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Preventing stress corrosion cracking of austenitic stainless steels in chemical plants

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1. INTRODUCTION

General-purpose austenitic stainless steels, namely types 304 and 316 (standards and compositions listed in Table 4) are common corrosion-resistant materials of construction in chemical process plants. One corrosion mode that occurs with these materials is stress corrosion cracking (SCC), a type of damage that often causes serious problems in equipment function and safety. This is because SCC occurs relatively frequently, its propagation is often fast, and it is often difficult to detect nondestructively.

This paper discusses cases of SCC that occur with stainless steels in chemical plants and describes the present state, focusing on SCC caused by chlorides and examining what causes SCC and how to prevent it.

2. EXAMPLES OF SCC OF AUSTENITIC STAINLESS STEELS

The results⁽¹⁾ of a study of 80 cases of SCC that occurred in chemical plants that the author became aware of over a span of about ten years are presented.

Figure 1 shows a breakdown of all the examples into the two modes; transgranular stress corrosion cracking (TGSCC) and intergranular stress corrosion cracking (IGSCC). About three-fourths of the examples are TGSCC.

Figure 2 divides the SCC examples into the number and type on the process side and on the non-process side (cooling water environment, atmosphere-side environment, etc.). The largest number of cases of SCC are from environments that contain

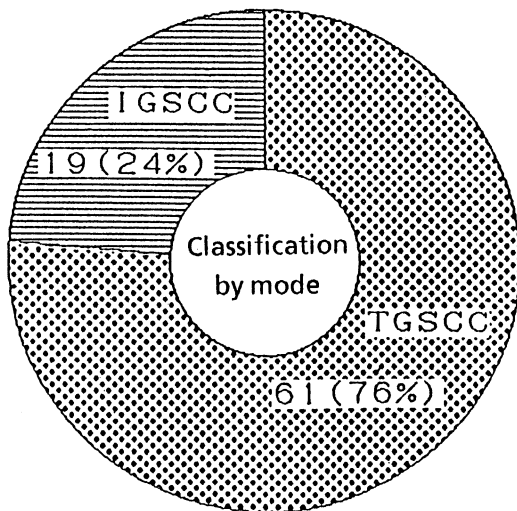


Fig. 1. Classification of examples of SCC by mode

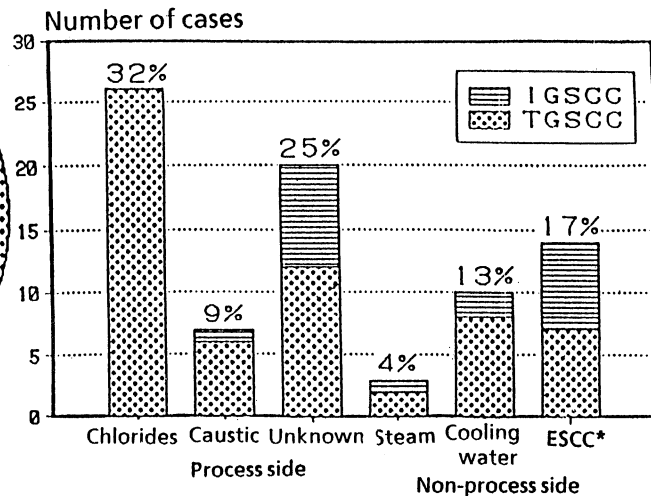


Fig. 2. Classification of examples of SCC by environment

(* ESCC: external Stress Corrosion Cracking)

chlorides on the process side, and they all are TGSCC. In addition, a relatively high proportion occur in cooling-water environments and by SCC from the external surface (ESCC), where chlorides are inferred to have played a major role. In these environments IGSCC also occurs.

Figure 3 gives the results classified by the temperature at which SCC occurs for each mode. These data show that TGSCC frequently occurs in the high-temperature region of 80°C and higher, while IGSCC frequently occurs at near-ambient temperatures.

Figure 4 gives the proportion of the occurrence of SCC for different types of

austenitic stainless steels. According to this data, the ratio of type 304 to type 316 is 7:3 for TGSCC and 9:1 for IGSCC. This ratio for TGSCC is believed to be higher than the use-ratio of type 316 to type 304 in chemical plants. The reason is thought to be because type 316 is frequently selected for severely corrosive environmental conditions.

