Calcium Wire Injection

Question

In our facility, we use calcium wire injection in aluminum killed heats with < 0.009% S to prevent the choking of ladle and tundish nozzles. While the process seems to work fine 95 % of the time, the other 5% is pure hell. Sometimes at the beginning of a sequence we experience tundish nozzle choking which then inexplicably clears up. At other times, the choking starts and never goes away forcing us to abort the sequence. What could be causing these problems? A.D., United States of America

Answer

Three factors come immediately to mind: improper injection practice, spinels and reoxidation. In simple terms, improper injection practice results from injecting too much or too little calcium wire. Many problems with alumina clogging are controlled with the judicial use of Ca wire injection when making aluminum killed steels. If your optical emission spectrometer is capable of determining total and metallic aluminum and calcium levels, you may want to determine the ratio of CaO to Al_2O_3. Just assume that all of the Ca in the steel sample is CaO since the solubility of Ca in liquid iron is very low. At a mole ratio of 12 CaO to 7 Al_2O_3, the melting point is as low as 2651°F (1455°C). Additionally, CaO and Al_2O_3 levels in the steel sample give a quantitative, but not definitive, measure of steel cleanliness.

As an example, consider the following situation. Lets say you are making low carbon aluminum killed steel with a liquidus temperature of 2780 °F (1527 °C). Assume your tundish temperature range is between 2815 to 2830 °F (1546 to 1554 °C). A spectro test determines that a tundish sample contains 0.006 % Ca, 0.040 % Total Al and 0.035% Metallic Al. By performing the stoichiometry, one finds that the sample contains 0.008 % CaO and 0.009 % Al_2O_3. This results in a CaO to Al_2O_3 weight ratio of 0.889. According to the binary phase diagram for CaO-Al_2O_3, the liquid inclusion range found at 2815°F (1546°C) has a corresponding CaO to Al_2O_3 weight ratio range from 1.5 to 0.67. The present example indicates that the calcium aluminate at a weight ratio of 0.889 will be liquid at casting temperatures. A binary phase diagram presents a simplistic model. Other non-metallic oxides present in the liquid steel will have an effect on the formation of liquid and solid inclusions.

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Spinels are the bane of all casters. If other strong deoxidizers are present such as titanium, magnesium, silicon, magnesium or rare earths, high melting point aluminate spinels can form which are nearly impossible to remove. As a friend said once, “You could stir the ladle, inject wire, modify the slag and reheat the steel until the sun blows up and the spinels would still clog the tundish nozzle.” Spinels tend to form in killed heats during long holding times between the melting furnace and caster. Heats that have a planned delay after tapping until casting start for over 60 min., should be held unkilled as long as possible. Of course this plan may only work if you have a ladle furnace or other method of reheating available.

Reoxidation of calcium wire treated aluminum killed steel causes choking. Perhaps the most common cause is ladle stirring. A hard stir after wire injection can cause the formation of more Al_2O_3 thus upsetting the ratio between CaO and Al_2O_3 and causing the formation of a solid inclusion phase at casting temperatures. Air leaks into the ladle to tundish shroud and tundish to mold shroud can have the same effect. A study of nitrogen pickup from the start of ladle treatment through the caster mold correlated to nozzle choking will help to define problems related to reoxidation.

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