EFFECT OF INJECTION OF CAO-CONTAINING POWDER ON INCLUSIONS AND MECHANICAL PROPERTIES OF ALUMINIUM-KILLED STEEL

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Effects of injection of $CaO-CaF_2-Al$ powder on inclusions and mechanical properties of aluminium-killed steel have been studied in the full-scale industrial trials. The results indicate that the powder injection positively affect the morphology, size and distribution of the remaining inclusions in the steel. This ultimately results in that the steel acquires better cleanliness and improved toughness in the transverse and short transverse directions.

INTRODUCTION

In view of the everincreasing demands for high quality steels, the steel industries have to supply products with extremely strict specification in terms of high strength, low temperature toughness, and weldability. To meet such demands, the industries are emphasising product quality improvement through effective deoxidation, desulphurization and elimination of non-metallic inclusions in the steel. In addition, considerable efforts are being made to improve steel quality through inclusion shape and composition control (1,2).

During recent years, a considerable amount of work on improving mechanical properties of aluminium-killed steel by removal of Al_2O_3-clusters and/or through modification of inclusions morphology has been reported (3,4). Out of the methods suggested, calcium treatment of the steel has acquired an increasing importance. It is known that calcium treatment provides CaO necessary for modifying Al_2O_3-clusters into $CaO.Al_2O_3$, and results in clean steel with improved mechanical properties. However, it should be possible to obtain similar beneficial effects by direct addition of CaO or CaO-containing powders into the steel.

The effect of injection of CaO-containing powder on non-metallic inclusions in aluminium deoxidized melts in the laboratory is reported in an earlier work (5). This work describes the effect of injection of CaO-containing powders on inclusions and mechanical properties of aluminium-killed steel in full scale production.

EXPERIMENTAL

Industrial trials were performed with steel containing about 0.17% C, 0.35% Si, 1.5% Mn, 0.03% S & 0.02-0.06% Al produced in an electric arc furnace at A/S Norsk Jernverk, Mo i Rana, Norway. The bath after the oxidizing and deslagging operations was subjected to the addition of specific amounts of ferromanganese, ferrosilicon, aluminium and lime+fluorspar. After a waiting period necessary to allow the slag forming materials to melt and to attain the bath temperature of about 1600°C, a predetermined amount of powder containing 70% CaO + 15% Al + 15% CaF_2 was injected into the melt. Nitrogen was used as a carrier gas. Afterwards, the bath temperature was adjusted, and the steel was then tapped into a ladle. In some experiments, the steel was also subjected to the powder treatment in the ladle. Metal samples were taken at predetermined stages. In addition, samples from the rolled products (universal mill plates and/or ship-profiles) were taken. The metal samples were taken in the as rolled condition. These were, according to need, later on subjected to a normalizing treatment. All the samples were subjected to complete chemical analysis. Selected samples from each heat were examined metallographically and with a microprobe analyser. Quantitative determination of inclusions in the steel was made by QTM 360 and, in some cases, also with PASEM. The steel samples taken from the rolled material were also subjected to the standard tests for determining mechanical properties of the steel.

RESULTS AND DISCUSSION

The liquid steel in the ladle after the injection treatment contained 0.006-0.009% S and 6-10 ppm oxygen. The sulphur concentration in the rolled material remained practically unchanged, while the oxygen content had increased to 12-15 ppm. The experimental results obtained in the present work are compared with those of conventional heats, and a normal heat produced with the desulphurized hot metal as a starting material (6), see Table 1.

Inclusions

Normally, inclusions in the steel produced by straight aluminium addition are Al_2O_3-clusters and type II manganese sulphides which form stringers and long, flat ribbons during hot-rolling, see Fig.1. Steel samples taken from the ladle contained mainly small, round and randomly distributed inclusions, see Fig. 2. The oxides were rather complex, containing a calcium aluminate phase together with a sulphide phase, see Fig.2A. Occasionally, we also observed large oxide inclusions surrounded with pure calcium sulphide, see Fig.2B. These inclusions were probably of primary origin because they contained some fluorine.

Table I.

