Ni- and Mo-Free Ferritic Stainless Steel with High Corrosion Resistance, JFE443CT†

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Abstract:

High corrosion resistant ferritic stainless steel JFE443CT has been developed. With the increase of Cr content to 21% and the addition of Cu, its corrosion resistance is equivalent to that of SUS304 in the neutral chloride environment. Moreover, without the addition of Ni and Mo, its price is stable even when the price of Ni and Mo soars. JFE443CT has been applied widely as the substitution for SUS304, the price of which is fluctuating severely.

1. Introduction

While stainless steels are available in many grades, SUS304 (18mass%Cr-8mass%Ni ("mass%" is hereinafter described simply as "%")) is the most frequently used grade on account of its excellent corrosion resistance and workability. Indeed, SUS304 grade stainless steels are the main products for stainless steel makers throughout the world. The production of SUS304 is estimated to account for about half the total production of stainless steels. However, SUS304 recently has had the disadvantage of an unstable price. The problem results from the unstable and sharply fluctuating price of Ni, one of the principal raw materials of SUS304. SUS430 (16% Cr), one of the typical ferritic stainless steels produced without Ni, has an inferior corrosion resistance compared with SUS304, and thus is applied to limited applications. To solve these problems, there were previously proposed two new stainless steels for the replacement of SUS304, namely, SUS430J1L (JFE Steel Specification: JFE430CuN, 19%Cr-0.5%Cu-0.4%Nb) and SUS436L (JFE Steel Specification: JFE436LT, 18%Cr-1.2%Mo-0.3%Ti). Neither of these proposed steels, however, serves as an appropriate substitute: the corrosion resistance of the former fails to match that of SUS304, and the latter requires the addition of Mo, an element whose price is rising steeply. Thus, the development of a stainless steel with corrosion resistance equivalent to that of SUS304 without the addition of expensive constituents had been demanded by stainless steel users.

JFE Steel stopped the production of SUS304 in 2004 and has since specialized in the production of Ferritic stainless steels. In 2005, earlier than any other steelmaker in the world, the companydeveloped JFE443CT as an Ni-free, Mo-free high-corrosion-resistance ferritic stainless steel that meets the above-described requirements.

This paper describes details of the development and the properties of the developed steel. Note, also, that this special issue includes reports on several applications of JFE433CT[1]. Please look through these reports for details on examples of application.

2. Background of Development

2.1 Development Targets and Policy

Though corrosion resistance improves when the Cr content increases, productivity and formability both decline. Thus, steps must be taken to suppress the increase in the Cr content. SUS304 is used in many applications and has excellent corrosion resistance in various environments. By suppressing the increase in the Cr content in the development of JFE443CT, JFE Steel sought to develop a substitute for SUS304, for articles

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such as kitchen appliances, building materials, electrical equipment, automobiles, and industrial machines for general indoor and outdoor environments.

In all of these uses, the principle corrosive in the stainless steel is the Cl^- ions (neutral chloride environments). The design target, therefore, is to ensure corrosion resistance high enough to prevent rusting caused by the Cl^- ions that induce corrosion, or at least to minimize any rusting that does occur, in order to preserve a good appearance. The corrosion resistance of SUS304 reaches this target, except in outdoor environments in coastal areas. The corrosion resistance of stainless steel is obtained by a passive film (an amorphous film of several nanometers in thickness, composed of oxides and hydroxides of both Fe and Cr) that forms on the stainless steel surface and protects its substrate. Thus, the above-described corrosion resistance is ensured by the following mechanisms:

(1) A passive film is less apt to be brokenby Cl^- ions.

(2) Even when a passive film is broken, the broken film is rapidly repaired (re-passivation) and the propagation of rust is prevented.

In our present development, we measured the pitting potential (JIS G 0577) and evaluated to what extent the passive film stood against Cl^- ions. Our development target was a pitting potential of the developed steel equivalent to that of SUS304. Furthermore, the Cr content in a passive film increased when SUS304 was subjected to field exposure[2,3], and the pitting potential increased at the same time[3]. Therefore, to assure that the developed steel maintained corrosion resistance equivalent to that of SUS304 for a long time, we aimed at obtainment of the pitting potential to be equivalent to or better than that of SUS304 even after extended exposure.

We also studied how various elements other than Ni and Mo affected (1) and (2). Based on our results, we developed the steel grade reported here by finding and exploiting a synergistic action between high Cr and the added Cu. This synergistic action will be described in the following section.

