Technical Report

# Development of Heat-resistant Stainless Steel NSSC™ 429NF for Automotive Exhaust Systems

Atsutaka HAYASHI* Jun-ichi HAMADA
Norihiro KANNO Nobuhiko HIRAIDE
Atsuhisa YAKAWA Yoshiharu INOUE
Shin-ichi TERAOKA

## Abstract

***In this study, an Nb-free heat-resistant ferritic stainless steel NSSC 429NF (14%Cr-1.2%Cu-Ti-Low C,N) was developed for alloy saving of the heat-resistant ferritic stainless steel used in automotive exhaust parts. The newly developed steel showed an enhanced thermal fatigue property in the automotive exhaust system due to the dynamic precipitation hardening of Cu particles. Furthermore, it exhibited an excellent high-temperature oxidation resistance due to the enhanced stability of the ferritic phase, which was achieved by adjusting the chemical composition. The newly developed steel showed superior heat-resistant properties and can be used as a substitute for the conventional heat-resistant ferritic stainless steel, namely: Type 429 (14%Cr-0.4%Nb-Low C,N).***

## 1. Introduction

The main use of stainless steel for automotive application is the exhaust system components of engines; the use of stainless steel sheets and pipes for exhaust manifolds directly below the engine has expanded rapidly since the 1980s.[1] While next-generation vehicles such as electric and fuel cell vehicles are expected to increase in the future, it is predicted that the majority of vehicles will still be driven by engines or hybrid units comprising engines and electric motors,[2] and therefore it is necessary to continue pursuing high heat resistance and low costs of the material of exhaust manifolds. This application requires high-temperature properties such as thermal fatigue, high-temperature strength, and oxidation resistance.[3] Ferritic stainless steel is superior to austenitic steel in terms of thermal fatigue owing to its smaller coefficient of thermal expansion.[3] It is superior also in high-temperature oxidation resistance because a protective film of $Cr_2O_3$ effective in high temperature environments forms more readily in the ferritic phase due to the quick diffusion of Cr.[3, 4] In appreciation of these advantages, heat-resistant ferritic stainless steel is used for the exhaust manifolds of many automobile types and models. To improve the high-temperature strength, Nb, Mo, Cu, etc. are added to heat-resistant ferritic stainless steel, and Nb-added steels of Type 429 (14%Cr-0.4%Nb) are used as conventional materials. In addition, as higher-grade steels, there are the Type 444 steels (18%Cr-2%Mo-0.5%Nb) with the combined addition of Nb and Mo, and recently developed steels with the combined addition of Nb and Cu.[5–8] In such existing steel grades, Nb is an essential element, but it is expensive, and since its resources are distributed unevenly, high risk is involved in its supply. It is therefore important from the viewpoints of economic efficiency and material procurement strategy to develop Nb-free heat-resistant ferritic stainless steel.

As an alternative element to Nb, we focused attention on relatively inexpensive Cu, and studied its effects on the steel strength in environments of thermal fatigue and high-temperature oxidation resistance.[9–11] As a result, we found that the particles of Cu precipitates in steel repeated dissolution and precipitation in the process of thermal fatigue, and by doing so, maintained their fine size, and that it was possible to actively utilize this dynamic precipitation hardening of Cu at high temperature for enhancing thermal fatigue properties.[7, 9, 10] We also found that in the use of Cu, which is an austenite-forming element, the stability of the ferritic phase of the matrix was important for high-temperature oxidation resistance.[11] Nb-free heat-resistant ferritic stainless steel NSSC 429NF has been developed based on these findings. The present paper outlines the basic studies

* Senior Researcher, Coil & Sheet Products, Automotive Products Research & Development Div., Research & Development Center, Nippon Steel Stainless Steel Corporation
3434 Ooaza-shimata, Hikari City, Yamaguchi Pref. 743-8550

for the development, and compares the characteristics of the developed steel with those of the existing Type 429 conventional steels.