Figure 5 shows the distribution of the number of years of service until SCC damage was observed, that is, the useful lifetime. The data indicate that TGSCC frequently occurs within a short period of a year or less, while the occurrence of IGSCC is after considerably longer periods of time.

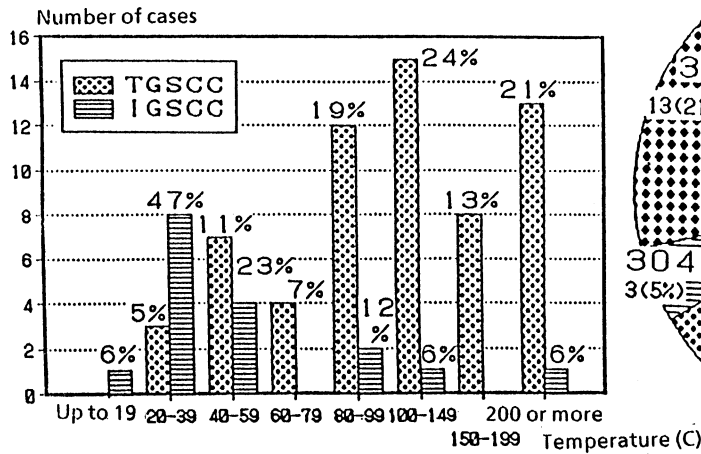


Fig. 3. Classification of SCC cases by temperature

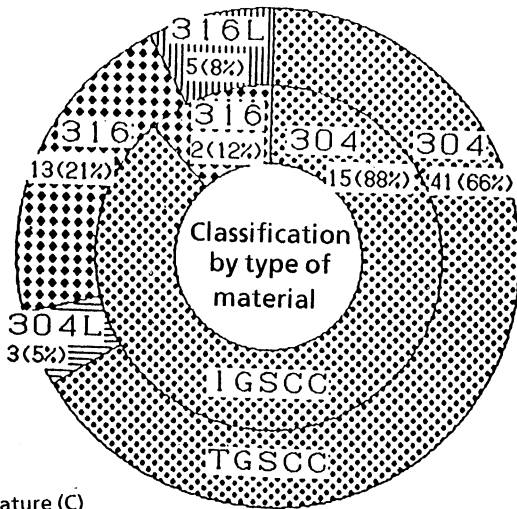


Fig. 4. Classification of SCC cases by type of austenitic stainless steels

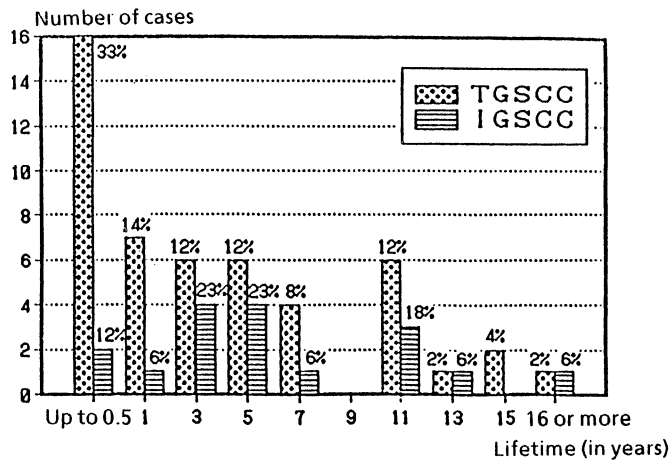


Fig. 5. Classification of SCC cases by lifetime

3. CAUSES AND PREVENTION OF SCC INVOLVING CHLORIDES

3-1. Causes of SCC

Among the modes of SCC, the main cause of IGSCC is believed to be sensitization of the material, with contribution of the environmental component (chloride ions) and of the stress component being relatively small. (However, even in IGSCC, since it represents a form of SCC, the presence of electrolytes on its surface and the existence of chlorides in them are inferred to accelerate the occurrence of IGSCC.)

