HAJI AMINI, S., OSTROVSKI, O., and BRUNGS, M. A study of dissolution of dense lime in molten slags under static conditions. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

A study of dissolution of dense lime in molten slags under static conditions

S. HAJI AMINI*, O. OSTROVSKI† and M. P. BRUNGS*

**School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Australia*

†School of Material Science and Engineering, The University of New South Wales, Australia

Static dissolution of CaO into a $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag and slags with additional fluxing agents (fluorspar, nepheline syenite and ilmenite) was studied. The slag was packed into dense CaO crucibles and heated to 1500ºC /1600ºC. After reaction, the crucible was air cooled and cross-sectioned. The development of the Ca_2SiO_4 phase and concentration profiles of various cations across the reaction zone were examined by Electron Probe Micro Analysis. At 1500ºC, a Ca_2SiO_4 layer was found to form at the CaO/slag interface. No such layer was evident at 1600ºC. Ilmenite and nepheline syenite were found to be effective substitutes for fluorspar, increasing the rate of CaO dissolution.

Introduction

Product quality in the steelmaking industry is influenced by the chemical and rheological properties of the slag produced as an integral part of the operation. The chemistry of the slag is controlled within wide limits by the addition of lime. This primary flux also provides some control over rheological properties. Fluxes are required in steelmaking basically for two purposes. Firstly, to lower the melting point of slags so that slags of higher basicity can be used to reduce the level of residuals in steel. Secondly, to decrease the viscosity of slags and thus speed up refining reactions.

Many investigations have been made into the mechanism of lime dissolution into slag[1-8]. Umakoshi, Mori and Kawai[9] studied the solution of a rotating burnt dolomite cylinder in $Fe_tO\text{-}CaO\text{-}SiO_2$ slag as a function of temperature (1350ºC—1400ºC) and rotational speed. From their analysis, they found that a film of Ca_2SiO_4 formed at a short distance from the CaO interface and hinder the dissolution of CaO. They also concluded that the dissolution rate was controlled by the dissolution of (Fe,Mg)O solid solution, which was formed on the surface of the burnt lime.

Matsushima *et al.*[10] investigated the dissolution of solid lime by dipping a crystalline lime cylinder into the static $CaO\text{-}SiO_2\text{-}Al_2O_3$ and $FeO\text{-}CaO\text{-}SiO_2$ slag bath at 1400ºC and 1500ºC and measured the concentration profile in the vicinity of interface. It was shown that Ca_2SiO_4 precipitated at places slightly apart from the interface, and the slag near the interface was enriched in Al_2O_3 or FeO, which indicated that the amount of silicon reaching the interface is small due to the formation of the Ca_2SiO_4 film. These results seemed to confirm the long-held belief that when lime is immersed in the slag; a layer of di-calcium silicate is formed that slows down the dissolution process.

Fluxes such as fluorspar are usually added to increase the rate of lime dissolution. However, fluorspar causes air pollution, environmental problems and refractory wear. The possibility of fluorspar substitution has been previously examined by a number of researchers[11-14]. Tribe *et al.*[15] presented a series of laboratory and industrial tests whereby fluorspar in steelmaking slag was partially or fully replaced with feldspathoid mineral (a group of sodium and potassium aluminosilicate). They found nepheline syenite tailing (NST) as a suitable substitute for the fluorspar. NST slag exhibited a similar rheological behaviour to the CaF_2 slag. Also, when using NST, the steel chemistry was not affected and adequate desulphurization was achieved.

Singh *et al.*[16] conducted extensive industrial trials to show that ilmenite ($FeTiO_3$) has the same fluidity as the fluorspar and it can be successfully used instead of fluorspar as a fluxing agent in open hearth steelmaking. Poggi and Lee[17] also found that the fluorspar and ilmenite have close melting points and both are very fluid when molten, and any degree of superheat does not decrease their viscosity.

