

Development of Ultra-fine Grained Stainless Steel by Nitrogen Absorption Treatment for Gaskets

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ABSTRACT

Desirable attributes for a material used in a cylinder head gasket are the strength required to form a combustion gas seal and sufficient fatigue strength such that the gasket may operate properly during engine operation. The high combustion pressure characteristic of diesel engines in particular creates a severe environment for the gaskets, necessitating the achievement of high levels of strength and fatigue in the material. In order to satisfy these requirements, a method of exploiting the difference in the solubility limit of the nitrogen in the martensite and austenite structures that form the composite structure of SUS301L stainless steel to enable the precipitation of Cr_2N by means of the application of an aging treatment to supersaturated nitrogen was examined. The achievement of high workability and refinement of the grains are effective in increasing fatigue strength. Workability was increased by employing a nitrogen absorption treatment in the intermediate annealing process to produce an austenite structure as the surface structure. In addition, the pinning effect of the precipitated Cr_2N during annealing refined the grains.

These innovations have enabled the development of a gasket displaying approximately 40% higher seal ability and an approximately 20% increase in fatigue limit in fatigue tests than those of a gasket formed from conventional materials.

1. Introduction

As the necessity of reducing the environmental impact of automobiles increases, the impetus towards the reduction of emissions of CO_2 , a leading factor in global warming, is increasing in pace. The achievement of increased fuel economy is an effective method of reducing CO_2 emissions, and sales of vehicles fitted with higher fuel efficiency diesel engines are increasing, in particular in Europe.

One major characteristic of diesel engines is their high combustion pressure. Because of this, the cylinder head gasket ("head gasket" below) which seals the combustion chambers is required to display reliable sealing performance in diesel engines.

As shown in Fig. 1, head gaskets are normally constructed from multiple thin sheets that are 0.2 mm in thickness and feature machined beads. The combustion chambers are sealed by the load reaction force of the beads. High strength is therefore a requirement of gasket materials. In addition, combustion pressure causes the cylinder head to lift when the engine is operating, and a

repeated stress is generated in the beads in response to this lift. High fatigue strength is therefore a further requirement of gasket materials.

The beads are formed in the thin steel plates that make up the gaskets by pressing. As shown in Fig. 2, a localized machining stress is generated in the surface layers of the steel plates during formation, resulting in a reduction of the fatigue strength of the gasket⁽¹⁾. This reduction in fatigue strength is caused by the occurrence of tiny cracks in the grain boundary due to machining stress. Refinement of the grain boundary and the achievement of a high level of workability are therefore effective methods of achieving high fatigue strength.

Based on the discussion above, the characteristics required of head gasket materials can be summarized as follows:

- (1) High strength and high fatigue strength when used in an engine
- (2) High workability when the component is machined

This means that antagonistic characteristics are required during engine operation and during machining.

This paper will discuss research on the further

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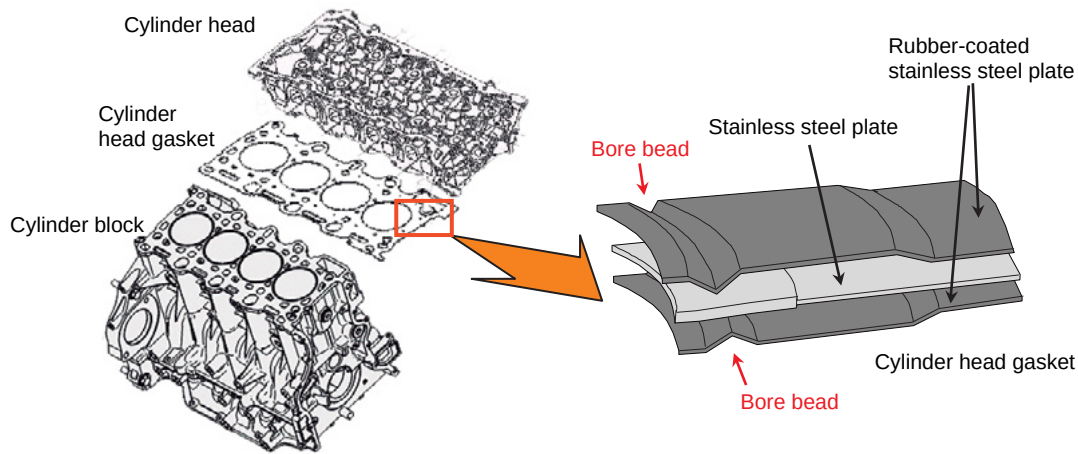


