ASK Chemicals

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The Volume Deficit of Iron-Carbon Alloys

The specific volume of the standard casting metals is larger in the liquid state than in the solid state. For this reason, these metals undergo contraction when solidifying and cooling. A volume deficit then occurs, taking the form of defects such as shrink holes, sink marks, microporosity, etc. (Fig. 1)

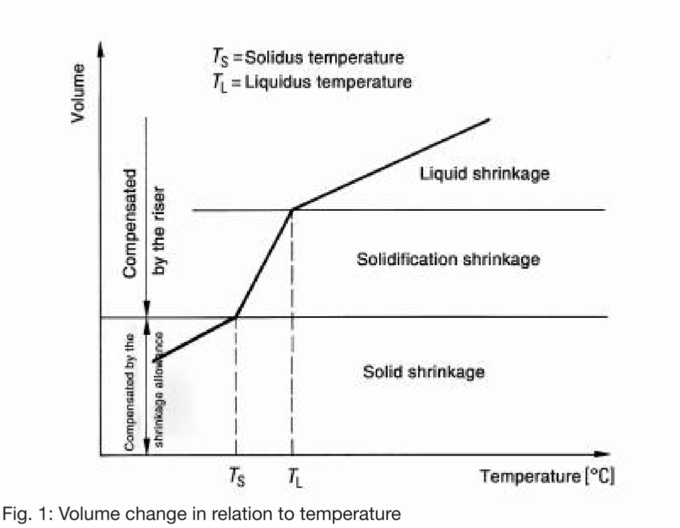

Fig. 1: Volume change in relation to temperature

Shrink holes are thus the result of the interaction between the physical volume deficit during the solidification process and the possibility of compensating it through additional feeding.
The size of the technological volume deficit in conjunction with the specific volume is first and foremost a function of the casting material. Compared with the total volume deficit, its distribution in the cast body and to the specified volume defect types depends on the solidification procedure. Specific influencing factors here are the gas content of the alloy, the mold wall movement in the case of sandcasting and the graphite expansion during solidification in the case of cast iron alloys.
Typical possibilities of the solidification procedure are shown schematically in Fig. 2 and are described briefly in the following.

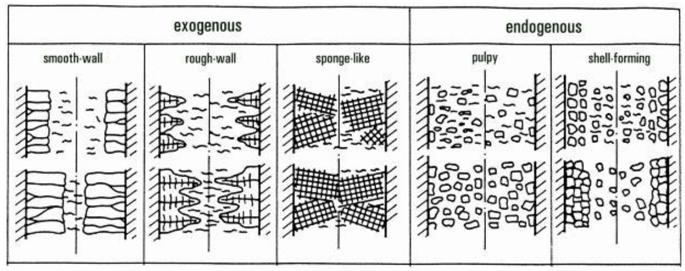

Fig. 2: Exogenous and endogenous solidification types at two consecutive times (according to Patterson and Engler, schematic)

Exogenous Solidification Types:

1. Smooth-wall solidification
Smooth-wall solidification involves the growth of exogenous crystals in a compact manner from the edge to the center of the cast piece. The boundary layer of the crystallites growing beside each other to the melt is relatively smoothly formed; the resulting microstructure is made up of what are known as columnar crystals.

2. Rough-wall solidification
If the exogenous crystals do not grow in a compact manner but instead dendritically, a crust that grows from the outside in forms - particularly if the dendrites are coarse and loosely structured. Unlike smooth-wall solidification, the boundary layer to the melt is roughened. Solidification ends when the crusts, which come from the sides, meet in the middle.

3. Sponge-like solidification
If the dendrites are delicately structured and have many side branches, the partially solidified cast piece area takes on sponge-like properties. It is made up of a dendrite network, which pervades the complete melt and is “saturated” with melt. Over the course of solidification, the dendrite branches become thicker and thicker until the melt in the cavities in-between has been sapped up.