The current study examines the dissolution of lime at temperatures normally encountered in the steel ladle during production (1600°C) with a view to examining the dissolution mechanism and the effect of the fluxing agents fluorspar, nepheline syenite and ilmenite on the rate of dissolution. While acknowledging that in industry, the burnt lime is porous (53 per cent porosity for soft-burnt lime and 26 per cent porosity for hard-burnt), it was decided to use a low porosity of 8.4 per cent lime to ensure a sharper lime/slag boundary and consequently better determination of the mass transfer mechanisms.

Experimental method

Materials

Lime crucibles were used to hold slag during the experiments. The limestone powder with 50–70 microns average particle size was ball-milled with alumina balls, which resulted in 0.8–1 micron particles that were then calcined to CaO and pressed in a mould and subsequently fired to provide the necessary density and strength. This

Table I
Chemical compositions of fluxes

Table I.a
Nepheline syenite

Oxides	Wt%
SiO_2	59.30
Al_2O_3	19.28
Fe_2O_3	2.25
CaO	0.91
MgO	0.09
Na_2O	8.33
K_2O	5.32
FeO	2.27

Table I.b
Ilmenite

Oxides	Wt%
TiO_2	59
Fe_2O_3	19.3
FeO	14.4
Al_2O_3	1
SiO_2	0.8
H_2O	0.6
P_2O_5	0.09
Cr_2O_3	0.06

technique has the potential for close control of the physical properties such as bulk density and apparent porosity, since it involves parameters that can be varied precisely. These include compacting pressure, sintering temperature, rate of heating and cooling in sintering, and the required time in the furnace. The experimental slags were prepared for the different experiments in a platinum crucible by allowing the mixture of slag components to melt, quenching the melt, and then re-melting to ensure production of homogeneous slags.

The master slag was a three component $CaO\text{-}SiO_2\text{-}Al_2O_3$ system with CaO: 45 weight per cent, SiO_2: 45 weight per cent and Al_2O_3: 10 weight per cent. Flux additions were made by adding 10 weight per cent of the chosen flux to the master slag. The flux compositions used in the present work are presented in Table I.a and I.b. In the case of the CaF_2 addition, subsequent analysis revealed that the CaF_2 content of the resultant slag was only 3.9 weight per cent indicating a loss of fluorine as reported by Shimizu *et al.*[18] (and consequent formation of additional CaO).

Apparatus

A CAMECA SX50 electron probe microanalyser (EPMA) was used in quantitative analysis of the samples. It is a fully automated instrument employing four wavelength dispersive spectrometers in order to analyse various elements. These elements were analysed with the TAP, PCO and PET crystals. All samples were examined using an accelerating voltage of 15 KV, a beam current of 20 nA and a beam size of 1 micron. The instrument was operated with SAMx application software. X-ray intensity distributions were acquired for the main constituents to produce elemental analysis across the area of interest. A MATLAB script program was developed to process the X-ray intensity distribution data. A JOEL 840 scanning electron microscope was used to obtain the backscattered electron images of various phases in the samples operated at 20 KV.

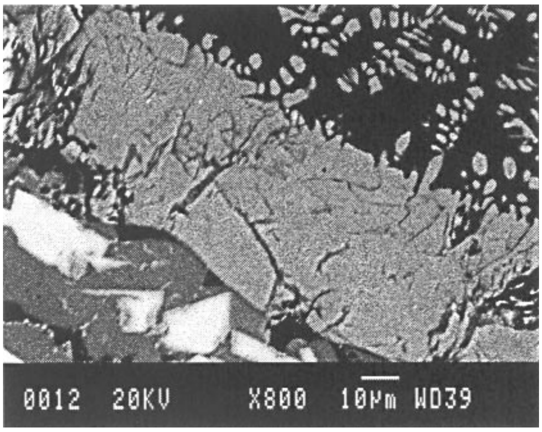

Figure 1. SEM of base slag at 1500°C for time = 0 with 1000x magnification.

