UDC 669 . 14 . 018 . 8 - 416 : 62 - 224

# Development of Stainless Steel Sheets for Cylinder Head Gasket

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### Abstract

Stainless steels with high strength and high fatigue strength for cylinder head gasket were developed to contribute to development of conventional automobiles and improvement of environment. In this paper, practicable steels were presented, fine grained metastable austenitic stainless steel "NSSMC-NAR-301L HS1 (HS1)", ultra-fine grained metastable austenitic stainless steel "NSSMC-NAR-301L HSX (HSX)" by nitrogen absorption treatment, and economical martensitic stainless steel "NSSMC-NAR-403 2D-Q (2D-Q)". (1) HS1 has average grain diameter within  $1.5 - 2.0 \mu m$ . The fatigue strength of HS1 is improved more than 30% as compared to one of conventional steel (SUS 301). (2) HSX has average grain diameter within  $1.2 \mu m$  near surface. The fatigue strength of HSX is improved around 20% as compared to one of HS1, with improvement of age hardening for increment of combustion pressure. (3) 2D-Q have average grain diameter around 10  $\mu m$ after quenching from dual-phase area at high temperature. The anisotropy of tensile properties in 2D-Q is improved as compared to one of temper rolled SUS 304.

#### 1. Introduction

The engine of an automobile is divided into a cylinder head ("head") and a cylinder block ("block"). A cylinder head gasket ("gasket") is inserted between the head and the block to prevent leaks of the high-pressure combustion gas, cooling water, etc. inside the engine. Until the 1990s, asbestos had been largely used for gaskets. In recent years, however, stainless steel sheets having high performance and durability, thinly coated with rubber on the surface, are widely used to prevent the leakage of internal fluids.

The construction of an automotive engine including a gasket is shown in **Fig. 1**. The gasket is generally composed of several layers of thin sheets. A convex part called a bead is press-formed around the combustion chamber to separate and seal the internal fluids by repulsive force. Therefore, a metastable austenitic stainless steel having both high strength and good formability is employed for gaskets. Stainless steels for gasket are characterized by the marked hardening that accompanies a strain-induced martensitic transformation. Ordinarily, they are cold-rolled into sheets approximately 0.2 mm in thickness and are then subjected to adjustment of the mechanical properties (temper rolling).<sup>1-3)</sup>

The stresses that act upon the gasket bead are shown in Fig. 2.





When the gasket is built in the engine, it is first sandwiched between the head and block as shown in Fig. 1, following which it is clamped tightly from both sides with bolts. Therefore, a high tensile stress occurs locally in the bead foot, etc. While the engine is running, the head is pushed up, creating a gap between the head and the block.

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Fig. 2 Tensile stress at bead of gasket during engine running

However, the bead follows up the head movement by elastic deformation to maintain the required sealing performance. At this moment, the tensile stress in the bead foot decreases. Thus, since a large repetitive tensile stress acts locally in the bead foot, adequate fatigue strength is also required of the material for bead. It is considered that the range of variation of the repetitive tensile stress is generally proportional to the amount of gap between the head and the block.<sup>3)</sup>

The number of automobiles sold still continues to increase, mainly in the NIES. In view of the aggravating global environmental problems, automakers are actively studying ways to improve the fuel efficiency of their cars and to reduce the  $CO_2$  emissions and other environmental pollutants. To those ends, it is effective to increase the combustion pressure (improve the combustion efficiency) and reduce the engine weight. On the other hand, reducing the engine weight can cause engine rigidity to decrease. Furthermore, the above measures tend to increase the gap created between the head and block. Therefore, the gasket material requires higher static strength and higher fatigue strength. Namely, an important task of every material maker is to develop high-performance materials that meet the abovementioned needs.

Incidentally, it has been clarified by Katsurai et al. that although the fatigue strength of the material (flat one) before it is made into a bead has a positive correlation with the static strength of the material,<sup>4</sup>) fatigue strength of the gasket does not always have a positive correlation with static strength.<sup>3</sup>) This is due to a fatigue fracture of the gasket originating in surface irregularities of a plastic-deformed part formed at the bead foot, i.e., the part subject to a stress concentration. To correctly evaluate any gasket material, it is necessary to establish a dependable fatigue test method that permits evaluating the influence of stress concentration in the material.

