KAWASAKI STEEL TECHNICAL REPORT
No.3 (September 1981)

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Isao Takahashi, Yoshihiro Matsumoto, Isamu Aruga

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Effects of Ti and C on fishscale formation and hydrogen diffusivity were examined using hot rolled titanium bearing steels. To clarify the traps for hydrogen, quenching and tempering experiments of iron-titanium-carbon alloys were carried out. It is concluded that hydrogen diffusivity of titanium bearing steels is indicative of thee fishscale suppres-siveness of the steels and that fine coherent TiC particles are main traps for hydrogen. Also the effect of TiC on mechanical properties of steels has been discussed. On the basis of these results, hot rolled sheet KHN for enameling use has been newly developed. Both-sided enameling of the KHN sheet prevents fishscale formation and its sag value is as small as that of cold rolled sheets for enameling.

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Isao TAKAHASHI** Yoshihiro MATSUMOTO** Isamu ARUGA***

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*On the basis of these results, hot rolled sheet **KHN** for enameling use has been newly developed. Both-sided enameling of the **KHN** sheet prevents fishscale formation and its sag value is as small as that of cold rolled sheets for enameling.*

1 Introduction

Enamel is a glassy substance having a low melting point and is ordinarily fired on steel sheets at 800 to 900°C. For this reason various characteristics are required of steels for enameling, such as excellent adherence of enamel to steel, no pinhole defects on enamel after the firing, a smaller sag (deformation of steel sheet during firing), and freedom from fishscale defects. Particularly, the fishscale defects are liable to occur not only immediately after firing but also several days after firing, thereby posing a most troublesome problem. According to some researchers[1-3], fishscales are generally caused to occur in the following manner: hydrogen which has penetrated the steel during enamel firing is released again from the steel as the hydrogen becomes less soluble in the steel along with the cooling, thus resulting in a hydrogen gas generation and a build-up of high pressure at the steel-enamel interface. Therefore, higher hydrogen occlusion in steels is required for preventing fishscales.

In general, for steels for enameling use, decarburized rimmed steel (JIS specification: SPP; Kawasaki Steel Standard: KTS-M) is used. This type of steel has improved fishscale suppressiveness, because nonmetallic inclusions and carbides contained in the steel form small microvoids during cold rolling and the microvoids trap hydrogen which has penetrated the steel[4-7]. Since the decarburized rimmed steel also lowers its C content to below 0.008% as a result of decarburized annealing after cold rolling, it is virtually free from pinhole defects and has a smaller sag value. Further, the steel during this annealing process forms a texture suitable for deep drawing, thereby making it excellent for press forming.

However, the decarburized rimmed steel has its upper limit of the thickness of sheet that can be manufactured, owing to restraints by the production process.

On the other hand, normal hot rolled steel sheets were usually enameled only on one side, because of their inferior fishscale suppressiveness—that is, because the hot rolled steel sheets were unable to form microvoids that would suppress fishscale generation by cold rolling.

The authors conducted basic experiments on the effects of various kinds of elements upon enameling properties, particularly, upon fishscale susceptibility of steels and found that Ti is effective in fishscale prevention; and thus the authors developed hot rolled steel sheets that can be enameled on both sides.

This report describes the effect of Ti on fishscale suppressiveness of steels and reviews the properties of the newly developed hot rolled steel sheet **KHN** for enameling use.

2 Effects of Ti on Fishscale Susceptibility

Conceivable hydrogen trap sites in Ti-bearing steel

* Originally published in *Kawasaki Steel Technical Report*, 12 (1980) 2, pp. 65–72 (in Japanese)
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are TiN, TiC, solid solute Ti and microvoids[6,8,9]. In order to clarify the effects of these hydrogen trap sites, 50 kg vacuum-melted steels containing different quantities of C and Ti (basic composition: 0.30%Mn-0.008%P-0.005%S-0.003 0%O-0.002%N) were made. After hot-forged into a thickness of 50 mm, these steels were reheated at 1 250°C for 1 hr. and hot rolled by 6 passes into a thickness of 4 mm. In order to simulate a coiling temperature, the hot rolled sheets were held at 600°C for 1 hr. and then air-cooled. After the sheets were descaled by shot blasting, enamel was fired on them by using conventional frits, to examine whether or not fishscales occurred. **Fig. 1** shows the effects of C and Ti on fishscale susceptibility of the steel sheets. The degrees of fishscale formation are indicated in four grades by varying the pretreatment and firing conditions. In each case of the C contents, fishscales decrease as the Ti content increases, until fishscales do not appear at 0.20%Ti or above.