2.2 Improved Corrosion Resistance via the Synergistic Action of High Cr and Added Cu

The pitting potentials of SUS304 and 20 to 22%Cr-0 to 0.4%Cu-0.3%Ti stainless steels were measured before and after exposure for 1.5 years in a coastal area of Chiba (1 km distant from a revetment) and **Figs. 1**(a) and (b) exhibit respectively each of the measurements. To prepare for measurement of the pitting potentials before the exposure, steps were taken in accordance with JIS G 0577, namely, the test pieces were polished with #600 abrasive paper, passivated using nitric acid, and polished again immediately before the measurement

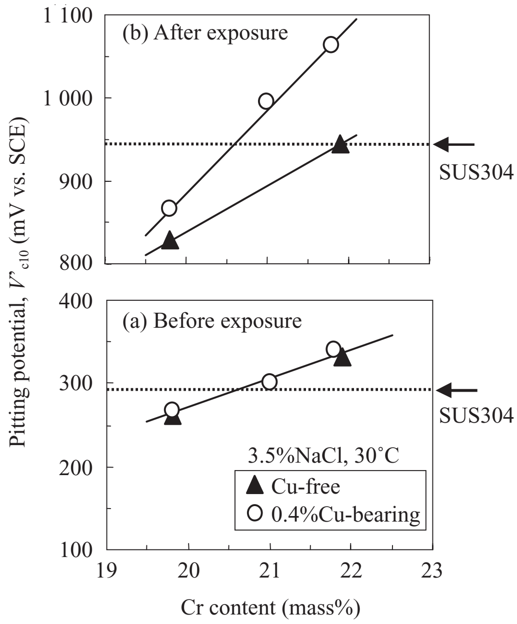

Fig. 1 Effect of Cr content and Cu addition on the pitting potential of 20–22%Cr-0.3%Ti stainless steels before or after 1.5 years field exposure (The pitting potential before and after exposure was measured by polished surface and as-exposed surface, respectively.)

with #600 abrasive paper. For the measurement after the exposure, the test pieces were polished with #600 abrasive paper, cleaned, and exposed. The measurements were taken after cleaning with water, without polishing. Further, rusting was not observed in any of the test pieces after the exposure. In both cases, a potential corresponding to a current density of 10 $\mu A \cdot cm^{-2}$ in an anodic polarization curve was designated as the pitting potential (V'_{c10}). It is certain that a more robust passive film, a film less apt to break by Cl^- ion, will form on a steel with a higher pitting potential: the higher the potential, the more robust the film.

The pitting potentials of 20 to 22%Cr-0 to 0.4%Cu-0.3%Ti stainless steels before the exposure increased with increasing Cr content, and at 21% Cr the pitting corrosion became equivalent to that of SUS304. Scarcely any difference in the pitting potential was found between the Cu-free and Cu-bearing steels. In all of the steel grades, the pitting potentials after the exposure exceeded those measured before the exposure. It is supposed that the passive films acquired a higher corrosion resistance as a result of the exposure. And both before and after the exposure, the pitting potentials rose as more Cr was added. Though added Cu had no effect before the exposure, it increased the pitting potentials of the high-Cr steels. In the Cu-free steels after exposure, the pitting corrosion of the 21% Cr steel was inferior to that of SUS304, while that of the 22% Cr steel became equivalent to that of SUS304. In the 0.4% Cu-bearing steels, in contrast, the pitting corrosion of the 21% Cr steel was superior to that of SUS304. This shows that an increase in the Cr content combined with added Cu is more effective in strengthening a passive film than an increase in the Cr content alone.

For the test pieces after the exposure shown in Fig. 1(b), we investigated the effect of the Cr content and the addition or non-addition of Cu on the Cr ratio (Cr/(Fe + Cr)) in a passive film measured semi-quantitatively by X-ray photoelectron spectroscopy (XPS) and thereby obtained investigation results are shown in **Fig. 2**. The addition of Cu promotes an increase in Cr content, and a higher Cr content leads to a greater increase.

