molten steel,

$[N]_L$: concentration (mass%) of N in molten steel, and

T : temperature (K) of molten steel.

Fig. 2 shows the range of concentration product for gross Ti and gross N measured at each step in the steelmaking process for the general high-carbon steel wire of Kobe Steel. The concentrations of gross Ti and N have been measured per JIS G 1258 and JIS G 1228, respectively. It should be noted, however, that the gross Ti concentrations have been less than the lower limit of quantification, and the concentration products of gross Ti and gross N have been calculated assuming that they are equal to the lower limit of quantification, 10 ppm. The figure also includes the solubility product of TiN calculated by Eq. (1), in which the Ti concentration is 10 ppm, and
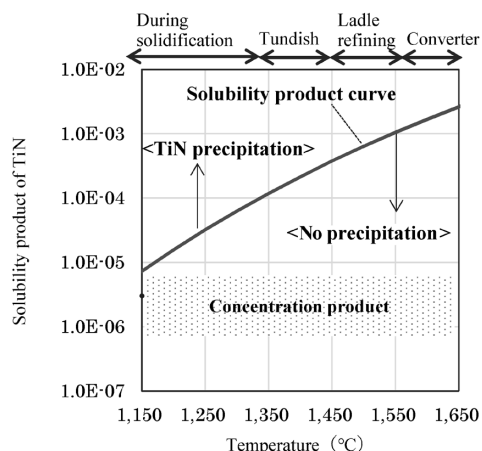

Fig. 2 Relationship between temperature and solubility product of TiN in molten steel[2]

N concentration is the maximum value of the actual measurement.

TiN is formed when the left side of Eq. (1) exceeds the right side, i.e., when the concentration product of Ti and N is higher than the solubility product of TiN in Fig. 2. The actual range of concentration product for Ti and N is below the solubility product curve in both of the temperature ranges, despite the higher-than-actual value for Ti concentration. Therefore, as far as shown in Fig. 2, TiN cannot be formed on the equilibrium calculation.

The TiN in steel products may be precipitated by heat treatment after the casting process. However, the TiN precipitates formed by solid phase diffusion are extremely small in size, generally in the submicron order,[3] and the size does not match the size of the breakage origin, TiN, of approximately 5 to 20 μm, which is the target of evaluation in this paper.

From the above, it is inferred that the breakage origin TiN is formed by the solute condensation associated with the temperature drop during solidification, i.e., the solubility product is locally exceeded by segregation. Hence, a study has been conducted on the mechanism of TiN generation by segregation and the critical Ti concentration that suppresses TiN formation.

Segregation morphologies are roughly classified as micro-segregation occurring in the microregion between dendrites and macro-segregation caused by the widespread movement of solute condensed by micro-segregation due to solidification shrinkage and convection. Scheil's equation[4] can predict the condensation of a solute component by micro-segregation, assuming that the liquid phase has a uniform composition and no diffusion in a solid phase. Bloody-Flemings' equation[5] predicts the same considering the diffusion in the solid phase. These equations suggest the possibility that the TiN solubility product in Fig. 2 is exceeded by segregation as the solidification progresses, even in the case of molten steel with an initial Ti concentration on the order of ppm. It should be noted; however, in the actual operation, it is unlikely that a TiN precipitate with a diameter of 10 μm would form in a micro-segregation region with a diameter of 100 μm, since the mass balance requires hundreds to thousands of times more Ti condensation than the initial concentration. Hence, it has been presumed that the breakage origin, TiN, is caused by macro-segregation rather than micro-segregation. This presumption has led to the examination of the critical Ti concentration to suppress TiN.

The critical Ti concentration was examined by the

following method. First, a high-carbon steel slab was made by Kobe Steel's continuous bloom caster, and the slab's longitudinal cross-section was analyzed by an electron probe micro analyzer (EPMA) to quantify the Mn concentration in the macro-segregation. Next, calculations were performed on the solid phase ratio when Mn condenses to this EPMA analysis value. The segregation calculation model by Ueshima et al.[6)-8)] was used to calculate the solid phase ratio. The parameters shown in **Table 1** were used for the calculation.[6), 9)-11)] Since the target is high-carbon steel in which solidification progresses in the γ single-phase region, Eq. (2) was used to calculate the liquidus temperature:[12]

$$
\begin{aligned}
T_L(^\circ C) = {} & 1625 - 110[\%C] - 25[\%Si] \\
& + 3[\%Mn] - 35[\%P] - 71[\%S] \\
& - 2[\%Ni] - 7[\%Cr] \quad\cdots\cdots\cdots\cdots\cdots\cdots (2)
\end{aligned}
$$

wherein [%M] is the concentration (mass%) of the component M in the liquid phase. The TiN with the stoichiometric composition is assumed to crystallize when the product of [%Ti] and [%N] in the liquid phase exceeds the equilibrium solubility product.[2] After crystallization, it is assumed to exist stably without moving among elements.