In the occurrence of TGSCC, the following items are believed to be involved as causes:

Environment:

- * chloride ions (abbreviated as Cl⁻)
- * pH
- * temperature
- * oxidizer (such as presence of oxygen or metallic ions in solution)
- * presence or absence of crevices (either adhesion or structural crevices)

Material:

- * quantity of Ni (alloys having a Ni content of 45% or more, or ferritic stainless steels)
- * resistance to crevice corrosion

Stress:

- * tensile stress (residual stress during welding, stress during operation)

3-2. Environmental causes

As shown by Nishino⁽²⁾ and a questionnaire survey by the Society of Chemical Engineers, Japan,⁽³⁾ Cl⁻ concentration and temperature play critical roles as environmental factors in the occurrence of SCC. From the results of

Truman's immersion experiments,⁽⁴⁾ Figure 6, pH is also affective. Figure 6 shows that the higher the Cl⁻ concentration and temperature, the more likely SCC will occur; and the lower the pH, the greater is the range of possibility for the occurrence of SCC. These results were obtained from immersion test pieces of type 304 pipe with butt welds in various sets of environmental conditions for up to 13,500 hours. No artificial crevices were formed in the test pieces, and the oxidizer was considered to be the oxygen in solution at equilibrium under atmospheric pressure.

Although the results of Figure 6 and other data hint at the effects of various other factors in the occurrence of SCC, it would be unreasonable to take these data as an absolute standard for the occurrence of SCC and to use the information as the basis for materials selection. The following two cases are examples.

Case 1

SCC was found to occur, starting from the cooling-water side, in a number of heat exchangers about ten years after they first went into service. These were horizontal multi-tube exchangers with process fluid inlet temperature of 60°C. Cooling water flowed on the shell side at a speed of 0.3 m/sec from an open circulation system. The water contained 120 ppm Cl⁻ and a concentration multiple of 5.

The damage was limited to the vicinity of the crevices between baffle plate and tube, and the crevices between tube plate and tube. In many cases the SCC starting point was crevice corrosion as shown in Photo 1, with TGSCC propagation. Also, in those heat exchangers where damage occurred, because

chemical cleaning was needed on the process side, the cooling water on the shell side was drained out two or three times a year and 80°C hot water was rinsed through the inside of the tubes. In heat exchangers made of type 304 having generally the same water quality system but without chemical cleaning, no SCC occurred even though the process inlet temperature was higher.

The operating conditions of these heat exchangers do not exist in the region of SCC occurrence shown in Figure 6 even if the

temperature of the type 304 tubing is assumed to rise to the process inlet temperature. Yet, SCC occurred nevertheless. From a comparison with other heat exchangers of the same system, the cause of SCC is believed to be due to the chemical cleaning. That is, during operation, contamination components (slime, sludge, etc.) built up on the shell side of the heat exchange, and during chemical cleaning dried on the surface of the tubes, forming firm crevices. During operation the concentration of chlorides is assumed to