## 2. Dynamic Precipitation Hardening of Cu in Thermal Fatigue Process [7, 9, 10]

Solid solution hardening and precipitation hardening are effective measures mainly employed for improving the steel strength at high temperature. Conventional heat-resistant ferritic stainless steel is strengthened mainly by means of a solid solution of Nb or Mo, and precipitation hardening has been regarded as a supplementary measure. This is because, even when fine precipitates are dispersed in a matrix structure, they coarsen when the material is kept at high temperature for a long period, their density is decreased, and so is their strengthening effect. However, little was known about the dynamic precipitation of alloy elements at high temperature,[12] and there had been no studies on their precipitation behavior under repetitive thermal strain cycles as with the exhaust systems of automobile engines. In view of this situation, we examined the dynamic precipitation behavior of Cu particles through a test of thermal fatigue, an important property for exhaust system components, using steel containing 1.2% Cu. Pipes 38.1 mm in outer diameter and 2 mm in wall thickness were used as the specimens, and to best simulate the environment of real exhaust manifolds, the condition of the cyclic thermal fatigue test was set as follows:[13] the lowest temperature (Tmin) of a heat cycle was set at 200°C; the highest temperature (Tmax) at 700°C as the temperature at which ε-Cu precipitates according to calculation by Thermo-Calc. (see **Fig. 1**); the holding time at Tmax at 120 s; and the restriction ratio at 50%. After repeating the cycles of heating and cooling from Tmin to Tmax and vice versa, a set of samples for structural observation were selected after 1 000 heat cycles, another set after 2 600 cycles, when a crack was found to have penetrated the pipe wall. Because the holding time at Tmax totaled 87 h a crack penetrated the wall, and a third set of comparative samples were prepared by subjecting the same steel to a static aging heat treatment at 700°C for 87 h. **Figure 2** shows photomicrographs of the samples taken through a field emission transmission electron microscope (FE-TEM). In the samples that underwent the thermal fatigue cycles, Cu particles are finer and more evenly dispersed than in that subjected to the static heat treatment, and crystal dislocations are found closely related to Cu particles. In addition, it is clear that Cu particles did not coarsen significantly from 1 000 to 2 600 cycles.

There have been several study reports on the shape change and dissolution of Cu particles due to material deformation. Yokoi et al. studied the fatigue of a Fe-1.5%Cu alloy at room temperature and reported that fine Cu particles were cut by crystal dislocations at a very early stage of fatigue, became unstable in terms of size, and went into solid solution again.[14] Tsuchiyama et al. reported the deformation and dissolution of Cu particles during cold forming work of Fe-Cu alloys, and demonstrated that dislocations were locally introduced to the inside of elongated Cu particles, and by dislocation shearing, the tips of such Cu particles acted as the starting points of their dissolution.[15] In high temperature deformation, on the other hand, an attractive interaction acts between dislocations and Cu particles, a dislocation disappears by the Srolovitz mechanism when it meets a Cu particle, after passing through it, reappears at the other side of it,[16, 17] and the Cu particle is not cut. However, dislocations move rapidly at high temperature, shear strain is concentrated on relatively soft Cu particles, and strain-induced dissolution and solid solution of Cu particles are likely to take place. Through an ultra-high-voltage electron microscope, we confirmed in situ the solid solution and spheroidizing of Cu particles during material deformation at high temperature, and it was inferred that Cu in solid solution diffused in the matrix mainly along dislocations, and precipitated again. It is considered from the above that, in an environment where deformation is repeated at the temperature at which Cu particles precipitate, Cu repeats the cycle of precipitation, particle dissolution, partial solid solution and re-precipitation, and as a result, it precipitates in spheroidized fine particles of a uniform granulometry. As stated above, the Cu precipitates forming in an environment of strain at high temperature are finer and more dispersed than those forming during a static heat treatment, and are expected to have a greater steel strengthening effect.[10]

Based on this finding, we studied how to define the amount of Cu addition with which the strength of 14%Cr steel at 800°C would be equal to that of the Type 429 steel. The result is shown in **Fig. 3**. With the addition of 1.2% Cu, the high-temperature strength of the 14%Cr steel is greatly improved, and becomes equal to that of the Type 429. Since Fig. 1 shows that Cu precipitates at 800°C when its addition amount is 1% or more, high strength at high temperature is obtained with Cu addition by 1.2%. In the alloy design of the developed steel, the contents of C and N were set low to prevent the intergranular corrosion of welded zones, and Ti was selected as a stabilizer.

Based on the above, the basic chemical composition of the developed steel has been defined as 14%Cr-1.2%Cu-Ti-LowC,N.