Steel	Number of heats	Total oxygen in ladle. ppm	Total oxygen & sulphur concentrations in the rolled products	
			%S	O ppm.
Treated with $CaO-CaF_2-Al$ powder	9	∿ 8	∿ 0.007	12 - 15
Conventional heats	2	∿35	∿ 0.021	30 - 38
	2	∿38	∿ 0.016	29 - 35
Made from the desulphurized hot metal	1	∿32	∿ 0.006	30 - 42

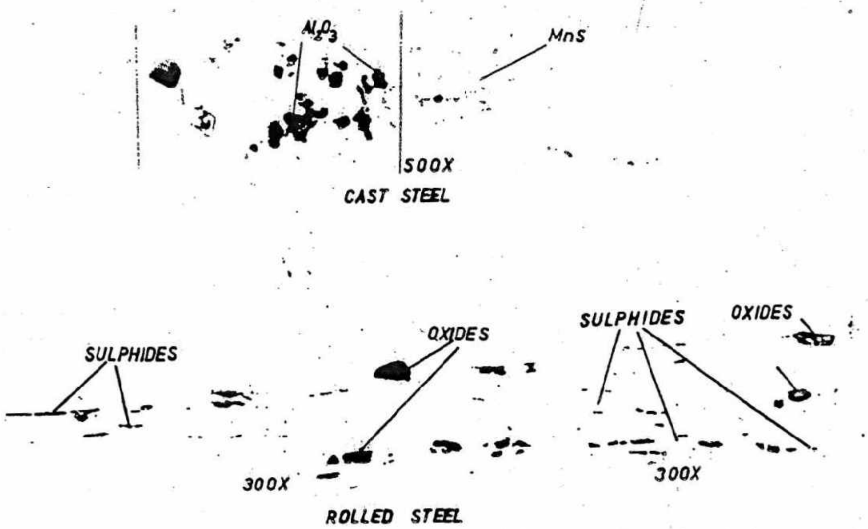

Fig.1: Inclusions in aluminium-killed steel made by straight aluminium addition.

