

from Northeastern University (2006) to Kyoto University (2008) to the University of New South Wales (2010) to Northeastern University (2012)

The 4th Australia-China-Japan Joint Symposium on Iron and Steelmaking

Ⅰ 主编 罗志国 邹宗树



The 4th Australia-China-Japan
Joint Symposium on Iron and Steelmaking



定价:85.00元

The 4th Australia-China-Japan Joint Symposium on Iron and Steelmaking



罗志国 邹宗树 主编

Shenyang, China 3-6 November 2012

© 罗志国 邹宗树 2013

图书在版编目 (CIP) 数据

第四届中日澳钢铁冶金学术会议论文集 = The 4th Australia-China-Japan joint symposium on iron and steelmaking: 英文/罗志国, 邹宗树编. 一沈阳: 东北大学出版社, 2013.11

ISBN 978-7-5517-0475-5

I. ①第··· II. ①罗···②邹··· III. ①钢铁冶金—国际学术会议—文集—英文 IV. ①TF4

中国版本图书馆 CIP 数据核字 (2013) 第 269989 号

出版者: 东北大学出版社

地址: 沈阳市和平区文化路 3 号巷 11 号

邮编: 110819

电话: 024 - 83687331(市场部) 83680267(社务室) 传真: 024 - 83680180(市场部) 83680265(社务室)

E-mail: neuph@ neupress. com

http://www.neupress.com

印刷者:沈阳市第二市政建设工程公司印刷厂

发 行 者: 东北大学出版社幅面尺寸: 210mm×297mm

印 张: 22.75

字 数:910千字

出版时间: 2013年11月第1版

印刷时间: 2013年11月第1次印刷

责任编辑: 孟 颖

责任校对: 子 敏

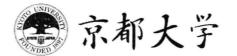
封面设计: 刘江旸

责任出版: 唐敏志

ISBN 978-7-5517-0475-5

定 价: 85.00元







from Northeastern University (2006) to Kyoto University (2008) to the University of New South Wales (2010) to Northeastern University (2012)

Introduction

The fourth Australia-China-Japan joint symposium follows the three successful Australia-China-Japan symposia (Shenyang 2006, Kyoto 2008 and Sydney 2010). The scope of the symposium has extended from raw materials to steel production, covering both fundamentals and applied researches into different processes or operations in iron and steel making. It involves a mix of industrial and academic participants from all three countries.

Consistent with the previous joint symposia, the objectives of this symposium are:

- to provide to researchers and technologists direct access to the three countries' leading science, technological development and forward planning in iron and steelmaking;
- to allow steel companies from the three countries to showcase their own research and technological development; and
- to offer a platform to exchange information and technology in iron and steelmaking, providing awareness of industrial needs in the three countries and exposure to industry representatives.

International Committee:

Professor Jiang Maofa (Northeastern University, China; Chair)

Professor Xue Xiangxin (Northeastern University, China)

Professor Tsukihashi Fumitaka (University of Tokyo, Japan)

Professor Kasai Eiki (Tohoku University, Japan)

Professor Young David (University of New South Wales, Australia)

Professor Yu Aibing (University of New South Wales, Australia)

Local Organizing Committee:

Professor Jiang Maofa

Professor Xue Xiangxin

Professor Shen Fengman

Professor Zou Zongshu

20

Schedule of the Symposium

Saturday 3rd November 2012 — Registration and Reception

Whole day	Registration (Shenyang Huangchaowanhao/Marvelot hotel for Australian and Japanese delegates; Yuning Hotel for Chinese delegates)
18:00—20:00	Reception (finger food and drinks) Place: Scholar Café

Sunday 4th November 2012 — Conference Sessions

(Room 634, Zhixing Building)