Another important task of materials maker is to develop resourcessaving type materials that consume lesser amounts of rare metals. This task is concerning certain environmental problems. Nippon Steel & Sumitomo Metal Corporation and other materials makers have already been tackling the task. Specifically, at present, it is effective to develop new martensitic stainless steels that do not contain Ni—one of the principal constituents of metastable austenitic stainless steels and an expensive element specified as a rare metal and that allow for heat treatment for obtaining such high strength as required to increase the combustion pressure of the engine.<sup>5</sup>

To carry out the above task, Nippon Steel & Sumitomo Metal has been pressing ahead with the development of new stainless steels for high-performance gaskets and the establishment of a fatigue strength evaluation method to expand the application scope of these new materials.<sup>6)</sup> This report describes "NSSMC-NAR-301L HS1,"<sup>7.9)</sup> a practical fine-grained stainless steel having high fatigue strength, "NSSMC-NAR-301L HSX,"<sup>10, 11)</sup> an ultrafine-grained version of HS1 having higher static strength and fatigue strength attained by nitrogen absorption, and "NSSMC-NAR-403 2D-Q,"<sup>5)</sup> an economical martensitic stainless steel.

#### 2. Features of Newly-developed Materials and Comparison of Properties between New and Conventional Materials

#### 2.1 NSSMC-NAR-301L HS1—a fine-grained stainless steel having high fatigue strength

The occurrence of microcracks during the forming of a bead is considered to be influenced by grain boundaries. Namely, it is expected that such microcracks will be restrained by increasing the grain boundary density in grain refinement and thereby dispersing uneven grain deformations at the grain boundaries. It is widely known that refining grains is an effective technique to increase the material strength without causing the material ductility to decrease much.

It has been reported that in the case of metastable austenitic stainless steels, including SUS301 used for gaskets, a fine-grained structure can be obtained through strain-induced martensitic transformation during cold working, and through reverse transformation to the mother phase of austenite during subsequent heat treatment.<sup>12, 13)</sup> To utilize that mechanism on a stable basis, (1) SUS 301L with low C content and high N content was selected as the raw material to prevent the fluctuation of  $\gamma$  stability caused by carbide precipitation and the deterioration of corrosion resistance caused by formation of a Cr-deficient layer in lowering the heat treatment temperature, (2) the material was added with Nb to restrain the growth of grains by the pinning effect of precipitates, and (3) the stability of austenite was optimized by adjustment of the alloying elements. Table 1 shows a typical example of chemical composition of NSSMC-NAR-301L-the base material for NSSMC-NAR-301L HS1 ("HS1"). The microstructure of heat-treated HS1 observed under a transmission electron microscope (TEM) is shown in Photo 1. HS1 has a unique fine-grained structure composed of equiaxed grains (average size:  $1.5 - 2.0 \,\mu$ m) having a low dislocation density, together with several parts leaving signs of the influence of working done before the heat treatment.

NSSMC-NAR-301L was subjected to temper rolling to adjust its hardness to 430-490 HV, equivalent to JIS G 4313 "H" specification for SUS 301, which is most widely used for gaskets. **Figure 3** shows the influence of average equiaxed grain size after heat treatment on the relationship between elongation and stress, obtained with tensile test specimens subjected to hardness adjustment. Both the elongation and maximum stress increase with the refinement of grains and reach their maximum when the grain size is  $1.8 \ \mu$ m. It should be noted, however, that the elongation decreased markedly when the grain size was  $0.8 \ \mu$ m. More than 50% of the material shows signs of the influence of working done before the heat treatment. Namely, it is considered that the heat treatment was insuffi-

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 Table 1
 Chemical compositions of NSSMC-NAR-301L (mass%)

С	Si	Mn	Cr	Ni	N	Nb
0.02	0.49	1.35	17.3	6.6	0.12	0.05



Photo 1 TEM image of NSSMC-NAR-301L HS1 after annealing



Fig. 3 Effect of grain size after annealing on relationship between elongation and stress in temper rolled NSSMC-NAR-301L (460HV)

cient to fully obtain the effect of grain refinement and, as a result, the elongation markedly decreased. **Figure 4** shows the relationship between hardness and elongation, obtained with the new finegrained steel and SUS 301 (conventional steel) after temper-rolling. It can be confirmed that the newly-developed steel is superior in hardness-elongation balance to the conventional steel.