The hot rolled steel sheets were machined to a thickness of 1 mm and subjected to a hydrogen permeability test at room temperature. The steel sheets were subjected to electrolysis (0.1N NaOH + 0.1N NaCN) at room temperature using a constant current density of 1 mA/cm² and the change in hydrogen permeation with time was measured. The apparent diffusion coefficient, *D*, of hydrogen was obtained by the time lag method[10] and the relation between this coefficient and fishscale formation was obtained as shown in **Fig. 2**. **Fig. 2** indicates that smaller *D* corresponds to lighter fishscale formation and that in the case of Ti-bearing steel, the hydrogen diffusion coefficient *D* can be used as a measure for fishscale suppressiveness.

In order to examine in more detail the effects of Ti on fishscale susceptibility of steel sheets, 0.05%C-0.2%Ti steel was quenched and aged. Variation in *D* due to the heat treatment was investigated. Namely, after water-quenching the steel from 1 250°C at which all C and Ti were considered to be in a solute state[11], the steel was held at varying temperatures for 1 hr. and water-quenched or air-cooled. The values of hydrogen diffusion coefficient, *D*, and the quantities of Ti precipitated by a chemical analysis were obtained. Simultaneously the precipitates were observed by an electron microscope.

The results are summarized in **Fig. 3**. When the sheets were quenched from various temperatures to 0°C, it was found that hydrogen diffusion coefficient *D* hardly varied at a temperature below 400°C, but suddenly decreased above 500°C, showing the minimum value at 600°C and again increased at higher temperatures. This result nearly agrees with the result of electrical resistivity measurement[7] and corresponds to precipitation and resolution processes of Ti There-

