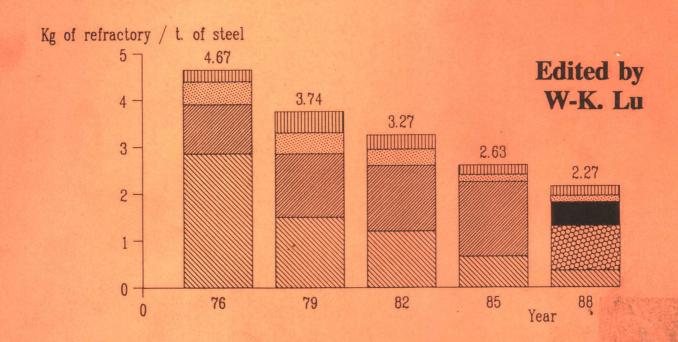
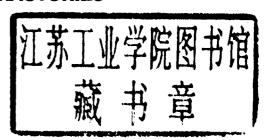
MCMASTER SYMPOSIUM NO. 18 MAY, 1990

EVOLVING ROLES AND EXPECTATIONS OF STEELMAKING REFRACTORIES



MCMASTER SYMPOSIUM ON IRON AND STEELMAKING, No. 18

EVOLVING ROLES AND EXPECTATIONS OF STEELMAKING REFRACTORIES



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Peter MacPhail, Algoma Steel
Wei-Kao Lu, McMaster University (Secretary)

McMaster Symposium on Iron and Steelmaking, No. 18

Evolving Roles and Expectations of Steelmaking Refractories

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PREFACE

This book contains the papers and discussions of the Symposium on EVOLVING ROLES AND EXPECTATIONS OF STEELMAKING REFRACTORIES. The discussions were recorded on tape during the proceedings and the resulting transcripts were sent to the individual contributors for editing.

Sincere thanks and appreciation go out to the many authors and other participants who made this 18th McMaster Symposium on Iron and Steelmaking both possible and successful. Special thanks are given to all the members of the Organizing Committee, particularly to Trevor Wright of Dofasco Steel, for his leadership as Chairman. Thanks and appreciation are also due to the Staff and students of the Department of Materials Science and Engineering of McMaster University, particularly to Linda Palmer, whose help was invaluable, and to the many people who worked behind the scenes to make this symposium an exciting and memorable event.

W-K. Lu

Symposium Secretary

OPENING REMARKS

As Chairman of the Organizing Committee, it is my pleasant task to open the 18th Annual McMaster Symposium.

To our participants from Australia, Japan and Europe and also our neighbours south of the border, welcome to Canada, and to everyone, welcome to Hamilton.

My name is Trevor Wright, and the other members of the Organizing Committee are: Terry Bonham of Stelco Steel, Peter MacPhail of Algoma Steel, and the corner-stone, from year to year, of this symposium, Professor Wei-Kao Lu of McMaster University. There is also a fifth person who is not named in your program, but without whose efforts, the next two days would not happen, Linda Palmer.

My apologies to our American friends for interrupting your Memorial Day Holiday to travel up here. However, when it came down to either interfering with our Victoria Day holiday last week or your Memorial Day holiday this week, well !!!

The topic of this year's Symposium is "Evolving Roles and Expectations of Steelmaking Refractories." We feel this is a very pertinent topic because as operators, we certainly have high expectations of our refractories. Over the next two days we will hear 15 papers on the subject. We keep the registration below 100 to encourage discussions, and we do expect some lively discussions. We have operations, and refractory experts (both Steel Plant and Manufacturers) with a sprinkling of academics, so we have a good mix for our discussions. I am sure that at the end of the two days, we will all have learned something new.

You will get a chance to edit the text before its published, so you don't have to worry about saying something now and getting hung out to dry at some time in the future. There is another item we have to mention, on the program there is a group photograph that was scheduled for the coffee break this morning, that has been delayed until this afternoon, pending more clement weather because the picture will be taken outside. I don't think there are any more official announcements, apparently there were some comments about how slides were operated last night, we do have a remote control at the front for slides.

We have representatives here from operations, refractory experts here from the steel companies, experts from the manufacturers and we also have a sprinkling of academics, I think a good mixture for a very good symposium. So with that, I would like to introduce Dr. Gary Purdy, who is the Dean of Engineering at McMaster University.

Trevor Wright Symposium Chairman

WELCOME ADDRESS

DR. G.R. PURDY - DEAN OF ENGINEERING MCMASTER UNIVERSITY

Thanks very much. I've just learned a collective noun for academics, "sprinkling". Its a pleasure on behalf of the University to welcome you here to the annual McMaster Symposium, this is the 18th I understand. It has become a tradition here that for a couple of days in May a number of people gather from all over the world, participate in open discussion, exchange ideas and to learn. I have just learned that you have the opportunity to edit what you say afterwards, this is a brilliant idea, I wish I could have it more often.

