

ELIMINATION OF SUB-SURFACE PINHOLE POROSITY DEFECTS IN ALLOY STEELS BY FERROSELENIUM ADDITIONS



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ARTICLE TAKEAWAYS:

- Understanding humidity and resulting porosity
- Elimination of Sub-Surface Porosity in High Alloy Steels
- Case study shows effective solution for preventing subsurface porosity

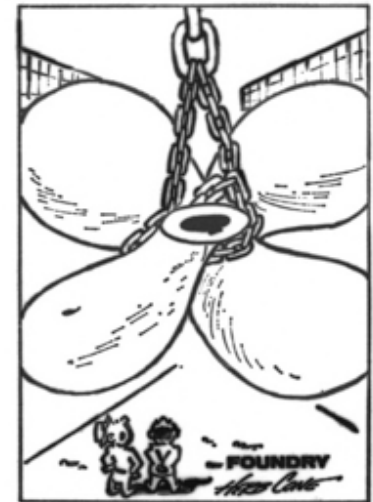
Introduction: Nothing is more frustrating in foundry operations than finding an outbreak of subsurface porosity after costly machining operations. (see Figure 1)

Outbreaks of subsurface porosity seemingly always occur during high humidity seasons, and especially during the spring. The prime culprit almost universally is blamed on hydrogen absorption into molten steels. The hydrogen atom is the smallest and simplest of all the elements. It must be noted here that hydrogen can only be absorbed in its mono-atomic state. Along with hydrogen, nitrogen can also play a significant role in the development of porosity, especially in the production of alloy and high alloy steel castings.

Both mono-atomic hydrogen

and nitrogen absorption in steel casting operations can result from alloy additions and reactions at the mold metal interface. The ability of molten steel to absorb large amounts of hydrogen and nitrogen is shown in Figure 2.

Molten steels can readily absorb hydrogen in excess of the solubility limit. When a casting that contains high hydrogen levels solidifies, subsurface porosity will inevitably result. Hydrogen pickup can occur from almost any source of moisture, such as refractories, green sand molds, chemical mold and core binder decomposition,



"Funny ain't it, how one little ol' pin-hole can ruin yer whole day?"

Figure 1: Cartoon from Foundry Management and Technology circa 1973

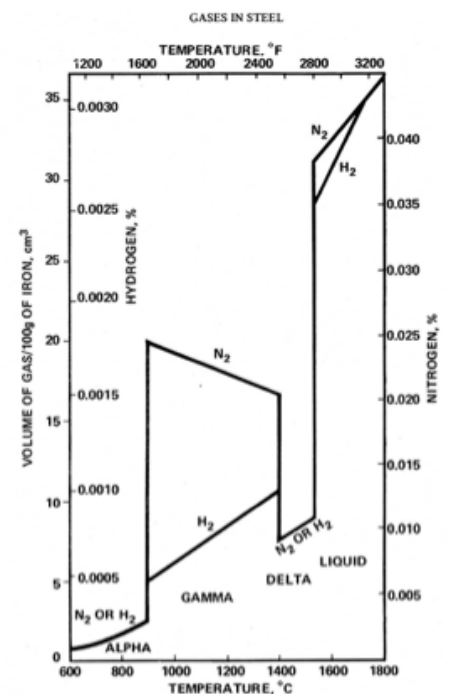


Figure 2: Solubility of Hydrogen and Nitrogen in molten iron (1)