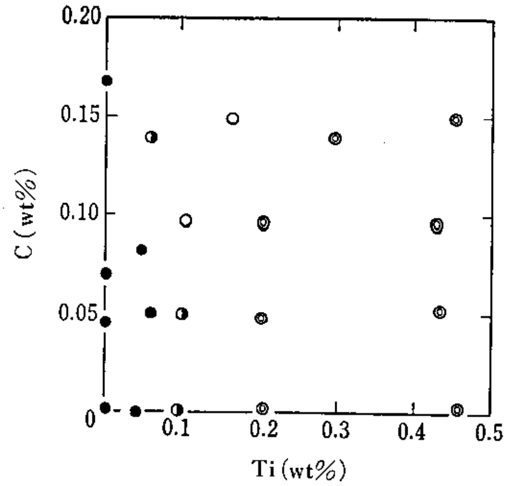


Fig. 1 Effects of C and Ti on fishscale susceptibility

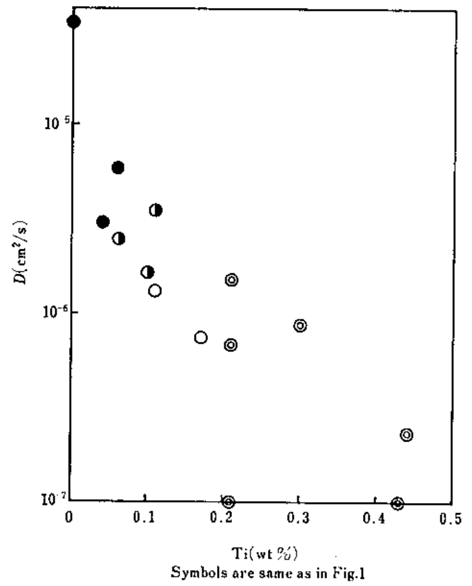
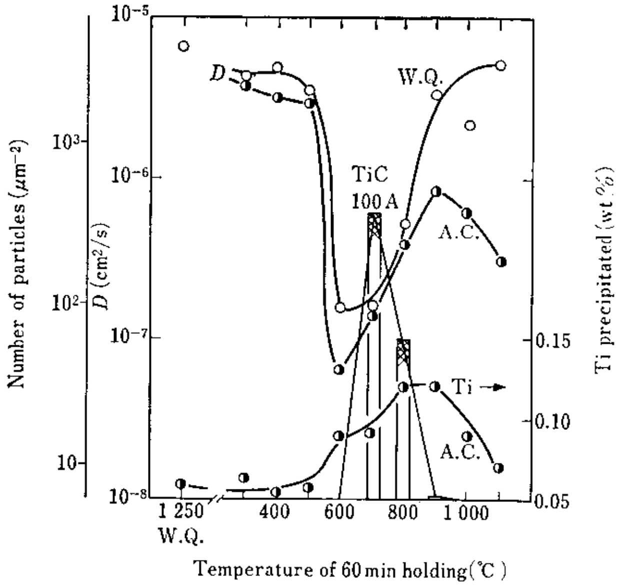


Fig. 2 Relation between hydrogen diffusivity *D* and Ti content

fore, the difference in the value of *D* between the water-quenched and the air-cooled materials at a higher temperature range may be attributed to partial precipitation of Ti during air cooling.

On the other hand, the quantity of Ti precipitates begins to increase at a temperature exceeding 500°C and shows a maximum value at 900°C. Namely, the decrease in the value of *D* agrees with the initial stage of Ti precipitation, but there is no correspondence between the quantity of Ti precipitates and the value of *D*. The results of X-ray diffraction have confirmed that the precipitates were TiC. In the transmission electron microscope observation of thin film, no Ti



TiC particles with the size of about 100 A were computed using transmission electron micrographs
W.Q. or A. C. :Water quenched or air-cooled from each temperature

Fig. 3 Effects of ageing temperature on hydrogen diffusivity D and Ti precipitates for 0.05%C-0.2% Ti steel

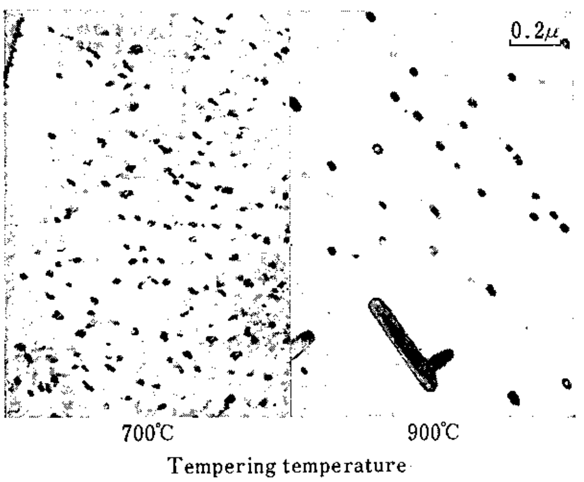


Photo. 1 Transmission electron micrographs showing the distribution of TiC particles in 0.05%C-0.2%Ti steel

precipitates were observed at 600°C. At 700°C, very fine coherent TiC particles were observed, as shown in **Photo. 1**. At 900°C, incoherent TiC particles existed having a particle size larger than that at 700°C. Therefore, at 600°C where D showed a minimum value, the existence of coherent TiC particles, which were finer in size than those at 700°C, or TiC clusters was suggested.

From the above-mentioned results, the hydrogen trap sites of Ti-bearing steel are discussed below. Asaoka et al. showed, from experiments using autoradiography, that the grain boundary has only a small trap effect and the boundary between the precipitates and the matrix is the most powerful hydrogen trap site in Fe-0.15%Ti steel[8], and Pressouyre and Bernstein reported that the most powerful trap site in Fe-Ti-C steel is TiC, and the grain boundary, dislocation and solute Ti are less powerful trap sites[9]. However, TiC particles which they observed were of several microns or a 1/10 micron. The results of quenching and ageing experiments indicated that TiC particles of 100 Å or smaller are powerful hydrogen trap sites and it is considered that coherent TiC precipitates, rather than incoherent TiC precipitates, trap hydrogen at the boundary between the TiC precipitates and the matrix or at the strain field surrounding the precipitates.