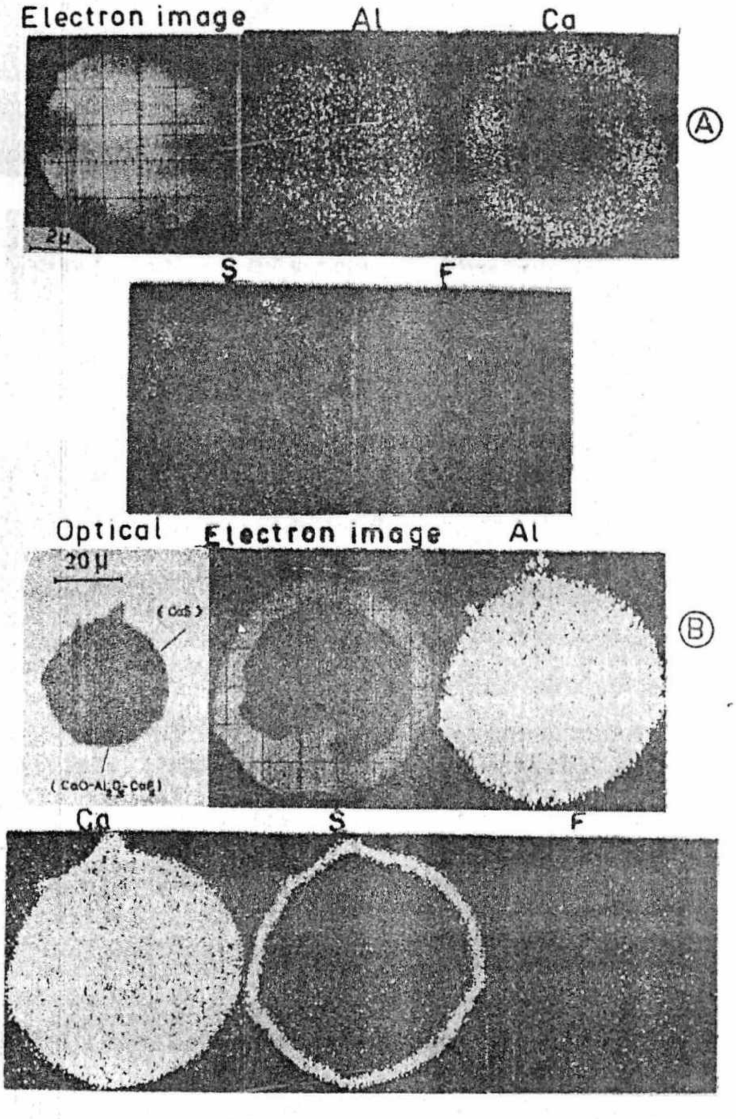

Fig.2: Typical oxides appearing in the steel subjected to the injection of $CaO-CaF_2-Al$ powder.

From these inclusions, it appears that the injected lime-based powder had changed Al_2O_3-clusters into low melting calcium aluminates. The presence of a pure calcium sulphide phase in such inclusions indicates that the injection treatment dissolutes some calcium into the melt. The calcium reacts with the dissolved sulphur and precipitates calcium sulphide. The primary inclusions act as nuclei for the precipitation of calcium sulphide, with the result that the calcium sulphide phase is confined to the outer surface. The duplex oxide inclusions are probably the secondary inclusions precipitated during the solidification process from dissolved Al, O, S and Ca in the steel.

Typical oxide inclusions appearing in the rolled product are shown in Fig.3. As can be seen from the figure, the oxides were small, hard, undeformed and of calcium aluminate type. In contrast to the alumina stringers which are normally found in aluminium-killed steels, the oxides in the treated steel were more or less randomly distributed. At no positions did we find any primary oxide. Probably because of their size, they separated from the steel before the start of, or during the teeming operation. Typical sulphide inclusions appearing in the rolled material are shown in Fig.4. For comparison, sulphides appearing in a steel having the same sulphur level

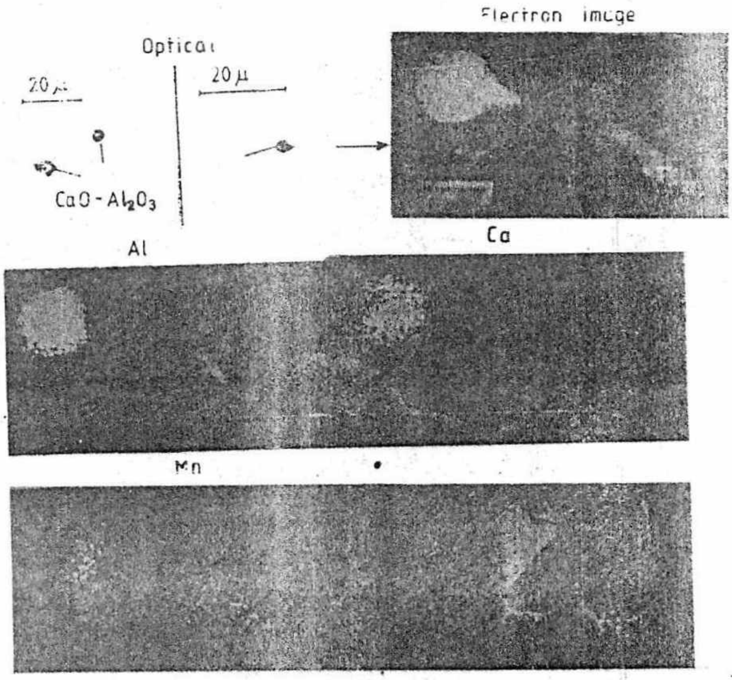

Fig.3: Typical oxides in universal mill plates produced from steel treated with the CaO-containing powder (reduction ratio R = 80)

and made from the desulphurized hot metal are also shown. As can be seen from the figure, the sulphides in the steel treated with the CaO-based powder were of duplex type, containing CaS and MnS. In contrast to the oxides, the sulphides were deformed during the mechanical working of the steel. However, the sulphide inclusions - despite the relatively high reduction ratio* - were thicker than those appearing in the steel made from the desulphurized hot metal. The reason that the sulphides were less deformed is probably the fact that during mechanical working, small and uniformly distributed inclusions are not so severely affected as the large inclusions. In addition, the sulphides contained a reasonable amount of calcium, which is reported to increase hardness of the manganese sulphide phase (7), thereby hindering its elongation during the rolling operation. This probably also explains why in the treated steel some small MnS-CaS inclusions retained their original appearance and did not elongate at all, see Fig.5. In no sample did we find pure manganese sulphide or isolated pure calcium sulphide inclusions. Manganese sulphides always contained some calcium sulphide. This confirms our laboratory results and is also in agreement with the results of H.Grunel et al. (8).