The topic this year concerns the development of refractories for steelmaking. I am pleased but not surprised to see such a representation from a number of countries, companies and sectors from all around the world. I am a physical metallurgist so I bring to this meeting no knowledge of refractories, but I am aware of the capital intensive nature of the steelmaking process and the consequent importance of evolutionary change in maintaining competitiveness in the global economy. Revolutionary change, abrupt paradigm switches within the ferrous metallurgy industry is rare. It is not often likely to occur in the working lifetime of a metallurgical professional, but incremental change toward an optimum assistance performance is the technological lifeblood of the steel industry.

So I welcome you today, I hope you take part, by giving and receiving information that will help you work towards that optimum. Several years ago I was called upon to perform this same kind of task to welcome the participants to the Symposium, I made the mistake of looking up the term Symposium in the concise Oxford Dictionary and the definition went something like this: Symposium, a conference; (which makes sense) a collection of essays on a particular subject; (and I think you will see that the outcome of this symposium to be something of that sort) a philosophical or friendly discussion; (I thought thats nice, it sets a tone for the kind of interaction you can expect to have in the next couple of days). The final definition is from the Greek, "a drinking party", it says that its a drinking party with song and dance. Now the first two fit very well, I hope you will find the discussions very friendly as well as informative and animated and perhaps the last definition of the Greek use of the word is not totally inappropriate, but we will see about that later on. Please enjoy your stay at McMaster, I hope the weather improves considerably and please come again.

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UNDERSTANDING THE BEHAVIOR OF OXIDE REFRACTORIES CONTAINING CARBON AND METAL ADDITIONS - SOME RECENT ADVANCES

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Abstract: - The marked improvements in refractory life enabled through the use of higher purity oxides and graphites and metal additions in resin-bonded shapes during the last decade far over ran the scientific awareness of the high temperature chemistry of these materials systems. Current efforts to gain fundamental understanding of these advanced refractory systems will be discussed together with challenges posed by testing and characterization requirements.

INTRODUCTION

Advances in BOF steel-making refractories have been accomplished in stages over the past 15-20 years largely through engineering studies. A feedback of evaluation data in the form of wear-rates in particular and post-mortem examination has allowed the refractory producers to move from plateau to plateau in a process of steady but discontinuous improvement of these products. The most notable assents to new levels have been:

- 1. The original introduction of the MgO-carbon refractory to replace dolomitic materials.
- 2. The replacement of pitch-type bonds with resin bonds for high wear applications.
- 3. The sharply increased use of graphite in the carbon component on the bricks.
- 4. The utilization of pure metal and alloy powders to suppress the rate of oxidation of the carbon at the working face of the refractory.

The parameters associated with the refractory components, the grains of MgO, the graphites and the binders have been extensively manipulated and moved to optimum levels in terms of wear performance. There are few doubts remaining as to the grades and physical characteristics one would use in the development of a refractory which would demonstrate maximum performance for a given set of demands and conditions, discounting economic considerations. Problems arise due to the fact that the demands and the conditions vary widely between use sites and even within use sites with the result that a refractory with a set of "good" parameters does not perform uniformly. In fact many contradictions exist between reports of improvements based on adjusting the materials parameters of BOF refractories.

For example, one study will show a pronounced effect of the purity of the MgO while a second study discovers no correlation to performance. Again, a particular study may point to an optimal graphite content or metal content which do not coincide with effective levels proven in yet another study. A large number of the process parameters also enter into refractory performance and this explains in part why so few systematic laboratory studies have been done to aid in explaining the many contradictions in reported experiences. The problem of simulation of the thermo-chemical conditions which take place in the contact zone between the slags, the atmosphere and the refractory is formidable.

I would like to proceed by reviewing the function of each of the components of the refractory system and then discuss those theories and ideas which purport to explain the functioning of the modern MgO-carbon-metal refractory systems which constitute products in active service.

I. MgO

Magnesia, with its simple crystal structure and absence of polymorphic forms and its straightforward thermochemistry has few demerits as the ideal refractory aggregate for contact with basic metallurgical slags. It was considered the sole candidate material for MHD (magnetohydrodynamic) combustors to be used for the production of coal plasmas at temperatures above 2100°C. It is also considered to be the only refractory which could serve as the turbine blade material for the Mach 25 National Aerospace Plane in very early stages of development in the U.S. The high thermal expansivity of MgO severely handicaps its use for the latter application. This problem with the thermal expansion of MgO is an old one for refractory technologists who have learned to accommodate it in various ways. A second relevant problem has to do with the relatively facile reduction of MgO in reducing atmospheres.

While direct vaporization is not a real concern in BOF applications it is interesting to recall the comparative vaporization of MgO and Al_2O_3 , presented in Table I, which lists results obtained in vacuum⁽¹⁾. MgO rates are several orders of magnitude greater than those for Al_2O_3 at 1900° C. Thirty percent of porosity approximately doubles the rate of vaporization and substantially increases the vaporization coefficient as is seen in Figure 1. Impurities tend to vaporize in proportion to their vapor pressure but not if they are initially present at a very low level or if they form spinels with MgO e.g. Al_2O_3 and Cr_2O_3 as depicted in Figure 2.

