Reoxidation and castability of aluminium-killed steels

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Synopsis

Steel was sampled after calcium treatment, to follow changes in inclusion composition during the processing of alumium-killed steel into continuously-cast billets, at Mittal Vereeniging. There is some shift in the distribution of inclusion compositions towards alumina, as the liquid steel moves from the ladle to the tundish. This shift may reflect some reoxidation. However, the effect on inclusion modification is small, since only a small fraction of the tundish oxide inclusions is fully solid—which agrees with the plant observation that these heats cast without clogging. Magnesium oxide in the inclusions contributes to liquid formation, substantially increasing the range of lime:alumina ratios over which the inclusions are partially or fully liquid.

Background

Liquid steel that has been deoxidized with aluminium contains alumina inclusions. Gentle stirring, for example by argon bubbling, causes the alumina inclusions to agglomerate and float out of the steel. However, some alumina inclusions remain in the steel melt. These can pose a problem in the continuous casting process by clogging the submerged-entry nozzle (SEN) through which the steel flows from the tundish into the mould. Clogging by alumina can be avoided by calcium treatment.

When calcium is injected into liquid steel, some of the calcium reacts with the alumina inclusions to form calcium aluminates, which are fully or partially liquid if the correct ratio of lime to alumina is achieved in the modified inclusions. The inclusion compositions that are liquid are shown by Figure 1. As this shows, partially or fully liquid inclusions fall within a narrow composition range for $CaO-Al_2O_3$ mixtures. However, the presence of even a small amount of MgO widens the fully liquid region considerably, and even more so for the partially liquid region. Calcium-treated inclusions often contain MgO,[1] which probably originates from the ladle lining or slag. In Figure 1, the broken line, which connects compositions that contain 50% liquid, is significant because it has been found that steels that contain less than 60% solid inclusions do not suffer SEN clogging during continous casting.[2] This implies that, if the majority of the oxide inclusions in the steel fall within the area bounded by the broken line, clogging is avoided (that is, inclusion modification has been successful).

After calcium treatment, inclusions that lie outside the liquid region can form if the steel comes into contact with a source of oxygen—this would cause reoxidation, which involves the formation of fresh, unmodified alumina. The possibility that this occurs at the Mittal Vereeniging plant was investigated in the work reported here.

Experimental procedure

Sampling

Steel samples were taken from three carbon steel heats, at the ladle furnace, in the tundish, and from solidified billets. The steels contained 0.4–0.6% C, 0.2–0.3% Si, 0.7–1.3% Mn, and were aluminium killed. Samples of liquid steel were taken with the sampler, which is depicted in Figure 2. As this shows, the sampling spoon was a steel cup with a wooden lid (with a steel handle—not shown in Figure 2—which was used to manipulate the sampler). Before sampling, the wooden lid was fastened to the cup using copper wire. The cup was then submerged in the steel, below the slag layer. After about 5 to 7 seconds of melting the copper wire released the wooden lid, allowing steel to enter the cup. Once the sampling spoon was removed, it was left to cool and the sample was subsequently removed. The sample from this spoon is well suited to cleanliness analysis, as it does not contain slag, and the sampler does not filter out inclusions from the steel.

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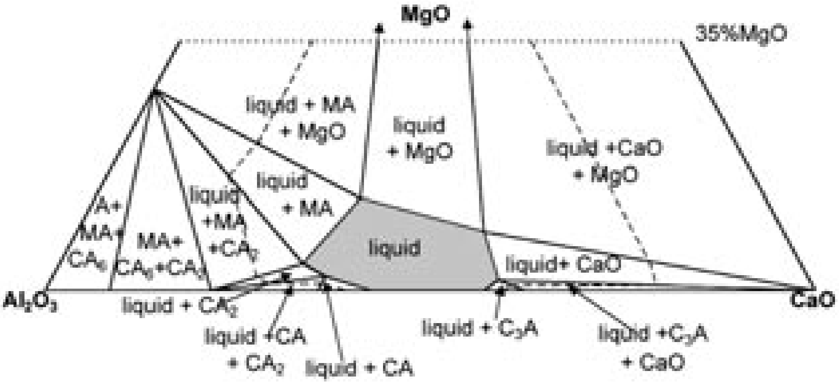

Figure 1—Isothermal section through the Al_2O_3-CaO-MgO system at 1550°C. Compositions in the shaded region are fully liquid, and compositions that lie within the broken line contain 50% liquid or more. Compositions are plotted as mass percentages. Constructed from the liquidus diagram for this system.[3] (Approximate diagram, neglecting solid-solution effects in the spinel phase.)