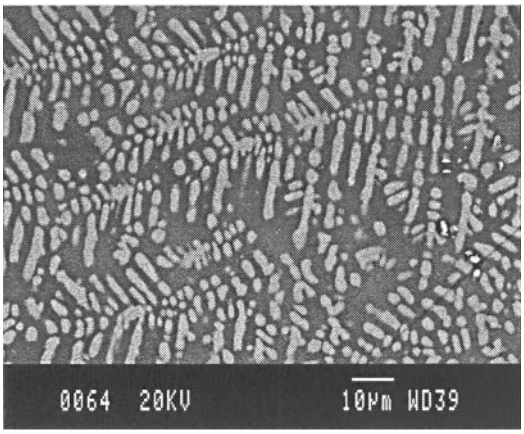

Figure 2. SEM of base slag at 1600°C for time = 0 with 1000x magnification

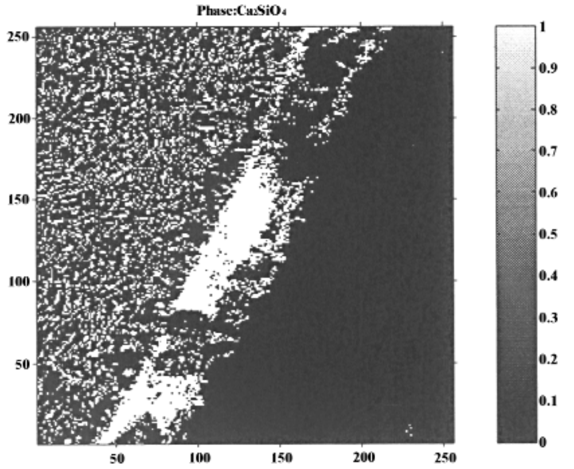

Figure 3. Identified Ca_2SiO_4 phase by MATLAB program for base slag at 1500°C for time = 0 in a 512 by 512 microns area and 256 by 256 image resolution

Experimental procedure

The dissolution of dense lime in molten slag was studied at 1500°C and 1600°C in the time range of 0, 30 minutes and 1 hour. The concentration profiles of different elements in the lime/slag interface were quantitatively measured by EPMA mapping. The CaO dissolved in the slag was also measured as a function of time and slag composition.

The CaO crucibles were filled with various slags and charged to the muffle furnace. The samples were heated slowly at 100°C/h up to 1250°C, which is below the melting point of the slags, in order to minimize the risk of thermal shock in the crucible and then heated quickly at 600°C/h up to 1500°C /1600°C. After the required reaction time, the crucible and slag were taken out of the furnace and quickly quenched in air. In this work, zero time is defined as when the crucible and its contents were taken out of the furnace immediately after reaching 1500°C /1600°C. The crucible

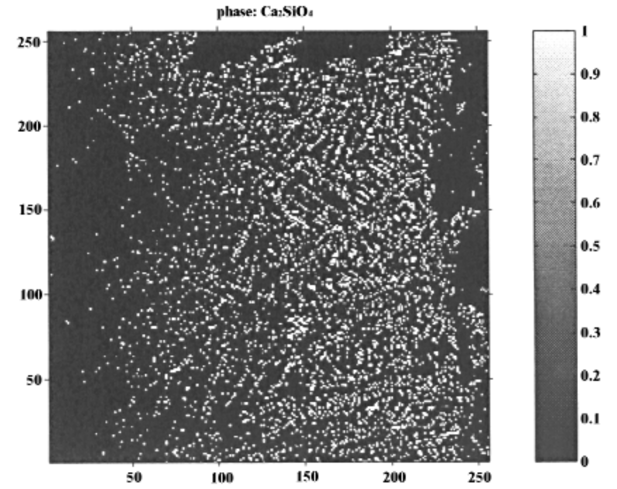

Figure 4. Identified Ca_2SiO_4 phase by MATLAB program for base slag at 1600ºC for time=0 in a 512 by 512 microns area and 256 by 256 image resolution.

