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Development of cobalt-free exhaust valve seat insert material for automotive engines

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Sintered materials have been widely used for valve seat inserts for automotive engines. They have possessed high flexibility in their alloying design to increase their performance in heat and wear resistance in comparison with that of conventional wrought steel and cast alloys. Especially several high cobalt containing sintered materials are used as exhaust valve seat insert materials because it's high wear and heat resistant properties. Recently, the circumstance of exhaust valve seat inserts has become sever due to A/F ratio (Air/ Fuel ratio) of recent engines is set to leaner than that of conventional. This trend is aim to reduce exhaust gases and fuel consumption. On the other hands, the reduction of use of high environmental burden materials such as cobalt has also been continually needed. This paper reports the development and the application detail of the cobalt-free and environmentally friendly exhaust valve seat insert material.

Key Wards: Powder Metallurgy, automotive, cobalt-free, valve seat insert, heat and wear resistance

1. INTRODUCTION

Exhaust valve seat inserts (VSIs) are used in such severe conditions as high temperatures, high sliding pressure and non liquid lubricant conditions. Accordingly, cobalt-contained sintered materials (material (A)), which have superior strength in high temperatures and good solid lubrication, are mainly used for exhaust VSIs. However, there is a now a demand that the use of cobalt as well as lead be reduced due to environmentally friendly point of view. In addition, cobalt has a shortcoming of a difficult of a stable supply, because cobalt is expensive and limited turn out area. Therefore, Nissan Motor Co., Ltd. and Hitachi Powdered Metals have developed a high speed steel based sintered material for exhaust VSIs (material (B)) which is both cobalt and lead free. But there still remains a subjects of machinability in mass production.

On the other hand, recently, because of the demand of further lean burn engines, it is expected that the condition which exhaust VSIs are used will be further high temperatures in the future. The development of an exhaust VSI with more superior wear resistance has been demanded. In this case, it has become apparent that exhaust VSIs need to be properly used both in the lean burn engines in the future or the conventional engines.

In this paper, the development of a new exhaust VSI with features of the following (1)-(4) will be reported; (1) a sufficient wear resistance in the conventional engines, (2) both cobalt and lead free, (3) good machinability, (4) Environmentally friendly material development and reduction in cost production.

2. CONCEPTI OF THE DEVELOPMENT FOR A COBALT-FREE VSI

Plastic flow was partially observed on the worn surface in case of endurance test on current exhaust VSIs, and adhesion of part of the VSI material on the valve face was also observed. Therefore, it was concluded that one of the factors of VSI wear was its adhesive wear caused by the sliding between the VSI and the valve face at high pressure. It was also concluded that this adhesive wear was affected by the combustion temperature, the combustion pressure and the wear surface. So, in order to obtain sufficient adhesive resistance, it was necessary to select a matrix and hard particles which have superior strength and hardness at a high temperature, lubrication and the capability to form non metallic film. The current material (A) containing cobalt shows good strength at high temperatures and good lubrication because of the existence of cobalt in the matrix and hard particles. The development objective of the new VSI material was to develop a cobalt free VSI which has comparably similar good properties at high temperatures to that of current material (A).

3. EXPERIMENTAL PROCEDURE

3.1 Materials and preparation of specimens

Some water atomized powders shown in table 1 were selected as base material and graphite were used as additive materials. Zinc stearate was added as a lubricant.

Each mixture was compacted at a pressure of 640MPa into a test specimen. Sintering was carried out in a dissociated ammonia gas at 1433K.

3.2 Evaluation method of anti−wear characteristics

Anti−wear characteristics was evaluated by using a VSI wear tester shown in Fig.1. This tester had been used for material screening.

A valve that had been used in an actual engine and specimens machined to the shape of an actual VSI were used for the VSI wear tester. The VSIs were indirectly heated by means of heating the valve.

4 SELECTION OF MATRIX

4.1 Investigation of components for the matrix alloy

In this development, high temperature hardness is considered as the main factor for the adhesive resistance. It was therefore decided to select a matrix with a high temperature hardness. Through an advance investigation, an Fe-Mo alloy was chosen as the matrix alloy, because the hardness of the Fe-Mo alloy was increased by the precipitated carbide and the decrease in hardness at a high temperature was not so critical.

