Modification of oxide inclusions present in aluminum-killed low carbon steel by addition of calcium

José Carlos S. Pires
Centro Federal de Educação Tecnológica de Minas Gerais, CEFET-MG, Brasil
E-mail: pires@fem.unicamp.br

Amauri Garcia
Department of Materials Engineering, State University of Campinas - UNICAMP, Brasil
E-mail: amaurig@fem.unicamp.br

Resumo

A crescente demanda por aços de alta qualidade com elevada limpeza interna tem levado a uma contínua melhoria nas práticas de produção do aço, em especial na etapa de refino secundário. O interesse especial é no controle das inclusões não-metálicas, devido ao seu efeito prejudicial nas etapas subseqüentes (lingotamento e conformação plástica) e devido às sua grande influência nas propriedades do produto final. Através do controle do tamanho, da quantidade e da composição química das inclusões, é possível obter um produto final de alta qualidade. O controle da formação das inclusões não-metálicas e a identificação de suas fases constituintes são de suma importância para a obtenção de aços limpos. Nesse trabalho, amostras de aço de baixo teor de carbono, desoxidado ao silício, coletadas em uma indústria siderúrgica, são analisadas e é demonstrado que, pela comparação do teor total de cálcio e de oxigênio no aço, é possível prever os tipos de inclusões presentes no aço.

Palavras-chave: Inclusões não-metálicas, refino secundário, indústria siderúrgica.

Abstract

The increasing demand in recent years for high-quality steel products has led to the continuous improvement of steelmaking practices. There is a special interest in the control of non-metallic inclusions due to their harmful effect on the subsequent stages and their great influence on the properties of the final product. Through the control of the amount, size and chemical composition of the inclusions it is possible to obtain a final product of good quality. The control of the formation of non-metallic inclusions and the identification of their constituent phases are of extreme importance for the obtaining of clean steels. In this work, samples collected in a steelmaking process are analyzed and it is demonstrated that by comparing the total calcium and oxygen contents in the steel, it is possible to have an overview of the types of oxide inclusions present.

Keywords*: Non-metallic inclusions, Secondary steel treatment, Steelmaking.*

1. Introduction

The presence of non-metallic oxide inclusions is a major cause of incompatibility between the attainable and desirable level of cleanliness in many grades of commercial steel. Generally, inclusions degrade the mechanical properties of the steel and thereby reduce the ductility of the cast metal and increase the risk for mechanical and/or corrosion failure of the final product[1-5].

Oxide inclusions originate from two sources: (i) - residual products resulting from intentionally added alloying elements to deoxidize the molten steel after oxygen treatment (endogenous or micro inclusions); (ii) - products resulting from reactions between the melt and atmosphere, slag, or refractory (exogenous or macro inclusions)[1,2,3,6,7].

According to Oertel et al.[8] the effectiveness of the steel refining process is heavily dependent on the characteristic of the slags employed in these processes. The selection of the most effective slags for ladle furnace treatment and the definition of steel-slag composition to achieve ideal non-metallic inclusions precipitation are typical problems that can only be solved if the slag behavior and its equilibrium with the liquid metal can be evaluated. Not only are processing costs directly related to this problem but also steel quality. Among the present quality factors, resulting directly from metal-non-metallic phase equilibrium, are: (i) - the prevention of nozzle clogging in continuous casting[5,8,9].(ii) - the increase in bearing steel fatigue life[7,8]; (iii) - the control of tire cord wire drawability[4,8]; (iv) - the achievement of high formability for sheet steel[4,7,8].

To prevent nozzle clogging in continuous casting by solid inclusions, calcium is added to steel to modify inclusions and desulfurize the steel. Calcium will convert solid alumina (Al_2O_3) inclusions into lower melting point calcium aluminates, which will help prevent the clogging of the casting nozzles[9,10]. However, when calcium is added to steel, it will also react with oxygen and sulfur and modify the sulfide inclusions. If the sulfur content of the steel is high, calcium will react with sulfur forming solid CaS, which could clog up the continuous casting nozzle[7,9,10].

