

Chromite Double Skin Defect on Heavy-Section Steel Castings

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ABSTRACT

This paper collates the relevant work done on chromite sand and its usage in steel foundries over the last 25 years. Many of these works have discussed the chromite "double skin" defect (or chromite glazing), but none have suggested solutions to the problem.

From practical assessment of foundry production data, and the installation of production control parameters used within many of Great Britain's leading heavy-section steel foundries, it has been possible to outline control parameters for chromite sand, binder content, zircon mould coatings and the drying procedure, pouring temperature, pouring speed, pouring time, and the oxygen activity within the liquid steel.

By exercising these controls, the chromite double skin defect has been virtually eliminated, which has resulted in a marked improvement in as-cast quality and cleanup times. It has also allowed chromite sand to be considered a viable alternative to zircon sand.

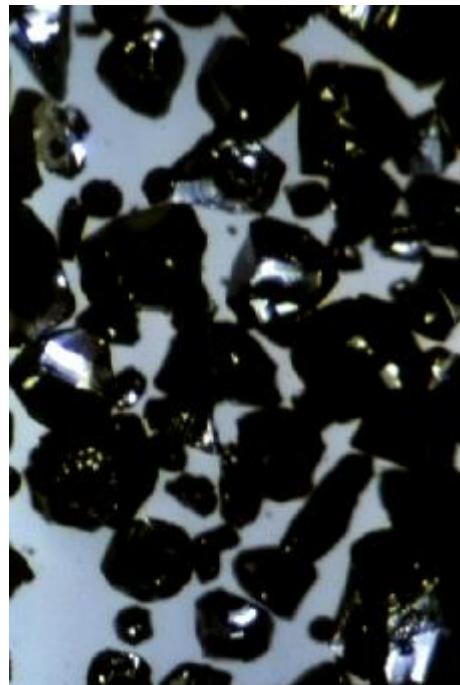


Fig.1 Chromite spinel sand A.F.S. 50 (sub angular).

CHROMITE SAND

Chromite is FeCr_2O_4 , a natural oxide of ferrous iron and chromium, usually with magnesium and aluminium present. It usually occurs in magnesium and iron-rich igneous rocks. Commercial qualities and quantities are available in the U.S.S.R., South Africa, Zimbabwe, Cuba, Turkey, and Finland. It is the only commercial source of chromium. When chromite and finely divided aluminium and carbon are heated, chromium is reduced.

Chromite spinel sand is the sand size fraction removed from the chromite ore. This size is not commercially practical for reducing chromium. Ideally, chromium content should exceed 48% and iron no more than 33% of the percentage chromium to make smelting attractive. Figure 1 shows a picture of chromite spinel sand. Figure 2 shows a typical chemical analysis. This is the material commonly used in foundries, and to which this paper will refer. Figure 3 shows the spinel structure. As is apparent, it is quite complex, although of a very regular cubic arrangement. As shown, eight units of formula make one unit cell. From Figure 2, the aluminium atoms may replace chromium atoms, and magnesium atoms may replace iron atoms within the spinel structure. These elements should not be viewed as impurities, but rather the nature of the beast. However, the other materials (i.e., silica, calcium, etc.) are not part of the spinel structure and are impurities. The silica fraction is part silica and various silicates, the most common being serpentine (magnesium silicate) and aluminium silicate.

These materials are often referred to as gangue or tramp elements. Unfortunately, most of these materials are not soluble or combustible, making removal very difficult and expensive.

	CHEMICAL ANALYSIS CHROMITE SHIPMENTS		
	Jan. '87	Feb. '88	Oct. '88
Cr_2O_3	46.71%	46.95%	46.75%
Fe_2O_3	28.76%	28.40%	28.48%
SiO_2	0.72%	0.52%	0.56%
CaO_2	<0.01%	0.10%	0.07%
MgO	10.20%	10.53%	10.46%
Al_2O_3	13.80%	14.48%	14.80%

Fig.2 Typical chemical analysis of chromite sand.

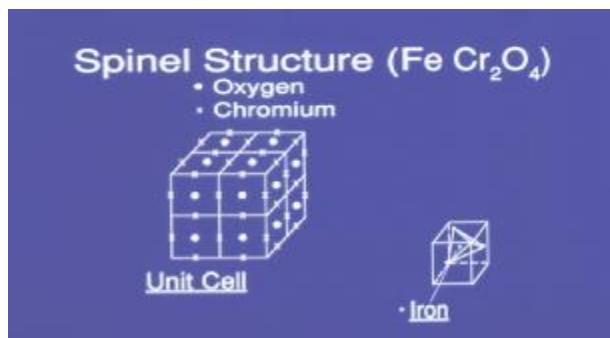


Fig.3 Atomic structure of chromite sand

Physical Properties

Figure 4 shows the heat transfer characteristics of various common moulding materials, and shows chromite to be superior to those commonly in use within foundries. Figure 5 shows a penetration test block casting designed by GD. Sylvestro. This test allows simulation of high ferrostatic pressure within the mould cavity, and the resultant effect on sample moulding materials. As can be seen, chromite out-performs the other common aggregates. Its penetration resistance is excellent. Figure 6 illustrates the expansion characteristics of the commonly used moulding mediums and highlights the low linear expansion characteristics of both chromite and zircon. It also confirms the need for care when using silica, if expansion defects are to be avoided. Figure 7 tabulates the other main physical properties of the common moulding aggregates.

In pouring steel castings, the longer the solidification time and the higher the calorific value, the higher the mould/metal interface temperature. Although tabular form tables of specific heat seem to indicate only small variations in value, remember that specific heat is measured in cal/g/deg C. Obviously, when dealing with a fifty tonne casting, the difference in calorific value becomes substantial.