		(Room 654, Zhixing Building)	
		sion 1 General Topics 8:20 am—10:00 am Chairpersons: Zhu Miaoyong, Yu Aibing	
1	Ding Lieyun Tsukihashi Fumitaka Yu Aibing	Welcome & introduction Introduction Introduction & opening	10 5 5
2	Jak Evgueni	Integrated experimental and modelling research methodology for the characterization of thermodynamic and physico- chemical properties in metallurgical slags	20
3	Watakabe Shiro	JFE Steel's Recent Development of Ironmaking Technology	20
4	Meng Qingbo	Progress and achievements of cokemaking industry in China—Solid foundation of iron and steel industry	20
5	Bai Chenguang	The progress of high efficiency iron ore granulation	20
	Session 2	Raw Material Preparation 10:40 am—12:00 pm hairpersons: Bai Chenguang, Gupta Sushil	
6	Pinson David	Analysing sintering and blast furnace performance by data mining	20
7	Kashiwaya Yoshiaki	Nondestructive analysis of coke with/without iron catalyst using μ -X-ray CT	20
8	Guo Rui	Relationship between coke properties and solution loss behavior and its influence on post reaction strength of coke	20

Chemistry, structure and quality of iron ore sinter

Lu Liming

Lunch: 12:00 pm—1:20 pm Place: Fengwei Dining Hall

Session 3 Raw Material & Ironmaking 1;20 pm—3:00 pm Chairpersons: Meng Qingbo, Kashiwaya Yoshiaki

10	Holmes Ralph	Effects of CaCl ₂ on sinter RDI and coke CSR	20
11	Xing Xing	Strength, micro-strength and microstructure of carbonaceous materials	20
12	Gupta Sushil	Simultaneous characterization of coke microstructure and mineralogy	20
13	Kasai Eiki	Carbothermic reduction behavior of iron oxide/carbon composite under high pressure	20
14	Wang Deyong	Distribution behavior of phosphorus during smelting reduction of steel slag in iron bath	20

Afternoon Break: 3:00 pm-3:20 pm

Session 4 Ironmaking 3:20 pm—5:00 pm Chairpersons: Wang Qi, Pinson David

Guo Zhancheng	Effects of mineral oxides on the precipitation micro- morphology of metallic iron in the reduction of iron oxides under CO atmosphere	20
Zhao Baojun	Viscosities of blast furnace slags	20
Zhang Wei Li Qiang	Revision of predominant area diagram of iron oxides reduction reactions with CO and $\rm H_2$	20
Shen Yansong	CFD modeling in blast furnace ironmaking	20
Zhou Zongyan	Discretemodeling of gas-solid flow in an ironmaking blast furnace	20
	Zhao Baojun Zhang Wei Li Qiang Shen Yansong	Guo Zhancheng morphology of metallic iron in the reduction of iron oxides under CO atmosphere Zhao Baojun Viscosities of blast furnace slags Zhang Wei Revision of predominant area diagram of iron oxides reduction reactions with CO and H ₂ Shen Yansong CFD modeling in blast furnace ironmaking Zhou Zongyan Discretemodeling of gas-solid flow in an ironmaking blast

Conference: Dinner 5:30 pm—7:30 pm Place: Scholar Café

Monday 5th November 2012 — Conference Sessions

(Room 634, Zhixing Building)