3 Relation between Tensile Strength and Hot Rolling Conditions

As mentioned in the preceding section, effective utilization of fine TiC precipitates made it possible to manufacture hot rolled steel sheets having reduced fishscale tendencies. TiC precipitation varied with the hot rolling conditions and affected not only the fishscale susceptibility but also the strength of hot rolled sheets. Steels with varying contents of C, Mn and Ti were made by the basic oxygen furnace and hot-rolled according to various hot rolling conditions, and the relation of tensile strength and yield strength with the rolling conditions was examined.

Assuming that the effects of TiC precipitation on mechanical properties of steel sheets follow Orowan's model, we obtain strength σ by

$$\sigma \propto \frac{\mu b}{l} \qquad \cdots\cdots(1)$$

μ: Shear modulus
b: Burger's vector
l: Distance of precipitates

If the number of precipitated particles is denoted by n, nucleation energy by ΔF, and the precipitation temperature by T_m, we obtain

$$\frac{1}{l} \propto n^{\frac{1}{3}}$$

$$n \propto \exp(-\Delta F/kT)$$

$$\Delta F \propto \left\{\frac{T_m}{T_m - T}\right\}^2$$

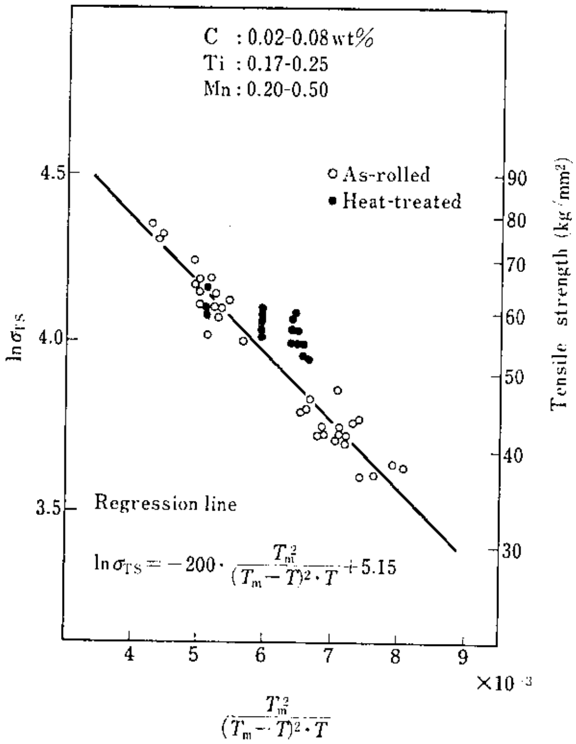


Fig. 4 Effect of hot rolling conditions on tensile strength σ_{TS} of hot rolled sheets

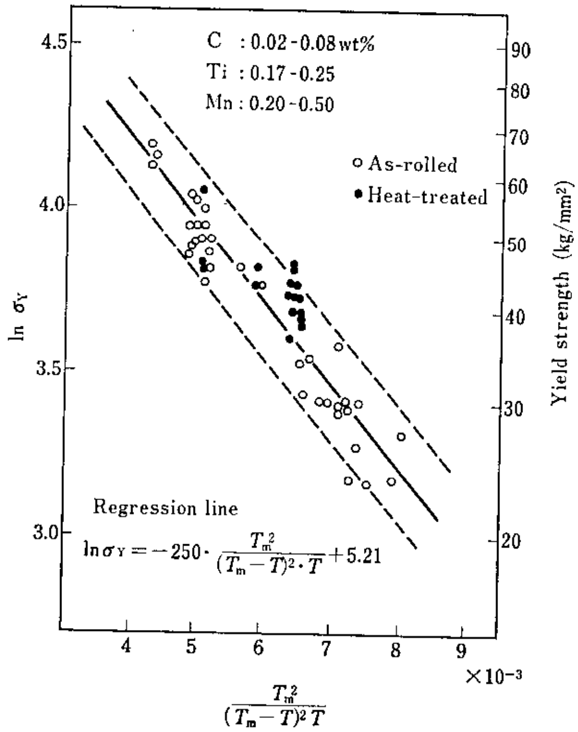


Fig. 5 Effect of hot rolling conditions on yield strength σ_y of hot rolled sheets