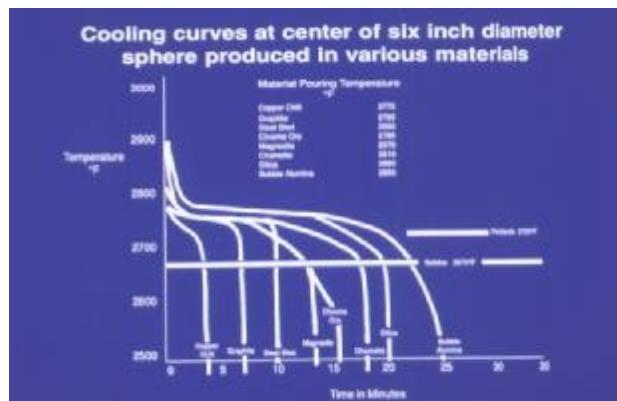


Fig.4 Heat transfer characteristics of common foundry moulding media (cooling curves at centre of six inch diameter sphere produced in various materials)

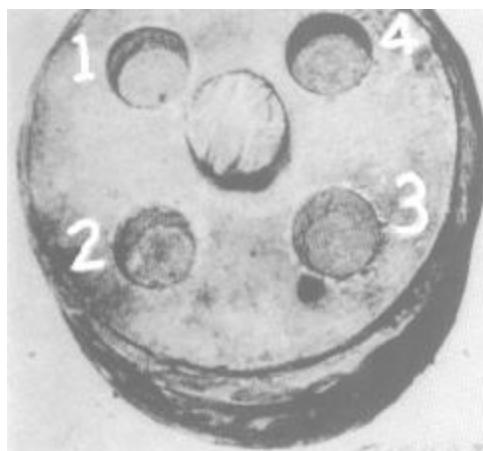


Fig.5 Penetration test block - 1. and 2. Zircon - 3. Silica - 4. Chromite (44 inch of ferrostatic head). Notice the superior resistance to penetration of Chromite

Casting Applications

Casting Applications

The pictures in Figures 8-15 show example castings made in chromite sand moulds. These castings are from different foundries, and are all of high as-cast quality. Special attention should be paid to ingate areas, as pouring rates rarely exceed 60 seconds. Chromite is used with any binder system in areas where: chilling is required, core removal is difficult, dimensional stability is necessary, ferrostatic pressure is high, or high pouring temperatures/long solidification times are encountered. It is also used extensively to avoid the manganese/silica reaction on manganese steel castings. In short, chromite is used in areas where silica is not up to the job.

The largest foundry users of chromite sand are heavy-section steel foundries where castings are in excess of 4 tonnes. It is usually used as a facing for both cores and moulds. It is apparent that production of this type of casting subjects the moulding material to the most exacting conditions experienced in the foundry industry, such as high pouring rate, high ferrostatic pressure, high alloying, and long solidification time. Although chromite is expensive in comparison to silica, this can easily be justified by reduced cleaning and rectification times in the cleaning room.

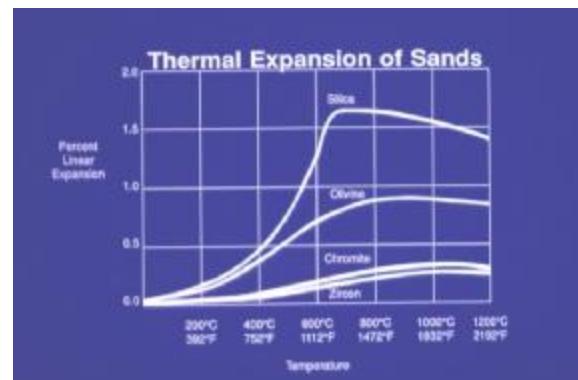


Fig.6 Expansion characteristics of common foundry moulding media

COMPARISON OF SANDS				
PROPERTY	SILICA	ZIRCON	OLIVINE	CHROMITE
Color	White	Yellow White	Green Grey	Black
Specific Gravity	2.2-2.4	4.4-4.7	5.2-5.6	4.5-4.8
Bulk Density	90-102	180-185	100-126	107-116
Thermal Expansion	0.018	0.003	0.006	0.005
High Temperature Reaction	Acid	Slightly	Basic	Neutral to Basic
Grain Shape	Rounded	Elongated Rounded	Sharp Angular	Sub-angular
Grain Distribution	2-6 Sieves	2-3 Sieves	2-4 Sieves	4 Sieves
AFS Fineness	90-190	98-190	50-140	80-90
Source	Mid-West USA	Florida Australia	Washington N. Carolina	S. Africa

Fig.7 Physical property comparison of common foundry moulding media.



Fig.8. Steam turbine casing, 15 tonnes Cr/Mo steel, Chromite facing.



Fig.11. Turbine casting, 40 tonnes, chromite facing sand. Pouring time 90 seconds.



Fig.9. Different view of figure 8



Fig.12. "Y" Connector casting, 18 Tonnes, Chromite facing sand. Pouring time 47 seconds.



Fig.10. Close up view of ingate area of figure 8.
No erosion even though the pouring time was less than one minute.



Fig.13. Pilger roll, 12 Tonnes, Chromite face in working areas and radii. Pouring time 40 seconds



Fig.14. Close-up of Figure 13.



Fig.15. Large roller casting, chromite facing sand.

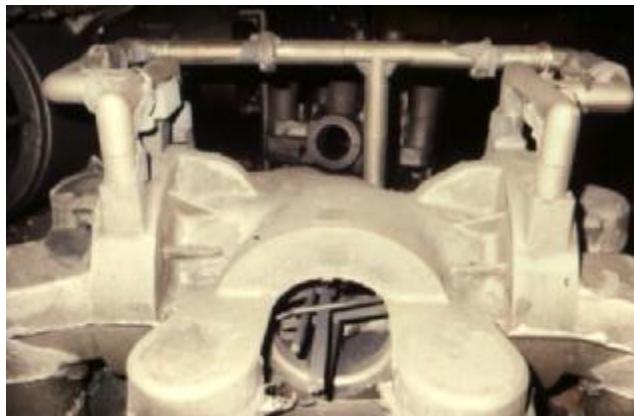


Fig.16. Double skin defect on a large valve body.