Fig. 1 Illustration of cylinder head gasket

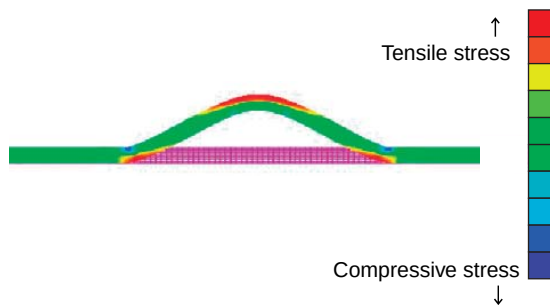


Fig. 2 Distribution of stress in section of bead-formed sheet

refinement of the grain size and the use of heat treatment following machining to increase the strength of the material as methods of reconciling these antagonistic characteristics, and will also discuss the composition and method of manufacture of the materials required to enable this.

2. Research on the Achievement of High Strength and Verification of Effect

2.1. Research on the Achievement of High Strength

Solution hardening, precipitation hardening, work hardening, and transformation hardening are the standard methods of increasing strength. SUS301, a metastable austenite stainless steel, is the main material used in the manufacture of head gaskets. This is a reliable material in which the necessary strength is provided by the transformation of austenite structures into hard, work-induced martensite structures during cold working. The project discussed here studied the possibility of achieving further strength increases by using other hardening methods in combination with this mechanism.

The research focused on the structural change occurring in SUS301L steel. The characteristics of the structures in the steel differ; one specific point of

difference is the difference in the solubility of elements in them. Interstitial solid elements generally display high solubility in austenite structures, which have large spaces in their crystal lattices, and low solubility in martensite structures, which have small spaces in their crystal lattices. This research studied the potential for exploiting this characteristic in order to achieve high strength in the material by aging at low temperatures as a method of promoting the precipitation of the interstitial solid elements that are supersaturated in the martensite structures following cold working.

Carbon (C) and nitrogen (N) are the normal interstitial solid elements present in this steel, but N was selected in this research due to the fact that the precipitation of C in the compound Cr_{23}C_6 would result in the formation of a chromium depletion layer, reducing the required corrosion resistance of the stainless steel.

2.2. Effect of the Aging Precipitation of Cr_2N

The project studied the effect of precipitation in NAR-301L HS1⁽¹⁾, a stainless steel that is employed in the production of gaskets and contains approximately 0.1% nitrogen. Figure 3 shows the change in hardness of NAR-301L HS1 after aging following final cold rolling. At the low temperature of 200°C the material displays a hardness increase of approximately HV40, reaching a hardness of HV520 following the completion of aging. Figure 4 shows the precipitates in the material following dissolution and removal of the parent phase, as observed using a transmission electron microscope (TEM). As Fig. 5 shows, electron beam and EDX analysis show that high quantities of fine Cr_2N are dispersed in the material following aging.

This indicates that the supersaturated N in the work-induced martensite has formed a compound (Cr_2N) with the Cr present in high quantities (approximately 17%) in the material and has precipitated during low-temperature aging hardening. Figure 6 shows the relationship between

the amount of martensite in the material and its hardness following aging. The hardness of the material following aging is proportional to the quantity of martensite. This is thought to be because the area of precipitation of Cr_2N increases with increased martensite content, a result that matched expectations.

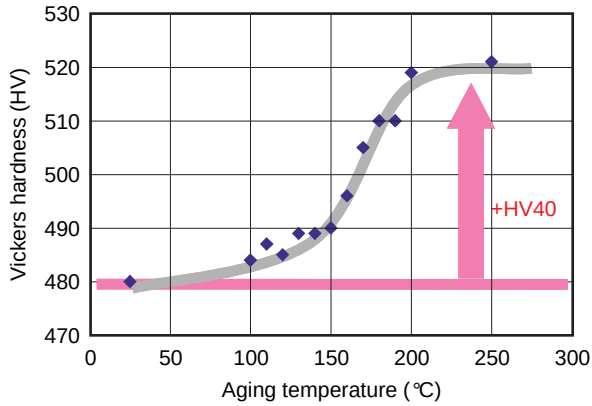


Fig. 3 Relationship between Vickers hardness and aging temperature in NAR-301L HS1

