MATERIALS OF THE VALVES

Subject: Materials Science

MSc presentation
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FUNCTIONS

Valves control the gas flowing into and out of the engine cylinder. The camshaft and valve spring make up the mechanism that lifts and closes the valves. The valve train determines the performance characteristics of four-stroke-cycle engines.

There are two types of valve, inlet and exhaust. The figure shows an exhaust valve. An inlet valve has a similar form. The commonly used poppet valve is mushroom-shaped.
FUNCTIONS

The figure illustrates the parts of the valve. A cotter which fixes the valve spring retainer to the valve, is inserted into the cotter groove.

Nomenclatures of the valve. The shape from the crown to the neck is designed to give a smooth gas flow.
FUNCTIONS

The figure shows the position and relative motion of each part of the valve mechanism. The motion of the cam lobe drives the valve through the valve lifter. The valve spring pulls the valve back to its original position. During the compression stroke, the valve spring and combustion pressure help to ensure an air-tight seal between the valve and the valve seat.
FUNCTIONS

One revolution of the camshaft gives the amount of valve lift shown in the figure. The valve stem moves in the valve guide and also revolves slowly around the stem. The revolving torque is generated by the expansion and contraction of the valve spring.

An engine basically needs one inlet valve and one exhaust valve per cylinder but most modern engines use four valves per cylinder.

This multivalve configuration raises power output, because the increased inlet area gives a higher volume of gas flow.

Contemporary five-valve engines use three inlet valves and two exhaust valves to increase trapping efficiency at medium revolutions.
FUNCTIONS

The shape of the neck, from the crown to the valve stem, ensures that the gas runs smoothly. In modern vehicles, various valve crown shapes are used. High-performance engines generally use recessed or tulip crown shapes.

The shape of the valve crown controls the flexibility of the valve face. Some high-speed engines need a flexible valve so that the valve does not bounce off its seat when closing. The recessed or tulip valve is elastically flexible as well as light.
REQUIREMENTS

- The valve typically receives an acceleration of 2000 m/s² under high temperatures. Valves must be of light weight to allow the rapid reciprocating motion.
- The combustion gas heats the inlet valve to around 400 °C, while the exhaust valve is heated to between 650 °C and 850 °C.

Temperature distribution (°C) of valves during operation. An aircooled 200 cm³ engine. (a) Inlet valve (b) Exhaust valve.

- Corrosion resistance because of the engine gas.
- Wear resistance because of the frictional motions at the stem end and the face surface of the head.
**MATERIALS OF VALVES**

Heat-resistant steels are classified into ferritic, martensitic and austenitic systems. The **ferritic** system is not suitable for engine valves because it is not strong enough at high operating temperatures.

<table>
<thead>
<tr>
<th>Valve material</th>
<th>Name</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Others</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martensitic heat-resistant steel</td>
<td>JIS-SUH3</td>
<td>0.4</td>
<td>2</td>
<td>0.6</td>
<td>0.6</td>
<td>11</td>
<td>1</td>
<td>Balance</td>
<td>–</td>
<td>30 HRC</td>
</tr>
<tr>
<td>Austenitic heat-resistant steel</td>
<td>JIS-SUH35</td>
<td>0.5</td>
<td>0.3</td>
<td>9</td>
<td>4</td>
<td>21</td>
<td>–</td>
<td>Balance</td>
<td>N: 0.5</td>
<td>35 HRC</td>
</tr>
<tr>
<td>Co-base heat-resistant alloy</td>
<td>Stellite</td>
<td>1.2</td>
<td>1.1</td>
<td>0.5</td>
<td>3</td>
<td>28</td>
<td>1</td>
<td>3</td>
<td>Co:</td>
<td>57 HRC</td>
</tr>
</tbody>
</table>

The alloyed **Cr forms a thick oxide film** on the surface and **prevents progressive corrosion at high temperature**. Since high concentration of **Cr does not make the alloy brittle**, it is always alloyed in heat-resistant steels.
MATERIALS OF VALVES

Since valves work under high-temperature (red heat) conditions, the materials need to be **strong and corrosion-resistant at elevated temperatures**.