THE "DOUBLE SKIN" DEFECT

Typical Occurrences

In the author's experience, double skin is only found on steel castings that have been produced in chromite moulds or with chromite cores. It is also known as glazing, frit, or elephant skin, dependent upon where you are or with whom you are talking. It is seen throughout the world in heavy-section steel foundries using chromite sand. It is a surface defect usually at its worst in hot spots or areas that have been exposed to long periods of radiant heat during mould filling, but can occur anywhere on mould or core surfaces. It is an occasional defect. In some cases, it is easily removed by shot blasting or heat treatment. In other cases, it can only be removed by chipping, grinding, or at worst by arc air cutting. Figures 16-25 show example castings with the defect.

From the illustrations, it is apparent that the binder system being used is unimportant; they are both organic and inorganic systems. The steel specification is only important in as much as the longer the solidification time, the worse the defect is likely to be. In practice, castings or foundries with extended pouring times, or castings or foundries pouring at high degrees of superheat, experience a higher incidence of the defect. Interestingly, the defect appears to occur more frequently in the winter months. Also, foundries using hot-air mould dryers appear to experience fewer difficulties.



Fig.17. Another view of Figure 16.



Fig.18. A close up view of Figure 16. Notice how the severity increases adjacent to the ingate areas.



Fig.19. End case casting. Severe double skin around ingate.

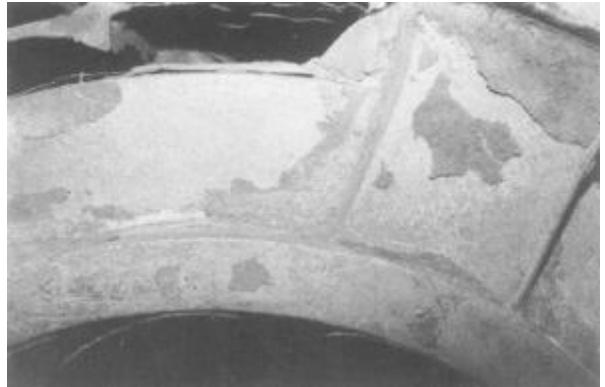


Fig.22. Example of an easily removed double skin.



Fig.20. Steam chest casting. Showing double skin emanating from the ingate areas.



Fig.23. Double skin on an ingate.



Fig.21. Example of a very difficult to remove double skin.



Fig.24. Pilger roll with double skin.

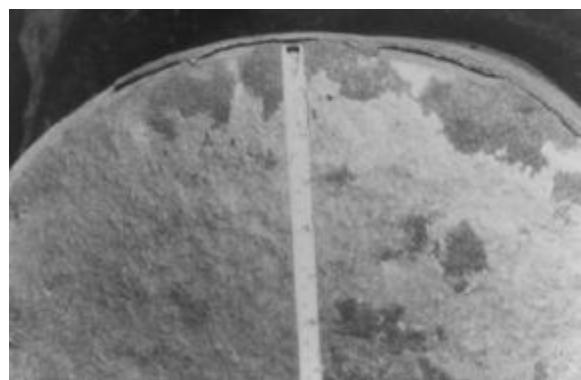


Fig.25 Close up of Figure 24.

Research Review

From the work done by Biel, Petro, and Finn, the defect is a mixture of chromite sand, glassy slag, and metal. Figures 26 and 27 show pieces of the defect that can very easily be removed, and leave a very good surface finish on the casting after removal. These pieces are, however, magnetic. If one calculates the mass of an equal volume of rammed chromite sand, and then calculates the volume and weight of one of these pieces, they are approximately the same, no penetration has occurred. This metalization has occurred through reduction of iron from the chromite sand. Work was carried out by Scheafer, and confirmed by Flinn, that under reducing conditions, iron droplets are reduced from the chromite grains (see Fig. 28) if sand temperatures rise to 1250C.

As these iron droplets migrate to the surface of the sand grains, the sand mass expands, and the droplets amalgamate. As cooling takes place and the resin binder in the sand burns out, air is drawn back to the interface, causing oxidation. This sticks the whole thing together. Figures 29 and 30 show pieces of the defect, which are very difficult to remove.

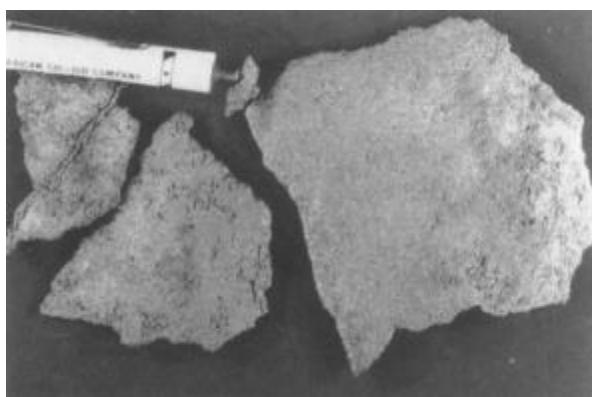


Fig.26 Fragments of the defect. Note the smooth surface on both sides of the pieces (easy to remove).

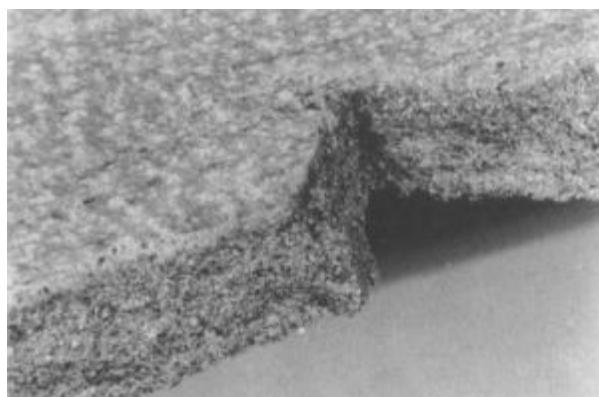


Fig.27. Close up of Figure 26. Note the sandwich effect.