Subsequently, the initial Ti concentration was changed stepwise to calculate the segregation concentration of components other than Mn at the above solid phase ratio. These concentrations were used as initial conditions, and the concentration of crystallized TiN in macro-segregation was calculated using the same model. Furthermore, assuming that the TiN particle is a cube each side of which is 10 μm, the crystallized TiN concentration in the macro-segregation was converted into the number of TiN particles to derive the relationship between the initial Ti concentration and the number of TiN particles (**Fig. 3**). Fig. 3 shows that the initial Ti concentration index value for not forming a TiN of 10 μm is 0.5 or less, compared with the standard
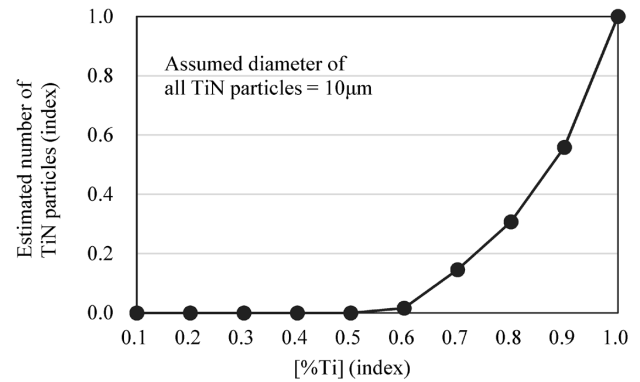

Fig. 3 Relationship between initial Ti concentration and number of TiN particles (index)

material, assuming the Ti concentration of 1 for Kobe Steel's general high-carbon steel wire.

2. Method for quantifying trace amount of Ti dissolved in steel

As described in the previous section, the gross Ti concentration in Kobe Steel's high-carbon steel for extra-fine wire is less than the lower limit of quantification according to JIS G 1258 (less than 0.001 mass%), requiring a more precise method of quantifying Ti. It is not the gross Ti concentration, but the concentration of Ti dissolved in the molten steel that affects the thermodynamic conditions for the formation of TiN.

However, the JIS method described above can only analyze gross Ti concentration and cannot distinguish between the Ti dissolved in the steel, and the Ti contained in inclusion particles. Hence, Kobe Steel investigated a method for quantifying the concentration of dissolved Ti using CAMECA's secondary ion mass spectrometry (SIMS) IMS7F owned by the Kobe Steel Group. Hitherto, the Kobe Steel group had conducted quantitative analysis using SIMS for the trace amount of Al dissolved in steel. In the SIMS analysis, it is necessary to eliminate the influence of Al-containing inclusions on the measurement results. To this end, secondary-ion mapping is performed on the sample surface of a steel product to select an area that is not affected by inclusions on the surface. Next, analysis in the depth direction is performed by ion sputtering to confirm that a stable concentration profile is obtained without sudden concentration increase due to inclusions before calculating the trace amount of Al.[13]

The present method adapts this method of quantitatively analyzing dissolved components using the SIMS to the quantitative analysis of dissolved Ti. The results have enabled quantifying

Table 1 Parameters for numerical calculation of micro segregation[6), 9)-11)]

Elements	$K^{\gamma/L}$	$D^{\gamma}(m^2/s)$
C	0.33	$7.61\times10^{-6}\exp(-1.35\times10^5/(R\cdot T))$
Si	0.52	$3.00\times10^{-6}\exp(-2.51\times10^5/(R\cdot T))$
Mn	0.13	$5.50\times10^{-6}\exp(-1.83\times10^5/(R\cdot T))$
P	0.79	$1.00\times10^{-6}\exp(-2.49\times10^5/(R\cdot T))$
S	0.035	$7.50\times10^{-4}\exp(-2.23\times10^5/(R\cdot T))$
Ti	0.07	$1.50\times10^{-5}\exp(-2.51\times10^5/(R\cdot T))$
N	0.48	$3.60\times10^{-5}\exp(-1.69\times10^5/(R\cdot T))$

