Y. PONTIKES*, P.T. JONES*, D. GEYSEN*, B. BLANPAIN*

OPTIONS TO PREVENT DICALCIUM SILICATE-DRIVEN DISINTEGRATION OF STAINLESS STEEL SLAGS

MOŻLIWOŚCI ZAPOBIEGANIA ROZPADOWI SIARCZANU DWUWAPNIOWEGO Z ŻUŻLI STALI NIERDZEWNYCH

In this paper, a short overview is given on the strategy for high dicalcium silicate stainless steel slags stabilisation along with some results from work done and currently being performed at the K.U.Leuven.

Keywords: slags, stainless steel, production, solidification, microstructure, utilization

W niniejszej pracy, znajduje się krótki opis strategii stabilizacji żużli stali nierdzewnych zawierających krzemian dwuwapniowy, także niektóre wyniki dokonanych i obecnie przeprowadzanych prac w K.U. Leuven.

1. Introduction

Slags are essential in high temperature metallurgical processing to purify molten metal at competitive prices. Large volumes are produced annually, leading to important economical and ecological issues regarding their afterlife. To maximise the recycling potential, slag processing has become an integral part of the valorisation chain [1].

Production of steel slags in Europe was 15 Mt in 2004 [2], of which, stainless steel slags constitute a more than proportional fraction due to the higher slag to metal ratio in stainless steel production. Stainless steel slags are currently used for a number of applications and some alternatives have been suggested in literature [3]: aggregates, additives or raw materials for cement making, carbon sink, as well as fertilisers and additives for soil treatment are only a few of the potential routes. Nonetheless, disintegration of stainless steel slags hinders the valorisation and increases considerably the landfilling cost.

It is well established that this kind of disintegration is driven by the presence of dicalcium silicate ($2CaO \cdot SiO2$ or C_2S) in the slag [4]. This mineral undergoes several phase transformations from one polymorph to another when the slag is cooled. As the athermal, martensitic-like transformation of the monoclinic β-polymorph to the orthorhombic γ-polymorph [5] is accompanied by a volume expansion of about 12%, high internal stresses finally cause the disintegration of the slag.

The potential routes to avoid the formation of γ-dicalcium silicate explored in this work are: a) chemical stabilization by additions, b) change in slag chemistry and c) fast cooling.

2. Chemical additions to stabilise the high temperature phases

2.1. Boron additions

In metallurgy, the option of inhibiting the β to γ transformation of C_2S was first elaborated in 1986 by Seki and co-workers [6], who developed a borate based stabiliser for stainless steel decarburisation slag. At the time, it was already known that borates stabilise the higher temperature polymorphs of pure C_2S to ambient temperatures by forming a solid solution. Seki proved that by adding borates to the high temperature slag, C_2S grains in the cooled slag can also be stabilised. The crystallographic mechanism is believed to be the partial replacement of SiO_4^{4-} units by BO_3^{3-} units [7]. Because of the large difference in ionic radius between Si^{4+} and B^{3+}, this replacement suppresses the Ca^{2+} migrations and SiO_4^{4-} rotations required for the β to γ transformation, even with only 0.13 wt% of B_2O_3 [8] (although this theory should be juxtaposed with the other suggested

* DEPARTMENT OF METALLURGY AND MATERIALS ENGINEERING, KATHOLIEKE UNIVERSITY OF LEUVEN, KASTEELPARK ARENBERG 44, B-3001, HEVERLEE (LEUVEN), BELGIUM

theory of martensitic-like β to γ transformation). As borates increase steel hardness and may lead to hot tearing during rolling or forging, they need to be added to the slag after slag/metal separation to avoid boron pick-up by the steel. Fortunately, the required level is so low that the heat content of the slag is sufficient to melt and dissolve the stabiliser. Because of its effectiveness and simplicity, borate stabilisation of air-cooled slags is widely implemented in industrial practice.