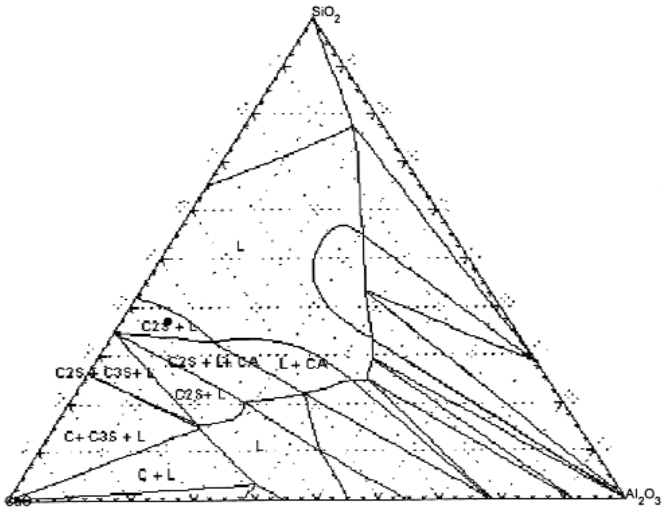

Figure 5.The composition of bulk slag at time = 30 minutes in phase diagram for basic slag at 1500ºC
C2S: Ca_2SiO_4, C3S: Ca_3SiO_5, CA: $Ca_2Al_2SiO_7$, C: CaO, L: liquid slag.

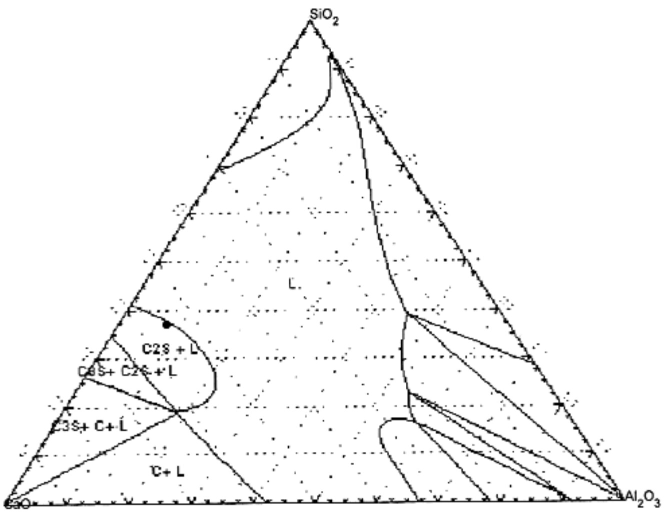

Figure 6. The composition of bulk slag at time = 30 minutes in phase diagram for basic slag at 1600ºC
C2S: Ca_2SiO_4, C3S: Ca_3SiO_5, C: CaO, L: liquid slag

was cut by a diamond saw parallel to the bottom of the crucible. The slice of the crucible and its contents was mounted in resin.

Samples must be provided with a flat and well-polished surface, finished to (0–1) micrometers for EPMA analysis. Therefore, they were polished initially with the Struers waterproof silicon carbide paper at consecutive grits sizes of 320, 800 and 1200 using a Struers Labopol-5 grinding machine at 300 rpm. Since the samples are very sensitive to moisture, a Shell Macron oil was used as the lubricating fluid. Diamond polishing of the specimen was done initially with a chemo-textile cloth (Leco-PAN-W) using polycrystalline diamond paste of 3 microns. The final mirror finish was obtained by using a silk-type cloth (Kemet-MSF) with 1 micron polycrystalline diamond paste. A LECO G25 rotary polisher was used for the final stage of polishing.