4.2 Effect of molybdenum amount

A suitable molybdenum amount was also investigated. To determine the amount of molybdenum necessary in the alloy powder for a matrix, the high temperature hardness and radial crushing strength was measured using an Fe-Mo alloy with a molybdenum amount of 1.5-5.0%. Specimens were shown in Table2

Fig.2 shows the relationship between the high temperature hardness and the amount of molybdenum. The matrix hardness increased at both room temperature and at high temperatures as the amount of molybdenum was increased. The hardness of Fe-Co which is the matrix for a current material (A) is also shown in Fig.2. The hardness of the Fe-Mo alloy with the molybdenum amount of 2.1% or more was more than equal to that of Fe-Co used in a current material (A).

Fig.3 shows the relationship between the radial crushing strength and the amount of molybdenum. The radial crushing strength increased in the molybdenum amount range of 1.5-3.5%, as the amount of molybdenum was increased. However, a sample that included 5% of molybdenum had a decrease in radial crushing strength compared with that of 1.5-3.5%, molybdenum. It was assumed that the decrease in radial crushing strength was due to the precipitation of the molybdenum carbide.

Judging from these results, it was determined that the amount of molybdenum to be included in the alloy powder for the matrix was 3.5%.

5 SELECTION OF HARD PARTICLES

5.1 Concept for hard particles

It was decided that two kinds of hard particles with different hardness (the first hard particle and the second hard particle) should be dispersed. The purpose of having additional hard particles in the first hard particles was to improve the wear resistance, it was therefore necessary to select particles with high hardness for the investigated VSI. However, the more addition of hard particles ,the more decrease of sintered materials because of the difficulties of diffusion in sintering. Therefore, it was necessary to select a particle with little influence for the strength . Additionally, it was decided to choose a particle which functions as the second hard phase with high hardness between both the matrix and the first hard particles in the investigated VSI. That is, the objectives of the second hard particles should maintain the strength and to function as hard particles in the sample VSI.

It was thought that the addition of two kinds of hard particles would make it possible to increase the total amount of hard particles while keeping an efficient amount of strength. Based on this idea, the development and selection of hard particles was conducted.

5.2 First hard particle

5.2.1 Development of the first hard particles

Powders containing cobalt or ferro-alloy powders such as Fe-Mo have generally been used as additional hard particles in conventional exhaust VSIs.

A Co-Mo-Cr-Si alloy powder has also been used for a current material (A). This powder has cobalt-based hard particles forming hard phases consisting of mainly molybdenum silicide in the VSI material, and the hard phases have greatly contributed to the improvement in wear resistance.

Based on the above, it was decided to select a hard particle containing molybdenum silicide but without cobalt in consideration of the environmentally friend ness and costs. A new hard particle Fe-Mo-Si was developed as a first hard particle satisfying these requirements. The hardness of the Fe-Mo-Si was equal to that of the Co-Mo-Cr-Si alloy powder used for a current material (A).

5.2.2 Influence of Si amount

The chemical composition of Fe-Mo-Si was

Table 1 Chemical compositions of raw material powder (mass%)

	Fe	Cr	Mo	V	Si	C	
Fe-Mo	Bal.	-	1.5-5.0	-	-	-	Base iron powder
Fe-Cr-C	Bal.	12	1.0	0.8	0.4	1.5	Hard particle
Fe-Mo-Si	Bal.	-	35	-	1.4	-	

Table 2 Mixing rate of test samples (mass%)

Base powder	Hard Particles		Graphite	Lub.
Fe-Mo	Fe-Cr-C	Fe-Mo-Si		
75.0	15.0	10.0	0.65	0.5

