Silicon Killed Steel Nozzle Clogging

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Tundish and ladle nozzle clogging is commonplace in silicon killed, high carbon, low dissolved oxygen grades. Symptoms of clogging manifest as a decrease in flow rate from the ladle to the tundish; a similar decrease in flow rate from the tundish to the mold with an associated decline in strand speed; and the formation of steel flow deflection buttons or "whiskers" on the bottom of the tundish nozzles. Signs tending to precede the occurrence of clogging in silicon killed steels include the following:

1. Aluminum levels greater than 0.003% for steels with carbon levels > 0.20%;
2. Dissolved oxygen levels under 20 ppm;
3. Sulfur removal levels greater than 30 % using a white slag practice;
4. Dolomitic or Mag Carbon ladle slag line material; and
5. Ladle Furnace heat working times in excess of 45 minutes.

Many solutions have been used to reduce the propensity for clogging in silicon killed steels: low aluminum ferro alloys; tundish slide gate nozzle change systems; calcium and calcium – silicon wire injection systems; and increasing the oxygen content of the liquid steel in the ladle and tundish. Operators since the start of continuous casting have been increasing the oxygen content of the steel in the tundish to eliminate nozzle clogging. This can often lead to the formation of slag on the billet surface, increased levels of internals inclusions (dirt), pinholes or blowholes, chemistry changes with respect to Mn, Si and C, strand breakouts and increased dissolved nitrogen and oxygen levels. In all cases, increasing the oxygen content of the steel is a poor option for eliminating nozzle clogs. Fig. 16.10 [1]shows that the ideal range for a beam blank grade is between 10 to 20 ppm.

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[1] A.W. Cramb, ed. The Making Shaping and Treating of Steel, 11th Edition, Casting Volume, The AISE Steel Foundation, 2003, Chapter 16, page 8.

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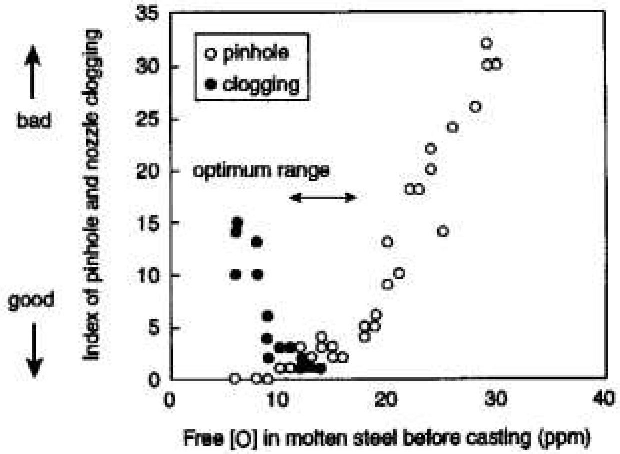

Fig. 16.10 Effect of steel deoxidation on pinhole occurence and nozzle clogging tendency. *From Ref. 19.*

In a majority of steel melt shops, the final product is a continuously cast billet, bloom, slab or beam blank. Liquid steel in the ladle is of no commercial value. Castability is a very good measure of steelmaking process control. Steelmaking using the lowest cost process and raw materials is futile if the liquid steel cannot be cast into a semi finished shape with the correct chemistry and level of cleanliness. A steel meltshop is producing at peak efficiency when the continuous caster is running smoothly and the strand operator is sitting in a chair taking very little action. If the caster operator needs to modify the liquid steel chemistry in the tundish or mold to correct existing nozzle clogging, then one can say there is a defect present in the steel making process.

White slag practices have been instituted in many silicon killed shops that reduce FeO levels in the slag to less than 1% which aids in the removal of sulfur from the liquid steel. While some have claimed to “invent” the white slag practice, a reference can be found in the 1951 edition of Making Shaping and Treating of Steel, pg. 517-518. In days of yore, the oxidizing slag in the EAF would be hand rabbled and replaced by a reducing slag. The major difference today is that the EAF can be tapped essentially slag free and a white slag can be built and used at the ladle furnace. Additionally, inert gas stirring in the ladle has greatly aided in the intermixing of steel and slag. Calcium carbide, calcium silicon fines and ferro silicon fines may be added to the ladle slag to reduce the FeO. As the FeO level drops in the slag likewise does the dissolved oxygen level in

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the steel. With a liquid slag and an accommodating V ratio, sulfur reductions of 60 % or better to levels less than 0.010 % S are possible at dissolved oxygen levels of 15 ppm. The big drawback to the white slag practice is that ladle and tundish nozzle clogging becomes much more commonplace.