If one again does a mass/volume calculation, the sample weight is too heavy; penetration has occurred. If one takes this further and calculates the void space, it works out at approximately 25% on well-rammed chromite sand, but the weight gain is in excess of 25% metal, and sand grains have been fluxed and void space increased (as per Flinn). Finn looked at this defect in great detail and found that reduced iron from the sand could be subsequently oxidized. During this reaction, iron would combine with the tramp silicates within the sand and form fayalite. Fayalite is a low melting point iron silicate slag that devours silica and is capable of softening or fluxing chromite sand grains. This, in turn, allows the chromite sand to be more easily wetted by liquid steel. Figures 31-35 show a brief resume of this work.

Finn also confirmed the work of Weber, Sontz, and Scheafer, which showed, that under oxidizing conditions, at temperatures of 1200C, chromite could break down into oxides, exuded along its crystalline planes. The surface would then be sealed by the bloating process, as referred to above. Figures 36-38 illustrate this work. Figures 39 and 40 show more work done by Finn on the effectiveness of zircon mould coating in preventing the defect and illustrate the refractory slag formed. However, in the author's experience, most steel foundries are using a zircon mould coating when making very large castings, yet they still experience the defect.

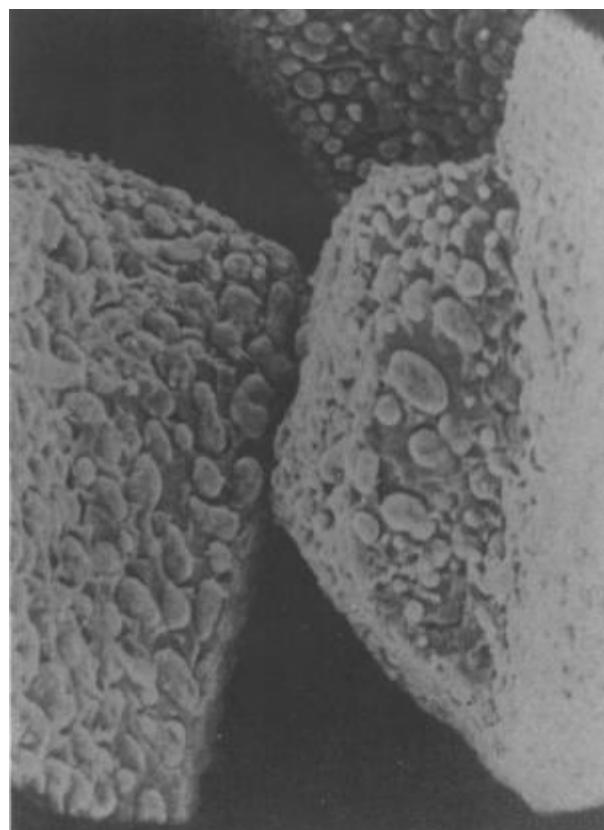


Fig.28. Iron droplets migrating to the surface of chromite sand grains, SEM, 1000X.

In summary:

- Iron can be reduced from chromite sand in a reducing atmosphere (most foundries use organic binders).
- If iron is subsequently oxidized in the presence of silica, fluxing agents are formed.
- Chromite is more easily wetted by liquid steel when coated with iron or softened by fayalite. Sand temperature at the interface is important, i.e., 1250C (2282F) approx. required.
- Zircon coatings help to reduce fusion to the casting.
- Excess gangue material (turbidity) in the chromite will increase the severity of the defect.
- Damp conditions or high moisture contents increase the risk of occurrence.



Fig.29. Fragments of the defect (difficult to remove)

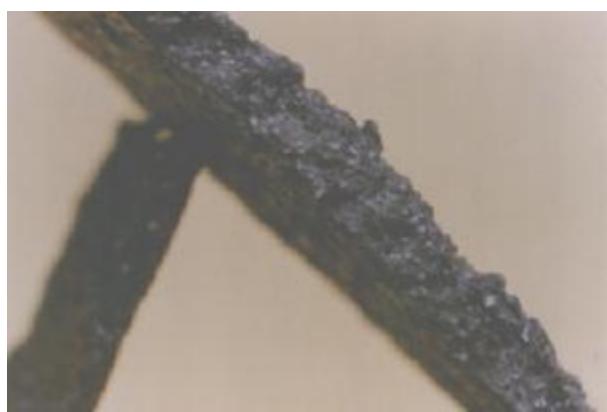


Fig.30. Close-up of Figure 29. Note the uniformity of the section density.



Fig.31. The double skin defect. 60X

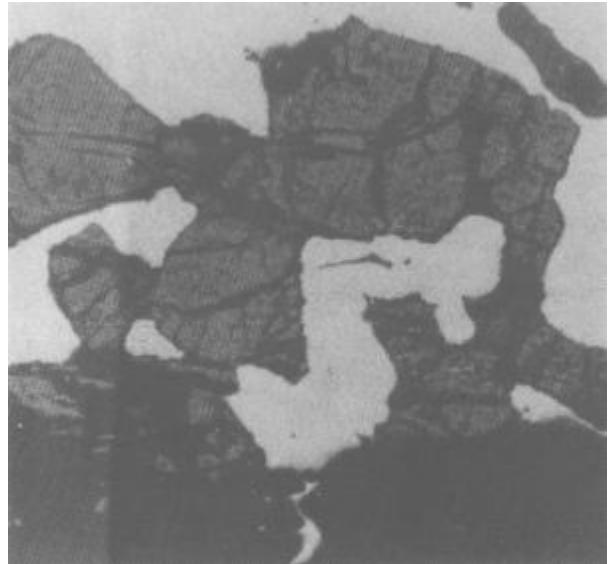


Fig.32.The defect X60 Slag and chromite dark gray colour.
Metal light grey colour.

