NKK has developed a wide variety of state-of-the-art flat-rolled products in response to demands from both domestic and overseas customers. This paper introduces typical new products for use in automobiles, electric appliances, can making, and enameling that were developed by NKK in the last decade based on its continuous annealing technology.

1. Introduction

A quarter of a century has passed since NKK started its first-in-the-world CAL (Continuous Annealing Line) for sheet-gauge production. During the subsequent period, the Japanese automobile companies showed remarkable growth and advancement, and also established overseas production plants. NKK responded to the needs of the Japanese automobile companies by providing an increasing amount of sheet steel and also by upgrading the quality. Since the 1990’s, in particular, there has been an increasing social requirement for automobiles to be designed based on global views of energy saving, environmental protection, and resource recycling, in line with the North American CAFE (Corporate Average Fuel Economy) regulation. The demand for structural members designed for passenger protection in case of collisions and other accidents has also been strong. NKK has endeavored to develop technologies for automotive materials based on the concept of “simultaneous engineering,” where all the activities for structural design, materials engineering, and production engineering are harmoniously carried out in parallel. As a result, NKK has successfully developed unique products for (1) body panels, (2) chassis and undercarriage parts, (3) safety parts and reinforcements, and (4) transmission parts. In addition, NKK developed unique technologies for automobile production. These include technologies for accurately forming high-strength steel sheets; for evaluating difficulties in forming steel sheets by CAE and selecting the most appropriate type of steel sheet for a particular application; for joining formed parts; and for evaluating the crashworthiness of automotive parts.

Since the latter half of the 1980’s, NKK has also endeavored to develop new business fields for sheet steel by giving them new functionality. NKK successfully commercialized advanced steel sheet products such as non-oriented electrical steel sheets and high-Ni Invar alloy sheets. Further, a number of unique products were developed in response to the needs of energy saving, particularly since the 1990’s. For example in the field of non-oriented electrical steel sheets, NKK developed the technology to mass-produce 6.5%Si steel sheets (NK Super Core) using CVD (Chemical Vapor Deposition) technology. This world first product opened the way to new applications such as high-frequency chokes and high-frequency transformers. For JIS-grade electrical steel sheets, NKK developed NK-B Core, a low-loss, high-induction type product that is superior to conventional products. NK-B Core has been used for the motor cores of EHV (Electric and Hybrid Vehicles). NKK also established an integrated production system for 36%Ni Invar alloy sheets, which are used as a shadow mask material for fine-pitch color display tubes, along with the technologies to achieve good photo-etching and magnetic-shielding properties.

Other major types of steel sheets include those used for can making and enameling. In the can-making industry, traditional cans formed by the DI (Draw & Ironing) process have increasingly been replaced since the 1990’s by the ones formed by the stretch-draw process using PET-film-laminated steel sheets. This change has rationalized the can-making process and made steel cans more advantageous in the competition against aluminum cans, as well as in reducing environmental loads. Against this background, NKK established the technology for integrated production of can-making steel sheets, based on an advanced technology to suppress inclusions originating in the steel-making process. For enameling steel sheets, NKK
has promoted the development of technologies for stable production and quality improvement of high-oxygen steel as a replacement for rimmed steel since the 1990’s, after establishing the relevant continuous casting technology in the 1980’s. As a result, NKK has maintained a leading position in the field of enameling sheet, as exemplified by the successful development of chromium-bearing, high-oxygen steel for producing steel sheets for direct-firing enameling.

This paper presents the technologies developed by NKK in the 1990’s for producing various steel sheets that are featured by strength and flexibility. In essence, these technologies originate from the continuous annealing technology firmly established by NKK in the preceding decades.

2. NKK’s steel sheets originating from continuous annealing technology

In 1972, NKK developed the prototype for a revolutionary, world-leading, NKK-CAL (Continuous Annealing Line) for steel sheet production based on operating experience from No.1 CAL in Fukuyama Works. The full NKK-CAL was commissioned in 1976 as No.2 CAL. This line has drastically trimmed the time required for annealing cold-rolled sheets. It uses a unique heat treatment method including a function for water quenching the steel strip that permits the production of various high-strength cold-rolled sheets, hitherto not possible by conventional batch annealing\(^1\).

NKK commissioned No.3 CAL in 1987 and No.4 CAL in 1993. In total, 18 NKK-CAL plants have been commissioned in the world to date, an indication of the high esteem for this technology both at home and abroad. While expanding the production capacity of the NKK-CAL, NKK developed a new direct-firing heating method that uses a reducing flame, and a new roll-quenching method\(^1\).