Intrinsically, silicon killed steel ladle and tundish nozzle clogging can be traced to the following sources:

1. Alumina;
2. Manganese silicates;
3. Manganese-Silicate-Alumina inclusions;
4. Magnesium aluminate spinels; and
5. Cold steel temperatures.

Alumina

Alumina, Al_2O_3 is the bane of all casters. Aluminum is the most cost effective deoxidizer but oxides of aluminum precipitate as alumina on nozzles surfaces and sinter together to block the flow of molten steel. Sometimes, metallic aluminum is used as a sacrificial deoxidizer in low carbon silicon killed steels. For silicon killed steels with more than 0.10 % C to which no sacrificial aluminum is added, the most common trace sources of aluminum are ferroalloys used in the steelmaking process. Calcium silicon wire may contain up to 1.5% aluminum. Other sources include calcium aluminate slag formers. While the use of calcium aluminate slag conditioner reduces the need for fluorspar to liquefy the ladle slag, metallic aluminum and vanadium oxide can be present depending on the source of the slag conditioner. The use of fluorspar is known to reduce ladle slag line life but if calcium aluminate is substituted for fluorspar, an operator runs the risk of increased aluminum levels in silicon killed steels and possibly a vanadium increase depending on the source of the calcium aluminate. Increased levels of vanadium lead to unpredictability in tensile strength. While refractory supervisors despise the use of spar, use of calcium aluminate slag liquifiers containing metallic aluminum and vanadium oxides on high carbon silicon killed grades limited to 0.003% Al, leads to nozzle clogging and chemistry problems so spar may be the only suitable slag liquifier.

Calcium and calcium silicon wire injection has been developed to promote the formation of a liquid calcium aluminate inclusion in steel. Calcium silicon lump is also added at various plants to aid in deoxidation and also help in the formation of a liquid calcium aluminate inclusion. In quite a few silicon killed shops, calcium silicon wire is injected as a primary deoxidizer and desulfurizer. While this is effective in sufficient quantities, the use of a white slag can be considered as a less expensive alternative. With the white slag practice, calcium silicon wire can be injected in at levels <1 lb/ton of liquid steel, to liquefy remaining alumina in the steel.

Manganese Silicates

In silicon killed steels, a liquid manganese silicate inclusion is typically produced at Mn/Si ratios greater than 3.4 to 1. At lower ratios, solid SiO_2 forms which can provide a base for tundish nozzle clogs. Lower Mn/Si ratios produce stronger deoxidation levels but with the use of a white slag practice, dissolved oxygen levels under 20 ppm can be produced under non-equilibrium conditions in 0.20 % C or greater steels with Mn/Si ratios in excess of 3.4 to 1. Fig. 2.127 [2]shows that at equilibrium a molten manganese silicate can be produced at certain temperatures and ratios. Obviously, either increasing the manganese or decreasing the silicon levels will increase the Mn/Si ratio. Decreasing the Si level is preferable and is entirely feasible when using a white slag practice. An operator must experiment to find the correct ratio for producing a molten manganese silicate but usually somewhere greater than 3.4 parts Mn to 1 part Si produces the desired result.

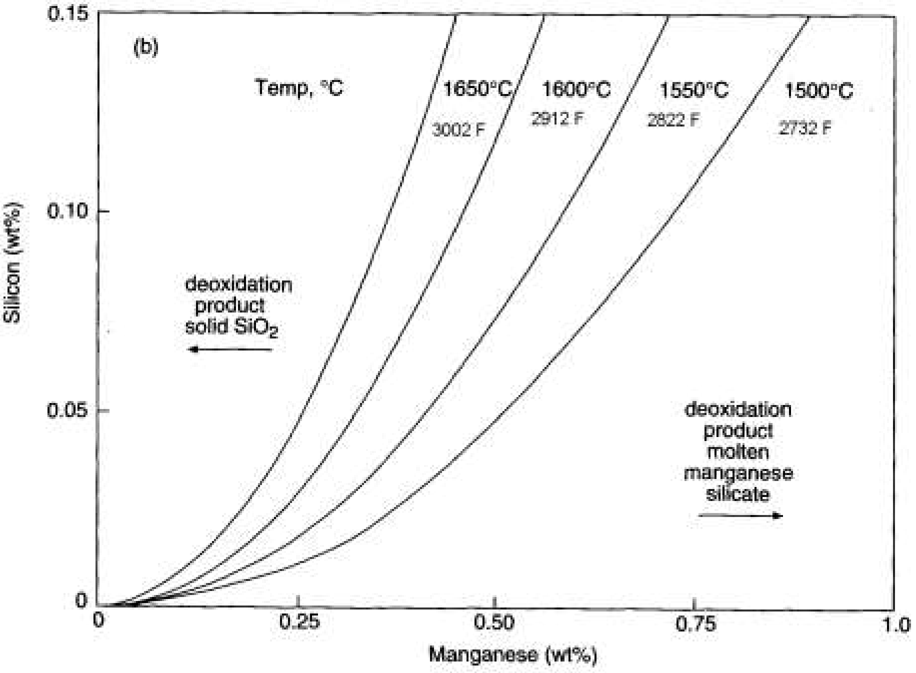

Fig. 2.127 Equilibrium relations for deoxidation of steel with silicon and manganese at 1600°C. *From Ref. 27.*