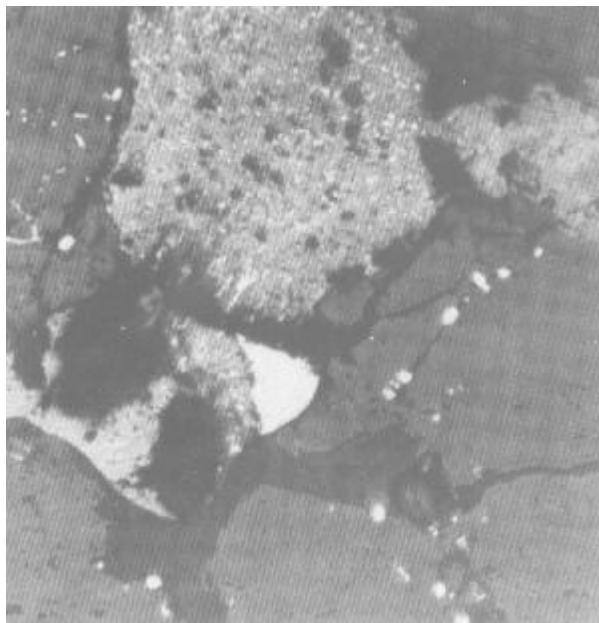


Fig.33. The defect – the bright spots are reduced iron oxide and slag. 250X

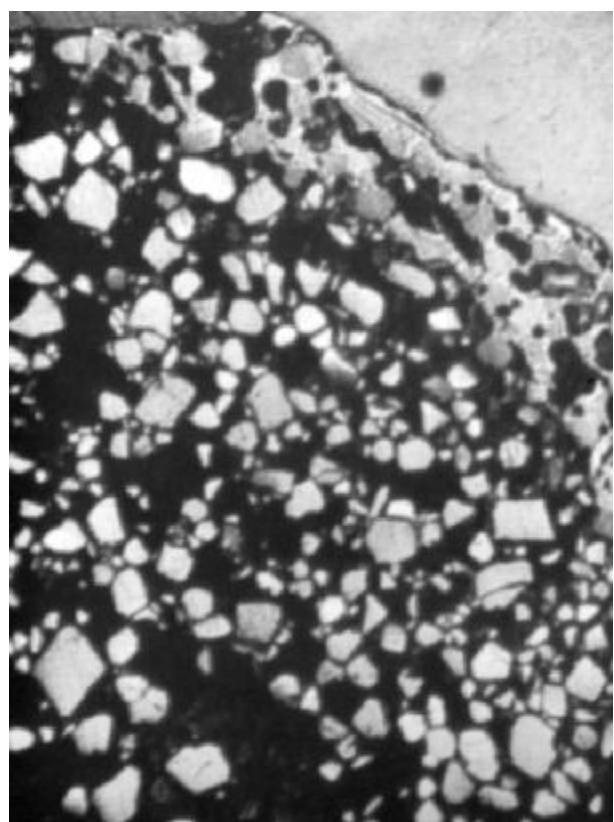


Fig.35. Chromite + 3% serpentine. 10x

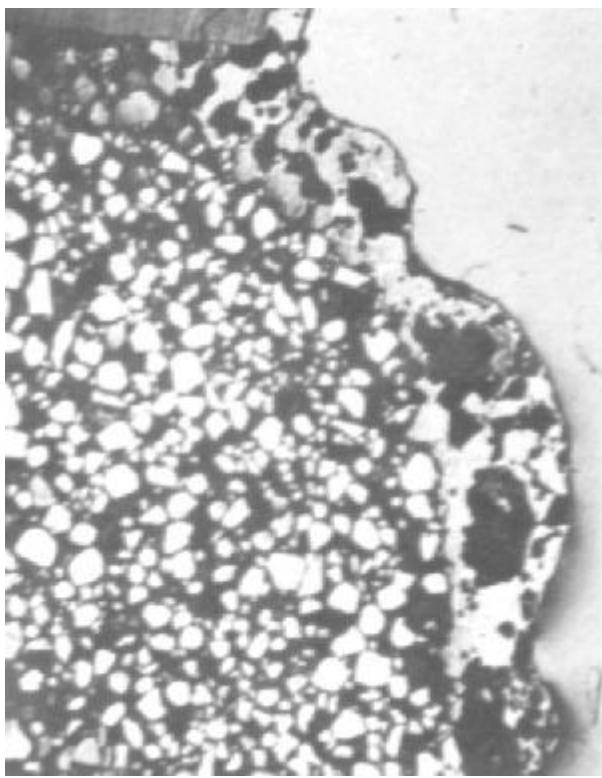


Fig.34. Chromite + 5% silica. 10X

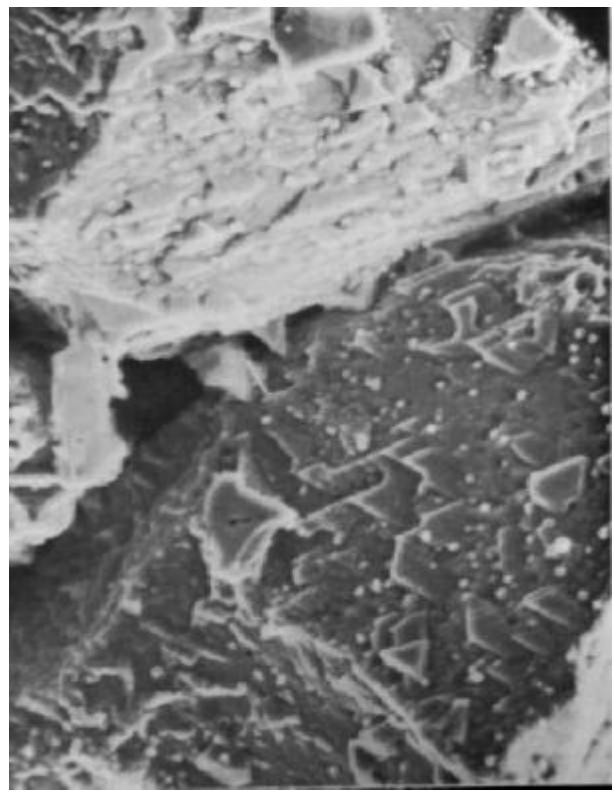


Fig.36. Early exudation of iron oxide and recrystallization of chromite grain. 1000X



Fig.37. Resin bonded chromite, fired at 1300C.
Note crystallographic planes.

