

# Development of NSSC<sup>®</sup> 420J1M—a Highly Corrosion-resistant Martensitic Stainless Steel for Cutlery

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## Abstract

*The martensitic stainless steel, NSSC 420J1M, was developed for cutlery knife. The corrosion resistance of SUS420J1 was deteriorated by precipitation of Cr carbide during air hardening. In the case of developed steel, sensitization was suppressed by increase of nitrogen and reduction of carbon. It would contribute to the productivity improvement with customer that the heating temperature to obtain quenching hardness necessary for knife usage could be lowered.*

## 1. Introduction

As the principal materials for cutlery, stainless steels are used for reasons of sanitation. To cite specific examples, austenitic stainless steels (e.g. SUS304) are generally used for spoons and forks, while martensitic stainless steels (e.g. SUS420J1) are commonly used for knives. Such marks as “18-8” and “18-10” impressed on the back of spoons and forks indicate stainless steel grades, 18-8 representing 18%Cr-8%Ni and 18-10 representing 18%Cr-10%Ni (both SUS304 stainless steels). SUS420J1 (13%Cr-0.2%C) is inferior to SUS304 in terms of corrosion resistance. When quenched, however, it affords the high wear-resistance required of knives.

There are several forms of table knives. Some knives are of solid construction having a blade and a handle in one unit. Others are of separate construction with a hollow handle. Still others have a handle made of resin. For the handle of two-part knives, SUS304 or some stainless steel other than the one used for the blade is used. Unlike table knives, kitchen knives and special knives are made of stainless steel from the SUS440 series, which is harder than SUS420J1 and contains more carbon and chromium. In this paper, we discuss the use of SUS420J1 for common table knives.

Since table knives are cleaned after use, it is extremely rare for corrosion to become a problem with them. Recently, however, there have been cases in which detergents with a high chloride concentration are used in dishwashers. As a result, corrosion of table knives has become more of a problem than in the past. Accordingly, we

evaluated the corrosion resistance of various types of table knives available on the market and studied ways to improve their corrosion resistance. On the basis of the study results, we developed NSSC 420J1M, which is equal or superior to SUS420J1 in hardenability, and has better corrosion resistance.

This paper describes the results of our evaluation of the corrosion resistance of table knives available on the market and the salient qualities of NSSC 420J1M.

## 2. Corrosion Resistance and Mode of Corrosion of Table Knives

The interior of a dishwasher was assumed to be the corrosive environment for table knives, and the salt spray test specified in JIS Z2371 was adopted as the corrosion test method simulating said environment. Comparing the salt spray test conditions with the conditions inside a dishwasher, the test temperature is set to 35°C, which is lower than the temperature inside the dishwasher, but the salt (NaCl) concentration specified for the test is about 5 percent, which is higher than that inside the dishwasher. It was considered, therefore, that the salt spray test could be used to roughly evaluate the corrosion resistance in a corrosive environment.

Domestic and imported table knives were subjected to the salt spray test for four hours. The results are shown in **Fig. 1**. In the corrosive environment mentioned above, rust was observed on all the knives, although there was a tendency for low-carbon stainless steels to exhibit relatively mild rust. Some of the table knives that

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were tested were of separate construction, and the hollow handles made of SUS304 were free of corrosion. Even knives made from the same stainless steel material showed noticeable differences in the degree of corrosion. This was considered due to the influence of manufacturing conditions. In many cases, martensitic stainless steels are air-hardened since they can effectively be quenched even in the air. However, if the air cooling rate is excessively low or the tempering temperature is inappropriate, it is thought that carbide  $(CrFe)_{23}C_6$  precipitate in the grain boundaries and Cr-depleted zones occur in their neighborhood, causing so-called sensitization—the phenomenon whereby the material’s sensitivity to intergranular corrosion increases. In the case of solid-type knives, in particular, it was considered that the air-cooling rate would decrease at their handle, which can be as thick as 6 to 8 mm.