Figure 5 shows the results of a fatigue test of HS1 gaskets temper-rolled to hardness around 460 HV.7) In the figure, "x" indicates that a fatigue crack through the specimen occurred after 10<sup>6</sup> cycles of prescribed gap displacement represented by the vertical axis, whereas "o" indicates that such a fatigue crack did not occur. With the refinement of grains, the newly developed steel increases in maximum amount of gap displacement ("critical gap displacement") within which the steel is free from fatigue cracks. It can be seen that the critical gap displacement of the newly developed steel is more than 30% larger than that of the conventional steel. Figure 6 shows the microstructures of cross sections of heat-treated steel samples observed under an optical microscope and the appearances of bead feet. In the case of the newly developed steel, microcracks in the surface of bead foot are restrained. Namely, the refinement of grains helped maintain a smooth surface of bead foot, thereby reducing the local tensile stress. Based on the above results, the grain size of HS1 was decided to be  $1.5 - 2.0 \,\mu m$  as mentioned earlier.

Table 2 shows examples of mechanical properties of HS1,



Fig. 4 Relationship between hardness and elongation on temper rolled sheets



Fig. 5 Effect of grain size on displacement of limit gap by fatigue test (10<sup>6</sup>cycles)



Fig. 6 Microstructure after annealing and surface of bead foot

Table 2 Mechanical properties of NSSMC-NAR-301L HS1

0.2% Y.S. (MPa)	T.S. (MPa)	Elongation (%)	Hardness HV
1,280	1,350	15.0	450

which was temper-rolled to the H specification (430 to 490 HV) for SUS 301.

# 2.2 NSSMC-NAR-301L HSX—an ultrafine-grained stainless steel having superior performance

On the basis of our experience in the development of HS1 described above, in developing NSSMC-NAR-301L HSX ("HSX"),

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we discussed further refinement of grains in the surface layer of steel through utilization of nitrogen absorption, paying our attention to the sheet surface deformed most during bead formation and cyclically subject to maximum tensile stress while the engine is running. In addition, to permit increasing the combustion pressure, we studied low-temperature age hardening utilizing the heating process for rubber coating after bead formation.

As in the case of HS1, the base steel for HSX is NSSMC-NAR-301L. The process for manufacturing HSX is schematically shown in **Fig. 7**, which shall be referred to in the following explanation. In the intermediate annealing, the base steel is made to absorb nitrogen in a nitrogen–hydrogen gas atmosphere. **Figure 8** shows the microstructure of the steel after the intermediate annealing and a line profile of the steel obtained by an electron probe microanalyzer (EPMA). Because of the increase in solute nitrogen as a result of nitrogen absorption, the austenite phase in the surface layer of the intermediately annealed steel was stabilized. In addition, the steel contained a martensite phase which was considered to have been strain-induced during surface grinding. From the result of the EPMA analysis, an increase in nitrogen concentration in a surface layer approximately 100  $\mu$ m in thickness can also be confirmed. As in the case of HS1, the intermediately annealed steel is subjected to coldrolling to effect the strain-induced martensitic transformation.

TEM images of the steel after the final annealing are shown in **Photo 2**. Observed in the surface layer are precipitates of many fine particles of the Cr-N compound. Here, equiaxed grains (average size: approximately  $1.2 \mu m$ ) having a low dislocation density had been formed. By contrast, the steel interior had few precipitates and was nearly the same in microstructure as HS1. Thus, grains in the surface layer could be further refined. After cold-rolling, the steel is subjected to temper-rolling to adjust its hardness to the "H" specification (430 to 490 HV) for SUS 301. **Table 3** shows examples of mechanical properties of the HSX.

Next, in order to strengthen the steel so as to allow for a higher combustion pressure in the engine, we studied the hardening of the steel by aging heat treatment taking the rubber coating into consideration. The age hardening characteristic of the HSX is shown in **Fig. 9**. It can be seen that the HSX sufficiently age-hardens at 200°C. This temperature corresponds to the baking and vulcanizing condition for rubber coating. Thus, it is possible to further strengthen the HSX without adding any age-hardening process in the manufacturing of gaskets.