2. Theoretical considerations

Alumina inclusions occur as deoxidation products in the aluminium-based deoxidation of steel. Pure alumina has a melting point above 2000°C, i.e., these alumina inclusions are present in a solid state in liquid steel. The addition of calcium to steel which contains such inclusions changes the composition of these inclusions from pure alumina to CaO-containing calcium aluminates, as it can be observed from the CaO-Al_2O_3 binary system, shown in Figure 1, the melting point of the calcium aluminates will decrease as the CaO content increases, until liquid oxide phases occur at about 22% of CaO, i.e., when the $CaO.2Al_2O_3$ compound is first exceeded at 1600°C. The liquid phase content continues to increase as CaO content rises further and is 100% at 35% of CaO. The minimum melting temperature for the liquid calcium aluminates is around 1400°C, i.e., such liquid calcium aluminates may be present in liquid form until, or even after, the steel solidifies[9].

Thermodynamically, if sulfur or oxygen is dissolved in the steel at moderate levels, or if Al_2O_3 inclusions are present in steel, calcium will react with these. According to Larsen et al.[10], Ca will react with oxygen or sulfur until the contents of reactants are very low (<2ppm).

$$Ca + O = CaO \tag{1}$$

$$Ca + S = CaS \tag{2}$$

$$Ca + Al_2O_3 = \text{Calcium aluminate} + Al \tag{3}$$

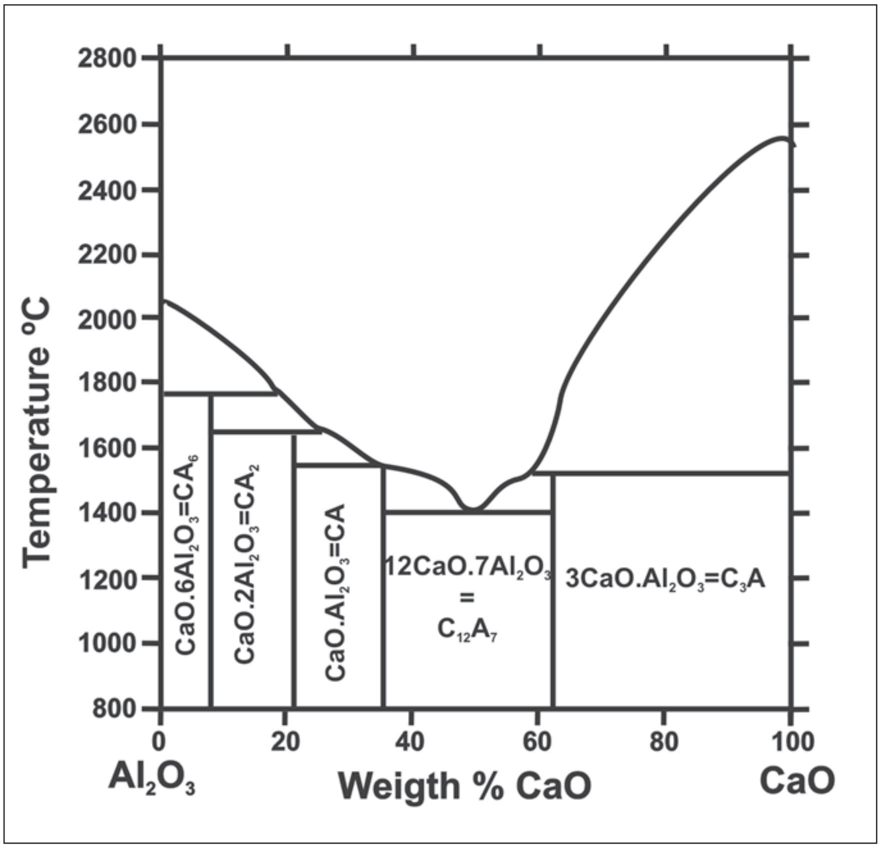

Figure 1 - Binary system CaO-Al_2O_3.

One of the critical questions is whether or not calcium added to steel will react with sulfur by reaction (2) and form CaS or modify Al_2O_3 to liquid Calcium aluminate by reaction (3).

