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# Nitrogen Defects in Iron Castings

By J. M. Greenhill and N. M. Reynolds*

**Recent changes in ironfounding practice have brought with them the risk that excessive nitrogen may be introduced into the iron. Sources of this nitrogen may be steel scrap, carburisers, mould- and core-binders, reclaimed resin-bonded sand, coatings and adhesives. Its adverse effects are examined, and ways of minimising them are indicated.**

Nitrogen may be absorbed by liquid iron during the melting operation or the filling of a mould cavity; levels between 0.004% and 0.009% are quite common in commercially produced grey cast irons. At these levels, nitrogen can have beneficial effects, promoting fully pearlitic structures and improving hardness and tensile strength[1]. At nitrogen levels above 0.009% the iron is less able to retain the gas; during solidification, nitrogen is liberated and forms pinhole or fissure defects, sometimes in combination with hydrogen.

### Pinhole Defects

During the past decade or so there has been considerable technological development in the ironfounding industry, particularly in metal production and in sand-binder systems. One of the principal changes has been a significant reduction in the amount of pig-iron used coinciding with an increase in the use of steel scrap, in both cupola and electric-furnace melting. Another has been in moulding and core-making, where there has been a great increase in the use of synthetic resins as binder materials; they replace conventional vegetable oils and the dry-sand moulding process. These changes, whilst having considerable economic and production advantages, can lead to nitrogen pick-up resulting in pinhole or fissure defects that may first be revealed by costly machining operations.

The principal sources of nitrogen, which can lead to defects in grey iron castings, are reviewed in this paper. In general, their effects are cumulative: the greater the number of sources of increased nitrogen, the greater is the danger that unsoundness in the form of pinholes, blowholes, or fissure defects will occur in castings. If hydrogen is present, a tolerable level of nitrogen may then become dangerous and the cumulative effect of both gases then results in the formation of fissure or pinhole defects.

### Melting Process as a Source of Nitrogen

The effects of melting in the cupola, and of electric melting, are now considered.

*Cupola melting*—The cupola furnace is the most widely used means for producing cast iron. During the past decade there has been a noticeable trend towards using higher proportions of steel in the charge, both for the production of high-duty irons, ie grades 260-350 (17-23), and for lower grades for general engineering applications. The greatest possible use of steel scrap is clearly economical when the higher price of pig-iron is considered.

A number of workers[1,2] have noted a progressive increase in the nitrogen contents of irons as the percentage of steel scrap in the charge is increased. Observations in foundries have frequently indicated that irons produced from high steel-scrap charges (in excess of 50%), are prone to fissure defects; fig. 1 shows a machined casting exhibiting such defects due to nitrogen.

Commercially produced irons can contain between about 0.004% and 0.013% nitrogen, the level chiefly depending on the quantity of steel in the charge. Generally, irons produced from charges containing low levels of steel, ie less than 15%,

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**Stickstoffdefekte in Gusseisenteilen**

**von J. M. Greenhill und N. M. Reynolds**

Anderungen bei Giessereiverfahren in letzter Zeit haben das Risiko mit sich gebracht, dass zu veil Stickstoff in das Eisen eingeführt werden kann. Quellen dieses Stickstoffes können Stahlschrott, Aufkohlungsmittel, Form- und Kernbindemittel, aufgearbeiteter harzgebundener Sand, Beschichtungen und Klebstoffe sein. Die ungünstigen Auswirkungen werden untersucht und Methoden für deren Verringerung angedeutet.

**Défauts dus à l'azote dans les pièces de fonte**

**J. M. Greenhill et N. M. Reynolds**

Les modifications intervenues récemment dans les méthodes de fonderie ont entraîné des risques d'introduction excessive d'azote dans la fonte. Cet azote provient de sources diverses dont la ferraile, les produits de cémentation, les liants de moule et de noyau, les sables de récupération liés à la résine, les revêtements et les colles. Cet article examine les effets indésirables de ce phénomène et les moyens de les éviter.

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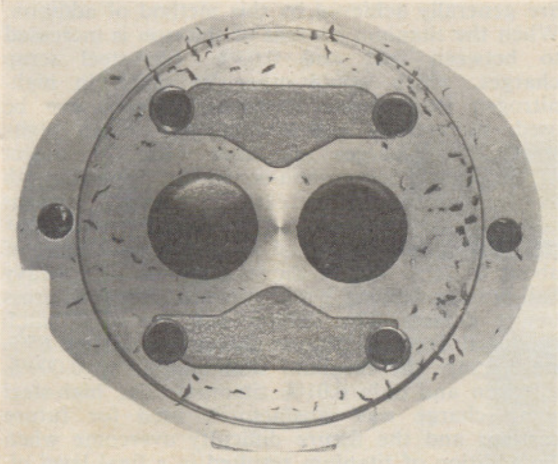

1 Extensive nitrogen fissure defects revealed after machining of pump casting.

## NITROGEN DEFECTS IN IRON CASTINGS

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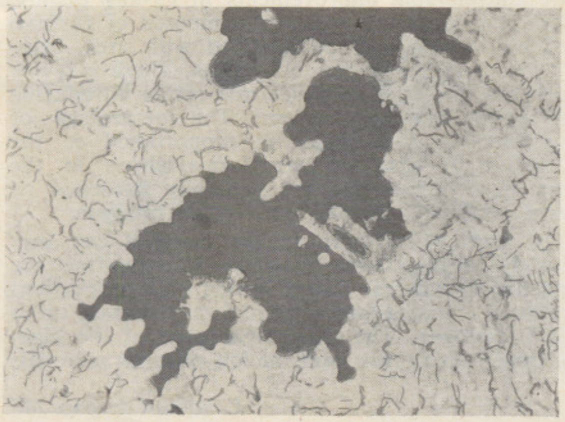
will have nitrogen levels in the range 0.003 to 0.005%. With high steel contents, ie greater than 50%, levels of nitrogen in the resultant iron will generally be greater than 0.007% and can be as high as 0.013%. The level of nitrogen in the resultant iron is affected by the nitrogen content of the steel scrap used, high nitrogen steels leading to high nitrogen in the iron. A significant amount of nitrogen is most probably picked up from the coke charge, coke usually containing between 0.4 and 1.0% nitrogen.

Experience has shown that when the nitrogen content of the iron is greater than about 0.009%, castings are prone to defectiveness as shown in fig. 1. Viewed under the microscope, the defects tend to be dendritic in form as in fig. 2, and often contain discontinuous graphite films. Increasing the nitrogen content modifies the graphite form by rounding of the flakes and at high levels severe compaction will take place as in fig. 3. The level of nitrogen in this instance being 0.0140% with a titanium of less than 0.01%.

2 Interdendritic form of nitrogen fissure defect, with discontinuous graphite film.



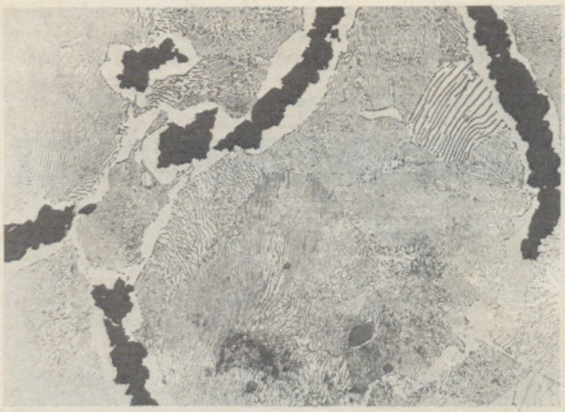
In borderline cases it is often found that the nitrogen content of the iron may be reduced to a safe level merely by reducing the steel content by 5%, and substituting for this either pig-iron, or suitable cast iron scrap.

*Electric melting*—Electric-furnace melting makes it possible to produce iron of closely controlled composition even when a high proportion of steel scrap is used in the charge. Many foundries are now producing irons from electric furnace installations, using only steel scrap and returned cast iron scrap. Frequently, steel scrap up to 80% is included in the charge; then it is necessary to add substantial quantities of carburiser, to arrive at iron having the required carbon content; often as much as 3% carbon as a carburiser is added to electric-furnace charges.

The quality of the carburiser is important, since these carburising materials may contain significant quantities of nitrogen. Certain petroleum cokes, used for carburising, may contain up to 0.5% nitrogen, and if enough of such material is used a dangerous level of nitrogen in the iron may result; whereas high-purity graphites contain about 0.0015% nitrogen and contribute insignificant quantities of the gas when used to carburise steel melts. It is important, therefore, to know the nitrogen content of the carburiser being used, and to be able to calculate the percentage of nitrogen added by the treatment. For example, a carburiser containing 0.3% nitrogen can contribute 0.003% of the gas for every 1% carbon addition; a 3% addition would certainly result in an iron having a high tendency for nitrogen fissure defects to occur. Davison and others[3] in 1961 encountered gross nitrogen fissure defects, in very large iron castings, only after conversion from cupola to electric-furnace melting. The main source of the nitrogen in the electric furnace charge was from Gilsonite, a carbonaceous material containing up to 2.4% nitrogen; when a more expensive, pure Mexican graphite containing only 0.1% nitrogen was used, the difficulty was overcome.

