KAWASAKI STEEL TECHNICAL REPORT

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An Outline of the Stainless Steel Continuous Annealing and Pickling Line at Chiba Works

Toshio Watanabe, Yoshio Nakazato, Ryuzo Sato, Hirokazu Takita, Masanobu Ochiai, Minoru Hoshino

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A new annealing pickling line has been put on stream at Chiba Works in October 1982. Meeting with the demands of the age, this large-scale line efficiently produces coils of large dimensions, i.e., maximum 8 mm thick and 1 600 mm wide, available from various kinds of stainless steel and high carbon special steel. In this construction careful consideration was given to the thoroughgoing protection of environment. Especially a new method to regenerate HNO3 and HF efficiently was successfully developed by introducing Fe-removing process. This development was commissioned to Kawasaki Steel by Research Development Corporation of Japan (J.R.D.C). This AP line and its auxiliary acid recovery plant, to which the above-mentioned new systems have been introduced, are now in smooth operation.

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The body can be viewed from the next page.

An Outline of the Stainless Steel Continuous **Annealing and Pickling Line at Chiba Works***



Toshio Watanabe Staff Assistant General Manager, Cold Rolling Technology Sec., Chiba Works



Hirokazu Takita Deputy Manager, Cold Rolling Mill Maintenance Sec., Chiba Works



Yoshio Nakazato General Manager, Electrical Steels & Stainless Steels Technology Dept., Steel Technology Division

Masanobu Ochiai

Assistant Manager.

Sec., Chiba Works





Minoru Hoshino Staff Deputy Manager, Technical Coordination Chemical Technology Sec., Chiba Plant, Chemical Division

1 Introduction

Stainless steel production at Kawasaki Steel was all made at Hanshin Works in the past except for the hot rolling process worked at Chiba Works, but as a part of rationalization, changes were made to the production system with only the cold rolling process left remained at Hanshin Works, and all the upstream processes integrated at Chiba Works.

Following the moving of the Steelmaking Division, a new continuous annealing and pickling line was constructed, which began to operate in October 1982. An outline of this new line is reviewed below.

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This AP line and its auxiliary acid recovery plant to which the above-mentioned new systems have been introduced, are now in smooth operation.

2 Construction Principles of Continuous **Annealing and Pickling Line**

This line is mainly aimed at annealing and pickling hot rolled coils of stainless steel to supply them to Hanshin Works and other general users.

To meet the growing demands for stainless steel expected in the coming years, this line is capable of treating large-dimension coils of 8 mm thick max, and 1600 mm wide max. in addition to those of conventional dimensions. It also produces general Ni- and Cr-based steels, various types of alloy steels and high carbon highgrade steels as well as cold rolled finished products for implementing a new cold rolled product manufacturing system.

Concepts of the continuous annealing and pickling line (hereinafter abbreviated to the "AP line") and its features are described.

^{*} Originally published in Kawasaki Steel Giho, 16(1984)2, pp. 109-115

2.1 Layout and Composition of AP Plant

AP plant was constructed as a separate building on the side of the annealing yard at No. 2 cold rolling mill, in order to improve annealing efficiency of ferritic stainless steel using a large-scale batch annealing furnace for carbon steel.

This AP plant has the CB (coil build-up) line, which can build up a coil for the above-mentioned batch annealing, along with the AP line.

Hot coils to be supplied to this AP line are transported by trailers from the hot rolling mill, and products are taken out of the AP line to the product warehouse by trailers. This trailer system is more efficient than the railroad system and can transport coils "just in time", thereby making the former process more effective in the mill design.

2.2 Improvement of Quality Control

Quality of the hot-rolled stainless steel strip can be realized only at the delivery inspection position of the AP line. Since all upstream processes down to the AP process are integrated at Chiba Works, feedback to processes such as steelmaking and hot rolling has become easier and faster than at Hanshin Works in the past, thereby help enhancing accuracy of quality control.

2.3 Reduction in Delivery Time and Reinforcement of Service System

Thanks to the AP plant, the distribution of steel strip became simpler than at Hanshin Works in the past. Moreover, delivery time to users in the Kanto District is reduced and the after-sales service system reinforced.

