

AN ABSTRACT OF THE THESIS OF

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(Name of Student) (Degree)

in Metallurgical Engineering presented on April 20, 1971
(Major) (Date)

Title: THE CONTROL OF NON-METALIC INCLUSIONS IN
CAST STEEL

Abstract approved: Redacted for Privacy
O. G. Paasche

Exogenous and indigenous inclusions are defined and described with respect to their origins and effects in cast steel. Means of minimizing exogenous inclusions thru prevention of their formation as well as entrapment in the mold filling system are discussed. Indigenous inclusions arise from elements normally present in steel, principally oxygen, nitrogen and sulfur, and to control these inclusions it is necessary to limit the concentration of the forming elements. Conventional steelmaking techniques for controlling the oxygen, nitrogen and sulfur levels are described. Absolute elimination of indigenous inclusions has not been attained, so it is necessary to treat the residual inclusions in such a way that their deleterious effects are minimized. This involves selection of the appropriate final deoxidizer. The various deoxidizer choices are discussed with

respect to their primary effect upon sulfide and nitride inclusions as well as precautions to be taken involving side effects.

The Control of Non-Metallic
Inclusions in Cast Steel

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1971

APPROVED:

Redacted for Privacy

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Date thesis is presented

April 20, 1971

Typed by Ilene Anderton for Philip Charles Belding

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THE CONTROL OF NON-METALLIC INCLUSIONS IN CAST STEEL

INTRODUCTION

Description of Non-metallic Inclusions

In general a non-metallic inclusion in steel can be defined as a foreign body present in the solidified steel and incongruent with the matrix. Although this is an all encompassing definition, it is hardly suitable to begin a discussion of so complex a subject as non-metallic inclusions in cast steel. Others faced with this problem have devised widely accepted categories in which the various inclusions are classified as to size, distribution and source. Those which are macroscopic in size and have originated entirely from outside the steel are termed exogenous, while those which are microscopic and have origin from elements found entirely present in the liquid steel are termed indigenous. A third classification is sometimes mentioned which involves reoxidation of some elements of the steel while in contact with the air before solidification. These have been called endogenous, but because of their form and distribution similarities with exogenous inclusions, even so far as inter-reacting with them, they are often not distinguished from them. That course will be followed in this paper.

Exogenous inclusions are entrapped material which arises generally from mechanical or chemical erosion of the refractories or other

substances with which the molten steel comes in contact. They are macroscopic in size and invariably haphazard in their distribution. Although they are often found near the surface of the casting, they can occur at any location where conditions are favorable for their entrapment.

Internally they may appear in several shapes. One investigator (33) found two distinct types; the first was a film defect and linear in shape whose severity was directly related to the aluminum addition; the second was a multiphase particle with many geometrical shapes.

A special case of the surface macroinclusion has been termed the ceroxide defect (25, p. 6-15). It is typified as a non-metallic material found at the surface, or slightly below the surface of steel castings. It appears as a white to green translucent slag-like material, composed of oxides of silicon, iron, aluminum and manganese covering areas up to two or three inches in diameter.

The composition of the inclusion depends largely upon its source. Slag inclusions in steel made by the basic process will contain substantial amounts of lime. If the inclusion is a reoxidation product of an aluminum killed steel then corundum will be the principal phase (33). Chemical erosion of an acid refractory by basic oxides of the metal, especially manganese oxide will always be found high in this oxide (37, p. 369-397). Because of its relation to the source, the

content of the inclusion is of first importance in planning corrective measures.

The indigenous inclusion is always a precipitate of a second phase from the steel, usually an oxide or sulfide and certain nitrides and carbides. The particles are usually small and uniformly distributed originating as either liquids or solids in a steel that can itself be either liquid or solid. Particles separating as liquids with a melting point below that of steel, such as type I^{1/} sulfides will have external globular shapes. Some inclusions, such as zirconium and titanium nitrides precipitate as solids from the liquid steel and will have well defined crystalline exteriors in the solidified steel. Another form is the film or eutectic precipitate which segregates toward and separates from the last solidifying steel and thus becomes concentrated at primary grain boundaries. Type II sulfide inclusions are formed this way. A solid state precipitation occurs when aluminum nitride particles separate at primary grain boundaries of the completely solidified steel.

The reactions by which the indigenous inclusion is precipitated include (37, p. 369-397):

1. Decreased solubility as the steel cools to and thru the solidification range.
2. Decrease in solid solubility as the steel further cools from the solidus, including phase change effects.

^{1/} See page 32.

3. Increased concentration of solutes from dendritic segregation during freezing.

Indigenous inclusions are primarily oxides, sulfides and nitrides which have extremely low solubilities in the solid steel. The total sulfur present then in the liquid steel determines the quantity of sulfides present after solidification. The degree of deoxidation imposed on the steel has a strong influence on the form of the sulfide precipitate. The degree of deoxidation also determines the amount of secondary oxides which precipitate in the solidified steel, because all available data indicate oxygen in excess of equilibrium with the deoxidizer precipitates as primary oxides which have the opportunity to float out according to Stoke's law, and are not found in the solidified steel. True indigenous oxide inclusions are formed only by the soluble oxygen which at the beginning of solidification is in equilibrium with the deoxidizer but which during solidification loses this solubility and precipitates as an oxide.

Significance of Non-metallic Inclusions

Non-metallic inclusions can have an effect on steel castings in two ways. They can add to the cost of production if they happen to be detectable and must be removed. Or, if they are internal, they can reduce the mechanical properties of the casting.

The subject of repair cost on castings because of inclusions is

difficult to approach quantitatively. Ceroxides and other surface inclusions can be relatively large and they must be removed by arc-air or grinding and the depression filled with suitable weld metal. This involves skilled labor for an unscheduled operation resulting in a direct labor cost plus disrupted production. The cost per defect can be small but if the incidence of ceroxide is high, the overall production cost can be substantial.

Some large sub-surface inclusions may cause specification castings to be radiographically rejected. Repair of these defects can be very costly because so much overlying sound metal must first be removed.

Small internal inclusions, if they are of the right type are a contributing cause of hot tears (9, p. 40-50). Hot tears in the extreme result in complete loss of the nearly finished casting, and in lesser degree require weld repair.

The effect of non-metallic inclusions on mechanical properties of steel castings has been better documented.

Tensile ductility values for reduction of area and elongation in medium carbon cast steel are significantly lowered by the presence of eutectic type II sulfide inclusions (11, p. 127-159). Low tensile ductility is also exhibited by steels with aluminum nitride grain boundary precipitates (8, p. 1-3, 23, 49). Unpublished test results by the author concerning ductility of ultra high strength steels showed a

decrease from 9.2 percent elongation to 0.20 percent elongation directly attributed to aluminum nitride precipitate.