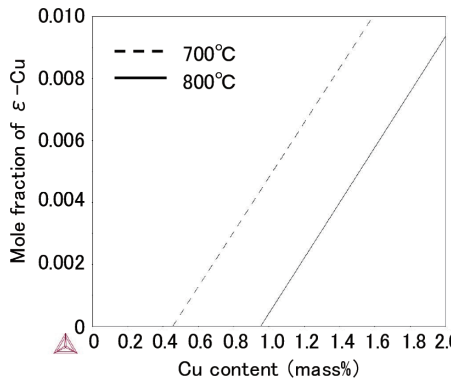


**Fig. 1 Mole fraction of ε-Cu precipitates in 14%Cr-0.1%Ti-Cu steel at 700 and 800°C calculated by Thermo-Calc.**

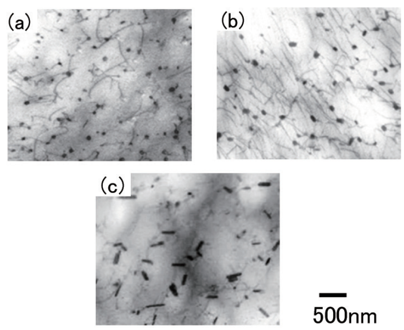


**Fig. 2 TEM photographs of 1.2%Cu steel after (a) 1 000 and (b) 2 600 cycles of thermal fatigue test from 200 to 700°C at 50% restriction ratio, and (c) after aging treatment at 700°C for 87 h**

## 3. Improvement of High-temperature Oxidation Resistance by Stabilization of Ferritic Phase

The high-temperature oxidation resistance of stainless steel results from the formation of a protective layer of $Cr_2O_3$ on the surface in a high temperature environment and consequent suppression of the rapid oxidation of Fe, often called breakaway oxidation; the upper limit temperature of use rises as the amount of Cr increases.[18] Regarding the effect of crystal structure on high-temperature oxidation resistance, Fujikawa stated that the diffusion rate of Cr in the austenitic phase was slower than that in the ferritic phase, and as a result, the formation of the Cr oxide was delayed with the austenitic phase.[4] Makiura et al. showed that breakaway oxidation of 11%Cr steel was accelerated by decreasing the amounts of ferrite-forming elements and increasing those of austenite-forming elements, and stated that this was related to the fact that the rate of Cr diffusion was slower in the austenitic phase than in the ferritic phase.[19] In consideration of the above, we studied whether or not there was a similar structural effect on the oxidation of the 14%Cr steel. Test pieces of the following steels were prepared: steel having a chemical composition of 14%Cr-Nb-Ti-LowC,N (hereinafter referred to as the Cu-and-Ni-free steel); the Cu-and-Ni-free steel with Cu addition by 1.0 and 1.8% (hereinafter referred to as the 1%Cu-added and the 2%Cu-added steels, respectively); and the Cu-and-Ni-free steel with Ni addition by 0.5 and 1.0% (hereinafter referred to as the 0.5%Ni-added and the 1%Ni-added steels, respectively). The test pieces were subjected to a continuous high-temperature oxidation test in normal atmosphere, where they were held at 950°C for 200 h, and the difference between their weights before and after the test per unit area was regarded as their mass gain by oxidation. **Figure 4** shows the effects of Cu and Ni on the mass gain. It was small with the Cu-and-Ni-free steel and the 1%Cu-added steel, which indicated their normal oxidation, but the mass gain rose significantly with the 2%Cu-added steel, which confirmed breakaway oxidation. Breakaway oxidation was observed also with the 0.5%Ni-added and the 1%Ni-added steels, which indicated that Ni lowered high-temperature oxidation resistance more than Cu did. **Figure 5** shows the result of calculation of the effects of the addition of Cu and Ni on the behavior of ferrite/austenite transformation by Thermo-Calc. The area in the Cr content-temperature plane in which austenitization occurred with the addition of Cu and Ni, and the effect of Ni is greater than that of Cu. With a high-temperature X-ray diffractometer (XRD) using synchrotron radiation, we analyzed in situ the mechanism of breakaway oxidation of ferritic stainless steel in detail.[11] It became clear as a result that the austenitic phase formed and grew in the Cr-depleted zone where $Cr_2O_3$ formed on the base metal, and that Fe oxidized in priority in such zone, leading to breakaway oxidation. In other words, with the addition of Ni, which accelerates austenitization more than Cu does, breakaway oxidation is likely to occur during a high-temperature oxidation test. From the above, to secure good high-temperature oxidation resistance of 14%Cr steel, it is necessary to design the amounts of the alloy elements including trace elements in a well-balanced manner in con-