Figure 3 shows the effect of added Cu on the depassivation pH of 21%Cr-0.3%Ti stainless steels and 18%Cr-0.3%Ti stainless steels. The test pieces were immersed in a sulfuric acid aqueous solution with varied pH values, subjected to cathodic reduction at −700 mV for 10 min, and then tested to measure the open-circuit potentials 16 h later. The depassivation pH was regarded as the maximum pH-value at which no potential increase due to re-passivation was observed. It is indicated that lower depassivation pH will readily facilitate re-passivation of the steel. Compared with the 18%Cr-0.3%Ti stainless steels, the depassivation pH of the 21%Cr-0.3%Ti stainless steels decreased remarkably as a result of the added Cu. This shows that a higher Cr content combined with added Cu is also effective in promoting re-passivation. Open-circuit potentials obtained at pH of 2 in the steel grades are shown in **Fig. 4**. The Cu-bearing steels showed nobler potentials than the Cu-free steels. This indicates that an increase in the Cr content combined with added Cu not only promoted re-passivation, but also strengthened the passive film after re-passivation. It is considered that simultaneous increase in Cr content and addition of Cu facilitate concentration of Cu on the steel surface, readily inviting not only re-passivation but also nobler potentials after re-passivation and resultant increase in Cr concentration in the passive film strengthens the film and thereby, corrosion resistance is improved[4)].

Figure 5 shows the rust area ratio of 20%Cr-0.3%Ti stainless steels with varied Cu contents after exposure in a coastal area of Chiba (10 m distant from a revetment) for 1 month. Compared to the Cu-free steels, the rust area ratio is small in the 0.3 to 0.6% Cu-bearing steels. This attests to the good corrosion resistance of these steels. The rust area ratio, on the other hand, increased when 1% or more Cu was added. Fine metal Cu on the order of tens of nanometers precipitated in the steel, providing initiation points for rusting. Based on these results, the amount of Cu added was set at 0.4%.

To investigate how the addition of Cu affected crevice corrosion, samples were examined after being sub-

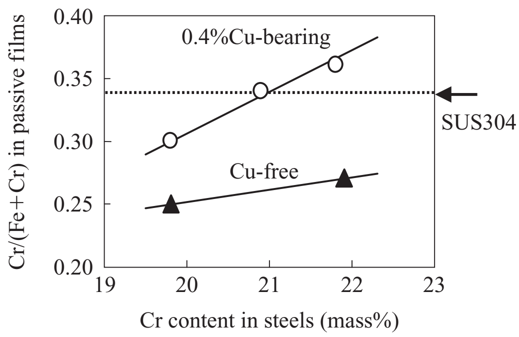

Fig. 2 Effect of Cr content and Cu addition on the ratio of Cr to Fe+Cr in passive films formed on 20–22%Cr-0.3%Ti stainless steels after 1.5 years field exposure

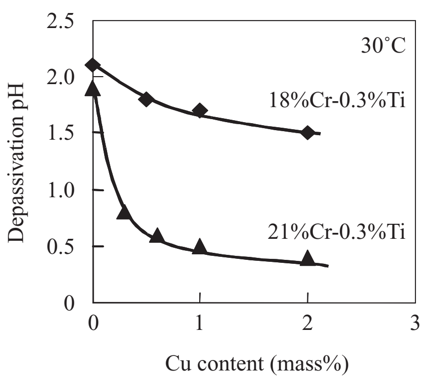

Fig. 3 Effect of Cu addition on the depassivation pH of 18%Cr-0.3%Ti stainless steels and 21%Cr-0.3%Ti stainless steels

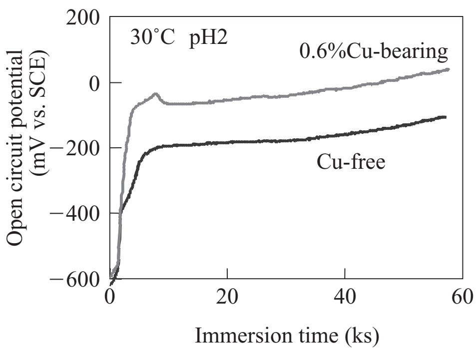

Fig. 4 Effect of Cu addition on the open circuit potential of 21%Cr-0.3%Ti stainless steels

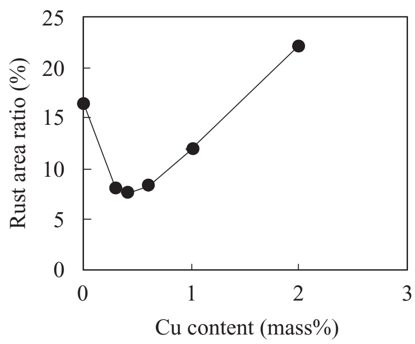

Fig. 5 Influence of Cu content on the rust area ratio of 20%Cr-0.3%Ti stainless steels after one month exposure