The history of the diversification of NKK’s steel sheet production since the NKK-CAL was commercialized is schematically shown in Fig.1.

Combined with secondary refining technology, which significantly contributed to progress in the 1980’s, the continuous annealing technology with its ability to anneal steel sheets at temperatures exceeding 800°C, enabled ultra-low-carbon IF (Interstitial Free) steels with high recrystallization temperatures to be extensively used as general-purpose steels. The extensive application of IF steels opened the way to the application of continuous hot-dip galvanized sheets for automobiles.

On the other hand, the water quenching technology in the NKK-CAL permitted the development of 440 MPa grade DP (Dual-Phase) steel sheets, which was followed by commercialization of up to the 1470 MPa grade ultra-high-strength steel. These technologies have played leading

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**Fig.1  History of the development of new cold-rolled products for automotive use based on NKK-CAL**
3. Development and application of high-strength steel sheets for automobiles

Automobile manufacturing has the largest share in the use of steel sheets. NKK has developed various high-strength steel sheets to help reducing the car weight, which is the essential factor for reducing fuel consumption and exhaust gas emissions. Major achievements in the technological development of high-strength hot-rolled and cold-rolled steel sheets and their application technologies are presented below.

3.1 High-strength hot-rolled sheets for automobiles

HSLA (High-Strength Low-Alloy) steel sheet strengthened using precipitation hardening was the main high-strength hot-rolled sheet for automobiles until the 1970’s. However, this material could only be used for automobile parts with limited configurations because of its poor press formability. Utilizing transformation hardening, NKK developed 590 - 780 MPa grade as-rolled-type DP steel sheets (NKHA590L, 780L) in the period of 1981 to 1984\(^2\). These steel sheets have a dual-phase microstructure of ferrite and martensite that is produced by controlling the cooling rate of material on the run-out table at exit side of hot strip mill. There are a number of ways to produce DP steel sheets, and NKK’s products are characterized by their unique production process. Steel with about 1.0% silicon is subjected to a two-step cooling process (rapid cooling - slow cooling - rapid cooling) on the run-out table after hot rolling and then coiled at low temperatures of lower than 200°C. This method stabilizes the formation of microstructure. These DP steel sheets exhibit low yield ratios, excellent work hardenability and good elongation, which make them highly suitable for parts such as wheel disks.

In the 1990’s, NKK intensively researched stretch-flangeability. A series of bainite-based steel sheets (NKHA440-780SF) that have excellent elongation and hole-expansion ratio were commercialized in 1994\(^3\). Until those days, single-phase bainitic steel had had the best hole-expansion ratio. NKK found that it was possible to increase elongation while maintaining the hole-expansion ratio by adding an optimum amount of ferrite to the bainite phase. Based on this finding, the SF series, which principally relied on strengthening by bainite, was developed to improve both the elongation and hole-expansion ratio by providing either a bainitic + ferrite dual-phase structure or a single-phase bainite structure. Generally, carbon deteriorates formability and weldability, while sulfides decrease the hole-expansion ratio. Therefore, the SF series products contain low C, Si and Mn and ultra-low S. For 590 MPa and higher grades, trace elements were added to prevent softening of the HAZ (Heat Affected Zone) by welding. Further, the SF series products have excellent fatigue resistance and were extensively employed for fabricating undercarriage parts such as suspension arms.

In reducing the gauge of undercarriage parts, the effect of pitting corrosion on the life of these parts has been a major concern. For some parts, their corrosion resistance is an important quality factor. Since blowhole defects are created by welding in galvanized steel sheets, high corrosion resistance is required for the substrate. Against this background, NKK developed an offspring of the SF series steel sheet with improved corrosion resistance in 1995. These products were marketed under the same grade name as the SF series, NKHK440-780SF\(^4\). The newly developed steels were produced by complex additions of P-Cu or P-Cu-Mo. These elements concentrate in the rust layers, and make them dense and stable, and consequently improve corrosion resistance. The steels improve 30 to 40% of the maximum corrosion depth on both accelerated corrosion test and atmospheric corrosion test over the general-purpose materials. These newly developed steels also have excellent formability, weldability, paintability, and fatigue resistance, in addition to corrosion resistance. Accordingly, they are used in suspension arms.