From the above relation we obtain

$$\ln\sigma \propto -\frac{T_m^{\ 2}}{(T_m-T)^2\cdot T} \cdots\cdots\cdots\cdots\cdots (2)$$

T_m was obtained from the following eq. (3)[12] and the hot rolling conditions were re-arranged with T as a coiling temperature as shown in **Figs. 4** and **5**:

$$\log[\mathrm{Ti}][\mathrm{C}] = -\frac{10\,580}{T_m} + 4.38 \cdots\cdots (3)$$

For both tensile and yield strength, the relation of eq.(2) is valid, namely, it is evident that the mechanical properties of hot rolled sheets vary widely depending upon cooling speed after hot rolling and the coiling temperature. Conversely, by controlling these conditions, variation in distribution of TiC particles can be utilized to give desired mechanical properties to the hot rolled sheets.

4 Characteristics of Hot Rolled Sheet KHN for Enameling Use

Characteristics of **KHN** manufactured on the basis of the above knowledge are given below. Chemical compositions are shown in **Table 1. KHN** is designed to be a low-carbon steel sheet in order to improve its formability and to prevent pinholes liable to occur during enamel firing. Its Mn and Ti contents were determined by taking into consideration sagging and fishscale suppressiveness.

The raw materials were melted in a basic oxygen furnace and, after degassing, cast by continuous casting or ingot making process. In the hot rolling process, attention was given to minimizing variation in mechanical properties and fishscale susceptibility over the entire length of the coil. For slab-reheating, finish rolling and coiling, temperatures of 1 250°C, over

Table 1 Chemical compositions of **KHN** (wt%)

Thickness (mm)	C	Si	Mn	P	S	Ti	Al	O	N
1.6	0.02	0.03	0.23	0.014	0.005	0.21	0.033	0.0029	0.0041
3.2	0.02	0.03	0.23	0.014	0.006	0.18	0.029	0.0023	0.0038

850°C, and 700°C were employed, respectively. After skin pass rolling, the sheets were shot-blasted.

4.1 Mechanical Properties

Table 2 shows tensile properties of hot rolled sheets of 1.6 mm and 3.2 mm in thickness manufactured by the above method. Tensile strength ranges from 36 to 41 kg/mm^2. **Table 3** shows tensile properties of enamel-fired sheets (heat treatment at 860°C). When the sheets are enamel-fired at 860°C, their tensile strength becomes lower by 1 to 5 kg/mm^2 than that of the as-hot rolled sheets. This result is more or less the same as those for SPHC and SS41.

Results of various formability tests are summarized in **Table 4**. The formability of **KHN** lies near the middle between SPHC and SS41, but owing to inclusion shape control using Ti addition[13], the difference between mechanical properties in the longitudinal and

Table 2 Tensile properties of **KHN** sheets

Thickness (mm)	Sampling position	Direction	Y.S.(0.2%) (kg/mm^2)	T.S. (kg/mm^2)	El. (%)
1.6	LE	L	23.3	36.7	31
		T	26.4	37.5	39
	TE	L	30.0	40.8	32
		T	29.9	42.0	27
3.2	LE	L	22.8	41.2	36
		T	25.7	42.8	32
	TE	L	29.2	40.9	36
		T	29.8	41.0	36

Test piece : JIS No. 5 (gauge length : 50 mm)
LE : Coil top, TE : Coil bottom
L : Rolling direction, T : Transverse direction