Cleanliness

The area fraction of inclusions appearing in the universal mill plates made from the conventional heats and the heats treated with the CaO-containing powder are shown in Fig.6. The area fraction of inclusions as well as the projected inclusion lengths in the steel were determined by optical image analyser, QTM 360. The result of each heat is based on about six mill plate samples taken from different predetermined positions. In each sample, an area of 160 mm^2 divided into 500 fields was examined. The analyser had a resolution limit of 1.0 μm. As can be seen from Fig.6, the steel treated with lime based powder had the lowest amount of impurities. The two main probable reasons for the improved cleanliness are:

1. Reduction in the contents of sulphur and total oxygen in the steel.
2. Presence of relatively small, hard, and randomly distributed inclusions in the steel.

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*) Reduction ratio "R" = $\frac{\text{average cross-section area of ingot}}{\text{cross-section area of the rolled product}}$

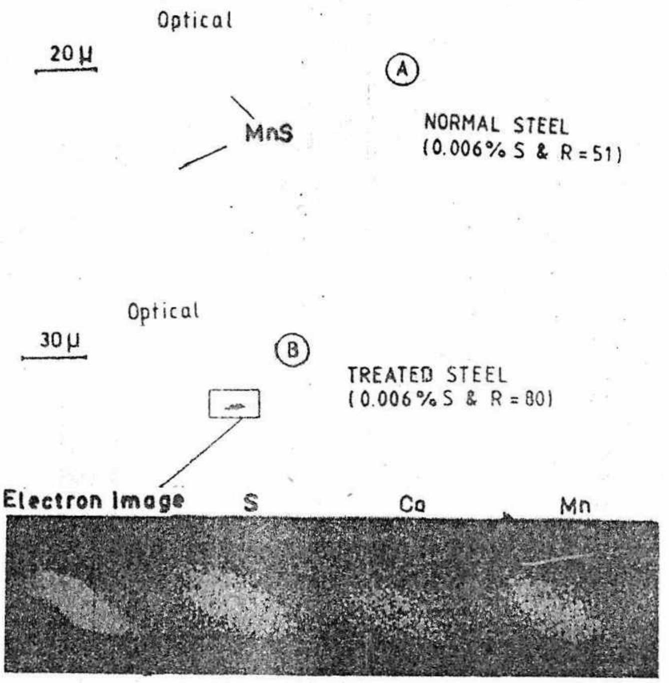

Fig.4: Typical sulphides in universal mill plates produced from steel made with desulphurized hot metal (A) and from the steel treated CaO-containing powder (B)

For comparison, area fraction of inclusions in the mill plates produced from different steels having the same sulphur level, were determined, see Fig.7. As can be seen from the figure, even at same sulphur level, the steel treated with lime-based powder reveals the best results. The main reason appears to be that during the treatment of steel with lime-based powder, the melt attained not only low sulphur level, but the content of total oxygen was also appreciably reduced. In the steel made from the desulphurized hot metal, the final total oxygen content remained practically the same as in conventional heats. Also addition of rare earth in such a steel did not appreciably reduce the total oxygen level. Rare earth treatment usually results in several oxides(La_2O_3, Ce_2O_3), oxysulphides ($La_2O_2S_2$, Ce_2O_2S) and sulphides (LaS & CeS). These inclusions are relatively heavy, and therefore probably remain in suspension in the melt for a considerable period of time. This may be the reason why the steel treated with rare earth contained relatively high amounts of inclusions (although QTM360 and PASEM can accurately determine the total area fraction of inclusions in rare earth treated steel, they cannot exactly differentiate between