$K^{\gamma/L}$: Equilibrium distribution coefficient between γ phase and liquid

D^{γ}: Diffusion coefficients in γ phase

R: Gas constant of 8.314 J·K^{-1}mol^{-1}

T: Temperature in Kelvin

the concentration of Ti dissolved in a range from ppm to ppb. In addition, the operation improvement of the actual machine has enabled quantitative evaluations of whether or not the concentration of dissolved Ti could be reduced to less than the index value determined in the previous section.

3. Development of method for extracting and evaluating TiN particles in steel

Inclusions in steel products are critical factors that affect the quality, making their evaluation key. The methods for evaluating inclusions include a chemical extraction and separation method. In this evaluation method, the base material of steel products is dissolved to extract only inclusions for evaluation. This method allows for three-dimensional evaluation of inclusions and is suitable for grasping their amount, number, and chemical composition. Therefore, many reports have been made.[14)-21)]

However, when multiple inclusions coexist in a sample, an excess of multiple types of inclusions will remain excessively on the filter during inclusion extraction, making the quantification difficult. On the other hand, to extract only the inclusions of the target chemical species to be evaluated, complicated separation procedures and operations must be performed, and depending on the series of operations, the target inclusions may disappear.[21)] In the case of the high-carbon steel wire in this study, there are multiple inclusions such as carbide and oxide in addition to TiN, and it is not easy to quantify TiN by the conventional technique. Hence, as the basis for developing the manufacturing process of high-quality wire, efforts have been made to develop a new technique to evaluate the number of TiN inclusions while considering the components of the steel products and the species of inclusions other than TiN.

TiN is often added proactively to steel products to improve their quality,[22), 23)] and there are many reports on extracting and evaluating TiN in steel products. Examples include the acid treatment method for extracting TiN particles using an acid such as hydrochloric acid or sulfuric acid,[15)] and an electrolysis method that separates TiN by constant current electrolysis using a solution of 10%AA system (10% acetylacetone-1% tetramethylammonium chloride-methanol) and by secondary processing using 10% bromine methanol solution.[24)]

In developing the evaluation method, a decision was made to apply the acid treatment method, which has more evaluation allowance than the electrolysis method. The electrolysis method has a low dissolution tolerance of steel products,[25)] and is not suitable for the trace amount evaluation of TiN originating from Ti mixed at an impurity level, the target of this study. Although it has been reported that TiN dissolves slightly in the acid treatment,[26)] the factor that causes breakage of extra-fine wire is the number of relatively coarse TiN particles sized 10 μm or greater. Hence, a slight dissolution of TiN is considered not to significantly affect the number evaluation, and the acid treatment method using hydrochloric acid has been chosen for the extraction.

SEM observations were performed on the residues on the filter after treatment with hydrochloric acid. The result is shown in **Fig. 4**. Fig. 4 b) schematically illustrates the residues on the filter and is based on the evaluation results from energy dispersive X-ray spectroscopy. The acid treatment does not dissolve inclusions other than TiN, and SiO_2, carbide-derived carbon, and P compounds remain over the entire filter surface in addition to TiN.

Hence, additional processing for extracting only TiN has been studied to establish the process shown in **Table 2**. The feature of the process shown in Table 2 is that TiN is converted to insoluble Ti oxide after the removal of carbon by atmospheric combustion. This process avoids the disappearance of TiN particles caused by the mixed-acid treatment in the back end, whose purpose is to reduce residues other than the Ti-based ones. The only residue on the filter finally obtained by the flow in Table 2 is Ti oxide derived from TiN (**Fig. 5**), and no inclusion of other chemical species is observed.
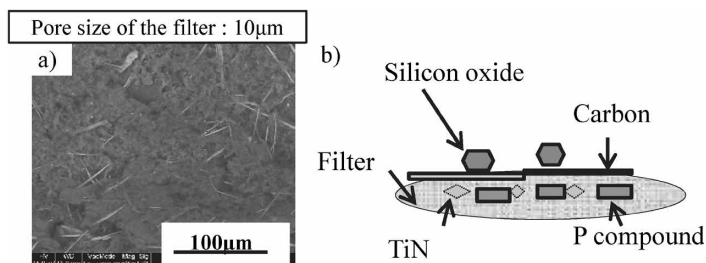