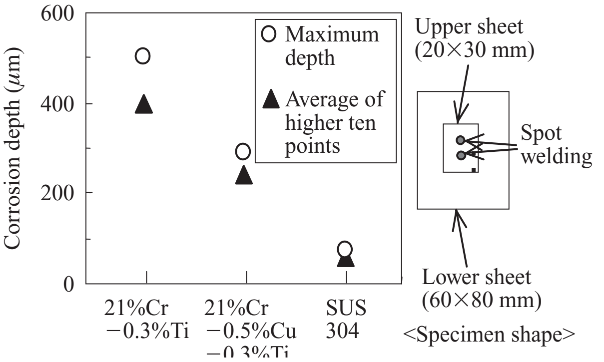

Fig. 6 Effect of Cu addition on the crevice corrosion depth of 21%Cr-0.3%Ti stainless steels after 90 cycles JASO M 609-91 mode cyclic corrosion test (JASO: Japanese Automobile Standards Organization)

jected to 30 cycles of a combined cyclic corrosion test in accordance with JASO M 609-91 (Society of Automotive Engineers of Japan, Inc.) (1 cycle: Salt spray (5% NaCl aqueous solution 35°C, 2 h) → Drying (60°C, relative humidity 20 to 30%, 4 h) → Wetting (50°C, relative humidity 95% or more, 2 h)). **Figure 6** shows the results of the investigation mentioned above. Though inferior to SUS304, the 21%Cr-0.3%Ti stainless steels exhibited a shallower corrosion depth due to the added Cu. Thus, the addition of Cu is also apparently effective in reducing the crevice corrosion.

From the above-described experiment results, a chemical composition of 21%Cr-0.4%Cu was selected as the basic chemical composition for JFE443CT.

2.3 Chemical Composition Designing

The chemical composition of JEF443CT is shown in **Table 1**. In this steel grade, the C and N contents in the steel are reduced as far as possible through refinement (in which the C and N contents are lowered to the order of 1/6 to 1/4 of those of SUS430) in the basic chemical composition of 21%Cr-0.4%Cu in order to maximize the effect of a high Cr content and added Cu. Moreover, by adding 0.3% Ti as a stabilizing element, the C and N remaining in the steel are made harmless as Ti-carbides and Ti-carbides. Thus, the corrosion resistance of the weld zones is ensured and the formability is improved.

Still more, Ti was selected as a stabilizing element in place of Nb as a means of lowering the recrystallization temperature of the steel sheets. This is advantageous, as a lower recrystallization temperature enables manufacture on an ordinary-steel production line (a tandem rolling-continuous annealing and pickling line (CAL)). As a result of this, JFE443CT became available for high-productivity, functional finished products (tandem-CAL-finished products) together with 2B (annealed and pickled products) and BA (bright-annealed products), the general surface finishes for stainless steels. Paint adheres better to functional finished products than to 2B-finished produced, as the former has a higher surface roughness.

Table 1 Chemical composition of JFE443CT

(Typical values, mass%)

Steel grade	C	Cr	Ni	Cu	Ti	Nb	N
JFE443CT	0.01	21	—	0.4	0.3	—	0.01
SUS430	0.04	16	—	—	—	—	0.04
JFE430CuN (SUS430J1L)	0.01	19	—	0.5	—	0.4	0.01
SUS304	0.05	18	8	—	—	—	0.03

2.4 Establishment of Manufacturing Process

High-Cr ferritic stainless steels with Cr concentrations of over 20% are difficult to mass produce for several reasons: a large manufacturing load in refining (the lowering of the C and N), the likely occurrence of surface defects during hot rolling, and the low toughness of the slabs and hot-rolled strips.

JFE Steel has established a manufacturing process for mass producing JFE443CT. Mass production can be achieved with a large-capacity, high exhaust speed SS-VOD (strongly stirred vacuum oxygen decarburization) furnace designed to efficiently remove the impurity elements C and N[5], together with various manufacturing techniques[6] accumulated by JFE Steel in the manufacture of many difficult-to-manufacture, high-Cr ferritic stainless steels such as SUS447J1 (30%Cr-2%Mo) stainless steels and 20%Cr-5%Al stainless steels).