		ssion 5 Steelmaking 8:40 am—10:20 am airpersons: Yang Jian, Tsukihashi Fumitaka	
1	Brooks Geoff	Modelling of oxygen injection and splashing in steelmaking	20
2	Abiko Takashi	Preventing rephosphorization during tapping in BOF steelmaking	20
3	Zhu Miaoyong	The characteristics of air gap formation between slab mold copper plate and solidifying shell during continuous casting of peritectic steel	20
4	Li Guangqiang	An experimental study on silicon-aluminum complex deoxidization of titanium bearing ultra-pure ferritic stainless steel	20
5	Ma Yonglin	Microstructural modification of Q345D steel by air-cooling solidification in different time	20
		Morning Tea: 10:20 am—10:40 am	
		ssion 6 Steelmaking 10:40 am—12:00 pm nairpersons: Li Guangqiang, Brooks Geoff	
6	Taniguchi Shoji	Model study on inclusion coagulation in liquid steel with large difference in initial particle	20
7	Yang Jian	Change in inclusions after MG deoxidation process	20
8	Ji Chenxi	Researches on the evaluation of surface defects of cold-rolled IF sheet	20
9	Matsuura Hiroyuki Tsukihashi Fumitaka	Physical chemistry of Al-Ti deoxidation reaction of molten iron and formed inclusions	20
		Lunch: 12:00 pm—1:20 pm	
		Place: Fengwei Dining Hall	
		ession 7 Steelmaking 1:20 pm—3:00 pm Chairpersons: Qin Liyan, Taniguchi Shoji	
10		ession 7 Steelmaking 1:20 pm—3:00 pm	20
10	(ession 7 Steelmaking 1:20 pm—3:00 pm Chairpersons: Qin Liyan, Taniguchi Shoji Effects of calcium treatment on low carbon Al-Killed steel in	20
	Zhu Wanjun	ession 7 Steelmaking 1:20 pm—3:00 pm Chairpersons: Qin Liyan, Taniguchi Shoji Effects of calcium treatment on low carbon Al-Killed steel in CSP process	
11	Zhu Wanjun Tanaka Toshihiro	ession 7 Steelmaking 1:20 pm—3:00 pm Chairpersons: Qin Liyan, Taniguchi Shoji Effects of calcium treatment on low carbon Al-Killed steel in CSP process Capillary refining of iron alloys by porous CaO with molten slag	20

Session 8 Other Topics & Closing 3:20 pm—5:10 pm Chairpersons: Guo Zhancheng, Tanaka Toshihiro			
15	Long Yue	The research on granulation of gas quenching steel slag by numerical simulation	20
16	Qin Liyan Wang Hongpo	Study on corrosion resistance of stainless steel bars of bridges	20
17	Long Hongming	The influence of dioxin reduction on sintering exhaust gas chemical composition with adding urea	20
18	Pan Yuhua	CFD modeling of slag atomisation by spinning disc	20
19	Akiyama Tomohiro	Combustion synthesis of β-SiAlON	20
20	Yu Aibing Tsukihashi Fumitaka Jiang Maofa	Closing	10
	Ba	rbeque Dinner: 5:30 pm—7:30 pm	
		Place: Foreigner's Dining Hall	
	Wra	np-up discussion: 7:30 pm—9:00 pm	

Tuesday 6th November 2012 — Sightseeing Tour

8:00 am —	Guided One-Day City Tour: Shenyang Imperial Palace etc.
36. 2 1000	, and any any and any

Notes:

- 1) The symposium is open to all individuals (registration is required), but oral presentations are to be given by official delegates representing Australia, China and Japan.
- 2) 20 minutes are allocated for each presentation which includes presentation, questioning and transition for next presenter. PowerPoint presentation is recommended (PC and data projector will be provided).
- 3) Name badge will be provided and is required for attending all technical sessions, morning/afternoon teas, lunches, conference dinners and reception.