Figure 10 shows the influence of combustion chamber internal pressure on the sealing performance of HSX gaskets.<sup>10</sup> The sealing





Fig. 8 Microstructure and line-profile of EPMA after intermediate annealing



Photo 2 TEM images of NSSMC-NAR-301L HSX after final annealing

Table 3 Mechanical properties of NSSMC-NAR-301L HSX

0.2% Y.S. (MPa)	T.S. (MPa)	Elongation (%)	Hardness HV
1,363	1,399	6.0	465



Fig. 9 Effect of aging temperature (300s) on hardness in NSSMC-NAR-301L HSX



Fig. 10 Relationship between cylinder pressure and seal ability of developed steels

1.0*µ*m

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Fig. 11 Effect of grain size on displacement of gap by fatigue test (10<sup>6</sup>cycles)

pressure was so adjusted that it became the same as the value when the gasket was installed in the engine. The sealing pressure when the combustion chamber internal pressure was increased was measured and indicated in terms of the pressure drop rate. Against the increase in combustion chamber pressure, the HSX gaskets show higher sealing performance than the HS1 gaskets. Figure 11 shows the results of a fatigue test of HSX gaskets. As in Fig. 5, "×" indicates that a fatigue crack through the sheet occurred after  $10^6$  cycles of prescribed gap displacement, and "o" indicates that such a fatigue crack did not occur in the fatigue test. The HSX was superior in fatigue strength to the HS1. It excelled in strengthening by grain refinement, which follows the Hall-Petch relationship, and achieved a 20% improvement in critical gap displacement. Those enhancements in performance are considered attributable at least in part to the strengthening of the steel by fine precipitates in the surface layer shown in Photo 2 and Fig. 9.

#### 2.3 NSSMC-NAR-403 2D-Q

As mentioned earlier, metastable austenitic stainless steels are widely used for gaskets. Although those steels can easily be strengthened by a martensitic transformation induced by cold working, they are not inexpensive because they contain approximately 7mass% Ni, which is specified as a rare metal. On the other hand, martensitic stainless steels, the principal component of which is 13Cr, can be strengthened by quenching and are economical because they do not contain costly Ni. Therefore, we developed a new martensitic stainless steel, NSSMC-NAR-403 2D-Q ("2D-Q"), with 13Cr as the principal component.

**Table 4** shows a typical chemical composition of the NSSMC-NAR-403 steel. An example of microstructure of 2D-Q observed under an optical microscope is shown in **Photo 3**. 2D-Q has a two-phase structure consisting mainly of martensite grains and partly of ferrite grains having an average size of approximately 10  $\mu$ m. **Figure 12** shows the relationship between martensite fraction and hardness/elongation, obtained with 2D-Q after quenching. The strength of 2D-Q can be controlled by adjusting the proportions of martensite and ferrite phases under suitable quenching conditions. **Table 5** shows examples of mechanical properties of 2D-Q.

**Figure 13** compares tensile properties between 2D-Q and SUS 304, both having a hardness of approximately 370 HV. It can be seen that 2D-Q is higher in strength and better in ductility than temper-rolled SUS 304, showing smaller anisotropy in mechanical properties. Namely, 2D-Q is expected to be capable of sealing the combustion gas effectively and efficiently. This is considered due in

Table 4 Chemical compositions of NSSMC-NAR-403 (mass%)

С	Si	Mn	Р	S	Cr
0.13	0.30	0.45	0.026	0.03	12.4



Photo 3 Microstructure of NSSMC-NAR-403 2D-Q



Fig. 12 Relationship between martensite fraction and hardness, elongation on NSSMC-NAR-403

Table 5 Mechanical properties of NSSMC-NAR-403 2D-Q



Fig. 13 Anisotropy of tensile properties on NSSMC-NAR-403 2D-Q and temper rolled SUS 304 (370HV)

part to the fact that it is not elongated grains stretched in the rolling direction but equiaxed grains that are retained in the sheet as a result of the quenching that accompanies a transformation.

