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[54] **VALVE SEAT MATERIALS FOR INTERNAL COMBUSTION ENGINES**

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[57] **ABSTRACT**

A valve seat material for internal combustion engine, which comprises at least one lubricating material selected from the group consisting of lead and glass in a phosphorus-containing precipitation hardened austenitic matrix which is strengthened by the addition of cobalt.

9 Claims, No Drawings

VALVE SEAT MATERIALS FOR INTERNAL COMBUSTION ENGINES

BRIEF SUMMARY OF THE INVENTION

This invention relates to a valve seat material for internal combustion engines and more particularly, it is concerned with a valve seat material containing a lubricating material in an austenitic base matrix.

A valve seat material for internal combustion engines should have the following properties:

1. Sufficient fatigue strength and creeping strength for an impact load at a high temperature
2. Excellent wear resistance
3. Excellent heat and corrosion resistance to combustion gases.

Up to the present time, ordinary cast iron, low alloy cast irons such as containing Cu-Cr-Mo and Ni-Cr-Mo and high chromium steels such as containing 2.0 % C -12.0 % Cr and 1.0 % C -8.0 % Cr have been used as a valve seat material for internal combustion engines. The vale seat is always exposed to a combustion gas in the operation of an internal combustion engine and subjected to not only a high temperature of from 300° to 700 °C but also an impact load by the valve beat and a sliding action by the irregular rotation of valve. In an internal combustion engine using the ordinary lead-containing gasoline, the lead in the gasoline reacts with sulfur, phosphorus, calcium and sodium contained in the oil or gasoline to form combustion products such as lead oxide, lead sulfate, calcium oxide, sodium oxide and phosphorus oxide, which may possibly form a film playing a role as an antioxidant or antifriction material at high temperature between the contact surfaces of the valve and valve seat. In another internal combustion engine using a lead-free gasoline, on the contrary, such lubricating products are not formed and the valve and valve seat are brought into direct contact at a high temperature, resulting in rapid wearing of the valve seat and, sometimes, the valve itself due to adhesive wearing. Consequently, the engine cannot be operated normally, since there is no tappet clearance due to such abnormal wearing. In order to solve this problem, at first, Monel alloys and high alloy die steels which are heat and wear resistant but expensive have been taken into consideration, but no satisfactory results are given except that the life is somewhat increased.

It is an object of the invention to provide a valve seat material for internal combustion engines, which overcomes this difficulty and which is resistant to oxidation and wearing at high temperatures.

It is another object of the invention to provide a valve seat material for internal combustion engines, which is suitable for use of lead-free gasolines.

Further objects of the invention will become apparent from the following description and embodiments.

As a result of our various studies, it is found that a sintered austenitic steel, in particular, precipitation hardened austenitic steel is suitable for use as a base matrix of the valve seat material of this kind, in which a lubricating material capable of softening, melting and thus forming a lubricating film at the faced surface temperature of a valve and valve seat is allowed to be coexistent.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there is provided a valve seat material for internal combustion engines, which comprises at least one lubricating material selected from the group consisting of lead and glass in a phosphorus-containing precipitation hardened austenitic matrix which is strengthened by the addition of cobalt.

As matrix elements, 3'30 % chromium, not more than 20 % nickel, 0.5–5 % molybdenum, 2–25 % copper, 0.5–2.0 % carbon and the balance iron are taken into consideration and compounded according to uses depending on the thermal expansion, heat conduction, heat resistance and wear resistance. For example, Fe 12.0%, Cr 40%, Ni 2%Mo, 2%, C and Fe 1.5%, C 20%, CR 10%, Ni are used as a wear resistant cast steel and Fe 5%, Cr 20%, Cu 1%, C 4%, Pb are used as a sintered alloy. In these alloys, however, there is a distribution of tenacious carbides in the matrices and, in particular, distribution of lead in the sintered alloy, but satisfactory results cannot be given always in engines requiring severer specifications.