Most valves are made from **heat-resistant stainless steels**, which are **resistant to sulphur corrosion** as well as **to oxidation at high temperatures**.

The **inlet valve** works at a temperature of approximately 400 °C, which is relatively low for iron-based materials. A **martensitic heat-resistant steel** such as JIS-SUH3 is commonly used.

By contrast, the **exhaust valve** reaches approximately 850 °C at the valve crown, **requiring an austenitic heat-resistant steel** such as JIS-SUH35.
MATERIALS OF VALVES: Martensitic steels

The **martensitic system** has a hard martensite microstructure. JIS-SUH3 is a typical alloy which gives **superior wear resistance** and **intermediate temperature strength**.

The figure shows the microstructure.

The **carbon content** is around 0.4%, which **raises hardness**, and the alloyed **Cr, Mo and Si** give oxidation resistance.

The **cost of this type of alloy** is relatively low.

Microstructures of JIS-SUH3, showing martensite with dispersed carbide
MATERIALS OF VALVES: Martensitic steels

The martensitic alloy is quench-hardened, and the process consists of holding it at 1,000 °C followed by quenching, tempering at 750 °C and finally quenching in oil.

The temperature used for tempering martensitic heat-resistant steel is higher than that for normal carbon steel, because the microstructure is stable at high temperatures.

The quenched steel softens more with higher tempering temperature.
MATERIALS OF VALVES:  Austenitic steels

The high Cr and Ni concentrations make the austenitic matrix.

These elements restrict $A_1$ transformation to widen the austenitic area in the phase diagram. As a result, a stable austenitic microstructure occurs even at room temperature.

SUH35 keeps the austenite structure in the range from low to high temperature without causing martensitic transformation, therefore austenitic steel cannot be quench-hardened in the same way as martensitic steel.
MATERIALS OF VALVES:  Austenitic steels

The figure shows the microstructure of SUH 35. The fine dispersion of carbide and nitride in the stable austenitic matrix makes it strong at high temperatures. The precipitated carbide in the austenitic heat-resistant steel increases creep resistance at high temperatures. For precipitation to occur, the following three heat treatment stages must be followed: firstly, solution treatment at 1,100 °C, secondly, quenching, and finally, age hardening at 750 °C.

Polygonal austenite grains with carbide precipitations are observable. The nitride layer of 20 μm thick (white layer at the right edge) improves wear resistance.
MATERIALS OF VALVES: Comparison of martensitic and austenitic steels

The strength depends on the environmental temperature, as shown in the figure.

In the low-temperature range below 500 °C, martensitic SUH3 is equal to or a little stronger than austenitic SUH35.

However, in the high-temperature range, the austenitic SUH35 is stronger.
MATERIALS OF VALVES: Comparison of martensitic and austenitic steels

The reason that austenitic heat-resistant steel is stronger above 500 °C is due not only to the fine carbide dispersion, but also to the slow diffusion rates of elements in the austenite structure (FCC). The slow diffusion rate of the included elements means that the microstructure generated by heat treatment hardly changes, thus maintaining strength at high temperatures.

Martensitic steel is hard below 500 °C, and is used in the mid-temperature range. By contrast, austenitic steel is used above 500 °C and is an appropriate choice where heat resistance is important.
BONDED VALVES:

Austenitic steel shows excellent strength at high temperatures, but, unlike martensitic steel, quench hardening is impossible due to the lack of martensitic transformation. Nitriding must be used as an additional heat treatment. To obtain high wear resistance at the stem and stem end, martensitic steel is bonded to an austenitic steel crown. For this, friction welding is generally used. The figure shows an as-bonded exhaust valve.

Friction-welded bond of an exhaust valve.
BONDED VALVES:

The figure shows an as-bonded exhaust valve and the microstructure at the weld joint.

Microstructure of the bond between austenitic SUH38 and martensitic SUH1.

Ferrite generated by the heat during friction welding appears in the SUH1 side.

The complete solution treatment and ageing can remove this ferrite.
FRICTION WELDING:

Friction welding was first conducted successfully in 1954. Friction welding is a method for producing welds whereby one part is rotated relative to, and in pressure contact with, another part to produce heat at the mating surfaces. The friction generates the heat necessary for welding.