Dynamic properties are likewise impaired. Notched-bar impact values can be reduced by as much as 50 percent if eutectic sulfides are present (24, p. 445-452). Another study showed that sulfide segregation reduced the fracture energy absorbed by room temperature Charpy V-notch specimens from 38 foot-pounds to 17 foot-pounds in quenched and tempered 130,000 psi tensile strength steels (6, p. 17-22). Further test of the effect of Type II sulfide inclusions on Charpy V-notch specimens show that of 150 low alloy cast steels tested, only five percent having Type II inclusions attained values over 50 foot-pounds while 94 percent with Type I inclusions exceeded 50 foot-pounds (10, p. 21-38). The similar effect has been shown with Izod specimens where the precipitate was aluminum nitride (23).

Fatigue of cast steel, contrary to what might be expected, is not generally affected by the presence of indigenous inclusions (24, p. 445-452, 19), although one study indicated qualitatively that brittle inclusions increase the rate of crack propagation (47). Exogenous inclusions do, however, act as stress raisers and initiate failure, especially when near the surface. Slag inclusions under high cycle, low stress conditions were found to determine the fatigue behavior of a crawler shoe casting (18). Large inclusions, or clusters of smaller inclusions present at the surface also affected fatigue strength

(3, p. 173-178). Finally it is held that any non-metallic inclusion of macroscopic size if it is located in a critical zone of a dynamically loaded part causes a great strength reduction under repeated stress (24, p. 445-452).

ELIMINATION OF EXOGENOUS INCLUSIONS

General Approach

Exogenous inclusions arise from conditions outside the steel so that, as will be contrasted in the case of indigenous inclusions later, little can be done to the steel itself to prevent the occurrence of the inclusions. The techniques devised for their control relate to the materials with which the steel come in contact - the furnace refractories and slags, oxygen in the air, ladle linings and molding media.

Early concepts of the origin of inclusions held that they were present suspended in the bath as an emulsion (34). Tests in which the furnace slag and metal were intimately mixed for the purpose of desulfurization in aircraft quality steel, however, contained no inordinate amounts of slag inclusions in the solidified steel. Likewise, spoon samples when taken from a furnace and allowed to solidify fail to contain any of the so-called suspended inclusions.

Most available data indicate that particles in liquid steel tend to float rapidly following Stokes' law of a suspended particle. The equation is simplified for the particular case of steel and the only important variable is the particle radius (37, p. 369-397). Calculations shows that a 30 micron particle will rise five feet in 30 minutes, and a 300 micron particle rises five feet in 21 seconds. With regard to

the exogenous inclusion then which is macroscopic in size, it becomes obvious that there is no need to be concerned with the presence of any particles in the steel prior to its placement in the final pouring ladle. Up to that time any inclusions present will have had adequate time to float out. Even a clean pouring ladle may hold the steel undisturbed sufficiently long that it represents a starting point where the exogenous inclusion count is negligible. This is not intended to dismiss the pouring ladle as a significant factor, because once pouring commences the agitation of the metal and the washing action on refractories can cause further erosion.

Also, ladles may not always be clean, so that slag, metal oxides and fluxed lining materials previously frozen on the ladle interior may be continuously melting during the time the steel is held. This material can become entrained in the metal stream during pouring and be deposited in the casting.

Reoxidation of metallic elements in contact with the air form compounds, which by themselves can become inclusions, as well as interacting with ladle and mold refractories to form complex fused products which are prominent inclusion source (25, p. 16-17). If the metal oxides could be prevented from forming then a significant reduction in the inclusion count should follow.

Ideally it should be possible to protect the exposed metal from oxygen in the air and prevent surface oxidation. Unfortunately, very

little quantitative work seems to have been done in this area. Protection of the stream with argon gas has been investigated, but this was in connection with billet production (2). The result of shrouding the stream from tundish to mold with argon results in 33 percent less dissolved oxygen and about 76 percent reduction in inclusion count and size in the billet. However, another study found no significant improvement of the billet surface with regard to linear indications or oxide inclusions (17, p. 6) using argon blanketed streams. These results are from billet tests, where there is freedom from oxygen which is found in binders and moisture in the average casting mold and the results may have no application to casting techniques. To use this with castings further requires enclosing the entire mold in a container of argon. For good results the air must be almost totally excluded. Air diluted 90 percent with argon is unsatisfactory. As a matter of practice argon protection is not used in foundries even though theoretically it could result in fewer exogenous inclusions.

Since reaction of metal oxides with the ladle refractories is a prominent source of inclusions, then some refractories should be better than others in minimizing this. Acid linings for instance, in the presence of a basic steel are poor in this respect although they are still used. A better material obviously is indicated.

Finally, somewhat as a last resort, inclusions instead of being

prevented from forming can be trapped in the mold filling systems so that they don't find their way into the mold cavity.

The general approach then in practice to eliminate exogenous inclusions involves selection of refractories with which the steel comes in contact and design of pouring systems.

Refractories Contacting Molten Steel

The Steel Founders' Society of America has conducted extensive research on the problem of surface or slightly sub-surface exogenous inclusions, which they have termed ceroxide (25, p. 6-15). Assuming that ceroxides are a surface manifestation of typical exogenous inclusions, then results from research on the former should be generally applicable to the latter. The laboratory research was quantitative in that the amount of ceroxide was determined by weighing the deposits formed on a standard test casting. Several variables were studied, among them were silica vs high alumina ladle linings and green sand molds vs baked oil sand, all of which represent refractories coming into contact with the molten steel. Radioactive tracers as well as chemical tracers were used in order to determine the origin of the ceroxide.

The results indicated that high alumina ladle linings seemed to have a more beneficial effect than silica although statistically the difference was not significant at the 95 percent confidence level. The

molding sand mixture, and perhaps by inference the mold atmosphere, did not influence ceroxide production.

Plant trials were conducted to affirm the conclusions derived from laboratory tests. The trials were quantitative, but unlike the lab tests, the parameter used was the time to repair the defect, including removal of the ceroxide, weld repair of the cavity and contour finishing grinding.

In practice, the 96 percent alumina ladle lining produced a significant improvement over the material which was currently being used. A ladle brick of 70 percent alumina also was significantly better than a clay brick that was in regular use.