For the production of iron from high-steel scrap charges in electric furnaces the nitrogen content of the carburiser must be known and restricted,

3 Compacted form of graphite associated with nitrogen fissure defects.



4 Nitrogen fissure defects in heavy ball-bearing lapping plate.

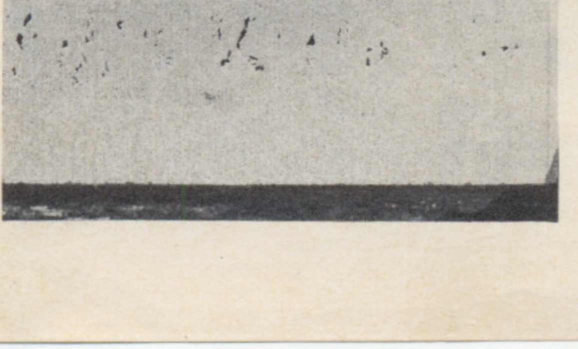
so that addition of significant quantities of the gas to the melt will be avoided. Nitrogen may also be introduced by the use of high-nitrogen steel scrap (some structural steels contain 0.01%) or cast iron borings; in recorded instances, cast iron borings containing over 0.008% nitrogen were contributing significant quantities of the gas to the melt, resulting in fissure defects.

Work has shown[4] that holding liquid metal in an induction furnace may either increase or decrease the nitrogen content, until it attains an equilibrium level; this level, dependent on the carbon content, is higher in low-carbon than high-carbon irons. This is important, since high nitrogen levels produced from high steel charges in either induction furnaces or cupolas can be reduced by holding in large receivers: the adverse effect of nitrogen on soundness is then considerably reduced.

### Neutralisation of Nitrogen

The adverse effect of nitrogen on soundness can be offset by an addition of titanium to the melt[1,3]. Fissure defects can be prevented by ensuring a residual titanium content in the iron of between 0.02 and 0.03%. Titanium combines with the nitrogen to form an insoluble compound, titanium cyanonitride, and so 'fixes' the gas. Generally, high steel charges result in irons having low residual titanium levels, in the range 0.003 to 0.008%. Titanium may conveniently be added to the electric furnace as ferrotitanium, or as commercially pure titanium scrap. Owing to the high melting point of ferrotitanium, it is unwise to add this alloy to cupola-melted iron as it is tapped from the furnace, unless temperatures of about 1500°C are obtained. It has been found in practice that pure titanium swarf or clipped sheet is a satisfactory means of addition, since it readily dissolves in molten iron. To ensure good mixing and complete solution, it is preferable to make the addition to the molten iron as it is flowing down the cupola launder. Recoveries as high as 95% are generally achieved by this method of addition. When the titanium content of the iron is increased to between 0.02 and 0.03%, high-steel scrap charges, which would otherwise result in high-nitrogen irons prone to fissure defects, can be used, successfully and economically. When high-steel scrap charges are used with the object of producing low-carbon-equivalent high-strength irons, or deliberate increases in nitrogen content of the iron are made, it is recommended that titanium should be added to give a final level of about 0.025%. Fig. 4 shows a section of a heavy ball-bearing lapping plate, rejected owing to gross fissure defects. The casting was one of a batch produced from a cupola charge containing 65% steel scrap, the resultant iron containing 0.009% nitrogen and only 0.01% titanium. The high-steel scrap charge was satisfactorily used for future castings and the fissure difficulty overcome when the addition of titanium resulted in a final level of 0.02%.

5 Nitrogen fissure defects in machine tool casting resulting from nitrogen pick-up from the mould material.



The use of titanium to prevent fissure defects has been found to nullify the beneficial effect of nitrogen on strength[1]; the amount used should therefore be kept to a minimum when high strength is required.

Aluminium has a similar effect to titanium[5], but its use to prevent fissure defects is not recommended because aluminium at levels as low as 0.005% can lead to hydrogen pick-up and give pinhole defects, especially in thinner castings. Pick-up of hydrogen through aluminium contamination can have a combined effect with nitrogen, and unsoundness due to both gases can result.

### Moulding and Coremaking Process as a Nitrogen Source

The contribution of nitrogen from moulding and coremaking is considered in relation to three processes: self-setting, using resin binders; hot-box; and the shell, or pre-coated sand, process.

*Self-setting processes using resin binders*—There has been a rapid growth during the past decade in the use of moulding and coremaking processes employing furan no-bake binders. These binders, together with continuous mixers, have had a significant impact on moulding and coremaking activities, permitting increases in productivity accompanied by considerable improvements in casting quality. Furan binders are basically composed of furfuryl alcohol which may be modified with urea, urea-formaldehyde and phenolic resins. There is a risk of urea and urea-formaldehyde resins introducing nitrogen into the system. The percentage of nitrogen in the binder is proportional to the amount of urea or urea-formaldehyde in the system. These resins are generally hardened by acid catalysts, which do not contain nitrogen.

The level of nitrogen in the material can vary widely. Some resins may be nitrogen-free (eg phenolics) whereas others having high proportions of urea (eg urea-formaldehyde) may contain up to 16% nitrogen. The chief advantages of the high-nitrogen urea resins over the low-nitrogen materials

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## Nitrogen Defects in Iron Castings

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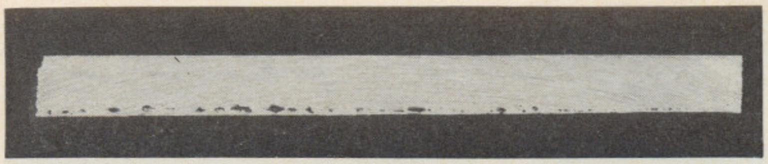


**6** Nitrogen pinhole defects on the water-jacket side of a cylinder bore.

are their lower cost and more rapid rate of cure. The high-nitrogen materials suffer a major disadvantage in that they may promote nitrogen fissure defects of the type illustrated in fig. 5. During the filling of the mould with molten metal, the urea in the binder decomposes and the ammonia gas produced dissociates into free nitrogen and hydrogen. Both gases are capable of dissolving in the liquid iron and may subsequently be liberated as fissures or pinholes during solidification of the casting.

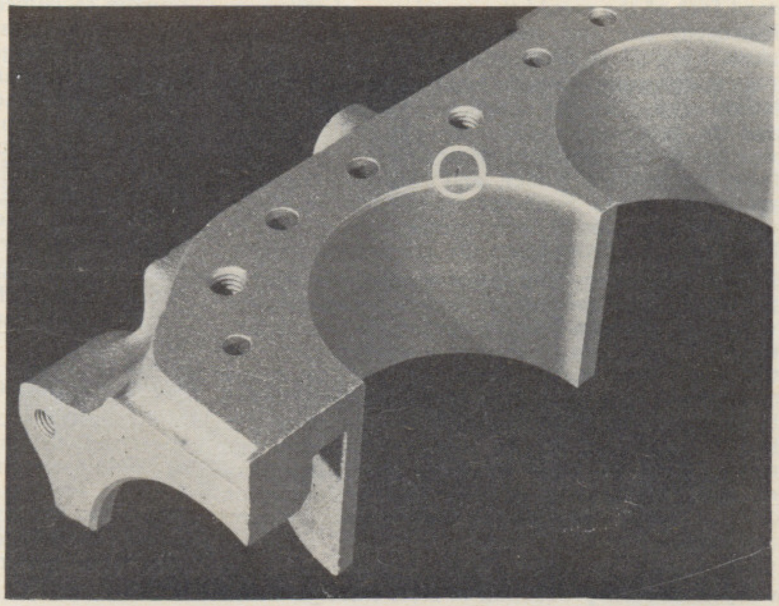
Such defects are often revealed only after extensive and costly machining. In heavy-section castings the gas often has time to diffuse through the solidifying metal; in consequence, the defects only occur in the last zones of the casting to solidify. Fig. 5 shows such an instance, where the gas has been evolved at some distance from the as-cast face. This is more likely to occur when there has been only a small amount of gas pick-up.

Experience has shown that if the nitrogen content of the mould or core is more than 0.15%, there is a serious risk of pinhole or fissure defects in the castings; levels of nitrogen over 0.25% are likely to produce gross forms of defect. The section thickness of the casting is also important: a three inch section would be most likely to be affected by mould material containing 0.15% nitrogen, whereas a casting with a half inch section would probably be perfectly sound. Where very heavy castings are being produced it is important, therefore, to select low-nitrogen systems and to use just enough resin to give the required properties and keep the nitrogen level down to 0.1% in the mould or core.

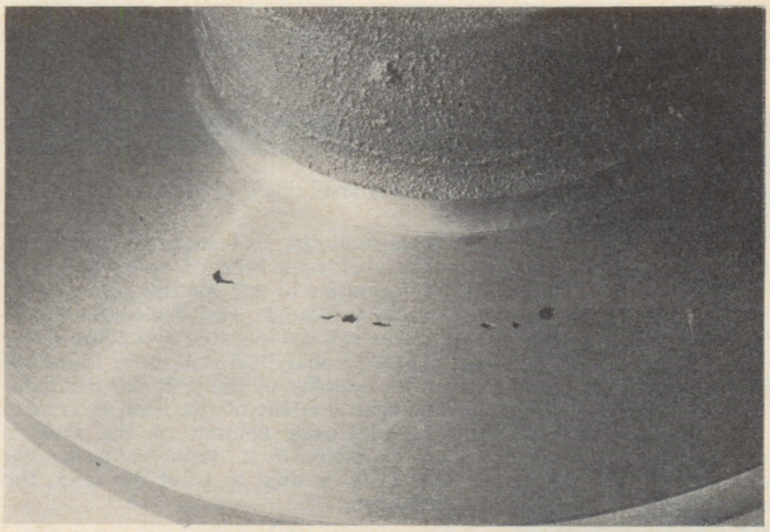
The resin manufacturers will generally quote the nitrogen content of each type of resin, and it is advisable for foundries to ask for this information with each batch delivered. The determination of nitrogen in resins is a complicated procedure needing a high degree of analytical skill; most foundries must rely on the supplier of the resin for this data. When the nitrogen content of the resin is known, calculating the nitrogen content of the sand is simple. For example, if a resin contains 7% nitrogen, and 1.5% is used to bond the sand, the resin will contribute

$$\frac{1.5}{100} \times 7 = 0.105\% \text{ nitrogen}$$

*The hot-box process*—The hot-box process involves the use of resins similar to those used in self-setting processes, based on furfuryl alcohol with either urea or phenol-formaldehyde. These resins are capable of curing rapidly, when heated above a certain temperature in the presence of a suitable catalyst such as ferric chloride, ammonium salts or dilute phosphoric acid. Any urea in the resin is a source of nitrogen. The urea-formaldehyde resins harden rapidly and this is advantageous where production rates are high. Because of their high nitrogen content, however, they have the severe disadvantage of promoting pinhole defects. Ammonium salts used as catalysts are also a source of nitrogen, and may contribute as much nitrogen as the resin itself. Fig. 6 shows



**7** Fissure-pinhole defect on head face of a cylinder block casting.



8 Fissure-pinhole defects in a disc brake, at the junction of a hot-box core and the greensand mould.

severe pinhole defects on the water-jacket side of a cylinder bore. The water-jacket core was bonded with a high-nitrogen resin-catalyst system, resulting in a nitrogen content in the core of 0.4%.