Contents · 1 ·

Contents

Session 1 General Topics

Integrated Experimental and Modelling Research Methodology for the Characterisation of Thermodynamic
and Physico-Chemical Properties in Metallurgical Slags Evgueni Jak, Peter Hayes (1)
JFE Steel's Recent Development of Ironmaking Technology Watakabe S, Sato M, Murao A, et al. (14)
Progress and Achievements of Cokemaking Industry in China—Solid Foundation of Iron and Steel Industry
Meng Qingbo, Liu Yang, Xu Xiuli, et al. (24)
Session 2 Raw Material Preparation
Analysing Sintering Performance by Data Mining
Nondestructive Analysis of Coke with/without Iron Catalyst Using μ-X-ray CT
Relationship between Coke Properties and Solution Loss Behavior and Its Influence on Post Reaction
Strength of Coke Guo Rui, Wang Qi (42)
Effects of CaCl ₂ on Sinter RDI and Coke CSR Lu L, Holmes R J, Hapugoda S, et al. (49)
Chemistry, Structure and Quality of Iron Ore Sinter Lu L, Hapugoda S, Adam M, et al. (52)
Strength, Micro-Strength and Microstructure of Carbonaceous Materials
Simultaneous Characterization of Coke Microstructure and Mineralogy
Gupta S, Lester E, Ismail M, et al. (63)
Carbothermic Reduction Behavior of Iron Oxide/Carbon Composite under High Pressure
Study on Sintering Solid Fuels Optimal Particle Size
Zhou Mingshun, Liu Jie, Wang Junshan, et al. (75)
Thermal Analysis Kinetics of Graphite-CO ₂ /H ₂ O Gasification
Liu Zhongsuo, Wang Qi, Zou Zongshu, et al. (81)
Discussion about Operation Technology of Low Fuel Ratio of Meigang Blast Furnace
Han Hongsong, Jin Ming (89)
Effect of Coke Micro-Textural and Basic Metal Oxide on Coke Strength Characteristics
Session 3 Ironmaking
Distribution Behavior of Phosphorus during Smelting Reduction of Steel Slag in Iron Bath
Cui Yuyuan, Zhang Tongsheng, Wang Deyong, et al. (99)
Effects of Mineral Oxides on the Precipitation Micro-Morphology of Metallic Iron in the Reduction of Iron
Oxides under CO Atmosphere Zhao Zhilong, Guo Zhancheng, Tang Huiqing (103)
Viscosities of Blast Furnace Slags Chen Mao, Zhang Dianwei, Zhao Zhixing, et al. (110)
An Overview of CFD Studies of Pulverized Coal Injection in Blast Furnace
Shen Yansong, Yu Aibing, Zulli Paul (118)
Discrete Particle Simulation of Gas-Solid Flow in an Ironmaking Blast Furnace
Zhou Zongyan, Liu Sida, Yu Aibing, et al. (131)

Thermodynamic Study on Solid Direct Reduction Process of Chromite	
Zhao Qing, Liu Chengjun, Jiang Maofa	(146)
Discussion on the Feasibility of Coke-Oven Gas Used in the Shaft Furnace	
	(152)
Study on the Effect of Caustic Calcined Magnesite to Quality of Green-Pellets	(156)
Reduction Kinetics of Carbon-Containing Bayan Obo Ore Pellets	(150)
	(159)
Effect of Chute Angle on Pile Structure under the Mixing Charging	
Li Haifeng, Luo Zhiguo, Han Lihao, et al.	(163)
Design and Maintenance of Prolonging the Campaign Life of Baosteel No. 3BF	
Liang Lisheng, Wei Guo, Shen Fengman Study on the Direct Reduction of Nickel Laterite and Separation Machanism of Direct Reduction	(169)
Study on the Direct Reduction of Nickel Laterite and Separation Mechanism of Direct Reduction of Nickel-Ore	(176)
Thermodynamics Behavior of Vanadium in the Chlorination Process of Vanadium-Bearing Titanomagnetit	
Session 4 Steelmaking	
Modelling of Supersonic Oxygen Jet Injection inside Steelmaking Furnace	
Morshed Alam, Geoffrey Brooks, Jamal Naser	(184)
Preventing Rephosphorization during Tapping in BOF Steelmaking	y 10 14310 (g)
Takashi Abiko, Takashi Sugitani, Atsushi Tazuke, et al.	(193)
The Characteristics of Air Gap Formation between Slab Mold Copper Plate and Solidifying Shell during Continuous Casting of Peritectic Steel	(199)
An Experimental Study on Silicon-Aluminum Complex Deoxidization of Titanium Bearing Ultra-Pure	(1)))
Ferritic Stainless Steel Li Guangqiang, Li Yongjun, Yuan Gang, et al.	(208)
Microstructural Evolution of Simulated Coarse-Grained Heat-Affected Zone of New HSLA Q690D	
Lu Hengchang, Li Zhe, Chen Zhongyi, et al.	(214)
Model Study on Inclusion Coagulation in Liquid Steel with Large Difference in Initial Particle Sizes	(210)
Change in Inclusions after Mg Deoxidation Process Yang Jian, Zhu Kai, Wang Ruizhi, et al.	
Researches on the Evaluation of Surface Defects of Cold-Rolled IF Sheet	(220)
	(232)
Physical Chemistry of Al-Ti Deoxidation Reaction of Molten Iron and Formed Inclusions	
Hiroyuki Matsuura, Wonjin Choi, Fumitaka Tsukihashi	(238)
Effcet of Calcium Treatment on Low Carbon Al-Killed Steel in CSP Process Zhu Wanjun, Ou Tie, Wang Chunfeng, et al.	(244)
Capillary Refining of Iron Alloys by Porous CaO with Molten Slag	(244)
	(250)
Study on Periodic Fluctuation of CC Slab Mould Level	
Jiang Zhongkuai, Cheng Nailiang, Chen Zhiping	(255)
Effect of Agitation on Crystallization of Calcium Silicate Based Slags	(9:0)
The Slag Melting Characteristic and its Recycling Use Effects for BOF Less Slag Smelting Wu Wei	
Development and Application of Online Mold Monitor System	(200)
Tian Yong, Zhang Xiangchun, Dai Wenmao, et al.	(273)
Microstructural Modification of Q345D Steel by Air-Cooling Solidification in Different Time	()
Li Zhe, Ma Ru, Liu Bingguang, et al.	