Table 3 Tensile properties of enamel-fired sheets

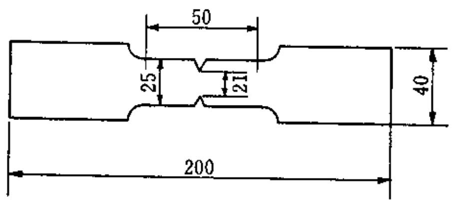
Thickness (mm)	Sampling position	As-hot rolled			After firing		
		Y.S.(0.2%) (kg/mm^2)	T.S. (kg/mm^2)	El. (%)	Y.S.(0.2%) (kg/mm^2)	T.S. (kg/mm^2)	El. (%)
1.6	LE	23.3	36.7	31	17.4	35.8	34
	TE	30.0	40.8	32	14.2	36.1	38
3.2	LE	22.8	41.2	36	16.5	36.1	44
	TE	29.2	40.9	36	18.8	35.8	43

Test piece : G.L.=50 mm, Rolling direction
Firing condition : 860°C, 4.5 min for 1.6 mm thick sheet
860°C, 7 min for 3.2 mm thick sheet

Table 4 Formability test results of **KHN** sheets

Thickness (mm)	Sampling position	Limiting drawing ratio, Blank holding force 1t	Limiting drawing ratio, Blank holding force 2t	Erichsen value (mm)	Bulge height (mm)	Side bend elongation*(%) L	Side bend elongation*(%) T	Notched tensile elongation**(%) L	Notched tensile elongation**(%) T	Bend radius
1.6	LE	2.10	2.00	11.0	54	54	40	31	28	0 T
	TE	2.10	2.06	11.2	54	42	49	30	29	0 T
3.2	LE	2.00	2.00	—	46	66	60	40	39	0 T
	TE	2.00	2.00	—	42	57	74	43	41	0.5T

*Test piece dimensions : 40 mm×170 mm
**



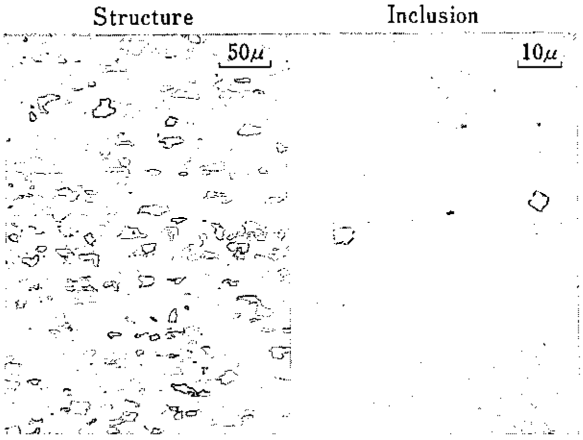


Photo. 2 Micrographs of hot rolled sheet, **KHN**

transverse directions of **KHN** is smaller and its anisotropy less than those of SPHC and SS41.

Photo. 2 shows the micrographs and inclusion shape of **KHN**. The grain boundary unique to Ti-bearing steel gives undefined microstructures, and Ti-containing inclusions are observed.

4.2 Enamel Properties

Three types of enamel pretreatment, namely, shot blasting, shot blasting plus picking (10% H_2SO_4, 75°C, 5 min.), and shot blasting plus pickling plus Ni flash (2%$NiSO_4$, pH = 3, 70°C, 5 min.) were applied to **KHN** of 1.6 mm and 3.2 mm in thickness, and these hot rolled sheets were sprayed on both sides with conventional frits and enamel-fired. After firing, the sheets were held at 160°C for 15 hr. as fishscale promotion treatment, and fishscale judgment was made by visual inspection. The results are shown in **Table 5.** Since sheets for enameling are enamel-fired after press forming, the results of fishscale tests performed on the worked sheets are also included in **Table 5.** No fishscales were formed on the as-hot rolled sheets and worked sheets.

After MIG welding or spot welding, the sheets were given the above-mentioned three types of enamel pretreatment and enamel-fired. The weld zones showed no fishscale formation.

After the three types of enamel pretreatment, the **KHN** sheets were subjected to two-coat enameling with conventional frits and enamel adherence was measured by the P.E.I. adherence tester[14]. As shown in **Fig. 6,** even with shot blasting alone, the **KHN** sheets gave satisfactory enamel adherence.