Results regarding the distribution of boron in the slag matrix have been reported in a previous work [9]. Both industrial and synthetic slags were investigated. For the synthetic slags a 200 g powder mixture with a composition of 52-wt% CaO, 39-wt% SiO_2, and 9 wt% MgO was made from dried CaO, MgO, and SiO_2 powders. This mixture was milled for 24 h in ethanol using zirconia balls for homogenisation. After drying, multiple samples of 20 g weighed. Sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$), containing 37 wt% of B_2O_3, was added as a stabilizer. The borate levels varied from 0- to 1.83 wt% B_2O_3. The samples were put into a Pt–Rh crucible and loaded in a bottom-loading furnace. The samples were heated in air to 1640°C at 5°C/min for 8 h and were subsequently cooled at 1°C/min. The industrial sample was stabilized with 2 wt% of $Na_2B_4O_7$ or 1.4 wt% B_2O_3. The mineralogy of the slag samples was determined using quantitative X-ray diffraction (QXRD). Spectra of samples mixed with 10 wt% ZnO as an internal standard were collected under ambient conditions with CuKα radiation using a laboratory Philips PW1830 Bragg-Brentano diffractometer. Quantitative results were obtained by performing a Rietveld refinement using the "Topas Academic" software. For microstructural characterization samples were embedded, grinded, polished, and carbon coated. Semi-quantitative analyses were performed with a JEOL 733 EPMA system equipped with an energy dispersive spectrometer (EDS), which can detect elements from sodium onwards. The borate distribution was determined using an ARL SEMQ EPMA system equipped with WDS and a multilayer Ni–C crystal. For each slag phase, three 7.6–5.8-nm wave scans were performed at different locations in the sample.

The addition of as little as 0.10 wt% of stabilizer or 0.04 wt% B_2O_3 proved to be sufficient to avoid disintegration. Although the minimal required level could not be determined exactly, it is <0.04 wt% for the experimental conditions used. Phase analysis proved to be very similar for the synthetic and industrial samples. The synthetic samples contain C_2S, C_7MS_4, C_3MS_2, C_2MS_2, and CS. As fluorine was added to the industrial slag to increase its fluidity, cuspidine formed in the later stages of solidification instead of C_2MS_2 and CS. Furthermore, the inevitable presence of CrOx in the industrial slag resulted in spinel formation. A $C_xS_yB_z$ phase was found in both types of samples. No sodium was detected by EDS. It probably evaporated as Na_2O during equilibration at high temperature. The borate distribution was determined using EPMA-WDS. The overall results are very similar for both types of samples. Figure 1 shows the result for the industrial sample. C_2S and C_7MS_4 show small but clear boron peaks. C_3MS_2 contains a borate level close to the detection limit. Cuspidine holds some borates but the major fraction is found in the $C_xS_yB_z$ phase. The latter phase has not been fully characterised, but there is indication that it is vitreous in nature. The microstructure is depicted in Fig. 2.

From quenching experiments, EPMA measurements and FactSage calculations it could be determined that the distribution ratio of borate between the C_2S phase and the liquid corresponds to approximately 0.1. Based on this observation and a mass balance calculation and additionally assuming a minimum level of borate necessary to stabilize the C_2S phase of 0.1 wt% an estimate can be made of the level of borate necessary to stabilize the C_2S phase as a function of C_2S level. As the distribution ratio is smaller than one, the borate level decreases as the C_2S fraction increases (see Figure 3). If this line is compared with experimental data, it is clear that the calculated level of borate is not in agreement with the experiments (dotted line) that indicate a minimum fraction of about 20 wt% C_2S before any stabilisation with borate becomes necessary as well as an increase in B_2O_3 content necessary to stabilize the slag with increasing C_2S levels. Evidently, chemical stabilisation of C_2S is not the only factor and other physical or mechanical stabilisation mechanisms need to be considered.
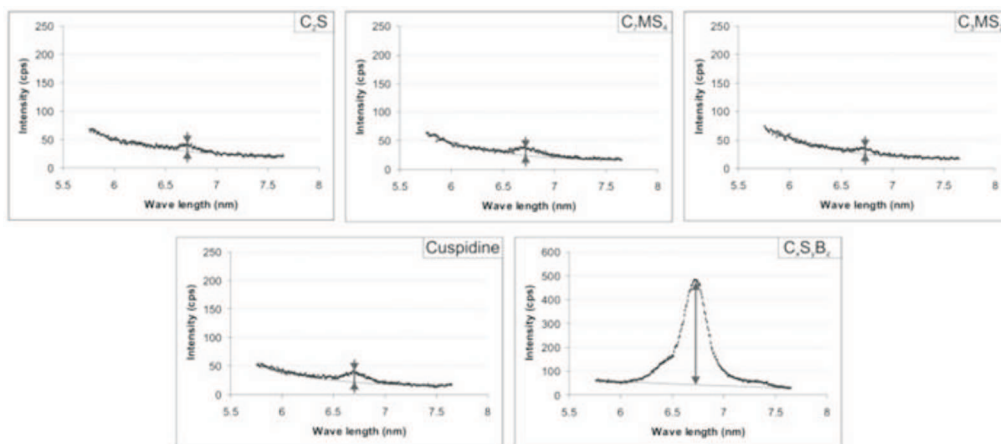
Fig. 1. EPMA-WDS wave scans for the different phases in the industrial stainless steel slag, net peak height correlates with B level
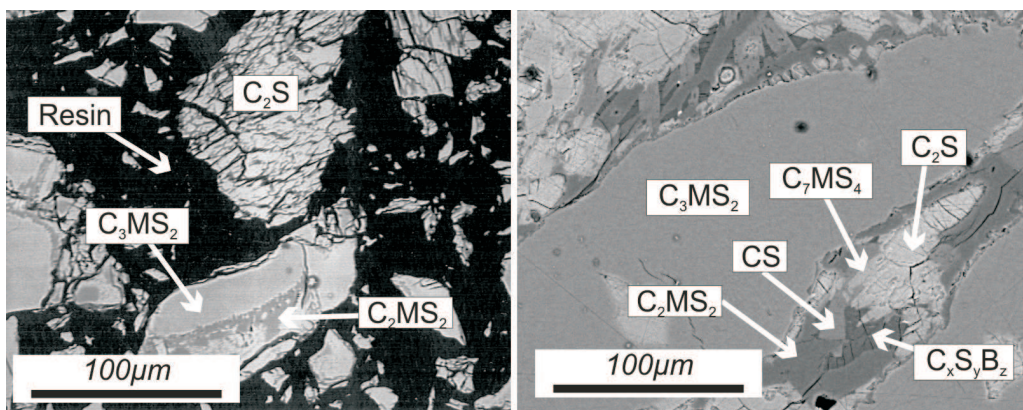