The formation of calcium sulfide can occur if calcium and sulfur contents are sufficiently high. Since calcium has higher affinity for oxygen than for sulfur, the addition of calcium initially results in a more or less pronounced conversion of the alumina into calcium aluminates until the formation of calcium sulfides starts as the addition of calcium continues. Calcium sulfides are solids at steelmaking temperatures and result in nozzle clogging similar to that caused by alumina[9,10]. As can be observed from the Figure 2, the conversion of alumina into calcium aluminates occurs until all the inclusions in the steel are present only in liquid form. The formation of solid calcium sulfides then occurs as an addition of calcium proceeds further. The range in which all the oxides have been liquefied and no solid sulfides have yet occurred is regarded as the "optimum window" for calcium treatment. The attainment of this window is the target in calcium treatment. Its precise location depends on the steel's sulfur and total oxygen contents.

In order to determine if calcium will modify Al_2O_3 inclusions or react with sulfur to form CaS, reactions (2) and (3) are combined and the thermodynamics analyzed[10].

$$3CaS + 19Al_2O_3 = 3(CaO.6Al_2O_3) + 2Al + 3S \qquad (4)$$

$$12CaS + 7(CaO.6Al_2O_3) = 19(CaO.2Al_2O_3) + 8Al + 12S \qquad (5)$$

$$3CaS + 4(CaO.2Al_2O_3) = 7(CaO.Al_2O_3) + 2Al + 3S \qquad (6)$$

$$15CaS + 33(CaO.Al_2O_3) = 4(12CaO.7Al_2O_3) + 10Al + 15S \qquad (7)$$

For liquid inclusions $12CaO.7Al_2O_3$ ($C_{12}A_7$) to form, the Al and S contents must be less than those for the equilibrium of reaction (7). The equilibrium constant for this reaction is given by[10]:

$$K = \frac{a_{C12A7}^{4} h_{S}^{15} h_{Al}^{10}}{a_{CaS}^{15} a_{CA}^{33}} \qquad (8)$$

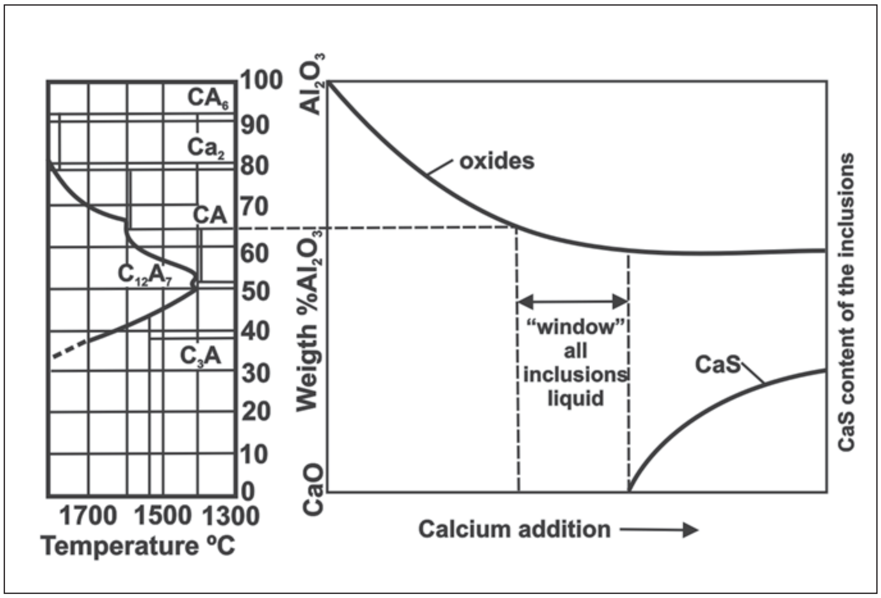

Figure 2 - Change of inclusions composition during calcium additions[9,10].

Where:

a_i is the activity for the pure standard state.

h_i is the activity for the 1wt percent standard state.