2.4 Reduction in Annealing Cost

Since ferritic stainless steel is built up to a coil weigh-

ing maximum 42 tons on the CB line and annealed in a large-scale 4-stack batch annealing furnace, its cost can be saved more significantly than at Hanshin Works in the past.

The continuous annealing furnace of the AP line, which anneals austenitic stainless steel, is a unified furnace having a preheating zone to economize on heat, and also preheats combustion air with the exhaust gas. The use of a large quantity of ceramic wool as a heat insulating material for the furnace has lowered heat capacity and shortened the time for starting and stopping the furnace.

The gas used for annealing is the C gas (cokeoven gas) generated at Chiba Works, resulting in further cost reduction than at Hanshin Works where LPG or electricity was used for heating.

2.5 Pollution Control Measures

Chiba works has taken up thoroughgoing pollution control measures to protect the environment, and the AP plant has been made completely pollution-free with full use of new techniques.

In particular, the problem of waste acid disposal at the AP line has been solved by developing a highly-efficient waste acid recovery method using the solvent extraction method to dispose of waste acids from HNO₃ and HF, contrary to the conventional method generally used at this type of equipment where waste acid was simply neutralized and disposed of.

3 Outline of Equipment

Figure 1 shows the schematic diagram of the AP line. The general views of the AP line are shown in Photos 1, 2 and 3.

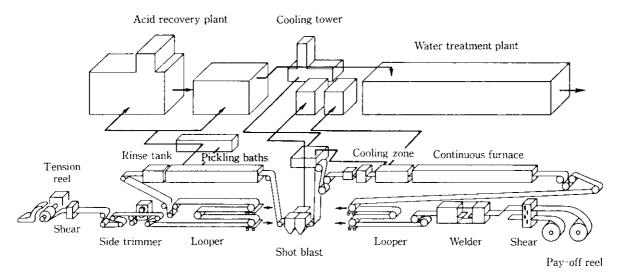


Fig. 1 Schematic diagram of APL

141



Photo 1 General view of APL (Entry section and furnace)

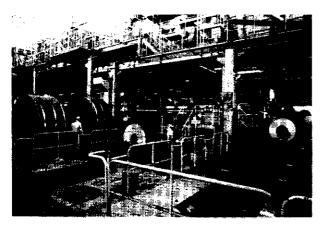


Photo 2 General view of APL (Large size coils at entry section)

3.1 Basic Specifications

3.1.1 AP line

- (1) Steel Strip: Stainless steels of general grade and special grade, and high carbon steel
- (2) Strip Thickness:

(Hot rolled) 3 to 8 mm ($\pm 10\%$) (Cold colled) 0.8 to 6 mm ($\pm 10\%$)

Strip Width: 650 to 1 600 mm

(3) Coil:

 (Entry side weight)
 (Delivery side weight)
 (Delivery side weight)
 (Inner dia.)
 (Outer dia.)
 (Duter dia.)
 (Duter dia.)

 (Duter dia.)
 (Duter dia.)

2 612 mm (#2) Delivery side: 2 134 mm (2193 mm

when including paper)

- (4) Speed: (Entry section) : 60 m/min max. (Center section) : 40 m/min max. (Delivery section): 60 m/min max.
- (5) Production Capacity: 20 000 t/month

3.1.2 CB line

- (1) Steel Strip: Same as at AP line
- (2) Strip Thickness and Width: Same as at AP line
- (3) Coil:
 (Entry side weight) 15 t
 (Delivery side weight) 3 to 42 t
 (Inner dia.) 510, 610 and 760 mm
 (Outer dia.) Entry side : 1 750 mm
 Delivery side: 2 612 mm
- (4) Speed: 100 m/min max.

3.2 Manufacturing Processes

Figure 2 shows the main manufacturing processes. Figures 3 and 4 show arrangement of AP and CB lines.