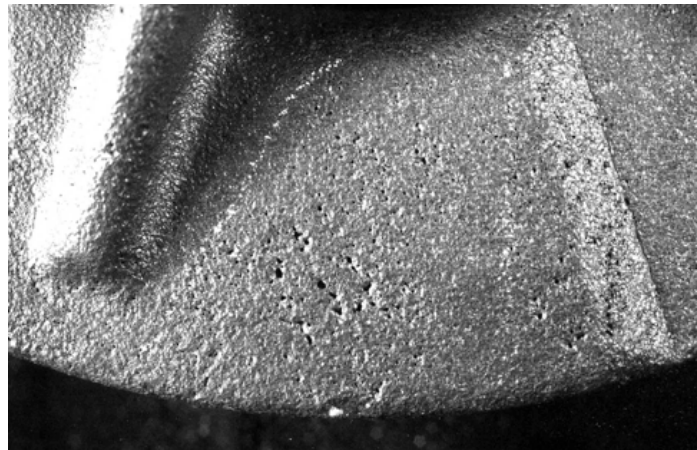
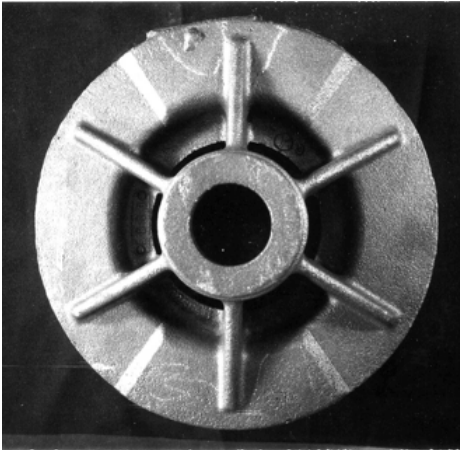


Figure 3:
Steel axle bracket
from a mining car
illustrating sub-
surface porosity

slag additives and atmospheric humidity. Nitrogen behaves in a similar manner and can result from the processing of some ferroalloys as well as decomposition products from chemical mold and core binders.

Appearance: Pinhole defects are a form of gas porosity. They are usually small, elongated holes (about 1/16 in. in diameter) at or immediately below the casting surface with the long axis of the pinhole perpendicular to the casting surface. The walls of pinholes in steel are often smooth and bright. When the pinholes extend to surface of the casting, the interior may appear oxidized and show a faint dendritic structure. Pinholes may

occur at or below any casting surface but will tend to occur more readily in thin and intermediate transition thicknesses, where re-entrant angles can serve as hot spots. Figure 3 illustrates typical subsurface pinholes in a high alloy steel casting.

Sources of Gas from Mold-Metal Interface Reactions:

With few exceptions, core and mold binders used in the steel foundry industry are organic based systems. Being organic, they are based on the elements carbon, hydrogen, and oxygen and in some cases nitrogen. The approximate chemical make-up of some of the common binder systems is shown in Table 1 (a typical Western Bentonite bonded green sand is

shown for comparison). Newer binder formulations have been developed in recent years to minimize hazardous air pollutants (HAPs), and these modifications have had a direct effect on the chemical makeup of the binder systems. More recently, TEOS solvent systems (a silicate-based solvent combining both organic and inorganic characteristics) have replaced traditional aromatic and aliphatic solvents. The primary performance advantages over aromatic hydrocarbon or biodiesel solvents is reduced smoke and odor. These newer binders can reduce HAP's at pouring, cooling and shakeout.

At ferrous casting temperatures, the presence of these elements (carbon, hydrogen, oxygen and nitrogen) and their subsequent decomposition products can produce a variety of casting defects. The following gaseous reactions are thermodynamically possible and under the right conditions may occur at the mold-metal interface⁵⁶.

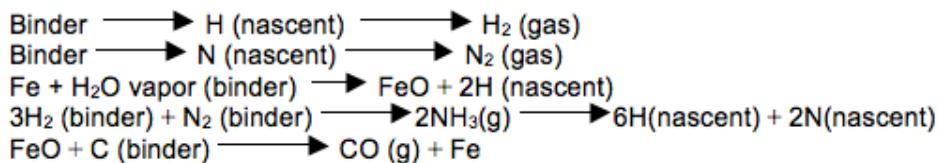
Hydrogen is absorbed into

Binder Type	% Carbon	%Hydrogen	%Nitrogen	% Oxygen
Phenolic Urethane Cold Box (2002 standard)	73.0	7.9	3.9	14.8
Phenolic Urethane Cold Box (2002 biodiesel)	68.4	8.1	4.0	20.0
(Biodiesel or vegetable oil based solvents)				
PU Cold Box (2002 all aromatic)	74.6	7.6	3.4	14.8
All Aromatic solvents				
PU No Bake (2002 standard solvents)	75.3	8.0	3.4	13.7
Premium Furan No Bake (2002)	52.9	6.6	0.56	38.4
Phenolic Ester No Bake (2002)	31.5	8.4	0.02	60.1
PU Coldbox (TEOS solvents) ⁽²⁾	65.0	7.0	3.8	25.0
PU No Bake (TEOS solvents) ⁽²⁾	65.0	7.0	3.8	25.0
Shell Sand (3.5% Binder, 12% Hexa) ⁽²⁾	71.1	5.8	4.3	18.8
Green Sand 3.2% moisture, 5% WB **	0	12.0	0	88.0
** Western Bentonite, ⁽²⁾ - Courtesy of Doug Trinowski, HA International				

