Explanations

Hydrogen and hydrogen-nitrogen pinholes

The formation of pinholes progresses in several stages:

1. The surface reaction of water vapour with other elements in the iron gives rise to metal oxides and atomic hydrogen which diffuses into the molten metal. Similarly, nitrogen-hydrogen compounds dissociate on the hot metal surface and diffuse into the molten metal. Dissociation of molecular nitrogen and hydrogen does not take place at the prevailing casting temperatures.

2. Due to enrichments in the slag, the metal oxides react with the carbon in the melt to form CO molecules which are precipitated from the melt and form micro-blowholes.

3. Hydrogen, and sometimes nitrogen, diffuse from the liquid metal into the CO micro-blowholes and increase their size.

Pinholes due to CO-slag reaction

These occur due to the reaction of heavily oxidizing, molten slags (mostly MnO / MnS-rich slags) with the carbon in the melt to form CO. Later in the process, hydrogen can also diffuse into these blowholes.

Pinhole porosity – surface blowholes

Differentiation is made between hydrogen pinholes, hydrogen-nitrogen pinholes and pinholes due to CO-slag reactions.

Characteristic features

- Pores or small blowholes with a smooth surface. Sub-surface blowholes often contain a thin graphite film. There is no differentiation between hydrogen and hydrogen-nitrogen pinholes.
- Pinholes due to CO-slag reaction also have smooth surfaces. The size of sub-surface blowholes can vary considerably. Blowholes occur in conjunction with oxygen-rich slag.

Incidence of the defect

Pinholes can appear individually or over an area. All areas of the casting can be affected. However, pinholes are more common in areas of the casting located away from the gate. Hydrogen and hydrogen-nitrogen pinholes occur in both grey and SG iron castings. Pinholes due to CO-slag reaction only occur in grey iron castings.

Fig. 32: Large areas of surface blowholes/pinholes on a grey iron casting.
Scale: 10 mm = 4 mm

Description of defects: Pinholes

Assistance for decisions ➔ P. 154
Sand control ➔ P. 181
Possible causes

Metallurgical
Ferrous metals
• Nitrogen content in the melt too high due to the charge composition.
• Proportion of oxides, hydroxides (rust) and other impurities in the charge materials too high
• Aluminium content in the melt too high
• Manganese and sulphur contents in the melt too high

Clay-bonded sand
• Nitrogen content in the sand too high
• Moisture content of the sand too high
• Lustrous carbon production in the moulding sand too low

Resin-bonded sand
• Nitrogen content in the core sand too high
• Proportion of nitrogen/hydrogen compounds in the core binder too high

Gating and pouring practice
• Pouring passages too long
• Too much turbulence and slag formation during pouring

Remedies

Metallurgical
• Use charge components with low nitrogen content, e.g. reduce the quantity of steel scrap.
• Use scrap and return material free of rust, water and oil impurities. Use circulating materials free of impurities adhering to sand and feeder auxiliaries.
• Use charge materials and especially inoculants and circulating materials with low aluminium and titanium contents.
• Deoxidize melts as well as possible. Avoid excessive supply of titanium or aluminium.
• Reduce the formation of slag, and particularly the formation of slags containing manganese sulphide, by adjusting the manganese and sulphur content.

Clay-bonded sand
• Reduce nitrogen content in the sand. Reduce the quantity of inflowing nitrogen-containing core sand. If necessary, add new sand to the circulating sand.
• Reduce the moisture content of the sand.
• Lower the bentonite content. Improve development of the moulding sand. If necessary, reduce inert dust content. Keep amount of lustrous carbon carrier at the minimum level.
• With an oxidizing atmosphere in the mould cavity, if necessary increase the quantity of lustrous carbon producer in the moulding sand. Avoid adding too much.

Resin-bonded sand
• Reduce the amount of binder. Use binder with lower nitrogen content.
• Improve core venting. Dress core if necessary.
• Add iron oxides to the core sand mixture.

Gating and pouring practice
• Increase pouring temperature
• Reduce flow rate into the mould
• Avoid turbulence when pouring.

Fig. 33: Section through the surface of a grey iron casting in the area of pinhole formation. Pinhole formation is promoted by surface oxidation, recognizable in the formation of ferrite. Scale: 10 mm = 0.08 mm
In the formation of CO bubbles, the surface tension of the melt is proportional to the work to be expended. According to Frenkel and Thompson, the intensity \( I \) of pinhole formation is described by the following equation:

\[
I = A \cdot e^{-\frac{A K T}{r}}
\]

The influence of surface tension on the formation of pinholes has been investigated. Higher surface tension suppresses pinhole formation.

Surface tension at 1400°C

Calculations of the gas pressure at which blowholes/pinholes can occur show that the melt must be considerably over-saturated with gases such as nitrogen and/or hydrogen.

Sub-surface blowholes can form on solid reaction products in the melt at considerably lower gas pressures (phase boundaries). Similarly, where CO bubbles are formed through the reaction of oxides with the carbon in the melt, the dissolved gases (nitrogen, hydrogen) diffuse into the molecular gas pockets and form pinholes.