Experience has shown here, as in the cold-setting systems, that cores containing more than 0.15% nitrogen are apt to promote nitrogen fissure or pinhole defects. To ensure freedom from such defects, suitably low-nitrogen resin-catalyst systems must be used (in least quantities compatible with the required properties) to give cores containing less than 0.15% nitrogen.

Fig. 7 shows a small fissure or pinhole defect on the head face of a cylinder block. Such an isolated defect is normally associated with borderline levels of nitrogen in the cores. During mould-filling, some nitrogen is absorbed by the metal, but not enough to cause a defect. On reaching the greensand face of the mould the metal may absorb some hydrogen, and the combined effect of the two gases is enough to promote defects.

Fig. 8 illustrates pinhole/fissure defects in a disc brake casting at the junction of a hot-box core and the greensand mould. The defect in this case was due to the combined effect of nitrogen pick-up from the hot-box binder, and hydrogen from the greensand mould. Such defects often occur in line with the junctions of cores containing a marginally high level of nitrogen and the greensand mould.

*The shell process*—The resins used in the shell or pre-coated sand process are phenol formaldehydes, which are nitrogen-free; but hexamine, which contains 40% nitrogen, is used as a catalyst to harden the resin when heated. Generally, shell sands are quite low in nitrogen, but where resin and hence hexamine contents are higher than normal, to give high strength, dangerous levels of nitrogen can result. It is in these instances, when levels of nitrogen can exceed 0.15%, that pinholing on casting surfaces adjacent to shell moulds or cores can occur.

Nitrogen-free pre-coated sands have been developed[6] for the production of steel castings, which are very prone to nitrogen pick-up. They have been used successfully in the production of grey-iron castings, and are particularly useful where the iron used has a high inherent nitrogen content due to its method of production.

## Nitrogen Build-up in Reclaimed Cold-setting Sands

Reclamation of resin-bonded sands has been adopted by many foundries, the most common method being dry crushing. If nitrogen-containing resins are used and steps are not taken to remove the binder residue, there will be a gradual accumulation of nitrogen during recycling—proportional to the percentage of binder used and the nitrogen content of the binder. Tables are available which present theoretical nitrogen build-up in reclaimed sands using nitrogen-containing binders. An indication of nitrogen build-up as sand is continually reclaimed is given in Table 1. The use of high percentages of reclaimed sand, particularly where the nitrogen content of the binder is high, can result in dangerous levels of nitrogen in the sand system. When reclamation is by dry crushing, it is important to consider the question of nitrogen build-up. As much as 80% of reclaimed sand may be used in the mixture when very low-nitrogen binders are used, but 50% should be regarded as a safe level[7]. The nitrogen level in reclaimed sand should preferably be maintained at less than 0.04%.

The nitrogen content of reclaimed sands containing urea-formaldehyde resins can be successfully reduced by heating the sand to between 500 and 850°C[7].

## Mould and Core Coatings as a Nitrogen Source

Many different coatings are available for moulds and cores; the majority of them are carbonaceous or contain zircon. In recent years there has been a trend towards using binder or filler materials other than the traditional, naturally occurring high-purity carbonaceous materials. Some of these alternative materials can be high in nitrogen and

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MATERIALS AND TECHNIQUES USED BY THE FERROUS FOUNDRY MELTING DEPARTMENT

**5** To minimise the possibility of defects arising from nitrogen pick-up from the mould or core, it is prudent to select a binder-catalyst system that will result in a nitrogen content not exceeding 0.15% in the mould or cores.

**6** Recycling of reclaimed resin-bonded sand can result in a gradual accumulation of nitrogen; and the level of nitrogen should therefore be monitored and maintained below 0.04%.

**7** Coatings, adhesives and materials used for repairing damaged areas of moulds or cores can contain nitrogen-bearing resin binders or carbonaceous materials. Careful use of such coatings, adhesives and materials used to repair cores is essential, to minimise the possibility of nitrogen defects.

## REFERENCES

[1] Mountford, A.; The influence of nitrogen on strength, soundness and structure of grey cast iron. *British Foundryman*, 1966, **59,** April, pp. 141-151.

[2] Morrogh, H.; Gases in Cast Iron. *Proceedings of the Institute of British Foundrymen*, 1955, **48,** pp. A324-A345; discussion, pp. A345-A361.

[3] Davison, M. H., Chen, F. P. H. and Keverian, J.; Solution to a Nitrogen Porosity Problem in Gray Iron Castings. *Transactions of the American Foundrymen's Society*, 1963, **71,** pp. 528-543.

[4] Greenhill, J. M. and Dawson, J. V.; Metallurgical Aspects of Melting and Holding in Electric Furnaces. Paper presented at BCIRA International Conference on Electric Melting and Holding Furnaces in Ironfoundries. University of Warwick, 1980.

[5] Dawson, J. V., Smith, L. W. L. and Bach, B. B.; Some Effects of Nitrogen in Cast Iron. *BCIRA Journal of Research and Development*, 1953, **4,** June, pp. 540-552.

[6] Le-Serve, F. L. and Lemon, P. H. R. B.; Nitrogen-free Resin-Coated Sand for Shell Moulding. *Modern Casting*, 1969, **56,** August, pp. 146-150.

[7] Cunningham, J. J.; Sand Conservation in a Jobbing Ironfoundry. *British Foundryman*, 1971, **64,** September, pp. 333-341.

[8] Winkler, H. J. and Bach, B. B.; Chemical determination of nitrogen in cast iron. *BCIRA Journal of Research and Development*, 1953, **4,** June, pp. 553-9.

[9] Bach, B. B., Dawson, J. V. and Smith, L. W. L.; Determination of oxygen, hydrogen and nitrogen in cast iron. *Journal of the Iron and Steel Institute*, 1954, **176,** March, pp. 257-63.

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**PROGRESS & DEVELOPMENT REPORT**

# Heat Pumps used for Process Control

Three Carlyle packaged heat pumps, supplied by Ductwork Engineering Systems Limited, authorised distributors for Carlyle air conditioning and refrigeration equipment, are providing a closely controlled environment in the shell room of Deritend Precision Castings Limited, Droitwich. Heat pumps are now generally accepted as being an energy efficient means of providing both heating and cooling in domestic and commercial premises, but this is believed to be the first time that they have been used for process control.

Deritend Precision Castings Limited was founded in 1948 to meet a growing post-war demand for close tolerance ferrous and non-ferrous parts, casting by the modern equivalent of the lost wax process. Wax assemblies are constructed and from these a ceramic shell is produced. The company has recently developed its own method of applying the initial ceramic coat, and backing coats are applied until the shell thickness is achieved. It is in this shell production area that close environmental control is essential. After each ceramic coat has been applied, the shell must be dried on a conveyor system at a constant temperature of 20° C ±1° C, 65% r.h. Any uncontrolled variations in temperature or hu-
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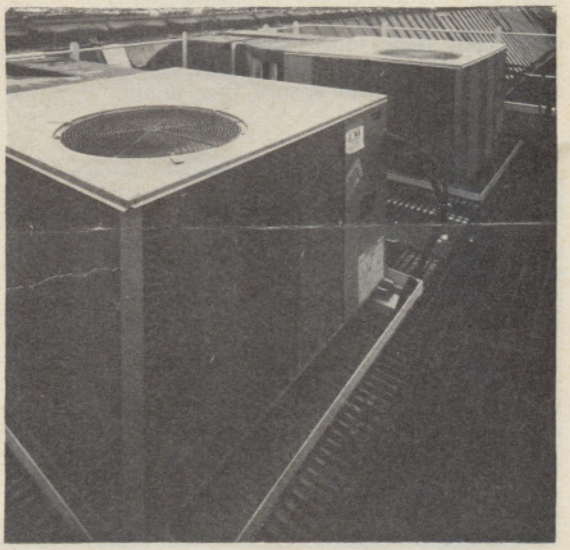
Deritend intends to have the system installed at its plant in Yeovil. The system was designed and installed by Project 77 (Environmental) Limited, Stourbridge.

The two Carlyle 50RQ010 mounted heat pumps at Deritend Precision Castings Limited.



