

Development of Low-Nickel Heat Resistance Alloy for Exhaust Valves

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ABSTRACT

The DY2 heat-resistant alloy was developed with lower nickel content than in the conventional heat-resistant nickel-based super alloy for use in exhaust valves. In order to compensate for the diminished strength that accompanies reduction in the nickel content, steps were taken with this alloy to optimize the additive elements (carbon, nitrogen, phosphorus, molybdenum) that contribute to solid solution hardening, increasing the quantities of these elements within the range that would not impair this material's hot workability. DY2 has reliable high-temperature strength and wear resistance, can be used to manufacture valves by hot forging, and achieved a 20% reduction in materials costs.

1. Introduction

Engine exhaust valves have the role of maintaining the airtight seal of the combustion chamber while being exposed to combustion gases at high temperatures and high pressures. They are important components, since deterioration of the airtight seal can lead to loss of power or loss of engine functionality. Given their function, exhaust valve materials require strength and wear resistance at high temperatures as well as corrosion resistance and oxidation resistance in the presence of combustion products.

In general, high-manganese heat-resistant steel SUH35 (21-4N steel) has been widely used in exhaust valves for automobiles. Since this material does not have adequate strength and hardness at high temperatures, alloy thermal spray (hard-facing) is applied to the valve seat face as necessary for high performance engines, or a highly heat-resistant material such as heat-resistant nickel-based super alloy is used.

Honda has consistently used heat-resistant nickel-based super alloy for automobile exhaust valve material since 1979. The company has developed material for exhaust valves to meet the particular needs of the times, and has been using heat-resistant nickel-based super alloy for automobile exhaust valves for the following reasons:

(1) It eliminates the need for hard-facing the valve seat face.

(2) It has reliable high-temperature strength and enables the valve stem to be made thinner.

(3) It has reliable oxidation resistance.

In order to reduce the costs of exhaust valves for automobiles, NCF3015 (30Ni-15Cr) has been used in mass-production vehicles and high-nickel heat-resistant alloy NCF440 (70Ni-19Cr) has been used in high-performance engines. Exhaust valves have been facing rising exhaust gas temperatures with the adoption of increasingly stringent exhaust emission regulations and heightened fuel economy measures. Greater strength at high temperatures is being required even in mass-production vehicles, while at the same time there are also calls for resource conservation and cost reductions. Rare metals have become essential materials for society today as motor vehicles and electronics take on increasing functionality, and the importance of these materials is steadily growing. At the same time, however, technology for resource conservation and recycling has become an important issue from the perspective of measures to curb the depletion of resources.

In order to meet these demands, the heat-resistant alloy DY2 was developed. Its purpose is to achieve a lower nickel content than in the present heat-resistant nickel-based super alloy NCF3015 and to reduce costs while also providing equal high-temperature strength and wear resistance.

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2. Development Goals

In taking steps to reduce the nickel content, the characteristics sought for the valve material were defined as equal to the heat-resistant nickel-based super alloy currently used as material in mass production (NCF3015). Development of low-nickel heat-resistant alloy content was pursued with the following four points as the main aims.

- (1) High-temperature fatigue strength and wear resistance at 800°C.
- (2) Oxidation resistance
- (3) Corrosion resistance
- (4) Hot workability

3. Alloy Design

Conventional high-nickel heat-resistant alloy is material made for greater strength and wear resistance at high temperatures by the precipitation of gamma-prime phase $\text{Ni}_3(\text{Al}, \text{Ti})$. Since nickel is the basic element composing the gamma-prime precipitation phase, which is the hardening phase, increased strength becomes less readily achieved through the use of gamma-prime phase when the nickel content is reduced, and the strength is diminished. By contrast, the developed material DY2 has reduced nickel content while simultaneously assuring high-temperature strength, wear resistance, and hot workability. The alloy design was therefore carried out using the following two types of strengthening technique.

DY2-D: Solid solution by the addition of molybdenum and carbide precipitation-hardening through an increase in the amount of carbon and the addition of niobium.