Line scan analyses were carried out from the CaO region in the crucible into the slag region. The step size for stage movement was 6 microns. Point analysis was performed for each distinct phase identified using back-scattered electron mode. The MATLAB program converted the concentration profile of each element in the matrix to the mole percentage of various oxides and determined the phase locations in the ternary phase diagram. The phase diagrams at different temperatures were obtained by thermodynamic modeling using the phase diagram module in FactSage[19].

The elemental distribution in the slag adjacent to the slag/crucible layer was mapped by 2 micron step size stage movement in an area of 512 by 512 microns size and at a 256 by 256 image resolution. A MATLAB program was also developed to analyse the results from mapping. This program incorporates a graphics user interface media, which changes the concentration intensity of the maps to the intensity images in order to illustrate the mole percentage of various phases. The program also enabled the recognition of the phases of interest such as Ca_2SiO_4 and Ca_3SiO_5 in the mapped area.

Experimental results

Electron Micrographs at 1500ºC (Figure 1) show formation of the Ca_2SiO_4 layer as per Matsushima *et al.*[10]. However, at 1600 ºC (Figure 2) there is no discrete layer of Ca_2SiO_4 and, moreover, the appearance of the crystallites suggests that they were not present in the liquid phase but only formed when the melt was quenched. Positive identification of the Ca_2SiO_4 phase was obtained via EPMA, mapping by MATLAB program (Figures 3 and 4). Thus it would appear from our results that at normal steelmaking temperatures of 1600ºC, a coherent layer of Ca_2SiO_4 was not observed, although it does not mean that it was not formed at this temperature. According to phase diagrams at 1500ºC and 1600ºC in Figures 5 and 6, it is apparent that the Ca_2SiO_4 crystallization field increases at the lower temperature such that for the given slag composition, Ca_2SiO_4 is expected to form at 1500ºC while at 1600ºC, the slag composition lies just at the boundary of the Ca_2SiO_4 field. However, one would expect the formation of Ca_2SiO_4 to take place at the lime/slag interface.

Figures 7–9 are the concentration profiles measured by EPMA for reaction between the dense CaO crucible and slags at 1600ºC for zero time. During heating from 1250ºC