3.3 Entry Section

The steel coil is transported to a coil skid by the overhead traveling crane and automatically inserted into the pay-off reels. Passing through a leveller, the leading end of strip reaches the double cut shear where off-gage parts and the leading strip are automatically cut-off. The tailing end of the preceding coil and leading end of the succeeding coil at both front and reverse faces, four faces in

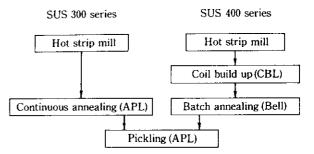


Fig. 2 Annealing and pickling process of stainless steel



Photo 3 General view of APL (center and delivery section)

KAWASAKI STEEL TECHNICAL REPORT

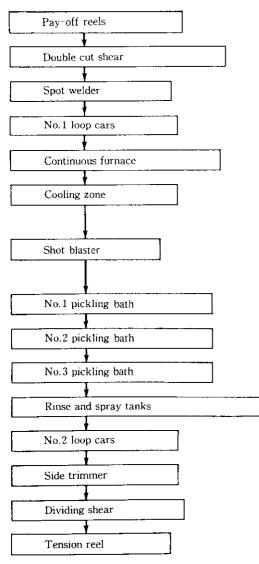


Fig. 3 Arrangement of AP line

total, are simultaneously polished automatically by the surface grinder. Then the two coils are spot-welded.

The tailing end of the preceding coil stops after automatic reduction in speed, and is cut. Then it is automatically moved to the polishing position and awaits the next process.

Punching for welding-point tracking is conducted immediately after spot welding, and notching at the coil end is executed just before the welder.

3.4 Center Section

The coil coming out of No. 1 loop car enters the continuous annealing furnace. Since the SUS 400 series stainless steel has been annealed beforehand at the batch annealing furnace, it passes through the continuous furnace without being heated. On the other hand, the SUS 300 series stainless steel is soaked at the con-



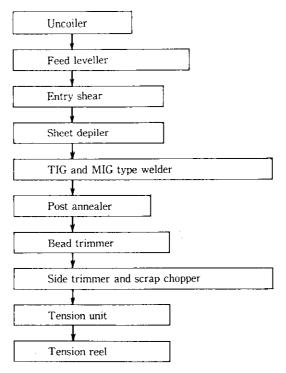


Fig. 4 Arrangement of CB line

tinuous annealing furnace and cooled first by air and then by water, thus completing the annealing process. **Figure 5** shows a typical example of a heating-cooling curve of the SUS 304 series.

The continuous annealing furnace is composed of preheating, heating and soaking, and cooling zones. It is a direct-heating catenary furnace where a coke-oven gas is used as fuel. Ceramic fiber is used for the furnace wall, and this furnace uses material preheating by waste gases and combustion air preheating by a heat exchanger to save energy. Figure 6 shows the overall structure of this furnace, and Table 1 shows its main specifications.

The strip which has been annealed is subjected to two shot blastings to have its surface oxide scale broken and removed.

Shot blasters, whose impellers are driven by DC motors, control momentum of projected shots to properly descale the strip surface and to adjust surface roughness and hardness. **Table 2** shows the specifications of the shot blaster.

The strip which has been shot-blasted enters pickling baths. No. 1 pickling bath is a neutral salt electrolytic bath (Ruthner method), and used only for finish-pickling of cold-rolled strip. No. 2 pickling bath is a sulfuric acid bath. No. 3 bath performs pickling by HNO_3 and HF, or HNO_3 . This combination has been the standard method of pickling stainless steel hot rolled strip since before.

The solutions in the pickling baths circulate between

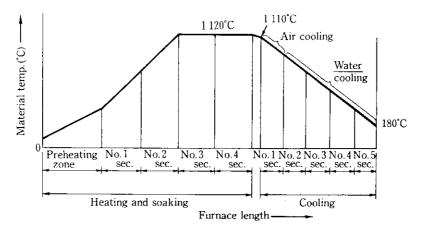


Fig. 5 Heat pattern for SUS 304

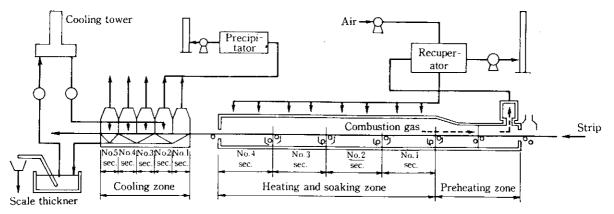


Fig. 6 Schematic diagram of continuous annealing furnace

 Table 1 Specifications of continuous annealing furnace

Item	Specification					
Furnace total length	62.5 m					
Preheating zone	17.5 m					
Heating and soaking zone	45 m					
Cooling zone	17.5 m					
Refractories	Ceramic fibre (Bricks for bottom)					
Fuel	Coke-oven gas					
Maximum furnace temp.	1 250°C					
Maximum burner capacity	13 900 × 10 ³ kcal/Nm ³					
Cooling zone precipitator ca- pacity	1 440 Nm³/min, 0.02 g/Nm³ max					