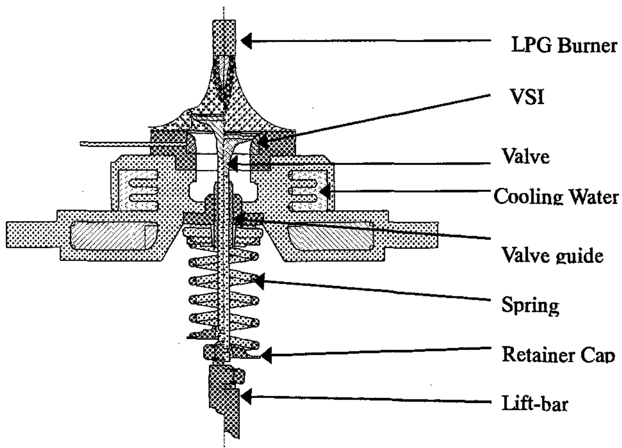

Fig.1 VSI wear test apparatus

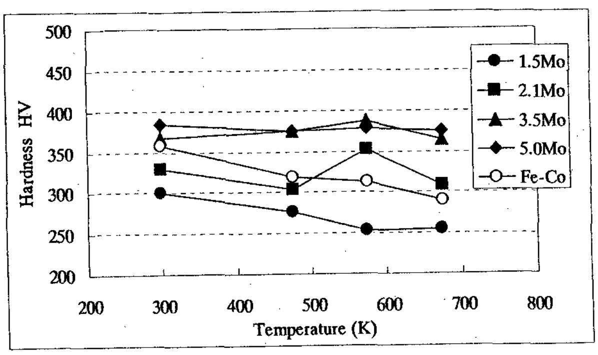

Fig.2 Relationship between high temperature hardness and amount of molybdenum

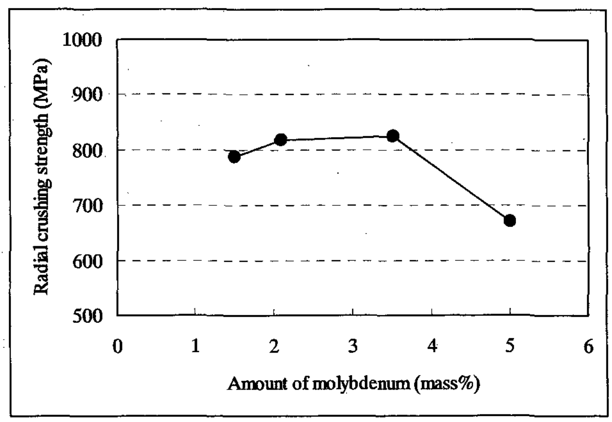

Fig.3 Relationship between radial crushing strength and amount of molybdenum

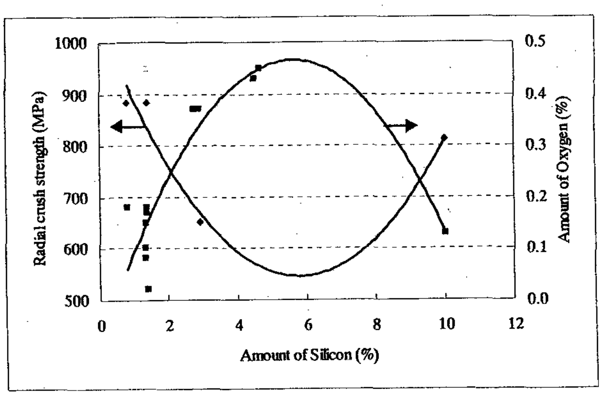

Fig.4 Relationship between radial crushing strength and the amount of Silicon, Oxygen

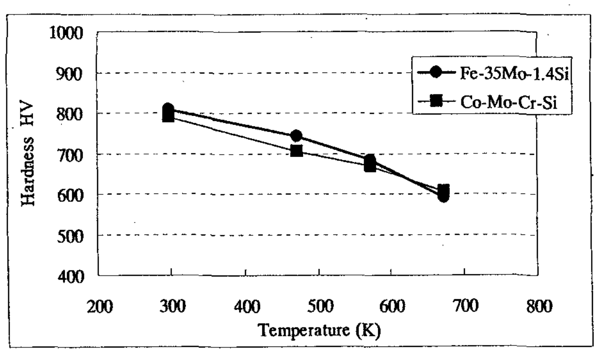

Fig.5 High temperature hardness of Fe-Mo-Si and Co-Mo-Cr-Si

determined based on the results of an investigation of the radial crushing strength, thermal conductivity, thermal expansion, proof strength, adhesion with the matrix and hardness of the hard particle phases. Especially, as it became clear in investigations that the amount of Si in the Fe-Mo-Si alloy greatly influenced several properties of the sintered body, the evaluation to decide a suitable Si amount was carried out. Fig.4 shows the relationship between the amount of Si, O and radial crushing strength. There was a good correlation between the radial crushing strength and the amount of oxygen in the hard particles. There was a tendency for the radial crushing strength to decrease, as the amount of oxygen was increased. It was considered that the cause which the radial crushing strength decreased was due to the precipitation of the silicon oxide at the grain boundary between the matrix and the first hard particles.