The picking weight loss in the 10% H_2SO_3 solution is shown in **Fig. 7.** The pickling rate of **KHN** is faster than that of the decarburized cold rolled sheet, KTS-M. Pickling time, therefore, can be shortened when pickling is performed as enamel pretreatment.

Table 5 Fishscale suppressiveness

(1) As-hot rolled

Thickness (mm)	Sampling position	Enamel pretreatment		
		As-shot-blasted	Shot blasting +pickling**	Shot blasting +pickling +Ni flash***
1.6	LE	0/3*	0/3	0/3
	TE	0/3	0/3	0/3
3.2	LE	0/3	0/3	0/3
	TE	0/3	0/3	0/3

(2) After cold reduction

Thickness (mm)	Reduction (%)	Enamel pretreatment		
		As-shot-blasted	Shot blasting +picking	Shot blasting +pickling +Ni flash
1.6	5	0/3	0/3	0/3
	10	0/3	0/3	0/3
	15	0/3	0/3	0/3
3.2	5	0/3	0/3	0/3
	10	0/3	0/3	0/3
	15	0/3	0/3	0/3

*0←Fishscaled specimen number
3←Total specimen number
**10%H_2SO_4, 75°C, 5 min
***2%$NiSO_4$, pH=3, 70°C, 5 min

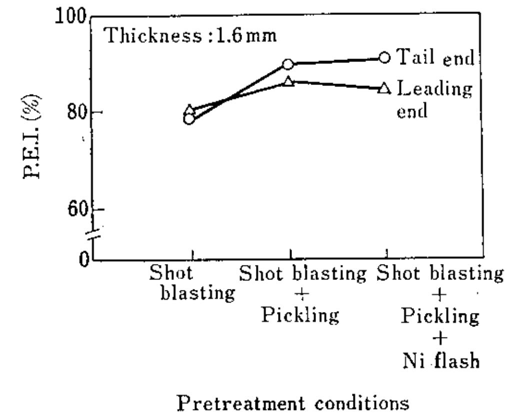


Fig. 6 Effect of pretreatment conditions on adhesion

The relation between sag and firing temperature is shown in **Fig. 8. KHN** has a smaller sag than does KTS-M, the decarburized cold rolled sheet, although **KHN** has a higher C content. This is attributed to fixing of C by Ti. Ti also suppresses generation of CO gas and greatly reduces the occurrence of pinhole defects.