A new type of high strength hot-rolled sheet steel began to be used for automotive parts in the early 1990’s that had high elongation obtained by transformation-induced plasticity of retained austenite. NKK also attempted to develop such steels\(^5\). However, the variance in mechanical properties of experimentally produced products was so large that NKK determined not to produce the TRIP steel sheets in the hot-rolling mill. Instead, NKK commercialized 590 and 780 MPa grades cold-rolled TRIP steel sheets. These products are easily produced by applying an austemper treatment in the NKK-CAL RQ (Roll-Quenching) process.

In succession to the development of various high strength hot-rolled sheets in the 1990’s, NKK successfully developed 780 and 980 MPa grade NANO HITEN\(^6\) in 2001. This is an entirely new type of high tensile strength steel in which single phase ferrite is strengthened by nano-sized precipitates\(^6\). In contrast to the conventional transformation hardened high strength hot-rolled sheets, NANO HITEN is produced by adding an optimized ratio
of C, Ti and Mo to form nano-sized TiMoC precipitates. Thus, an ultimate level of precipitation hardening was achieved. Since NANO HITEN does not contain low-temperature transformation phases, its balance between elongation and hole-expansion ratio is superior to that of the highly formable SF series sheets. Because the precipitates have particularly high thermal stability, NANO HITEN exhibits very little variance in mechanical properties compared to the conventional hot-rolled steel sheets, as shown in Fig.2. The low rolling load is another advantage to produce NANO HITEN, which facilitates the manufacture of thinner and wider sheets. In addition, NANO HITEN contains only a small amount of silicon, which makes it suitable for applications as a hot-rolled substrate sheet for hot-dip galvanizing.

3.2 High strength cold-rolled and galvanized steel sheets

Exposed automobile panels need excellent deep drawability and dent resistance. NKK developed a new material design in the 1990’s for a 340 MPa grade bake-hardenable high strength cold-rolled sheet (BH steel sheets) based on ultra-low-carbon steel. This steel was successfully used as a substrate sheet for hot-dip galvannealing, thereby realizing stable operation and quality improvement. Since that time, automobile manufacturers began to demand to export automotive steel sheets from Japan to their overseas plants. However, exporting BH steel sheets was constrained because of their poor aging property. NKK then developed BH steel sheets for exporting that is accommodated to both bake hardenability and anti-aging properties.

IF steel has been extensively used since the latter half of the 1980’s. NKK promoted the development of high-r-value-type high strength cold-rolled sheets for automobile panels that have a strength of over 340 MPa grade. These grades were accomplished through solid-solution hardening of IF steel using adding elements such as Si, Mn, and P. In the first half of the 1990’s, NKK successfully developed 390-440 MPa grade high strength cold-rolled sheets, chiefly by utilizing solid-solution hardening by Mn. This element does not inhibit the adherence of alloy coating layers in hot-dip galvannealing. However, there was a limit to relying on solid-solution hardening for further improving the formability and surface quality of hot-dip galvannealed steel sheets. NKK overcame these difficulties by a threefold increase in the carbon content over conventional IF steel, and bearing Nb as exceeding the atomic equivalence to produce a dispersed precipitation of fine Nb carbides. Thus, in this method, strengthening by grain refinement was effectively combined with strengthening by fine dispersed precipitation. This is how NKK successfully developed a fine-grained high strength steel (SFG-HITEN), which is an entirely new type of steel sheet that excels in deep drawability and is suitable as a substrate for hot-dip galvannealed steel sheets. When galvannealed, the SFG-HITEN exhibits good surface quality required for exposed automobile panels. This is due to the reduced additions of solid-solution-hardening elements such as Si, Mn and P. Further, as shown in Fig.4, SFG HITEN demonstrated the possibility of realizing high r-values that has not been previously achievable by conventional technologies owing to its fine grain structure. SFG-HITEN has various other features, one of which is a low yield ratio,
NKK’s State-of-the-art Flat-rolled Products Developed in the Last Decade

Despite its fine grain structure, the automobile industry has high expectations for SFG-HITEN as a steel sheet that can meet increasing demands for stronger internal structural panels and exposed panels.