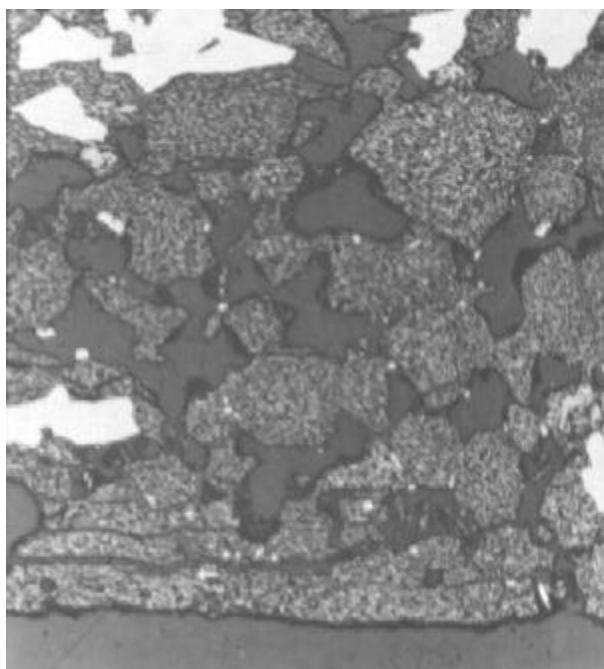


Fig.38. Chromite bloating. Note how the surface has sealed.

PROBLEM AREAS

From speaking to foundrymen, and from experience, it is apparent that the areas listed below most influence the formation of the defect. However, one of these alone is unlikely to create a severe form of the defect.

Turbidity (Impurities)

Turbidity is a measure of the colloidal particles within the raw chromite sand. It is measured in ppm and is a reflection of the amount of tramp material present. Figure 41 graphs the routine tests of material running through our plant. As one would expect, acid demand (pH), AFS No., and pan follow one another very closely. However, turbidity is not apparently affected by these other properties, which is surprising. The higher these impurities, the more fayalite can be formed.

Pouring Temperature and Time

The higher the degree of superheat, the higher the risk of the interface temperature reaching the critical point. The longer the pouring time, the higher the sand temperature when the metal reaches the interface and, thus, the lower the heat abstraction rate. The interface temperature is higher, which extends the time period during which the reactions can take place.

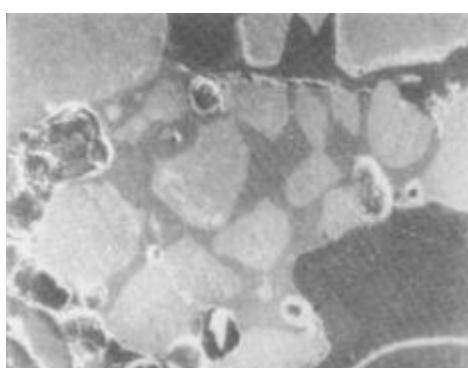


Fig.39. Chromite + alkyd resin, no mould coating.
Note fluid-fused slag

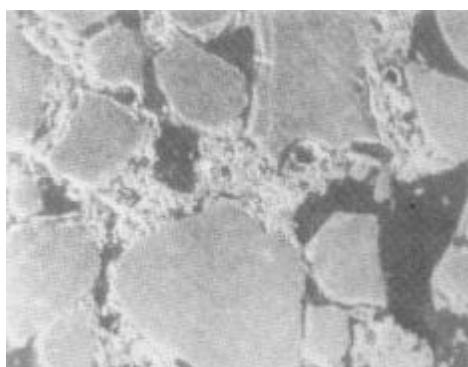


Fig.40. Same as Figure 39 (chromite + alkyd resin), but with zircon mould coating. Note refractory slag.

Oxygen Activity in Steel Melting

High levels of oxygen within the steel promote the formation of slags and ceroxides. These reaction products are capable of attacking the mould coating and acting as a silica flux. (Interestingly, the zircon used in mould coatings is really zirconium silicate, i.e., 34% silica, and there is also a free silica fraction present.) It is, therefore, important to try to reduce oxygen content within the liquid steel to 10 ppm max. It is necessary to have a good melting procedure, and the correct amount of aluminium should be plunged at tapping.

Turbulence

Turbulence at ingates or within the mould cavity could cause erosion of the mould coating or generate slags. Once the coating has been damaged, and iron droplets have been reduced from the sand, mechanical penetration can easily take place while ever-reducing conditions prevail.

Mould Refractory Coating

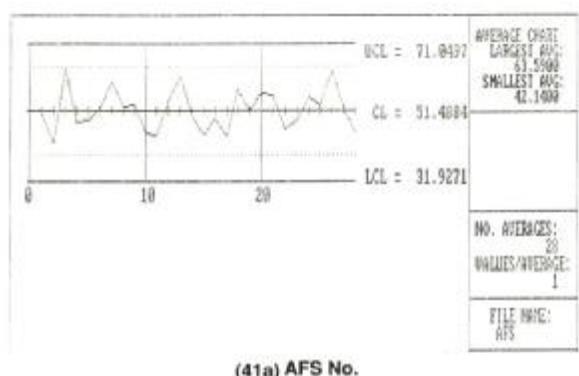
Zircon, as indicated, is approximately 64.5% Zr, 34% SiO₂, the main impurities being iron, and free silica.

The iron content dramatically reduces the fusion point of the material, and the free silica can combine with the reduced iron from the chromite or excess metallic aluminium in the steel to form aggressive slags.

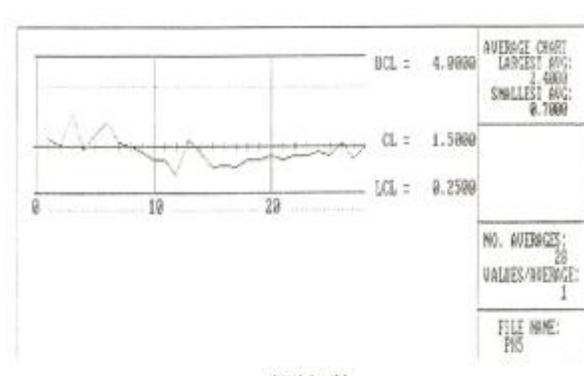
Most steel foundries use a water-based coating. If this coating is not dried properly, it is possible to envisage a wet layer being formed in the sand mass behind the mould coating. Obviously, this could create ideal conditions for formation of the defect (i.e., a reducing sand mass with an oxidizing layer near the interface).