3. Properties of JFE443CT

3.1 Corrosion Resistance

The pitting potentials of JFE443CT and conventional steels are shown in **Fig. 7**. Although SUS430J1L has the highest corrosion resistance of all Mo-free ferritic stainless steels of JIS standard steel grades, the pitting potential of SUS430J1L is lower than that of SUS304 and the

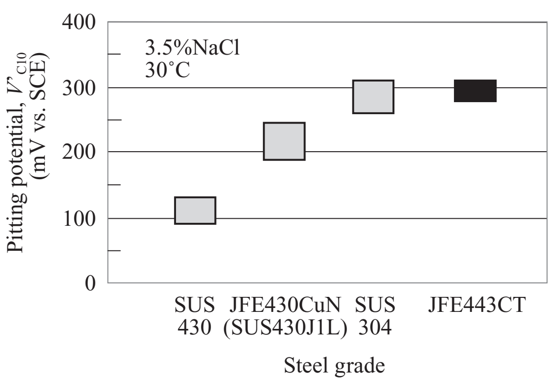

Fig. 7 Pitting potential of JFE443CT

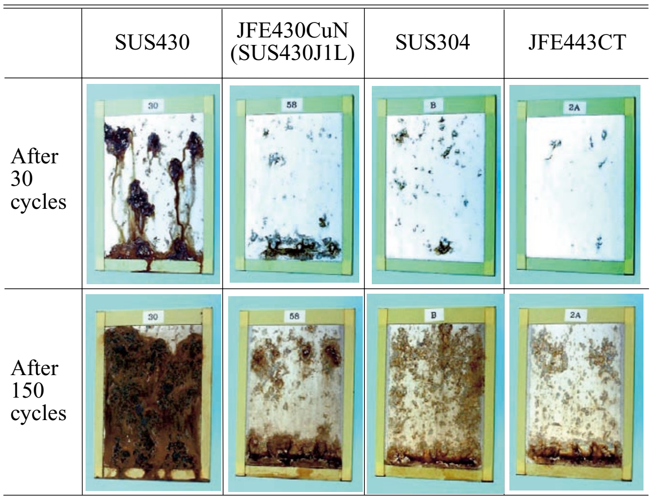

Photo 1 Appearance of various stainless steels after JASO M 609-91 (JASO: Japanese Automobile Standards Organization) mode cyclic corrosion test (#600 polished surface, Sample size: 60 × 80 mm)

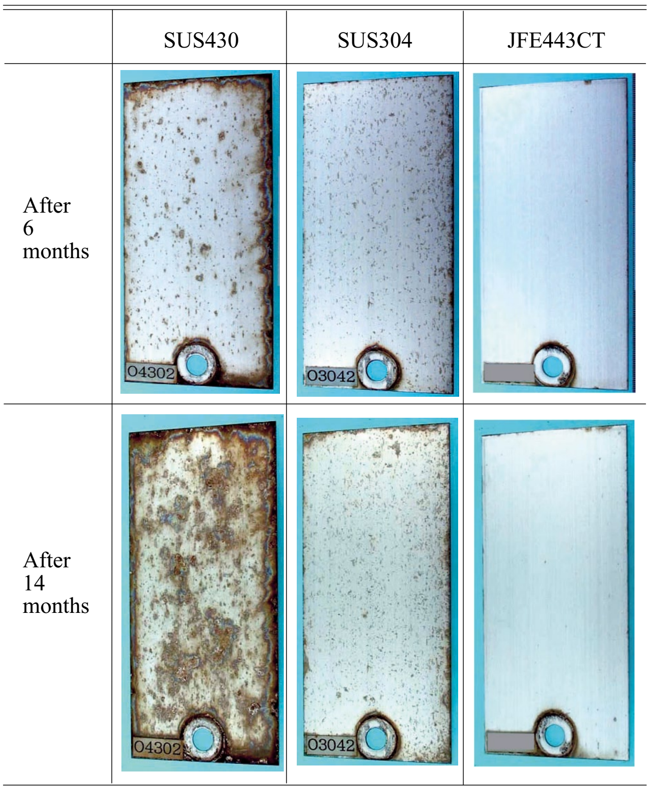

Photo 2 Appearance of JFE443CT, SUS304, and SUS430 after 6 and 14 months filed exposure test in a coastal area at Okinawa (#800 surface finished, Sample size: 75 × 150 mm)

corrosion resistance of SUS430J1L does not match that of SUS304. In contrast to this, the pitting potential of JFE443CT is equivalent to that of SUS304.