Fig. 2. Effect of B_2O_3 additions to a C_2S containing slag. Left: The untreated slag contains fractured γ-C_2S grains and disintegrates during cooling. Right: The treated slag contains stable β-C_2S and does not disintegrate
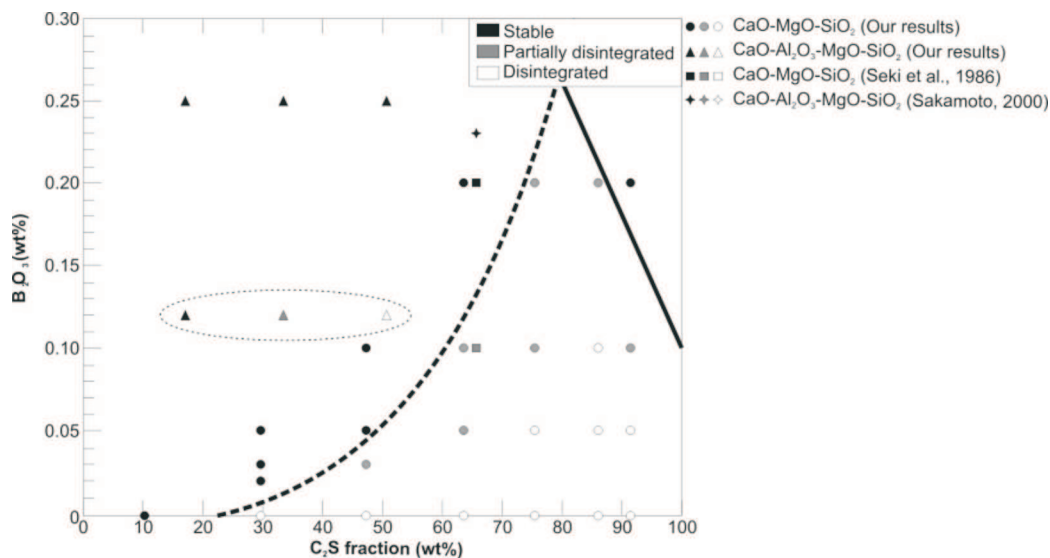

Fig. 3. Stability diagram as a function of B_2O_3 content and C_2S fraction. The full line is the result of a mass balance and partition calculation, the dotted line is based on experimental results

The very efficient action of B in conjunction with the need to couple waste streams and achieve their valorisation through this waste synergy strategy, was the incentive for the use of other boron sources. Already in the literature, a similar attempt was performed by Branca *et al.* using boron containing glazing powders [10] with promising results.