DY2-H: Grain boundary precipitation-hardening through the addition of phosphorus

3.1. DY2-D Material

Making a solid solution with molybdenum or tungsten and precipitation-hardening through the addition of carbides are effective ways⁽¹⁾ of making high-strength material from the austenite heat-resistant steel generally used as a heat resistance alloy.

The addition of molybdenum to the DY2-D alloy increases high-temperature strength by solid solution-strengthening, but larger amounts will cause embrittlement phase to precipitate and diminish hot workability⁽²⁾. Based on Fig. 1, concern over the precipitation of a Laves phase, which is an embrittlement phase, arises when the molybdenum content exceeds 3.5% or when the tungsten content exceeds 3.2%. Furthermore, the strengthening amount of elements for strengthening a solid solution is generally related to the atomic concentration, and as the dotted line in the figure indicates, tungsten, which has approximately twice the atomic weight of

molybdenum, has approximately one-half the solid-solution effect even at the same mass concentration. For DY2-D, therefore, the choice was made to add molybdenum alone, for its greater effectiveness by comparison with the addition of tungsten alone or in combination with molybdenum, and the amount of 3.2% molybdenum was decided on.

Increasing the amount of carbon in order to utilize carbide precipitation-hardening is effective in promoting the carbide precipitation of M_{23}C_6 -type material (chromium carbide) and increasing its high-temperature strength and wear resistance. However, the amount of carbon needs to be set within the range that will not degrade toughness. Since adding a small amount of niobium is effective in enhancing toughness⁽³⁾, 0.1% of niobium was added to DY2 and a portion of the carbon was replaced by the carbide precipitation of MC-type material (niobium carbide). When the amount of carbon exceeds 0.6%, hot workability is degraded. In consideration of productivity, therefore, the amount of carbon was set at 0.52%. MC-type carbide is effective in heightening the wear resistance of the valve seat face area, and one feature of this alloy, as shown in Fig. 2, is that in DY2-D, the total amount of carbide precipitation is increased and the composite reinforcement by the solid solution is further increased, yielding greater heat resistance.

Since molybdenum and niobium are ferrite stabilizing elements, reducing the amount of nickel raises concerns regarding the precipitation of delta ferrite phase when manufacturing the material. When delta ferrite phase is precipitated, the nitrogen that is a component will cause

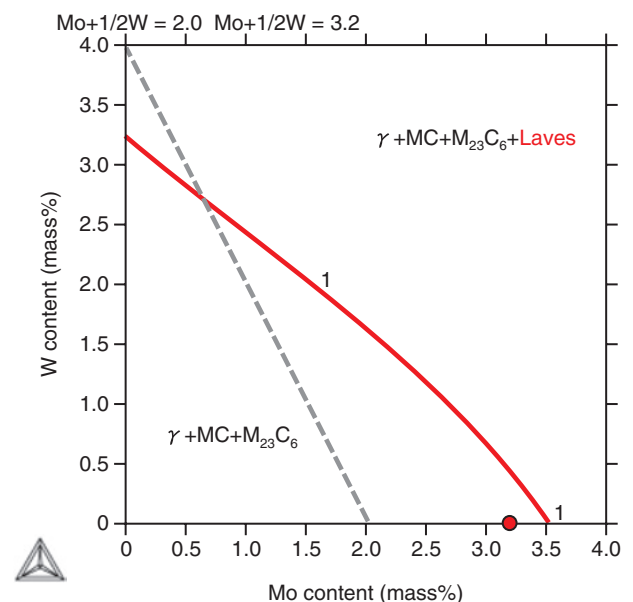


Fig. 1 Phase diagrams of Fe-0.52C-0.1Si-9Mn-6Ni-0.1Nb at 800°C

nitrogen-blow when melting, which may result in the formation of defects within the material. Therefore, there is a need to prevent reduction in microstructural stability. Figure 3 shows the nickel content on the horizontal axis and the temperature on the vertical axis. Since delta ferrite is precipitated during manufacturing of the material when the nickel content is 4% or lower, casting doubt on microstructural stability, the amount added in DY2-D was set at 6% to suppress the precipitation of delta ferrite.