Thus the base matrix of our valve seat material must be an austenitic phosphorus-containing precipitation hardened steel having an excellent strength and heat resistance at a high temperature of higher than 400 °C. That is to say, the features of the alloy according to the invention consists in:

a. The base matrix is made more excellent in strength and heat resistance at a temperature of 400°C or higher by the addition of cobalt.

b. In addition to the primary carbides excellent in wear resistance being evenly distributed in the matrix, iron phosphide (Fe_3P) and fine chromium carbide are precipitated by the addition of small amounts of phosphorus followed by the solution and age treatment, whereby the matrix is more strengthened.

c. The valve seat material of the invention is a composite material in which a lubricating material is dispersed or impregnated in such base matrix, said lubricating material being selected from the group consisting of lead and glass.

The valve seat material of the invention, as one embodiment, consists of 10–35 % chromium, 8–45 % nickel, 0.1–6.0 % molybdenum, 0.2–2.5 % carbon, not more than 3 % silicon, 0.05–0.7 % phosphorus, 0.02–0.2 % sulfur, 0.02–0.20 % nitrogen, 0.1–15 % cobalt, and 0.3–10 % lead and 0.5–5 % glass, and the balance iron except for impurities associated usually with these elements. In this composition, carbon combines with chromium and molybdenum to form carbides, thus raising the wear resistance, and at the same time, dissolves in the austenite to raise the strength. However, the carbon is preferably added in a measured quantity of 0.2–2.5 %, since if more than 2.5 %, the toughness lowers and if less than 0.2 %, the wear resistance becomes inferior. The nickel is effective in austenitizing the structure, thus raising the corrosion resistance as well as the strength at a temperature of from room temperature to high temperatures, and simultaneously, holding the toughness and increasing the plastic adaptation to the surface of a valve. However, the nickel is preferably added in a measured quantity of 8–45 %, since if less than 8 %, these effects are little and even if more than 45 %, these effects are not so increased. Manganese may be added in place of a part or all of the nickel. The chromium is effective in forming a surface film, thus raising the oxidation resistance as well as the wear resistance, but is preferably added in a quantity of 10–35 %, since if more than 25 %, the toughness lowers and if less than 10 %, the wear resis-

tance and strength are not adequate. Phosphorus is necessary for the precipitation hardening but is preferably added in a quantity of 0.05–0.7 %, since if less than 0.05 %, the hardening effect is not enough, and if more than 0.7 %, the toughness rather lowers and the workability deteriorates. In general, the phosphorus component is added to the base matrix in the form of an element or oxide, but the addition thereof may be omitted when a glass of phosphorus type is used as a lubricating material. In this case, however, only about 10 % of the phosphorus component in the glass enters the base matrix, so the former addition method is preferred. The nitrogen dissolves in the austenite to raise the hardness, strength at high temperatures and wear resistance and to improve the plastic adaptation to an engine valve, but is preferably added in a measured quantity of 0.02–0.2 %, since if more than 0.2 %, the workability lowers and if less than 0.02 %, these effects are little. The molybdenum is effective in raising the hardness at a high temperature, strengthening the austenitic matrix and improving the wear resistance, but is preferably added in a measured quantity of 0.1–6.0 %, since if less than 0.1 %, these effects are inadequate and if more than 6.0 %, these effects are rather decreased. The cobalt is effective in strengthening the austenitic matrix as well as improving the wear resistance, but is preferably added in a quantity of 0.1–20 %, since if less than 0.1 %, these effects are not enough and even if more than 20 %, these effects are not so increased for the cost increased. The sulfur is added so as to improve the sealing effect and to raise the tendency to be cut, but preferably in a quantity of 0.02–0.2 %, since if less than 0.02 %, these effects are little and if more than 0.20 %, the toughness rather lowers. Since selenium, bismuth and silver have the similar effects, a part or all of the sulfur may be replaced by one or more of them. In order to raise the heat conductivity, moreover, 30 % or less of copper may be added.