Sufficient oxygen enrichment near the surface of the melt is necessary for the formation of CO bubbles. According to Gibbs, the formation of molecular CO blowholes is determined through the work to be expended:

\[
A_k = \frac{4}{3} \sigma r^2
\]
In addition to pure CO pinholes, molecular CO bubbles can be regarded as the nucleus for hydrogen and hydrogen-nitrogen pinholes.

**Hydrogen pinholes**

Hydrogen is primarily introduced into a melt through the reaction of strong oxygen binding agents in the melt, e.g. aluminium, magnesium and titanium, with water vapour.

\[
\text{Me} + \text{H}_2\text{O} \rightarrow \text{MeO} + 2\text{H}
\]

The atomic hydrogen is immediately absorbed by the melt. Water vapour is produced by moist refractories, rust-containing input materials and the binding clays used in the moulds, and is also present in the mould cavity air during pouring.

Table 1 shows how long a melt absorbs hydrogen from the lining of a cupola.

<table>
<thead>
<tr>
<th>Tapping time</th>
<th>Hydrogen content [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00</td>
<td>5.6</td>
</tr>
<tr>
<td>7.20</td>
<td>4.2</td>
</tr>
<tr>
<td>7.40</td>
<td>3.0</td>
</tr>
<tr>
<td>9.00</td>
<td>2.2</td>
</tr>
<tr>
<td>11.00</td>
<td>1.8</td>
</tr>
<tr>
<td>12.00</td>
<td>1.4</td>
</tr>
<tr>
<td>14.15</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Cold blast test cupola, tap weight in each case 400 kg.
Cupola diameter 140 cm
Acid furnace lining
The furnace was lined 24 hrs. previously.

**Pinholes due to CO-slag reactions**

In the formation of this defect, low-viscosity silicate slags rich in manganese oxide and enriched with manganese sulphide react with the carbon in the melt and form CO. With high manganese and low silicon contents, the manganese reduces silica from slags and the refractory lining, forming highly liquid manganese oxide slags. High sulphur contents enable the formation of MnS, which is enriched in the slag and makes the slags even more reactive.

In addition to sulphur, titanium and tellurium content on surface tension and pinhole formation in grey cast iron.

**Surface tension at 1400°C**

Fig. 37: Influence of sulphur, titanium and tellurium content on surface tension and pinhole formation in grey cast iron.

**Fig. 38: Influence of manganese and sulphur content and pouring temperature on the formation of pinholes.**
The formation of pinholes can also be avoided if there is sufficient lustrous carbon producer in the mould. The reducing atmosphere prevents the formation of CO bubbles. Various authors have highlighted that admixtures of pit coal dust and other lustrous carbon producers can help to prevent pinholes.

**Nitrogen-hydrogen pinholes**

In addition to hydrogen pinholes, nitrogen-hydrogen pinholes occur where nitrogen-containing binding agents are used. Such defects are primarily generated through the use of binders containing urea. The nitrogen-hydrogen radicals are broken down near the surface of the melt, which immediately absorbs them in the atomic state.

These surface blowholes often have a graphite film and a ferrite seam like the hydrogen pinholes. They form in a similar way to that described under hydrogen pinholes. Many reports have been published on these pinhole phenomena.

**Avoidance of nitrogen-hydrogen pinholes**

These pinholes can occur where there is a high nitrogen content in the melt resulting from the use of charge materials such as steel scrap or nitrogen-containing carburizing compounds. Here, too, a crucial contribution is made by the combined action of gases from the mould cavity and the mould. High nitrogen contents in the melt (over 100 ppm), in the carburizing agent, in the core binder and in the bentonite-bonded sands should be avoided.

The use of increased proportions of lustrous carbon producers in the moulding sand to achieve a reducing atmosphere has also proved to be effective.

In the case of cores, the addition of iron oxides and barium sulphate will help to prevent this defect.

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**Fig. 39**: Blowholes/pinholes over the complete surface of a grey iron casting. Scale: 10 mm = 8 mm
**Pinholes due to CO-slag reactions**

Under certain conditions, oxygen-rich slags can react with the carbon in the melt to form CO. Liquid iron oxide-rich slags also react this way:

\[
\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}
\]

The pinholes may be observed on the surface of the casting but are sometimes not visible until it is machined. All slags formed during melting and pouring can become highly fluid through enrichment with FeO or MnO, and then react with carbon to form blowholes/pinholes.

Pinholes of this type mostly have slag inclusions in the pockets, such inclusions often containing MnS precipitations. The large influence of MnS on the formation of the pinhole can be traced back to the liquefaction of the slag and thus its increased reactivity.

Hydrogen also negatively influences this defect.

**Avoidance of slag-CO surface pinholes**

In order to avoid this surface defect, it is necessary to increase the pouring temperature, reduce the sulphur content and restrict the manganese content.

BCIRA recommends foundries to keep to a 0.7 % manganese content.

Other authors recommend that the manganese content be kept no higher than 0.4 % of the Si content.

It is also recommended that the melt be given little opportunity to oxidize. Turbulence during filling should be avoided and liquid-metal flow paths kept short. As water vapour has a strongly negative effect, the bentonite content in the moulding sand should be as low as possible.

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