Development of Processing Technology for Flat Sheet Products

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1. Introduction

Over the last few decades, the production technology for flat sheet products has developed with the aim of producing products having higher quality, better functionality, and improved productivity. Of the many fruits of such development, this paper focuses first on the manufacture of deep-drawing sheets and high-tensile sheets through continuous annealing. Second, we address the production of highly corrosion-resistant sheets for automotive use through continuous hot-dip galvanizing. Finally, we determine measures to homogenize the coating weight of electrolytic tinplates and to enhance labor productivity.

2. Advances in Continuous Annealing Technology

2.1 Technical development for production of deep-drawing sheets through continuous annealing

In Japan, the commercial production of cold-rolled sheets began in 1940 with the commissioning of a five-stand tandem cold mill in the Tobata Area of Yawata Works of the Nippon Steel Corporation. At that time, batch-type electric furnaces were used for the annealing process, and resulted in as-cold sheets having the desired mechanical properties. With the increasing demand for cold-rolled sheets after WWII, new cold-rolling facilities were built one after the other, but for a long time, batch processing continued to be the principal method of annealing, and it took a long time for the realization of commercial uses of continuous annealing to enable higher productivity, homogeneous product quality, shorter lead time, etc.

In 1959, the first continuous annealing line in Japan was constructed at Hirohata Works, and this was followed by the construction of many others. However, all of those lines were dedicated to the production of tinplate stock of hard grades that did not require suppressed-aging properties because while the carbon solute in ferrite precipitated as cementite during cooling by batch annealing, it remained in supersaturation after cooling by continuous annealing. This was due to the higher cooling rate when compared to batch annealing. As a result, continuously annealed sheets were hard and exhibited aging properties.

Meanwhile, there was a growing demand for cold-rolled sheets for deep drawing use mainly from the automotive and electric appliance industries, which called for the establishment of technology to enable their production through continuous annealing. In light of this, in 1968, Nippon Steel began fundamental studies for the production of deep drawing sheets by continuous annealing.

The intention of the studies performed by Nippon Steel was to control the steel chemistry adequately through the steel making processes and to set the cooling temperature of hot rolling to be up to about 700°C, so that AlN, FeC, etc. would precipitate in coarse grains before annealing. This would decrease both the fine precipitates that hinder the crystal growth during annealing and the solute elements that adversely affect crystal growth in the [111] direction. In addition, the application of over-aging treatment (maintaining the strip temperature at 400 to 450°C after heating, soaking and rapidly cooling) to the annealing process made it possible to have supersaturated solute carbon precipitate rapidly in the form of cementite, and to obtain suppressed-aging properties. Nippon Steel was the first to successfully commercialize the above process, and in June 1972, they accordingly commissioned the No.1 Continuous Annealing and Processing Line (C.A.P.L.) at Kimitusu Works.

Kimitsu No.1 C.A.P.L. integrated five processes (from electrolytic cleaning to recoiling) and had a heat treatment furnace for over-aging treatment in the annealing section; this epoch-making processing line attracted widespread attention because it enabled the manufacture of steel sheets having excellent material homogeneity, surface quality, and shape at lower costs and in a shorter time than what could be realized by employing conventional batch processing. Another C.A.P.L. was then commissioned at Yawata Works (Yawata No.1 C.A.P.L.) in February 1979, and this line produced products ranging from cold-rolled sheets for general working use to entirely non-aging sheets for ultra-deep drawing use. All of these had the same quality as what could be obtained through conventional batch annealing.

2.2 Development of accelerated cooling method

For the primary cooling of the strip, both Kimitsu No.1 C.A.P.L. and Yawata No.1 C.A.P.L. adopted the gas-jet cooling method whereby the furnace atmosphere gas was cooled and blown to the strip surfaces. The cooling rate realized using this method was roughly 10°C/s, but for this cooling rate, solute carbon precipitated at grain boundaries, the distance between the precipitates was large, and as a result, over-aging treatment took a long time. On the other hand, another continuous annealing process developed by another company used water quenching for the primary cooling. With this method, the cooling rate was about 1,000°C/s, at which rate carbides precipitated in fine particles inside the crystal grains and at their boundaries, making the distance between the precipitates smaller, and reducing the over-aging time, although the figures of elongation, n-value, etc. tended to be lower.