The Iron Deficit of Iron Carbon Alloys

Exogenous Solidification Types:

1. Pulpy solidification
Here, the endogenous crystals grow in a radial pattern at different points in the melt relatively evenly distributed. The mixture from the liquid and solid phase takes on the consistency of a pulp, which becomes more and more rigid as solidification continues. Solidification is finished when the individual crystals meet and the residual melt has been sapped up.

2. Shell-forming solidification
Here, the pulp-like properties of the solidifying material are lost to a large extent if there is a steep decline in the grain sizes of the growing crystals from the edge of the piece towards the inside. The low mobility of the crystals in the edge areas causes a shell with a certain carrying capacity to form.

On the basis of the solidification types, it is possible to support the view that

- The development of solidification holes is related to the formation of a solid peripheral shell, which in turn implies a corresponding temperature range. The conditions for this are smooth-wall, rough-wall or endogenous shell-forming solidification;
- The earlier a peripheral shell exists, the larger the solidification hole will be. If it has contact with the atmosphere, it is an exterior shrink hole. However, if the temperature range is such that a shell which is closed on all sides forms, an interior solidification hole develops.

In rough-wall and sponge-like solidification, and particularly with the endogenous solidification types, the strength of the peripheral shell can be lowered so far that it gives in to the forces (air pressure, metallostatic pressure, expansion pressure in the case of graphite precipitation) applied to it. The result is that sink marks and microporosity are more likely to occur.

The yielding of the peripheral shell initially manifests itself in the fact that the solidifying cast body connects to the mold walls and only the upper horizontal surfaces sink due to contraction. Due to better heat dissipation conditions, solidification then advances faster at the edges and corners than on the surfaces. After some time, the edges with their increased carrying capacity form a rigid external frame and the contraction of the cast body can now be seen not only in the external shrinkage but also in the indentations of the surfaces in comparison to the edges around them. Here, it is evident that micropores with a vacuum particularly promote the sinkage of the sides.

The close relationship between microporosity (shrinkage pores) and sink marks is manifested in the fact that both volume defects can be expected with the same solidification types. In addition, the feeding capacity is good with exogenous smooth-wall and exogenous rough-wall solidification but decreases in the specified order.
In the same direction, the formation of interior and exterior shrink holes also decreases and the propensity for sink marks and microsinkage increases.

To summarize, the result is that the difference between the specific volumes when liquid and solid is the prerequisite for the occurrence of volume defects. The different types of volume defects are determined by the temperature range and the solidification procedure. However, it must always be taken into account that for one same alloy, the preference for one type of volume defect is connected with the reduction of others; the total number of volume defects remains constant and equal to the volumetric deficiency given by the difference between the specific volumes.

Exogenous Solidification Types:

Characteristic of the volume deficit of gray cast iron are the differences between the specific volumes of the individual microstructure components (Table 1).

Microstructure component	Specific volume in m^3/g
Ferrite	0.1271
Iron carbide	0.1303
Austenite (C-saturated)	0.1360
Graphite	0.4475

Table 1: Specific volumes of individual microstructure components of cast iron

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The Iron Deficit of Iron Carbon Alloys

In eutectic solidification, the expansion of the precipitating graphite counteracts the solidification shrinkage of the austenite. With a certain graphite content, it is possible that the contraction occurring during solidification is compensated during the formation of the austenite. This means that depending on the chemical composition, the cooling conditions and the nucleation, "self feeding" may take place. If the volume of graphite precipitated eutectically is large, the volume expansion caused by the formation of the graphite may be larger than the solidification contraction of the metallic phase, meaning that expansion takes place on the whole.

Cast iron with lamellar graphite shows a decreasing shrink hole tendency as the chromo-saturation level increases up to the eutectic point. The volume deficit is lowest there. This applies to both the size of the exterior shrink hole and the proportion of microshrinkage. In the hypereutectic range, the shrink hole tendency increases again (Fig. 3).