In the 1990’s, NKK studied applications of high strength cold-rolled sheets exceeding 590 MPa grade for internal structural parts as side-members and center-pillars in view of improving the crashworthiness of automobiles. In particular, there was a strong desire to use hot-dip galvannealed steel sheets for structural parts under the car body from the viewpoint of corrosion resistance. NKK’s alloy design, with particular emphasis on galvanizability and spot-weldability, led to the development of HSLA type steel sheets and 590 MPa grade DP type low-yield-ratio high strength steel sheets. NKK also endeavored to develop 780 and 980 MPa grade high strength steel sheets, possibly as materials for the TWB (Tailor Weld Blank). In these endeavors, NKK improved the press-formability by increasing the elongation and lowering the yield ratio, and anti-HAZ-softening property by combing the effect of precipitation hardening.

Regarding 780 MPa or higher grade, ultra-high strength cold-rolled sheets, NKK applied the NKK-CAL WQ (Water-Quenching) process to obtain stable quench hardening effect at low alloy contents. Thus, NKK commercialized steel sheets up to 1470 MPa grade by the first half of the 1990’s. Ultra-high strength steel is used for safety enhancement parts such as bumper-reinforcement and door impact beams. It is also used for roll-forming and tubing parts. Delayed fracture in a corrosive environment was a concern for 1200 MPa or higher grade ultra-high strength steels, but was overcome by an alloy design with low carbon equivalent values and morphology control of the carbides in tempered martensite

In the latter half of the 1990’s, there was an increasing need for applications of ultra-high strength steels to parts with complex shapes. In addition to improved elongation, the suppression of fractures that start from the blank edges in stretch-flange forming became important. In response, NKK developed ultra-high strength steel sheets comparable in stretch-flangeability to 590 MPa grade high strength cold-rolled sheet by reducing the difference in strength between the ferrite and martensite phases in DP steels, which were featured by excellent elongation. To improve the lack of press-forming accuracy resulted from spring-back in high strength steel sheets, NKK controlled the WQ conditions to homogenize the strengths in the longitudinal and transverse directions of coils. NKK also achieved a small variance in strength comparable to that of the 590 MPa grade high strength cold-rolled sheet by the strict composition control at the steelmaking stage and the feed-forward control of factors affecting the strength.

Further, for 980 MPa grade ultra-high strength steel, NKK developed a high elongation and low yield ratio type DP steel sheet for parts mainly formed by stretching, and a super $\lambda$ type steel sheet for parts formed by extreme bending. The super $\lambda$ type steel sheets, in particular, achieved hole-expansion ratios that exceed those of the 440 MPa grade steel sheets. Hence, the super $\lambda$ steel sheets are well suited to mechanical clinching, which was previously applied only to low strength materials such as mild steel and aluminum. This sheet has led to new applications including lightweight seat frames for automobiles.

Fig. 5 shows the $E\lambda$ balance of the newly developed 980 MPa grade ultra-high strength steels.

![Fig. 5 Typical $E\lambda$ balance of newly developed 980 MPa grade cold-rolled ultra-high strength steels](image_url)
3.3 High-carbon steel sheet

High-carbon steel sheets have been extensively used for the transmission parts and other mechanical components in automobiles. Technologies have been developed to manufacture automobile parts such as link gears and drive plates by press-forming of high-carbon cold-rolled steel sheets followed by heat treatment, instead of the conventional casting and forging methods, to reduce the part manufacturing cost. However, the manufacture of gear parts to very high dimensional accuracy requires a method to rectify incorrect shapes caused by anisotropy of steel sheets. Since the latter half of the 1990’s, NKK has developed non-oriented high-carbon cold-rolled steel sheets with very little planar anisotropy but superb formability and hardenability. These products respond to the need to use high-carbon steel sheets to manufacture difficult-to-form and high-precision parts. NKK successfully developed a new highly formable high-carbon steel sheet by introducing a fine dispersion of cementite and controlling the recrystallization texture. This high-carbon steel sheet can be formed by deep drawing into axially symmetrical parts with minimum earing deformation and excellent circularity, as shown in Fig.6.

Fig.6 Appearance of drawn cups made of newly developed S35C and conventional S35C cold-rolled steel sheets

3.4 Evaluation and application technology of high strength steel sheets for automobiles

In the 1990’s, the automobile manufacturers began seriously studying the use of high strength steel sheets to manufacture lighter automobile parts. There were increasing needs to develop production technologies, such as die design, press-forming and welding, in addition to technology for evaluating the crashworthiness of safety parts and reinforcements.