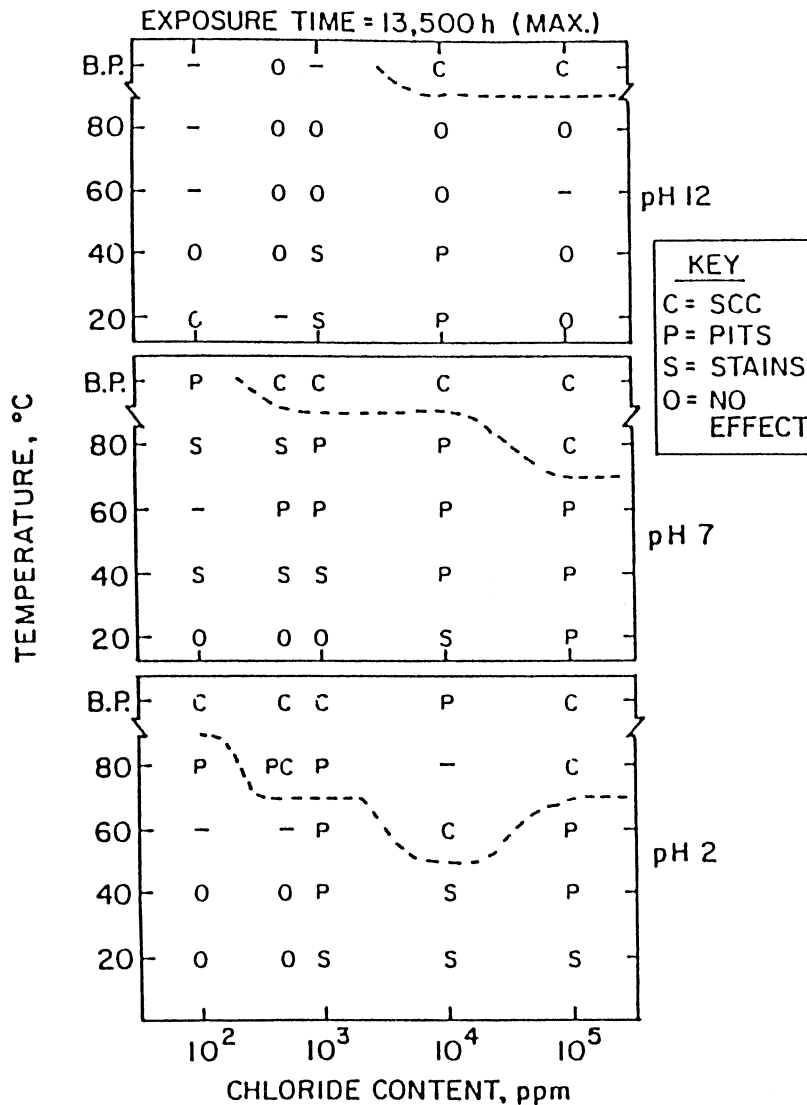


Fig. 6. Effect of Cl⁻ concentration, temperature and pH on type 304 corrosion mode in sodium chloride solution⁽⁴⁾

increase at these cervices, leading to the occurrence of crevice corrosion and then to initiation of SCC.

Table 1 shows the results found when, during five years, sample tubes were placed into the heat exchangers where SCC occurred (see Table 4), and later removed for

examination. Crevice corrosion was found in types 304 and 444 but not in type 316. Even under the same conditions of operation, type 316, which has better crevice corrosion resistance, is believed to suppress (retard) the occurrence of SCC and to be a better material for SCC prevention.

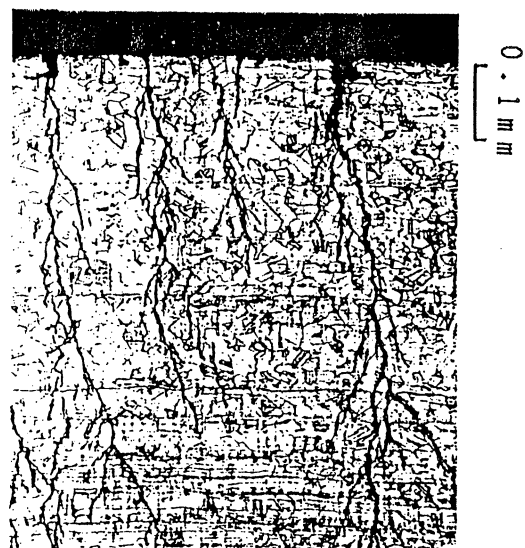
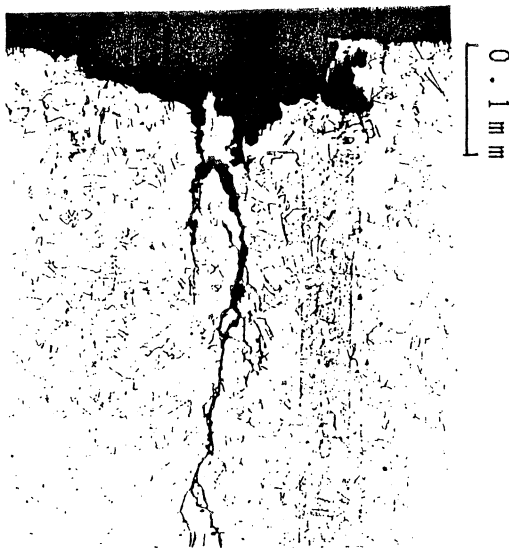


Photo 1. Electron micrograph of metal cross-section showing crevice corrosion SCC

Photo 2. Electron micrograph of metal cross-section showing direct penetrating SCC

Table 1. Results of corrosion tests on stainless steel in a cooling-water environment (*1)

Type	Baffle crevices	Tube plate crevices
304 (3 tubes)	Crevice corrosion (*2) Maximum depth 0.16 mm (3/24) (*3)	Crevice corrosion Maximum depth 0.25 mm (5/6)
316 (1 tube)	None (0/24)	None (0/6)
444 (1 tube)	None (0/8)	Crevice corrosion Maximum depth 0.12 mm (1/2)