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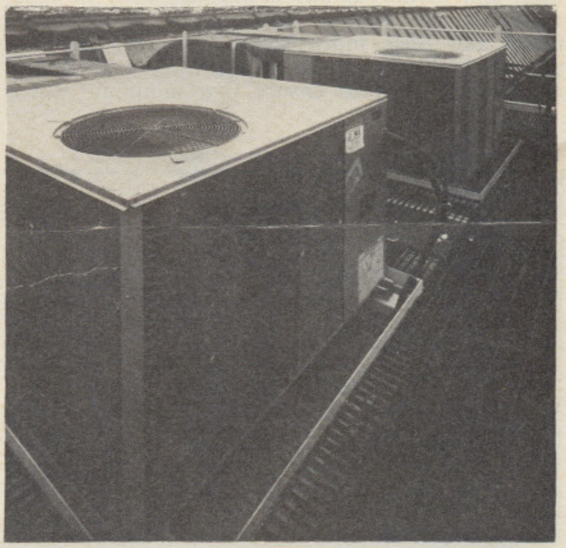

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## Nitrogen Defects in Iron Castings

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so lead to pinholing and fissure defects, particularly in castings of heavy section. As for binder systems, levels of nitrogen above 0.15% in mould or core are hazardous, levels of nitrogen above 0.15% in coatings can also be dangerous if the nitrogen is not present in the unreactive or stable form. The suppliers of the mould and the core coatings are generally aware of these problems and will recommend suitable materials to avoid nitrogen defects.

The one risk is of possible pick-up of nitrogen from the coatings; an additional danger is that the presence of hydrogen will lead to a combined effect of the two gases. If a water-based coating is used and is inadequately dried, hydrogen pick-up can occur, particularly if the metal is contaminated with aluminium, even at levels as low as 0.005%. Similarly, hydrogen pick-up can occur from any water that contaminates a spirit-based coating which has not been completely dried, and heat from 'flame-off' may not suffice to remove the dampness, arising from water contamination of such coating materials.

To minimise the risk of the nitrogen-hydrogen pinhole defect resulting from coatings, it is essential that low-nitrogen materials are used, and coatings should be completely dried after application.

### Adhesives, Fillers and Sealants as a Nitrogen Source

It is often found necessary to join individual cores, or to produce multi-core assemblies for complex castings. These operations require the use of commercially produced adhesives, or of pastes made up by the foundry, which are sometimes based on flour. Damaged cores are often repaired by carbonaceous fillers which may be bonded with resin.

It may be necessary to seal cores into a mould assembly or use a sealant on joint faces to prevent flash and metal run-out problems. Many of these materials can contain nitrogen-bearing resins or fillers and their indiscriminate use can promote pinhole problems due to nitrogen. Care, therefore, is always needed to ensure that minimum use is made of core fillers, and that sealants and adhesives are kept well away from cast faces, since gas evolution rates from such materials can be very high.

### Determination of Nitrogen

Nitrogen in cast iron may be determined by chemical means, using the steam distillation method[8] in which the sample is digested in acid, the nitrogen is evolved as ammonia, and the ammonia determined colorimetrically or titrimetrically. This method has been modified for nitrogen determination in resins and sands, and may also be used for carbon materials and carburisers, with modifications to ensure complete decomposition of nitrogen compounds contained in them.

Vacuum-fusion[9] or inert gas fusion are long established methods for determining nitrogen. Modern equipment is commercially available which performs the analysis on an automatic routine basis involving extraction in a stream of inert gas followed by thermal-conductivity measurement of the gas mixture.

### Summary

**1** Cupola charges containing more than 50% steel scrap produce irons containing high percentages of nitrogen, which are prone to give rise to fissure defects in castings.

**2** Certain carbonaceous materials used to carburise irons contain high proportions of nitrogen. When significant quantities of such carburisers are used, irons with dangerously high levels of nitrogen may be produced.

**3** The adverse effect of nitrogen on soundness may be offset by increasing the titanium content of the iron to between 0.02 and 0.03%. This may conveniently be done by making a suitable addition of ferrotitanium or titanium to the metal. Where strength is important, it is advisable to add the minimum amount of titanium necessary, since this element will nullify the effect of nitrogen on strength.

**4** Nitrogen may be picked up from mould or core materials bonded with resin-catalyst systems containing nitrogen.

TABLE 1: *Theoretical nitrogen build-up in reclaimed sand using nitrogen-containing binders*

| Nitrogen % | | 2.0 | | | | 7.58 | | | |
|---|---|---|---|---|---|---|---|---|---|
| Addition rate % | | 1.0 | | 1.5 | | 1.0 | | 1.5 | |
| Reclamation % | | 50 | 75 | 50 | 75 | 50 | 75 | 50 | 75 |
| Cycle | 0 | 0.020 | 0.020 | 0.030 | 0.030 | 0.075 | 0.075 | 0.111 | 0.111 |
| | 1 | 0.030 | 0.035 | 0.045 | 0.052 | 0.112 | 0.131 | 0.167 | 0.195 |
| | 2 | 0.035 | 0.046 | 0.052 | 0.069 | 0.131 | 0.173 | 0.195 | 0.257 |
| | 3 | 0.037 | 0.054 | 0.056 | 0.082 | 0.141 | 0.205 | 0.208 | 0.304 |
| | 4 | 0.038 | 0.061 | 0.058 | 0.091 | 0.145 | 0.228 | 0.215 | 0.339 |
| | 5 | 0.039 | 0.065 | 0.059 | 0.098 | 0.147 | 0.246 | 0.219 | 0.366 |
| | 6 | 0.039 | 0.069 | 0.059 | 0.103 | 0.148 | 0.259 | 0.220 | 0.386 |
| | 7 | | 0.071 | | 0.107 | 0.149 | 0.269 | 0.222 | 0.400 |
| | 8 | | 0.073 | | 0.110 | 0.149 | 0.277 | 0.222 | 0.412 |
| | 9 | | 0.075 | | 0.113 | | 0.283 | | 0.42 |
| | 10 | | 0.076 | | 0.114 | | 0.287 | | 0.42 |
| | 11 | | | | 0.116 | | 0.290 | | 0.4 |
| | 12 | | | | 0.117 | | 0.292 | | 0. |
| | 13 | | | | 0.117 | | 0.294 | | 0. |
| | 14 | | | | | | 0.295 | | 0. |
| | 15 | | | | | | | | 0. |

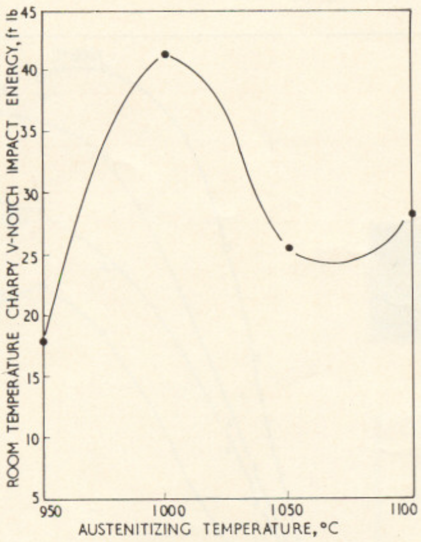


*Fig. 3—Effect of austenitizing temperature on Charpy V-notch impact value at room temperature*

hardness value as untempered martensite is produced. There is also a very marked decrease in transition temperature when tempering temperature is raised from 650°C to 750°C; for example, the 15 ft lb impact transition falls from +63°C to —43°C (Fig.4).

## EFFECT OF VARIATIONS IN COMPOSITION

The effect of variations in composition that could be obtained during normal steelmaking practice, but still within the range permitted by BS 1630, have been investigated using both air- and vacuum-melted steels.

### Effect of phosphorus

The chemical analyses of the steels made in this series are given in Table III. Comparison of V196 and V197 (Fig.6) show that small additions of phosphorus slightly reduce the maximum impact value of material tempered at 750°C and also tend to decrease the slope of the transition curve and move it to the right. Larger additions up to the maximum permitted in BS 1630, (i.e. 0·050%P) begin to have a greater effect on maximum impact value and on the position and slope of the curve. Very large additions, much in excess of those found in commercial material, have a catastrophic effect (V199 and V200, Fig.6). Phosphorus also appears to affect the impact peak obtained on tempering at 750°C and shown in Fig.5. With increase in phosphorus this peak moves and is obtained with a tempering temperature above 800°C (Fig.7).

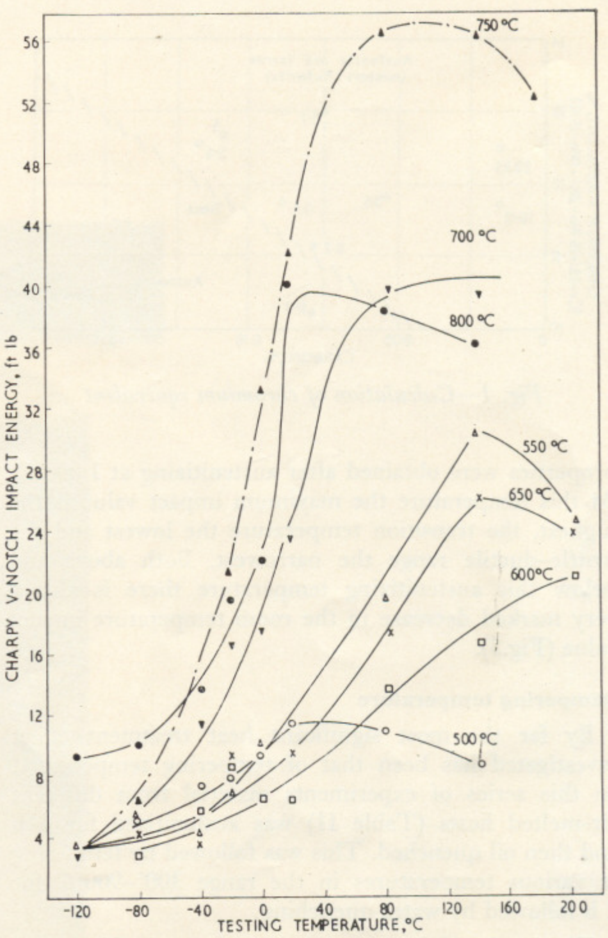


*Fig. 4—Effect of tempering temperature on Charpy V-notch impact transition curve*

The evidence of these experiments suggests that to obtain optimum impact properties the phosphorus content should be kept as low as possible.