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Manganese-Silicate-Alumina Inclusions

Paradoxically, increasing the silicon level leads to the formation of a liquid Manganese-Silicate-Alumina inclusion. Fig. 2.129 [3]shows that with increasing levels of aluminum, increasing the silicon level can lead to the formation of a liquid inclusion. Many steel plants produce high carbon silicon killed heats with about 0.20% Si. According to Fig. 2.129, solid Al2O3 is formed at Al levels greater than 0.003%. In many melt shops, occurrences of tundish nozzle clogging or whiskering correspond well to levels of Al greater 0.003%. So, based on Figure 2.129 an operator should increase Si content when the Al is greater than 0.003% but the major problem with this approach is that as the Si content is increased, the Al content likewise increases due to trace amounts of Al in the FeSi. The problem with increasing the Si level, in addition to incurring unnecessary costs, is that the Mn/Si ratio is decreased thus promoting the formation of solid silica.

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[3] R.J. Fruehan, ed. The Making Shaping and Treating of Steel, 11th Edition, Steelmaking and Refining Volume, The AISE Steel Foundation, 1998, Chapter 2, page 144.

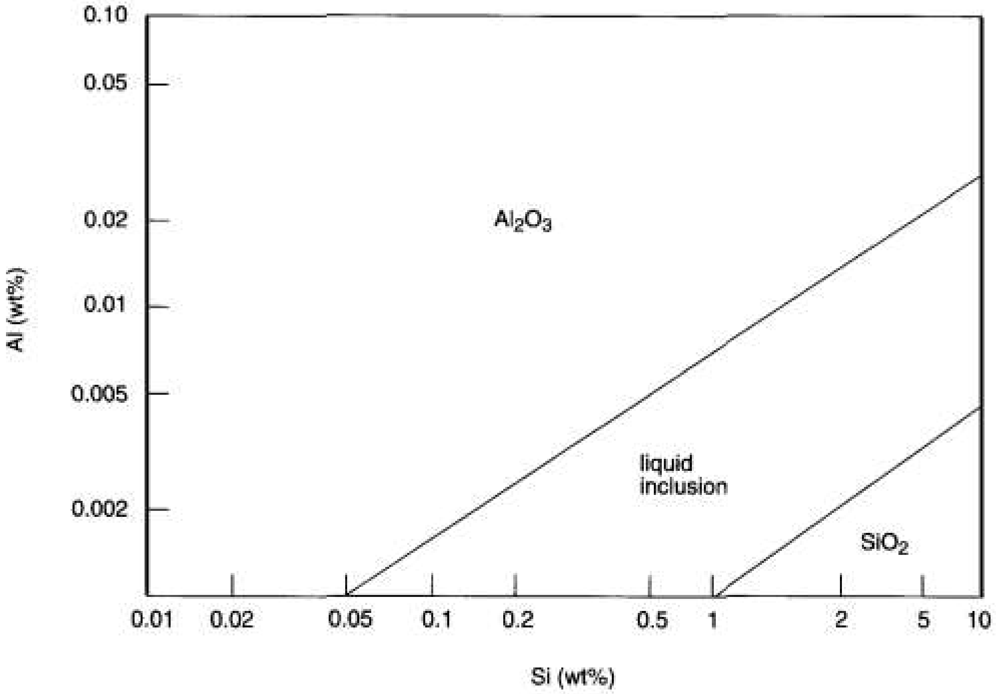

Fig. 2.129 Equilibrium inclusions for an Fe–Al–Si–1.0% Mn steel at 1600°C. *From Ref. 178.*

Magnesium Aluminate Spinels

Another factor in tundish nozzle clogging is the formation of magnesium aluminate spinels. This problem occurs at dissolved oxygen levels under 20 ppm in high carbon heats. Under reducing conditions in high carbon, low dissolved oxygen steels, magnesium can be liberated from dolomitic or MgO-C slag line brick.[4] Fig. 16-10 shows that clogging tends to start and get worse at free oxygen levels under 15 ppm for A-36 grades. When a high carbon heat is worked for 45 minutes or longer with a white slag practice, the occurrences of magnesium aluminate spinel clogging become much more prevalent. Several treatments can be used to minimize tundish nozzle clogging due to spinels. First, white slag treatment of a heat should not be started until a caster delivery time is certain. The addition of slag deoxidizers such as calcium carbide, ferro silicon or calcium silicon fines should not be used to excess. Next, the white slag treatment time should be minimized. Finally, lime additions at the ladle furnace should be very limited since the slag V ratio would tend to increase. Lowering the slag V ratio increases the capacity of the slag to absorb MgO, Fig. 2.57.[5]

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[4] C.R.Taylor, ed., Electric Furnace Steelmaking, The Iron and Steel Society Inc., 1985, pg. 312.