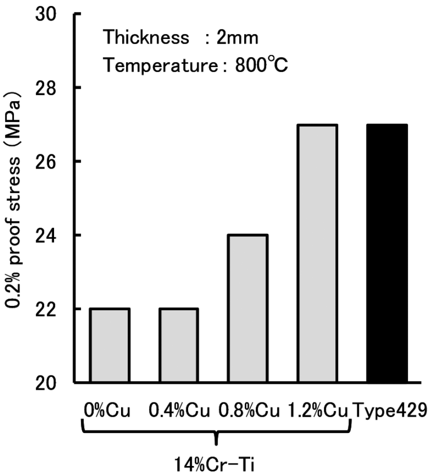


**Fig. 3 Effect of Cu content on 0.2% proof stress at 800°C of 14%Cr-Ti-LowC,N steels**

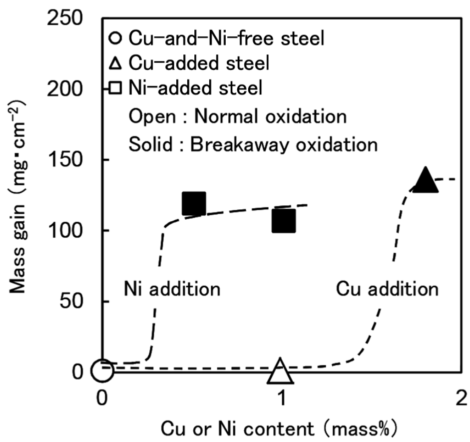


**Fig. 4 Effects of Cu and Ni on mass gain of 14%Cr steel oxidized at 950°C for 200 h**

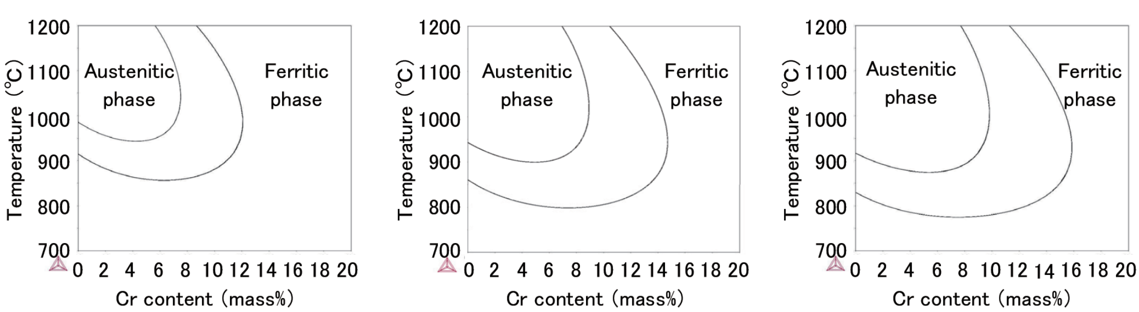


**Fig. 5 Calculated phase diagrams of (a) Cu-and-Ni-free steel, (b) 1%Cu-added steel and (c) 1%Ni-added steel**

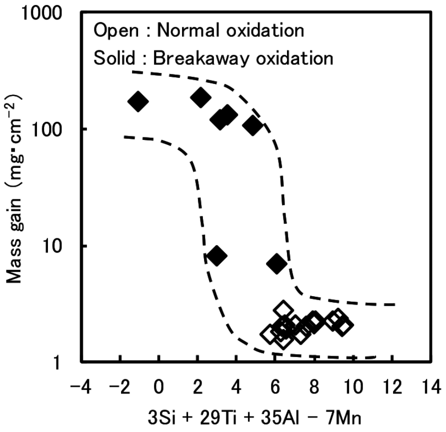


**Fig. 6 Relationship of oxidation mass gain of 14%Cr-1.2%Cu steels oxidized at 950°C for 200 h with ferritic stability indicator**