### Effect of nitrogen

Chromium content can markedly affect the solubility of nitrogen in molten metal and, in fact, will raise the nitrogen solubility of a binary iron–chromium alloy at 1 600°C from about 0·04% at 0·0% Cr to 0·1% at 13% Cr; this solubility will in turn be affected by

**TABLE III Analysis of vacuum melts made from Swedish iron and pure chromium metal to which phosphorus was added**

| | *Chemical composition, %* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *Heat no.* | *C* | *Si* | *Mn* | *S* | *P* | *Cr* | *Ni* | $N_2$ | $N_2$ *as AlN* | *Al* |
| V196 | 0·16 | 0·08 | Tr | 0·013 | Tr | 11·79 | Tr | 0·010 | 0·0001 | 0·024 |
| V197 | 0·15 | 0·12 | Tr | 0·014 | 0·012 | 11·59 | Tr | 0·010 | 0·0004 | 0·012 |
| V198 | 0·18 | 0·02 | Tr | 0·013 | 0·062 | 11·60 | Tr | 0·006 | 0·0004 | 0·006 |
| V199 | 0·15 | 0·03 | Tr | 0·010 | 0·140 | 11·59 | Tr | 0·011 | 0·0001 | 0·006 |
| V200 | 0·15 | 0·10 | Tr | 0·013 | 0·420 | 11·59 | Tr | 0·009 | 0·0003 | 0·008 |

Tr = trace

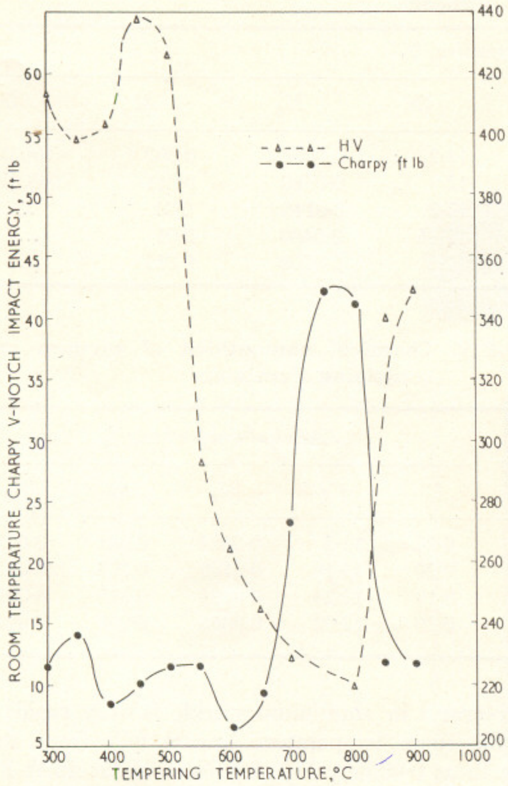


Fig. 5—*Effect of tempering temperature on Charpy V-notch impact value at room temperature*

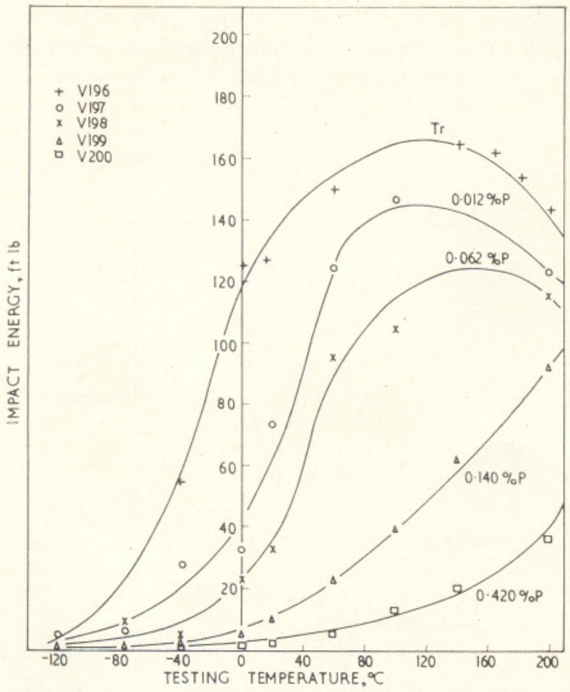
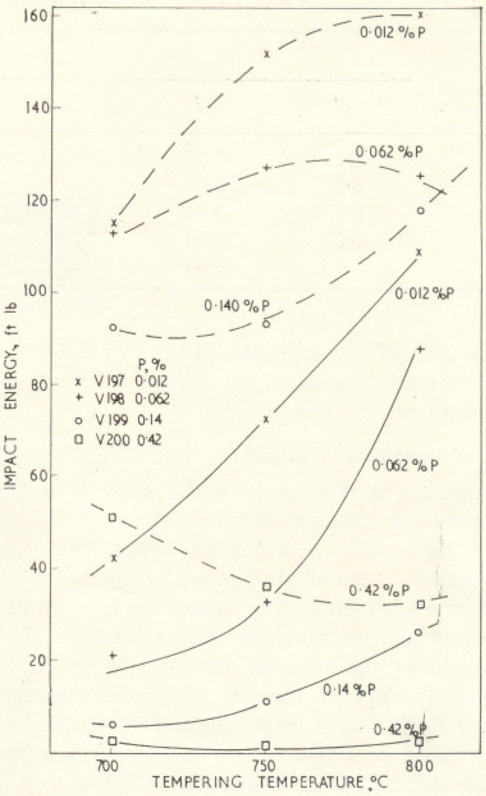


Fig. 6—*Effect of phosphorus content on the impact transition curves of material tempered at 750°C*



Broken lines: maximum impact value
Continuous lines: room temperature impact value

Fig. 7—*Variation in room temperature and maximum impact energy with tempering temperature for different phosphorus contents*

other alloy additions. The nitrogen content of the molten metal can therefore vary considerably from heat to heat and can be affected by a number of factors. Among these are the nitrogen content of the ferrochromium, which can also vary between wide limits, and the amount of atmospheric contamination. This contamination will depend to some extent on the length of time the steel bath is in contact with air, on the type and physical shape of the furnace and on the nature of the slag cover.

Investigations into the effect of variations in nitrogen content (Table IV) made on vacuum-melted alloys indicate that there is an optimum nitrogen content of about 0·04%, which in the absence of aluminium gives the highest room temperature impact value and the lowest transition temperature (Fig.8). At this optimum content it also appears that the brittle/ductile transition takes place over a narrower temperature range.

### Effect of aluminium

Although it is not generally recommended because of the possible formation of aluminium nitride in association with nitrogen, aluminium is occasionally used as a deoxidant. Examination of a number of vacuum-melted alloys containing various amounts of necessary level of tin. The following charge would be suitable.

The percentage of pearlite in a casting is clearly a function of cooling rate and the level of pearlite stabilising elements in the iron. The longer the cooling rate, and in particular the thicker the section, the higher these elements have to be to guarantee fully pearlitic structures.

Rather than taking the individual elements in isolation, it is very sensible to assess the pearlite stabilising effect of each element and then by taking one as the standard, calculate the equivalent amount of the others required to produce the same effect.

Several workers have used tin as the reference standard using the term tin equivalent to provide a typical formula as follows:—

$$\text{Tin Equivalent} = \%\text{Sn} + \frac{\%3\ \text{As}}{4} + \frac{\%\ \text{Cu}}{24} + \frac{\%\ \text{Mn}}{24}$$

In the author's experience the formula for use in any foundry will depend very much on the type of charge being used. The above may hold good where elemental additions are made to "pure" melts, but may not be totally acceptable where the elements are inherent in the metallic materials used in the charge. This is no doubt due to the presence of other pearlite stabilising elements present in very small quantities, but which are not normally checked as routine in control laboratories. It is reasonable for most foundries to use only the above four elements and then to determine the tin equivalent for each basic charge by collecting information over an extended period.

Referring back to the analysis for the cupola charge shown in Table III, the above formula gives a tin equivalent of 0.131 being generally suitable for ensuring pearlitic structures in S.G. castings of 0.75/1" thick.

### 2.2.1.2 Elements affecting the formation of nodular graphite structures

To date researches have failed to find ways and means of neutralising the pearlite stabilising properties of such elements as tin, arsenic and copper which, as previously stated, means that raw materials containing these elements cannot be used or have to be strictly controlled where substantially ferritic structures are required in the as cast condition.

Fortunately, this is not the case with the so called subversive elements; lead, bismuth and antimony whose effect in preventing the formation of nodular graphite structures using the conventional magnesium process can be neutralised by small additions of cerium, e.g. 5% MgFeSi containing either 0.25% or 0.5% of cerium. This does not mean that one can tolerate excessive quantities of these elements and limits have to be set following which control must be exercised over the raw materials in the charge.

Levels as low as 0.005% of lead and bismuth can result in the formation of inferior graphite after magnesium treatment when cerium is not used. Antimony has a similar deleterious effect when present in excess of 0.03/0.04%. It is essential therefore that these elements are controlled at very low levels and where significant quantities of scrap are charged, to use cerium containing magnesium treatment alloys.

### 2.2.2 Grey irons

When cupola mixtures were confined to the use of virgin pig iron, return scrap and cast iron scrap with little or no steel scrap being charged, it was very easy to predict the tensile strength of the irons produced and often the surface hardness of castings by reference to the carbon equivalent of the iron. Most reference books give tables or graphs relating tensile strengths on a standard test bar to the carbon equivalent value. Line A of Figure 1 is a typical example.

Unfortunately these conditions do not apply in foundries which have replaced at least some of the pig iron previously used with scrap. Where low phosphorus irons are required, the use of cast iron is limited to such materials as cylinder scrap, briquetted cast iron turnings of known low phosphorus content and hematite scrap. The metallurgist has often therefore no alternative other than to use more steel scrap.