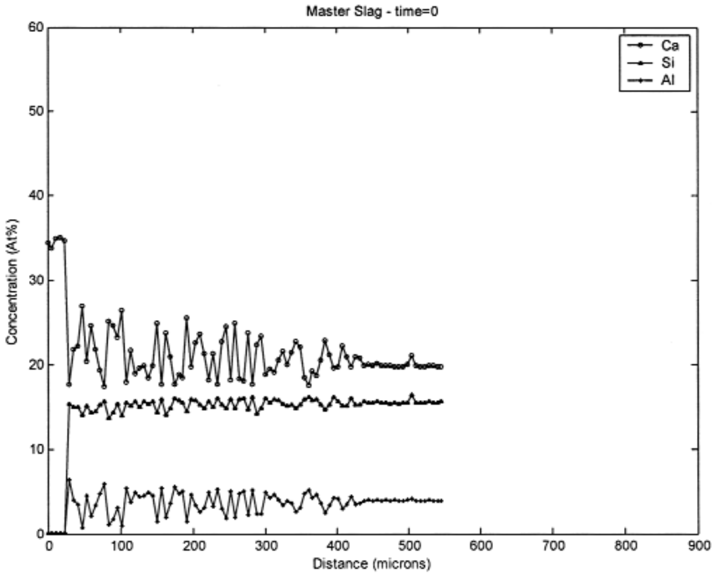

Figure 7. Master slag at 1600ºC for time = 0

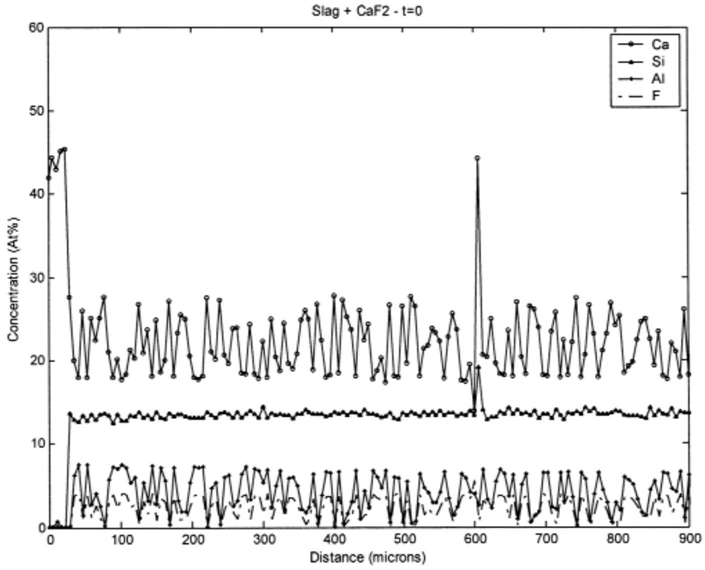

Figure 8. Slag+CaF$_2$ at 1600ºC for time = 0

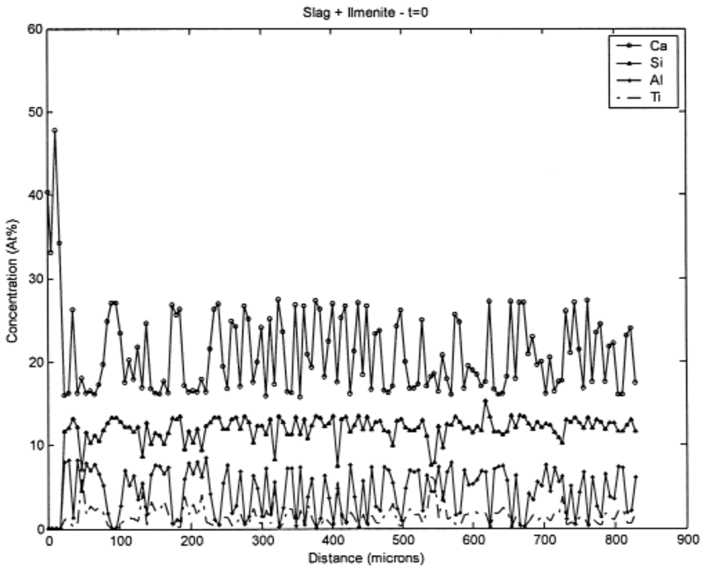

Figure 9. Slag+ ilmenite at 1600ºC for time = 0

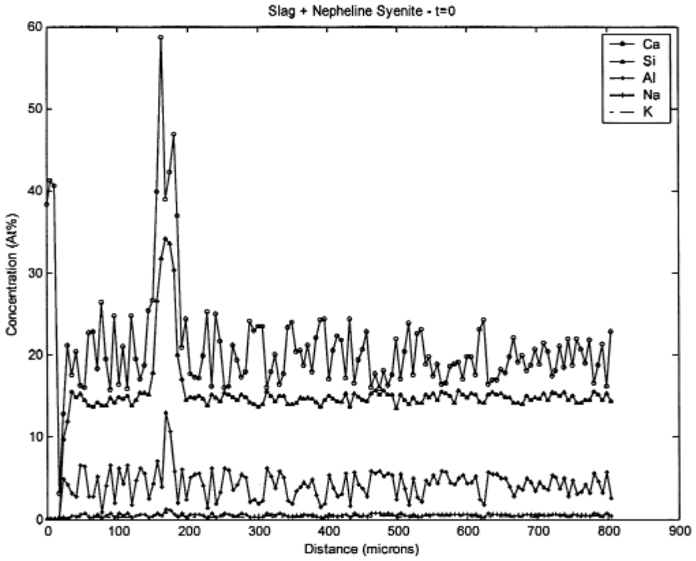

Figure 10. Slag + nepheline syenite at 1600ºC for time = 0

to 1600ºC, some reaction was expected. Individual point analysis was carried out to identify the composition of the slag at different locations of the sample as well as in the di-calcium silicate phase. It is evident from the figures that with the base slag, there is no Ca_2SiO_4 phase in the middle of the crucible while in slags containing flux, Ca_2SiO_4 has crystallized throughout the melt indicating either higher Ca_2SiO_4 concentration and/or better distribution of calcium throughout the melt.