The activity of CA ($CaO.Al_2O_3$) is unity and the activity of $C_{12}A_7$ varies from about 0.8 to 1.0 depending on the actual inclusion composition. The activity of CaS is estimated to be 0.75 ± 0.10. In steel containing Mn, the activity of CaS is not necessarily unity; CaS is usually found in a solution with MnS at a reduced activity. The amount of CaS in the inclusion will depend on the Mn content of the steel. The higher the Mn, the lower the CaS content and its activity. However, the change in CaS activity with the Mn content in steel has a relatively minor effect. In Figure 3, an invariant equilibrium is shown. Above the $C_{12}A_7$ line the equilibrium oxide phase is CA. So as to obtain liquid calcium aluminates, the composition of the steel must be below the $C_{12}A_7$ line. If Ca is injected into steel with Al and S contents above the $C_{12}A_7$ line, the alumina inclusions will be converted to CA. The calcium must then react with sulfur until the sulfur content goes below the line where liquid oxide inclusions form. Usually not enough Ca is injected to desulfurize below the line when a Ca wire is used and the inclusions present are CA and CaS-MnS. These inclusions can clog casting nozzles[9].

Figure 4 shows the castability curve as a function of the steel's inclusion composition. A steel containing inclusions consisting of pure alumina has only a moderate castability. Castability deteriorates drastically at the start of conversion of inclusions into calcium aluminates. Only when the first liquid phases occur, i.e., at calcium to total oxygen ratio of approximately 0.4, does castability improve. When the calcium to total oxygen ratio reaches 0.6, the castability is better than that of steel containing inclusions of pure alumina[9].

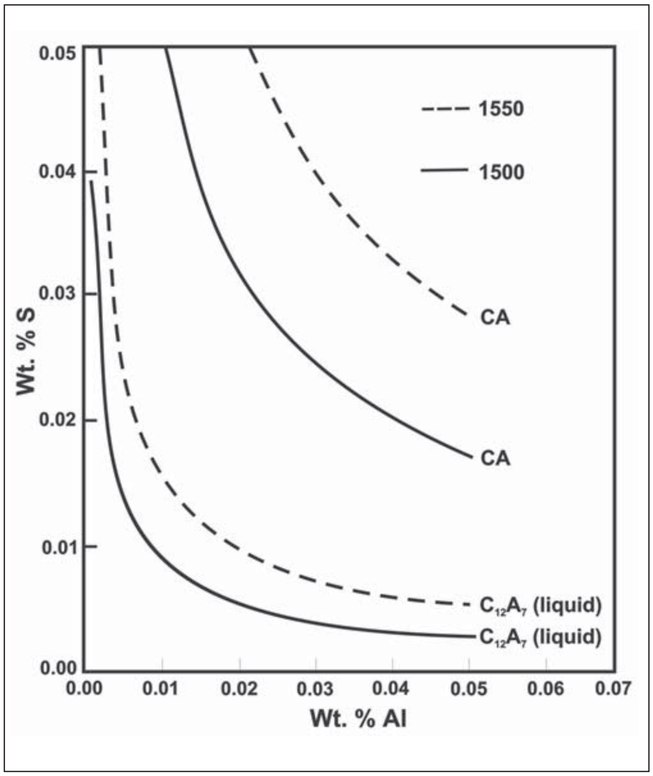

Figure 3 - Invariant equilibrium for CaS and $C_{12}A_7$ or CA as a function of percent Al and S at 1500ºC and 1550ºC [9].

3. Experimental procedure

The industrial process of steel production was accompanied, and samples were collected in the different stages of elaboration of aluminum-killed low carbon steels, in a Brazilian Steelmaking company. Table 1 shows the chemical composition of SAE 1015 steel obtained by optical spectrometry in the plant.

The choice of aluminum-killed low carbon steel is due to the fact that aluminum is a highly deoxidizing element and is added to the liquid steel in order to reduce the percentage of oxygen dissolved in the same. The lower the final level of carbon in the liquid steel, the greater the percentage of dissolved oxygen in it, and consequently the greater the quantity of inclusions formed. Therefore, in a sample of this steel it is possible to find many kinds of non-metallic inclusions of different sizes, shapes and chemical composition. Composition analysis of the non-metallic inclusions present in this sample were performed by using a scanning electron microscope with energy-dispersive spectroscopy.