Thermodynamic Research of MnS Precipitation in the Process of the Slab Continuous Cast	
Zhang Ning, Guo Xiaobo, Zhao Cheng-lin, et al.	(284)
Thermodynamic Study on Precipitation Behavior of Inclusions in 09CuPCrNi Steel with Rare Earth	
during Solidification Li Yandong, Liu Chengjun, Jiang Maofa	(291)
BOF End-Point Prediction Model Based on Nonlinear Homotopic BI Algorithm	(/
Feng Mingxia, Chen Ren, Li Qiang, et al.	(295)
Occurrence State of Niobium and Titanium in High Pure Ferritic Stainless Steel	(=>0)
	(302)
Aging Behavior of Boron Bearing Low Carbon Steel with Various Copper Contents	(002)
Zhang Zhihong, Xue Xiangxin	(306)
Mold Flux Design in Terms of Crystallization Control	(500)
Masahito Hanao, Yuichi Tsukaguchi, Masayuki Kawamoto	(310)
viasainto Tianao, Tulcin Tsukagucin, wasayuki Kawainoto	(310)
Session 5 Other Topics	
The Research on Granulation of Gas Quenching Steel Slag by Numerical Simulation	
Long Yue, Cai Zhenlei, Zhang Yuzhu	(315)
Study on Corrosion Resistance of Stainless Steel Bars for Bridges	<u>,</u>
	(319)
The Influence of Dioxin Reduction on Sintering Exhaust Gas Chemical Composition with Adding Urea	(,,
Long Hongming, Li Jiaxin, Wang Ping	(324)
CFD Modelling of Slag Atomisation by Spinning Disc Pan Yuhua	
Combustion Synthesis of β-SiAlON	
The Research on the Effect of Cooling Rate on Isothermal Crystallization Kinetic of C ₂ S in Gas Quenchin	
Steel Slag	_
Entang Tabha, Bao silver, Bong Tae, et al.	(334)
Experimental and Calculation Analysis on Characteristics of Combustion Jets	(334)
Experimental and Calculation Analysis on Characteristics of Combustion Jets	
Akihide Kaizawa, Takeo Inomoto, Yuji Ogawa, et al.	
	(339)

Integrated Experimental and Modelling Research Methodology for the Characterisation of Thermodynamic and Physico-Chemical Properties in Metallurgical Slags

Evgueni Jak, Peter Hayes

PYROSEARCH, Pyrometallurgy Research Centre, School of Chemical Engineering, The University of Queensland, Brisbane, Queensland, 4072, Australia E. Jak@uq. edu. au

Abstract After decades of careful experimental studies a great deal of fundamental information on the phase equilibria, and the thermodynamic and physico-chemical properties of the major slag systems encountered in metallurgical processes has been obtained. With the availability of advanced fundamentally-based modelling tools it is now possible to critically analyse these data with the aim of incorporating this information into self consistent databases, and accurate thermodynamic and physico-chemical property models of these systems.