An independent foundry test using graphite test molds compared 70 percent alumina brick side walls and 80 percent alumina bottom material to the clay materials regularly used in their ladles (29). In this test they measured the surface area of the inclusion at the cope as a measure of the severity. They concluded that the test material was significantly better - reducing the inclusion area by 40 percent in the test mold. The additional cost of the better refractories somewhat offset their advantage. There also were wide variations in the inclusions found for any combination of ladle refractories indicating some uncontrolled variable was operating.

The cost premium for high alumina ladles led other investigators (40) to prefer a zircon-silica lining which seemed to produce no

difference in the amounts of inclusions compared to alumina linings. In this regard, another study (1) found in practice high alumina linings were better when compared to clay or silica linings, but not appreciably better when the comparison was with zircon, olivine, or magnesia materials.

Besides ladle refractories, gating system materials were found to be a source of inclusions. If the gate is made of sand bonded with conventional mold or core binders, there is always a chance of some erosion as the steel is poured. The use of aluminum silicate refractory tiles, although substantially more expensive than sand were found to reduce the man-hours for cleaning a selected group of castings by 22 percent (21). Over a four year study the consumption of welding rod for repair of inclusion defects dropped from nine pounds per ton to five pounds per ton.

In brief summary, the proper choice of ladle lining and mold gating materials can reduce but not eliminate exogenous inclusions. Suggested ladle linings of high alumina refractory produced significant improvement although zircon, olivine and magnesia appeared equally effective when compared with clay or silica. Mold media itself did not effect the amount of inclusions produced, but aluminum silicate gate tiles reduced the amount.

Design of the Pouring System

The pouring system for steel castings includes the ladle, which may be a bottom pour, lip pour or tea pot spout type, the pouring cup which accepts the steel from the ladle and the gate thru which the steel flows from the pouring cup to the mold cavity.

Pouring ladles have been shown to have a significant effect on the amount of ceroxide found. A foundry experiment comparing bottom pour ladles vs lip pour ladles found that at the 95 percent confidence level, bottom pour ladles produced a lower weight of ceroxide on the test casting than the lip pour ladle (25, p. 18-20). This might be attributed to inherently cleaner metal from the bottom pour ladle as well as less exposure to the atmosphere. However, it did not entirely prevent the formation of ceroxide, it merely lessened the amount.

Because of the greater freedom of design, pouring cups and gating systems have been given greater attention with the intent of preventing exogenous inclusions from entering the mold. Investigators studying the problem agreed that a pouring basin should be used and that it should be rectangular in shape (39). This tends to prevent the formation of a vortex which causes greater metal surface exposure as well as inspiration of air. The presence of a full pouring basin permits the design of a gating channel which will be full at all times. For the same reasons, rectangular channels are proposed for the

entire system.

Tapered down sprues with an enlarged base were found to permit a well controlled metal stream with a low entry velocity. This seems to be an essential practice for minimizing exogenous inclusions; a full system, unpressurized and running at low velocities.

Entrained non-metallic material can be trapped in the gating system before it reaches the mold. Studies show that a whirl gate of the proper design can significantly reduce exogenous inclusions (20, p. 19-23, 48). Similarly, the so-called Battelle streamlined gate was found to trap exogenous inclusions and at the same time reduce the amount of ceroxide found in castings using this style of gate. Conversely, some devices commonly used in practice to trap slag such as strainer cores were found to be ineffective in preventing the presence of ceroxide in test castings.

Many different gating practices were being used in foundries, some of which have been carefully devised to achieve some end other than minimization of non-metallic inclusions. When reduction of inclusions is the intent, the methods described are effective. However, no practical means have yet been found to make steel castings entirely free of exogenous inclusions, and work is continuing toward this goal.

ELIMINATION OF INDIGENOUS INCLUSIONS

General Approach

Indigenous inclusions are reaction products of elements present in the liquid steel just prior to solidification. If it were somehow possible to cast steel free of these inclusion forming elements then the steel would probably not contain any inclusions when it solidified. As a practical matter, however, it is impossible to cast steel in this condition, primarily because oxygen, one of the inclusion forming elements which is in equilibrium with the molten steel would evolve as a gas during solidification and cause the casting to be spongy. It is necessary to add certain elements which will combine with the oxygen to form solid oxides and prevent the evolution of the gas. Rimming steels are made without benefit of deoxidizers, and so develop pin holes, but subsequent rolling welds the voids shut and the steel shapes come from the rolling mill solid. Castings, of course, must be solid as-cast, so some oxygen containing inclusions will be present.

Other inclusion forming elements, principally sulfur and to a lesser degree nitrogen might theoretically be removed from the steel before it is cast, but in practice it is more of an unattainable goal than a reality.

Therefore, even though it may not be possible to completely eliminate indigenous inclusions by the exclusion of the forming elements, the reduction of these elements to the lowest practical limit will lead to the least amount of inclusions in the steel. The control of oxygen, sulfur, and nitrogen then is the essence of inclusion control.

Oxygen Control

Oxygen is unique among the inclusion formers because it is essential to the steel making process. It serves a two-fold purpose. First, carbon and oxygen dissolved in the bath of electric arc furnace steel reach an equilibrium according to the approximate equation: % carbon x % oxygen = .003 (27). With this relationship, the carbon content of the steel may be adjusted downward by the addition of oxygen either as iron ore or gaseous oxygen. All electric furnace steel is made using this procedure, so that up to the time of final deoxidation the bath has a relatively high concentration of oxygen.

Its second purpose is closely related to the first. As equilibrium is established between carbon and oxygen during carbon adjustment, the reaction product is carbon monoxide. The evolution of this gas causes the steel to boil, a phenomenon essential to the production of high quality steel, because it purges other dissolved gases, particularly hydrogen.

It is evident then that oxygen is not controlled by limiting its input sources, but rather by removing it in the final stages of the heat. Removal of oxygen is not difficult, the problem is that most oxygen scavengers produce solid or liquid particles on reaction with oxygen, and in this portion of the discussion we are trying to minimize inclusions by the removal of oxygen rather than increase them.

The general exception to this is the use of carbon as a deoxidizer. Carbon and oxygen react to form carbon monoxide under steel making conditions, and being gaseous the carbon monoxide boils off without leaving a solid or liquid oxide phase. By carefully halting the boil during the carbon adjustment period at the highest permissible carbon level, the oxygen will be at its minimum, and deoxidation with stronger agents should produce the minimum amount of oxide particles (32).

Additionally the carbon-oxygen equilibrium is affected by pressure. Carbon is a much more effective deoxidizer under vacuum (37, p. 173) and this should permit casting very low oxygen steel. If the steel were melted under vacuum and cast under pressure, then it is possible that no oxygen would evolve on solidification even in the absence of a stronger deoxidizer.

