1. Introduction

Nickel (Ni) is an extremely useful metal which is used in electrical components, plating materials, alloying elements for heat resistant steels, Ni-based superalloys, and other applications. Stainless steel accounts for the largest part of demand for Ni, at approximately 60% of total consumption.

The total world production of stainless steels exceeded 24 million tons in 2005, and austenitic stainless steels occupied approximately 70% of it. The grade of 18%Cr–8%Ni (Type 304) is the most typical austenitic stainless steel. The price of Ni raw materials represents as much as 40–45% of the price of the austenitic stainless steels such as Type 304. Figure 1 shows the variation of the price of Ni raw materials on the London Metal Exchange (LME). The price has been increasing in recent years and at present it remains persistently high at around $32000/ton. It would appear that this high price level is mainly due to the supply-and-demand imbalance, which is attributable to the strong growth of demand for stainless steels in the Asian economies. Also, the effect of the speculation in the Ni market is pointed out.1)

The increase in the price of Ni raw materials causes the increase in that of stainless steels containing Ni. Then, in order to avoid higher material prices, stainless steel users try the use of substitute stainless steels with reduced Ni contents (referred to in the following as “Ni-saving”). They may also shift to other metal materials. In fact, they often tried ferritic stainless steels2) and the austenitic stainless steels in which N or Mn was substituted for Ni3–7) when the price of Ni rose or the consumption of Ni was limited.

Type 304 offers excellent cost performance, formability, and corrosion resistance. This grade is therefore used in a wide range of applications, including household products, building materials, automobile parts, and materials for the chemical and food industries. However, these applications do not require all the properties of Type 304. In other words, other types of stainless steels can be used as substitutes for Type 304 if only the necessary properties for the application are satisfied.

The purpose of this study is Ni-saving of Type 304. In this review, strategies for Ni-saving and the properties of candidate Ni-saving stainless steels are reviewed, and related problems are discussed.

KEY WORDS: nickel saving; austenitic stainless steel; ferritic stainless steel; martensitic stainless steel; duplex stainless steel; manganese; mechanical property; pitting potential; formability.

Fig. 1. The variation of Ni price on LME.
2. Strategies for Ni-saving in Type 304

Stainless steels are classified by chemical composition and microstructure, as shown in the examples in Fig. 2. Classified by composition, stainless steels are divided into the Cr stainless steel, Cr–Ni stainless steel, Cr–Mn–Ni stainless steel, and precipitation-hardening stainless steel. By metallic microstructure, the Cr stainless steel is further classified as martensitic or ferritic stainless steel, while the Cr–Ni stainless steel is classified as austenitic or ferritic-austenitic (in the following, the latter are called “duplex”) stainless steel. The present study investigates Ni-saving strategies for Type 304. Steels in which a one-half reduction in Ni content can be expected in comparison with Type 304 are considered candidates for Ni-saving.

The Cr stainless steels contain virtually no Ni, and are therefore considered Ni-saving. Although the Cr–Ni stainless steels contain Ni, the duplex stainless steels have low Ni contents in comparison with Type 304, and thus are also Ni-saving. The Cr–Mn–Ni stainless steels are austenitic stainless steels in which either part or all of the Ni content is replaced with Mn, N, or other austenite formers.

As outlined above, four alternatives for Ni-saving are possible, these being the martensitic, ferritic, duplex, and Cr–Mn–Ni stainless steels.

3. Features and Problems of Ni-saving Steels

Table 1 shows the typical chemical compositions of the steels identified as candidates for Ni-saving. Tables 2 through 4 show the mechanical properties, cold formability, and pitting potential of the materials, respectively. With the exception of the martensitic stainless steels, cold-rolled steel sheets with a 2B finish were used with all steel types, and measurements conformed to the respective JIS standards. However, these properties were changed in some cases, depending on the manufacturing process, manufacturing conditions, and chemical composition.

3.1. Cr–Ni Stainless Steels

The Cr–Ni stainless steels have excellent ductility and toughness, satisfactory cold formability, including deep drawing and bending forming properties, and excellent weldability. Corrosion resistance, high temperature properties, and low temperature properties are also excellent. The fact that the Cr–Ni stainless steels possess these properties is presumably the reason why this type accounts for approximately 70% of all stainless steels. The representative Cr–Ni material is Type 304.

As problems, the austenitic stainless steels are susceptible to season cracking, which is a type of cracking that occurs in cold-formed products several minutes to several months after processing, stress corrosion cracking (SCC), and rust. The occurrence of these phenomena is influenced not only by the material, but also by processing conditions and the use environment.

Thus, even though the Cr–Ni stainless steels possess excellent properties as stainless steel and are widely and generally used, care is required as accidents are possible if use is not based on correct knowledge.