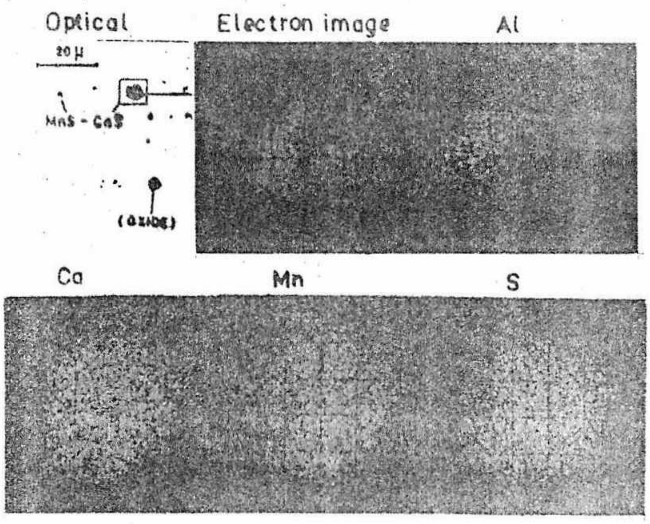

Fig.5: Small undeformed inclusions in universal mill plates made from the steel treated with CaO-CaF_2-Al powder (reduction ratio R= 80)

the rare earth sulphides and its oxysulphides. Hence, the values of area fraction of sulphides and oxysulphides are uncertain). However, the area fraction of the inclusions says very little about the sulphide and oxide shape factors which strongly affect the steel's ductility, particularly in the transverse and through thickness directions. This effect is better revealed by looking at inclusions size distribution in the steel.

Fig.8 shows the size distribution of sulphide inclusions in universal mill plates produced from different steels. As can be seen from the figure, the decrease in sulphur content reduces the number and size of the non-metallic impurities in the steel. The injection of lime-based powder affects the steel's cleanliness in a special manner. It considerably reduces the amount of large inclusions, whereas the content of small inclusions (2-6 μm)- which are less harmful to the steel quality - is increased. At the same sulphur levels, the content of large inclusions, (10-25 m) in the treated steel is 10-15% of those appearing in the steel made from desulphurized hot metal. It is somewhat surprising that the plates - despite the higher reduction ratio - contained relatively few elongated sulphides. This further confirms that the injection treatment had positively affected the morphology, size and plasticity of the remaining inclusions in the steel. One of the important beneficial effect of the powder injection

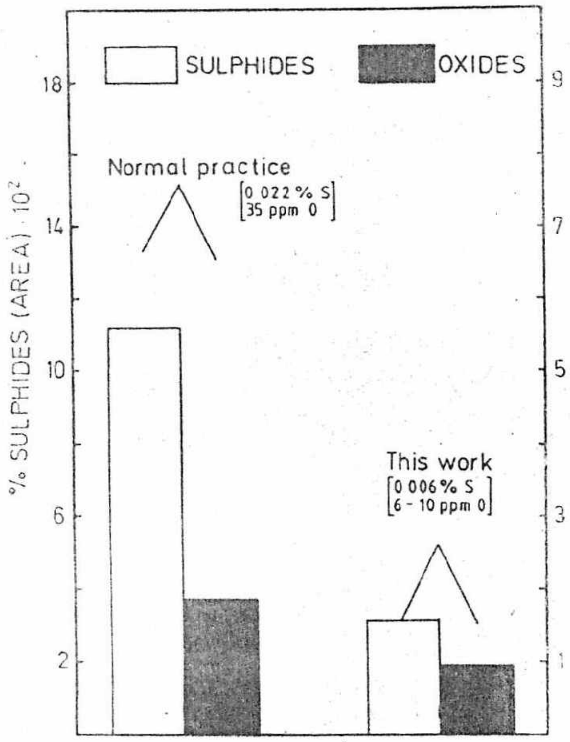

Fig.6: Effect of injection of CaO-containing powder on the sulphide and the oxide cleanliness of universal mill plates.