The boron source used is a form of boron waste originating in Turkey. These wastes are produced during the refining of the boron ores. Their volume amounts to 400.000 tons/y and are currently disposed in tailing dams. More information regarding the wastes can be retrieved elsewhere [11, 12]

The boron waste was mixed with a synthetic slag of basicity 2. Additions in the range of <1wt.% of boron waste have been proven successful in terms of C_2S stabilisation. The analysis of results is underway.

2.2. Non-boron additions

Borate additions are not the only possibility to avoid the expansive transformation of C_2S and the associated slag disintegration of the slag [8, 13-15]. The crystallographic coordination number, the ionic radius and the ionic valence of the doping ion all affect the deformation of the C_2S crystal and, as a consequence, the stabilisation. Recently, a qualitative criterion based on ionic radius, ionic valence and crystallographic structure of the additive was developed [16], which is capable of predicting whether or not a compound will stabilise the β-polymorph. In practice, different oxides have been reported to stabilise the different polymorphs of dicalcium silicate. The α and α polymorphs have been reported to be stabilised by oxides such as MgO, Al_2O_3, Fe_2O_3, BaO, K_2O, P_2O_5 and Cr_2O_3. The β polymorph can be stabilized by the addition of Na_2O, K_2O, BaO, MnO_2, Cr_2O_3 or their combinations [13]. The difference in the stabilising ability of each oxide provides a certain degree of flexibility if the goal is to avoid the formation of the γ phase.

Based on this knowledge, the effect of phosphate additions to disintegrating stainless steelmaking slags was investigated. Satisfactory stabilisation was obtained [17], but compared to borate additions a significantly larger amount of phosphates (~ 2 wt%) is required to avoid disintegration. Working on a similar direction, Yang et al. [18] used a feed grade mono-calcium phosphate, originating from iron ore processing. The P addition prevented the formation of γ- C_2S and only β- and α-C_2S were detected, for additions in the range of 0.46-0.69 wt%.

2.3. Changing the chemistry

Alternatively, slag disintegration can be averted by modifying the slag composition in order to avoid the presence of C_2S. Already in 1942, compositional limits were defined for disintegrating slags .....[19], based on the stability field of C_2S in the CaO-MgO-SiO_2-Al_2O_3 system, with an adjustment for the sulphur content (S) in the slag:

$$CaO + 0.8\ MgO \leqslant 1.20\ SiO_2 + 0.39\ Al_2O_3 + 1.75\ S$$

$$CaO \leqslant 0.93\ SiO_2 + 0.55\ Al_2O_3 + 1.75\ S$$
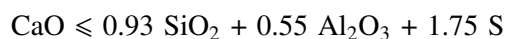
with the compounds referring to their respective weight fractions. However, in many cases, slags that meet these conditions do not have the appropriate high temperature metallurgical functionality. In stainless steelmaking, C_2S free, low basicity slags cause rapid refractory degradation and low chromium yields [20]. To avoid making such compromises towards production cost, the slag composition must be adjusted after slag/metal separation. Adding a relatively large amount of silica seems to be the best way to avoid C_2S. This was proven on a laboratory scale by Sakamoto [21], who stabilised a stainless steel decarburisation slag with 12 wt% of waste glass, containing 70-75 wt% SiO_2. The authors have also demonstrated the potential of this method in trials with waste glass in the slag pot. However, an additional slag treatment process is probably required in order to dissolve the waste glass. The principle of this step can be similar to the method developed by Kühn *et al.* [22, 23]. It permits the dissolution of a large amount of quartz sand in a basic oxygen furnace steelmaking slag by co-injection of oxygen. The injected oxygen reacts with FeO in the slag to form Fe_2O_3, whilst generating the additional heat required for the sand dissolution. This method has been adopted by Thyssen Krupp Stahl AG for years. In the case of slags containing little or no FeO, an alternative solution for the heat generation is required.

An alternative option, as described by Kitamura *et al.* [24], is to mix stainless steel slag with cold or preheated non-ferrous fayalite slag. In this way, the basicity of the slag can be substantially reduced, avoiding the formation of C_2S. The FeO from the non-ferrous slag is used as an additional energy source (exothermic reaction to Fe_2O_3 results in additional heat to dissolve the SiO_2. However, this method has only been shown to work on a lab-scale level. To scale this up to the industrial level is not straightforward. Heat balance calculations by Kitamura *et al.* [24] have shown that a mixing ratio of maximum 15% (non-ferrous slag to stainless steel slag) can be achieved. This would be insufficient to reduce the C/S ratio to a low enough level. In addition, it is possible that around the cold fayalite slag particles a solidified

stainless steel slag shell will be formed as soon as it is added to the hot slag, thereby blocking any further dissolution. This means that this method may be difficult to be used in practice, unless additional measures are taken.