Therefore, in our laboratory, we prepared test pieces of 6-mm thick SUS420J1 plate and subjected them to a salt spray test. The test pieces were prepared as follows. First, the plate was heated at 1,050°C for 10 minutes. Next, it was subjected to air hardening or oil quenching. Finally, the plate surface was subjected to #600 grinding with SiC paper. The appearance of each of the test pieces after the salt spray test is shown in Fig. 2. The air-hardened specimens corroded, whereas the oil-quenched ones were free from corrosion. The origin of corrosion on an air-hardened specimen and on the knives was observed under a microscope. The observation results are presented in Fig. 3. Both the knife and the specimen revealed inter-

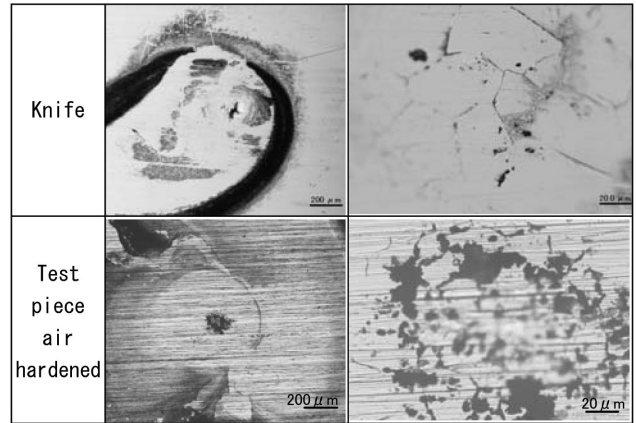


Fig. 3 Intergranular corrosion appeared on SUS420J1 after salt-spray test for 4 hours

granular corrosion grooves around the pits, suggesting that sensitization had occurred during air hardening. Namely, it was considered that Cr-based carbides had precipitated in the grain boundaries and, as a result, Cr-depleted zones were formed in their neighborhood, causing the corrosion resistance of the steel to deteriorate.

### 3. Guidelines on Development of New Stainless Steel with Better Corrosion Resistance

It has been reported that in order to restrain the sensitization of stainless steel, it is effective not only to reduce the content of carbon but also to add nitrogen. For example, concerning the effect of solute nitrogen on intergranular corrosion, there are various reports in studies carried out using austenitic stainless steels. According to those reports, nitrogen improves the resistance to sensitization of stainless steel<sup>1)</sup>, and helps restrain the decrease of Cr concentration in the grain boundaries<sup>2)</sup>. Since the sensitization temperature when a martensitic stainless steel is hardened is in the single-phase region of austenite before the martensite transformation, it was considered that nitrogen would have beneficial effects similar to those mentioned above.

In order to obtain the quench hardness required of martensitic stainless steel, an appropriate amount of carbon is necessary. For SUS420J1 stainless steel, JIS specifies that the carbon content shall be 0.16 percent to 0.25 percent. However, it was considered possible to secure the required quench hardness by substituting nitrogen for carbon.

Therefore, in the development of a new material for table knives, we placed the primary emphasis on restraining the sensitization of stainless steel during air hardening. By optimizing the C-N balance of the present SUS420J1, we could develop and bring to market a new stainless steel, NSSC 420J1M, which has the same hardenability as SUS420J1, but with better corrosion resistance.

### 4. Quality Characteristics of NSSC 420J1M

#### 4.1 Specimens

As specimens, 6-mm thick hot-rolled and annealed plates of NSSC 420J1M and SUS420J1 were used. The chemical composition of NSSC 420J1M is shown in Table 1. Characteristically, NSSC 420J1M contains a larger proportion of nitrogen and a smaller proportion of carbon than SUS420J1 (0.2%C-0.015%N). Nitrogen is an element which improves pitting resistance. As an index of pitting resistance, pitting resistance equivalent (PRE) given by Equation (1) has been proposed as follows.