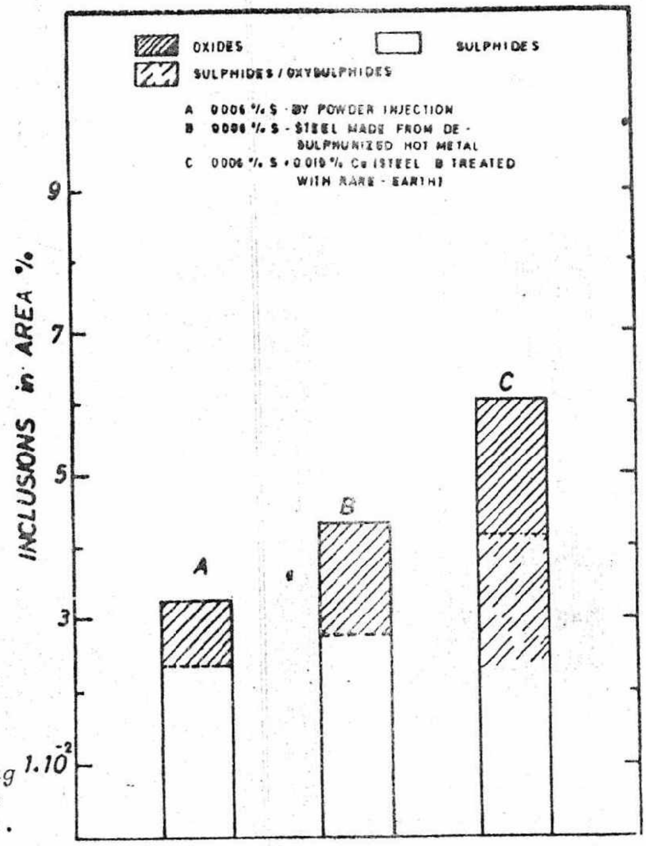

Fig.7: Area fraction of inclusions in universal mill plates made from different steels having the same sulphur level.

was that it resulted in appreciably smaller inclusions in the melt. During hot rolling, these inclusions either did not deform or deformed to a lesser degree. This may also be a reason why the mill plates made from the above mentioned steel contained only a few large, elongated inclusions.

Mechanical properties

It is widely known that non-metallic inclusions provide not only initiation sites for fracture, but also a path through which a crack can propagate. Normally, the mechanical properties of steels, particularly total ductility at fracture and charpy shelf energy, are affected by the volume fraction, shape, and distribution of non-metallic inclusions. When inclusions are aligned in arrays and have an elongated morphology, the mechanical properties of the steel are markedly anisotropic. This ultimately results in that many flat-rolled steel products reveal splitting during bending, low transverse notch toughness, lamellar tearing during welding, and low through-thickness ductility (RA_Z).

Toughness

The notch impact toughness of universal mill plates produced from different steels is shown in Fig.9. The toughness values are the average of 6-9 tests performed at each temperature. As can be seen from the figure, the injection of CaO containing powder appreciably improved the transverse impact toughness of the steel. It is interesting to see that the steel - despite the relatively high reduction ratio - had a higher toughness than that of the steel produced from the desulphurized hot metal. This improvement appears to be primarily because of absence of the usual alumina stringers and large planar sulphide inclusions. The injection treatment had also appreciably improved the notch impact toughness along the rolling direction. The reason for this improvement is not very clear. Improved cleanliness and inclusions morphology in the steel do have some positive effects on the toughness along