3.2. Martensitic Stainless Steels

Martensitic stainless steels are used in applications which require high strength and high hardness. Main applications include cutlery, turbine blades, wear-resistant parts, shafts, valves, and bearings.

Table 2 shows mechanical properties after quenching and tempering. The mechanical properties of martensitic stainless steels vary depending on heat treatment conditions. Cold forming is possible in the as-annealed condition, but
scale and deformation due to quenching and tempering after forming may be problems.

It should be noted that the martensitic stainless steel displays corrosion resistance only in extremely weak corrosion environments because the corrosion resistance of this steel is inferior to that of the other stainless steels.

Although the martensitic stainless steels are used in applications such as structural members which require strength, welding tends to be difficult. Martensitic steels are prone to hardening of the heat affected zone (HAZ), cold cracking, and grain boundary corrosion by welding.

Because the corrosion resistance and formability of the martensitic stainless steels are markedly inferior to those of Type 304, as described above, there are very few applications where martensitic materials can be used as a substitute for Type 304.

3.3. Ferritic Stainless Steels

The ferritic stainless steels, represented by Type 430, are widely used in kitchen equipment and tableware, home electrical appliances, fittings for construction, and other applications.

The corrosion resistance (pitting potential) of Type 430 is inferior to that of Type 304, as shown in Table 4, but corrosion resistance is adequate for use in everyday products in indoor environments. For use in coastal areas, ferritic stainless steels with corrosion resistance superior to Type 304 are produced by adding Cr and Mo. Resistance to stress corrosion cracking is an advantage of the ferritic stainless steels.

Where cold formability is concerned, the Lankford value (r value), which is an index of the drawing property, can be improved to exceed that of Type 304 by optimizing the chemical composition and manufacturing conditions, but in some cases ridging (roping) and brittle cracking may occur in the formed products.

On the other hand, strength and weldability are problems with the ferritic stainless steels. Because the strength and toughness of the ferritic stainless steels are inferior to those of Type 304, these steels are rarely used in strengthening members. The weldability of Type 430 and related materials is also a problem, as ductility and toughness are deteriorated by the formation of martensite in welds. Moreover, virtually all ferritic stainless steels display a poor bending property and toughness due grain coarsening in the HAZ and are prone to grain boundary corrosion. For this reason, it is necessary to apply different welding control from that used with Type 304 and other Cr–Ni stainless steels.

With proper adjustment of the Cr and Mo contents, the ferritic stainless steels possess satisfactory corrosion resistance for a wide range of applications, from mild to severe corrosion environments. Therefore these steels can be substituted for Type 304 if used in drawing applications. These steels also have the advantage of low stress corrosion cracking susceptibility. However, use of the ferritic stainless steel is difficult in applications which require strength and in processing which involves stretch-forming. Care is also required in the area around welds, as the ferritic stainless steel is susceptible to hardening and coarsening of the metallic microstructure.

3.4. Duplex Stainless Steels

The duplex stainless steels are stainless steels with a composite microstructure consisting of an austenite phase and a ferrite phase. Because they are characterized by excellent pitting resistance, crevice corrosion resistance, grain boundary corrosion resistance, and stress corrosion cracking resistance, they are used in severe corrosion environments, in applications such as chemical plants, heat exchanger/piping, and structures in coastal areas.

As shown in Tables 2 and 3, the cold formability of the duplex stainless steels is close to that of the ferritic stainless steels. Because the duplex stainless steels have high proof stress and deformation resistance, the die life of the press used in forming and the springback in the formed products differ in some cases.

The weldability of the duplex stainless steel is satisfactory, as the strength and toughness of the weld are equivalent to those of the base material. However, if the phase ratio changes due to the effect of welding heat, corrosion resistance and toughness may be reduced in the affected parts.

As problems, the toughness of duplex stainless steel is sharply reduced in hot forming and during cooling after forming because the σ phase precipitates in these processes. In particular, work strain accelerates precipitation of the σ phase. Therefore the duplex steels are prone to cracking during hot rolling, which reduces product yield. As a result, this type of stainless steel is inherently expensive, irrespective of the current rise in the price of Mo.

From the viewpoints of corrosion resistance and strength, the properties of the duplex stainless steels are superior to those of Type 304. However, due to their poor manufacturability and high content of Mo, duplex materials tend to be expensive. In order to apply duplex stainless steels as a substitute for Type 304, it appears necessary to adopt a policy of developing more economical materials, even if this requires some sacrifice of corrosion resistance.

3.5. Cr–Mn–Ni Stainless Steels

The Cr–Mn–Ni stainless steels have austenitic structure. As shown in Table 1, the austenite microstructure is maintained by adding C, N, and Mn as substitutes for the reduced Ni content of Type 304. However, at present the applications of the Cr–Mn–Ni stainless steels are limited to spring materials and electronic/electrical components. In these applications, the material is not used as a Ni-saving steel, but rather, to take advantage of the properties of the Cr–Mn–Ni steels as a high strength and nonmagnetic steels.