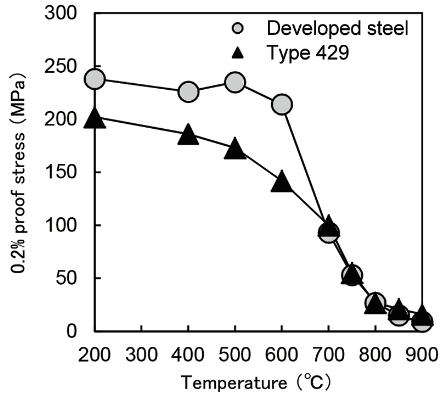


**Fig. 7 0.2% proof stress of developed and Type 429 steels at high temperature**

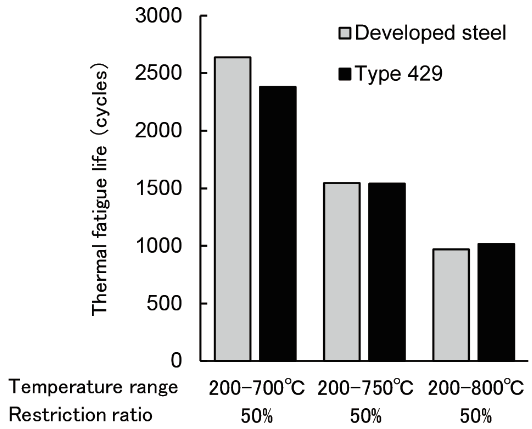


**Fig. 8 Thermal fatigue life of developed and Type 429 steels in different temperature ranges**

sideration of the stability of the ferritic phase.

As stated in Section 2, from the viewpoints of high-temperature strength and thermal fatigue property, the basic chemical composition of the developed steel was defined as 14%Cr-1.2%Cu. Excessive Cu addition was avoided in consideration of the mechanical properties and high-temperature oxidation resistance, but the stability of the ferritic phase is affected not only by Cr and Cu, but also by trace elements such as Si, Mn, Ti, and Al. In consideration of this, the same atmospheric continuous high-temperature oxidation test as described earlier was conducted at 950°C for 200 h using modifications of the 14%Cr-1.2%Cu steel containing other elements by different amounts as the specimens. In addition, the increase and decrease of ferritic and austenitic phases in the steel with the addition of Si, Mn, Ti, and Al were calculated by Thermo-Calc., and based on the calculation result, an indicator of the ferritic stability was formulated as 3Si+29Ti+35Al−7Mn. **Figure 6** shows the relationship of the oxidation mass gain during the oxidation test with the ferritic stability indicator. With alloy compositions having large values of the indicator, which means the ferritic phase is stable, the mass gain is small, breakaway oxidation does not occur, and good high-temperature oxidation resistance is obtained. It has to be noted that with Si addition, $SiO_2$ forms at the interface between the $Cr_2O_3$ scale and the base metal, whereby oxide acts as a barrier to prevent the outward diffusion of metal ions and inward diffusion of oxygen, and suppresses accelerated oxidation.[20] Ti and Al are considered to prevent breakaway oxidation by internally oxidizing in the base metal immediately below the scale to prevent the oxygen potential from increasing and Fe from oxidizing; this effect of Ti and Al is called the “oxygen getter” effect.[21, 22] In contrast, Mn is considered to accelerate the oxidation of Cr, which leads to short supply of Cr from the base metal to the interface with the scale, making breakaway oxidation likely.[23]

To secure good high-temperature oxidation resistance of the developed steel based on these findings, the ferritic phase was stabilized by delicately controlling the amounts of Si, Mn, Ti, and Al added to the base composition of 14%Cr-1.2%Cu.

## 4. Characteristics and Properties of Developed NSSC 429NF[7–9]

As stated in the previous section, Nb-free heat-resistant ferritic stainless steel NSSC 429NF has been developed on the basis of an alloy composition of 14%Cr-1.2%Cu-Ti-LowC,N. The characteristics and properties of sheets of the developed steel (2 mm in thickness) manufactured through commercial processes are presented below in comparison with those of the Type 429 steels.

**Figure 7** shows the 0.2% proof stress of the developed steel and the Type 429 at 200 to 900°C. The former is stronger than the latter at 600°C or lower, and exhibits the same high-temperature strength as that of the latter at 800°C or lower. Especially at 500 to 600°C, the developed steel is stronger than the latter thanks presumably to Cu precipitation in fine particles.