the pickling baths and the circulation tank at the tank yard while their temperatures are kept at constant levels, to add and discharge constant amounts of acid to and from the system, thereby permitting stabilized acid concentration control.

The strip coming out of the pickling baths is dried by

Table 2 Specifications of s	shot blast	machines
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Item	Specification					
Number of machines	2					
Type	Impeller type					
Number of impellers	2×4					
Shot blasting density	100 kg/m²					
Impeller motor capacity	$2 \times 4 \times 75 \mathrm{kW}$					
Bag filter capacity	2 × 350 Nm³/min, 0.02 g/Nm³ max					

the dryer after passing through the hot rinse bath, and pickling is completed. **Table 3** shows specifications of the pickling baths, and **Fig. 7** shows the schematic diagram of the pickling system.

3.5 Delivery Section

The strip coming out of No. 2 loop car, is edgecut with the side trimmer, has its width and thickness measured, and its surface and reverse side visually inspected at the inspection section. Then it is sheared by the delivery shear, and its defective portion is cut off. Finally it is wound up by the tension reel.

KAWASAKI STEEL TECHNICAL REPORT

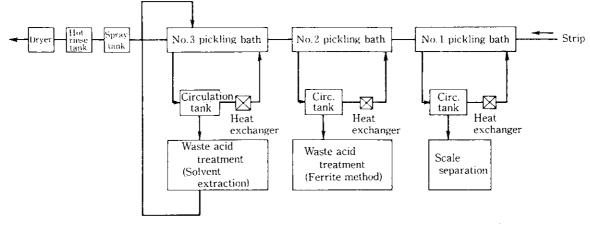


Fig. 7 Schematic diagram of pickling system

Table 3Specifications of pickling baths

Tank No.	Type of bath	pe of bath Solution		Length (m)	
1	Ruthener type electrolytic bath	Na ₂ SO ₄	4 × 90	21	
2	Catenary type dipping bath	H ₂ SO ₄	180	20	
3	Catenary type dipping bath	HNO ₃ +HF or HNO ₃	60	18.5	

3.6 Waste Acid Treatment Plant

Various waste acids discharged from the pickling baths are recycled for the purposes of pollution prevention and recovery of resources such as metal and acids $(HNO_3 \text{ and } HF)$ which are contained in the waste liquid.

Pickling waste liquid in each pickling bath is given independent treatment. Neutral salt waste liquid in No. 1 pickling bath has its scales removed by the centrifuge, and waste water is sent to water treatment equipment, where it is neutralized by calcium chloride to separate its gypsum.

Sulfuric acid waste liquid in No. 2 pickling bath is neutralized by caustic soda and is forced-oxidized by air, thereby being made into ferrite. Sludge is removed by centrifuging and waste water is sent to water treatment equipment where it is neutralized by calcium chloride to separate gypsum.

Waste liquid of HNO₃ and HF in No. 3 pickling bath has its Fe, Ni, and Cr contents and HNO₃ and HF separated and recovered by the solvent extraction method mentioned below. This is an epoch-making energysaving method which efficiently recovers acid by introduction of the Fe-removing process using a solvent.

No. 13 September 1985

3.7 Dust Collection, Fume Cleaning and Water Treatment

Pollution substances other than those mentioned above which are discharged from the AP line are removed by the following equipment to attain thoroughgoing environmental protection.

First at the continuous annealing furnace, low NO_x burners developed by Kawasaki Steel are used to control NO_x quantity at the stack. Scale powder dust generated at the furnace outlet and cooling zone is collected by the wet type dust collector (Rotoclone), and powder dust arising from shot blasting is collected by the bag filter. Scale sludge is given exclusive-use water treatment. Fumes from Nos. 1 and 2 pickling baths are treated by the wet type fume scrubber, and those from No. 3 pickling bath are completely treated by the dry type ammonia catalytic reduction method.