In another embodiment of the present invention, the composition of the valve seat material consists of 10–35 % chromium, 8–45 % nickel or manganese, 0.1–20 % cobalt, 0.1–6.0 % molybdenum, 1–8 % tungsten, 0.2–2.5 % carbon, 0.05–0.7 % phosphorus, 0.02–0.4 % at least one of sulfur, selenium, bismuth, antimony and silver, and 0.2–10 % lead and 0.5–8 % glass, and the balance iron except for impurities usually associated with these elements, the relationships of $Cr + Ni < 60$ %, $Ni + Co < 40$ % and $W + Mo < 10$ % being satisfied. Cobalt and nickel stabilize similarly the austenite but increase the laminate defect energy. Therefore, the both should preferably satisfy the relationship of $Co + Ni < 40$ %. In addition to molybdenum, tungsten is also used in a quantity of 1–8 % so as to strengthen the austenitic substrate and to raise the heat and wear resistance like molybdenum. However, molybdenum and tungsten should preferably satisfy the relationship of $Mo + W < 10$ %. Furthermore, chromium and nickel are preferably added in quantities of 10–35 % and 8–45 % respectively for the purpose as mentioned above, but should not exceed 60 %, since the workability markedly lowers. As occasion demands, the addition of the phosphorus component may be omitted, that is, the content of phosphorus may be reduced to less than 0.05 % since the base matrix is considerably strengthened by the joint addition of cobalt and tungsten.

In any case, as a lubricating material, at least one substance selected from the group consisting of lead and glass is used, which are capable of softening, melting and thus forming a lubricating film at the faced surface temperature of a valve and valve seat during the operation of an internal combustion engine. Lead melts and forms a lubricating film on the surface of a valve, thus preventing the metal adhesion and, simultaneously, raising the cutting workability. Preferably lead is added in a proportion of 0.2–10 % based on the valve seat material, since if less than 0.2 %, such effect is little and if more than 10.0 %, the strength of the valve seat material itself lowers. Glass forms similarly a tenacious lubricating film, thus preventing the adhesion of the valve and valve seat. Preferably glass is added in a proportion of 0.5–8.0 % based on the valve seat material, since if less than 0.5 %, the lubricating property at high temperatures is inadequate and if more than 8.0 %, the strength of the valve seat material lowers. As such glass, a glass having a softening point of lower than 800°C, for example, containing lead oxide, zinc oxide, phosphorus oxide, boron oxide and lithium oxide is preferably used. In the case of using lead as a lubricating agent, the lubricating effect can be shown well at a relatively low temperature range, whilst in the case of using glass, it can be shown well at a relatively high temperature range. Therefore, the use of lead and a glass in combination results in better results, that is, more stabilized lubricating effect and wear resistance at a temperature range of from room temperature to high temperature. In particular, a combination of lead and a glass of phosphorus oxide type is desired in view of that some of the phosphorus component enters the base matrix to cause the precipitation hardening thereof.

The valve seat material of the invention can be manufactured by the mass production system and is so excellent in fatigue strength, creeping strength, wear resistance and heat resistance at high temperatures that the severer requirements of an internal combustion engine may favourably be satisfied.

The following examples are to illustrate the invention in more detail without limiting the same.

TEST OF DURABILITY

Using a 360 cc, water-cooling, two cylinder-and two carburetter-engine at 7500 rpm with full throttle and full load, the tappet gap was firstly adjusted to 0.1 m/m and a period of time was measured irrespective of the right and left cylinders when the gap became zero. The life of a ring for the valve seat was defined by the measured period of time. A gasoline was used having an octane number of 87 containing lead in a quantity of 0.002 g/gallon.

EXAMPLE 1

Steels A to C having the following composition, for comparision, were molten in a high frequency furnace, cast in a ring of $40\phi \times 20\phi \times 15$, subjected to a certain heat treatment and cutting working, inserted in aluminum head and then subjected to the above mentioned test of durability.

	Composition	Hardness (MHV)*
Steel A	Fe -2.0%C -12.0%Cr -0.4%Mo	360
Steel B	Fe -1.5%C -20.0%Cr -10.0%Ni	320

-continued

	Composition	Hardness (MHV)*
Steel C	Fe -2.0%C -12.0%Cr -40.0%Ni	330

*Hardness by Micro-Vickers

The test results of durability of these materials were as follows:

Table 1

Material	Life of Valve Seat (hr) Life (hr)*
A	6, 3
B	16, 20
C	42, 40

*The measurement was carried out two times in each case.