3.2. DY2-H Material

A solid solution with molybdenum is effective in increasing high-temperature strength, but molybdenum is a rare metal and is also high in cost.

In DY2-H, grain boundary precipitation (phosphorus)-hardening, which is effective in increasing high-temperature fatigue strength, was used and the solid solution with molybdenum was reduced. The setting of

the phosphorus content will be discussed next. As shown in Fig. 4, increasing the added amount of phosphorus causes M_3P to form and high-temperature strength is enhanced, but when the amount becomes excessive, the grain boundary becomes brittle and hot workability is diminished. In consideration of manufacturability, therefore, the amount of phosphorus was set at 0.22%, where microstructural stability is reliable. Figure 5 shows the total precipitation amounts of carbides and phosphides.

The chemical compositions of the DY2-D and DY2-H produced by the above alloy design as well as the chemical compositions of existing heat-resistant nickel-based super alloys are shown in Table 1. The material DY2 has a nickel content 20 or more points lower than the high-nickel heat-resistant alloy NCF3015, and also possesses greater high-temperature strength.

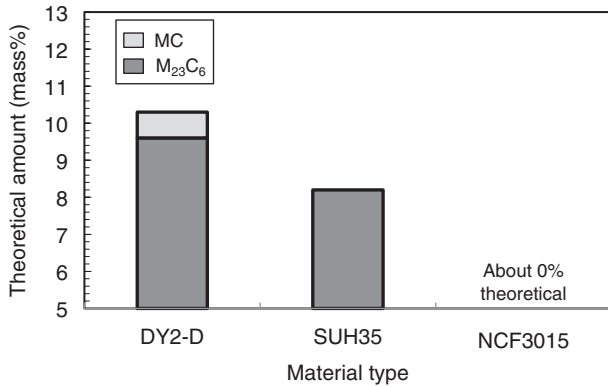


Fig. 2 Theoretical amount of carbides at 800°C

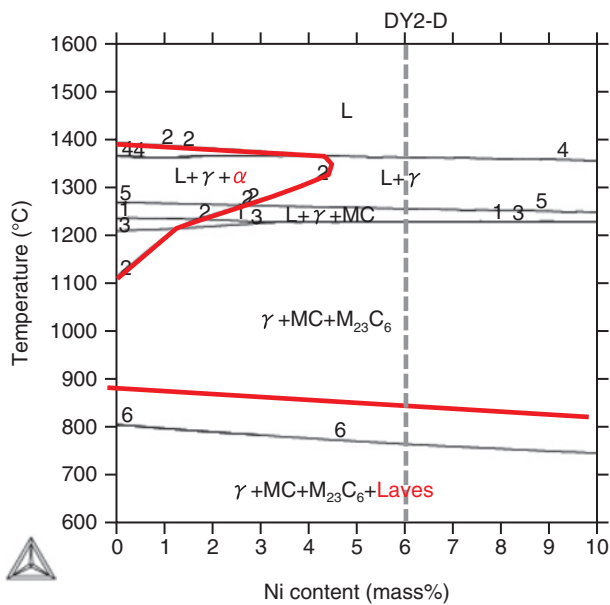


Fig. 3 Phase diagrams of Fe-0.52C-0.1Si-9Mn-3.2Mo-0.1Nb