By and large, however, the control of oxygen is accomplished by the use of strong deoxidizing agents which precipitate as inclusions. The oxygen which was in equilibrium with carbon rapidly reaches equilibrium with the deoxidizer, with the difference being precipitated as

the oxide. In general, it appears that these oxides float out according to Stoke's law (14, p. 459-489, 34). However, deoxidation should be accomplished as early as possible to allow the most time for flotation. Steels deoxidized at the mold, for example, have higher oxide contents than when the deoxidizer is added earlier. Oxides which precipitate as liquids, tend to coalesce forming a larger inclusion with much faster rate of rise, and more rapid elimination (32). Unfortunately, this type of liquid particle is associated with silicon, one of the weaker deoxidizers, and one which frequently cannot prevent porosity. Therefore, silicon is rarely used alone as the final deoxidizer.

As the oxygen in the bath reaches equilibrium with the final deoxidizer, the excess oxygen is expected to float out as the oxide. That which remains is still in solution, and it is this oxygen which precipitates on cooling and solidification and is found in the casting as an inclusion. The choice of deoxidizers and the amount used determines the final solution oxygen level. However, the formation of inclusions is a very complex process and the deoxidation used affects not only the resultant oxide but the other inclusions formed as well, so the choice of deoxidation should not be made exclusively on its ability to lower the oxygen level.

Deoxidizers commonly used in steel making are aluminum, calcium, titanium and zirconium. Other elements such as silicon,

manganese, chromium and vanadium might be considered as well except that they so weakly reduce oxygen levels that they are usually unable to suppress oxygen bubble formation on solidification. They are used in steel making normally for other reasons.

Aluminum is by far the most common deoxidizer used in steel castings. It is a very powerful deoxidizer and both theory and experimental studies show that the dissolved oxygen content of steels containing aluminum is exceedingly small. Evidence has shown that the aluminum content as alumina, of these solidified steels reaches a level of 0.006 percent and remains relatively constant regardless of the total aluminum content (37, p. 369-397, 38). Difficulties arise with the use of aluminum because of its widely variable recoveries -30 percent to 50 percent of the amount added-and because of its side effects. At less than 0.02 percent depending somewhat on the rest of the steel composition, deleterious Type II^{2/} sulfides are quite likely to be formed (16, 45). At levels higher than about 0.05 percent some deterioration from Type III sulfides back to Type II is noted, and the formation of aluminum nitride becomes a risk. Further, the incidence of ceroxide increases at high aluminum levels. Therefore, aluminum can be the most satisfactory deoxidizer provided its use is carefully controlled.

Calcium deoxidation is far more controversial than any of the other elements. It has some unfavorable properties such as a boiling

^{2/} See page 32.

point of 2625°F , below that of molten steel temperatures and a very low solubility in steel. These have made it doubtful that any calcium was actually introduced into the steel at all, but recent tests have found spectrographically the presence of as much as 0.02 percent (38). The development of complex calcium alloys such as calcium-barium-silicon and calcium-manganese-silicon which reduce the calcium activity have permitted better recoveries.

The fact that CaO is more stable than Al_2O_3 would tend to make it a better deoxidizer than aluminum. However, in practice, calcium is never used alone as a deoxidizer, but most often in conjunction with aluminum. Its effect is to enhance the cleanliness of straight aluminum deoxidation as well as convert in some cases Type II sulfides to the more desirable Type III.

The stability of titanium oxide is less than that of aluminum oxide so that titanium ranks somewhat below aluminum as a deoxidizer. However, it is a powerful deoxidizer with characteristics that make it desirable for use in steel. Much like aluminum, it forms primary oxides of a reasonable size, greater than 10 microns, which rapidly rise out of the molten steel and leaves only slightly more dissolved oxygen than an equal amount of aluminum (38). Unlike aluminum, an excess will not result in Type III sulfides, but rather produces a eutectic Type II sulfide which at moderate sulfur levels is damaging to the steel's ductility. If the steel is low in sulfur,

titanium can be a very useful deoxidizer which produces a minimum of oxide inclusions and protects outstandingly against aluminum nitride intergranular fracture.

The last conventional deoxidizer is zirconium. On the basis of reducing the activity of oxygen in the bath, it is a more powerful deoxidizer than aluminum. From the standpoint of oxide inclusions, however, it is less desirable than aluminum. Whereas aluminum remaining in the steel as the oxide stabilized at about 0.006 percent regardless of residual aluminum, zirconium as the oxide remained nearly constant at 70 percent of the total zirconium present (37, p. 369-397). Metallographic examination of the steel confirmed the presence of large quantities of oxides in the higher zirconium steels. In another study, as residual zirconium exceeded 0.08 percent, steel ductility rapidly diminished and inclusion amounts increased as zirconium increased (16). As a protection against nitrogen porosity or intergranular fracture, however, it is unexcelled, even in the presence of high sulfur content.

In summary, oxygen is an essential element in making quality steel. Once it has served its purpose it must be removed so that a sound casting can be made. Carbon deoxidation under vacuum should produce steel with the least oxide inclusions. Where this is not practical, some deoxidizer must be added to the molten steel which removes most of the oxygen as primary oxides which float out.

Secondary oxides will form on solidification. Of our four strong deoxidizers aluminum, calcium, titanium and zirconium; aluminum or aluminum with calcium under careful control should produce the lowest oxide inclusion amounts.

Sulfur Control

Sulfur, unlike oxygen is not essential to the steelmaking process and except for some free machining grades of steel where sulfur content must be high, it is never intentionally added. Its liquid solubility is quite high, being about two percent sulfur in a low carbon steel at 2900^oF. The solid solubility is conversely very low being less than 0.003 percent, which means that virtually all the sulfur precipitates as a sulfide during the last stages of solidification, when dendritic segregation has increased its localized concentration to near its liquid solubility limit. Estimates of when this limit is reached indicate it occurs at about 95 percent solidification (34).

Under these conditions the sulfides will be trapped at primary grain boundaries or interdendritic sites, with no possibility of floating out. Since sulfides account for well over 50 percent of all indigenous inclusions and are a direct function of the sulfur content, a most profitable means to promote steel cleanliness is to eliminate sulfur.

The most direct approach is to exclude from the cold charge

those materials which are high in sulfur. Steel scrap is the largest single item of the charge, and contributes most of the sulfur. Structural shapes, plates and mill croppings usually contain the least sulfur, while free cutting machine stock and scaled boiler tubes are particularly bad. Undetected cast iron or rubber can introduce substantial sulfur and rust on scrap can be an appreciable source. Steel scrap is a heterogeneous material and it is not easy to determine a general sulfur level, but if low sulfur steel must be produced, the efforts to find and exclude high sulfur scrap is rewarding.