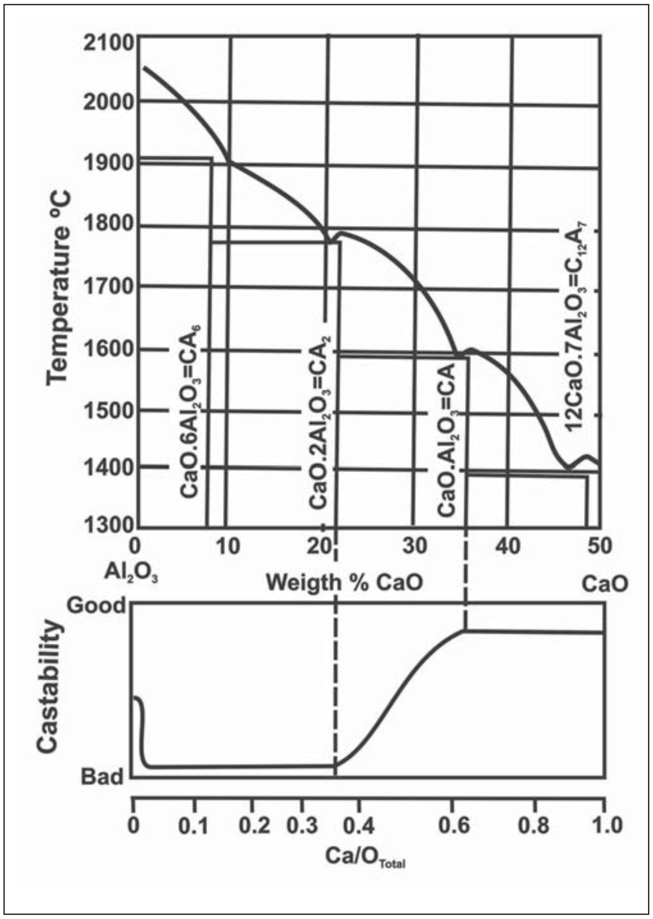

Figure 4 - Steel castability dependent on oxide composition[9].

4. Results and discussion

In most samples, several different types of inclusions were found. Figures 5 and 6(a,b,c,d) show photomicrographs of inclusions present in the low carbon steel analyzed.

In Table 2, the elementary composition and the oxide composition for any inclusions, in the ladle furnace sample, are presented.

The addition of calcium reduces the oxygen content dissolved in the liquid steel and it enlarges the existing field of liquid phases. That means in the presence of calcium, the addition of aluminum can be increased maintaining the liquid inclusions, which are favorable to facilitate the inclusion flotation and casting. On the other hand, the inclusions of calcium aluminates are spherical, during the solidification of the steel, and they are larger than alumina inclusions (Figure

Table 1 - Chemical composition of the SAE 1015 aluminum-killed steel, (wt %).