Mass balance calculations were used to estimate the quantity of calcium oxide dissolved by the slag. The underlying assumption was that the increased alumina content of the glassy phase had to be the result of precipitation of Ca_2SiO_4. The mass of slag was calculated from the Al_2O_3 mass balance and the mass of di-calcium silicate was evaluated from SiO_2 mass balance, and finally the CaO dissolved in the slag was found by mass balance of CaO. It is acknowledged that the accuracy of the EPMA results will have a significant effect on the accuracy and thus value of the resulting mass balances. At the same time, the results obtained (Table II) are reasonably self consistent. They indicate that loss of fluoride from the fluorspar flux with consequent increase in slag; CaO content has actually decreased the lime dissolution. With both the ilmenite and nepheline syenite fluxes, there has been an increase in dissolution of CaO with time and flux addition.

EPMA analysis of the CaO crucible indicated that the slag penetrated the intergrannular pores, confirming that porosity of the test specimen would be important in determining rate of dissolution.

Conclusion

The dissolution of dense lime in molten CaO-SiO_2-Al_2O_3 slags was studied at temperatures of 1500ºC and 1600ºC by

Table II Mass (grams) of CaO dissolved in the slags (per 100 grams of slag)

Slags	T=0	T=30 minutes	T=1 hour
Master slag	15.27	21.55	23.76
Slag + CaF_2	11.32	13.9	17.04
Slag + N.S	18.76	23.31	26.39
Slag + ilmenite	29.49	30.89	30.04

reaction of slags with a static lime crucible. The effect of different fluxing agents and time of reaction were investigated. Ilmenite was the most effective flux and nepheline syenite was comparable to fluorspar, increasing the lime dissolution. At 1500ºC a di-calcium silicate layer was formed between the slag and CaO crucible. However, at 1600ºC no di-calcium silicate layer was evident though Ca_2SiO_4 did crystallize out in the slag on cooling. This will be studied further *in situ* using confocal scanning laser microscopy.

Acknowledgments

The project is financially supported by an Australian Research Council grant in conjunction with Abel Metal Services Pty. Ltd. The authors also acknowledge the assistance in EPMA and SEM by Barry Searle at Electron Microscopy Unit, The University of New South Wales.