Discharged water generated from the abovementioned respective treatment is collected and made completely pollution-free by water treatment equipment.

3.8 Utilization of Computer

Figure 8 shows the computer system which is used by the AP plant. Production, quality and operation are controlled by the system.

The following shows main functions of each computer:

- (1) Line Computer
 - On-line production control is performed.
- (2) Process Computer

Receiving production specifications from the upperrank line computer, the process computer presets speed, tension and welding conditions, electrolysis conditions, etc., tracks welding-point control, and performs operations including the furnace and pickling conditions, collection of quality data, transmission of actual data and transmission of the set

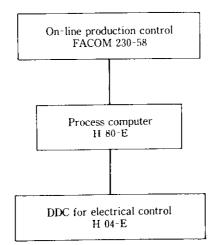


Fig. 8 Computer control system

value to DDC.

(3) Operation-control DDC

This DDC performs input/output automatic operation control and line operation main control (speed, tension, etc.).

These respective functions are smoothly operated and in the completely satisfactory condition.

4 Features of Waste Acid Treatment Plant

The conventional waste acid treatment in this kind of plant was mainly the neutralization method, which generates a large amount of waste. In the present construction, a new waste acid treatment method was developed to attain the reuse of resources and adopt full-scale environmental countermeasures.

Since the pickling waste liquid contains large amounts of metal ions (main elements: Fe, Cr and Ni) and free acids (H_2SO_4 , HNO_3 and HF), the development of an efficient acid recovery method and metal treatment method was necessary when these kinds of waste acid were treated.

The following conditions were set up as the target:

- (1) Effective ingredients shall be recovered as usable elements.
- (2) Materials recovered shall be reused as resources.
- (3) For nitrogen on which regulation is expected to be imposed in the future, its discharge amount shall be

minimized.

(4) The amount of dissolved metallic ions in the waste water shall be made less than the environmental standard value.

As a result, it was decided to obtain ferrite from waste acid in No. 2 pickling bath and to treat mixed waste acids in No. 3 pickling bath using the solvent extraction method.

4.1 Ferrite Treatment Plant

The ferrite treatment method is used for manufacturing spinel-type ferrite¹⁻³⁾ by neutralizing (pH 10 to 12) the waste acid which contained heavy metals in the presence of ferrous iron, and by oxidizing them by forced air under the conditions of a temperature of 70 to 80° C.

The ferrite treatment method was conventionally used for treating a low-concentration waste liquid, and this is the first time that the method is used for treating a high-concentration waste liquid.

The following are reaction formulas of ferrite: Neutralization reaction;

$$x M^{2+} + (3-x)Fe^{2+} + 6OH^{-}$$

 $\longrightarrow M_xFe_{(3-x)}(OH)_6$

Oxidation reaction;

$$M_x Fe_{(3-x)}(OH)_6 + \frac{1}{2}O_2$$

 \longrightarrow M_xFe_(3-x)O₄ + 3H₂O

Table 4 shows plant specifications, and Fig. 9 shows the production process.

4.2 Solvent Extraction Equipment

Mixed waste acids (HNO₃ + HF) generated from No. 3 pickling bath are treated by the solvent extraction method.^{4,10)} This equipment was developed as a research project commissioned to Kawasaki Steel by the Research Development Corporation of Japan (J.R.D.C.), based on the techniques of the Nishimura and Watanabe Extraction Laboratories.¹¹

This equipment was designed to improve the recovery of HNO₃ and HF. As the first stage, Fe is extracted from mixed waste acids by solvent A (alkyl phosphoric acid-based extracting agent), and removed by the fluoride-based separator. The resultant crystals are heated to recover ferrous oxide. At the second stage, metallic

Capacity	Com	position of	waste acid	(g/l)	Treated water (mg/l)				Moisture (%)	
(3/L)	Total acid	Fe ⁺²	Cr	Ni	Fe ⁺³	Total Cr	Cr+6	S.S.	Ferrite sludge	Plaster
2	230	54	12	10	<1.0	<0.1	<0.05	<50 (ppm)	<85	<15