The new approach to the characterization of these systems, involving the integration of both experimental and modelling studies is necessary in order provide more accurate descriptions of complex chemical systems.

The approach not only enables the critical data required to construct accurate models to be identified but also minimizes the experimental efforts required to characterize these systems. The advantages of an integrated approach to future thermodynamic and other slag property studies will be discussed, new experimental techniques and approaches that can be used for the characterisation of phase equilibria and physico-chemical properties in complex systems described, and examples of the approach provided.

Keywords slags; phase equilibria; thermodynamic modelling; viscosity modelling

1 Introduction

After decades of experimental studies a great deal of fundamental information on the phase equilibria, and the thermodynamic and physico-chemical properties of the major slag systems encountered in metallurgical processes has been obtained. These data are readily available in compilations such as Phase Diagrams for Ceramics^[1] and Slag Atlas^[2]. Many of these previous studies have focused on lower order systems, binaries and ternaries. The slags of interest in industrial practice, however, consist of multicomponent, multi-phase systems, and there is still

relatively little experimental information available on these higher order (4, 5 or more component) systems. Accurate measurement of high temperature slag phase equilibria and physico-chemical properties is particularly difficult and very time consuming.

The increased chemical complexity of industrial systems brings with it an exponential increase in the number of variables to be considered and associated practical difficulties so that a solely experimental approach in characterising these multi-component systems becomes increasingly prohibitive with the increasing number of components^[3].

The increase in the memory and speed of computers over the recent decades, along with development of theoretical knowledge about slags, has set the foundation for the development of advanced fundamentally-based, computer modelling tools. These tools describe can chemical thermodynamic and physicochemical properties over wide ranges of conditions rather than empirical fits to data sets that are valid over limited ranges of process conditions. This modern approach is reflected in the CALPHAD methodology used in thermodynamic modelling. The ultimate aim of this type of analysis is to incorporate this information into self-consistent databases, and accurate thermodynamic and physicochemical property models of these systems; these models will then be available to interpolate and extrapolate into compositional areas that are sparsely populated or contain no experimental information. These then are the key design tools for the future to improve operations and efficiencies.

2 Integrated Experimental and Modelling Approach

Historically the approach to thermodynamic and

physico-chemical database development has been to first undertake experimental work and subsequently, after the experimental work was completed, to incorporate available experimental data into a model. In the integrated experimental and modelling approach experimental studies and model development are undertaken in parallel, not sequentially. Significant advantages to the overall research progress can be achieved if this integrated approach is implemented right from the start of the work. The thermodynamic and property assessments based on the existing models can be used to plan individual experiments, the results of the experiments can then be used to iteratively adjust the set of model parameters, and the improved model can then be used to inform the next stages of the research. This makes it possible to more accurately target the critical data that are required to improve the description of the system, to enhance the quality of the research outcome and to improve the productivity of the research effort. Implementation of such an integrated approach combining advanced experimental and modelling methodologies in practice is a challenge. Some experiences in development of this integrated approach by the authors of this paper over the previous decade are outlined below.

3 Phase Equilibria and Elemental Partitioning in Complex Multiphase Systems

3. 1 Thermodynamic Modelling

Chemical thermodynamic databases not merely compilations of measurements but mathematical descriptions of the thermodynamic properties of the system. These databases developed through an optimisation process involves both the selection of appropriate thermodynamic models for all phases in a given system, and the critical evaluation of all available thermodynamic and phase equilibrium data. The thermodynamic model parameters are selected so as to obtain a self-consistent set best reproducing the experimental data as functions of temperature and composition[4].