Because the austenite forming capacities of Mn and Cu, which are added in place of Ni, are smaller than that of Ni, large quantities of C and N are also added to maintain the austenitic microstructure. Therefore, as shown in Table 2, tensile strength, proof stress, and hardness of these steels are higher than those of Type 304. However, addition of Mn and Cu deteriorates proof stress.

As shown in Table 3, the cold formability of the Cr–Mn–Ni stainless steels is substantially the same as Type 304. However, because proof stress is higher than that of Type 304, deformation resistance and work hardening may
Creased corrosion loss. However, because the Cr–Mn–Ni reduced Ni content and higher Mn content results in insufficient corrosion resistance. Care is necessary in applications where chemical corrosion resistance is required, as the Cr–Mn–Ni stainless steels are also susceptible to season cracking.

As other problems, although the high temperature strength of the Cr–Mn–Ni stainless steels is higher than that of Type 304 and other Cr–Ni stainless steels, the high content of added Mn reduces resistance to high temperature oxidation. Accordingly, care is necessary when using the Cr–Mn–Ni stainless steels in high temperature environments. On the other hand, in spite of their austenitic structure, high N-added steels display a ductile-brittle transition temperature (DBTT).

Because the weldability of the Cr–Mn–Ni stainless steels, including the quality of welds, is basically identical to that of Type 304, there is no need for special welding control like that required with the ferritic stainless steels. Mn-added steels have a high content of solid solution C. These steels therefore show lower susceptibility to grain boundary cracking than Type 304.

Figure 3 shows the effects of alloying elements on pitting potential in 1 000 ppm Cl– aqueous solution at 80°C. Pitting potential is proportional to Cr+3.3Mo+30N–Mn (%). This means that Mn addition has the effect of reducing corrosion resistance. Care is necessary in applications where chemical corrosion resistance is required, as the reduced Ni content and higher Mn content results in increased corrosion loss. However, because the Cr–Mn–Ni stainless steels possess adequate corrosion resistance for comparatively mild environments, such as indoors and inland, application in these environments is possible. In addition, corrosion resistance can be improved by addition of Cr, Mo and N. Like the Cr–Ni stainless steels, stress corrosion cracking occurs in Cr–Mn–Ni stainless steels in certain cases.

The most important feature of the Cr–Mn–Ni stainless steels is their resistance to the deformation-induced martensite transformation (α’). For this reason, these materials are enjoying expanded application as spring materials and electronic/electrical components, taking advantage of their above-mentioned features as a high strength and nonmagnetic steels.

In passing, it may be noted that the applications of Cr–Mn–Ni stainless steels are still limited in spite of a long history of research and development. As factors in this, there were numerous problems in the manufacturability of this material, and it was difficult to obtain cost merits corresponding to the reduction of Ni. However, manufacturability is improving with progress in refining and rolling technologies in recent years.

As described above, the Cr–Mn–Ni stainless steels possess substantially the same strength and formability as Type 304. And these steels also have adequate corrosion resistance for indoor, inland, and other mild environments. These suggest the possibility of use as a substitute for Type 304 in these environments.

4. Future Trends in Ni-saving Materials

4.1. Ferritic Stainless Steels

It is possible that the ferritic stainless steels have corrosion resistance equal or superior to that of Type 304 by the additions of Cr and Mo. However, there are restrictions on formability and strength. These restrictions must be overcome if ferritic stainless steels are to penetrate fields where the Cr–Ni stainless steels presently hold a large share.

To impart high strength to ferritic stainless steel, material with a dual-phase microstructure consisting of ferrite and martensite has been developed. On the other hand, ferritic stainless steel with corrosion resistance equal to Type 304 has been developed by addition of a high content of Cr without use of expensive Mo, while ferritic material with improved weldability has been developed using a low C, low N, and Ti-added composition design.

Because the ferritic stainless steels have a different crystal structure from the austenitic stainless steels, it is natural that both have different physical, mechanical, and chemical properties, and their fields of application are also different.

4.2. Cr–Mn–Ni Stainless Steels

The Cr–Mn–Ni stainless steels are somewhat inferior to the Cr–Ni stainless steels in corrosion resistance. However, the evaluation of corrosion resistance will differ depending on added alloying elements and the use environment. In addition, mechanical properties of the Cr–Mn–Ni steels are almost equal to those of Type 304. For these reasons, it would seem that the Cr–Mn–Ni stainless steels have advantages of other Ni-saving steels.