To solve the above problem, in the early 1980s, Nippon Steel developed a new cooling method which was called the Accelerated Cooling (AcC) process (see Fig. 1). With this method, the strip was cooled by blasts of air-water mixture sprayed from cooling nozzles,
each having a water header and a gas header. The cooling rate was approximately 100°C/s, and the rate and the final temperature of cooling were both controllable by changing parameters such as the amount of water and gas and the number of headers. This method made it possible to shorten the time for over-aging treatment and to obtain the prescribed material properties.

Meanwhile, the demand for high-tensile sheets began to increase from the second half of the 1970s to satisfy the needs for lighter car bodies. As a result, the high cooling rate and temperature control capacity of the AcC process made it possible to efficiently produce high-tensile sheets of the solid-solution hardening and the precipitation hardening steels, as well as those of the steels developed by transformation strengthening, which have strengths of 1,180 MPa. The AcC was applied to No.1 C.A.P.L. of Nagoya Works, which was commissioned in July 1982, and to H-C.A.P.L. of Hirohata Works, which started up in August the same year, becoming the core of Nippon Steel’s continuous annealing technology.

3.2 Development and commercial production of heavy-coating galvannealed sheets for car body use

Ordinary galvanized (GI) sheets have coating layers of soft pure zinc. As a result, under press forming work, the coefficient of friction with dies increases, and the influx of material to the space between the dies is restricted, making the formation of complex shapes of car parts difficult. Another problem with GI sheets arose because zinc corrodes rapidly, and therefore when the paint coating is damaged, the paint layer forms blisters, which spoils the appearance. To solve these problems, GA sheets were manufactured by heating the galvanized strip (alloying treatment) immediately after the coating process. Nippon Steel developed the electromagnetic pump process and the roll coating process for one-sided galvanizing, and began to produce them at Yawata and Nagoya Works.

In the mid-1980s, the Nordic Code then specified that there should be “no perforation corrosion for six years and no surface corrosion for three years”, making it necessary to use two-sided galvanized sheets for better corrosion resistance. Subsequently, in the second half of the 1980s, North American carmakers specified another corrosion resistance target of “no perforation corrosion for ten years and no surface corrosion for five years”. Since then, steelmakers have struggled to develop and supply corrosion-resistant sheets capable of meeting the revised target. Eventually, heavy-coating galvannealed (GA) sheets that are excellent in corrosion resistance, weldability, and press formability became dominant in Japan.
carmakers, in addition to good corrosion resistance due to the alloy coating layers.

At first, heavy coating GA had two coats per side (called AS-E sheets): the undercoat layer, which was thicker than the upper one, enabled long-term corrosion resistance, and the upper coat layer of a high-Fe alloy provided good press formability and paintability. In 1986, Nippon Steel began to produce the AS-E sheets commercially using a two-step method, forming the undercoat layer through a continuous galvanizing line (CGL) and the upper coat layer through an electrolytic galvanizing line (EGL). After modifying a CGL, they then switched to a one-step method in 1988. On one occasion, the production of AS-E attained an annual maximum of 424,500 t, but automobile makers then became concerned about costs, and Nippon Steel subsequently developed a new type of GA sheet that satisfied customer requirements with a single coat per side, and this became the dominant material for car body use.