In general the provision of suitable equipment in the melting shop has allowed the foundryman to use higher proportions of steel scrap often of questionable quality and analysis.

As in ductile irons this has given rise to higher levels of pearlite in castings and also to finer pearlite structures with consequent higher tensile strengths and hardness levels for a given carbon equivalent. In order therefore to ensure that hardness levels and machineability are controlled, this being the main criterion for any machine shop, it is often necessary to increase the proportion of pig iron in the charge and/or increase the carbon equivalent to compensate by increasing the metal carbon and/or silicon levels. The following is a typical example for grade 17 and 14 irons.

| Grade of Iron | Carbon Equivalent | |
|---|---|---|
| | Conventional Mixtures | Mixes Containing High Proportion of Steel Scrap |
| 17 | 3.9 | 4.1) Containing 0.46% Sn, |
| 14 | 4.2 | 4.4) 0.022% As, 0.4% Cu. |

Figure 1 compares the effect of high tramp elements resulting from the use of steel scrap (B) with conventional mixtures (A) at different carbon equivalent levels.

As is the case for S.G. iron production, it is not generally possible to use high proportions of the cheaper scraps, e.g. black bales, destructor scrap and detinned scrap as to do so will present problems in the foundry, e.g. hot cracks and shrinkage defects and which will almost certainly result in machine shop complaints.

As is the case for S.G. iron one has to strike a balance between cost and product quality and the best advice is to move slowly when introducing or increasing the proportion of steel scrap in the cupola charge, this being particularly true where cheaper, lower quality scraps are being introduced.

It is best to gain experience by carrying out detailed remelt analyses, make checks on casting quality and above all get an adequate feedback from the customer's machine shop as the levels of scrap are progressively increased and the back scrap is further affected.

Table IV shows the effect on tensile strength and Brinell hardness on a 1.2" diameter test bar from the use of different charges at a given carbon equivalent value.

Often the effect on hardness from the use of high steel scrap charges is greater than that on tensile strength. This is because castings produced from steel scrap charges have a greater tendency to produce edge chill coupled, in some cases, to the formation of finer graphite structures.

### 2.2.2.1 Nitrogen and hydrogen in grey irons

One element which is not a problem when producing S.G., but which can be a major source of trouble in grey irons is nitrogen. The use of high steel scrap charges often plays a major part in lifting the nitrogen in the iron during casting above 100 p.p.m. (0.01%) which is generally accepted as the level at which nitrogen fissuring will occur in light to medium castings.

In addition to causing waste due to fissuring, nitrogen can have a marked effect on graphite form which, under certain conditions, can be advantageous in that it increases tensile strength by up to 2–3 Tonf/in$^2$ in an otherwise similar iron. Very high levels, above 0.01%, can promote the formation of fine pearlite

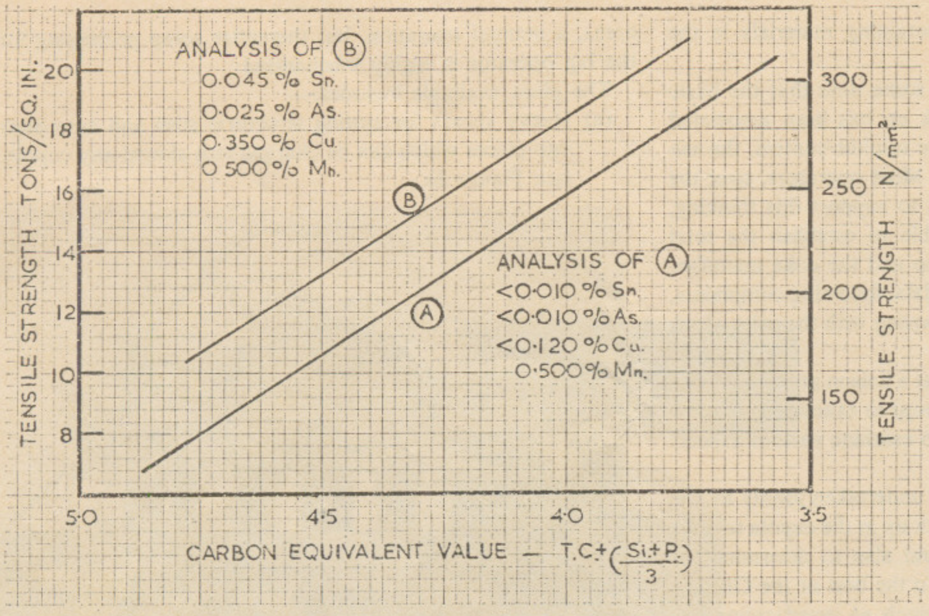


*Fig.1—Graph showing effect of carbon equivalent on tensile strength for (a) conventional cupola charges and (b) charges containing high proportions of steel scrap.*

**Table IV Effect of steel in cupola charges on tensile strength and hardness of a 1.2″ diameter test bar**

| Charge | Carbon Equivalent | % Sn | % As | % Cu | % Mn | Brinell Hardness | Tensile Strength Tonf/in$^2$ |
|---|---|---|---|---|---|---|---|
| 1. 25% Black Bales<br>25% Structural Steel<br>50% Returns | 3·9 | 0·04 | 0·023 | 0·33 | 0·5 | 260/270 | 20/22 |
| 2. 20% Hematite<br>20% Structural Steel<br>10% Black Bales<br>50% Returns | 3·9 | 0·22 | 0·016 | 0·21 | 0·55 | 245/250 | 18/20 |
| 3. Conventional Charge | 3·9 | 0·01 | 0·01 | 0·12 | 0·5 | 230/235 | 17/19 |

and may lead to white iron structures, both of which can affect machineability in engineering castings.

When making ingot moulds from cupola charges containing high proportions of steel scrap, nitrogen can result in the formation of compacted graphite which is detrimental in that it lowers their resistance to thermal shock. The effect on ingot moulds can often be offset by the addition of aluminium to give a residual level in the iron of 0.03/0.05%. This should not be used to neutralise the effect of nitrogen in thin or general engineering castings as it can lead to hydrogen pinholing defects. In such cases where it is found essential to lower the nitrogen content, an addition of ferro titanium to give a residual content in the iron of 0.02/0.03% is often effective. Ferro titanium in addition to reducing the risk of waste castings due to fissuring, also neutralises the effect on the graphite and thereby lowers the tensile strength.

The best advice where nitrogen is a problem, is to reduce the level of steel scrap in the cupola charge and to replace it with other materials, e.g. pig iron.

Hydrogen can also lead to defective castings due to the formation of pinholes. Generally pinhole defects in castings are associated with the presence of aluminium in the iron. It is important therefore that every effort is made to eliminate aluminium containing materials in the cupola mix by a careful and continuous inspection of incoming scrap, which can contain alloy parts, e.g. old cylinder engines with pistons still attached. Levels of aluminium as low as 0.005/0.02% are enough to give rejects due to hydrogen pinholing. It is essential therefore that all suspect material be rejected. One other source of aluminium comes from ferro silicon which is often used in cupola mixes to lift the silicon level of charges containing steel. Where this is a major problem it is often necessary to replace at least part of the steel in the charge with pig iron.

### 2.3 Carbon Pick Up

With the increased consumption in cupola charges of materials low in carbon, e.g. steel scrap and pre-reduced iron pellets, the solution of carbon in the cupola becomes a very important factor, particularly for those operators who have no external treatment facilities, such as shaking ladles, quirls, porous plug ladles or electric furnaces. Most operators are increasingly aware that it is difficult, if not impossible in cases where high proportions of steel scrap are being charged, to control final metal carbon contents within specified limits without post treatment outside of the cupola. This is particularly true for the production of S.G. irons, but an ever increasing requirement for grey irons where customer specifications are becoming more stringent without necessarily a compensating change in what they are prepared to pay for castings.

In the end the foundryman has to decide which is the best and lowest cost route to him. He cannot expect to get the best of all worlds, i.e. he cannot expect to use low cost mixtures without giving due consideration to improving his control equipment and often post treatment of the liquid iron to produce metal of the requisite quality at the casting station.

Accepting that control systems are all important, the metallurgist using charges containing materials low in carbon knows only too well from experience that he can suddenly and unexpectedly get changes in tapped carbon contents without any change in operating practice. When such changes occur, the normal practice is to change the coke rate, make alterations to blast rate and/or oxygen consumption where used, or to inted only by a reduction in the phosphorus content. In castings like cylinder heads subject to a pressure test, phosphorus should be held below 0.2%. A high phosphorus content can, however, be tolerated in castings of uniform section like pipes, where in fact it is intentionally raised to confer fluidity.

It is reported that the manganese-sulphur ratio also influences soundness of grey iron castings to some extent. Although this may not be critical from soundness point of view, when sulphur is high (0.15%) and manganese low, inverse chill defect is likely to occur. As such the sulphur content should be low enough and the manganese content should be adequate to balance the sulphur in accordance with the formula $\% \text{Mn} = 1.7 \times \% \text{S} + 0.3$.

### Improper Pouring Temperature

Generally little attention is paid to a proper pouring temperature, which is conditioned sometimes by the melting unit as in the case of a cupola. If any, as high a pouring temperature as is generally feasible is preferred to avoid the dangers of cold shut or misrun particularly when pouring of both thin and thick section castings at the same time is involved. It should, however, be noted that excessively high pouring temperatures cause shrinkage defects and lower pouring temperature should be prefered to the extent possible. There is an optimum pouring temperature for each type of casting depending upon whether green sand or dry sand moulds are used. A green sand mould aggravates the effects of a high pouring temperature in increasing shrinkage defects while high pouring temperatures will be permissible in dry sand moulds. The optimum pouring temperature for the various castings can only be determined through experience by each foundry. Very often, certain castings poured from the first ladle nearest to the melting unit may exhibit pronounced shrinkage defects while when poured farthest away may be found to be absolutely sound, indicating that a lower pouring temperature is necessary in their case. A rearrangement of the pouring schedule in such cases, having regard to the various items under production, will help to minimise the shrinkage defects due to an improper pouring temperature.