C	Mn	S	Si	P	Al	Ca	N_2
0.145	0.340	0.009	0.062	0.010	0.027	0.0063	0.0036

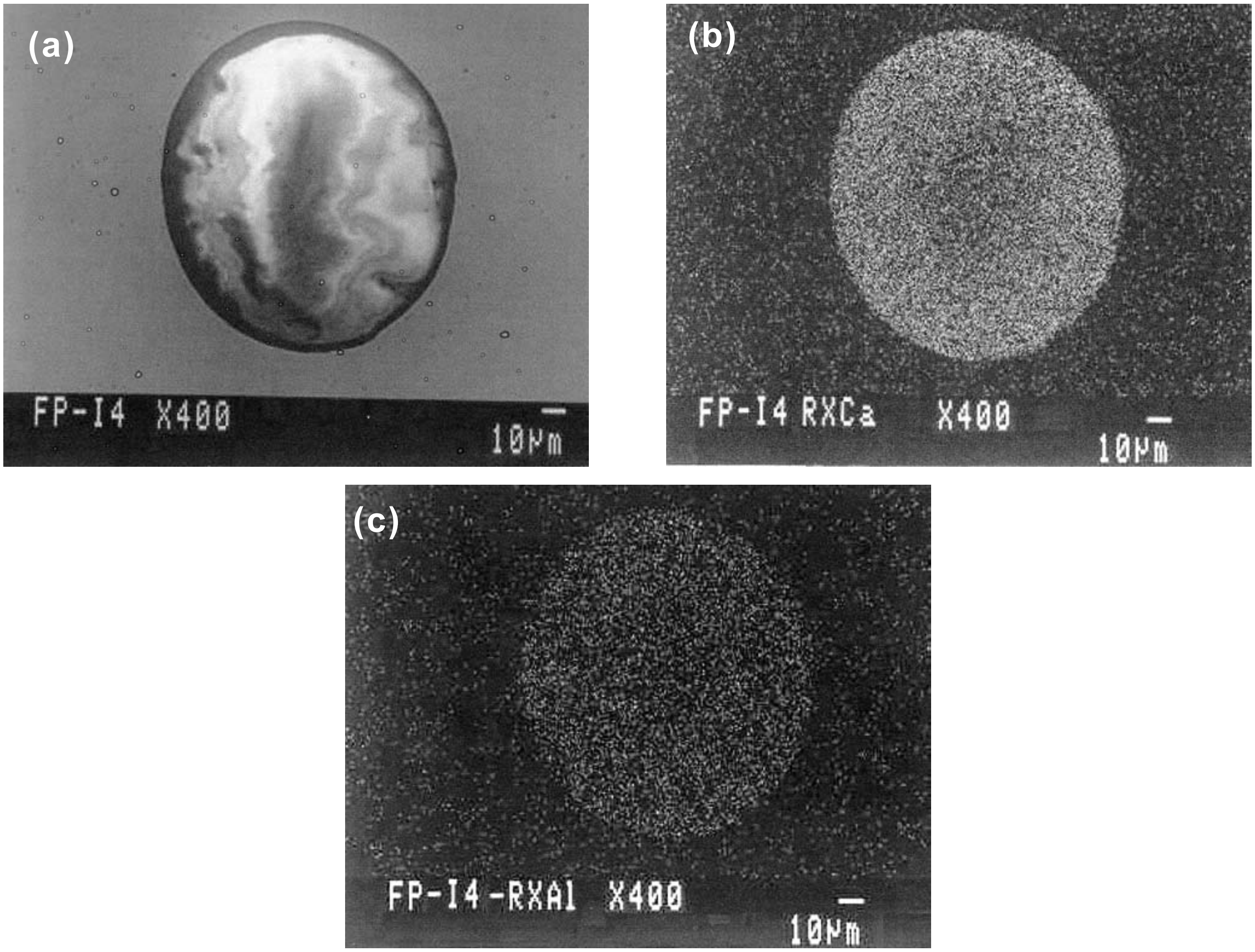

Figure 5 - (a) Typical calcium aluminate inclusion, (b) X-ray of Ca, (c) X-ray of Al.

5). Thus, special care should be taken to promote the flotation of those inclusions, during the ladle furnace treatment of the steel, in order to guarantee an improvement in the surface quality and in the mechanical properties of the product.

The great advantage of steel deoxidation with aluminium and the use of calcium to modify the form of the alumina inclusions is that they reduce the dissolved oxygen activity in the liquid steel, resulting in a final product with a larger index of cleaning and a smaller tendency for porosity formation.

The calcium aluminate inclusions that present high contents of Ca have a higher capacity of absorving sulfur. The concentration of sulfur in equilibrium in calcium aluminate inclusions can be very high and, therefore, absorve most of the sulfur present in the melting. During the cooling and steel solidification, the solubility of the sulfur in the calcium aluminate inclusion decreases and precipitates in the ring form of CaS, involving the nucleus of calcium aluminates. Besides, the solubility of the residual calcium in the melting decreases with the cooling of the steel. It can react with the sulfur on the surface of the inclusions of calcium aluminates to form superficial layers of CaS present in those inclusions (Figure 6).