The reason for using two coats for each side of the AS-E sheets was that the heavy coating of GA did not have both good press formability and adhesion to the base metal. When manufacturing GA by letting Fe be diffused into the Zn coating layers, if the Fe diffusion amount is low (insufficient heating), a large quantity of soft \( \gamma \) phase \((\text{FeZn}_{1-3})\) forms in the outer surface layer, increasing the friction between the coating and forming dies during formation to deteriorate formability. On the contrary, if the Fe diffusion amount is high (excessive heating), a hard, brittle and thick layer of \( \gamma' \) and \( \gamma'' \) phases \((\text{FeZn}_{0.5-0.3} \text{ and FeZn}_{0.1-0.05}, \text{respectively})\) forms between the base metal and the coating, and at pressing formation, this layer easily breaks, causing the zinc coating to flake off. Since the heating time increases with increased coating thickness, when producing heavy coating GA sheets, a very narrow range of operation is ideal to obtain good formability and coating adhesion. Furthermore, the diffusion rate of Fe changes depending on steel chemistry, the Al concentration in the plating bath, and the heating temperature. Therefore, to stably manufacture heavy, single-coat GA sheets which are easily formed by carmakers, (as opposed to the two-coat sheets), it is necessary to minimize fluctuations in the coating weight, and to optimize the alloying conditions.

Since the mid-1980s, Nippon Steel has focused on establishing an optimum method for producing heavy, single-coat GA, and based on the results, Nagoya No.4 CGL was modified in July 1988 and Iwata No.4 CGL in May 1991, followed by No.1 CGL of Unigal, Brazil, in April 2001 (No.2 CGL in May 2011), and No.1 CGL of BNA, China, in April 2005 (No.3 CGL in February 2010). Other CGLs are expected to begin operating in Mexico and Thailand. Nippon Steel also expanded its own GA production capacity in Japan, and prepared itself for increasing demands of high-functionality and high-strength sheets that are necessary to improve the fuel economy and collision safety of light-weight car bodies by commissioning the Continuous Galvanizing Annealing and Processing Line (GAPL) of Iwata in April 2002, No.5 CGL of Kimitsu in June 2006, New No.2 CGL of Nagoya in September 2006, and No.2 CGL of Hirohata in December 2006.

3.4 Future Prospects

The social awareness of the need to decrease CO\(_2\) emissions to conserve global environment is expected to rapidly increase. In response, our aim is to develop and supply new products that have higher functionality and strength, and which will enable lighter car bodies and establish high-efficiency production with a minimum amount of waste and loss of materials by continuing to enhance our manufacturing expertise. The alloying elements added to high-strength steels often interfere with the workability with the zinc bath and the alloying of the coating layers. Other problems remain unsolved: for example, various restrictions were imposed on the heat schedule of a CGL consists of many small lots of products having different sizes and material specifications, depending on the final application of their users, and these lots must be continuously processed without interruption. Excellent appearance suitable for exposed car body use is realized only through integrated manufacture and quality control extending from steelmaking to hot and cold rolling. The GA sheets are products of CGL processing and a delicate integration of base metal prepared through many closely linked upstream processes and baking of quality in the galvanizing process, in accordance with the material conditions of the base metal.

When embarking upon overseas production, Nippon Steel began by embarking on joint ventures with local partners, and after the plant facilities were constructed, transferred integrated production technology to the partners and jointly fostered it with them. Accordingly, No.1 CGL of I/N Kote began operations in the U.S.A. in March 1991, followed by No.1 CGL of Unigal, Brazil, in April 2001 (No.2 CGL in May 2011), and No.1 CGL of BNA, China, in April 2005 (No.3 CGL in February 2010). Other CGLs are expected to begin operating in Mexico and Thailand. Nippon Steel also expanded its own GA production capacity in Japan, and prepared itself for increasing demands of high-functionality and high-strength sheets that are necessary to improve the fuel economy and collision safety of light-weight car bodies by commissioning the Continuous Galvanizing Annealing and Processing Line (GAPL) of Iwata in April 2002, No.5 CGL of Kimitsu in June 2006, New No.2 CGL of Nagoya in September 2006, and No.2 CGL of Hirohata in December 2006.