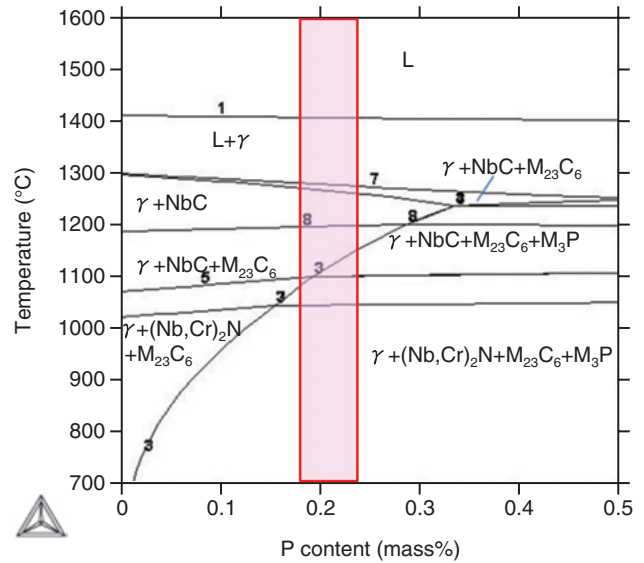


Fig. 4 Phase diagrams of Fe-0.33C-0.30Si-1Mn-0.5Mo-10.5Ni-0.2%Cu-0.12Nb-0.18N

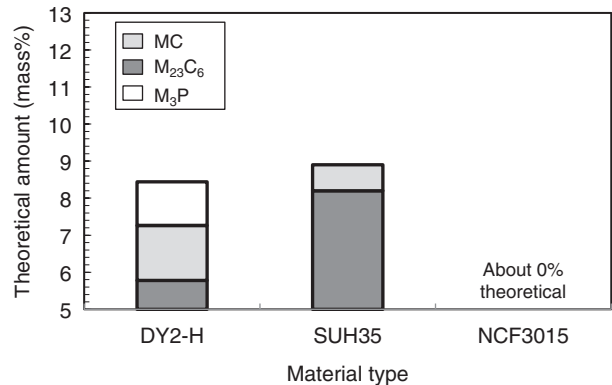


Fig. 5 Theoretical amount of carbides and phosphide at 800°C

Table 1 Nominal chemical composition

Material	Composition (mass%)												
	C	N	Si	Mn	Ni	Cr	Fe	Mo	Ti	Al	Nb	P	Other
DY2-D	0.52	0.40	0.10	9.0	6	21	Bal.	3.2	-	-	0.10	-	
DY2-H	0.33	0.18	0.10	1.0	10.5	20	Bal.	0.5	-	-	0.12	0.22	
SUH35	0.50	0.40	0.10	9.0	4	21	Bal.	-	-	-	-	-	
NCF3015	0.03	-	0.10	0.10	32	16	47	-	2.70	1.20	0.80	-	0.004B

4. Phase Stability

Figure 6 shows a photograph of the structure following solution and aging heat treatment of the developed materials at 800°C for 400 hours. It is apparent from the structure photograph that Laves phase and delta ferrite phase precipitation, which reduce the materials' strength, are not present after aging heat treatment at 800°C for 400 hours.

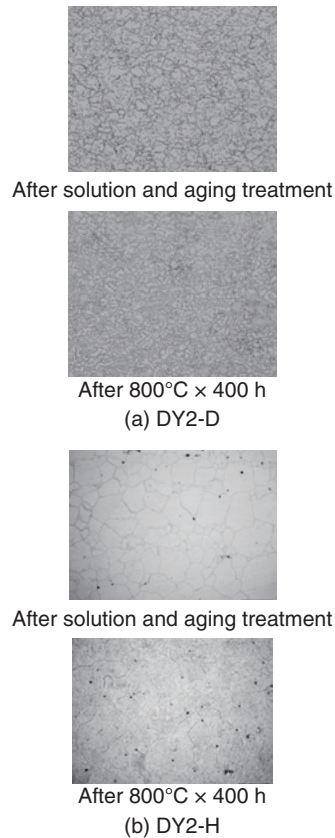


Fig. 6 Microstructure of developed materials

5. Material Characteristics

5.1. High-Temperature Fatigue Strength

High-temperature fatigue strength is an important characteristic indicating the fatigue strength of the valve stem. Figure 7 shows the results of rotary bending fatigue

testing at 800°C and a speed of 3500 rpm. DY2-D and DY2-H demonstrate fatigue strength on a par with that of the target heat-resistant nickel-based super alloy NCF3015 at 800°C.