## GAS HOLE DEFECTS

Gases are emitted during pouring of moulds. The free escape of these gases during solidification of the molten metal will depend upon a number of factors like the duration for which the metal remains molten or in other words the pouring temperature, the amount of gas generated, the ease with which the evolving gases can escape out, etc. Any or a combination of these factors can give rise to conditions which may lead to entrapment of the gases produced. Such entrapment will give rise to a number of defects, which may take the form of blowholes, fissures or pinholes. Defects due to entrapped gases constitute a major cause of rejections in many foundries and their elimination also is not particularly easy as more than one factor may be responsible for the different types of gas hole defects. Modern foundry technology and several new methods and materials introduced have also given rise to new problems, complicating the diagnosis of gas hole defects. Determination of the gas content of the metal, by no means simple and easy, or examination of the microstructure are by themselves not adequate to identify the cause of the defect and to take steps to prevent its recurrence, for which a clear understanding of the manner of formation of gas hole defects is necessary.

The following are the sources of gases which give rise to gas hole defects :

(i) dissolved gases in the molten iron
(ii) reaction gases
(iii) gases evolved by moulds and cores.

The manner of formation of defects, attribut ble to gases evolved from each of the abo sources, is detailed below.

### Defects due to dissolved gases in molten iro

The dissolved gases involved are hydrogen nitrogen. Both are soluble in liquid iron, but relatively insoluble in the solid state. Thus dissolved gases will be rejected during solid tion. The usual concentrations of diss hydrogen and nitrogen in liquid iron are re tively 0.8 to 1.8 ppm and 20 to 80 ppm. they are present in excess of the above the amount rejected during solidification w be able to fully diffuse out within the ti metal is still in the molten state in the mou a part may, therefore, get entrapped in th castings. The resulting defects are refe as 'blowholes'.

Of the two gases, nitrogen has a muc rate of diffusion through iron. As such, casting sections are more prone to the caused by entrapment of nitrogen ga thinner casting sections are more prone gen gas defects. In thicker sections, can escape out by diffusion through skin of the casting due to the longer so time available, while similar time w available in thinner sections.

(Depending upon the amount of disso the gas entrapment defects may tak of rounded holes or long thin fissures gen content is high enough to caus of rounded blowholes, it also causes ing of the risers on the top of the ca does not occur with hydrogen at levels sufficient to cause rounded blockholes. The more common form of occurrence of the defect, however, is long thin fissures. Fissures caused by hydrogen occur near to the heat centre of the casting or at the bisection of the angle between two solidification fronts as shown in Fig. 2, while fissures due to nitrogen will be more uniformly dispersed throughout the casting as shown in Fig. 3.

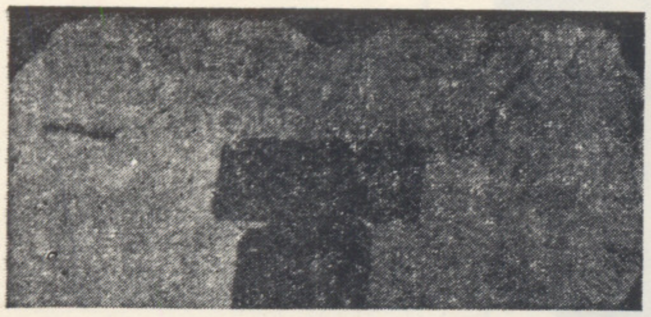


Fig. 2 — Typical fissure defects caused by hydrogen.

Fig. 3 — Typical fissure defects caused by nitrogen

A situation may arise when both hydrogen and nitrogen may be present together. In such a case, defects may be caused by their combined effect at levels below those required for each alone to cause the defects. Since both the gases cause similar types of defects, it is not easy to distinguish the defects caused by their combined action from those caused by either alone. However, the tendency for fissuring produced by the combined action of the two gases to concentrate at the centre of casting as shown in Fig. 4 can provide some clue.

The factors in a foundry that cause pick-up of nitrogen and hydrogen above the normal tolerable levels, are referred to below briefly.

Although nitrogen forms a mojor portion of the atmospheric air, it is present in the molecular form. In this form, it is only slightly soluble in the liquid iron, while at the temperatures n mally involved in the melting of grey iron a serious pick-up by its decomposition to libera atomic or nascent nitrogen, is not likely. Th hydrogen content of the atmosphere is very low while the normal humidity range of a cupola blas is not high enough to cause any significant variation in the hydrogen content of the molten iron. As such, it is always (the introduction of nitrogen and hydrogen containing materials in foundry practice that are primarily responsible for excess quantities of these gases.)

Conditions conducive to sufficient pick-up of nitrogen to cause the fissure type of defect exist in cupola melting of low carbon equivalent irons of 3.5 C.E. and less. However, production of such low carbon equivalent irons is not a routine practice in many foundries and nitrogen defects are most unlikely in irons of 3.9 C.E. and over. At times, nitrogen can be introduced through the recarburiser used in the production of synthetic irons. However, the principal source of nitrogen pick-up is the decomposition of a nitrogen-bearing compound such as a core binder. The deleterious effects of nitrogen can be neutralised by addition of 0.05% titanium.

The most common source of hydrogen in a foundry is water vapour, decomposition of which in contact with molten iron liberates hydrogen in the atomic or nascent form which is readily soluble in molten iron. The sources of such water vapour are invariably damp refractories, inadequately dried ladle linings, wet patching of ladles after some use, wet swabbing and rebuilding of ladle spouts or lips without proper attention to their drying and high moisture content of green sand mixtures.

A major and perhaps more common defect than the blowhole defects, attributable to hydrogen is 'pinholing'. Pinholes are small sub-surface rounded holes generally revealed only after shotblasting, annealing, light machining or fracturing. Certain thin section castings are particularly prone to pinholing. This defect is related to the

Fig. 4 — Typical fissure defect caused by the combined effect of hydrogen and nitrogen

degree of hydrogen concentration on the surface layers, inrrespective of the total hydrogen content throughout the section. Hydrogen pick-up by the surface layers is markedly influenced by elements which accelerate the rate of reduction of the water vapour, thus increasing hydrogen availability for solution. Most important in this respect as far as grey cast iron is concerned is aluminium. Amounts of aluminium as low as 0.005-0.02 per cent are sufficient to exercise a harmful influence. Influence of aluminium itself varies depending upon other factors. For instance, relatively lower amounts of aluminium can lead to severe pinholing in the presence of higher managenese contents. The principal sources of aluminium are contaminated scrap and ladle inoculants. Late additions of sizeable amounts of ferro-silicon for inoculation can introduce sufficient aluminium to cause a severe outbreak of the pinholing defect particularly in certain types of castings.

A convenient way in practice to diagnose the primary causes for the defects arising from dissolved gases in the metal will comprise the following steps :

(a) Assess if the defects are occurring in thick or thin sections and whether they are dispersed or localised. A simple experiment in the foundry with thick and thin section block castings will prove helpful to bring out the effect clearly.

(b) Assess the time of occurrence of the defects. If the defects occur throughout the duration of a melt, nitrogen is the likely cause; otherwise, hydrogen is the more likely cause.

(c) Assess if an addition of 0.05% titanium to each ladle markedly reduces the gas hole defects. If so, nitrogen is the cause of the defects.

(d) Look for metal agitation at the furnace or ladle spout or in the ladle. If there is agitation, dampness and hence hydrogen is the cause of the trouble.

(e) Hydrogen is the most common cause of the pinholing defect.

Blowing of a dry inert gas for a few minutes through the liquid metal can help to decrease hydrogen, but such a practice is not common. When trouble is suspected, the metal could be pigged for subsequent reuse. However, corrective action can normally be implemented in future production only after establishing the correct diagnosis of the cause of the defects as outlined earlier. The diagnosis itself will assist in deciding on the remedial measures to be initiated. In the case of pinhole defects, addition of coal dust will lessen their incidence, but obviously, because of its gas producing potential, it cannot be increased beyond a certain limit. Particular attention will have to be paid to the moisture content of the sand and the amount of inoculating additions that introduce aluminium. If introduction of a certain amount of aluminium becomes inescapable, pinholing can be tackled to a certain extent by attention to other aspects by which hydrogen pick-up can be minimised. One such aspect is to reduce the traverse of the molten iron over the green sand surface. This is secured by using shortest possible runners and downsprues. This is illustrated in Fig. 5. It will be apparent that this method will suggest itself to be applicable when pinholing has been found to be occurring in a casting or castings farthest away from the ingate or sprue.

### Defects due to reaction gases

Under certain conditions, a reaction may take place between the carbon in the molten iron

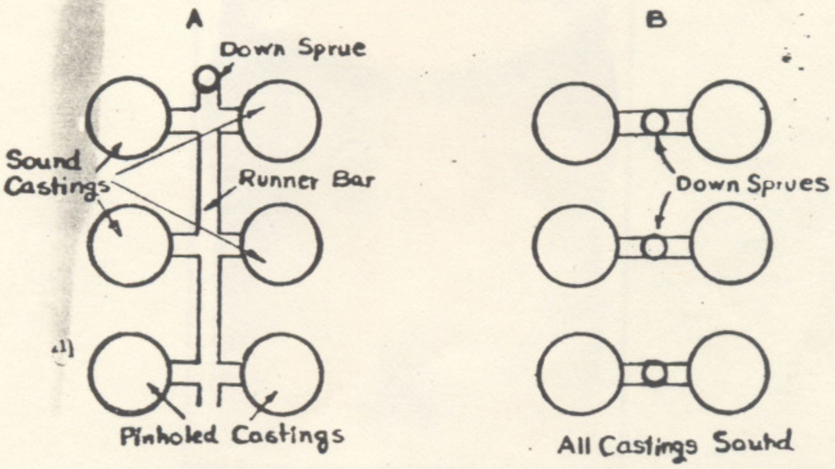


Fig. 5 — Avoiding pinholing defects by improving the gating system

and oxygen in intimate contact with it, producing carbon monoxide gas. Entrapment of this gas in the solidifying metal can lead to blowholes. Such blowhole defects may be referred to as reaction gas defects. They are usually revealed after machining, but may also appear as glassy depressions on the surface.