2.4. Fast cooling

Fast cooling in order to prevent the γ polymorph is standard practice for the cement industry. Dedicated studies have also proved the interconnection between cooling rate, final mineralogy and hydraulic properties [25]. In metallurgy, the efficiency of the method is also demonstrated [26]. According to the laboratory experiments [27, 28] the required slag cooling rate is about 5°C/s. This stabilisation method was further developed by showing on a laboratory scale that a granulation process transforms a disintegrating slag into a slag product suitable for construction applications [29]. Similar results have been reported also recently [18]. The authors have also stabilised synthetic slags of basicity 2 by applying high cooling rates, arresting the β polymorph.

3. Conclusions

Increasing environmental awareness has created incentives for metallurgical companies to tackle various slag issues. Regarding air-cooled slags, C_2S-driven disintegration during cooling is one of the main issues, as it not only creates dust problems but also complicates the slag valorisation in construction applications.

Borate additions to the slag during or immediately after slag/metal separation have proven to be an effective and easy-to-implement method to stabilise these slags and avoid disintegration. The technique is commonly used for treating stainless steelmaking slags at the moment, but its potential for treating ladle refining slags has also been shown. Other additions besides boron have been also proven promising, although it is possible that higher levels are required.

Change in the slag chemistry is also an option. However, it is possible that an additional step in slag processing will be required in order to enhance the dissolution of the materials. Finally, fast cooling can offer an alternative route.

REFERENCES

[1] D. D u r i n c k, F. E n g s t r ö m, S. A r n o u t, J. H e u l e n s, P.T. J o n e s, B. B j ö r k m a n, B. B l a n p a i n, P. W o l l a n t s, Hot stage processing of metallurgical slags. Resour. Conserv. Recy. **52**, 10, 1121-1131 (2008).

[2] The European Slag Association. Legal Status of Slags, Position Paper, Duisburg, Germany, 2006.

[3] D. G e y s e n, P. J o n e s, A. S a n d e r, Y. P o n - t i k e s, Ö. C i z e r, T. V a n G e r v e n, M. C r a p s, J. E y c k m a n s, B. B l a n p a i n, Slag valorisation, as an example of high temperature industrial ecology. In EPD Congress 2010. 2010 TMS Annual Meeting & Exhibition, 2010, Washington State Convention Center. Vidal, E., Ed. 877-884.

[4] L.M. J u c k e s, Dicalcium silicate in blast-furnace slag: a critical review of the implications for aggregate stability. Mineral Processing and Extractive Metallurgy: Transactions of the Institute of Mining and Metallurgy, Section C, **111**, 120-128 (2002).

[5] G.H. T h o m a s, I.M. S t e p h e n s o n, The beta to gamma dicalcium silicate phase transformation and its significance on air-cooled slag stability. Silic. Ind., 195-200 (1978).

[6] A. S e k i, Y. A s o, M. O k u b o, F. S u d o, K. I s h i z a k a, Development of dusting prevention stabilizer for stainless steel slags. Kawasaki Steel Giho **18**, 1, 20-24 (1986).

[7] J.G. F l e t c h e r, F.P. G l a s s e r, Phase relations in the system $CaO-B_2O_3-SiO_2$. J. Mater. Sci. **28**, 10, 2677-2686 (1993).

[8] A. G h o s e, S. C h o p r a, J.F. Y o u n g, Microstructural characterization of doped dicalcium silicate polymorphs. J. Mater. Sci. **18**, 10, 2905-2914 (1983).

[9] D. D u r i n c k, S. A r n o u t, G. M e r t e n s, E. B o y d e n s, P.T. J o n e s, J. E l s e n, B. B l a n - p a i n, P. W o l l a n t s, Borate distribution in stabilized stainless-steel slag. J. Am. Ceram. Soc. **91**, 2, 548-554 (2008).

[10] T.A. B r a n c a, V. C o l l a, R. V a l e n t i n i, A way to reduce environmental impact of ladle furnace slag. Ironmaking and Steelmaking **36**, 597-602 (2009).