5.2. Wear Resistance

High-temperature hardness is an important characteristic value that indicates the wear resistance of the valve seat face. Figure 8 shows the hardness of DY2-D and DY2-H from room temperature to high temperature. The developed material has greater hardness than SUH35 from room

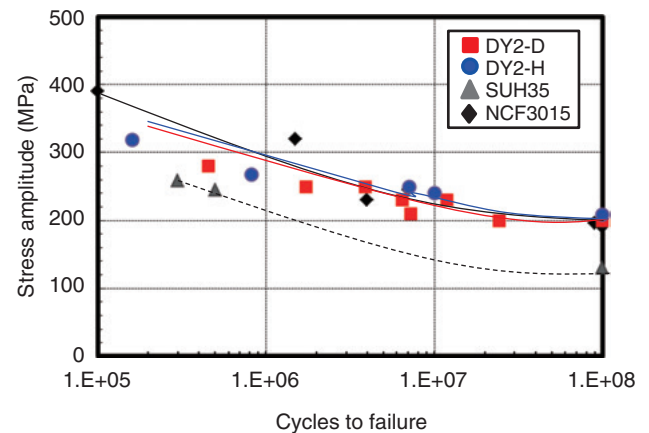


Fig. 7 Fatigue strength at 800°C

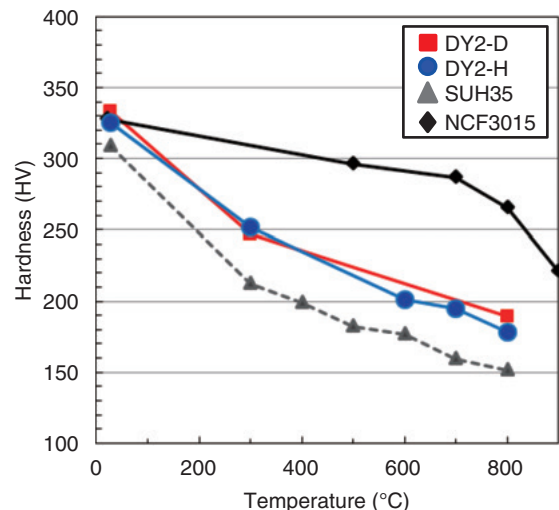


Fig. 8 Hardness at high temperatures

temperature to the high temperature of 800°C, but less than that of NCF3015.

Since these alloys have been given greater wear resistance by increased carbide precipitation, their wear characteristics were verified by endurance testing in an actual engine and by stand-alone slide testing as described below in Chapter 6.

5.3. Oxidation Resistance

Exhaust valves are used under a thermo cycle accompanying a high-temperature oxidation environment and engine acceleration and deceleration load change. Oxidation of the valve generates oxide scale on the valve surface. This increases wear and sometimes causes leakage from the valve face. Figure 9 shows the increase in amount of oxidation after the valve is heated at 850°C for 400 hrs. DY2-H is on a par with NCF3015, and, together with DY2-D, shows greater oxidation resistance than SUH35.

5.4. Corrosion Resistance

Exhaust valves are exposed to sulfides that are a product of combustion. Figure 10 shows the results from sulfur attack testing (heated at 870°C for 80 hours in corrosion

ashes mixed with $\text{CaSO}_4\text{-BaSO}_4\text{-NaSO}_4$). DY2 demonstrates greater corrosion resistance than NCF3015.

5.5. Physical Characteristics

Among the various physical characteristics, the coefficient of thermal expansion indicates the elongation characteristic of the valve material, which affects the tappet clearance. Thermal conductivity affects the heat-reducing ability of the valve. The specific gravity affects the weight of the valve. In general, the coefficient of thermal expansion should be small in order to reduce thermal stress and minimize the effect on the tappet clearance, while thermal conductivity should be large in order to enhance the heat-reducing ability, and the specific gravity should be small from the viewpoint of lightness⁽⁴⁾. Figure 11 shows the coefficient of thermal expansion, Fig. 12 shows thermal conductivity, and Table 2 shows specific gravity. DY2 has a coefficient of thermal expansion and thermal conductivity that are higher than NCF3015. Testing in an actual engine