	Type of stainless steel	Blade part of knife
1	SUS420J1 (13. 2Cr-0. 2C)	
2		
3	SUS420J2 (13. 5Cr-0. 3C)	
4	--- (14. 3Cr-0. 5C)	

Fig. 1 Appearance of knives after salt-spray test for 4 hours



	SUS420J1
Air hardning	
Oil quenching	

Fig. 2 Effect of quenching method on corrosion resistance of SUS420J1 ( salt-spray test for 4 hours )

Table 1 Chemical compositions of NSSC 420J1M (mass%)

	C	Si	Mn	P	S	Cr	Ni	N
Range	0.15 - 0.17	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.03	13.00 - 14.00	0.20 - 0.60	0.04 - 0.06
Typical	0.16	0.51	0.43	0.025	0.01	13.3	0.23	0.0533

$$PRE = \%Cr + 3.3 (\%Mo) + 16 - 30 (\%N)^{3,4} \quad (1)$$

Since the nitrogen content of NSSC 420J1M is approximately 0.04 percent higher than that of SUS420J1, the PRE of NSSC 420J1M is about 0.6 to 1.2 more than SUS420J1. In the quality evaluation described below, stainless steel products manufactured by actual production equipment were mainly used. In some of the tests carried out for the evaluation, however, stainless steels (13%Cr-0.05%N-0.10 to 0.18%C) prepared in the laboratory were also used for reference.

#### 4.2 Evaluation of various characteristics

##### 4.2.1 Hardenability

The heating temperature was varied between 950°C and 1,150°C, and the specimens were air-hardened after they were maintained at each of these temperatures for 600 seconds. A Vickers hardness tester was used to measure the hardness of each specimen. The hardness was measured at five points using a test force of 9.8N and the average hardness was obtained. In addition, with the aim of measuring the influences of amounts of solute C and N on quench hardness, each specimen was quenched at two different cooling rates—air cooling and water cooling—after it was held at 1,050°C for 600 seconds, and then the hardness of the specimen was measured. At the same time, the amounts of insoluble Fe, Cr and N in the specimen were measured by an extractive residue analysis using the SPEED method. Furthermore, the carbide composition of each specimen was analyzed using the CALPHAD method (Thermo-Calc ver. S, Data Base TCFE5) and compared with the measured composition. The presence or absence of residual austenite in the hardened structure was evaluated by X-ray diffraction.

##### 4.2.2 Corrosion resistance

The corrosion resistance of NSSC 420J1M was evaluated using the following conditions. For (1) salt spray test (JIS Z2371) and (2) pitting potential (JIS G0577), a 6-mm thick flat plate was heated at 1,050°C for 600 seconds and air-hardened or oil-quenched. Then, the entire surface of the plate was ground with #600 SiC paper. For (3) oxalic acid etching test (JIS G0571) and (4) sulfuric acid/cupric sulfate corrosion test, each specimen in the form of a strip was heated at 1,050°C for 600 seconds by a high-frequency induction heater and then cooled down to room temperature at a rate of 1°C to 70°C per second. In the sulfuric acid/cupric sulfate corrosion test, since the Cr concentration of the steel to be evaluated is low, a test solution (0.5 wt% H<sub>2</sub>SO<sub>4</sub> + approx. 6 wt% CuSO<sub>4</sub> + Cu chips)<sup>5)</sup>, the sulfuric acid concentration of which is lower than that specified in JIS G0575, was used and the specimen surface was ground to #600 as in tests (1) and (2).

## 5. Test Results

### 5.1 Hardenability

Fig. 4 shows the relationship between the hardening temperature and hardness of NSSC 420J1M and SUS420J1, respectively. The quench hardness of SUS420J1 sharply increases with the rise in hardening temperature from 950°C to 1,100°C. By contrast, the change in quench hardness of NSSC 420J1M in that temperature range is small. The hardness of NSSC 420J1M reaches about 450HV at a hardening temperature of 950°C. This was considered to be due to the fact that