(*1) Test duration: 5 years. Heat exchange conditions: process fluid inlet temperature 60°C, shell-side water flow, cooling water flow speed 0.3 m/sec, implementation of process-side chemical cleaning (2-3 times/year, 80°C, shell-side falling water)

(*2) Corrosion form: pitting corrosion, no occurrence of SCC found

(*3) Values in ()s show the proportion of occurrence of corrosion in parts subject to the same conditions

As this case shows, in a neutral low-concentration chloride ion environment the occurrence of SCC often propagates from a point of origin caused by crevice corrosion or pitting. It further demonstrates that SCC can occur even in the apparent safe region for the occurrence of SCC indicated in Figure 6.

Case 2

This case is an example of SCC that occurred when selection of the material of construction for a new piece of equipment was being made. The equipment is used for treating resin containing chlorine with fluorine-based solvent. In this process, under the environmental conditions of No. 1 in Table 2, TGSCC occurred extensively. This type of TGSCC progressed directly from the surface as shown in Photo 2 and not via crevice corrosion; it is hereafter called direct penetrating SCC. Also, pitting was found in SUS329J2L.

These results prompted a search for a suitable solvent composition that would give a less corrosive process environment. A new set of environmental conditions were determined, No. 2, and once again corrosion tests by immersion were carried out. No corrosion occurred, not even crevice corrosion, in the second environment.

In this case, the process conditions could be changed so that SCC (and pitting) were checked. Since TGSCC was of the direct penetrating type, measures such as prevention of crevice corrosion are inadequate, and it was considered necessary to drastically change the environment or change the materials of construction.

3-3. Material factors

There are two materials approaches on how to prevent SCC.

- i) Fundamental method:
Use an alloy having a Ni content of 45% or more, or a ferritic stainless steel
- ii) Retarding methods:
Use a stainless steel or alloy such as type 316, type 329J4L or type 20-25MT: (see Table 4.) (that have good resistance against crevice corrosion)

The Copson diagram,⁽⁵⁾ Figure 7, was determined from corrosion tests in an environment of boiling magnesium chloride. It shows that in a high-temperature (about 150°C) chloride environment, SCC neither occurs in materials that contain at least 45% Ni, nor in materials that contain no Ni (ferritic stainless steels). Thus, the

Table 2. Corrosion tests results of Case 2

Test	Environmental conditions			Results of immersion tests	
	Solvent	Alcohol	Temperature	type 316	type 329J4L
No. 1	A	Present	80°C	SCC	Pitting
No. 2	B	Absent	40°C	No corrosion	No corrosion

Testing conditions: test pieces bent into a U shape, immersed for 100 hours

selection of either of these is considered a rational approach for preventing SCC in many environments. But it is not always clear whether the criterion in Figure 7 will also be applicable for chloride environments in which the temperature exceeds 150°C, and confirmation is considered necessary.

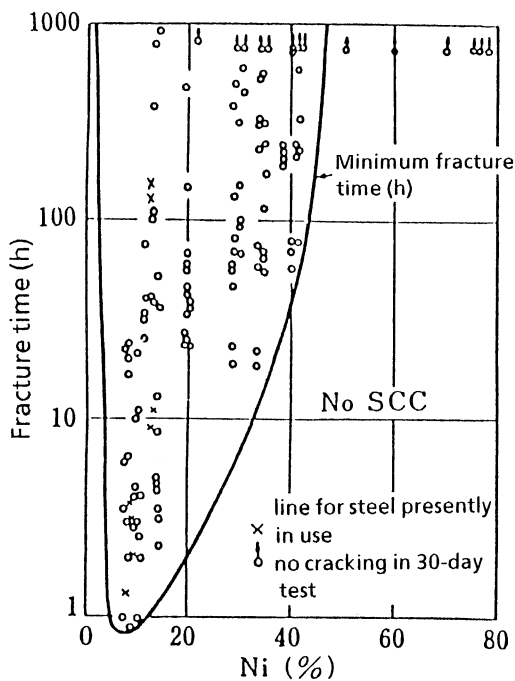


Fig. 7. SCC fracture time of Fe-Cr-Ni wire in an environment of 42% boiling $MgCl_2$ ⁽⁵⁾

On the other hand, when SCC occurs in existing equipment that has been in use for a long period of time (although it depends on the length of time that elapses before it occurs, and on its extent), the cost of changing over to a material that contains at least 45% Ni is prohibitive. Further, in many cases a ferritic stainless steel is not adopted because of its poor weldability. In addition, SCC that occurs over a long period of time often is of the type that starts in a crevice. Thus, even if it is impossible to completely prevent SCC as in

Case 1, the measures listed in ii) are sometimes adopted for the purpose of retarding its occurrence for long periods of time.