In recent years, the market for Cr–Mn–Ni stainless steels has expanded, centering on India and China. According to the International Stainless Steel Forum (ISSF) held in Korea in May 2004, the Cr–Mn–Ni steels achieved a 7.5% share of stainless crude steel production in 2003. These Cr–Mn–Ni stainless steels contain from 1 to 5% Ni. And these steels are used in applications such as tableware and pipes for construction material which do not require particularly high corrosion resistance. However, data on the formability and corrosion resistance of the Cr–Mn–Ni stainless steels are not as abundant as those of the Cr and Cr–Ni stainless steels. This means that it will be necessary to collect proper data for the application in order to further expand the applications of the Cr–Mn–Ni stainless steels.

Research on Mn-added stainless steels began in 1912. In recent years, research and development has taken two
main directions,\(^{59}\) one being stainless steels with new functions realized by Mn addition, such as a nonmagnetic property or high strength, and the other, stainless steels in which Mn addition is used for Ni-saving.

In the Cr–Ni stainless steels, the relationship between chemical composition and properties, for example, Ni equivalent and Cr equivalent,\(^{60,61}\) Md\(^{30,63,63}\) and mechanical properties\(^{64,65}\) can be expressed by a first-order linear equation for the chemical composition. This relationship is frequently used as a guideline for the development of new steels. On Cr–Mn–Ni stainless steels, however, such relations have not been suggested. Even though the materials have the same austenitic microstructure, the effects of alloying elements on properties and structures may be different between Cr–Ni and Cr–Mn–Ni steels. In order to develop rapidly the steel with appropriate properties for application, it is necessary for Cr–Mn–Ni stainless steels to investigate the relationship between the chemical composition and the properties.

Incidentally, in control of scrap in the market,\(^{11}\) the difficulty of distinguishing between Cr–Mn–Ni and Cr–Ni stainless steels has been pointed out. However, use of chemical analysis kit and portable X-ray analysis device\(^{66}\) developed for scrap sorting is continuing to grow. And it can be said that the establishment of control methods for scrap using these techniques is also one key to expansion of the applications of Cr–Mn–Ni stainless steels.

### 5. Conclusion

Ni is a valuable metal in the modern industries. Therefore Ni should be supplied stably at an appropriate price and utilized effectively in the alloys. Ni-saving in austenitic stainless steels can be one of the methods in which Ni is used in an effective manner.

According to “the Annual Stainless Steel Statistics by Application for fiscal 2005 (Japan Stainless Steel Association)”, Cr–Ni stainless steels are mainly used in applications which require high strength such as construction applications, industrial machinery, ships, and railroad cars, while Cr stainless steels is used in automobiles and other transportation machinery and equipment. This is one of the examples in which suitable types of stainless steels are chosen for practical applications.

Currently the ferritic and Cr–Mn–Ni stainless steels are mainly used in terms of Ni-saving, and in some fields the duplex stainless steels are under examination. Table 5 shows the comparison of properties of Ni-saving stainless steels and Type 304. Not every candidate steel for Ni-saving satisfies all the properties of Type 304, but in some cases equal or even better properties are indicated. This suggests that the substitution for Type 304 is sufficiently possible, depending on the application. In the future, the use of these Ni-saving stainless steels would increase if an adequate grade is chosen considering applied conditions and necessary properties.

### REFERENCES


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<p>| Table 5. Comparison of properties of Type 304 with those of stainless steels to save Ni. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Structure</th>
<th>Martensite</th>
<th>Ferrite</th>
<th>Ferrite</th>
<th>Austenite</th>
<th>Austenite</th>
<th>Note</th>
</tr>
</thead>
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<tr>
<td>Corrosion resistance</td>
<td>×</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>S.C.C.</td>
<td>○</td>
<td>Insensitive</td>
<td>Insensitive</td>
<td>○</td>
<td>Depend on alloy</td>
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<td>Oxidation</td>
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<td>○</td>
<td>△</td>
<td>△</td>
<td>△</td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>High temp.</td>
<td>△</td>
<td>×</td>
<td>brittle</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>Room temp.</td>
<td>High*</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>○</td>
<td>*After quenching</td>
</tr>
<tr>
<td>Low temp.</td>
<td>brittle</td>
<td>brittle</td>
<td>brittle</td>
<td>○</td>
<td>○</td>
<td>tempering</td>
</tr>
<tr>
<td>Fatigue</td>
<td>△</td>
<td>△</td>
<td>△</td>
<td>△</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>Workability</td>
<td>Drawability</td>
<td>×</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
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<tr>
<td>Stretch-ability</td>
<td>×</td>
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<td>○</td>
<td>○</td>
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<tr>
<td>Weldability</td>
<td>×</td>
<td>△</td>
<td>○</td>
<td>○</td>
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</tr>
<tr>
<td>Season cracking sensitivity</td>
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<td>Possess</td>
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<tr>
<td>Magnetism</td>
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<tr>
<td>Productivity</td>
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<td>×</td>
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<tr>
<td>Cost</td>
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<td>Cheap</td>
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