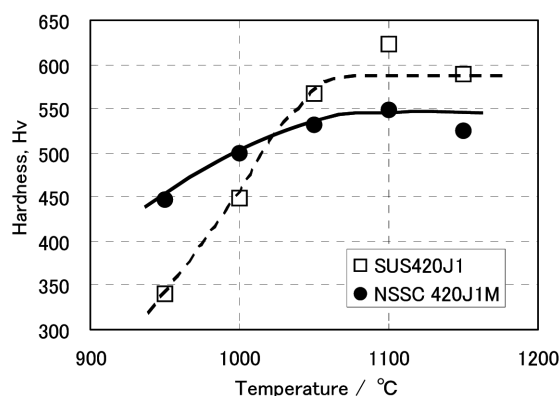


Fig. 4 Effect of solution treatment temperature on hardness of martensitic 13% Cr steels, solution-treated for 600s and then air hardened

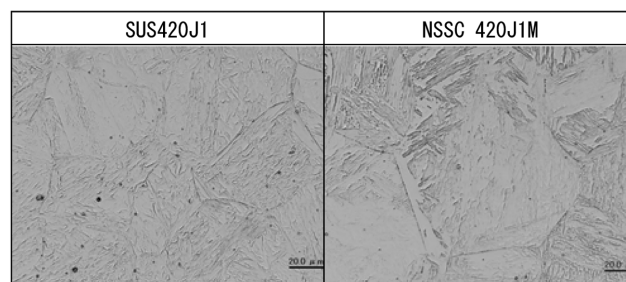


Fig. 5 Optical micrographs showing martensitic structure of steels, solution-treated for 600s at 1,050°C and then air hardened

the solution treatment temperatures for the carbides and nitrides in NSSC 420J1M are lower than those of SUS420J1. Fig. 5 shows the hardened structures of the two steels at 1,050°C. The entire structure of each of the steels was martensite, containing no ferrite. X-ray diffraction revealed no residual austenite.

Concerning the influence of carbon on the hardness of martensite that contains insoluble carbides, Tsuchiyama et al.<sup>6)</sup> presented the following equation for 12-percent Cr steel:

$$Hv = 25 + 1250\sqrt{[C]} + 500 (C - [C]) \quad (2)$$

(0.11% < C < 0.34%, [C]: solute carbon)

In addition, it has been reported that the influence of solute nitrogen is 0.4 to 1.0 times that of carbon<sup>7,8)</sup>. Therefore, we studied the effects of solution-precipitated C/N on quench hardness using NSSC 420J1M and the reference steels (SUS420J1 (0.2%C-0.016%N) and steels prepared in the laboratory (13Cr-0.10% to 0.18%C-0.05%N)). An extractive residue analysis revealed that all the steels contained insoluble carbide M<sub>23</sub>C<sub>6</sub> and that nitrides in the steels had been dissolved almost completely.

Fig. 6 shows the amounts of Fe and Cr in the above carbide. The Cr/Fe ratio was constant, at about 1.66, regardless of the cooling conditions during hardening. SUS420J1 contained a larger amount of insoluble carbide than the reference 0.05-percent N steel, and air-

hardened SUS420J1 contained still more insoluble carbide than water-hardened SUS420J1. As an example, Fig. 7 shows the composition and calculated full-solution temperature of  $M_{23}C_6$  in NSSC 420J1M. It can be seen that the higher the temperature, the lower the Cr concentration becomes. We interpreted this as follows. Although the steel was heated at 1,050°C—higher than the calculated full-solution temperature of 928°C—for 10 minutes before quenching, the carbides did not completely dissolve into solution within that time, causing carbides of relatively low Cr concentration to remain.