Table 1. Approximate chemical composition of current foundry binders systems

Continued on next page

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molten steel from moisture in atmosphere and refractory materials, deoxidation and alloying elements, and slag additives. Because hydrogen is such a small atom, it can diffuse rapidly once it's absorbed, creating pinholes. Hydrogen absorption can also result from the decomposition of water vapor in green sand molds, from chemical mold or core binder decomposition or from high humidity conditions on the melt deck. Increased usage of recycled metallic borings containing residual cutting fluids will also contribute to hydrogen pick-up.

Nitrogen can also readily be absorbed in molten steels from gaseous decomposition products from mold and core binders as well as certain charge materials. Roach and Simmons (3) reported that all stainless steels will tend to pick up nitrogen when melted in air. The ability to retain nitrogen has been shown to be dependent on chrome and manganese levels in steel. Higher chromium and manganese will permit retention of great amounts of nitrogen.

Nascent or mono-atomic hydrogen and nitrogen are readily soluble in molten irons and steels. While the first four reactions are likely to generate both surface and subsurface porosity defects, the last reaction usually results only in surface defects, such as surface pockmarking or more often, lustrous carbon laps and surface wrinkles (4).

Sources of Gas from Alloying

Materials: The solubility of nitrogen in chromium alloys can be quite high, unless the foundry specifies the need for a low nitrogen ferrochrome grade. In one reported instance, a stainless steel foundry was experiencing severe subsurface porosity and upon further investigation, it was found that the low carbon (0.05% carbon) ferrochrome that was being used contained over 10,000 ppm (1.0 pct) nitrogen. The foundry had no idea that they should put a nitrogen specification on the low carbon chrome that they were purchasing.

Nitrogen and hydrogen are also very soluble in manganese alloys so great care must be taken by the foundrymen to specify low hydrogen and nitrogen grades, particularly with electrolytic grades of manganese metal. Hydrogen has also been found to be present in electrolytic nickel cathode squares.

The observation that hydrogen and nitrogen are additive in promoting porosity is supported by some analytical data. Rassbach, Saunders, et al (5) found in experimental heats of type 410 (11 to 13% Cr) stainless steels containing 230 ppm nitrogen (0.023%) and 5 ppm hydrogen (0.0005%) were sound. Increased nitrogen levels of 300 ppm nitrogen (0.030%) and 4 ppm hydrogen were also sound. However, an increase of 3 ppm in hydrogen (7ppm or (0.0007 total) on the heat containing 300 ppm

nitrogen (0.030%) produced severe pinholes. This pattern indicated that in type 410 stainless steel, even with nitrogen as low as 300 ppm (0.03%), hydrogen to the extent of 7 ppm level was excessive. This anomaly has come to be known as complex nitrogen/hydrogen pinholing.

Elimination of Sub-Surface Porosity in High Alloy Steels:

Research work conducted in the late 1960's identified that the use of ferroselenium can substantially eliminate subsurface porosity in green sand molds (6). At the time of the research, chemical binder technology was in its infancy so none of binders systems shown in Table 1 were investigated. However, it has since been found that the addition of ferroselenium can also be effective when using chemically bonded sand.

One of the primary uses of ferroselenium in the foundry industry is the control of hydrogen porosity. Small amounts of FeSe can virtually eliminate hydrogen porosity (pinholes) in carbon, medium, and high alloy cast steels, wear resistant iron castings such as Ni Resist, and stainless steels poured in green sand or chemically bonded molds. Typical addition rates are 0.005% Se to 0.02% Se (0.10 lbs to 0.40 lbs per ton) but as much as 1 lb. per ton can be added. Because such small additions are used, FeSe is briquetted into a uniform shape to facilitate accurate weight additions. It is generally believed that selenium prevents pinhole porosity by its influence on the surface tension of the melt, so that solid surfaces are not wetted and the probability of heterogeneous gas bubble nucleation is reduced.(6) It is also reported that selenium additions of 0.10% can reduce the rate of nitrogen absorption in liquid steel.