In the beginning of the 1990’s, the hydraulic counter-pressure forming method was a highly regarded press-forming technology for high strength steel sheets. But, it had problems, notably, the low productivity and large sizes of the machines. NKK solved these problems by developing the high-pressure liquid lubrication method, in which press forming is conducted while a high-pressure pump injects fluid into the space between the steel sheet and die-face at the blank holding portion, as shown in Fig.7. This technology effectively prevents breakage and flange wrinkles during press forming of high strength steel sheet by reducing the resistance to the flow of material from the flange portion to the die cavity portion. The method drew much attention because it provides a wide formable range for high strength steel sheets without modifying a press-forming machine itself.

Fig.7 Schematic diagram of the high-pressure liquid lubrication method

The need for stronger steel sheet is inevitable if thinner steel sheets are used to make automobile parts for weight reducing. In 1993, NKK developed a unique device called the “dynamic crash testing machine with constant folding speed” to quantitatively evaluate the ability of light automobile parts to absorb the energy of impacts. This machine has been used to perform detailed studies of the effects of the strength and thickness of steel sheets on energy absorption. One result of these studies is shown in Fig.8. These tests indicated that making automobile parts lighter by increasing the sheet strength increases difficulty as the steel sheets used for forming these parts become thinner.

Fig.8 Effects of thickness and yield strength of steel sheets on crashworthiness (Fave: Average Folding Force)
Together with CAE-based sheet-forming and crashworthiness evaluation technologies, these testing and evaluation technologies were used to develop TWB (Tailor Weld Blank) technology, which was viewed as promising for making parts lighter. NKK embarked on the TWB manufacturing business in 2001, targeting the domestic market.

4. Development of electrical steel sheets to support environmental protection

In 1988, NKK established a system for manufacturing and marketing non-oriented electrical steel sheets that meet the highest JIS quality specification. Since then, social awareness for the environment has been increasing, as exemplified by obligatory recycling of home appliances enforced by the Home Appliances Recycling Law; mandated energy saving for these appliances, as specified in the revision of the Law concerning the Rational Use of Energy; and the development of environmentally friendly hybrid and electric vehicles. NKK developed energy efficient electrical steel sheets against this background. Further, in response to the trend of electric machines toward using higher frequencies, NKK was the first in the world to commercialize 6.5%Si electrical steel sheets.

4.1 Non-oriented electrical steel sheet

In 1988, NKK commissioned a horizontal continuous annealing line (NKK-EFL) in the Fukuyama Works for exclusively manufacturing electrical steel sheets. Since then, the facility has been used to produce a series of non-oriented electrical steel sheets up to the highest JIS grade product (NK E-CORE series). NKK-EFL incorporates quality control technologies, such as the latest furnace control and line tension control, as well as quality assurance technologies such as an on-line continuous core-loss tester and an on-line coating thickness meter. The NK E-CORE series products consist of the EF series (full-processed) and the ES series (semi-processed). Fig. 9 shows the magnetic flux density versus core-loss characteristics of the 0.5 mm thick EF series. NK E-CORE series are highly regarded by customers for their good balance between magnetic flux density and core-loss characteristics, and are extensively employed as core materials for electric motors[16,17].

Further, NKK developed NKBF-CORE and NKBFA-CORE products as high-efficiency motor core materials. NKBF-CORE has outstanding low core-loss and high magnetic flux density, while NKBFA-CORE is a semi-processed product[19]. NKBF-CORE provides low core-loss and high magnetic flux density with low hardness. In order to accommodate these mutually conflicting properties, the steel was highly purified, and the grain size was optimized to substantially reduce the hysteresis-loss. The sulfur content was reduced to an extremely low level because lowering the MnS content was known to have a beneficial effect on the grain growth. Further, surface segregation type elements were added to prevent surface nitriding resulted from the ultra-low sulfur content of the steel. The magnetic flux density versus core-loss characteristics of the 0.5 mm thick BF-CORE and BFA-CORE products are shown in Fig. 9. The BF-CORE and BFA-CORE products achieve substantially higher magnetic flux density and lower core-loss than the JIS EF grade products.