Fig. 4 Residue after acid treatment with HCl (a: SEM Image, b: Schematic diagram of residue on filter)

Table 2 Procedure for evaluation of TiN particle number

Procedure	Purpose
Sample preparation ↓	—
Acid treatments with HCl ↓	Extraction of inclusion
Filtration ↓	—
Heated in air atmospere ↓	Dissolution of residue derived from carbon Modifing of TiN
Treatment with ammonium hydrogen fluoride ↓	Dissolution of residue derived from SiO_2
Treatment with mixed acid ↓	Dissolution of residue derived from Phosphorus
Filtration ↓	—
SEM observation	Evaluation of size and number of Ti oxide derived from TiN

Fig. 5 Ti oxide on filter after mixed acid treatment

Table 3 Chemical compositions of production materials

(mass%)

	C	Si	Mn	P	S	Cr	Dissolved Ti (index)
Steel A	1.05	0.20	0.29	0.004	0.005	0.22	1.2
Steel B	1.04	0.19	0.30	0.006	0.006	0.21	1.5
Steel C	1.04	0.20	0.31	0.008	0.004	0.22	1.0
Steel D	1.04	0.19	0.29	0.004	0.005	0.20	0.5

Measuring the size and number of inclusions by SEM has enabled quantitative evaluation of the number of TiN particles in steel products.

4. Example of application of analysis evaluation method

The following describes the results of the quality evaluation of production materials at Kobe Steel using the new analytical method described in the previous section.

4.1 Results of evaluation of concentration of dissolved Ti and TiN particle count

When making high-carbon steel wire, multiple alloying elements and auxiliary feedstock are added during molten steel refining. Here, the steel was melted while appropriately controlling the Ti concentration in four batches at Kobe Steel's Kakogawa Works (250 tons/batch) and hot rolled to ϕ5.5 mm by a Kobe Steel wire rod mill.

Table 3 shows the chemical compositions of the four batches. The concentration of dissolved Ti was measured by the method described in Section 2 and was confirmed to be quantifiable even if the concentration was less than 10 ppm. Table 3 includes the index value with the concentration of dissolved Ti in Steel C, which is equivalent to Kobe Steel's general high-carbon wire steel, being 1.0, and Steel D corresponds to the material that satisfies the improvement guidelines shown in Fig. 3 of Section 1. It should be noted that the results hereinafter will be described by index value, with Steel C being 1.0.

Fig. 6 shows the relationship between the concentration of dissolved Ti in Steels A to D and the number of TiN particles evaluated by the TiN particle extraction method newly developed. A positive correlation was confirmed between the concentration of dissolved Ti and the number of TiN particles. In addition, no TiN particles were detected in Steel D, which satisfied the guidelines for improving the concentration of dissolved Ti.

4.2 Effect of TiN particles on breakage rate
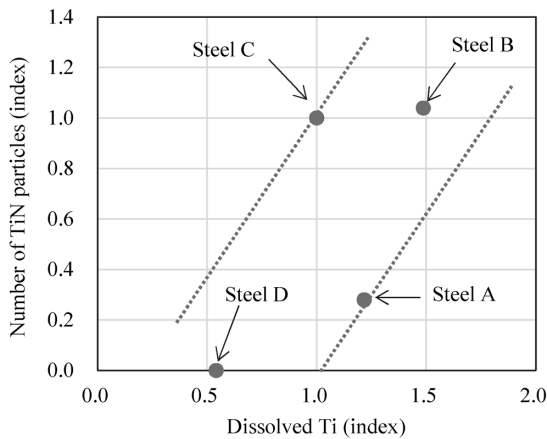
The following method has been used to examine

Fig. 6 Relationship between dissolved Ti concentration and number of TiN particles (both of index in Steel C: 1.0)
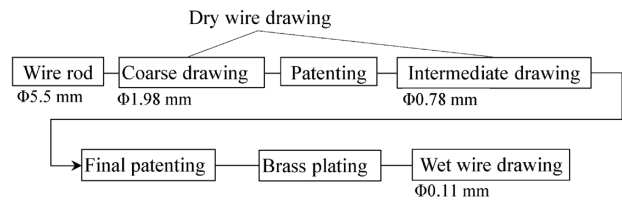