Mould Atmosphere

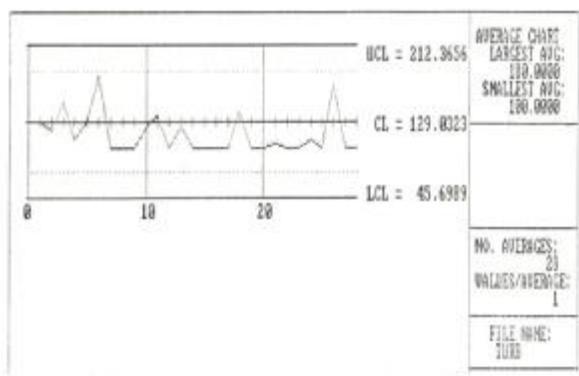
Within the sand mass, it is apparent that, with an organic binder, a reducing atmosphere at, or just below, the interface will prevail. However, resin binder systems do contain large quantities of water, which is driven back from the interface during casting. If this moisture could then re-condense to form a wet layer, it would induce an oxidizing condition in this area. In very large moulds, we have a great deal of air, which can be very humid. This may promote condensation on the mould surface. It is, therefore, possible to have a reducing sand layer at the interface sandwiched between an oxidizing mould cavity, and an oxidizing sand layer some distance from the interface.



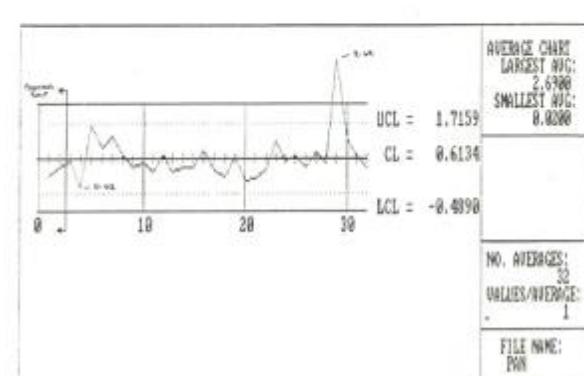
(41a) AFS No.



(41b) pH



(41c) turbidity



(41d) fines

Fig.41. Quality control graphs for chromite sand production plotting - AFS No, pH, turbidity and fines.

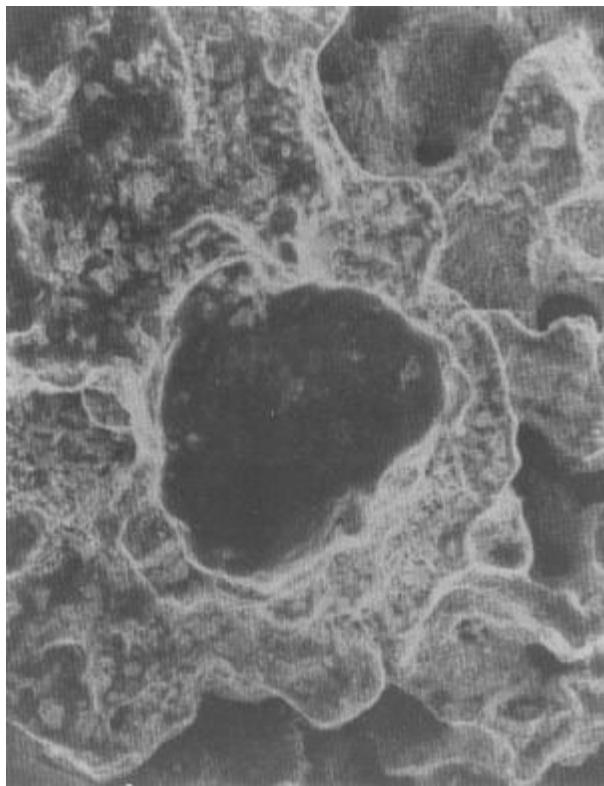


Fig.42. Single metal entry through a zircon mould coating.
85X

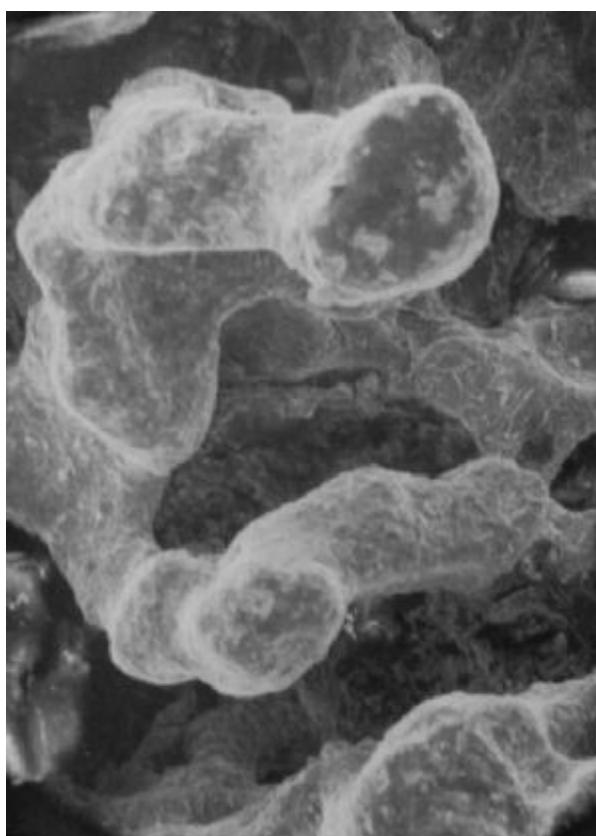


Fig.43. Same as Figure 42 (single metal entry through a zircon mould coating), but 180X

POSSIBLE SOLUTIONS

As a result of this analysis, the following theory was put forward. A number of the above factors have come into play. This has resulted in the silica being removed from the coating, allowing steel to penetrate the easily-wetted, iron-coated, or fluxed chromite grains. This explains why there is a good surface under the defect, because the zircon, minus the silica, is still acting as a parting line, but adhesion is severe due to 34% possible contact area (see Figs. 42-43). The pieces of double skin removed from a duplex steel multi-stage pump (Fig.44) show the attachment points as bright spots, created as the liquid steel penetrated the zircon coating. This was highlighted when the high-iron-content skin rusted, yet the stainless steel attachment points remained bright.

