(150) EXPERIMENTAL DETERMINATION OF CaO AND CaS SOLUBILITIES IN LIQUID STEEL CONSEQUENCES FOR INCLUSIONS SHAPE CONTROL BY CALCIUM

○ C. GATELLIER, M. JOYANT, P.V. RIBOUD

IRSID - 57210 Maizières-les-Metz (France)

I. Introduction

Nowadays calcium alloys are frequently used to eliminate non-metallic elements from liquid iron base alloys, and to control the composition of remaining oxide and sulfide inclusions. However experimental data, on the stability of calcium compounds in liquid steel, are scarce and results are quite scattered.

II. Experiments and results

This laboratory study has been made in an induction furnace under argon atmosphere. Precise analytical methods involved oxygen activity measurements with ThO_2-Y_2O_3 sensors and chemical analysis of soluble and non soluble calcium in the sampled steel.

- The influence of Cr and Ni on calcium activity has been determined :

$$\log a_{Ca} = \log [\%\ Ca] - 18.\ [\%\ Ca] + 0.02\ [\%\ Cr] - 0.049\ [\%\ Ni] + 0.0018\ [\%\ Ni]^2$$

- Solubility products at 1600°C for CaO and CaS have been evaluated

$$K_{CaO} = \frac{a_{Ca} \cdot a_O}{a_{CaO}} = 9.10^{-7} \qquad K_{CaS} = \frac{a_{Ca} \cdot a_S}{a_{CaS}} = 1.7.10^{-5}$$

III. Discussion

One should note that, in the usual steelmaking concentration range of non-metallic elements, these solubility products are much larger than the one computed using existing thermochemical data (figure 1). These results imply that part of the added calcium remains in solution in steel and is available to participate to the formation of oxide inclusions during reoxydations and of sulfide inclusions during solidification.

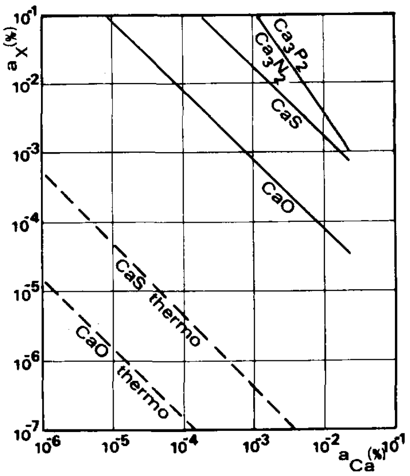

Fig. 1. Solubility of calcium compounds in liquid steel at 1600°C.

The range of stability of liquid calcium aluminate in equilibrium with aluminum killed steel has been calculated using our experimental value of K_{CaO} (figure 2). There is good agreement with results obtained in industrial treatments : the points plotted on figure 2 correspond to treatments in which alumina clusters have been completely transformed into liquid calcium aluminates. In this analysis, an estimation of dissolved calcium by mass balance assuming the formation of liquid inclusions (CaO-Al_2O_3 : 50-50 in weight %) gives the relationship

$$[\%\ Ca]_{in\ Fe} = [\%\ Ca]_{tot} \cdot (1 - 93 \cdot [\%\ O]_{tot})$$

This relation is very similar to the one determined experimentally by EMI et al. concerning the amount of Ca having reacted during solidification to form sulfides (1).

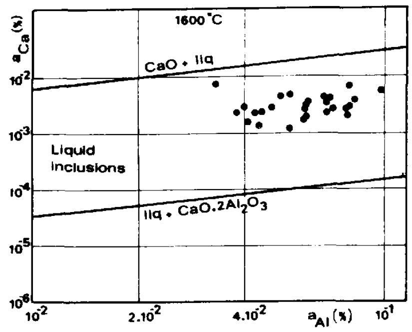

Fig. 2. Stability field of liquid calcium aluminates in steel at 1600°C (our data).
• industrial results with completely globular inclusions.

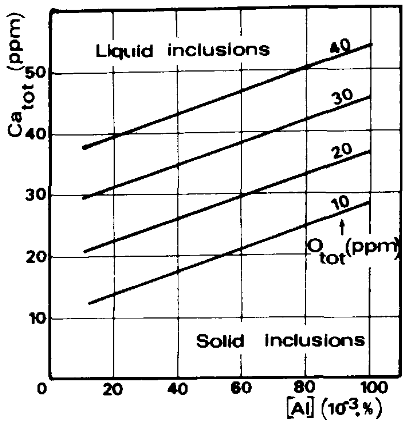

Fig. 3. Ca, O, and Al contents corresponding to the complete transformation of alumina clusters.

The minimum amount of calcium that should remain in solid steel to obtain the complete transformation of alumina clusters is plotted on figure 3 : it is dependent on both total oxygen and aluminum contents.

(1) O. Haida et al. Tetsu to Hagane, 64, (1978), 10, 1538.