[11] A. C h r i s t o g e r o u, T. K a v a s, Y. P o n t i k e s, S. K o y a s, Y. T a b a k, G.N. A n g e l o p o u l o s, Use of boron wastes in the production of heavy clay ceramics. Ceram. Int. **35**, 1, 447-452 (2009).

[12] A. C h r i s t o g e r o u, T. K a v a s, Y. P o n t i k e s, C. R a t h o s s i, G.N. A n g e l o p o u l o s, Evolution of microstructure, mineralogy and properties during firing of clay-based ceramics with borates. Ceram. Int. **36**, 2, 567-575 (2010).

[13] S.N. G h o s h, P.B. R a o, A.K. P a u l, K. R a i n a, Review. The chemistry of dicalcium silicate mineral. J. Mater. Sci. **14**, 7, 1554-1566 (1979).

[14] G.C. L a i, T. N o j i r i, K. i. N a k a n o, Studies of the stability of β-Ca_2SiO_4 doped by minor ions. Cem. Concr. Res. **22**, 5, 743-754 (1992).

[15] J. G e i s e l e r, Properties of iron and steel slags regarding their use. In 6th Conference on molten slags, fluxes and salts, 2000.

[16] D.V. L o p a t i n, V.M. C h i z h i k o v a, The new stability criterion of crystal-chemical stabilization of β-C_2S. In Advances in metallurgical processes and materials, Dnepropetrovsk, Ukraine 481-482 (2007).

1172

[17] Q. Yang, L. Nedar, F. Engström, M. He, Treatments of AOD slag to produce aggregates for road construction. In Aistech 2006, Ohio, USA, 573-583 (2006).

[18] Q. Yang, F. Engström, B. Björkman, D. Adolfsson, Modification study of a steel slag to prevent the slag disintegration after metal recovery and to enhance slag utilization. In 8th International Conference on Molten Slags, Fluxes and Salts – MOLTEN 2009, 2009, Santiago, Chile. Mario Sánchez, Roberto Parra, Gabriel Riveros and Díaz, C., Eds.

[19] T.W. Parker, J.F. Ryder, Investigations on 'falling' blast furnace slags. Journal of the Iron and Steel Institute **11**, 21-51 (1942).

[20] M. Guo, D. Durinck, P.T. Jones, G. Heylen, R. Hendrickx, R. Baeten, B. Blanpain, P. Wollants, EAF stainless steel refining – Part I: Observational study on chromium recovery in an eccentric bottom tapping furnace and a spout tapping furnace. Steel Res. Int. **78**, 2, 117-124 (2007).

[21] N. Sakamoto, Effects of MgO based glass addition on the dusting of stainless steel slag (development of control process of stainless steel slag dusting-3). Current Advance in Materials and Processes **14**, 4, 939 (2001).

[22] M. Kühn, H. Behmenburg, Decreasing the scorification of chrome., Report EUR 19382, Primary Steelmaking, European Commission 39, Luxembourg, 2000.

[23] M. Kühn, P. Drissen, H. Schrey, Treatment of liquid steel slags. Proceedings of the 2nd European slag conference, (2000).

[24] S. Kitamura, N. Maruoka, Modification of stainless steel refining slag through missing with nonferrous smelting slag. In First International Slag Valorisation Symposium, 2009, Leuven, Belgium. Jones, P. T., Geysen, D., Guo, M. and Blanpain, B., Eds.

[25] J. Stark, A. Müller, R. Schrader, K.R. Rumpler, Contributions to active belite cement, part 2: Influence of cooling conditions of cement strength. Silikattechnik **31**, 2, 50-52 (1980).

[26] C.J. Chan, M.W. Kriven, J.F. Young, Physical Stabilization of the $\beta_¿\gamma$ Transformation in Dicalcium Silicate. J. Am. Ceram. Soc. **75**, 6, 1621-1627 (1992).

[27] N. Sakamoto, Effect of cooling process to crystallization of stainless steel slag (development of control process of stainless steel slag dusting-1). Current Advance in Materials and Processes **9**, 4, 803 (1996).

[28] N. Sakamoto, Inhibition mechanism of dusting on stainless steel slag with additive B_2O_3 (development of control process of stainless steel slag dusting-2). Current Advance in Materials and Processes **13**, 4, 862 (2000).

[29] Q. Yang, F. Engström, M. Tossavainen, M. He, AOD slag treatments to recovermetal and to prevent slag dusting. In 7th Nordic-Japan symposium on science and technology of process metallurgy, 2005.