Schematic illustration of friction welding process:

Welding is carried out in solid state without melting the materials. The rotating rod (left) is slightly pressed to the stationary rod (right), so that friction heat is generated at the rubbing plane.
FRICTION WELDING:

The joint portion does not melt, so the welding takes place in the solid phase.

Since this mechanical solid phase process does not form macroscopic alloy phases at the bond, the joining of similar or some dissimilar materials is possible.

For example, fused welding of aluminum with iron is generally impossible as the brittle Fe-Al compounds generated at the weld make the joint brittle.

However, friction welding is possible because it does not form brittle compounds, and this method is typically used to combine carburized steel with stainless steel and to bond between two cast iron parts without generating brittle chill.

These mechanical, solid-phase welding processes give highly reliable joints with high productivity and low cost.
MANUFACTURING PROCESS OF THE VALVES:

First, the sheared rod is *friction-welded (process 3)* and the part which will form the crown is made larger than the stem portion. To raise the material yield, *upset forging is used to swell* the crown portion from the stem diameter. The rod end is heated by resistance heating and upsetted (process 5).
MANUFACTURING PROCESS OF THE VALVES:

Die forging stamps the swollen portion into the crown shape (process 6) and the stem of the bonded valve is heated and quench hardened (process 18).
MANUFACTURING PROCESS OF THE VALVES:

Exhaust valves reach very high temperatures and their strength at such temperatures relies on selecting a suitable material. However, there is also a way to control the temperature of the valve structurally, by using a hollow valve containing sodium. The Na in the stem melts during operation and the liquid metal carries heat from the crown to the stem. Na is solid at room temperature, but melts at 98 °C and the valve stem works as a heat pipe.

Reciprocating aero-plane engines used this technique during the Second World War, as do high-power-output car engines at present. Historically, a valve enclosing a liquid such as water or mercury was first tried in the UK in 1925, and also tried with a fused salt, KNO₃ or NaNO₃, in the USA.

Friction welding is used to enclose Na in the valve stem. In the frictionwelded valve, the crown side is first drilled to make a cavity for the Na. Na and nitrogen are then placed in the hole and the crown side is friction-welded to the shaft.
INCREASING WEAR RESISTANCE: Stellite coating

The carbon soot formed by combustion can stick to the valve, hindering valve closure and consequently causing leakage.

To prevent this, the valve revolves during reciprocative motion. The rotation rubs off the soot and prevents uneven wear of the valve face and seat.

The face is exposed to high-temperature combustion gas and so this rubbing occurs without oil lubrication.

The valve material itself does not have high wear resistance, so must be hardened to improve wear resistance at high temperatures.
INCREASING WEAR RESISTANCE: Stellite coating

Wear resistance in the valve face is improved by a process known as hard facing. The valve face is gradually coated with melted stellite powder, a cobalt-based heat-resistant alloy, until the entire circumference is overlaid. A plasma welder or a gas welder is used to melt the powder. The figure shows a cross-section of an exhaust valve crown. The microstructure of the stellite is a typical dendrite, characteristic of cast microstructures. The result is a hardness value of around 57 HRC.
INCREASING WEAR RESISTANCE: Stellite coating

Cobalt-based heatresistant alloys have excellent heat resistance compared to Fe or Ni-based alloys but are costly. Hence, a small amount is used only where their high heat-resistant properties are required.

Among stellite alloys, there are alloys with increased Ni and W, which are much more wear resistant. Recently, instead of stellite, Fe-based hard facing materials have been developed to reduce costs. The typical composition is Fe-1.8%C-12Mn-20Ni-20Cr-10Mo.
INCREASING WEAR RESISTANCE: Stellite coating

Wear in the valve lifter results from contact with the valve stem end. The valve stem end is also coated with stellite to increase wear resistance as a substitute for quench hardening.