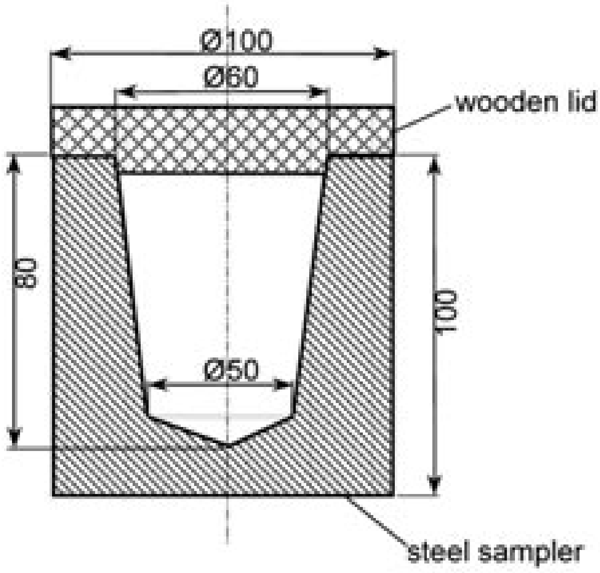

Figure 2—Schematic drawing of sampler used to collect liquid steel samples. Dimensions are in millimetres

Other information which was recorded for each heat included the following:

- *Electric arc furnace*—level of active oxygen (from electrochemical oxygen probe), and the amounts of Al, Si, C (graphite) and Mn used for de-oxidation.
- *Ladle Furnace*—Spoon samples were taken at the ladle furnace, before calcium addition, and approximately 2 min after calcium addition. Plant data was obtained to determine the amounts of calcium and aluminium added per heat. Alloy additions, temperatures and active oxygen readings were also recorded.
- *Cast billet*—a sample was taken at billet inspection

During casting, the tundish level was constant at approximately 12 tons; casting temperatures and superheats were noted. All three heats cast without clogging, indicating that calcium treatment had successfully modified the alumina inclusions.

Inclusion analysis

Samples were analysed using the scanning electron microscope (SEM) in the Department of Materials Science and Metallurgical Engineering at the University of Pretoria. The SEM includes an energy-dispersive X-ray (EDX) microanalysis facility. Samples were prepared for analysis by wet grinding cross-sections to 1200 grit, followed by diamond polishing. Inclusions were detected by imaging the sample surface at 800x magnification, using backscattered electron imaging. The inclusions were then analysed by EDX at higher magnifications, generally using 100 seconds of live time per inclusion. The amounts of manganese, magnesium, aluminum, calcium, sulphur and silicon in the inclusions were quantified. Modified inclusions generally contained calcium, aluminium, magnesium, sulphur, and oxygen.

To estimate the degree to which the inclusions had been liquid at the casting temperature, the inclusions were plotted on the Al_2O_3-CaO-MgO diagram, which is shown in Figure 1. All sulphur in the modified inclusions was assumed to be present as CaS, and subtracted from the inclusion composition.

Results

As examples, compositions of inclusions as found in the ladle (after calcium treatment), in the tundish, and in the solidified billet, are shown in Figure 3. The distribution of inclusions between different phase fields is given in Figure 4. Immediately after calcium treatment (samples labelled 'ladle furnace' in Figures 3 and 4), most inclusions are fully or partially molten. Note the substantial MgO content of these inclusions—the MgO had probably been present as spinel inclusions before calcium treatment; after calcium treatment the MgO contributes to liquefaction of the inclusions, by expanding the composition range over which inclusions are fully or partially molten.