BF-CORE substantially raised motor efficiency. A good example is application of BF-CORE to a motor for driving an EPS (Electric Power Steering) system. Although the EPS system achieves a fuel saving of 3 to 5% compared to a conventional hydraulic power steering system, materials with low hysteresis-loss are desired to suppress the loss of torque that occurs when motors run idle, which affects steering response. Fig. 10 shows the improvement in loss torque achieved by using the BF-CORE in a DC-type EPS motor. The figure shows about a 40% reduction in the loss torque. BF-CORE is also used in motors for driving hybrid and electric vehicles. BF-CORE is looked at with great anticipation as a material for supporting various environmentally friendly technologies.
4.2 High-Si electrical steel sheet

NKK has promoted research and development into mass production technology for 6.5%Si electrical steel sheet, which has minimal high-frequency core-losses and zero magnetostriction. The company successfully developed for the first time in the world a continuous manufacturing technology for 6.5%Si electrical steel sheet employing CVD (Chemical Vapor Deposition). In 1993, a CVD line (NKK-SEL) was commissioned to mass-produce the 6.5%Si electrical steel sheet, which was marketed under the trade name of NK SUPER E CORE. Taking further advantage of the merits of the CVD technology, NKK developed a gradient high-Si steel sheet in which Si content varies in the thickness direction, and marketed it under the trade name of NK SUPER HF CORE.19,20) The Si content gradient in the thickness direction of NK SUPER HF CORE induces a skin-effect that reduces core-losses by 20 to 30% over NK SUPER E CORE at frequencies above 10 kHz.

Fig.11 schematically shows the CVD process employed in the NKK-SEL for producing the 6.5%Si electrical steel sheet. The CVD process heats a cold-rolled 3%Si steel sheet in a non-oxidizing atmosphere while feeding silicon tetrachloride (SiCl₄) to the surface of the steel sheet. Silicon from the SiCl₄ substitutes the iron atoms on the sheet surface and forms Fe₃Si. The steel sheet is then subjected to heat treatment in a non-oxidizing atmosphere to uniformly diffuse the Si from the Fe₃Si into the sheet to obtain the 6.5%Si electrical steel sheet.

NK SUPER-E-CORE is manufactured in two thicknesses, 0.1 mm and 0.05 mm. Table 1 shows the typical magnetic properties. The high frequency core-loss is marvelously small, with the loss at 10 kHz being about half that of a grain-oriented electrical steel sheet, and 40% of that of a non-oriented electrical steel sheet of the same thickness. The magnetostriction, which is a source of noise, is also very small. The magnetostriction is about 1/10 that of a grain-oriented electrical steel sheet, and as low as about 1/80 that of a non-oriented electrical steel sheet.

Today, NK SUPER-E-CORE is used as a low core-loss and low noise material for high frequency applications such as photovoltaic power supplies, uninterruptible power supplies, inverters, and high speed motors.

Table 1  Magnetic properties of NK SUPER E CORE

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Core loss(W/kg)</th>
<th>Magnetostriction (x 10⁻⁶)</th>
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<tbody>
<tr>
<td></td>
<td>W₁₀/₁kHz</td>
<td>W₁/₁₀kHz</td>
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<tr>
<td>0.05</td>
<td>18.8</td>
<td>5.3</td>
</tr>
<tr>
<td>0.10</td>
<td>18.7</td>
<td>8.3</td>
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5. Production and future prospects of steel sheets for CRT

In the 1970’s, NKK was among the first in the world’s steel industry to commercialize aluminum-killed steel sheet for color TV shadow masks. Since the 1980’s with the dawn of the multi-media age, NKK had successfully developed various shadow mask materials such as Invar alloy sheets for use in fine-pitch color display tubes and large-sized color TV tubes. These new products were developed by drawing upon NKK’s time-honored technology for producing high-purity steel, and by effectively employing the most advanced cold-rolling mill and bright annealing facility21). Fig.12 schematically shows various high performance steel sheets and their locations in a CRT, along with newly developed products such as an inner shield with high magnetic shielding properties and a shrink band.
5.1 Aluminum-killed steel sheet for shadow mask

A CRT shadow mask is produced through a series of processes consisting of photo-etching, annealing, press-forming and blackening treatment. For this reason, the steel sheet for producing shadow masks must have extremely high purity and uniformity of mechanical properties. In the early period of producing color TVs, rimmed steel was used for shadow masks. In order to eliminate defects caused by press-forming due to non-uniform elongation, NKK developed a new aluminum-killed steel sheet (NKTV-X) that is structurally uniform and has low yield-point elongation. NKTV-X gained a high reputation because of its excellent properties when used as a press-forming material for shadow masks. Since the 1990’s, NKK has continued further research and development for reducing the required coercive force and for applying continuous annealing to the production of this type of steel sheet.