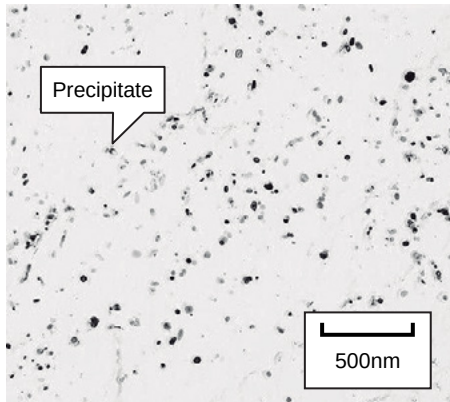


Fig. 4 TEM image of NAR-301L HS1 after aging treatment

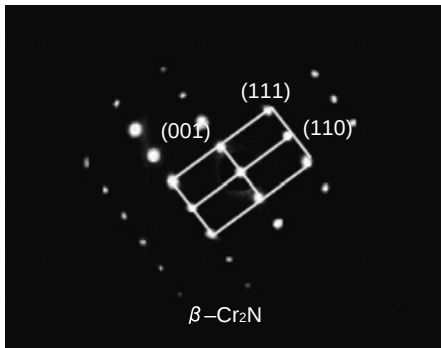


Fig. 5 Identification of precipitates by electron beam diffraction pattern

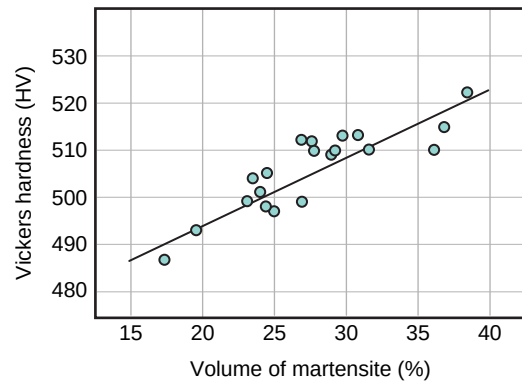


Fig. 6 Relationship between volume of martensite and Vickers hardness after aging treatment

3. Research on the Achievement of Increased Fatigue Strength and Verification of Effect

3.1. Research on the Achievement of Increased Fatigue Strength

As previously indicated, the refinement of the crystal grains in the surface layer of the steel plates used in the manufacture of head gaskets is an effective means of increasing fatigue strength. This method was therefore studied in this research. A method that involves heating the work-induced martensite structures to promote their reverse transformation into austenite and recrystallization⁽²⁾⁻⁽⁴⁾ is available as a method of refining the crystals in SUS301L stainless steel. This method is already applied to the NAR-301L HS1 steel mentioned above⁽¹⁾, and, by optimizing both the rolling conditions prior to final annealing and final annealing conditions, results in the achievement of a grain diameter of approximately 2 μm , around one-tenth the average grain diameter of a normal stainless steel. In order to achieve further refinement of the grains, in addition to this method, the research discussed here studied the use of the pinning effect of the precipitated substances to control grain growth during recrystallization.

3.2. Research on Methods of Precipitation

Bright annealing in a non-oxygenated environment is widely used as a technique that enables stainless steels to retain their surface gloss. A mixture of hydrogen and nitrogen is widely used as the ambient gas in this process. Because of this, a large amount of research has been conducted on nitrogen absorption, which is expected to increase corrosion resistance, among other effects^{(5),(6)}.

Figure 7 shows the process of manufacture of NAR-301L HS1. Low temperatures are employed in the final annealing process, compared to the other annealing processes, in order to control grain growth and achieve fine grains. Because the solubility limit of nitrogen in

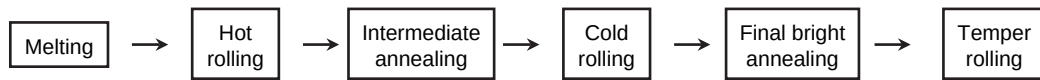


Fig. 7 Production process of NAR-301L HS1

steels is generally proportional to temperature⁽⁷⁾, if the temperature of the intermediate annealing process is set higher than that of the final annealing process, the difference in the solubility limit of nitrogen at each temperature would enable nitrogen precipitation to be exploited. The method selected in this research was therefore to promote precipitation of supersaturated nitrogen during a low-temperature final annealing process following the absorption of high quantities of nitrogen in a high-temperature intermediate annealing process.