Fig.5 shows the high temperature hardness of Fe-Mo-Si in the new VSI. The high temperature hardness of Fe-35Mo-1.4Si at 673K was equal to that of current cobalt contained hard particles.

There was a tendency for the thermal conductivity to increase, as the amount of silicon in the particle was decreased.

As a result of the above mentioned results, the Fe-35Mo-1.4Si powder was selected as the first hard particle without containing cobalt

5.3 Second hard particle

There were two objective to adding a second hard particle; one was to increase the amount of hard particles for the improvement of wear resistance, and the other was to maintain the strength of the new VSI. An advance investigation was performed to select a second hard particle which would satisfy these two requirements, and SKD11(Fe-Cr-C) was selected SKD11 functioned as the hard phase in the new VSI, since the chromium carbide precipitated. And it was considered that the radial crushing strength increased because of the diffusion of the chromium in SKD11. In addition, the diffusion of the chromium had a secondary effect other than the above mentioned two objectives, and that was of increasing the matrix hardness facilitating the generating of an oxide film.

According to observations of the microstructure of a sintered material added SKD11, chromium carbide was observed in the SKD11 phase. The hard part where the chromium carbide precipitated was about 600 HV at the room temperature, and this hard phase has sufficient hardness as a second hard particle. Fig.6 shows the relationship between the radial crushing strength and the additional amount of SKD11. There was little decrease in the strength between the additional amount of SKD11 from 5 to 25 %. It was possible to increase the amount of the total hard particles added to the new VSI while maintaining the sufficient strength. Because the chromium in SKD11 diffused into not only the matrix but also the near Fe-Mo-Si hard particles, the hardness of Fe-Mo-Si also was increased.

5.4 Optimization of hard particles mixing ratio

The amount of additional hard particles was decided based on the results of an investigation of the radial crushing strength and wear resistance. Fig.7 and 8 shows the results of the evaluation of the wear resistance and the radial crushing strength with a difference in the additional amounts of hard particles.

It was seen that there was a tendency for the wear of the VSI to decrease, as the amount of Fe-Mo-Si was increased. And the radial crushing strength decreased linearly, as the amount of Fe-Mo-Si was increased.

It was seen that there was also a tendency for the wear of the valve seat insert to decrease, as the amount of SKD11 was increased in the range of between 5-15%. However, there was little improvement at the point of radial crushing strength where there was an addition 25%.

Judging from the results mentioned above, it was concluded that the most suitable addition of hard particles was 10% of Fe-Mo-Si and 15% of SKD11.

By means of selecting these two types of hard particles, it was possible to increase the total amount of hard particles by 25% while maintaining a sufficient strength level. As a result, a sufficient wear resistance was obtained.

6. MECHANICAL PROPERTIES

Photo.1 shows the microstructure of the new VSI material. The matrix is bainite, and the Fe-Mo-Si and SKD11 hard phases were dispersed throughout the matrix. Table3 shows the mechanical properties of the new VSI material. The manufacturing process of the new VSI material was 1P1S(single press single sintering), while the manufacturing process of the current material (A) was 2P2S(double press double sintering). Therefore, the density of the new material was lower in comparison with that of current material (A); nevertheless the new material has a high radial crushing strength and the hardness is more than equal to that of current material (A).

7. MACHINABILITY

Machinability tests of the developed material were carried out. The developed material which was impregnated with resin to improve the machinability was also evaluated. To compare it with a presently used material, a current material (A) (with a small amount of lead) and a current material (B) (with resin

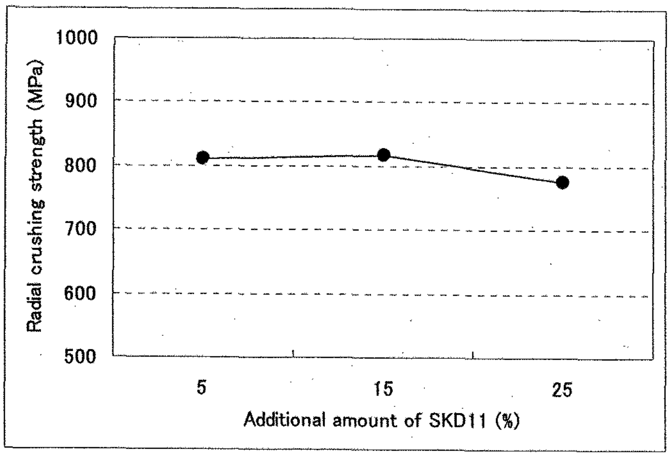

Fig.6 Relationship between radial crushing strength and the additional amount of Fe-Cr-C (SKD11)