EXAMPLE 2

At least one of lead and glass in various proportions and raw materials, based on the following recipe:

	Composition	Hardness (MHV)
D (martensite, for comparison)	Fe -1.0%C -8.0%Cr -0.8%Mo	350
J (austenite)	Fe -1.5%C -20.0%Cr -10%Ni -2.0%Mo -0.2%P -0.1%Co	345
K (austenite)	Fe -1.5%C -20.0%Cr -10%Ni -2.0%Mo -0.2%P -5%Co	345
L (austenite)	Fe -1.5%C -20.0%Cr -10%Ni -2.0%Mo -0.2%P -10%Co	345

were mixed, molded in a density of 6.0 g/cc, sintered at 125 °C in a reducing atmosphere to give a density of 6.8 g/cc, subjected to a predetermined heat treatment and cutting working, inserted in an aluminum head and then subjected to the above mentioned test of durability.

The test materials, D, J, K and L contained further small amounts of elements such as 0.05 % sulfur, 0.05 % nitrogen and 1 % silicon.

The test results of engine durability represented by hr were tabulated below (Table 2):

Table 2

Lubricating component, glass, %	Matrix	Life of Valve Seat (hr) (Test of two times) Lubricating component, lead, % 0	0.5	4	10
0	D			7, 12	
	J	40, 45	64, 59	85, 83	88, 93
	K	57, 62	81, 75	101, 99	102, 105
	L	68, 73	92, 88	113, 111	116, 121
0.5	D				
	J			90, 84	
	K			125, 121	
	L			138, 132	
2	D	13, 17		14, 19	
	J		94, 92	102, 105	94, 96
	K		128, 125	139, 148	131, 138
	L		139, 135	145, 151	145, 141
5	D				
	J			85, 89	
	K			135, 128	
	L			133, 138	

As is evident from the results of the above table, the life of the valve seat tends to increase with the increase of the content of cobalt when keeping constant the content of phosphorus (0.2%).

EXAMPLE 3

At least one of lead and glass in various proportions and raw materials, based on the following recipe:

	Composition	Hardness (MHV)
K-1 (austenite)	Fe -1.5%C -20.0%Cr -10%Ni -2.0%Mo -5%Co	345
K-2 (austenite)	K-1 + 0.2%P	350
K-3 (austenite)	K-1 + 0.4%P	370

were mixed, molded in a density of 6.0 g/cc, sintered at 1250 °C in a reducing atmosphere to give a density of 6.8 g/cc, subjected to a predetermined heat treatment and cutting working, inserted in an aluminum head and then subjected to the above mentioned test of durability.

The test materials K-1, K-2 and K-3 contained further small amounts of elements such as 0.05 % sulfur, 0.05 % nitrogen and 1 % silicon.

The test results of engine durability represented by hr were tabulated below (Table 3):

Table 3

Lubricating component, glass, %	Matrix	Life of Valve Seat (hr) (Test of two times) Lubricating component, lead, % 0	0.5	4	10
0	K-1			82, 80	
	K-2			101, 99	
	K-3			90, 91	
0.5	K-1			88, 82	
	K-2			125, 121	
	K-3			105, 103	
2	K-1		70, 68	90, 89	85, 88
	K-2		128, 125	139, 148	131, 138
	K-3		85, 81	103, 99	99, 89
5	K-1			92, 89	
	K-2			135, 128	
	K-3			92, 98	

As is evident from the results of the above table, the life of the valve seat tends to increase by the addition of phosphorus and to reach the maximum value at a phosphorus content of approximately 0.2 % when keeping the content of cobalt at 5 %.

EXAMPLE 4

At least one of lead and glass in various proportions and raw materials, based on the following recipe:

	Composition	Hardness (MHV)
M (austenite)	Fe -1.0%C -13%Cr -10%Ni -10%Co -5%W -2%Mo -0.2%P	340–395
N (austenite)	Fe -1.2%C -20%Cr -10%Ni -7%Co -3%W -3%Mo -0.2%P	"
Q (austenite)	Fe -1.0%C -31%Cr -20%Ni -10%Co -5%W -4%Mo -0.2%P	"
N-1 (austenite)	Fe -1.2%C -20%Cr -10%Ni -7%Co -3%Mo -0.2%P	"
N-2 (austenite)	Fe -1.2%C -20%Cr -10%Ni -7%Co -8%W -3%Mo -0.2%P	"

were mixed, molded in a density of 6.0 g/cc, sintered at 1250°C in a reducing atmosphere to give a density of 6.8 g/cc, subjected to a predetermined heat treatment and cutting, inserted in an aluminum head and then subjected to the above mentioned test of durability.