3.3. Refinement of Grains Using Nitrogen Absorption and Precipitation and Effect of Aging Precipitation

Based on the research in Section 3.2., a mixture of hydrogen and nitrogen was employed as the environment for the intermediate annealing process. Figure 8 shows the structure of the material following intermediate annealing. Analysis of a cross-section using an optical microscope shows high austenite stability from the surface to a depth of approximately 70 μm . This is due to the absorption of nitrogen, an element that stabilizes austenite, by the surface layer. Abrasive stress has promoted the transformation of the austenite into work-induced martensite in the deeper layers which did not absorb nitrogen. As Fig. 9 shows, analysis using an electron probe micro-analyzer (EPMA) indicates that the austenite structures have absorbed approximately 0.3% nitrogen, three times the amount in the parent material. This figure is close to the solubility limit of nitrogen at the temperature employed in intermediate annealing, and a pinning effect due to the precipitation of Cr_2N in the final annealing process can therefore be expected.

Figure 10 shows the results of study of the area close to the surface layer and the center of the steel plates using transmission electron microscopy. While the average grain diameter at the center of the plates was approximately

2.0 μm , an ultra-fine grain structure was achieved close to the surface layer, with an average grain diameter of 1.2 μm . In addition, a higher amount of precipitation of compounds occurred close to the surface layer. Electron beam and EDX analysis showed the precipitated substances to be Cr_2N compounds as in the case of the aging discussed above.

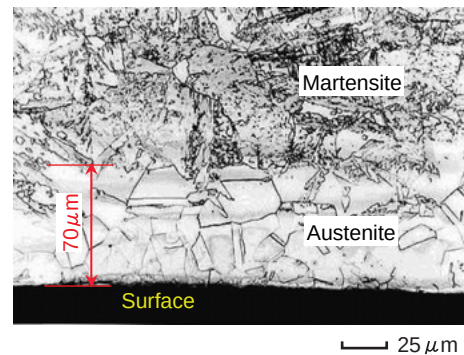


Fig. 8 Optical microscope image of surface structure after intermediate annealing process

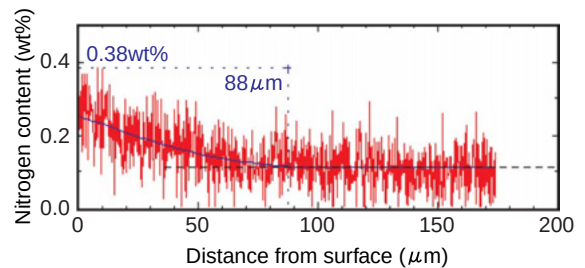


Fig. 9 Result of nitrogen content by EPMA

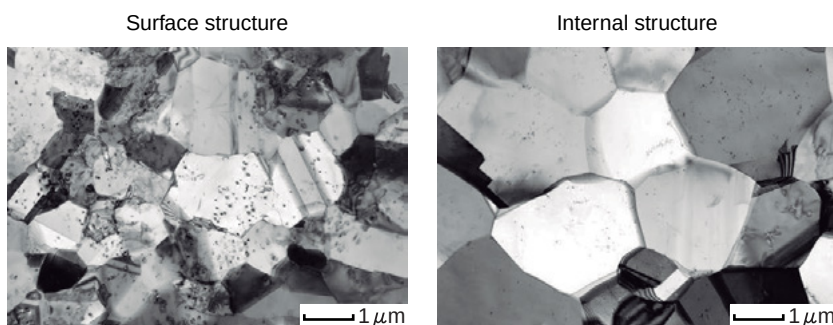


Fig. 10 TEM images of surface and internal structure after final annealing process

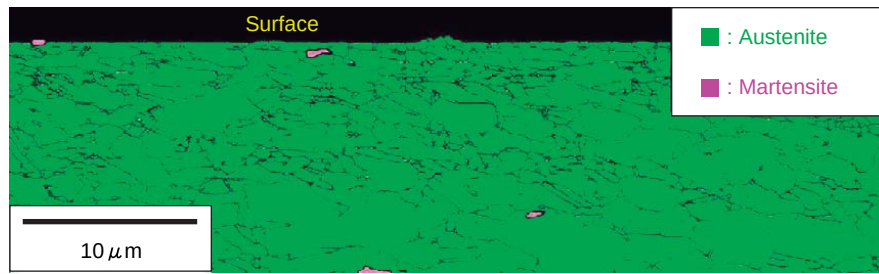


Fig. 11 Phase identification in surface structure after final annealing by EBSD analysis

Figure 11 shows the results of a study of the structure of the material using an electron back scattering pattern (EBSP). The grains in the surface layer are finer than those in the center of the plates, and the grains are almost all in the austenite phase.