3-4. Stress factors

Often in stainless steels there is as much welding residual stress or residual stress from processing as the yield stress of the material, and these stresses often are at a higher level than the operating stress. (With tube made of type 329J4L, processing residual stress of about 20 kg/mm² has been measured). In an attempt to reduce these two types of stresses, shot peening,⁽⁶⁾ the selection of appropriate welding methods and the improvement of pipe fabrication methods (reduction of processing residual stress) are being tried. But, at present these stress-related measures are often adopted only as a supplementary means as compared with the other approaches involving changing the environment or selecting a more SCC-resistant material. In the future, it is expected that the effects of stress-related measures will become clearer as data is accumulated in chemical plants and elsewhere.

4. CONCLUSION

The foregoing discussion of aspects relating to environment, material, and stress are summarized in Table 3. Even with the same TGSCC, if its mode is of the type via crevice corrosion, its occurrence will be difficult to clarify when selecting a material; there are many cases where the damage becomes apparent only after a relatively long time (such as 5-10 years). Moreover, in cases where

SCC occurs in existing plants, it is difficult to rationally improve the environment or to make a major change in the material (such as to use material that has a Ni content of 45% or more), so measures are adopted that lie within the range of the possible.

On the other hand, when TGSCC of the direct penetrating type occurs, the damage becomes apparent in a relatively short time (several days to a year), and in many cases the

extent of the damage is substantial. In such cases it becomes necessary to take radical measures concerning the environment or the material, as in Case 2. Thus, different measures are adopted for prevention of SCC, depending on its mode, the extent of its occurrence, and the importance of the equipment. These factors are classified qualitatively in Table 3.

Table 3. Transgranular stress corrosion cracking (TGSCC) measures for austenitic stainless steels

	Direct penetrating type stress corrosion cracking	Crevice corrosion mediated stress corrosion cracking
Environment	Lowering temperature Lowering Cl ⁻ concentration (example: using pure water for the cooling water) Raising pH Reducing oxidativeness (removing oxygen in solution, changing type of metallic ions) Cathodic corrosion prevention (Al plating) Corrosion-resistant design (eliminating structural crevices, eliminating parts that get repeatedly wet and dry out, etc.)	Making it difficult for crevices to form (example: in a cooling-water environment, increasing the flow speed, changing the route of flow, adding dispersants) Corrosion-resistant design (eliminating structural crevices, eliminating parts that get repeatedly wet and dry out, etc.) Improving environment (lowering temperature, reducing Cl ⁻ concentration) Cathodic corrosion prevention (Al plating)
Material	Using 45% + Ni alloys Using ferritic stainless steels Using mild steels (in some cases)	Using pitting-resistant materials (type 316, type 20-25MT:) Using two-phase (duplex) stainless steels (type 329J4L)
Stress	Using member material that has low processing residual stress (low-residual-stress pipes) Selecting correct welding methods (water-flow cooling)	Shot-peening the welds Heat treatment after welding (risk of sensitization)
Remarks	When material for a new plant is being selected, or shortly after the plant beings operation	After long period (at least several years) of use in an existing plant

Table 4. Stainless alloys standards and main compositions (wt. %)

Type	JIS	UNS	C	Ni	Cr	Mo	Else compo.
304	SUS304	S30400	<0.08	8.00-10.5	18.00-20.00	–	
316	SUS316	S31600	<0.08	10.00-14.00	16.00-18.00	2.00-3.00	
20-25MTi	–	N08320	<0.05	25.00-27.00	21.00-23.00	4.00-6.00	Ti>C×4
444	SUS444	S44400	<0.025	–	17.00-20.00	1.75-2.50	Ti, Nb, Zr
329J4L	SUS329J4L	S31260	<0.03	4.50-7.50	22.00-26.00	2.50-4.00	N:0.08-0.30

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