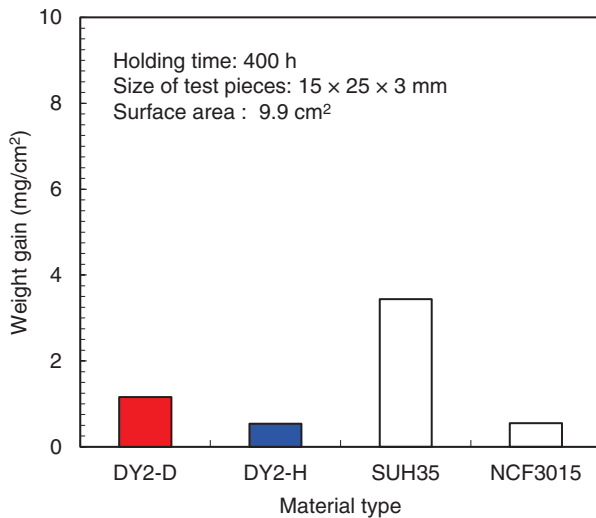


Fig. 9 Oxidation resistance at 850°C

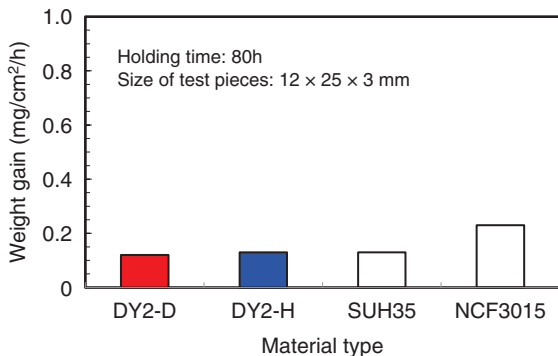


Fig. 10 Sulfur attack resistance at 870°C

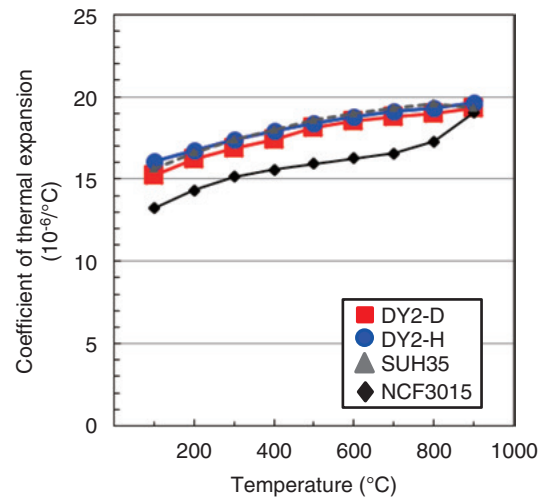


Fig. 11 Coefficient of thermal expansion

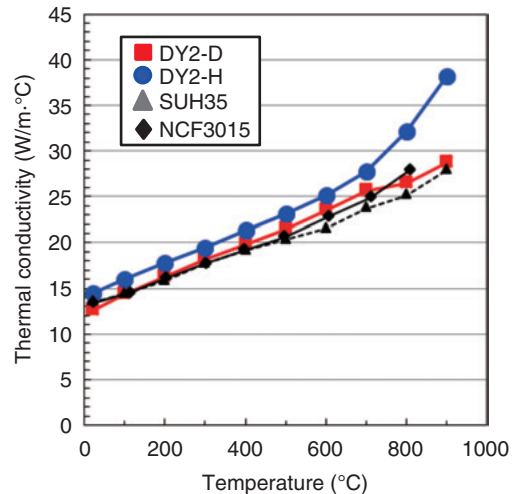


Fig. 12 Thermal conductivity

Table 2 Specific gravity

DY2-D	DY2-H	SUH35	NCF3015
7.83	7.86	7.75	7.89

was performed to verify the characteristic of thermal elongation, and this showed that there were no issues regarding effects on tappet clearance. The specific gravity has been lowered by reducing the nickel content.

5.6. Cost

Reduction of the nickel content has enabled a reduction of approximately 20% in the cost of materials for DY2-D and DY2-H.

6. Characteristics of Parts

6.1. Hot Workability

Hot workability is used to evaluate the formability of the valve. Figure 13 shows the results of performing a hot high-speed tension test using a Greeble testing machine. In general, the temperature region in which a reduction in area of at least 50% can be obtained in the Greeble test is the formable range. The temperature region in which DY2-D and DY2-H show a reduction in area of 50% or more has a range of 250°C or more, and these materials have workability on a par with NCF3015.