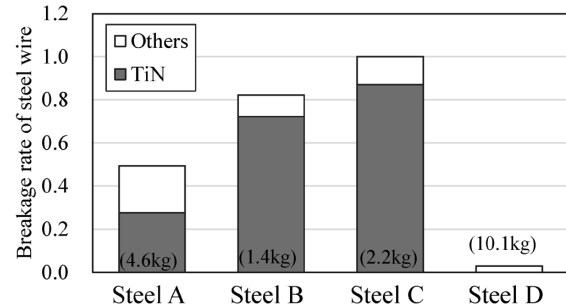Fig. 7 Wire drawing process for evaluation of breakage rate

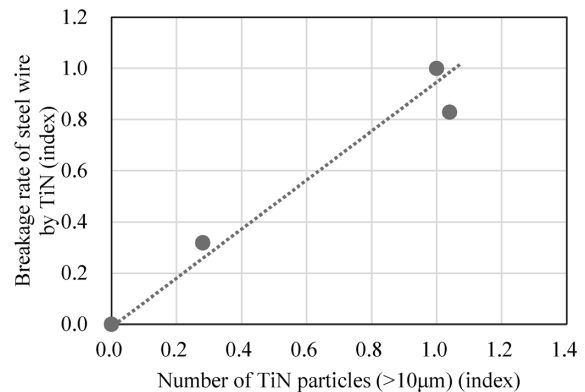Fig. 8 Results of breakage rate of steel wire with wet drawing (index in Steel C: 1.0)

Fig. 9 Relationship between number of TiN particles and breakage rate of steel wire caused by TiN (both of index in Steel C: 1.0)

the effect of the number of TiN particles in steel on the breakage rate during wire drawing. **Fig. 7** describes the wire drawing process for evaluating the breakage rate. A wire of $\phi 5.5$ mm was roughly drawn, followed by an intermediate wire drawing to $\phi 0.78$ mm. After the subsequent patenting and brass plating, the wire was wet-drawn to $\phi 0.11$ mm to evaluate its breakage rate. Typical low-angle dies were used for the first 19 passes of wet drawing, and high-angle dies were used for the final 5 passes to increase the shear stress around the TiN particles to facilitate the evaluation of the effects of the number of TiN particles.

Fig. 8 shows the evaluation results for the breakage rates of Steels A to D. The numbers in parentheses indicate the wire drawing evaluation value. In the case of frequent breakage rates, it gives higher reproducible evaluations with fewer samples than for infrequent breakage rates. Therefore, the evaluation value was changed as appropriate, and the breakage results were converted to the number of breakages per 100 km of line drawing distance to exclude the effect of the difference in the evaluation value. The breakage origin was investigated and evaluated for broken wires, distinguishing between TiN and other inclusions.

In this wire drawing test, a fractographic study was conducted after the breakage to confirm that the breakage from TiN origin predominates in Steels A, B, and C. The result proves that this wire drawing condition evaluates the breakage characteristics with TiN origin. In addition, the breakage rate with TiN origin in Steel A, B, and C was 0.3 to 0.9, whereas the breakage with TiN origin was zero in Steel D, whose index value for the concentration of dissolved Ti was 0.5 or less than that of Steel C. This result supports the validity of the improvement guideline shown in Fig. 3 of Section 1.

Fig. 9 shows the correlation between the number of TiN particles in Steels A to D and their breakage rate. The number of TiN particles was counted by applying the TiN particle extraction and evaluation method described in Section 3. A linear correlation is observed between the two, and quantifying the number of TiN particles in steel by the newly developed method has enabled the prediction of the breakage rate with TiN origin in the wire drawing process of extra-fine wire.

Conclusions

As the diameter of high-carbon steel wire is reduced, the breakage originating from TiN has become apparent. In order to suppress this breakage, a quantitative analysis technology for dissolved Ti in steel using SIMS and technology for evaluating TiN particle count applying the acid treatment method

have been established.

The concentration of Ti dissolved by the trace amount, the number of TiN particles, and the breakage rate were evaluated for the materials manufactured. These results have revealed that the number of TiN particles in the steel decreases with the reduced trace amount of dissolved Ti, suppressing the breakage from TiN. Besides, the correlation between the number of TiN particles and the breakage rate has enabled the prediction of the quality of extra-fine wire of high-carbon steel by the newly developed TiN particle count evaluation technology.

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