Fig. 8 shows the influence of the solute carbon/nitrogen in martensitic 13-percent Cr steel, obtained from the amounts of precipitated carbide/nitride, on the hardness of the steel. The air-hardened specimen is not as hard as the water-quenched specimen. This was considered to be due not only to the smaller amount of solute carbon but also to the progress of tempering of the martensite as a result of slow cooling below the  $M_s$  point. Next, we analyzed the influence of insoluble carbides on hardness taking into account the influence of solute nitrogen on hardness on the basis of Equation (2). As a result, it was found that there was a good correlation between insoluble carbide and hardness as shown in Fig. 9. Since there were only two different levels of nitrogen content in the specimens, it is insufficient to make an accurate comparison of the influence between nitrogen and carbon. However, the contribution of solute nitrogen atoms to

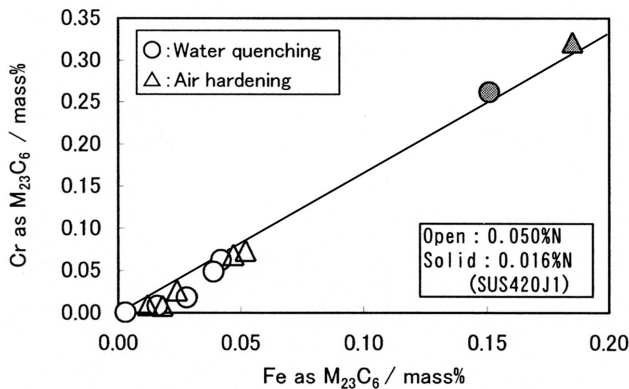


Fig. 6 Ratio of Fe, Cr content in insoluble carbide extracted from hardened specimens

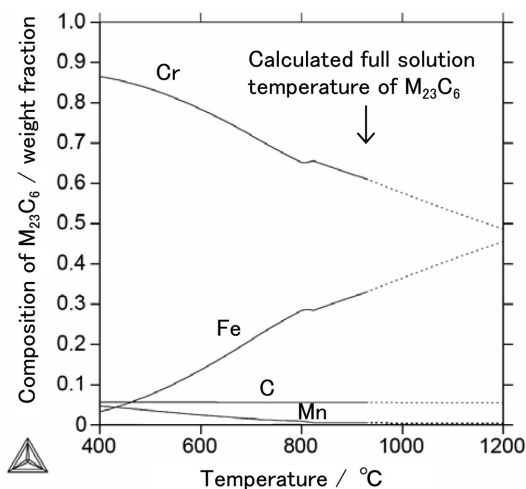


Fig. 7 Effect of solution treatment temperature on composition of  $M_{23}C_6$  in NSSC 420J1M

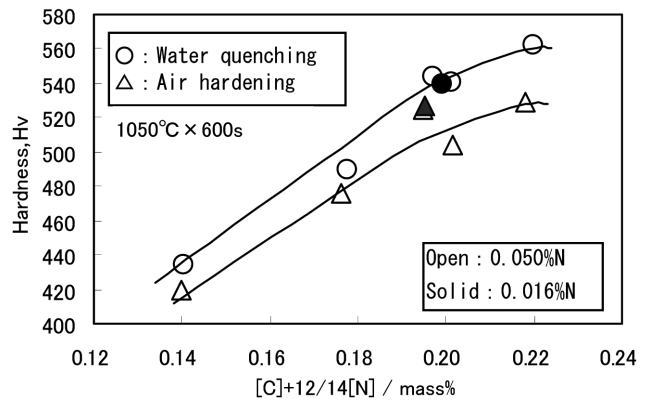


Fig. 8 Effect of solute carbon [C] and nitrogen [N] on hardness of martensitic 13%Cr steels

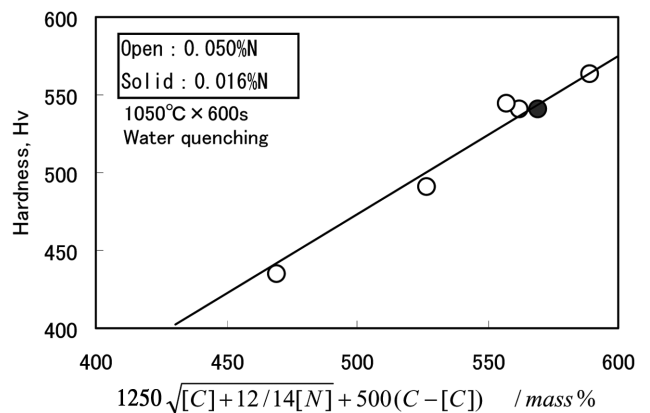


Fig. 9 Effect of solute carbon [C], nitrogen [N] and insoluble carbon on hardness of martensitic 13%Cr steels

the hardness of martensite was comparable to that of carbon.