In the thermodynamic "optimisation" of a system, all available thermodynamic and phase equilibrium data for the system are evaluated simultaneously to obtain one set of model equations for the Gibbs free energies of all phases as functions

of temperature and composition. From these equations, the thermodynamic properties and the phase diagrams can be back-calculated. Thermodynamic property data, such as, activity data, can aid in the evaluation of the phase diagram, and conversely phase diagram measurements can be used to deduce thermodynamic properties. In this way, the thermodynamic databases are developed and all the data are rendered self consistent and consistent with thermodynamic principles [4].

The types of data incorporated in the databases include not only phase equilibria data such as solubility limits in complex solutions, liquidus, solidus, but also many other types of data including heats of formation, heat capacities, Gibbs free energies compounds reactions. thermodynamic activities in solution phases, crystal structure information and data on special transition reactions including magnetic transformations, and other relevant information. In an optimised database the same model parameters should be valid over the whole composition range from binary and ternary to multi-component systems. To achieve this outcome the optimisation of the parameters is performed in a number of cycles from binary and ternary to the multicomponent systems and back, so that binary and ternary parameters are re-optimised to reach agreement with the data sets in multi-component space.

Examples of the application of this thermodynamic modelling approach to the development of the key slag databases used in the FactSage computer system are described elsewhere $^{[4\text{-}12]}$. In particular this approach has been successfully applied to the Al $_2$ O $_3$ -CaO-"FeO"-Fe $_2$ O $_3$ -MgO-SiO $_2$ system $^{[10]}$, which is central to the chemistry of iron and steelmaking processes.

3. 2 Experimental Techniques

In addition to using the computing power in the analysis and modelling of these systems new advanced characterisation tools are now available to enable the identification of phases and phase compositions at a microscopic level. The powerful tool that has emerged over the past decade for applications involving the determination of phase equilibria in complex slag systems has been electron microprobe X-ray analysis (EPMA).

The use of the equilibration/quenching/EPMA experimental approach has significant advantages over

conventional approaches to liquidus and phase equilibria determination [4, 13-15]. The approach can be clearly explained with reference to Fig. 1. A small quantity of oxide mixture, with bulk composition X, is prepared from pure powders, pelletised and equilibrated at temperature T_1 below the liquidus so that two phases (or more in higher order systems) are formed. Following equilibration the sample is cooled rapidly by quenching, the result is that the phases present at high temperature and their compositions are retained to room temperature. The liquid phase is retained as an amorphous glass phase, and the solid phase(s) present at temperature are readily identified in the microstructure. The compositions of the glass (liquid) and solid phases are then measured using EPMA. The equilibration temperature is controlled to within 6 K or better, and compositions are measured with EPMA with accuracy within 1 wt% better^[4, 13-15]

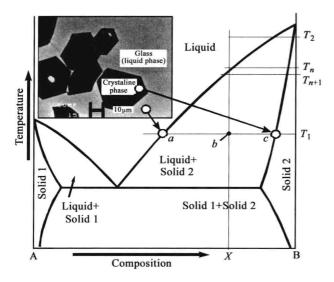


Fig. 1 Quenching experimental technique (conventional and based on EPMA measurements) for phase equilibrium $\det(A, 13-15)$

Utilization of the quenching technique enables the advantages of static phase equilibrium determination techniques, in particular, accurate control and verification of achievement of equilibrium to be exploited. This is particularly important for systems in which the approach to equilibrium is slow, and dynamic techniques (such as DTA) run the risk of providing inaccurate information originating from metastability.

The advantages of the equilibration/quenching/ EPMA technique are discussed by the authors in more detail in previous publications^[4, 13-15]; a number of main points particularly important for the expansion of the range of applications of this technique to various complex production slags are listed below.