[5] R.J. Fruehan, ed. The Making Shaping and Treating of Steel, 11th Edition, Steelmaking and Refining Volume, The AISE Steel Foundation, 1998, Chapter 2, page 83.

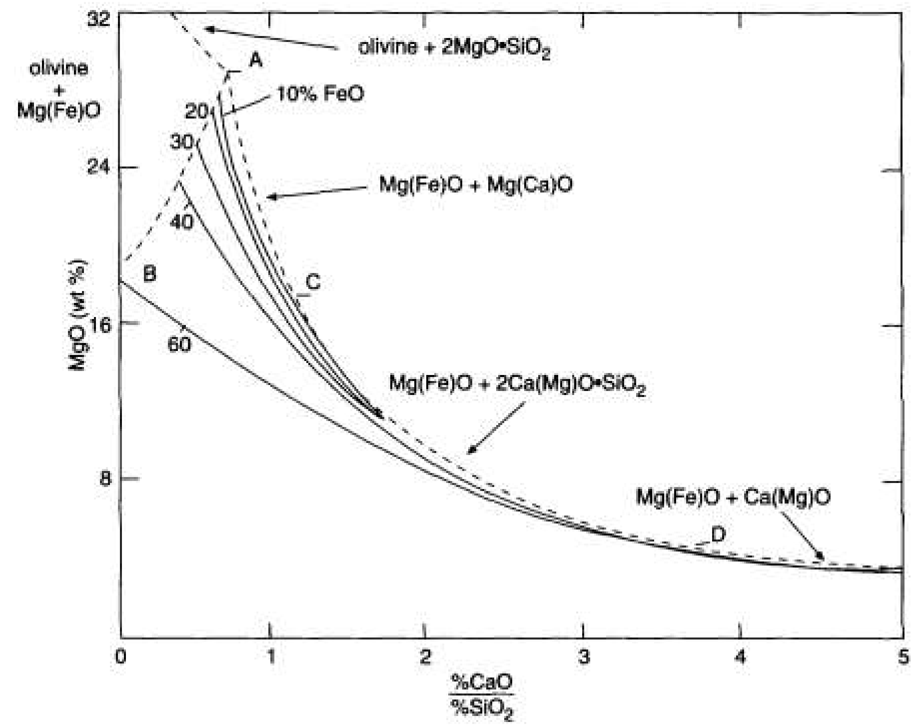

Fig. 2.57 Solubility of MgO, as magnesio–wustite, in the system CaO–MgO–SiO$_2$–FeO at 1600°C as a function of slag basicity and FeO concentration. *From Ref. 97.*

Cold Steel Temperatures

With the ready availability of liquidus formulae and years of casting experience, cold steel temperature is not a major factor in high carbon silicon killed steel caster nozzle clogging. Most steel temperature problems occur due to false temperature readings, cold ladles and tundishes and excessive inert gas stirring in the ladle. A vigorously stirred ladle can lose 5 °F per minute. Uniform training of operators in taking immersion temperatures needs to be enforced due to variabilities in insertion depth and position. Furthermore, testing and

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calibration of temperature measuring equipment needs to be conducted on a regularly scheduled basis.

Summary and Conclusions

High carbon silicon killed steels can experience ladle and tundish nozzle clogging on a regular basis. Causes of the clogging are non-metallic inclusions and cold liquid steel temperature. Making a liquid inclusion, minimizing the formation of spinels or absorbing a solid particle into the slag is key to preventing clogging problems. To avoid clogging problems the operator needs to be aware of the following:

1. Minimize the aluminum level to 0.003 % if possible;
2. Add calcium or calcium silicon wire or calcium silicon lump to liquefy aluminates;
3. Maintain a Mn/Si ratio greater than 3.4 to 1;
4. Minimize the white slag treatment time to reduce the formation of magnesium aluminate spinel;
5. Reduce the ladle slag V ratio by adding sand or wollastonite at the ladle furnace after all desulfurization is completed;
6. Increase the steel dissolved oxygen by blowing an oxygen lance in the open stirring eye or add mill scale to the slag and
7. Maintain the temperature measuring equipment and insure that operators follow a uniform temperature measurement protocol.

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