According to Larsen et al.[10], in order to obtain full oxide modification to liquid calcium aluminates in aluminum-killed steels, the sulfur content must be quite low. Another important consideration is the casting temperature. The higher the temperature, the easier it is to form liquid ($C_{12}A_7$) inclusions. Therefore, the order of reaction of calcium in steel depends on the aluminum and sulfur contents. For example, for 0.02 percent Al and 0.015 percent S, calcium will first convert Al_2O_3 to CA inclusions. Then it will react with sulfur to form CaS until the sulfur content reach a value below 0.01 percent, and then it will convert the CA inclusion to a liquid inclusion ($C_{12}A_7$).

5. Conclusions

Calcium is used in steel for desulfurization, oxide inclusion modification and sulfide inclusion modification. Depending on the composition of the steel, calcium sulfide or various forms of calcium aluminates may form.

Table 2 - Inclusion analysis of the steel sample collected in the ladle furnace treatment.

Element	EDS analysis wt%	Calculated Oxides	Compound %	CaO/Al_2O_3	Inclusion
Al	10.19	Al_2O_3	19.25	3.2	$3CaO.Al_2O_3+SiO_2$
Si	4.99	SiO_2	10.68		
Ca	44.13	CaO	61.74		
Mg	1.65	MgO	2.74		
Mn	---	MnO	----		
O	36.16				
Al	13.16	Al_2O_3	24.86	2.1	$12CaO.7Al_2O_3+SiO_2$
Si	6.55	SiO_2	14.01		
Ca	37.92	CaO	53.06		
Mg	2.24	MgO	3.72		
Mn	----	MnO	---		
O	37.79				
Al	20.58	Al_2O_3	38.89	1.4	$12CaO.7Al_2O_3$
Si	0.38	SiO_2	0.80		
Ca	38.28	CaO	53.56		
Mg	1.29	MgO	2.13		
Mn	---	MnO	---		
O	36.48				
Al	20.45	Al_2O_3	38.65	1.3	$12CaO.7Al_2O_3$
Si	0.58	SiO_2	1.24		
Ca	37.18	CaO	52.02		
Mg	1.43	MgO	2.37		
Mn	---	MnO	---		
O	36.58				
Al	20.56	Al_2O_3	38.85	1,4	$12CaO.7Al_2O_3$
Si	0.44	SiO_2	0.94		
Ca	39.55	CaO	55.34		
Mg	0.37	MgO	0.62		
Mn	---	MnO	---		
O	36.40				
Al	49.23	Al_2O_3	93.02	---	Al_2O_3
Si	---	SiO_2	---		
Ca	---	CaO	---		
Mg	---	MgO	---		
Fe	4.89	FeO	6.29		
O	45.55				
Al	0.16	Al_2O_3	0.30	---	CaO
Si	---	SiO_2	---		
Ca	68.44	CaO	95.76		
Mg	0.33	MgO	0.55		
Fe	2.08	FeO	2.68		
O	28.70				