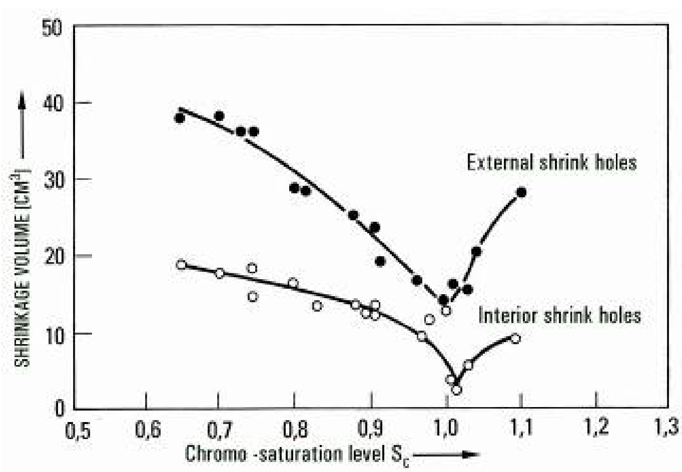

Fig. 3: Shrink hole volume of Fe-C alloys in relation to the chromo -saturation level

At the same chromo -saturation level, the expected shrink hole volume decreases as the carbon content increases. Phosphor increases the propensity for the formation of microporosity, particularly for P contents > 0.3% due to the formation of a phosphor-rich residual melt (phosphorous eutectic).

Provided that a non-inoculated iron would also have solidified as a gray cast iron, the inoculation of cast iron with lamellar graphite also causes an increased propensity for shrink holes, porosity and sinking. A stronger "swelling" of the cast piece occurs through increased expansion due to heavy eutectic graphite precipitation and the solidification type also changes toward "pulp-like" solidification, meaning that the cast piece contour follows the mold cavity expansion based on the mold material more closely.

Cast iron with nodular graphite shows a greater tendency for shrink holes than cast iron with lamellar graphite. If a gray iron melt is treated with magnesium, the shrink hole volume increases from 0.5 cm3 to 5 cm3.

Unlike the endogenous shell-forming solidification of cast iron with lamellar graphite, the solidification of cast iron with nodular graphite is endogenous and pulpy. As well as the liquid contraction, which can be controlled by the feed and gating system, and a secondary shrinkage, an expansion occurs during the solidification process.

Based on the different time phases of solidification, graphite can take effect during its precipitation in a peripheral shell and bulge or expand it if it and the mold material yield to this pressure from inside. If the liquid metal sinking in the cast body is not topped up, this alone can cause shrink holes to form. Later on in solidification, the graphite is precipitated in a larger area of the cast body. As the peripheral shell can already shrink, the conditions for self-feeding become more favorable. If the peripheral shell is also still in a state of eutectic solidification, increased expansion is to be expected.

Provided the mold is rigid, the exploitation of this expansion phase leads to a compensation of the secondary shrinkage and thus to cast pieces without sink holes and with a high yield. Significantly hypo- and hypereutectic compositions, missing inoculation, excessive casting times at temperatures that are too high and magnesium contents that are too high foster the shrink hole susceptibility of cast iron with nodular graphite.

Alloyed cast iron types generally also show a higher shrink hole tendency, as do increased pig iron additives in the charge make-up. However, this latter impact can always be seen in conjunction with the melting process.

The Iron Deficit of Iron Carbon Alloys

Decreasing the Volume Deficit by Feeding

The productivity of a foundry is significantly determined by the cleaning work required on the finished cast part. As a result, the riser system masses must be kept as low as possible without affecting the actual task of the risers, i.e. compensating for the volume change during solidification of the melt. As well as riser insulation, the operative riser size can also be reduced effectively by heating the riser. The heat released in exothermic mixtures extends the riser solidification time. This results in the option of reducing the riser dimensions and thus improving the casting yield. Numerous experiments to investigate the impact of exothermic mixtures on the required riser size have shown that the solidification-delaying effect of the heat-emitting reactions of these exothermic substances allows the riser dimensions to be reduced considerably.