References

1. NATALIE, C.A., and EVANS, J.W. Influence of Lime Properties on Rate of Dissolution in $CaO-SiO_2-FeO$ Slags. *Ironmaking and steelmaking*, vol. 6, no. 3. 1979. pp. 101–109.
2. EVANS, J.W., and NATALIE, C.A. Kinetics of Lime Dissolution in Steelmaking Slags. *Proceedings International Iron and Steel Congress, 3rd*, 1979. pp. 365–372.
3. NOGUCHI, F., UEDA, Y., and YANAGASE, T. The Mechanism of Calcium Oxide Dissolution into Slag Melts. *Jt. MMIJ-AIME Meet. proceedings World Min. Met. Technol.*, 1976. vol. 2, pp. 685–692.
4. SCHLITT, W.J., and HEALY, G.W. Kinetics of Lime Dissolution in Calcium Oxide-Ferrous Oxide-Silicon Dioxide Slags. *Amer. Ceram. Soc., Bull.*, vol. 50, no. 12. 1971. pp. 954–957.
5. YADAV, U.S., KACHHAWAHA, J.S., and TARE, V.B. Dissolution of Lime in Steelmaking Slag. *Tool Alloy Steels*, vol. 22, no. 10. 1988. pp. 297–302.
6. WILLIAMS, P., SUNDERLAND, M., and BRIGGS, G., . Interactions between Dolomitic Lime and Iron Silicate Melts. *Ironmaking and steelmaking*, vol. V 9, no. 4. 1982. pp. 150–162.
7. SATYOKO, Y., and LEE, W.E. Dissolution of Dolomite and Doloma in Silicate Slag. *British Ceramic Transactions*, vol. 98, no. 6. 1999. pp. 261–265.
8. KIMURA, H., YANAGASE, T., NOGUCHI, F., and UEDA, Y. Studies on the Mechanism of CaO Dissolution into Slag Melts. *J. Jap. Inst. Met.*, vol. 38, no. 3. 1974. pp. 226–232.
9. UMAKOSHI, M., MORI, K., and KAWAI, Y. Dissolution Rate of Burnt Dolomite in Molten Iron Oxide-Calcium Oxide-Silicon Dioxide ($Fe_tO-CaO-SiO_2$) Slags. *Trans. Iron Steel Inst. Jpn.*, vol. 24, no. 7. 1984. pp. 532–539.
10. MATSUSHIMA, M., YADOOMARU, S., MORI, K., and KAWAI, Y. A Fundamental Study on the Dissolution Rate of Solid Lime into Liquid Slag. *Trans. Iron Steel Inst. Jpn.*, vol. 17, no. 8. 1977. pp. 442–449.
11. CALEY, W.F., and MACDONALD, J.B. Influence of Slag Mineralogy on Apparent Viscosity in Secondary Steelmaking. *Ironmaking and Steelmaking*, vol. 28, no. 2. 2001. pp. 96–100.
12. MACLEAN, J.R., KINGSTON, P.W., MACDONALD, J.B., and CALEY, W.F. Potential Role of Feldspar/Feldspathoid Minerals in Secondary Steelmaking. *Ironmaking Steelmaking*, vol. 24, no. 5. 1997. pp. 406–411.
13. TRIBE, T.S., KINGSTON, P.W., and CALEY, W.F. Rheology and Constitution of the $CaO-SiO_2-MgO-CaF_2$ System. *Canadian Metallurgical Quarterly*, vol. 36, no. 2. 1997. pp. 95–101.
14. KINGSTON, P.W., and CALEY, W.F. Nepheline Syenite as a Synthetic Slag Addition in Secondary Steelmaking. *Miner. Eng.*, vol. 2, no. 2. 1989. pp. 207–215.
15. TRIBE, T.S., KINGSTON, P.W., MACDONALD, J.B., and CALEY, W.F. Reduction of Fluorspar Consumption in Secondary Steelmaking. *Ironmaking and Steelmaking*, vol. 21, no. 2. 1994. pp. 145–149.
16. SINGH, B.N., RAVAT, Y.F., CHATTERJEE, A., and CHAKRAVARTY, P.K. Use of Ilmenite Sand as a Substitute for Fluorspar in Open-Hearth Steelmaking. *Ironmaking Steelmaking*, vol. 4, no. 3. 1977. pp. 170–175.
17. POGGI, D., and LEE, H.Y. Massive Ilmenite as a Slag Thinner in Steelmaking. *Canadian Metallurgical Quarterly*, vol. 13, no. 3. 1974. pp. 529–533.
18. SHIMIZU, K., SUZUKI, T., JIMBO, I., and CRAMB, A.W. An Investigation on the Vaporization of Fluorides from Slag Melts. *Ironmaking Conference Proceedings*, 1996. vol. 55, pp. 727–733.
19. BALE, C.W., CHARTRAND, P., DEGTEROV, S.A., ERIKSSON, G., HACK, K., BEN MAHFOUD, R., MELANCON, J., PELTON, A.D., and PETERSEN, S. Factsage. Vers. 5.2. Computational Thermochemistry software and database. École Polytechnique CRCT, Canada and GTT-Technologies GmbH, Germany. 2003.