**Figure 8** shows the result of the thermal fatigue test of ERW pipes 38.1 mm in outer diameter and 2 mm in wall thickness, wherein the lowest temperature (Tmin) of one heat cycle was 200°C, the highest temperature (Tmax) was 700, 750, and 800°C, the holding time at Tmax was 120 s, and the restriction ratio was 50%. The developed steel has been confirmed to have the same thermal fatigue life as that of the Type 429 under any one of the test conditions.

**Figure 9** shows the parabolic rate constant $k_p$ obtained through the atmospheric continuous high-temperature oxidation test at 800, 850, 900 and 950°C for 200 h. It is the oxidation rate constant under an assumption that the oxidation reaction progresses according to the parabolic law; it was calculated by the following formula, where $\Delta W$ is the mass gain by oxidation and $t$ is the test time:

$$\Delta W^2 = k_p \cdot t.$$

At 950°C or lower, the values of $k_p$ of the developed and the

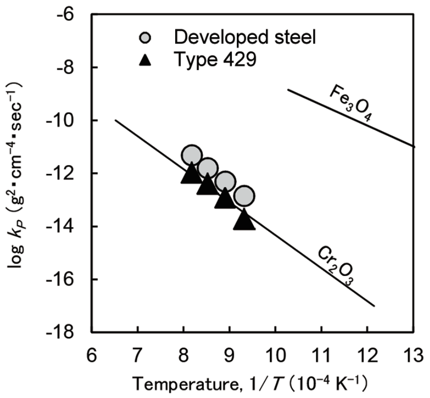


**Fig. 9 Parabolic rate constants of developed and Type 429 steels oxidized at 800, 850, 900 and 950°C for 200 h**

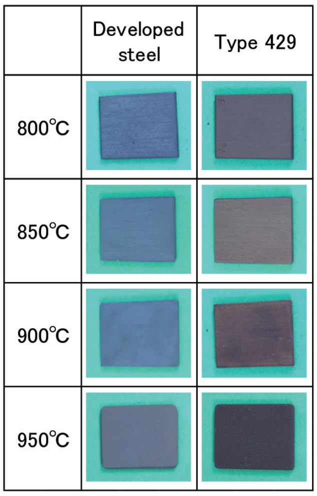


**Fig. 10 Appearances of developed and Type 429 steels oxidized at 800, 850, 900 and 950°C for 200 h**

**Table 1 Mechanical properties of the newly developed steel when compared to those of Type 429 at room temperature**

| | 0.2% proof stress (MPa) | Tensile strength (MPa) | Total elongation (%) | Average r-value |
|---|---|---|---|---|
| Developed steel | 326 | 447 | 34 | 1.3 |
| Type 429 | 300 | 470 | 35 | 1.1 |

Type 429 steels change in the same manner as the reported $k_p$ value of $Cr_2O_3$,[24] which corroborates that the steel oxidation was well controlled. **Figure 10** shows the appearances of some specimens after the oxidation test. The specimens exhibit satisfactory oxidation resistance owing to adhesive scale without spallation.

**Table 1** shows the mechanical properties of the developed steel at room temperature. Although the developed steel is a little harder than the Type 429, its r-value is higher, which demonstrates its excellent deep drawability. The high r-value of the developed steel is secured not only by the alloy design, but also by the metallographic control through the manufacturing processes.[6, 8]

## 5. Conclusion

The addition of Cu as a substitute to Nb, which had long been added to heat-resistant ferritic stainless steel as a strengthening element, was studied, and based on the findings of the dynamic precipitation hardening of Cu under deformation at high temperature and its effect on high-temperature oxidation resistance, Nb-free and heat-resistant ferritic stainless steel NSSC 429NF has been developed. The following conclusions were obtained through the development studies:

(1) Based on the dispersion mechanism of Cu in fine particles under deformation at high temperature, the basic alloy composition of the developed Nb-free steel was defined as 14%Cr-1.2%Cu-Ti-LowC,N.

(2) In 14%Cr steel, the stability of the ferritic phase affects its high-temperature oxidation resistance. The ferritic phase of the developed steel is stabilized and high-temperature oxidation resistance is ensured by optimally controlling the addition amounts of Si, Mn, Ti, and Al.