5.2 Invar alloy sheet for shadow mask

A basic property required of Invar alloy sheets used for producing shadow masks is low thermal expansion. In addition, these sheets need to have various material properties corresponding to the shadow mask production processes. NKK established a high-yield and high-quality integrated production system that covers all of the processes from melting the Invar alloy to production of etching substrate coils. This production system employs a high purity refining technology based on an electric furnace and secondary refining process, a hot strip mill equipped with a high-precision-shape-controlling function, and a large width, high-precision cold-rolling mill (12-rolles reversing mill). Fig.13 is an enlarged photo of an Invar shadow mask. NKK’s product shows no photo-etching defects caused by inclusions, indicating good etchability. Recently, NKK has diversified the product lineup to meet the needs of TV-set maker to include products with high strength and good magnetic shielding for tension masks, and products with extremely low thermal expansion for use in computer displays.

Fig.13 Appearance of fine pitch CRT Invar shadow mask

5.3 Inner shield and shrink band material

Metallic materials for TV parts such as inner shields and shrink bands must provide excellent magnetic shielding against geomagnetism so that electron beams can be targeted with an accuracy in the order of micrometers. NKK promoted development of these materials with particular emphasis on anhysteretic permeability, which is an important magnetic property considering the actual conditions in which TV sets are used. Fig.14 shows the demagnetizing process of metallic parts during the degaussing process after a TV set is energized. During the degaussing process that is done by applying an alternating current of decreasing amplitude, the material exhibits a minor loop due to a bias magnetic field from the influence of geomagnetism. Therefore, the material does not return to the origin of the B-H curve. Instead, the material remains in an unsteady magnetization state depended on the material properties (the point ⑧ in the figure). In order to improve the magnetic shielding of the TV tube from geomagnetism, the material must have enhanced anhysteretic permeability (as expressed by the inclination of the line ①→⑧ in the figure) rather than regular permeability (as expressed by the inclination of the line ①→② in the figure)22). By pursuing this concept, NKK succeeded in commercializing inner shielding sheets with enhanced anhysteretic permeability by optimizing the chemical composition and microstructure of the steel. Other new products successfully developed include high strength steel sheets for shadow mask frames, in which the creep deformation is suppressed by increasing the applied tension, and steel sheets with both high strength and superb magnetic properties for shrink bands.

Fig.14 Schematic diagram showing the demagnetizing process under geomagnetism
Comprehensive design technologies such as computer simulation of their structures and positions in a TV tube must be used to make these newly developed products fully exhibit their magnetic shielding property. All of these technologies were fully applied to the product design.

6. Development of other major steel sheets and expansion of product lineup

6.1 Can-making steel sheet

Since the 1990’s, NKK has promoted the development of can-making steel sheets with the objectives of responding properly to environmental issues, increasing the cost competitiveness against other can-making materials, and creating unique new products.

In response to the environmental concerns, cans made from film-laminated steel sheets are replacing conventional painted cans. The stretch-draw process was developed for making two-piece cans from PET-film-laminated steel sheets. In this process, high gripping pressure is applied on the flange portion to suppress wrinkles, and the material sheet is formed and thinned while being held in tension by the gripping pressure. Steel sheets used for this process must have better resistance to earing deformation than ever before to make the width of the flange uniform. To satisfy this need, NKK conducted crystallographic texture analysis of earing deformation. Crystallographic texture control was used to develop a steel sheet with a built-in capacity to suppress earing deformation. The process of this analysis is shown in Fig.15.

Since the cost of steel sheets accounts for a substantial portion of the total cost of producing steel cans, reduction of the sheet thickness was pursued in order to decrease the consumption of steel. For two-piece cans, the decline in the buckling resistance at the bottom and the decline in necking formability at the neck portion are problems with thinner-gauge sheets, as shown in Table 2. The mechanical properties that need to be improved to solve these two problems are mutually contradicting; therefore, steel sheets were desired to satisfy these two requirements. NKK succeeded in satisfying these two requirements by a mechanical property design that imparted bake-hardenability to the steel sheet while suppressing the work-hardenability. The sheet steel developed is widely used in Japan and abroad as two-piece can material.

Three-piece welded cans with constricted shaped bodies are drawing particular attention because they make quick retort treatment possible and their designs easily catch the eyes of consumers. The steel sheets for three-piece cans need to have both formability to obtain the particular body shape and strength to give the formed body rigidity. NKK developed new steel sheets for constricted shaped cans by optimizing the sheet thickness and material properties. Studies on the material properties and panel strength including FEM analyses on buckling resistance led to the new sheets, which provide both sufficient formability and strength, as shown in Fig.16.
Can-making steel sheets are under fierce competition with other materials such as aluminum and PET. NKK continues its best endeavors for research and development for creating new steels and their applications.