It is apparent that no single action will resolve the problem, and that it is necessary to institute both quality and production control procedures to avoid formation of the defect. The following procedures and limitations were therefore instituted, and the practical outcome assessed, within foundries.

Raw Materials

Chromite sand should have a turbidity level of 150 ppm max., and SiO_2 1.0% max.

Zircon mould coating should have an iron content of 0.5% max. and free silica of 2.0% max.

In-Process Control

Pouring Temperature/Pouring Speed. On large castings (modulus 5 cm or 2 in. and over), the casting temperature should be in the range 30-50C (77-112F) above liquidus. At these pouring temperatures, the equation below should be used to calculate the pouring speed.

$$GZ = 5.06 \times G^{0.236}$$

where

GZ = pouring time in seconds

G = casting weight in kg.

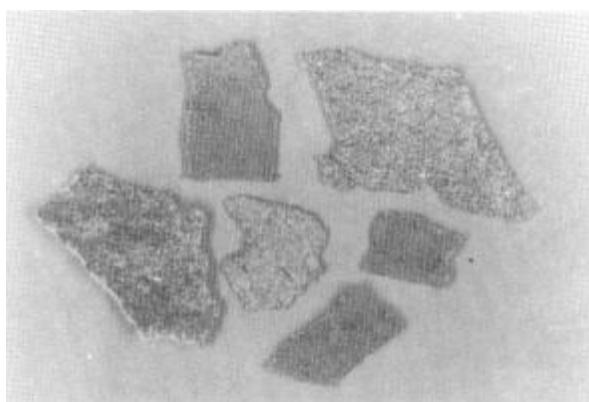


Fig.44. Pieces of double skin showing the bright attachment points.

For example, take a 5000 kg casting where

$$\begin{aligned}GZ &= 5.06 \times (\log 5000 \times 0.236) \\GZ &= 5.06 \times (\log 0.8729) \\GZ &= 5.06 \times 7.4637 \\GZ &= 37.8 \text{ sec.}\end{aligned}$$

The flow rate within the running system and mould cavity should be within the following limits.

Sand running system	1.0 m/sec max. (3.25 ft/sec)
Refractory running system	3.5 m/sec max. (11.5 ft/sec)
Ingate velocity	1.0 m/sec max. (3.25 ft/sec)

If these parameters are followed, a solidified steel layer should rapidly be formed at the interface. This layer is not washed away by the flow of steel as the mould cavity is filled, yet still maintains a sufficiently slow-growing solidification front to maintain properties.

Moulding Sand

Because most foundries face moulds with chromite and back up with silica sand, it is important that the thickness of the chromite face is sufficient to avoid silica contamination, and also to ensure high enough heat abstraction rates. From previous work done, it seems that 2-6 inches should be used, dependent on section thickness and pouring temperature. Resin and hardener contents should be kept to a minimum, as this will minimize possible condensates (in the author's experience, the resin required to bond chromite is between 30% to 50% less than that used on silica to produce comparable sand properties).

Melting Procedure

Oxygen activity should be kept to a minimum (10 ppm) in order to minimize slag formation around turbulent ingate areas.

Mould Coating

Water-based mould coatings should be thoroughly dried. If two coats are applied, the first should be properly dried before application of a second coat. The use of a mould dryer is recommended after closing the mould, if practicable, as this will avoid condensation within the mould cavity, and should allow a further reduction in binder additions. The mould dryer should not be removed until the ladle is in position for casting.

CONCLUSIONS

When we started this work, in conjunction with many of the U.K.'s leading large steel casting producers, there was a high incidence of double skin defects. As we have shared our experiences and ideas, the parameters for elimination of the defect, as outlined above, have developed and have been in place for approximately nine months. During this period, the double skin defect has become an extremely rare occurrence, and can now usually be traced back to a deviation from the outlined procedure.

ACKNOWLEDGMENTS

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BIBLIOGRAPHY

- Ableidinger, K.; "Steel Foundry Methoding of Integrity Castings" (1977).
Asanti, P.; "Interface Reactions of Chromite, Olivine, and Quartz Sands with Molten Steel," *AFS Cast Metals Research Journal*, vol 5, no 1 (Mar 1968).
Asanti, P.; "Mold Materials and Burn On in Steel Castings," *Modern Castings*, vol 49, no 4(1969).
Biel, J., A. Petro, and R. A. Flinn; "Variables Affecting Chromite Sand Performance in Molds" *AFS Transactions*, paper 80-111(1980).
Middleton, J. M., and F. F. Bownes; "The Properties of Chromite and its Application in the Foundry," *The British Foundryman* (Aug 1970).
Saunders, C. A., and R. L. Doelman; "Heat Abstraction into Molding Sand" *AFS Transactions*, vol 79 (1971).
Saunders, C. A., and R. L. Doelman; "Review of Sand Surface Area Relationships" *AFS Transactions*, vol 76 (1968).
Saunders, C. A., R. L. Doelman, and A. C. Den Breejen; "The Relationship of Bond Deactivation, Molding Media and Casting (v/sa) to Heat Abstraction Rates from Castings for Various Metals" *AFS Transactions*, vol 81(1973).
Scheafer, K. D.; "Behavior of Chromite in Steel Casting Molds and Cores," *AFS Transactions*, paper 75-16(1975).
Sontz, A.; "Recovery of Chromite Sand," *AFS Transactions*, pp 1-12(1972).