(3) The newly developed steel is excellent in high-temperature strength, thermal fatigue properties, high-temperature oxidation resistance, and mechanical properties at room temperature. Its performance has been confirmed to be equal to or better than that of the Type 429 steel, conventional heat-resistant ferritic stainless steel for general applications, in the temperature range where the latter is widely used (up to 800°C).

### References

1) Hosoi, Y. (editorial supervisor): Science and Latest Technology of Stainless Steel. 1st edition. Tokyo, Jpn. Stainless Steel Ass., 2011, p.222–228
2) Ministry of Economy and Industries: Materials for 1st Meeting, Conference on Automobile Strategy for New Era (Apr. 18, 2018) / original literature: IEA: ETP (Energy Technology Perspectives) 2017
3) Kajimura, H.: Bull. Iron Steel Inst. Jpn. 11 (2), 67 (2006)
4) Fujikawa, H.: Tetsu-to-Hagané. 70 (11), 1541 (1984)
5) Tomita, T. et al.: Nisshin Steel Tech. Rep. (90), 30 (2009)
6) Hamada, J. et al.: Proc. Academic Conf., Soc. Automotive Engrs. Jpn, Inc. (46-14), 13 (2014)
7) Hamada, J. et al.: Materia Japan. 56 (1), 33 (2017)
8) Hamada, J. et al.: International Journal of the Italian Association for Metallurgy. (5), 33 (2018)
9) Kanno, N. et al.: Trans. Soc. Automotive Engrs. Jpn. 48 (4), 939 (2017)
10) Kanno, N. et al.: Tetsu-to-Hagané. 103 (9), 539 (2017)
11) Hayashi, A. et al.: International Symposium on High-Temperature Oxidation and Corrosion 2018, 2018, p.191–194
12) Kanno, N. et al.: CAMP-ISIJ. 25, 1175 (2012)
13) Miyahara, M. et al.: High Temperature Properties of Stainless Steel and Applications, Iron & Steel Inst. Jpn. (9672), (Oct. 2003)
14) Yokoi, T. et al.: Journal of Materials Science. 36, 5757 (2001)
15) Tsuchiyama, T. et al.: Acta Materialia. 113, 48 (2016)
16) Nakajima, K. et al.: Tetsu-to-Hagané. 89 (5), 524 (2003)
17) Kobayashi, S. et al.: Tetsu-to-Hagané. 101 (6), 315 (2015)
18) Nemoto, R.: Corrosion Engineering. 31 (9), 597 (1982)
19) Makiura, H. et al.: Report of No. 123 Committee on Heat-resisting Metal and Alloys, Japan Society for the Promotion of Science, 21, 83 (1980)
20) Inoue, Y. et al.: Tetsu-to-Hagané. 102 (12), 704 (2016)
21) Inoue, Y. et al.: Materials Transaction. 60 (9), 1968 (2019)
22) Ike, H. et al.: J. Japan Inst. Metals. 42, 509 (1978)
23) Inoue, Y. et al.: ISIJ International. 58 (10), 1850 (2018)
24) Otsuka, N. et al.: Netsu Shori. 33, 251 (1993)


Atsutaka HAYASHI
Senior Researcher
Coil & Sheet Products, Automotive Products Research & Development Div., Research & Development Center
Nippon Steel Stainless Steel Corporation
3434 Ooaza-shimata, Hikari City, Yamaguchi Pref.
743-8550


Jun-ichi HAMADA
General Manager, Dr.Eng.
Coil & Sheet Products, Automotive Products Research & Development Div., Research & Development Center
Nippon Steel Stainless Steel Corporation


Norihiro KANNO
Manager
Intellectual Property Div.
Nippon Steel Stainless Steel Corporation


Nobuhiko HIRAIDE
Group Manager, Dr.Eng.
Solution Development Dept.
Research & Development Center
Nippon Steel Stainless Steel Corporation


Atsuhisa YAKAWA
General Manager
Products Development Div.
Nippon Steel Stainless Steel Corporation


Yoshiharu INOUE
Senior Manager, Dr.Eng.
Products Development Div.
Nippon Steel Stainless Steel Corporation


Shin-ichi TERAOKA
Chief Researcher, Ph.D.
Kyushu R & D Lab.
R & D Laboratories
Nippon Steel Corporation