# Behaviour of Calcium Aluminates During Hot Rolling of Continuous Casting Steels

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**Abstract**

*New data are presented on the behaviour of Ca-aluminate inclusions during the hot working of Al-Killed, Ca-Treated steels. The influence of rolling temperature and inclusion chemistry on their relative deformability was studied. The Ca-aluminates studied were not deformed at rolling temperature lower than 1150°C, and slightly deformed at 1200-1250°C. In the range 1300-1350°C, they were broken into small pieces rather than deformed plastically. Such decohesion in small, slightly deformed particles was attributed to their low $CaO/Al_2O_3$ ratios. Decohesion at high rolling temperature was sharply lowered by higher Mg contents. Ca aluminates with Zr precipitated as a second phase were very decohesed when rolled at 1300°C. An ultrasonic testing procedure proved to be very effective in detecting inclusions and clusters through the thickness of the rolled specimens of clean steels.*

**Riassunto**

Il comportamento degli alluminati di calcio durante la laminazione a caldo degli acciai da colata continua.
Vengono presentati alcuni dati nuovi sul comportamento delle inclusioni di alluminato di Ca durante la lavorazione a caldo degli acciai calmati all'Al e trattati con il Ca. In particolare lo studio ha valutato l'influenza sulla deformabilità di dette inclusioni della loro composizione chimica e della temperatura di laminazione. Gli alluminati studiati non vennero deformati a temperatura di laminazione <1150°C, mentre se ne è verificata una leggera deformazione nell'intervallo 1200-1250°C. Fra i 1300 ed i 1350°C, però, si è assistito alla loro frammentazione in piccoli pezzi piuttosto che alla deformazione plasatica. La decoesione a temperature di laminazione che portava così alla formazione di particelle piccole e poco deformate viene attribuita ai bassi rapporti $CaO/A_2O_3$ degli stessi alluminati. Inoltre si ridusse drasticamente in quelli con più alti tenori di Mg, mentre la laminazione con lo Zr precipitato qual seconda fase. Per la rilevazione delle inclusioni e dei relativi aggregati si è rivelata molto efficace una procedura di prova ad ultrasuoni sullo spessore dei laminati.

## Introduction

The relative deformability of non-metallic inclusions in hot rolled steels largely depends on its chemical composition and rolling temperature ($T_R$) [1-2]. In Al-Killed, Ca-Treated steels, inclusions belong to the system $CaO-Al_2O_3-SiO_2$. When the modification treatment is complete most of them are Ca-aluminates with a varying $CaO/Al_2O_3$ ratio [3]. Kiessling [4] reported that $Al_2O_3$, Ca-aluminates and rare earth oxides are not deformable at usual rolling temperatures (1200-1300 °C). Ekerot and Klevebring [5] found that contents of above 15 wt% $Al_2O_3$ in the inclusions raised their melting point and reduced their relative deformability. More recently, Jacobi et al [6] found that Ca-aluminates with up to 32 wt% $Al_2O_3$ and 47 wt% CaO were apparently deformated at $T_R = 1200$ °C. In the present paper, new data on the behaviour during hot working of Ca-aluminates found in continuously cast steel billets is presented, as a function of their chemical composition and rolling temperature.

## Experimental

The investigation was performed on commercial heats of 80 tons of Al-Killed Ca-treated 0.35 wt% C-1.2 wt% Mn steel. Were machined 50 samples from continuously cast billets and hot rolled in a experimental roller, at $T_R$ in the range 1100-1350 °C. Average thickness reduction was six times.

The rolled specimens were ultrasonically inspected, and metallographic samples were taken from locations where a high density of inclusions was detected. Shape analysis and size measurement was performed on the inclusions together with the identification of phases within them, all with the aid of a scanning electron microscope (SEM). Also, quantitative chemical analysis of the phases and matrix in the inclusions was performed via energy dispersive X-ray analysis (EDAX). Finally, their apparent relative deformability was calculated.

## Results and discussion

The through-thickness ultrasonic testing was very effective to detect clusters and deformed inclusions. It was possible to locate clearly the areas with total loss of bottom echo in each sample. In all cases, the metallographic analysis of samples taken from areas with positive ultrasonic indications confirmed the presence of particles in those locations.

After SEM/EDAX examination, the oxide particles found were identified as Ca-aluminates. Nevertheless, differences both in the $CaO/Al_2O_3$ ratio and in the content of several elements, like Mg, Zr, Na and K, were observed. These variations account for the different behaviour of the particles observed during hot working. Typical inclusion chemistries obtained by EDAX are shown in Table 1, both in the matrix and internal precipitates (when present).