### 5.2 Corrosion resistance

The results of a salt spray test on air-hardened NSSC 420J1M specimens are shown in Fig.10. The specimens were free from the pitting accompanying intergranular corrosion that was observed on the SUS420J1 specimens. Fig.11 shows the measured pitting potential of NSSC 420J1M, together with that of the laboratory-prepared reference steels, which differ in carbon content. The pitting potential varies according to the carbon content. We considered that when the carbon content is on the low side, the pitting potential decreases as the sensitization of steel is promoted by the residual ferrite and that when the carbon content is on the high side, the pitting potential decreases as the increase in the amount of insoluble carbide sensitizes the steel and thereby causes intergranular corrosion.

On the other hand, the pitting potential of the oil-quenched specimens was 0.15 to 0.26 V for the 0.10 to 0.18%C-0.05%N steels and 0.06 to 0.20 V for SUS420J1 (0.21%C-0.016%N) steel. Thus, as long as the PRE was the same, the pitting potential did not change significantly, regardless of the carbon content. We interpreted this as follows. The specimens that substitute N for C showed an improvement in PRE because the decrease in the amount of Cr caused by insoluble carbides during quenching was small and because the amount of solute nitrogen was appreciably large. All this helped improve the pitting potential slightly during oil quenching.

Next, we carried out an oxalic acid etching test to study the influ-

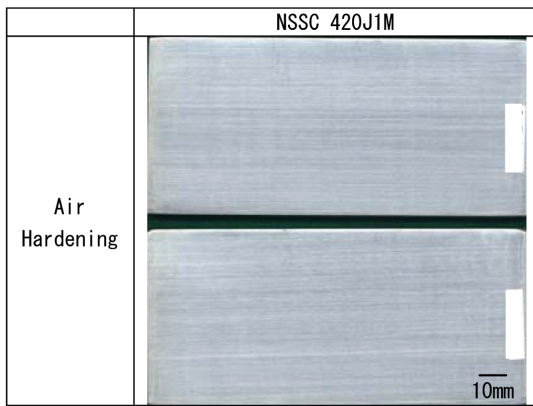


Fig. 10 Appearance of air hardened NSSC 420J1M test pieces after salt-spray test for 4 hours

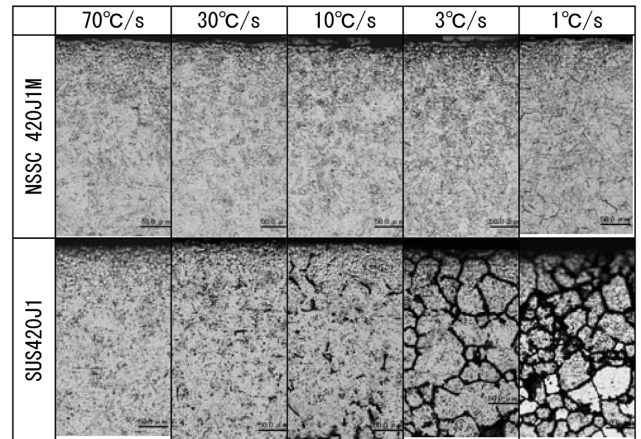


Fig. 12 Optical micrographs showing the effect of cooling rate on corrosion resistance of martensitic 13%Cr steels (oxalic acid etching test)