The most important source of oxygen to start such a reaction is the presence of a thin fluid iron-oxide rich slag in the molten iron. The chief sources of liquid iron-oxide slag are (i) cupola slag (ii) ladle refractories and (iii) ladle surface slag produced by oxidation at the metal surface in contact with the atmospheric air. The cupola slag, however, is not a major source of trouble, as, being viscous, it gets removed easily to the metal surface. Improperly dried ladle linings evolve steam when carrying molten metal. This steam oxidises the metal and gives rise to a thin fluid iron-oxide rich slag, which is an important source of reaction gas blowhole defect trouble. The trouble from this source can be overcome with properly dried ladle linings.

By far the most important source and which accounts for a high scrap rate in practice, is the ladle surface slag. Defects due to this source for the reaction gas usually occur at some depth from the surface of the casting and are only revealed after machining. A high moisture content in the moulding sands aggravates this defect. High manganese and sulphur contents and low pouring temperatures are reported to be responsible for the sub-surface blowholes caused by ladle surface slags. This may be explained as follows.

Manganese reacts with iron sulphide in the liquid iron as per the reaction $Mn + FeS \rightarrow MnS + Fe$. An increase in either the manganese or the sulphur content will precipitate manganese sulphide. The reaction proceeds to the right as the temperature falls. The iron-oxide slag produced by surface oxidation is not liquid at the eutectic temperature when graphite is precipitated, but becomes thin and fluid when the manganese sulphide precipitated as above is dissolved in it. An intimate contact between such a slag and the graphite precipitated causes the reaction to produce carbon monoxide gas. It will be seen that the action of manganese sulphide is essentially to promote the reaction to liberate carbon monoxide gas. It also helps in identifying the cause of the blowhole defect from this source by its characteristic segregation adjacent to the blowhole, which can be observed under the microscope. Also associated with this gas hole defect will be found a crystalline slag. Both these can be seen at low magnifications under the microscope in the unetched condition.

The manner of formation of reaction gas hole defects due to ladle surface slag will suggest that either increasing the pouring temperature or decreasing the manganese or sulphur contents will overcome the trouble. The balancing of sulphur by higher manganese contents, which will help to counteract the inverse chill defect, can introduce the reaction gas hole defect. To avoid the reaction gas hole efect, it is desirable to hold the manganese content below 0.7%. With higher manganese contents, it would be necessary to lower the sulphur content and employ higher pouring temperatures.

**Defects due to mould and core gases**

The binders and other additives added to moulding and core sands, evolve gases when heated during pouring. Some of these gases may get entrapped, giving rise to true blowhole defects. The principal gas producing additives are moisture and coal dust in the case of moulds and oil and binders in the case of cores. While good sand permeability and proper venting of moulds and cores aid in the smooth escape of the gases, good control is achieved only by limiting the additives.

In the case of green sand moulds, there is an optimum moisture content to be used depending upon the type of clay and the amount of fines in the sand. Moisture in excess of this level will decrease mould permeability, besides having a higher gas producing potential. Thus a high moisture sand will be worse than a low permeability sand and is certain to cause blowholes. Coal dust also reduces permeability besides requiring more moisture to make the mix workable. Thus, coupled with its own gas producing potential, an excess of coal dust is certain to increase the blowhole risk.

In the case of cores, a number of factors affect the volume and rate of gas evolution, which in turn influence the risk of blowhole formation. For instance, the degree of gas evolution by linseed oil cores will very much depend upon the extent of baking. An underbaked core may evolve nearly twice as much gas as a correctly baked core, while an overbaked core is liable to break or crack which will lead to metal penetration and blocking of the vents and thus not allow the free escape of the gases. It should, however, be noted that the principal gas producing additive is the green binder and not the oil. Several types of green binders are used in modern core making practice, like glucose, resins and furfuryl alcohol. Of these, the phenolic resins are reported to give the lowest amount and rate of gas evolution.

Besides the above, factors which influence mould and core permeability such as sand permeability, the degree of compaction or hardness of the moulds and cores and the extent and type of venting will also have a vital bearing on the tendency for gas entrapment. One recommendation for the permeability of moulding sand is that it should be at least 25 permeability points for each 1" section of the casting involved, upto a maximum of 100. Core sands no doubt should have a much higher permeability. A high mould hardness so very desirable for mould rigidity to prevent mould wall movement and hence for ensuring soundness in castings, will however, substantially decrease mould permeability as can be seen from Fig. 6. A copromise may be necessary at times in practice depending on various factors on the needs of mould hardness to ensure required mould rigidity and mould permeability.

Many practical means are resorted to to increase mould and core permeability. These consist of insertion of coke lumps where the sand mass permits, use of perforated tubes, placing the moulds on perforated bottom plates etc. in the case of moulds, and adequate venting with 1/8" to 1/4" dia wires or rods, use of special vent tubes, well-fitted maximum permissible size of prints and effectively venting through the same etc. in the case of cores. In the case of complex cores, wax venting is common; however, care should be taken to ensure that the wax is completely melted out during baking. More effective alternates to wax venting are glass fibre tubes and perforated steel tubes which do not decompose and liberate further gas on heating.

Another important source of blowholes are the metal inserts such as denseners, chaplets etc. or the inserts involved in composite constructions. These blowholes, usually bubble-shaped, may occur at some distance from the source. Such defects are attributable to the metal parts coming in contact with molten iron, not being absolutely free from moisture, rust and dirt. Use of metal inserts coated with high purity tin or suitably shot-blasted and warmed up prior to use to remove moisture, is recommended when blowhole defects due to metal inserts occur.

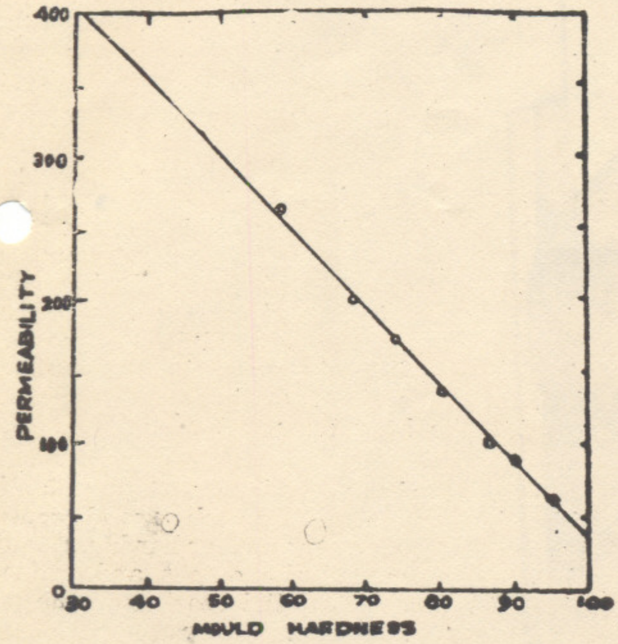


Fig. 6 — A typical mould hardness-mould permeability relationship

## SAND EXPANSION DEFECTS

The above is only a nomenclature based on the cause of occurrence of the well-known defects, scabs and rat tails. The manner in which these defects are formed may be explained as follows.

As the molten metal fills the mould, the cope gets dried by the heat radiated from the rising surface of the metal and the temperature rises further rapidly. With rise in temperature, the sand expands as shown in Fig. 7. While the expansion is not uniform with temperature, it will be seen that at 573°C there is a sudden expansion. This is due to change of $\alpha$ — quartz to $\beta$ — quartz at this temperature. The steam that is evolved when the surface layer is dried is driven to the cooler regions of the mould, where it condenses. The moisture content of the zone where the steam condenses is thereby increased substantially. Thus, immediately behind a narrow zone of dried sand there will be a narrow zone of very wet sand. The stresses accompanying the expansion of the dried surface skin can cause a crack in this wet layer, depending upon what is described as its 'wet tensile strength.' When a crack is initiated and propagates further, the surface layers detach to form a buckle. After the mould is completely filled, the rising metal enters the crack developed in the wet layer through the buckle in the dried layer. The resulting defect will have a layer of sand, usually about 1/6" to 1/8" between two layers of metal, which is typical of the ex-

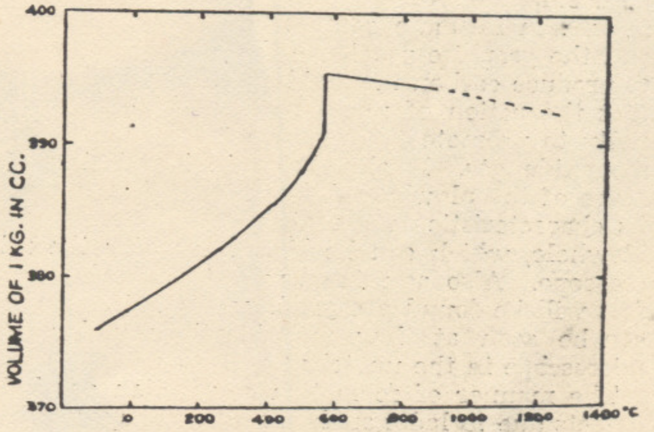


Fig. 7 — Temperature volume curve of quartz (after Sosman)