The valve stem also rubs against the inside of the valve guide. To improve wear resistance here, salt bath nitriding or hard chromium plating are used. Salt bath nitriding is preferred for high-chromium heat-resistant steel, and can produce a more homogeneous nitrided layer compared to gas nitriding.
INCREASING WEAR RESISTANCE: Ni-base superalloys

Stellite is expensive to use. Valves that use **Ni-based superalloys**, such as Inconel 751 or Nimonic 80A, **have been developed as an alternative** to hard facing.

Valves without a stellite coating are becoming increasingly common as exhaust valves in high-output engines. The table shows the chemical compositions of Inconel 751 and Nimonic 80A. Both are **stronger at high temperatures than austenitic heat-resistant steel**, however, these are cast alloys and are impossible to shape by forging.

<table>
<thead>
<tr>
<th>Ni base superalloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni Balance</th>
<th>Cr</th>
<th>Co</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
<th>Nb+Ta</th>
<th>Hardness</th>
</tr>
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<tbody>
<tr>
<td>Inconel 751</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>Balance</td>
<td>15.0</td>
<td>–</td>
<td>2.5</td>
<td>1.0</td>
<td>7.0</td>
<td>1.0</td>
<td>38 HRC</td>
</tr>
<tr>
<td>Nimonic 80A</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>Balance</td>
<td>20.0</td>
<td>2.0</td>
<td>2.5</td>
<td>1.7</td>
<td>5.0</td>
<td>–</td>
<td>32 HRC</td>
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</tbody>
</table>
INCREASING WEAR RESISTANCE: Ni-base superalloys

Ni-based superalloys get their *increased strength due to precipitation hardening*. The hardening mechanism is the same as for austenitic valve steels (and Al-alloys). Coherent precipitation gives high strength by raising the internal stress of the matrix.

In the Ni-based superalloy, the high temperature strength is at a maximum when a coherent precipitate Ni$_3$(AlTi) appears.

Ni-based superalloys make the *valve face strong to remove the need for stellite*, but *cannot give enough wear resistance at the stem* or stem end. *Nitriding is not possible* for Ni-based superalloys. To overcome this, a *small piece of martensitic steel is friction-welded to the valve stem end*. 
LIGHTER VALVES USING OTHER MATERIALS: Ceramics

New materials for producing lightweight valves have been tested. For engines with large diameter valves, lightweight materials are a definite advantage. Silicon nitride \((\text{Si}_3\text{N}_4)\) valves have been researched extensively.

\(\text{Si}_3\text{N}_4\) weighs as little as 3.2 g/cm\(^3\). It has a bending strength of 970 MPa at room temperature and 890 MPa even at 800 °C.

By contrast, the austenitic steel SUH35 shows a bending strength of only 400 MPa at 800 °C.

It has been reported that the weight reduction from using \(\text{Si}_3\text{N}_4\) instead of a heat-resistant steel valve is 40%.
LIGHTER VALVES USING OTHER MATERIALS: Ceramics

Ceramic materials are brittle under tensile stress conditions, so design and material quality are very important. Silicon nitride powder is first molded and then baked. To increase reliability, particular attention is paid to the purity of the materials, grain size and the baking process.

Some ceramic parts have already been marketed as engine parts. These include:

- insulators for ignition plugs,
- the honeycomb for exhaust gas converters,
- turbo charger rotors,
- wear-resistant chips in a valve rocker arm, and
- the prechamber for diesel engines.

However, despite vigorous research efforts, ceramic valves have not yet been marketed.
LIGHTER VALVES USING OTHER MATERIALS: Ti-alloys

Titanium alloys have also been used for valves.

The Toyota motor company marketed an exhaust valve in 1998 made from a Ti matrix composite alloy, Ti-6%Al-4Sn-4Zr-1Nb-1Mo-0.2Si-0.3O, containing TiB particles (5% by volume).

The relative weight was about 40% lower, which also enabled a 16% decrease in valve spring weight.

It was reported that a

- 10% increase in maximum rotational velocity and
- 20% reduction in friction were obtained.
LIGHTER VALVES USING OTHER MATERIALS: Ti-alloys

**Powder-metallurgy** is the process used to produce an **extruded bar for hot forging**.

A mixture of TiH$_2$, TiB$_2$, and Al-25%Sn-25Zr-6Nb-6Mo-1.2Si powders is sintered at high temperatures. During this sintering, densification through diffusion takes place and the chemical reaction forms TiB particles. This process is called **in-situ reactive combustion synthesis**.