Other steelmaking materials beside scrap can be sulfur sources. Slag making material, particularly burnt lime in the basic process can be as high as 0.28 percent sulfur and for electric furnace steel lime exceeding 0.10 percent should not be used. Both magnesite and dolomite are suitable for furnace bottoms, but dolomite can be as high as 0.22 percent sulfur so that magnesite is preferred. Carbon for recarburizing a heat is commonly derived from pig iron, and high grade pig iron is very low in sulfur. However, some other sources such as cast iron should be avoided (36, p. 175-209).

If sulfur is to be controlled and input sulfur is too high, then fundamentally the basic steelmaking process must be adopted since removal of sulfur in the acid process is virtually impossible. With proper slag control, the basic process can successfully remove sulfur. For the most rapid results, slags must be highly basic, with

a lime to silica ratio of about three to one, have a very low iron oxide content and be intimately in contact with the molten bath, for relatively long periods-about two hours. These conditions are met most suitably by the open hearth furnace, and basic open hearth steels are notably low in sulfur.

In the electric arc furnace, however, holding the molten bath under strongly reducing slags - low iron oxide content - for extended periods causes the steel to absorb hydrogen and nitrogen making it unsuitable for any but the least demanding service. To circumvent this obstacle, a technique of pneumatically injecting a powdered slag mixture directly into the bath has been developed (42). Using lime or lime with magnesium, injected thru a graphite lance into a reduced bath, sulfur was significantly removed. Injections were from 15 to 30 kilograms per ton of steel in four to six minutes, and sulfur dropped from as high as 0.060 percent to as low as 0.004 percent. In the short time of injection some increase in hydrogen was noted especially if the dry lime had attracted moisture before injection.

The Steel Founders' Society has investigated basically the same process with the idea of avoiding any final hydrogen pickup at all, or at least keeping it under two parts per million hydrogen. Their approach was to desulfurize by injection prior to the boil rather than afterwards which is the normal sequence of events (4, p. 5-14, 43, p. 6-12). In this way, the sulfur was lowered to an average of less

than 0.020 percent sulfur in the bath after which the sulfur containing slag was removed. The oxidizing boil followed for carbon adjustment and hydrogen elimination. The process proved satisfactory provided magnesite and not dolomite was used as refractory in the hearth. A substantial sulfur reversion was found using dolomite.

In summary, virtually all sulfur in liquid steel precipitates as sulfide inclusions, so late in the freezing process that they all are trapped. These sulfide inclusions account for a major portion of all inclusions in steel, so that sulfur elimination is the single best way to produce cleaner steel. Sulfur can be most directly minimized by charging low sulfur materials. Sulfur removal from the bath is possible in a basic lined furnace using suitable slag controls, but invites hydrogen pick-up which can be more deleterious than the inclusions themselves.

Nitrogen Control

Nitrogen does not result in formation of inclusions at the same degree as oxygen and sulfur, but can form an extremely small, quite often sub-microscopic, particle on reaction with aluminum. These aluminum nitrides while not detracting from the steel's apparent cleanliness can produce extreme brittleness and are to be avoided. Early investigation showed the precipitate would form at about 1500^oF depending upon aluminum and nitrogen contents and cooling

rate at this temperature (23). If nitrogen could be held low, slower cooling rates as in heavy section castings and higher aluminum contents could be tolerated. For this reason, nitrogen control in cast steelmaking is practiced.

The melting furnace used in making the steel has a characteristic effect on the nitrogen level. Open hearth and basic oxygen furnace steels seldom exceed 0.006 percent nitrogen which is quite low, while acid and basic electric steels range from 0.008 percent to 0.014 percent which at the high side can readily produce nitride inclusions. If a choice of steel is permitted and low nitrogen is desired, then simply exclude electric arc furnace steel from consideration.

Nitrogen sources in the electric arc furnace are nitrogen bearing ferroalloys, scrap charge and furnace atmosphere. Except for some ferroalloys which are used for the express purpose of raising nitrogen in special steels, the furnace atmosphere is the primary nitrogen source. Molecular nitrogen is relatively insoluble in liquid steel and nitrogen used as a flush results in no discernable pick-up in the steel (32). Around the electric arc, however, the air breaks down into nascent nitrogen or possibly even ammonia if moisture is present, and has a solubility limit of about 0.05 percent nitrogen in the liquid steel, depending upon temperature and alloy content (32, 37, p. 95-178).

Several methods are available for the reduction of nitrogen from liquid steel. During the carbon oxygen boil both hydrogen and

nitrogen are known to be diminished. A survey of several three to ten ton basic electric heats showed a melt-down nitrogen content of 0.0056 percent to 0.0127 percent.

After the boil the content was 0.0047 percent to 0.0076 percent (7, 8, p. 4-20). In three specific two ton heats the nitrogen level prior to the boil was 0.0064, 0.0059 and 0.0051 percent and after an oxygen injection rate of 150 cubic feet per minute for one to three minutes, the nitrogen was found to be 0.0042, 0.0032 and 0.0034 percent (4,p. 9) respectively. Good furnace practice then, where an oxygen boil is used, will lower the nitrogen level significantly.

Since the nitrogen removed by the carbon oxygen boil is actually transported by the carbon monoxide bubble, other gases injected into the bath causing the same boiling action should act similarly. Where this has been done using argon with a simple lance in the furnace, no apparent degassification has occurred (7). However, tests of a porous plug in the base of a holding ladle thru which argon is injected show significant removal of both nitrogen and hydrogen (12). These test results have been verified in practice by at least one steel foundry (15).

Vacuum treatment is also effective in removing dissolved gases, particularly hydrogen with a lesser effect on nitrogen. The techniques used include furnace and ladle evacuation as well as stream degassing. The literature details several tests on the effect of

vacuum on dissolved nitrogen (7, 31, 44p. 16-19, 46, p. 8-11).

Finally, denitrification is possible by the use of elements having and affinity for nitrogen and forming stable precipitates at liquid steel temperatures. Only two elements, zirconium and titanium fulfill the requirements. They form very stable nitride particles which precipitate as solids from the liquid, and very effectively decrease soluble nitrogen (13, p. 48-55, 37, p. 95-178). The intent, however, is to remove nitrogen in order to minimize inclusions, and both of these elements increase the number. Some of these particles no doubt float out of the bath, however, they are very small and flotation time is long, and practically, there will always be some of these nitrides in the solidified steel.