# 3. Establishment of Fatigue Strength Evaluation Method

To develop high-performance stainless steels that are suitable for gaskets, it is necessary to accurately grasp the fatigue strength of gaskets made from them. With this in mind, efforts have been made to establish a convenient method of evaluating the fatigue strength of gaskets. An example is given below.<sup>6</sup>

In general, either axial load or bending load is used in a fatigue test of a steel sheet. For example, a method of fatigue test using bending load is specified in JIS Z 2275: Method of Plane Bending Fatigue Test of Metallic Sheets. However, with a flat test piece, it is impossible to evaluate the influence of microcracks which occur in the surface during the formation of a bead. Besides, even if a test piece having a formed bead is used, it is difficult to simulate the dynamic condition of an actual engine when a simple axial load or bending load is applied to the gasket sandwiched between the head and the block.<sup>3)</sup>

Therefore, to accurately evaluate the fatigue strength of a gasket, we studied an evaluation method in which a ring-shaped bead simulating an actual gasket is first formed on the stainless steel sheet and then a cyclic load appropriate to the working environment of the actual engine as shown in **Fig. 14** is applied to the bead. The shape and dimensions of a fatigue test piece are shown in **Fig. 15**. The test piece is a disk provided with a hole simulating a combustion chamber in the center and with a ring-shaped bead 0.1 mm in height around the hole. After forming the bead using prescribed dies, we reshaped it by compression before the test so that it would not be subjected to excessive plastic deformation by compression at the early stages of the test. In the fatigue test, an electro-hydraulic servo fatigue tester was used.

**Photo 4** shows the appearance of the tester and the construction of the testing jig. First, the test piece is positioned on the lower part of the jig and fixed at the outer periphery. Then, a cyclic compres-



Fig. 14 Load wave form for fatigue test



Fig. 15 Shape and dimension of fatigue specimen with bead

sive load is applied to the bead by the upper part of the jig. The fatigue test was carried out in the open air at room temperature under controlled load. The load waveform used was a 20-Hz sine wave. The maximum compressive load was kept at 40 kN in view of the condition of coupling between the head and the block and the noncombustion state of the engine, and the minimum compressive load was varied between 1.5 and 5.0 kN. The relative displacement between the upper and lower parts of the testing jig that corresponds to the amount of gap displacement was accurately measured using a differential transformer type displacement gauge. During the fatigue test, the presence or absence of a fatigue crack in the test piece cannot be confirmed. Therefore, after  $2 \times 10^6$  cycles of repetitive loading, the test piece was taken out from the jig and the bead foot was checked for a fatigue crack under an optical microscope. Figure 16 shows an example of fatigue cracking. In this particular example, the fatigue crack occurred in the bead foot, indicating that the repetitive compressive fatigue test reproduces stress load conditions for actual gaskets.

Figure 17 shows the results of a repetitive compressive fatigue test. The maximum displacement at which no fatigue cracks occurred is indicated by a horizontal line. In terms of the marginal displacement for fatigue cracking, HS1 is approximately 6  $\mu$ m higher than SUS 301. As in the fatigue test results obtained with actual gaskets (Fig. 5), the HS1 improves the fatigue strength of gaskets by approximately 30%.

#### 4. Conclusion

We have been pressing ahead with the development and commercialization of new environment-friendly stainless steels for highperformance gaskets that can be widely applied to automobiles. In this report, we have described "NSSMC-NAR-301L HS1" ("HS1"), a fine-grained metastable austenitic stainless steel, "NSSMC-NAR-301L HSX" ("HSX"), an ultrafine-grained stainless steel utilizing



Photo 4 Testing apparatus



Fig. 16 Fatigue crack at bead foot



nitrogen absorption, and "NSSMC-NAR-403 2D-Q ("2D-Q") utilizing an economical martensitic stainless steel.

- (1) HS1 attained a grain size as small as  $1.5-2 \mu m$  and fatigue strength approximately 30% higher than that of SUS 301.
- (2) HSX has attained a still smaller grain size of 1.2  $\mu$ m in the sur-

face layer by means of nitrogen absorption. Thanks to age hardening that allows for higher combustion pressure, it has fatigue strength approximately 20% higher than that of the HS1.

(3) The 2D-Q maintains an average grain size of approximately 10  $\mu$ m by means of quenching in the two-phase region. It has reduced the anisotropy in tensile properties of temper-rolled SUS 304.

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