4. Advance in Production Technology for Tinplates

4.1 Use of insoluble anodes only for electrolytic tinning line

Electrolytic tinplates, which are a kind of surface-treated steel sheet, have been long used as the material for containers. Conventionally, cast tin anodes were used in the electroplating process to
produce tinplates: tin in the anodes are electrolytically dissolved and supplied to the base metal surfaces. However, this method has some problems in the product quality and equipment operation (which is explained later), and the long term dream of persons related to tinplate production was to replace all of the anodes of an electrolytic tinning line (ETL) with insoluble ones.

After years of research and development, Nippon Steel developed a method for chemically dissolving tin and supplying it in the form of ions and other related elementary technologies. Based on these technologies, they established a technology for the all-insoluble-anode ETL, and was first to apply it to commercial production (see Fig. 2)\(^{(4)}\). This section outlines the developed technology.

The problems with soluble anodes are as follows:

(i) The replacement of consumed tin anodes with new ones is labor-intensive.

(ii) Tin anodes cannot be spent until they are completely depleted, which implies a waste of expenses incurred to form them by casting.

(iii) As tin anodes wear out, they change shape, requiring manual position adjustment. For this reason, it is difficult to shorten the anode-cathode (strip) distance to save power.

(iv) Since individual tin anodes wear out unevenly, the anode-cathode distance becomes uneven, leading to inhomogeneous coating thickness in the width direction.

(v) Because anode efficiency (tin dissolution) is higher than cathode efficiency (tin deposition on base metal surfaces), the tin ions accumulate in the electrolyte, making it necessary to discharge the electrolyte partially (liquid loss) and dilute it with fresh liquid at regular intervals.

(vi) The edge overcoat is inevitable, which means that some of the tin is wasted. (To allow the anode to easily change work, it is not possible to install edge masks to prevent edge overcoat.) Insoluble anodes as used in electrolytic galvanizing, and tin-free steel lines can solve all of these problems. The reason for the extended use of soluble tin anodes for ETLs was that the only industrially applicable method of dissolving tin was the electrolytic ionizing method.

### 4.2 Development of tin ion supplying method

Whereas with conventional electrolytic tinning involving soluble tin anodes, the anodes serve as the supply sources of tin ions with insoluble anodes. In contrast, they cannot be considered as the supply sources, and therefore, it is necessary to supply them from outside of the system. However, tin is chemically stable and does not dissolve much under most conditions.

The chemical dissolution of metallic tin in a plating liquid is expressed by the following formula:

\[
Sn + 1/2O_2 + 2H^+ \rightarrow Sn^{2+} + H_2O
\]

The rate of chemical dissolution of metallic tin depends on the supply of oxygen solute in the electrolyte and the rate of its diffusion. Therefore, the dissolution rate is very low if tin is simply dipped into it. It follows that to raise the dissolution rate to an industrially useful level, it is necessary to reduce the thickness of diffusion zones, maintain a high concentration of solute oxygen, and secure a sufficient area of reaction surfaces. The following measures were taken to solve the problem:

(i) Use of a fluidized bed for tin dissolution;

(ii) Increasing the concentration of solute oxygen in the fluidized bed by applying high pressure and injecting oxygen; and

(iii) Forming metallic tin into small grains to increase the reaction surface area.

### 4.3 Dissolution of tin grains in fluidized bed

The amount of solute oxygen consumed by the dissolution of tin according to Equation (1) in a fractional height \(dz\) of a fluidized bed can be expressed as follows:

\[
L \cdot dC = -kf \cdot a \cdot (1 - \epsilon) \cdot (C - C^*) \cdot A \cdot dZ
\]

where, \(C\) is the solute oxygen concentration in the liquid in the fluidized bed, \(C^*\) is the solute oxygen concentration at the solid-liquid interface, \(k_f\) is the mass transfer coefficient in the fluidized bed, \(a\) is the specific surface area of tin grains, \(L\) is the liquid flow rate, \(\epsilon\) is the void ratio of the fluidized bed, \(A\) is the sectional area of the fluidized bed, and \(Z\) is the height of the fluidized bed. Assuming that the flow in the fluidized bed is a piston flow, that \(C^*\) is negligibly small compared with \(C\), and from the integration of Equation (2), the oxygen consumption due to tin dissolution, or the dissolution rate of tin, is given by the following equation:

\[
G = C_0 \cdot L \cdot \left[1 - \exp\left(-\frac{V}{L} \cdot k_f \cdot a \cdot (1 - \epsilon)\right)\right]
\]

where, \(G\) is the dissolution rate of tin in the fluidized bed, \(C_0\) is the solute oxygen concentration at the entry to the fluidized bed, and \(V\) is the effective volume of the fluidized bed. As seen in Fig. 3, the
measured dissolution rate agreed well with Equation (3).

4.4 Control of tin dissolution rate

Fig. 4 shows the outlines of the fluidized bed system used to dissolve metallic tin. As seen in Fig. 5, with this method, the dissolution rate of tin can be accurately controlled over a wide range by changing the rate of oxygen injection into the fluidized bed.

4.5 Related Elementary Technologies

(i) Tin granulation
Metals tin is formed into small grains by melting it and having it drip through a perforated plate into water.

(ii) On-line analysis of tin ion concentration
A system for the on-line analysis of tin ion concentration was developed applying X-ray fluorescence spectrometry.

(iii) Selection of anode materials and improvement
Titanium and platinum were selected as the materials of the anodes, and their service life was extended by modifying the method of platinum coating.

(iv) Removal of iron ions
By using only insoluble anodes, the electrolyte became confined to within a closed system, which led to an accumulation of iron ions. This was solved by applying an ion exchange process that was developed to remove them from the electrolyte.

(v) Recovery of metallic tin from tin sludge
Tin sludge SnO$_2$ forms in the electrolyte as a result of oxidation of tin ions Sn$^{2+}$, and settles at the bottom of the tanks. Due to the developed all-insoluble anode method, more tin sludge is generated than is the case with the conventional soluble anode method because of nascent oxygen that is generated at the anode surfaces and solute oxygen from the fluidized bed. A system was constructed to recover metallic tin from the sludge by baking and reducing it with hydrogen.

4.6 Results of all-insoluble anode operation

The developed technology presented above made it possible to produce electrolytic tinplates using only insoluble anodes (see Fig. 6), solving all the past problems$^{5,6}$.

(i) Improvement in product quality

Fig. 7 compares the coating thickness distribution in the width direction of tinplates manufactured by both the conventional and developed methods. Resulting from the all-insoluble anode operation and provision of edge masks, very homogeneous transverse thickness distribution was obtained. Therefore, the welding work was significantly improved at car manufacturing plants.

(ii) Improvement in labor productivity

The all-insoluble anode operation rendered the anode change and position adjustment work as unnecessary and thus greatly reduced labor load. In addition, anode casting was no longer required. As a result, the number of operators was significantly decreased enabling significant improvement in labor productivity.
4.7 Future prospects

The all-insoluble anode system for ETLs that was first developed worldwide by Nippon Steel has expanded its applications in Japan and at overseas-based joint venture companies. In addition, the system has found applications at several overseas steelmakers through license, and many others are considering its introduction, which confirms the industrial value of the technology. New types of tinplate products that make use of the advantages of this epoch-making technology have been developed and marketed.

From the viewpoint of environmental protection, thinner gauges and lighter coating weights will be required for container materials, and the advantages of the insoluble anode method will be more significant.

5. Conclusion

We have presented information pertaining to Nippon Steel’s technical development in the field of strip processing, which focused mainly on continuous processing (in the general sense of the word), and was aimed both at transversally and longitudinally homogeneous product quality and high productivity. To continue producing high-quality products economically and stably, we are committed to remaining a world leader by taking approaches such as the enhancement of equipment technology which makes use of rapidly advancing computer and measurement technologies, and the development of software technology that will uniformly distribute the expertise of seasoned operators among all of our team members through advanced application of the latest information technology.

References

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