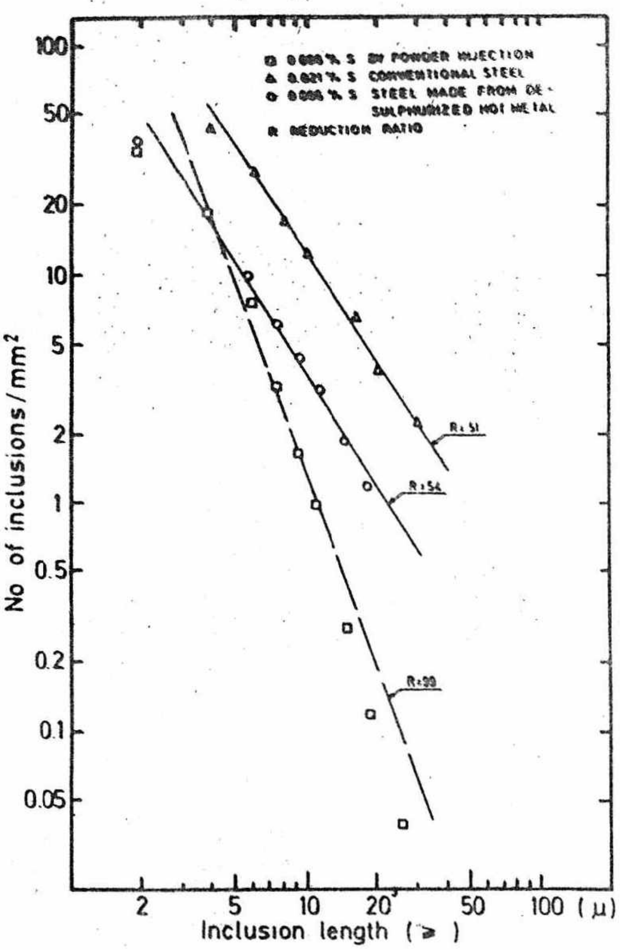

Fig. 8: Number of inclusions per unit area greater than (or equal to) a given size in universal mill plates made from different steels.

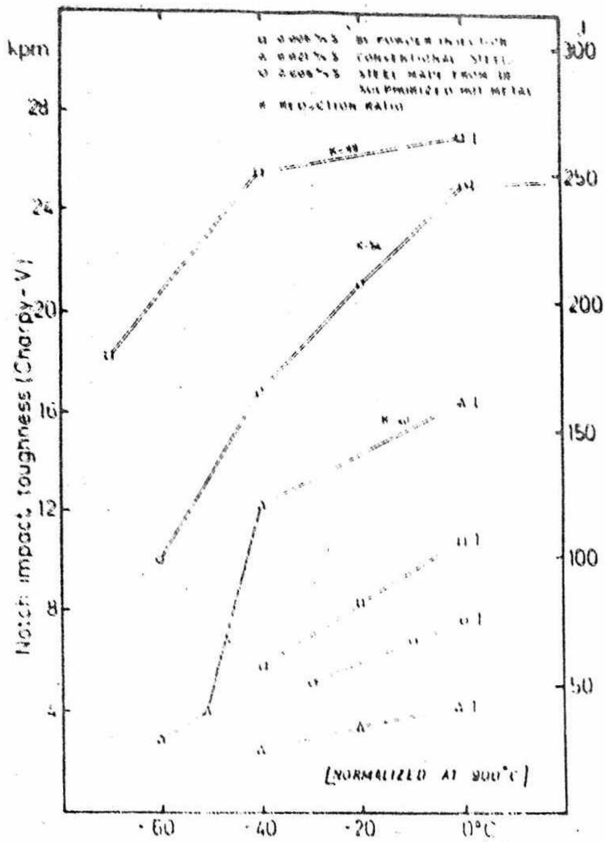

Fig. 9: Comparison of the impact strength of the universal mill plates produced from steel treated with CaO-containing powder and from normal steel containing different sulphur concentrations.

the rolling direction, but how these can produce such an improvement over the conventional and normal low sulphur steels is unclear. The grain size measurements of the above steels did not reveal any appreciable difference. The probable reason could be the relative reduction ratio. The steels treated with the lime-based powder were rolled to 15-20 mm compared with 30-35 mm plate thickness of the conventional/normal low sulphur steels.