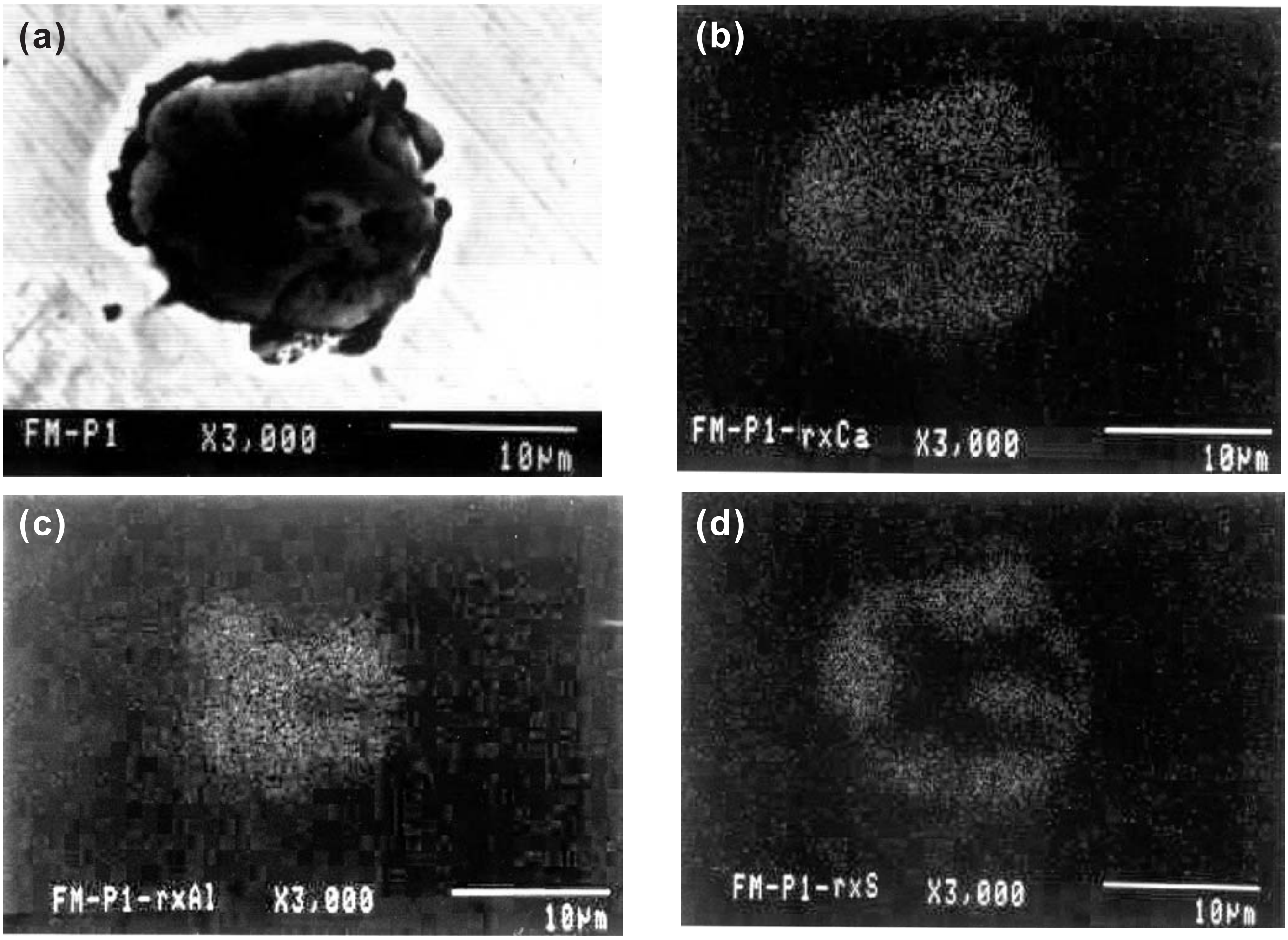

Figure 6 - (a) Calcium aluminate inclusion with superficial layer of CaS, (b) X-ray of Ca, (c) X-ray of Al, (d) X-ray of S (sulfide ring).

In the present results shown in table 2, it can be noted that the complete inclusion modification in the ladle furnace treatment was not reached.

To achieve complete oxide shape control of liquid calcium aluminates ($C_{12}A_7$), the sulfur content must be low. The casting temperature is also very important; it is much easier to form liquid inclusions ($C_{12}A_7$) at higher temperatures than at lower temperatures.

6.Acknowledgements

The authors wish to thanks FAPESP (The Scientific Research Foundation of State of the São Paulo, Brazil), and CNPq (The Brazilian Research Council) for financial support for the research. We would also like to thank the Belgo Mineira S.A. for supplying steel samples and the technicians of the material characterization laboratory of DEMA/FEM/UNICAMP, for their support during the analysis of the samples in SEM.

7. References

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Artigo recebido em 08/03/2004 e aprovado em 21/09/2004.