Changes in the inclusion compositions are evident as the steel is processed through the continuous caster. Unmodified alumina was detected to a limited extent—as shown by the data for the tundish sample of heat 5974 in Figures 3 and 4. This fresh alumina indicates reoxidation. In addition to the observation of isolated fresh alumina, the entire distribution of inclusion compositions moves towards the alumina corner as the steel proceeds through the caster—as is quite evident in Figures 3 and 4. This shift in the entire distribution is

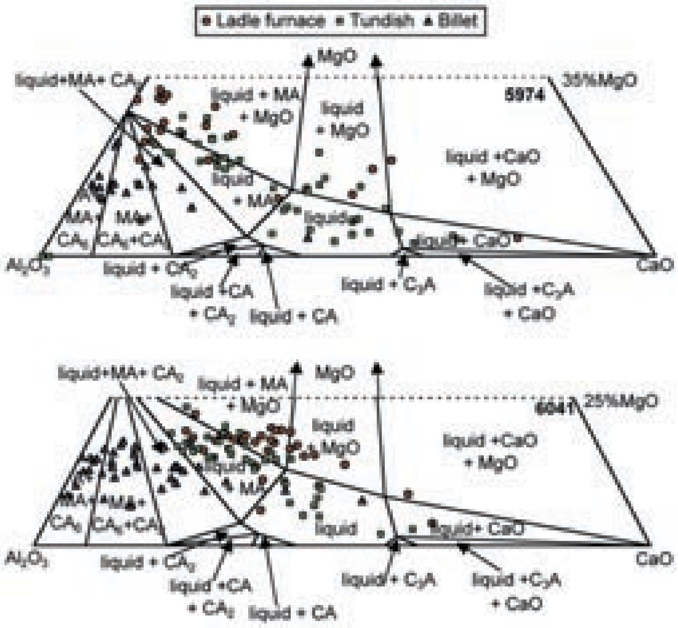

Figure 3—Inclusion compositions in steel of two different heats (5974 and 6041), as sampled at three different stages of the continuous casting process, namely in the ladle furnace after calcium treatment, in the tundish, and after solidification in the billet. Compositions plotted as mass percentages

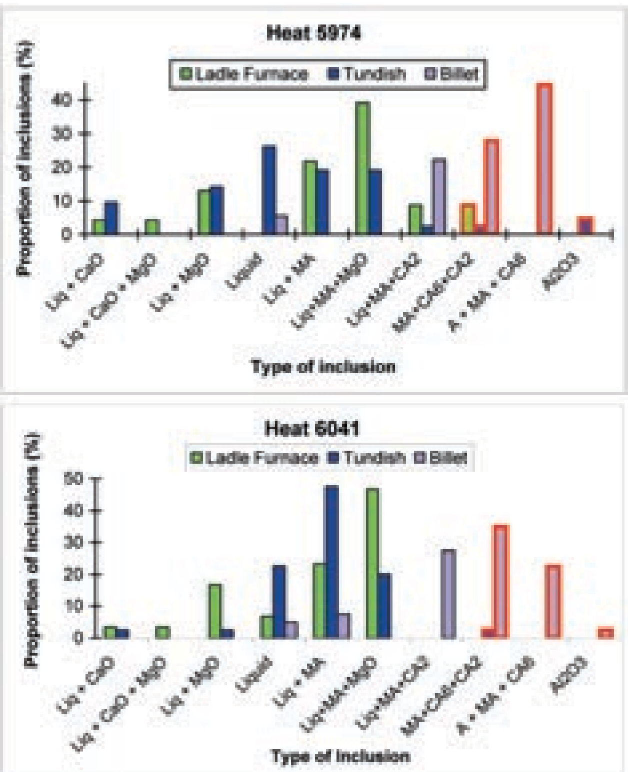

Figure 4—Distribution of inclusion compositions between different phase fields at 1550°C, for the two heats of Figure 3. All inclusions are fully or partially liquid, excepting those that fall in the three phase fields listed at the right of each graph

rather surprising, and seems to indicate that the exisiting inclusions in the steel come into contact with and react with fresh alumina, which forms through reoxidation. The net effect is that, while the distribution shifts, most inclusions in the ladle and tundish remain fully or partially molten—a conclusion that is supported by the observation that these heats cast without any clogging problems. The origin of the high alumina content (and hence low liquid content) of the inclusions in the solidified billet is not clear, but this may reflect floating-out of the more highly modified liquid inclusions in the mould (whereas alumina-rich solid inclusions are trapped more readily by the advancing solidification front and so remain in the solidified product).

Conclusions

For the heats sampled here, slight reoxidation occurred as the steel moved from the ladle furnace to the tundish. However, the majority of the inclusions remained fully or partially molten, and no clogging problems were encountered during casting. The results confirm that modified inclusions cannot be adequately described with an average composition: the distribution of compositions must be considered. The analyses indicate a strong effect of MgO—which probably originates from the ladle lining—in promoting liquid formation in the inclusions.

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