- (1) The phase compositions are measured at the completion of the equilibration so that changes of bulk composition of samples during experiment that usually take place in high-temperature phase equilibria studies due to a) vaporization, b) reactions with containment material, or c) reactions between phases (e.g. metal/slag/gas phases) do not affect the accuracy of final results.
- (2) Only a small sample size (down to 10-50 needed for μm) is accurate composition measurements using EPMA — this essential factor means that only small sample mass is required. The consequence of this is that of extremely rapid cooling rates within the liquid phase to be achieved (105-106 $K \cdot s^{-1}$) especially when the sample can be directly exposed to the quenching medium rather than being retained in a crucible. This has been particularly important in enabling the development of substrate suspension techniques, where a slag film is supported by surface tension forces as a film on the outside of the substrate.
- (3) The compositions of all phases in equilibrium are measured enabling the determination of not only liquid compositions, but, importantly, the compositions of solid solutions coexisting with these liquids. These tie-lines provide valuable information required for model development.
- (4) The methodology is readily extended to the determination of multi-component, multi-phase equilibria. The solid phases can be identified exactly from their compositions, and accurately measured with EPMA.
- (5) The achievement of equilibrium within the system can be directly tested by measuring compositional profiles across phases; at equilibrium each phase should have a uniform composition. Any compositional variation with the individual phases, indications that equilibrium has not been achieved, can be detected. The presence of metastable phases can also be identified.
- (6) The use of very small slag masses (0.1g) means that gas/slag equilibria are readily obtained and equilibrium can be achieved in relatively short times.
- (7) The rapid quenching rates achievable ($10^5 \, \text{K} \cdot \text{s}^{-1}$) greatly extends the range of compositions that can be characterised; recent work has demonstrated that the technique can be used to characterise silica-free slags,

mattes and selected alloys.

- (8) Minor element partitioning in multiphase systems under controlled gas, e. g. $P_{\rm O_2}$, $P_{\rm S_2}$ conditions can also be determined using this approach.
- (9) In systems in which vapour phase losses of metal components are unavoidable it is still possible to establish, through the use of EPMA, local equilibria between condensed phases in the samples.
- (10) The use of the primary phase substrate support technique avoids contamination of the melts; enabling liquidus isotherms to be readily and accurately determined in reactive chemical systems. The accuracy of the analysis is in most cases comparable to that achievable in wet chemical analysis. The selection of compositions to be studied can be assisted through the use of existing theoretical

knowledge including the phase rule, Alkemade theorem, lever rule, Schreinmeher's rule and through thermodynamic modelling tools $^{[4,\ 13-15]}$.

3. 3 Examples of Multi-phase Equilibria in Controlled Gas Conditions

The integrated experimental and modelling approach, and the use of improved experimental techniques, has enabled critical data to be obtained from systems that could previously not be characterised using conventional techniques. An example of this is the successful measurement of liquidus isotherms in the systems FeO_x-CaO-SiO₂ under controlled oxygen partial pressures using platinum metal support and primary phase substrate support techniques (Figs. 2 and 3) [16].

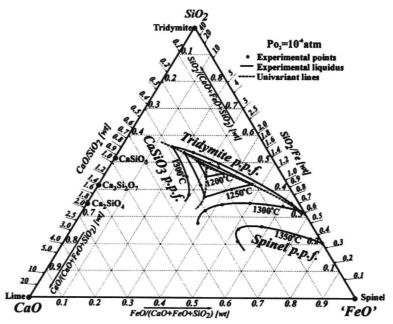


Fig. 2 Liquidus isotherms in the "FeO"-CaO-SiO $_2$ system at 1200°C, 1250°C, 1300°C, and 1350°C at a $P_{O_2} = 10^{-6}$ atm^[16]

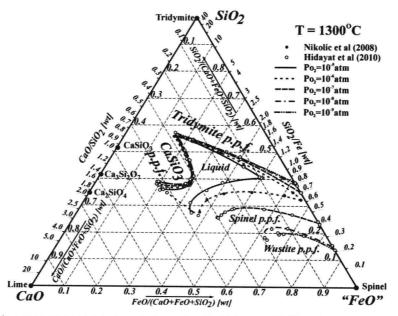


Fig. 3 Effect of oxygen partial pressure on liquidus surfaces in the system Ca-Si-Fe-O at 1300°C and projection onto the FeO-CaO-SiO₂ plane^[16]