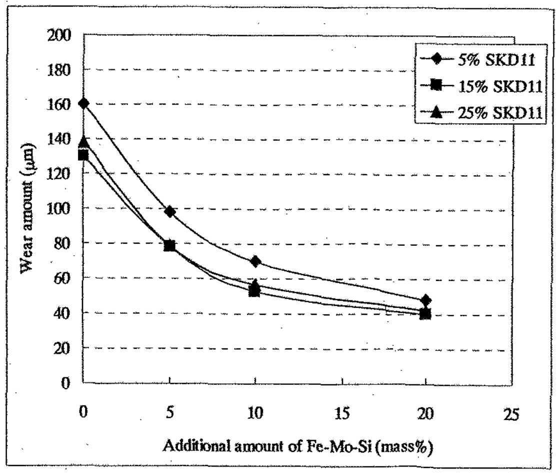

Fig 7 Relationship between wear amount and amount of hard particles

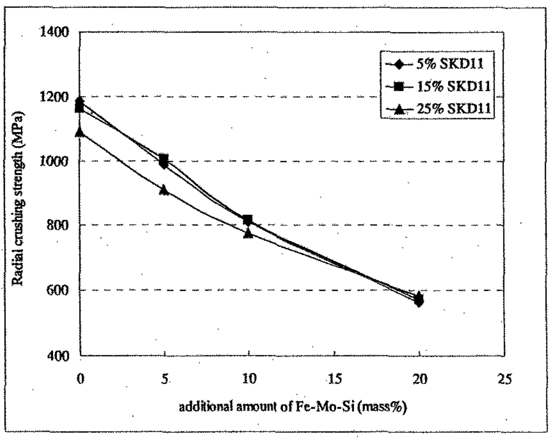

Fig.8 Relationship between radial crushing strength and amount of hard particles

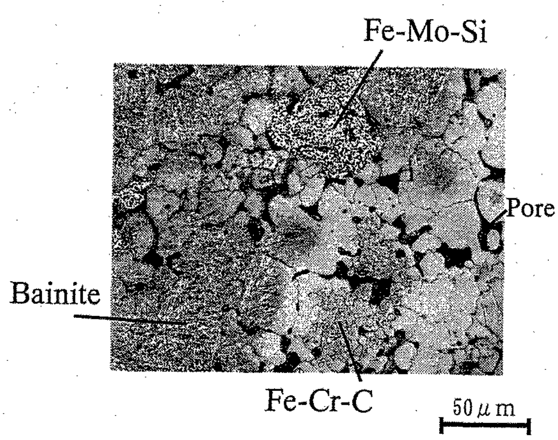

Photo 1 Microstructure of developed VSI

Table 3 Properties of developed material.

	Radial crashing strength at 300℃ (MPa)	Hardness HRA	Density (g/cm3)
Developed material	>830	60	7.0
Current material (A)	>780	60	7.2