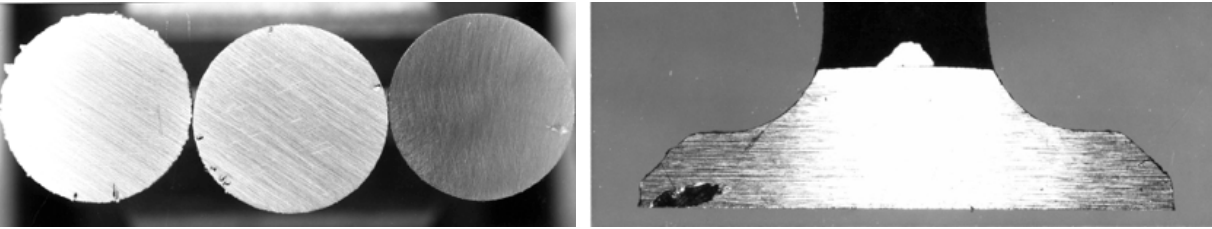


Figure 4:
Macrophotographs of sub-surface pinholes found in high chrome nickel valves. Top of valve head and longitudinal section.

Example of FeSe additions at Foundry X:

To illustrate how effective the addition of FeSe to a high chrome-nickel alloy valve casting (nominally 1.6% C, 21% Cr, 6% Mn, 4% Ni, 0.2% N) is shown in this example from Foundry X. Nitrogen (2000 ppm) is intentionally added to stabilize austenite and added as a nitrogen bearing FeCr. Foundry X is a shell sand foundry pouring a variety of high chrome-nickel stainless steel castings. In the spring during the rainy (high humidity) season, outbreaks of subsurface porosity would inevitably occur. Due to the seasonal nature of this problem, finished scrap has occasionally risen to as high as 80% for a given month. During the investigation it was thought that complex hydrogen/nitrogen pinholing arising from breakdown of the nitrogen-bearing synthetic resin binders used for shell molds was partly responsible for the porosity. Examples of the type of subsurface porosity are shown in sectioned valve castings (see Figure 4).

In an effort to reduce overall gas levels, Foundry X embarked on an extensive study of variables that might be the cause of the subsurface porosity. This included:

- Varying metal pouring temperatures from 2800°F to 3050°F
- Melting under a protective argon cover
- Rapid melting and minimizing metal holding times

- Adding iron ore and nickel oxide to initiate a moderate carbon boil
- Deoxidation practice using various CaSi, CaSiBa, Aluminum and Misch Metal additions
- Additions of ferrozirconium, ferrotitanium and a complex alloy consisting of (Fe-Si-Mn-Al)
- Reducing the charged nitrogen levels

To determine the effect of charged nitrogen, heats made without nitrogen additions contained 0.05% to 0.07% (500 to 700 ppm) nitrogen. Three factors were responsible for the increase in nitrogen levels:

1) melting in air ⁽³⁾, 2) nitrogen pickup from the shell molds and 3) increased nitrogen solubility from chrome and manganese in the alloy. Even at these lower nitrogen levels, intermittent porosity still occurred.

Extensive analytical work was conducted along the way to determine if nitrogen and/or hydrogen was responsible for subsurface defects, extreme care was taken in analyzing for hydrogen. Test castings were immediately quenched and stored in liquid nitrogen to prevent diffusion of hydrogen from the samples.

Almost without exception, no definitive variable was identified as the culprit for the sub-surface pinholes. Only when adding 0.02% FeSe to the ladle after deoxidation with 0.10% aluminum

and 0.06% ferrotitanium did the porosity problem disappear. It appeared likely that the subsurface porosity was the result of complex hydrogen/nitrogen interactions.

Conclusion: The addition of small controlled amounts of ferroselenium (up to 0.02%) and keeping the charged nitrogen on the lower end of the specification was the only foolproof method that was effective in preventing subsurface porosity at Foundry X.

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