Photo 1 shows the test pieces after 30 and 150 cycles of a combined cyclic corrosion test in accordance with JASO M 609-91. SUS430 rusted significantly. Although SUS430J1L showed a smaller rust area ratio than SUS304, the rust in each test piece had propagated more deeply. JFE443CT had less rust than SUS304 and showed good corrosion resistance.

Photo 2 shows the test pieces after a field exposure in a coastal area of Okinawa (20 m distant from a revetment). In SUS304, pitting corrosion is observed on the whole surface. JFE443CT is almost entirely free from rusting and shows better corrosion resistance than SUS304.

As described above, JFE443CT has corrosion resistance equal to or better than that of SUS304 in general indoor and outdoor environments (neutral chloride environments) where the present steel grade is intended for use.

3.2 Mechanical Properties

The mechanical properties of JFE443CT are shown in **Table 2**. The mechanical properties of this steel grade are equivalent to those of SUS430J1L. Compared to SUS430, JFE443CT has high ductility, a high *r*-value (Lankford value), and excellent formability. It also has a markedly better *r*-value compared to SUS304, and very good performance in deep drawability. **Photo 3** shows results of a measurement test of the limiting drawing ratio (LDR), an index of deep drawability. In a pure drawing such as this, JFE443CT can be drawn more deeply than SUS304.

3.3 Physical Properties

The physical properties of JFE443CT are shown in **Table 3**. The physical properties of this steel are equivalent to those of other ferritic stainless steels. This steel

Table 2 Mechanical properties of JFE443CT

(Typical values, Specimen thickness: 0.8 mm)

Steel grade	0.2% proof stress (MPa)	Tesile stress (MPa)	Elongation (%)	Mean *r*-value
JFE443CT	305	483	31	1.3
SUS430	320	490	29	1.0
JFE430CuN (SUS430J1L)	356	496	29	1.3
SUS304	260	645	60	1.0

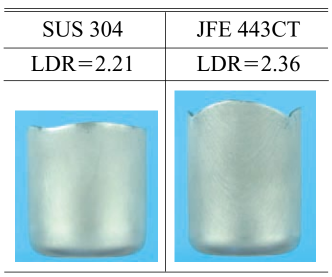

Photo 3 Comparison of Limiting Drawing Ratios between JFE443CT and SUS304 (Thickness of specimen 0.8 mm)

Table 3 Physical properties of JFE443CT

Steel grade	Density (g/cm^3)	Electroc resistivity ($10^{-6}\Omega\cdot cm$)	Magnetism	Specific heat 25°C (J/kg·°C)	Thermal conductivity 100°C (W/m·°C)	Thermal expansion coefficient 20–100°C (10^{-6}/°C)	Young's modulus (GPa)
JFE443CT	7.74	58	Magnetic	440	22.5	10.5	204
SUS430	7.70	60	Magnetic	460	26.1	10.4	200
JFE430CuN (SUS430J1L)	7.73	61	Magnetic	460	24.0	10.5	203
SUS304	7.93	70	Non-magnetic	500	16.2	17.3	193

has magnetic properties and can be used in magnet type utensils and accessories. Compared to SUS304, this steel has a small thermal expansion coefficient and excellent thermal conductivity. As a result, deformation due to welding can often be reduced. JFE443CT has a lower density than SUS304 (7.74 vs. 7.93), hence the former saves weight by 2.5% compared to the latter.

4. Conclusion

JFE443CT has excellent corrosion resistance (equivalent to that of SUS304) in neutral chloride environments. It acquires this property by virtue of its higher Cr content (21%) and added Cu (0.4%). JFE443CT is also less expensive than SUS304, as no Ni or Mo is added. Thus, JFE443CT is most suitable as a substitute for SUS304 in applications where this steel is used in neutral chloride environments.

The price of Ni has risen sharply since 2006, hence the price of SUS304 has been rising as well. The demand for JFE443CT has been increasing rapidly. At present, this steel is widely used as a substitute for SUS304 in kitchen appliances, building materials, household electrical appliances, automobiles, industrial machines, etc. Examples of these applications are shown in **Photo 4**.

JFE443CT is expected to become a world standard for steel as a replacement for SUS304. When realized, this steel grade will save energy and stabilize the supply of stainless steels.

Photo 4 Applications of JFE443CT

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