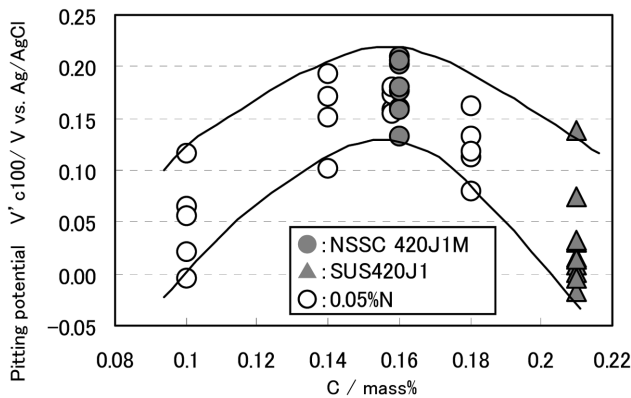


Fig. 11 Effect of carbon content on pitting potential of martensitic 13%Cr steels after solution treated at 1 050°C for 600s and then air hardened

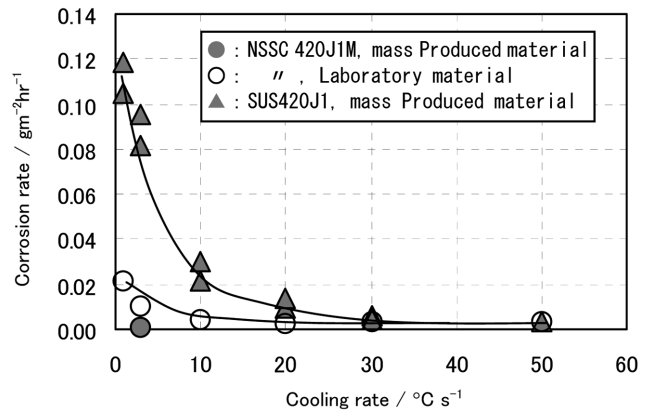


Fig. 13 Effect of quenching rate on corrosion resistance of martensitic 13%Cr steels in copper sulfate-sulfuric acid

ence of the cooling rate during quenching on the corrosion resistance of the specimens. The test results are shown in Fig.12. In addition, the results of a sulfuric acid/cupric sulfate corrosion test we also carried out are shown in Fig.13. In the sensitization temperature range, both NSSC 420J1M and SUS420J1 consist entirely of austenite before martensitic transformation. Nevertheless, SUS420J1 clearly revealed intergranular corrosion grooves even at a cooling rate of 10°C/s, whereas NSSC 420J1M was free from intergranular corrosion even at a cooling rate as low as 3°C/s.

In the sulfuric acid/cupric sulfate corrosion test too, the difference between the two steels was conspicuous. With the decrease in cooling rate, the corrosion loss in weight of SUS420J1 increased. The corrosion of this steel was especially conspicuous when the cooling rate was 10°C/s or less. In the case of NSSC 420J1M too, the corrosion increased with the decrease in cooling rate. Even so, the degree of corrosion was about one tenth that of SUS420J1. The specimens that were subjected to the salt spray test mentioned above were 6-mm-thick air-hardened steel plates. In the salt spray test, the average cooling rate from 1,050°C down to 400°C was about 3°C/s at which the difference in corrosion resistance between the two steels became conspicuous. When rapid cooling (e.g. oil quenching) is applied, the difference in corrosion resistance between the two steels narrows down. When it comes to manufacturing table knives using air-hardened steel, however, we considered that the advantage of

NSSC 420J1M having better corrosion resistance than SUS420J1 would become self-evident.

## 6. Conclusion

In this paper, we have described the general corrosion resistance of table knives made from SUS420-series martensitic stainless steel. In addition, we have described NSSC 420J1M, which has better corrosion resistance than SUS420J1, because steel sensitization during air hardening is effectively restrained.

It is now clear that many table knives available on the market corrode even in short salt spray tests, that the mode of corrosion is pitting accompanied by intergranular corrosion, and that the corrosion is apparently caused by the sensitization of steel during air hardening, etc. in the manufacturing process, but this can be restrained by oil quenching.

In addition, as a martensitic stainless steel which displays excellent corrosion resistance even with air hardening, we have developed NSSC 420J1M that utilizes nitrogen effectively. By carrying out various types of tests, we have demonstrated that the corrosion resistance of NSSC 420J1M is relatively unaffected by the cooling rate during hardening. NSSC 420J1M is now being mass-produced as stainless steel for table knives.

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