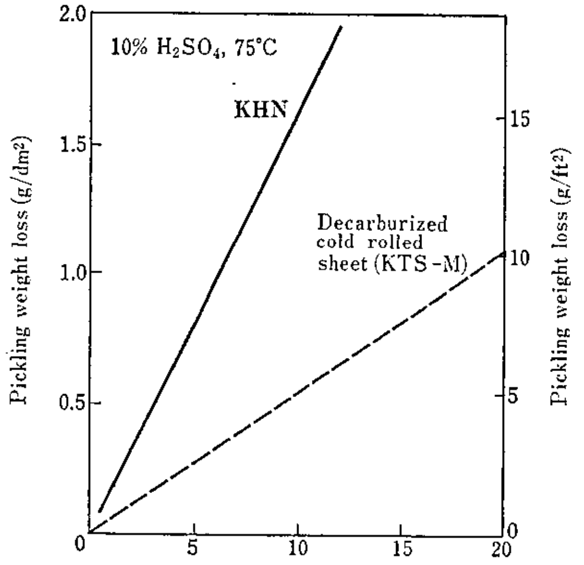


Fig. 7 Pickling weight loss

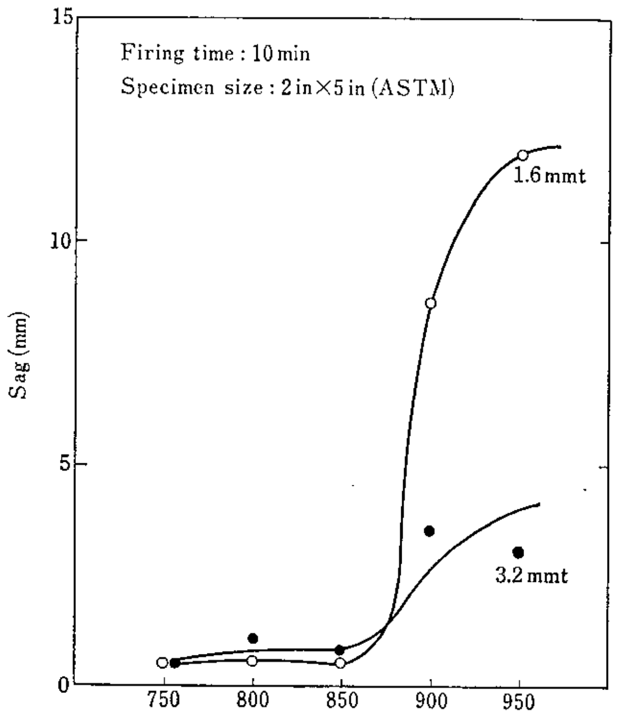


Fig. 8 Relation between sag value and firing temperature

Conventionally, hot rolled sheets such as SPHC and SS41 were used for enameling, but they were usually used as single side enameled sheets owing to fishscale. For instance, only the internal surface of the water heater that was to contact water was given enamel treatment, and the external surface was painted. In such application, **KHN** can be used for both-sided enameling. In addition, **KHN** can find many applications in kitchenware such as the range, grate of the range and handles of pots and pans, as well as boilers, tanks, construction panels and silos.

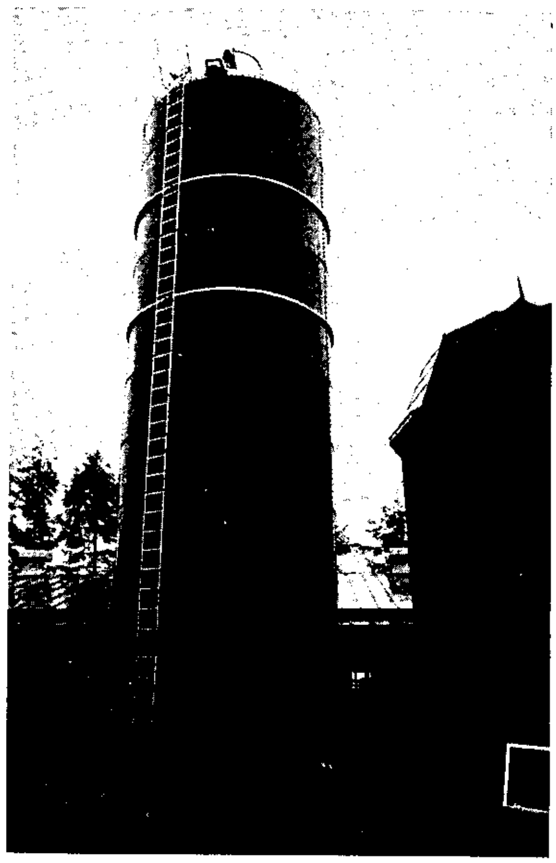


Photo. 3 An application example of **KHN** for enameled silo

Photo. 3 shows a silo made of **KHN** sheets enameled on both sides. Enameled sheet silos are neat in appearance and hermetically sealed, thereby exemplifying one of the most suitable applications of **KHN**.

5 Conclusions

As a result of examining the effects of Ti in steels on their fishscale susceptibility, it was found that very fine coherent TiC particles are most effective hydrogen trap sites and have a great effect in preventing fishscale formation.

By utilizing the above finding, **KHN**, the hot rolled sheets for both-sided enameling, was developed. **KHN** has excellent fishscale suppressiveness and, owing to its C being fixed by Ti, is practically free of sag and pinhole defects. It is also possible to change the strength level of **KHN** according to its applications.

Therefore **KHN** is expected to open a new field of enameled sheets which has been closed to conventional hot rolled sheets and the cold rolled sheets which have thickness restrictions.

Thanks are due to Kawatetsu Metal Industry, Co., Ltd. and Nichiyuu Kouki Co., Ltd. which have kindly made the photograph of the silo available for this paper.

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