To summarize then, nitrogen may not cause steel to be visibly dirty, but does form, on reaction with aluminum, under favorable circumstances, a very damaging nitride inclusion. Primarily because of this, nitrogen levels in aluminum killed steels must be controlled. Open hearth and basic oxygen furnace steels are inherently low in nitrogen and no special treatment is necessary. Electric furnace steels can be high in nitrogen so that precautions are necessary to avoid excessive amounts. Good electric furnace practice with an oxygen blow can significantly reduce this nitrogen and further treatment especially with argon or even evacuation can drive it still lower.

Treatment of the liquid steel with zirconium and titanium tends to lower the soluble nitrogen content but nitride inclusions of these elements will be present after solidification.

CONDITIONING OF SULFIDE AND NITRIDE INCLUSIONS

Necessity of Conditioning

Non-metallic inclusions have a detrimental influence on cast steel properties, especially as greater demands are placed on the steel's strength, and ultimately steels may be made completely free of any inclusions. In the meantime, however, no practical ways have been devised to make a perfectly clean steel. This paper has discussed some of the ways to control the concentrations of the inclusions forming elements and thus minimize inclusions. Unfortunately, in some cases as with argon purging of nitrogen, the means are not very effective; or, as with furnace desulfurization, where hydrogen pickup is common, the cure may be worse than the illness. It is often better to form the least harmful inclusion than to remove it entirely. Precisely because of this, deoxidation of steel has been intensely studied, for the deoxidation practice not only fulfills a primary objective of preventing oxygen evolution during solidification, it also determines the distribution and morphology of the oxide, sulfide and nitride inclusions to be found in the solid casting. Proper choice of final deoxidizers then can condition the inclusions that inevitably remain so that their harmful effects are minimized.

Sulfide Conditioning

In discussing sulfides in castings, some ground rules should be established. The base composition of most carbon and low alloy steels is included in the range 0.15 to 0.50 percent carbon, 0.60 to 1.60 percent manganese, 0.30 to 0.50 percent silicon and 0.01 to 0.05 percent sulfur. Under these restrictions, the sulfides are predominantly MnS. As mentioned earlier, sulfur solubility is high in the liquid steel and very low in the solid so that virtually all the sulfur precipitates as MnS, but only in the final stages of solidification. Since steel is known to solidify thru dendritic growth the final repository of the sulfides is in the primary grain boundaries or interdendritic channels. To refer to the most damaging type of sulfide inclusions as grain boundary sulfides is inappropriate since even the least damaging types are also in the grain boundaries.

Sulfide inclusions have been extensively studied in the literature (30, 34, 35, 38, 45). Type I sulfides, such as occur in silicon killed steels, are characteristically globular in shape and are frequently duplexed with a silicate phase. Closely examined all Type I sulfides will be found to contain some oxide content. In the absence of a strong deoxidizer, the oxygen level in the steel at the time of solidification is high enough that the liquid oxides and sulfides, which are miscible, precipitate together. Their freezing points are lower than

that of the steel so that they assume a characteristic spherical shape.

Type II sulfides are eutectic in shape and distribution. On a flat polished specimen they appear as round or oval dots or films depending upon how they were sectioned, and tend to be strung out in a chain. The change from Type I to Type II is brought about by deoxidation with a strong deoxidizer such as aluminum, titanium, zirconium, calcium or carbon in vacuum. Transition from Type I to Type II occurs at about 50 PPM oxygen and is quite sharp. As little as an 0.005 percent residual aluminum can cause the change. These sulfides contain no silicates as contrasted to Type I and although they may completely enclose some primary grains, the network is not continuous.

Finally, Type III sulfides, while they have some characteristics in common with Type I such as larger size and less tendency to outline grains, they differ markedly in that they take on an external crystalline form. Microprobe analyses indicate that they are pure manganese sulfide which has a freezing point above that of the steel and precipitate as solids in a liquid medium. Transition from Type II to Type III is not so clean as from Type I to Type II. Even though they can usually be produced in steels with 0.02 to 0.04 percent residual aluminum the mechanism which causes the change from Type II is not known. It certainly is not due to greater deoxidation since vacuum deoxidized steels at 3 PPM oxygen have contained Type II sulfides and aluminum will not lower the oxygen more than this. Recent study

of this type sulfide indicates that the formation is a complex mechanism involving carbon, manganese, silicon and sulfur together with aluminum plus an oxygen build-up during solidification (30, 35).

The ideal sulfide, if one must be present is definitely Type I since ductility values remain high in steels where they are exclusively present. As a matter of fact, however, the oxygen level tolerable in cast steels is lower than that needed to produce Type I inclusions and they are seldom produced. Both Type II and Type III sulfides lower ductility values but the former is by far the most damaging so the aim in conditioning sulfide inclusions is to produce Type III and avoid Type II.

The progression of sulfide inclusions from Type I thru Type II to Type III seems to follow an orderly increase in aluminum. However, in practice, it is not always consistent and several considerations besides the amount of aluminum added must be made to assure the formation of Type III sulfides.

The optimum aluminum residual range seems to be 0.02 to 0.04 percent. In order to achieve this regularly, the amount and means of addition must be controlled. Aluminum, for instance, which upon addition becomes separated from the steel by a slag layer, most often burns up before it can dissolve. The aluminum recovery is not of itself as important as the consistency. Repeatable recovery is essential. Exposure of the molten steel to the air, as for instance

during extended periods in a holding ladle or during reladling and pouring, can cause significant loss of aluminum. Long runners in wet sand molds likewise cause aluminum losses. If these practices are followed then additional aluminum must be added at the start to compensate for the loss.

The ill effects of an overdose of aluminum can be serious also. It has been reported that above a residual of 0.06 percent aluminum, Type III sulfides revert to what appears to be Type II (38). High aluminum content also increases the likelihood of aluminum nitride formation and ceroxide problems are aggravated. Therefore, it is not safe to merely add an abundant excess of aluminum to avoid eutectic sulfides.

Calcium used with aluminum seems to offer added insurance since under some conditions, where aluminum alone produces Type II or mixed Types II and III, the addition of calcium yields pure Type III sulfides.

Titanium used as a deoxidizer substitute for aluminum adequately controls oxygen level, but cannot condition sulfides well. Residual content of 0.015 percent titanium produces eutectic Type II manganese sulfides. Larger amounts, instead of forming Type III manganese sulfides, preempts the manganese to form a titanium sulfide which has a low melting point and precipitates as a eutectic much the same as Type II sulfides with the same damaging effects on physical

properties.