6.2 Enameling steel sheet

Enameling sheets must have formability that is equivalent to other cold-rolled sheets along with good enamellability. Enamellability is evaluated by factors such as enamel adherence and resistance to fish scales, bubbles, black spots, and other surface defects. When the enamel coating is applied by direct firing, the enameling steel sheets must have particularly good enamellability so as not to occur detects, because the cover coating is applied directly onto the sheet without ground coating that provides adherence-promoting agents.

Conventionally, enameling steel sheets for direct firing were manufactured by decarburized annealing of rimmed steel sheets made by ingot casting. In contrast, NKK employed continuous casting, which can more efficiently produce steels that have uniform mechanical properties, and developed an ultra-low-carbon, high-oxygen enameling steel sheet containing about 600 ppm oxygen. The new enameling steel sheets have good enamellability equivalent to the rimmed steel sheets. Today, in NKK all enameling substrates for direct firing are high oxygen steel sheets made by continuous casting. NKK also developed enameling steel sheets for two coat-two firing processing, such as titanium-bearing steel sheets that have excellent deep drawability, and boron-bearing steel sheets that are well suited for light forming, both made by continuous casting. Recently, NKK successfully employed the CAL process for producing chromium-bearing, high-oxygen enameling steel sheets that have excellent formability and enamellability. The CAL process is advantageous in cutting the lead-time for delivering the final products to customers by eliminating otherwise necessary processes and for securing uniform quality. Table 3 lists NKK’s enameling sheet products.

Table 3 NKK’s enameling steel sheet products

<table>
<thead>
<tr>
<th>Enameling type</th>
<th>Press formability</th>
<th>SPCC</th>
<th>SPCD</th>
<th>SPCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct-firing</td>
<td>Cr bearing high oxygen steel</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two coat-two firing</td>
<td>B bearing steel</td>
<td>B decarburized steel</td>
<td>Ti bearing steel</td>
<td></td>
</tr>
</tbody>
</table>

The excellent formability of chromium-bearing, high-oxygen enameling steel sheets was developed by the application of oxide metallurgy for optimizing the morphology of oxide inclusions\(^\text{28}\). Fig.17 compares the oxide morphology of the newly developed steel sheet to that of a conventional high-oxygen enameling steel sheet. The latter contains several \(\mu\)m MnO inclusions in diameter and very fine (Cr, Mn)-O inclusions that have a diameter of several tens nm. These fine oxide inclusions inhibit grain growth. NKK intended to mitigate this effect by making the size of oxide inclusions larger. Chromium was added to the steel to form chromium oxide precipitates at high temperatures. These precipitates act as nuclei for forming larger complex oxides such as (Cr, Mn)-O. Accordingly, the number of fine oxide inclusions becomes smaller than in the conventional steel. The developed steel, even though continuously annealed, possesses formability comparable to that of conventional steel sheet manufactured by decarburized annealing, with excellent enamellability and good resistance against fish scales.

![Fig.17 Morphology of oxide inclusions in Cr-bearing, high-oxygen enameling steel sheet](image)

Improvement of the adherence of enamel on titanium-bearing steel was also an important development theme, and NKK studied improvement methods based on morphology control of the enamel/steel interface\(^\text{29}\). NKK was able to deposit Ni in granular form by optimizing the pickling weight loss during enameling pretreatment and Ni deposition weight. This roughened the enamel/steel interface during the firing stage, which improved the enamel adherence. This has become the standard technique for improving enameling steel.

7. Conclusion

This article introduced the sheet steels that NKK has recently developed. These sheet steels exhibit good property and flexibility for almost all automobile, electric appliance, container and similar applications. NKK’s steel sheet production technology originated from the NKK-CAL technology and has been continuously devel-
oped with a good balance of basic and application technologies. The basic technology relies on the creativity of people engaging in the development, while application technology reflects the requirements of customers. These products have enjoyed excellent reputation both in Japan and abroad. NKK’s time-honored culture for technological development will be transferred to JFE Steel Corporation in April 2003, together with Kawasaki Steel’s culture for technological development. These two cultures will compete in a creative manner and merge to form an even stronger culture at JFE that will lead in the world for technological development for steel sheets.

References