**TABLE 1 - Rolling Temperatures, Inclusion Deformabilities and Chemistry (wt%)**

| # | T (C) | Deform (%) | $Al_2O_3$ | CaO | MgO | FeO | $K_2O$ | $Na_2O$ | $ZrO_2$ | CaO/Al | Fig. # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1100 | 0 | 33.61 | 53.27 | 1.47 | 0 | 1.7 | 1.47 | 6.54 | 1.58 | 1A |
| 2 | 1150 | 0 | 49.38 | 40.24 | 3.34 | 6.37 | 0.66 | 0 | 0 | 0.81 | – |
| 3 | 1200 | 0.11 | 27.92 | 60.89 | 1.52 | 1.92 | 0.88 | 0.81 | 5.94 | 2.18 | 1B |
| 4 | 1300 | 0.97 | 82.74 | 13 | 1.48 | 2.09 | 0.53 | 0 | 0 | 0.16 | 3 |
| 5M | 1300 | 0.89 | 45.44 | 50.02 | 0 | 4.17 | 0.35 | 0 | 0 | 1.10 | – |
| 5P | 1300 | 0.89 | 8.16 | 12.02 | 0 | 0 | 0 | 0 | 79.8 | 1.47 | – |
| 6 | 1350 | 0.89 | 47.39 | 49.08 | 0.33 | 1.95 | 0.79 | 0.44 | 0 | 1.04 | – |
| 7M | 1350 | 0.86 | 35.54 | 60.12 | 0.25 | 2.31 | 0.85 | 0.92 | 0 | 1.69 | – |
| 7P | 1350 | 0.86 | 67.67 | 0.21 | 28.29 | 2.27 | 0 | 1.26 | 0 | 0 | – |
| 8M | 1350 | 0.43 | 38.64 | 58.42 | 0.16 | 2.1 | 0.61 | 0 | 0 | 1.51 | – |
| 8P | 1350 | 0.43 | 85.71 | 0 | 14.27 | 0 | 0 | 0 | 0 | 0 | – |
| 9M | 1350 | 0.03 | 39.05 | 53.57 | 3.31 | 1.37 | 0.32 | 0.1 | 0 | 1.37 | – |
| 9P | 1350 | 0.03 | 78.15 | 6.53 | 15.3 | 0 | 0 | 0 | 0 | 0.08 | – |
| 10M | 1350 | 0.03 | 39.45 | 51.91 | 3.71 | 2.54 | 0.22 | 0 | 0 | 1.32 | 2 |
| 10P | 1350 | 0.03 | 6.48 | 11.21 | 82.3 | 0 | 0 | 0 | 0 | 1.73 | – |

M = matrix, P = precipitate/$SiO_2$ content is in the range 1.4-1.8 wt% in #1, 9 and 10.

The deformability of the Ca-aluminates was a function of their chemical composition at the different rolling temperatures. In all cases, they were undeformable at $T_R$ <1150 °C and slightly deformed at $T_R = 1200$°C, as shown in Fig. 1 (photo), and Fig. 4 (scheme). Voids and small cracks were observed at the tip of the inclusions when the deformability factor was less than 0.5, as reported also by Rudnik [2].

Most of the Ca-aluminates showed an apparently high deformability at $T_R = 1300$ and 1350°C. In fact, those inclusions were broken into small, slightly deformed particles dispersed and aligned along the rolling direction, Fig. 2. Those aligned particles formed a stringer that should play an important role in lowering through-thickness mechanical properties. In some cases, a low $CaO/Al_2O_3$ ratio is thought to be responsible for the observed decohesion of the inclusions, as also observed by Ekerot & Klevevring [5].

Mg is an element usually found in modified oxides in steels. It may also be related to contamination with refractories. In the present study, lower deformabilities were noticed as the MgO content of the inclusion matrices rised, even at levels at which it precipitated as a second phase. In Mg-bearing inclusions (MgO>1.5 wt%), low deformabilities were observed at $T_R$ up to 1350 °C, Figs. 3 and 4.

Elements like Na and K exert a fluxing action that improves the deformability of inclusions as it can be seen in those of the system $CaO$-$Al_2O_3$-$SiO_2$, where traces of those minor components lower the melting temperature [6, 7]. Such softening effect of Na is noticed in this investigation when comparing samples N° 7 and 8, Table 1. The presence of 0.92 wt% $Na_2O$ in the matrix of the inclusions in sample 7 (7M) against none in 8M, with similar contents of the rest of the compounds, can be correlated to the rise in deformability from 0.43 (8M) to 0.86 (7M).

Zr is rarely seen in microinclusions. Nevertheless, it may appear since it is sometimes used as a deoxidizer or inclusion modifier [9]. In the present investigation, its presence is due to the erosion of refractories such as the sub-entry nozzle. In sample N° 5 there were found inclusions where $ZrO_2$ had precipitated as a second phase. They were highly decohesed after being rolled at $T_R = 1300$ °C, thus showing an apparently high deformability.