This matches the requirement for a gasket material, and indicates that the austenite structure has been stabilized by the absorption of nitrogen, a powerful austenite stabilizer, making it possible that the austenite structures will help ensure that the material maintains superior workability.

4. Verification of Characteristics of Developed Material

4.1. High Strength and High Fatigue Strength

Exploiting the difference in the solubility limit of nitrogen in the austenite and martensite structures that form the composite structure of SUS301L steel, the supersaturated nitrogen in the martensite structures was precipitated as Cr_2N using low-temperature aging as a method of achieving high strength. This resulted in an increase of around HV40 in hardness, representing an increase of approximately 20% in strength.

The absorption of nitrogen into the layers of the plates contiguous to the surface layer during intermediate annealing was employed to achieve high fatigue strength. Reducing the temperature of the final annealing process against the temperature of intermediate annealing enabled the difference in the nitrogen solubility limit to be exploited. Supersaturated nitrogen was precipitated as Cr_2N during the final annealing process, and the pinning effect of this Cr_2N resulted in the refinement of the grains to a diameter of approximately $1.2 \mu\text{m}$. In addition, nitrogen is a powerful austenite stabilizer, and the fact that the structures in the surface layer are austenite structures helps ensure a high level of workability.

In order to effectively exploit these characteristics, the material was aged following machining of the beads, producing a gasket material that balanced the antagonistic characteristics of high strength and high workability.

4.2. Effect of Employment of Material in Component

Figures 12 and 13 show examples of the results of testing of the sealing performance and fatigue strength of a gasket manufactured using the developed material. Aging was conducted following formation of the beads.

The gasket manufactured using the developed material displayed an increase of approximately 40% in sealing performance against a conventional gasket, and its fracture limit was approximately 20% higher in fatigue tests. In durability tests conducted using an actual diesel engine, the new gasket displayed a high level of sealing performance under conditions of high combustion pressure, in addition to high fatigue strength.

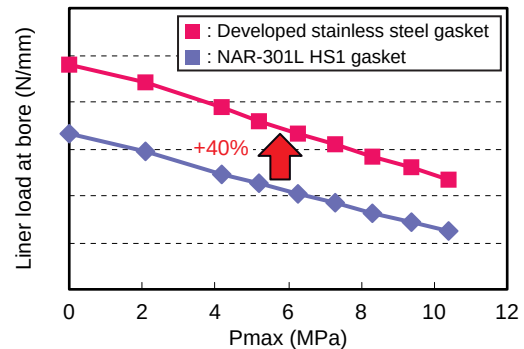


Fig. 12 Gasket sealability

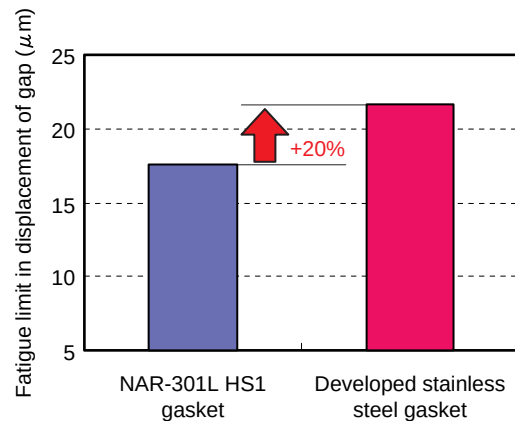


Fig. 13 Result of gasket fatigue test

5. Conclusion

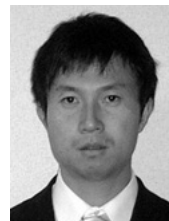
Research was conducted on the use of nitrogen absorption treatment during intermediate annealing and aging precipitation of Cr_2N in SUS301L stainless steel as methods of achieving increased gasket performance. This research produced the following results:

- (1) Nitrogen absorption treatment at high temperatures enabled the achievement of a nitrogen concentration of 0.3% and above from the surface layer of the material to a depth of 70 μm .
- (2) Precipitation of the absorbed nitrogen as Cr_2N during the final annealing process produced a pinning effect. This controlled the growth of crystal grains during recrystallization, resulting in the achievement of ultra-fine grains of approximately 1.2 μm in diameter.
- (3) Aging enabled the dispersion of the supersaturated nitrogen in the martensite as Cr_2N . This precipitation hardening enabled the achievement of high strength.
- (4) A head gasket manufactured using the developed material displayed an increase of approximately 40% in sealing performance and an increase of approximately 20% in fatigue strength against a gasket manufactured using a conventional material.

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