Through-thickness ductility

For many applications, particularly steel plates for the production of ships, oil or gas pipes and offshore structures, there is a demand for high through-thickness ductility in the steel. This is simply because this property directly indicates the susceptibility of a steel to lamellar tearing. The through-thickness ductility is directly affected by the amount and shape of non-metallic inclusions in the steel. Normally, tearing starts as a result of decohesion at the matrix/inclusion interface, followed by void formation around the inclusions and in the last stages, void linking and tearing of the intervening matrix. Therefore, the tearing susceptibility depends on the inclusion surface area as well as on the distances between the inclusions in the steel. The projected inclusion length per unit area is the best parameter to quantify the above aspects of inclusion population and their effect on lamellar tearing. The projected inclusion length per unit area and through-thickness ductility of universal mill plates produced from different steels are given in Table II. As can be seen in the table, the RA_Z decreases with increasing projected length of inclusions and sulphur content in the steel. The treated steel, even when its sulphur level is not lower than that of the steel

Table II

Universal mill plate made from steel	% Sulphur	Plate thickness & Reduction ratio	Projected inclusion length. mm/mm^2	Test samples	$\%RA_Z$-range	$\%RA_Z$-average
Treated with CaO-containing powder	0.006	20 mm/99	0.17	6	48-53	50
	0.008	15 mm/149	0.19	9	43-49	44
Produced from desulphurized hot metal	0.006	35 mm/54	0.23	3	-	38
Produced by conventional method	0.016	35 mm/50	0.55	4	13-20	16
	0.021	35 mm/51	0.75	5	3.2-7.5	5.9

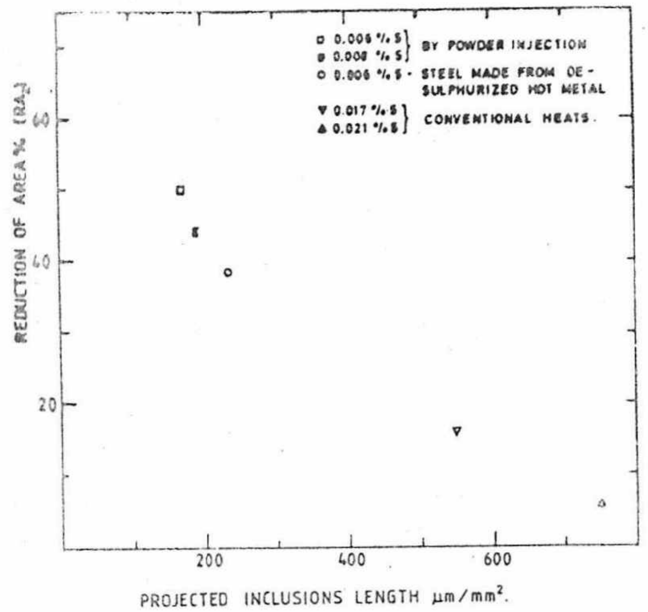

Fig.10: Comparison of the through-thickness reduction of area as a function of projected inclusions length for the different steels.

made from desulphurized hot metal, reveals the highest RA_Z values, see Fig.10. This again confirms the presence of relatively small, hard, and randomly distributed inclusions in the mill plates. Normally, the RA_Z value in the Z-grade steel has to be at least 25% to eliminate the danger of lamellar tearing (9). As can be seen from the figure, the conventional steel containing 0.016-0.021% S has 6-16% RA_Z. The injection treatment raises this value to above 45-50%, revealing an appreciable improvement. Even at the same sulphur level, the injection treatment improves the RA_Z value by about 10%.

SUMMARY AND CONCLUSIONS

Experiments have been performed with 65 tons electric furnace melts to study the effect of injection of CaO-containing powders on inclusions and mechanical properties of aluminium-killed steel. The results indicate that:

1. The injection treatment modifies alumina clusters into low melting calcium aluminates which easily coagulate and separate quickly from the bath.
2. The type II sulphides are changed to small, relatively hard, and randomly distributed MnS-CaS sulphides.
3. The injection treatment improves cleanliness of the steel. The area fraction of inclusions in the steel is reduced to 1/4 of the normal level.
4. At the same sulphur level, and equal or larger reduction ratio, the content of large inclusions (10-20 μm) is reduced to 10-15% of that appearing in a steel made from desulphurized hot metal.
5. The injection treatment improves the transverse notch toughness in the rolled product.
6. The injection treatment, at the same or somewhat larger reduction ratio, increases the through-thickness ductility of the steel, RA_Z, to about 50%.

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