A summary of the relative deformability measurements in the inclusions investigated is presented in Fig. 4. There, the observed lower average deformabilities when rolling at 1350 °C can be attributed to lower decohesions due to higher average $CaO/Al_2O_3$ ratios.

## Conclusions

— Ca-aluminates resulted undeformable when rolled below 1150 °C and only sligthtly deformed in the rolling temperature range 1200-1250 °C. In the range 1300-1350 °C, decohesion in small, slightly deformed particles was usually observed, thus resulting in an apparently high relative deformability. Such effect is attributed to low $CaO/Al_2O_3$ ratios (0-1.7).

— The deformability of Ca-aluminates at high rolling temperatures (range 1300-1350 °C) is strongly dependent on their chemistry. As Mg content increased, the deformability decreased sharply. Also, the softening effect of minor components, like Na and K oxides, may account for some of the observed higher deformabilities.

— Those Ca-aluminate inclusions where the presence of Zr was observed as second phase precipitates showed a high decohesion when rolled at 1300 °C. Thus, they also gave rise to an apparently high relative deformability.

— The ultrasonic testing was effective in detecting particles accumulated trough the thickness, even in the case of uniaxial rolling. Consecuently, this method proved to be useful for the assessment of macroinclusions and clusters in clean steels.

## References


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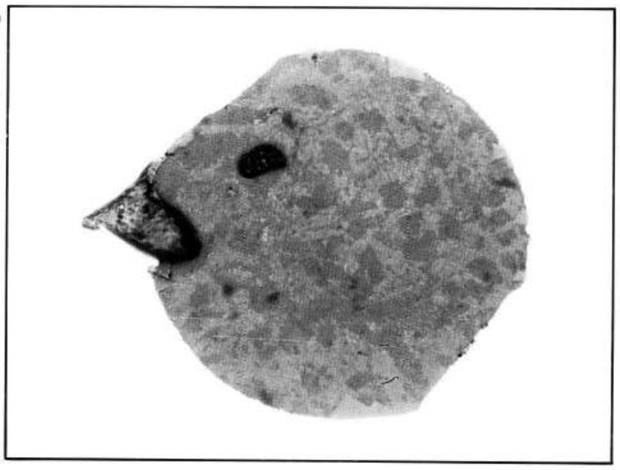
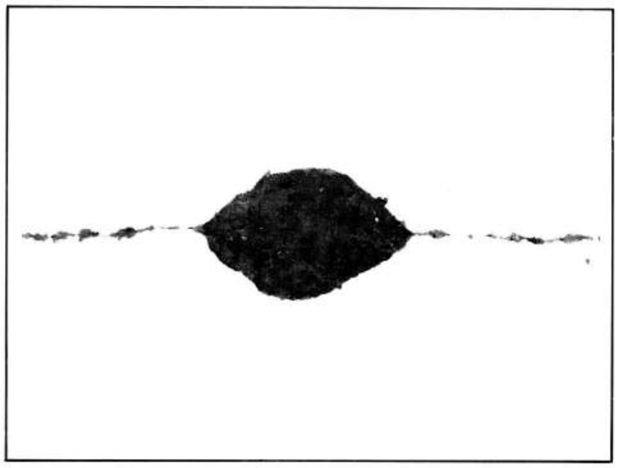
(a)  (b) 

Fig. 1:
Ca-aluminate inclusions with low deformability, 480X.

a) 33.61 wt% $Al_2O_3$, 53.27 wt% CaO, 1.47 wt% MgO, 1.47 wt% $Na_2O$, 1.7 wt% $K_2O$.
Rolling Temperature: 1100°C.
Deformability: nul.

b) Stringers of isolated particles at the tips, while the body of the inclusion is not much deformated (0.11).
27.92 wt% $Al_2O_3$, 60.89 wt% CaO, 1.02 wt% MgO, 0.88 wt% $K_2O$, 0.81 wt% $Na_2O$.
Rolling Temperature: 1200°C.
Deformability: 0.11

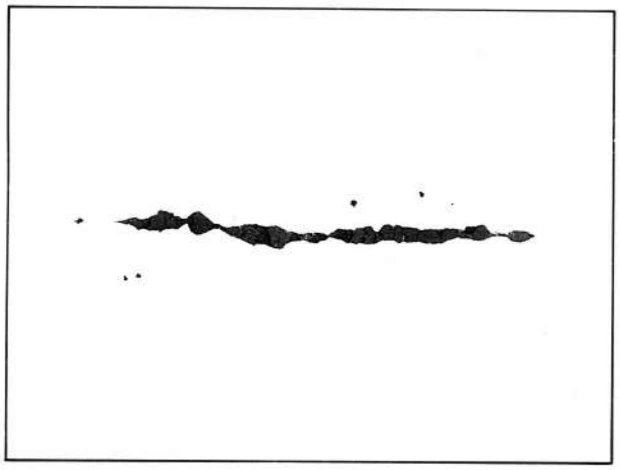


Fig. 2:
Decohesion of Ca-aluminates with $CaO/Al_2O_3 = 0.16$ (low $CaO/Al_2O_3$ ratio).
82.74 wt% $Al_2O_3$, 13 wt% CaO, 1.48 wt% MgO, 0.53 wt% $K_2O$.
Apparent Deformability: 0.97
Rolling temperature: 1300°C
240X.