The test materials M, N, Q, N-1 and N-2 contained further small amounts of elements such as 0.05 % sulfur, 0.05 % nitrogen and 1 % silicon.

The test results of engine durability represented by hr were tabulated below (Table 4):

Table 4

Lubricating component, glass, %	Matrix	Life of Valve Seat (hr) (Test of two times) Lubricating component, lead, % 0	0.5	3	10
0					
0.5	M			120, 103	
	N			137, 148	
	Q			162, 173	
	N-1			126, 136	
	N-2			143, 158	
2	M		105, 115	128, 112	116, 102
	N		136, 135	146, 158	136, 140
	Q		159, 170	183, 171	161, 170
	N-1		118, 130	135, 145	121, 135
	N-2		146, 150	156, 169	146, 152
5	M			118, 100	
	N		142, 136		
	Q			160, 169	
	N-1			136, 121	
	N-2			142, 150	

In this case, the best results are obtained where 3 % lead + 2 % glass are added. The life of the valve seat tends to increase with the increase of the content of chromium in view of M, N and Q and to increase with the increase of the content of tungsten when keeping constant the contents of chromium and cobalt as is apparent in view of N, N-1 and N-2.

We claim:

1. A valve seat material for internal combustion engines, which consists essentially of at least one lubricating material selected from the group consisting of 0.2–10% lead and 0.5–8% glass in a phosphorus- containing precipitation hardened austenitic matrix which is strengthened by the addition of cobalt, said austenitic matrix consisting of 10–35% chromium, 8–45% nickel, 0.1–6.0% molybdenum, 0.2–2.5% carbon, 0.05–0.7% phosphorus, 0.1–20% cobalt and the balance iron except for impurities associated usually with these elements.

2. The valve seat material of claim **1** wherein said lubricating material is dispersed or impregnated in said phosphorus-containing precipitation hardened austenitic matrix.

3. The valve seat material of claim **1** wherein said glass is a glass containing phosphorus oxide.

4. A valve seat material for internal combustion engines, which consists essentially of at least one lubricating material selected from the group consisting of 0.2–10% lead and 0.5–8% glass in a phosphorus-containing precipitation hardened austenitic matrix which is strengthened by the addition of cobalt, said austenitic matrix consisting of 10–35% chromium, 8–45% nickel or manganese, 0.1–20% cobalt, 0.1–6% molybdenum, 1–8% tungsten, 0.2–2.5% carbon, 0.05–0.7% phosphorus, and the balance iron except for impurities usually associated with these elements, the relationships of CR + Ni<60%, Ni + Co<40% and W + MO<10% being satisfied.

5. The valve seat material of claim **4** wherein said lubricating material is dispersed or impregnated in said phosphorus-containing precipitation hardened austenitic matrix.

6. The valve seat material of claim **4** wherein said glass is a glass containing phosphorus oxide.

7. A valve seat material for internal combustion engines, which consists of 10–35 % chromium, 8–45 % nickel, 0.1–6.0 % molybdenum, 0.1–20 % cobalt, 0.2–2.5 % carbon, 0.05–0.7 % phosphorus, and 0.2–10 % and 0.5–8 % glass, and the balance iron except for impurities associated usually with these elements.

8. A valve seat material for internal combustion engines, which consists of 10–35 % chromium, 8–45 % nickel, or manganese, 0.1–20 % cobalt, 0.1–6.0 % molybdenum, 1–8 % tungsten, 0.2–2.5 % carbon, 0.05–0.7 % phosphorus, and 0.2–10 % lead and 0.5–8 % glass, and the balance iron except for impurities usually associated with these elements, the relationships of Cr + Ni < 60 %, Ni + Co < **40** % and W + Mo < 10 % being satisfied.

9. A valve seat material for internal combustion engines, which consists of 10–35 % chromium, 8–45 % nickel, or manganese, 0.1–20 % cobalt, 0.1–6.0 % molybdenum, 1–8 % tungsten, 0.2–2.5 % carbon, not more than 0.05 % phosphorus, and 0.2–10 % lead and 0.5–8 % glass, and the balance iron except for impurities usually associated with these elements, the relationships of Cr + Ni < 60 %, Ni + Co < 40 % and W + No < 10 % being satisfied.

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