The sintered material is extruded into a bar, which is then forged into a valve using the same process as that used for steel valves. **Additional surface treatments are not necessary because of the high wear resistance of this composite.**
LIGHTER VALVES USING OTHER MATERIALS: Ti-alloys

Another Ti exhaust valve has also been marketed. This valve is not manufactured using powder-metallurgy, but instead uses cast and rolled Ti-6%Al-2Sn-4Zr2Mo-Si alloy, which is widely found in the compressor disk of jet engines. It has a dual structure, where the crown portion has an acicular microstructure and the stem portion an equiaxed one. The acicular microstructure is stronger than the equiaxed one above 600 °C, and is generated by upset forging of the crown portion above the β-transus temperature (995 °C). Plasma carburizing is used to increase wear resistance.
LIGHTER VALVES USING OTHER MATERIALS: Ti-alloys

A Ti inlet valve can also reduce weight.

Since inlet valves do not require the same high heat resistance properties as exhaust valves, normally Ti-6%Al-4V alloy is used.

Exhaust valves made from a Ti-Al intermetallic compound have also been investigated but are not yet commercially available.
THE VALVE SEAT

The valve seat insert has a cone-shaped surface. The seat is pressed into the aluminum cylinder head and seals in combustion gas, so needs to have good wear resistance to ensure an accurate and air-tight seal. Since heat escapes through the cylinder head, the operating temperature for the seat will be lower than that of the valve.

Valve seat inserts for inlet (right) and exhaust (left).
THE VALVE SEAT

In the past, the lead additives in fuel lubricated the contact points between the valve and valve seat, since lead acts as a solid lubricant at high temperatures.

However, unleaded fuel by its very nature does not contain lead-type lubricants.

When leaded petrol was replaced with unleaded alternatives, valve seat materials had to be developed to cope with the changed lubrication conditions.

<table>
<thead>
<tr>
<th>Valve seat materials:</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve seat material</td>
<td>C</td>
<td>Ni</td>
<td>Cr</td>
<td>Mo</td>
<td>Cu</td>
<td>W</td>
<td>Co</td>
<td>Fe</td>
<td>Hardness</td>
</tr>
<tr>
<td>Exhaust</td>
<td>1.5</td>
<td>2.0</td>
<td>8.0</td>
<td>0.8</td>
<td>18.0</td>
<td>2.0</td>
<td>8.0</td>
<td>Balance</td>
<td>35 HRC</td>
</tr>
<tr>
<td>Inlet</td>
<td>1.5</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
<td>4.0</td>
<td>–</td>
<td>–</td>
<td>Balance</td>
<td>100 HRB</td>
</tr>
</tbody>
</table>
THE VALVE SEAT

In the past, valve seats were manufactured from cast iron, but now sintered materials are more common.

Generally, valve seat materials are iron-based sintered alloys containing increased Ni, Co, Cr and W. The high Cr and W compositions increase carbide dispersion.

The exhaust valve seat contains the highest levels because it is exposed to more severe wear at higher temperatures. Cu and/or Pb22 are included as solid lubricants.

<table>
<thead>
<tr>
<th>Valve seat material</th>
<th>C</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>W</th>
<th>Co</th>
<th>Fe</th>
<th>Hardness</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exhaust</td>
<td>1.5</td>
<td>2.0</td>
<td>8.0</td>
<td>0.8</td>
<td>18.0</td>
<td>2.0</td>
<td>8.0</td>
<td>Balance</td>
<td>35 HRC</td>
<td>Quench &amp; temper</td>
</tr>
<tr>
<td>Inlet</td>
<td>1.5</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
<td>4.0</td>
<td>–</td>
<td>–</td>
<td>Balance</td>
<td>100 HRB</td>
<td>Quench &amp; temper</td>
</tr>
</tbody>
</table>
REFERENCE, SOURCE

Hiroshi Yamagata: The science and technology of materials in automotive engines, Woodhead Publishing Limited and CRC Press LLC, 2005