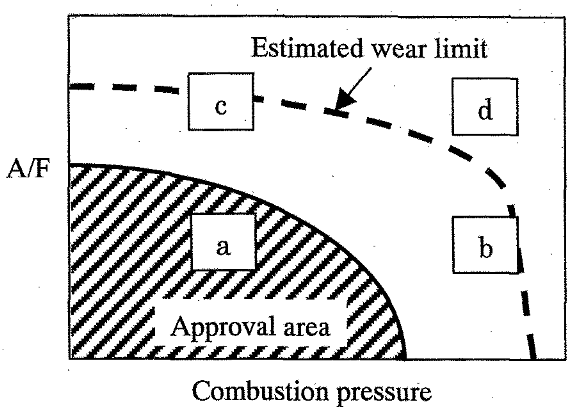

Fig.9 Diagram of condition of engine tests

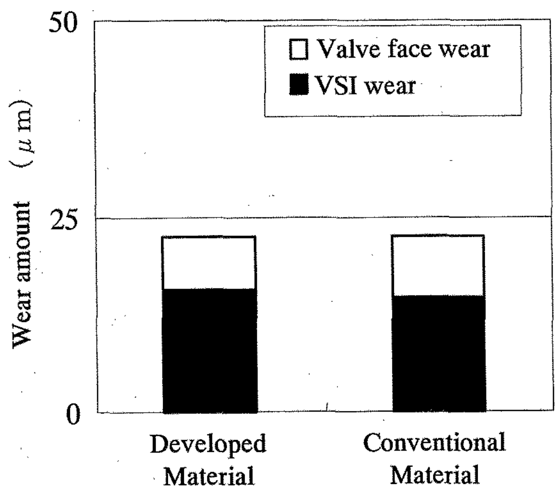

Fig.10 Results of actual engine test

impregnation) were machined, too.

Machinability was evaluated by using a CNC lathe. The cutting conditions were identical to that of mass production, and the relationship between the cutting distance and the amount of tool wear was investigated.

It was confirmed that the machinability of the newly developed material performed, with resin impregnation, better than the current material (A) and (B).

8. APPLICATION IN ACTUAL ENGINES

8.1 Clarification of adaptable condition of the new material

The conditions in which the new VSI would be able to be used were investigated for reference data so as to select the most applicable engines.

It was found that the A/F ratio, combustion temperature and combustion pressure in an engine influences the wear of a VSI considerably. Actual engine bench tests were carried out under different combustion pressures and A/F ratios conditions.

Fig.11 shows a diagram of the conditions of the engine tests for analysis. Wear of the new VSI tested under the condition (a) was small and equal to that of a current material (A). The wear surface of the new VSI was steady. This result means that the new VSI could be used under condition (a). In the case where the combustion pressure was increased; condition from (a) to (b), the wear amount of the new VSI tested under condition (b) was three times that of condition (a). In the case where the A/F ratio is increased; condition from (a) to (c), the wear amount of the new VSI tested under the condition (c) was twice that of condition (a). Resultantly, it was possible to conclude that the new VSI could be used under conditions (a), (b) and (c), because the absolute values of the wear amount of the new VSI under all three conditions were equal to that of a current material (A).

However, wear of the new VSI tested under the condition (d) was twice as large as that of the current material (A), though it was considered that a gasoline engine driven under those type of conditions of (d) would be extremely rare. This particular wearing was due to plastic flow being observed on the wear surface of both the new VSI and the current material (A), it was thought that superior strength and good lubrication would be required for a VSI that had to undergo such high combustion pressures and a high A/F ratio.

Judging from the results of the above mentioned engine tests analysis, the driving conditions in which the new VSI can be applied were clear. And it was determined that the application of the new VSI was advanced enough for some engines to the extent of the oblique line shown in Fig.9.

8.2 Durability

Judging from the analytical experiment mentioned above, an engine in which the new VSI material was able to be used was approximated, and an endurance test was carried out using such an engine Fig.10 shows the results of the actual engine test. The wear amount of the new VSI material was equal to that of a current material (A). The wear surface after the test was shown a steady wear shape without any falling off of the hard particles or any cracking of the matrix, though some plastic flow was observed. From these results, it was concluded that the new VSI material was able to be used as an exhaust VSI in engines at the condition over the extent of the oblique line shown in Fig.9.

9. CONCLUSIONS

In this study, a cobalt and lead free and low cost new exhaust valve seat insert material for gasoline engines was developed. The conclusions are as shown below.

1) Fe-Mo alloy which has superior high temperature hardness, thermal conductivity, wear resistance and detachment resistance can be selected for the base matrix. Suitable amounts of molybdenum are 3.5%.

2) The new Fe-Mo-Si hard particles with molybdenum silicide have high temperature hardness, the same hardness as that of conventional cobalt-based hard particles.

3) The wear resistance of the developed VSI is increased by optimizing the mixing ratio of Fe-Cr-C and Fe-Mo-Si. The optimum additional amounts are 15% of SKD11 and 10% of Fe-Mo-Si.

4) The wear resistance under combustion conditions of a conventional engine is equal to that of a current material (A).

5) The machinability of the developed material is superior to that of a current material (A) or current material (B).

6) The cost of producing this newly developed material is greatly decrease, compared with that of a current material (A) by being cobalt-free and having a simpler manufacturing process.

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