6.2. Wear Resistance Characteristic

Figure 14 shows the results from stand-alone sliding tests of valve parts. DY2-D and DY2-H have wear resistance characteristic on a par with NCF3015.

6.3. Durability in an Actual Vehicle

Figure 15 shows the amount of valve seat face wear after 100 hours of operation at 6800 rpm in a 1.5-liter direct-injection engine. DY2-D and DY2-H show the same wear characteristic in an actual engine as NCF3015.

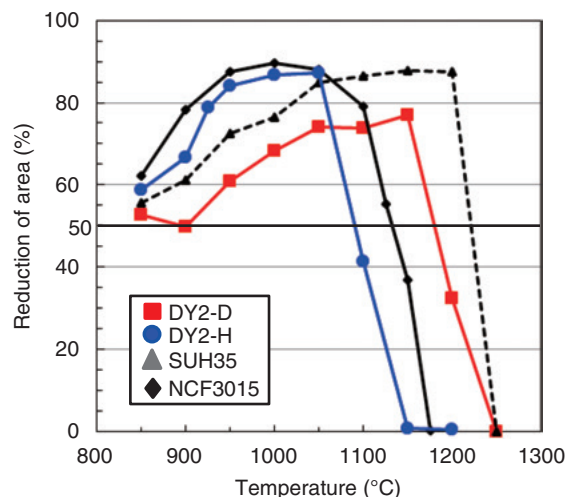


Fig. 13 Hot forgeability

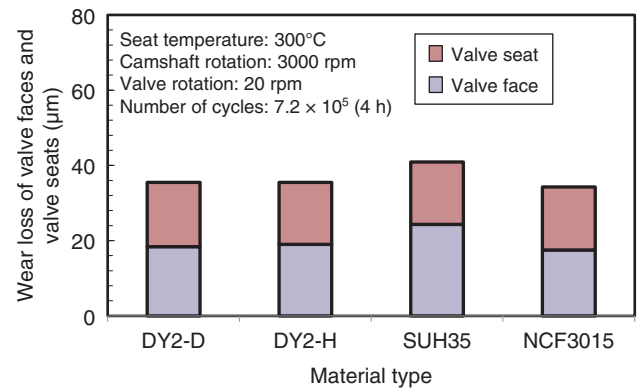


Fig. 14 Valve sliding test

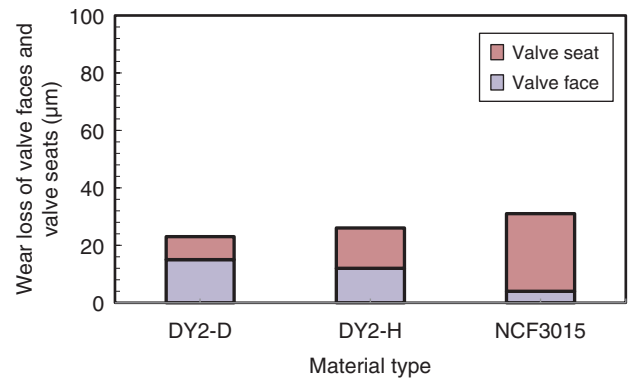


Fig. 15 Wear loss of exhaust valve face and valve seat

7. Conclusion

DY2 materials that save resources and have lower cost were developed in response to the exhaust valve material characteristics that are being called for.

Carbides were increased within the range that would not degrade hot workability while also achieving a reduced nickel content. The addition of optimal amounts of molybdenum, which is an element for strengthening solid solution, and phosphorus, which is a grain boundary strengthening element, is also a feature of these materials, which have achieved high-temperature fatigue strength, wear resistance, oxidation resistance, and corrosion resistance on a par with heat-resistant nickel-based super alloy NCF3015, which is the material previously used. The use of this alloy has enabled a cost reduction of approximately 20% over the conventional heat-resistant nickel-based super alloy.

Use of these developed materials in mass-production vehicles has begun with the 2014 model FIT.

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