Table 4 Specifications of ferrite plant

KAWASAKI STEEL TECHNICAL REPORT

compound anions are replaced by HCl, then the HNO₃ and HF solution is treated by extraction of HNO₃ and HF using solvent B (neutral phosphate) and water sepa-

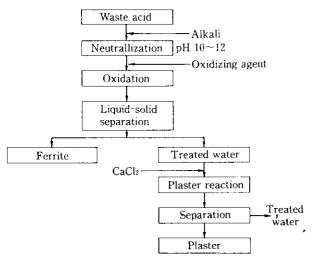


Fig. 9 Block diagram of waste acid treatment plant

ration. Raffinates such as Cr and Ni in the form of hydroxides are recovered as ferrite by the above-mentioned ferrite treatment plant. Ferrous oxide, which is secondly produced in this process, is expected to be of high purity.

Table 5 shows the plant specifications, Fig. 10 the production process and Photo 4 the general view of the equipment.

5 Operation

The subject plant has been smoothly increasing its production since the initial operation in October 1982. Steel types produced include mainly SUS 304 and SUS 430 followed by Mo-bearing alloy steel. It is stably producing steels of specified qualities, including 8-mm thick plates and 1 600-mm wide materials in accordance with the demands.

Waste acid recovery by solvent extraction, featuring the Fe-removing process, is giving satisfactory results as expected, based on some new knowledge obtained as a

Table 5 Specifications of solvent extraction plant

Capacity	Composi	vaste ac)	Composition of recovery acid (g/l)					Yield (%)		
(m ³ /h)	HNO3	HF	Fe	Cr	Ni	HNO3	HF	Fe	Cr	Ni	HNO3	HF
1	156~180	40	28	16	18	>165	>30	<0.5	<15	<16	>95	>90

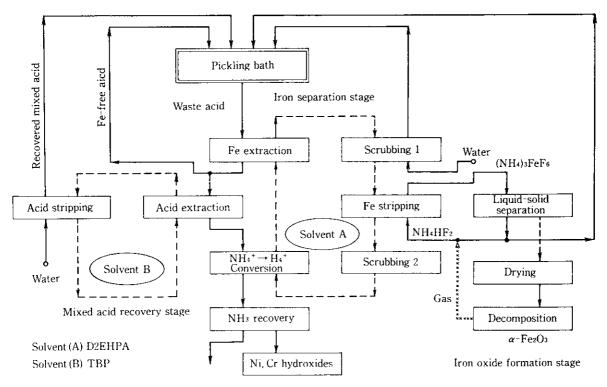


Fig. 10 Block diagram of nitric-hydrofluoric acid recovery plant

No. 13 September 1985

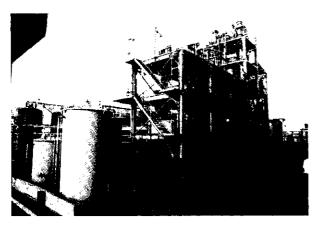


Photo 4 General view of solvent extraction recovery plant

result of research and development efforts.

6 Concluding Remarks

The continuous annealing pickling line for stainless steel hot rolled strip, the line installed at Chiba Works for the first time has been outlined.

This line is aimed at producing all grades of stainless steels including thicker and wider coils meeting the growing demands of the forthcoming years.

On the other hand, new lines in the future naturally must take into consideration thoroughgoing environmental protection. From this viewpoint, the AP line has been provided with drastic countermeasures.

What is particularly significant is that the development of acid recovery featuring Fe-removing of the HNO₃ and HF waste liquid which was unsolved in the past, has now been realized as the research project commissioned to Kawasaki Steel by the Research Development Corporation of Japan, and the new way is opened for the future in treating steel pickling waste liquids.

Kawasaki Steel will use this new AP line to manufacture stainless steel to meet the new needs of stainless steel of higher quality and to promote an effective use of natural resources by full operations of this AP system.

Finally, the authors would like to express their deep appreciation to the Research Development Corporation of Japan for having granted the above-mentioned development project which was indispensable for realizing the AP line, and to many manufacturers for their kind cooperation extended to us during the construction and the operation start-up of the AP line, and further to all other persons who participated in the meaningful project development.

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