An exothermic reaction is a chemical reaction in which energy is released and emitted into the environment. The course of these reactions reveals the following: The initial materials have a certain energy level to which further energy is added, thereby raising the level. If what is known as the “energy hill” is reached, the reaction starts running; the energy required for this is what is known as the activation energy. Energy is then released and emitted into the environment. The final materials have less energy than the initial materials, since the energy released was emitted into the environ-

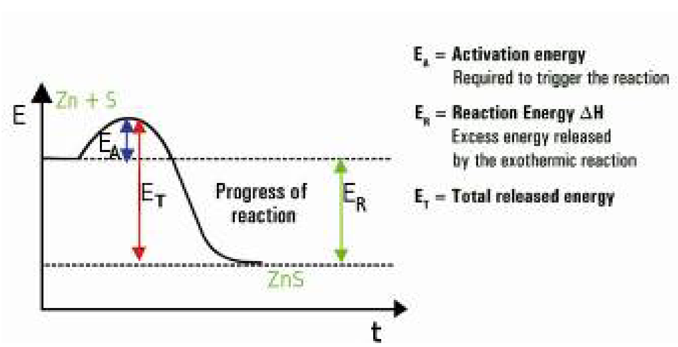

Fig. 4: Energy diagram of an exothermic reaction (source: Wikibooks.de)

Generally, much more reaction energy is released than was previously added in the form of activation energy. Many exothermic reactions occur spontaneously: The lower the activation energy, the more likely it is that a reaction like this will occur spontaneously.

The basis of exothermic reactions is the Goldschmidt process. In this process, the following exothermic reactions occur, reaching temperatures of up to 2400°C:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$
$$4Al + 3O_2 \rightarrow 2Al_2O_3 + energy$$

These reactions are the basic modes of operation for exothermic risers, exothermic covering materials and exothermic mixtures. The standard composition for exothermic risers is generally made up of aluminum, an oxygen dispenser and a fluorine carrier or nowadays increasingly magnesium, a filler and a binder.
It goes without saying that state-of-the-art risers are free of carcinogenic fibers and only have minimal organic emissions thanks to the inorganic binder. This reduces the odor pollution in the foundry and reduces the occurrence of gas defects. Thus, ASK Chemicals Feeding Systems GmbH principally provides waterglass-bonded risers, Fig. 5 and Fig. 6 show the significant

Fig. 5: Unfavorable binders in the riser can cause additional emissions to occur; left shows a waterglass-bonded riser and right shows a resin-bonded riser (ASK Chemicals Feeding Systems)

The Iron Deficit of Iron Carbon Alloys

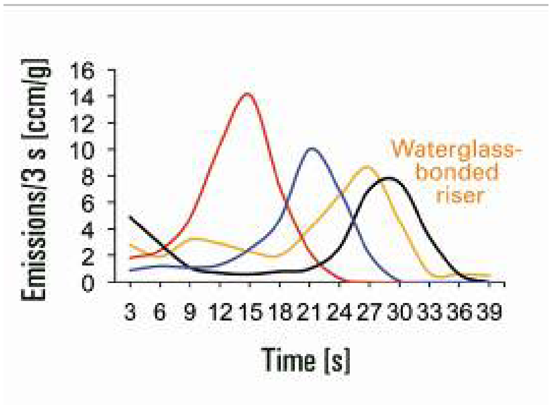

Fig. 6: Comparison of emissions of waterglass-bonded riser with various res-in-bonded risers

Fig. 8: Comparison of natural, exothermic and mini-risers in terms of cleaning costs (ASK Chemicals Feeding Systems)

In the mid-1990s, ASK Chemicals Feeding Systems was the first manufacturer to produce risers that were not just low in fluorine but completely free of fluorine. This was an important contribution to improving the quality of the circulation sand in the foundries and preventing surface defects (Fig. 7). It also helps to cut disposal costs when disposing of old sand.

Fig. 7: Possible fluorine defects on cast pieces due to fluorine contents in exo-thermic riser material

The mini-riser, developed and patented back in 1977, represents a quantum leap in feeding technology. The feeding volume can be reduced significantly, thus saving costs. The obvious advantages of the mini-riser compared with natural and exothermic risers are clearly shown in Fig. 8.

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