Zirconium behaves more as aluminum and can produce both Type II and III sulfides, and would be an acceptable sulfide conditioner. However, it produces other inclusions, mostly zirconium silicates, in proportion to its residual content and results in a dirty steel which makes it less desirable than aluminum.

Other factors play a part in Type III sulfide formation. The manganese content, or better, the Mn/S ratio, if high enough tends to produce favorable sulfides. A ratio of 20 has been found the minimum. Low sulfur content also favors Type III sulfides, but may be due to the effect on the Mn/S ratio. If either carbon or silicon are as low as 0.10 percent, it is almost impossible to have all sulfides Type III.

In summary, sulfide inclusions in cast steel have been classified as three types. Type I, a spherical inclusion found in high oxygen steels and known to be the least damaging, is not readily formed in fully deoxidized steel. Type II has a eutectic morphology and because of this is the most deleterious. Residual aluminum content of up to 0.02 percent leads to formation of this sulfide type. In practice, Type III sulfides represent a compromise for they can be readily produced in cast steel and are less damaging than the eutectic sulfide. Careful control of residual aluminum between 0.02 and 0.05 percent is necessary along with a correct balance of other steel making

elements. Titanium is incapable of producing Type III sulfides and zirconium which can produce them, also makes the steel generally dirty.

Nitride Conditioning

A particular type of intergranular fracture in cast steel has been called rock candy fracture, a name derived from the appearance of the fracture surface. In words, rock candy fracture is typified by smooth, undulating surfaces that may be shiny, but more often have a satin finish. Examination of these specimens indicates the surfaces represent primary austenite grain boundaries established as the casting cooled from solidification. Even though the castings may have been heat treated, and thus undergone a secondary austenitic state whose grain size was much smaller, fracture occurred along the much larger primary grain boundary loci. This form of intergranular fracture is always associated with low tensile ductility and low impact strengths.

Early investigations of this phenomena found that upon deep etching these steels developed a hairline network which approximated the primary grain boundary pattern (23). In addition, metallographic samples showed the presence of rod-like grain boundary precipitates visible at about 1000 diameters, which were identified as aluminum nitride. Later studies concurred in general that the precipitate was

aluminum nitride and that its precipitation at the primary grain boundaries was the principal cause of rock candy fracture (22, 41, 45, 49).

The parameters affecting the precipitation were found to be the aluminum content, the nitrogen content and the cooling rate. As either aluminum or nitrogen or both increased the degree of intergranular fracture increased. Also, as the cooling rate decreased, especially in the region above 1500^oF, the degree of intergranular fracture increased. This latter circumstance is generally accepted as the cause for heavy section castings to be more vulnerable to rock candy fracture than light section castings. It was further determined that by holding a steel known to contain nitride precipitates at a temperature of 2300^oF or higher, it was possible to redissolve the precipitate, which if the subsequent cooling were rapid enough, could be held in solution and prevent intergranular fracture. In fact, this test has been proposed as a simple method of distinguishing aluminum nitride as the cause of intergranular fracture in any particular case.

While it may be obvious that low nitrogen and aluminum may prevent the formation of the nitride precipitate, practice has shown this approach is not reliable. For one, using the most common melter, the basic electric furnace, the nitrogen level easily attainable is still high enough to cause trouble. For another, aluminum additions in practice tend to be higher than necessary in order to insure Type III sulfide formation. Finally, section sizes in castings can be so

massive and have such low mold cooling rates that even with very low nitrogen and aluminum, some nitride precipitation can occur. Therefore, from a practical viewpoint, it is more reliable to treat the nitride inclusion rather than eliminate it. In this instance, the steel will contain more visible inclusions after treatment and seem to be a dirtier product, but have vastly superior mechanical properties.

It has been suggested that aluminum nitride particles may be dissolved and held in solution by heat treatment so that they will not lead to intergranular fracture. Unfortunately, the 2300^oF temperature necessary to do this is considerably higher than most conventional heat treat equipment is designed for. In addition, 2300^oF is too high as far as grain growth is concerned, so that even if it could be done, a subsequent heat treatment to develop good mechanical properties would have to follow, and the nitride particles will again be precipitated although at new austenite grain boundaries. Therefore, correction of potential intergranular fracture thru heat treatment is impractical.

The aluminum nitride problem is best treated by using an addition of some element which forms a more stable nitride. The two most frequently discussed, and used in practice are titanium and zirconium. In their early investigations, Lorig and Elsea (23) attempted to avoid rock candy fracture by the use of titanium or zirconium as nitrogen scavengers while still using aluminum as the

primary deoxidizer. Their experience showed that, contrary to their expectations, neither appreciably changed the susceptibility to intergranular fracture unless it was substituted for part of the standard aluminum addition. Under this circumstance, both titanium and zirconium were effective.

Later studies by Woodfine and Quarrell (49) seemed to indicate that while zirconium and titanium by themselves could prevent rock candy fracture, only titanium, when used with aluminum continued to protect the steel from the defect. Zirconium, on the other hand, in additions of 0.08 percent was unable to prevent brittle fracture when 0.20 percent aluminum was added. They also found with the use of titanium that a tan colored eutectic phase could be formed, identified as titanium - manganese - iron sulfide.

However, contradictory evidence developed by the Steel Founders' Society of America (5, p. 25), in tests with high nitrogen steel illustrated the effectiveness of both titanium and zirconium in the presence of aluminum. In these tests, the steel exhibited not only intergranular fracture when deoxidized with aluminum alone, but also nitrogen worm-hole porosity. Additions of 0.07 percent zirconium and 0.085 percent titanium with a constant aluminum addition of 0.225 percent not only halted the nitrogen porosity but prevented intergranular fracture. Metallographic inspection confirmed the presence of typical zirconium and titanium nitrides, which rendered

the nitrogen harmless.

Further intensive investigation of the effects of zirconium (16) on steel castings afflicted with intergranular fracture when deoxidized with aluminum seem to substantiate the effectiveness of zirconium when used with aluminum. This study attempted to first eliminate aluminum entirely, but it was found that zirconium alone could not prevent pinhole porosity. Optimum properties were developed when deoxidizer additions were 0.085 percent aluminum and 0.065 percent zirconium. Larger zirconium additions - above 0.08 percent increased the amount and size of inclusions in localized areas, and was associated with rapid decline of the steel's ductility.