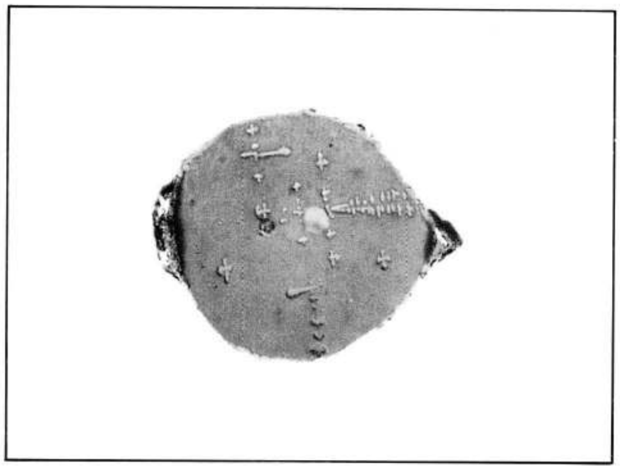


Fig. 3:
Mg-bearing particle.
Matrix: 39.5 wt% $Al_2O_3$, 51.9 wt% CaO, 3.7 wt% MgO, 0.2 wt% $K_2O$.
Precipitates: 82.2 wt% MgO.
Deformability: 0.03
Rolling temperature: 1350°C
480X

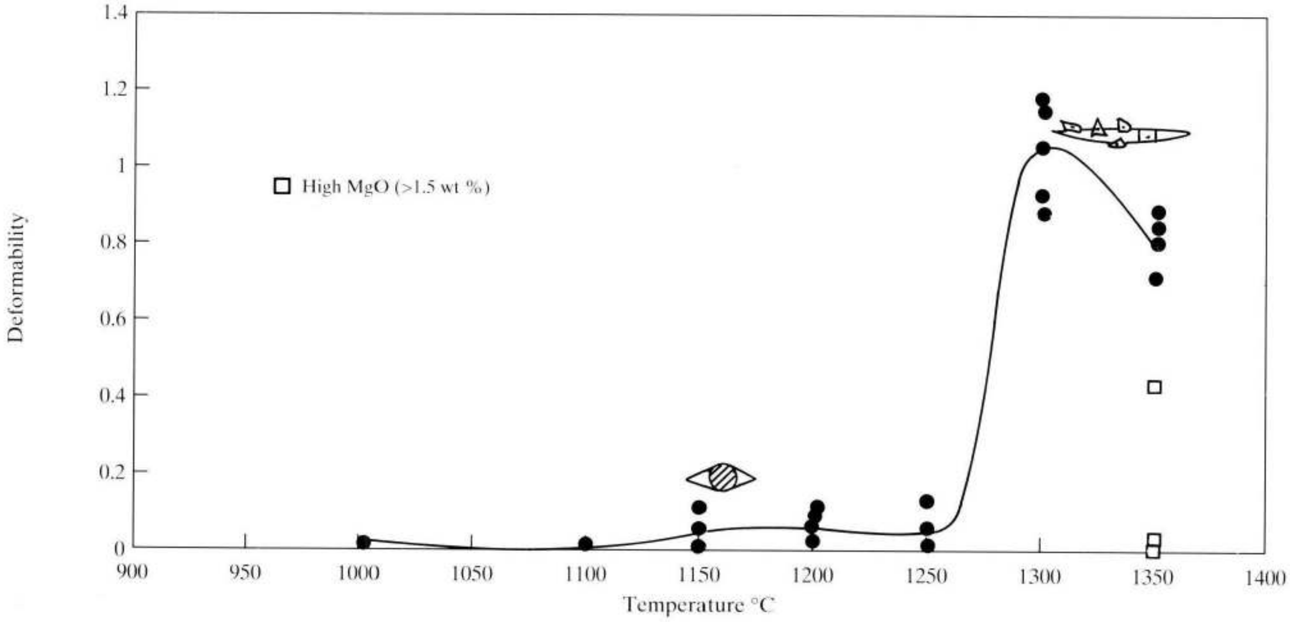



Fig. 4:
Apparent relative deformability of calcium Aliminates.