Finally, the author has conducted tests on high strength steel having tensile strengths over 200,000 pounds per square inch which suffered from intergranular fracture. When aluminum alone was the deoxidizer, rock candy fracture was common and tensile ductility reached as low as 0.20 percent elongation. Titanium with aluminum seemed to halt the intergranular fracture and resulted in about 4.0 percent elongation. Metallographic evidence of titanium nitrides as well as eutectic titanium sulfides was found in this steel. Zirconium with aluminum likewise stopped intergranular fracture, but the tensile ductility rose to 9.2 percent. The additions now established as standard are 0.10 percent aluminum and 0.05 percent zirconium.

Although both titanium and zirconium are effective in stopping

intergranular fracture due to aluminum nitride precipitation, the side effects of both must be considered. Titanium is incapable of producing Type III sulfide inclusions and in the presence of much sulfur actually produces a bad Type II titanium sulfide eutectic. Zirconium, on the other hand, conditions sulfides well, but excess zirconium leads to a high inclusion count. The evidence at hand seems to favor zirconium.

SUMMARY AND CONCLUSIONS

Non-metallic inclusions in cast steel are small foreign bodies incongruent with the matrix. They have been classified as exogenous, those which are macroscopic and have originated entirely from outside the steel and indigenous, those which are microscopic and originate entirely from elements found in the steel. Exogenous inclusions consist of trapped material unable to float out during solidification having widely varied morphology and are haphazardly distributed. Indigenous inclusions are always a second phase precipitated from the liquid or solid steel, usually oxides, sulfides or nitrides. They are uniformly distributed throughout the steel and their morphology is closely related to the amount and types of final deoxidation used.

Because they have a generally damaging effect upon steel castings, inclusions must be controlled. Inclusions found at the surface must be removed and the void repaired, adding to the cost of the part. Large sub-surface inclusions may cause radiographic rejection of the part. Certain sulfide inclusions are contributors to hot tearing of steel castings and this can result in complete loss.

Tensile ductility of castings is significantly lowered by the presence of some indigenous inclusions and dynamic properties such as impact strength are likewise impaired. Fatigue strength does not seem to be affected by inclusions unless the particle appears at or near the

surface of a highly stressed area.

The general approach, in practice, to minimize exogenous inclusions involves selection of refractories with which the steel comes in contact and design of pouring systems.

The proper choice of ladle lining and mold gating materials can reduce but not eliminate exogenous inclusions. Suggested ladle linings of high alumina refractory produced significant improvement, although zircon, olivine and magnesia appeared equally effective when compared with clay or silica. Mold media does not affect the amount of inclusions produced, but alumina silicate gate tiles reduces the amount.

The pouring system for steel castings includes the ladle, the pouring cup and the gate and runner system. Bottom pour ladles are preferred over lip pour and tea pot spout types because they produce fewer inclusions in practice. Pouring cups that are rectangular rather than circular tend to prevent formation of a vortex thus minimizing metal exposure to the air. The gating system design for best results should permit a full channel, unpressurized, with metal running at low velocities. Other devices such as whirl gates and streamlined gated have been found effective. It must be noted, however, that no practical means have yet been devised to make steel castings entirely free of exogenous inclusions and work is continuing toward that goal.

If it were possible to completely eliminate the inclusion forming elements, oxygen, sulfur and nitrogen from steel before it is cast then it might be possible to eliminate entirely indigenous inclusions. This has not been attained in practice. The reduction of these elements to the lowest practical level does minimize inclusions however, and is the essence of inclusion control.

Oxygen is an essential element in making quality steel. Once it has served its purpose it must be removed so that a sound casting can be made. Carbon deoxidation under vacuum should produce steel with the least oxide inclusions. Where this specialized technique is impractical, some deoxidizer must be added to the molten steel which removes most of the oxygen as primary oxides which float out. Secondary oxides will form on solidification. Of the four strong deoxidizers - aluminum, calcium, titanium and zirconium - aluminum or aluminum with calcium under careful control should produce the lowest oxide inclusion amounts.

Virtually all sulfur in liquid steel precipitates as sulfide inclusions, so late in the freezing process that they are all trapped. These sulfide inclusions account for a major portion of all inclusions in cast steel, so that sulfur elimination is the single best way to produce cleaner steel. Sulfur can be most directly minimized by charging low sulfur materials. Sulfur removal from the bath is possible in a basic furnace using suitable slag controls, but invites

hydrogen pick-up which can be more deleterious than the sulfide inclusion.

Nitrogen may not cause steel to be visibly dirty, but does form, on reaction with aluminum, under favorable circumstances, a very damaging nitride inclusion. Primarily because of this, nitrogen levels in aluminum killed steels must be controlled. Open hearth and basic oxygen furnace steels are inherently low in nitrogen and no special treatment is necessary. Electric arc furnace steels can be high in nitrogen so that precautions are necessary to avoid excessive amounts. Good furnace practice with an oxygen blow can significantly reduce nitrogen and further treatment especially with argon or even evacuation can drive it still lower. Treatment of the liquid steel with zirconium or titanium tends to lower the soluble nitrogen but nitride inclusions of these elements will be present after solidification.

As with exogenous inclusions, there is as yet no way to make cast steel completely free of indigenous inclusions. If, then, inclusions must be expected, it is prudent to have them in the least damaging form. Final deoxidation has a profound effect upon the morphology of sulfide and nitride inclusions, and the proper choice of deoxidizer will condition the inclusion to this end.

Sulfide inclusions in cast steel are classified as three types. Type I, a spherical inclusion found in high oxygen steels and known to be the least damaging is not readily formed in fully deoxidized steel.

Type II has an eutectic morphology and because of this is the most deleterious. Residual aluminum content of up to 0.02 percent leads to formation of this sulfide type. Type III represents a compromise for they can be readily produced in cast steel and are less damaging than Type II. Careful control of residual aluminum between 0.02 and 0.05 percent is necessary along with a correct balance of other steel making elements. Titanium is incapable of producing Type III sulfides. Zirconium behaves like aluminum but has a bad side effect of making the steel generally dirty.

Aluminum nitride precipitates form on primary grain boundaries during cooling below the solidus. They form planes of weakness which cause intergranular brittle fracture under stress. High temperature heat treatment followed by rapid quench can dissolve and retain the inclusion but the practice is generally incompatible with normal heat treatment practices. Nitrogen may be pre-empted from aluminum by using nitrogen scavengers such as zirconium and titanium. Both are effective in stopping intergranular fracture due to aluminum nitride precipitation but their side effects must be considered. Titanium is incapable of producing Type III sulfide inclusions and in the presence of much sulfur actually produces a bad Type II titanium sulfide eutectic. Zirconium on the other hand, conditions sulfides well, but excess zirconium leads to a high inclusion count. The evidence at hand seems to favor the use of zirconium.

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