Table I. Langmuir's Vaporization Rates of MgO and Al₂O₃ Single Crystals

	Oxide Temp. (°C)	Vaporization Rate (x10 ⁵ g∙cm ₋₂ ∙S ₋₁)	
	Oxide Temp. (C)	(x10° g°ciii ₋₂ °5 ₋₁)	
MgO	1400	0.53	
	1500	4.66	
	1550	14.9	
	1600	38.9	
	1640	79.3	
	1700	242	
	1800	1260	
	1900	1390	
Al ₂ O ₃	1850	0.773	
	1900	2.02	
	1955	7.10	

The effect of pO_2 on the vaporization of MgO by either of two reactions is straightforward:

$$MgO(s) = Mg(g) + *O_2$$
$$MgO(s) = MgO(g)$$

Figure 3 is a plot of the vapor pressures of MgO and Mg as a function of pO $_2$ at 1600°K and 1900°K, respectively, and shows that Mg has the higher vapor pressure with pO $_2$ = 10⁻² at 1900°K and at pO $_2$ = 10⁻⁸ at 1600°K. Consequently, gaseous MgO will not be expected under any of the conditions in a BOF process.

II. Magnesia-Carbon

The principal chemical effect of carbon in a magnesia aggregate/matrix powder system is to limit the extent of slag penetration and many studies have shown that the slag incursion does halt at the interface between the carbon depleted and undepleted zones. These extend no more than 6-8 mm from the slag surface layer and render the carbon free zone susceptible to the effects of reactions between the slag constituents and the magnesia impurities and impurities from the pyrolysis of the carbon sources. The excellent non-wetting properties of carbon are advantageous here as well.

The main thermo-physical effects of introduced carbons were to introduce some sufficient level of bonding and to provide pyroplasticity to allay effects of temperature change. Discontinuous spalling was the Achilles heel of direct and silicate bonded basic refractories in use before the "carbon" era and has been completely eliminated by optimal levels and types of carbon for various applications.

The carbon derived from binder carbon behaves variably as is well shown in a study by Fitchett and Wilshire⁽²⁾. The following figures from their work show the effects of carbon source (pitch versus cured resin-bonded) on magnesia brick hot strength, with and without graphite. The graphite diminishes the low temperature strength of a tempered pitch bonded material more than the intermediate temperature strength and greatly diminishes the strength of the resin bond at all temperatures. Effects of temperature on resin bond toughness is seen in Figure 4. The pitch bond has the advantage of toughness to a much higher temperature (of coking) than does the resin bond. Effects of mixing are pronounced as illustrated in Figure 5. Plastic collapse can occur at temperatures as high as 600°C in a poorly mixed resin-magnesia system.

At the working temperature of a BOF the carbon from whatever source has the capacity to reduce the MgO via the reaction:

$$MgO + C = Mg(g) + CO$$

Early authors had observed and speculated on the mode of formation of a dense MgO layer and on the ramification of the layer for the service life of the lining (3,4). The layer is inconsistently observed in practice in the melt region as well as in the slag contact region. The source of oxygen for the reaction to form the dense layer is variously considered to come from the iron oxide in the slag, from the furnace atmosphere or from the reaction gases developed within the refractory. Watanabe et.al. produced dense zones in laboratory studies of MgO-C mixes confined in a graphite crucible or in contact with an iron-free slag (5). They postulated that build-up of pressure of Mg(g) and CO(g) in the interior of the refractory could release through fissures in the dense MgO layer effecting "repair".

An often encountered effect of the CO atmosphere produced by the carbon presence is the blackening of the MgO grains due to precipitation of metals including Si, Al and Ca⁽⁶⁾. The authors presumed that by 1400°C the reaction between MgO and C is so rapid that equilibrium is reached i.e., for:

$$MgO(s) + C(s) = Mg(g) + CO(g)$$
 (1)

Al 1527°C and assuming that furnace pressure is about 1 atm., the CO(g) pressure, pCO \le 1. Further assuming the equilibrium

$$C(s) + *O2(g) = CO(g)$$
 (2)

the respective partial pressures for the three gases were calculated to be, at the MgO grain surface;

$$PMg \ge 10^{-2.7}$$

$$pO_2 \le 10^{-15.6}$$

These pressures of Mg and O_2 are graphed as a function of pco in Figure 6 which shows that the Mg(g) pressure is relatively very high at the temperature of the hot face. Due to a thermodynamically predicted shifting of the pressures of Mg and O_2 in pores relative to the surface a sharp reduction of pO_2 in pores allows Ca, Al and Si to vaporize and to subsequently crystallize on cooling to produce the familiar darkening of MgO grains.

The kinetics of the basic reaction were addressed recently by Tabata et.al. who cited early studies by Leonard and Herron⁽⁴⁾ and by Carniglia⁽⁸⁾. Incorporating pure graphite and two different sizes of pure magnesia, resin bonded specimens were exposed under vacuum (.001 atm.) for varying times and temperatures. The data in Figures 7 and 8 show the results for the test specimens. (A pure MgO specimen lost a relatively small amount of weight at 1600°C). The effect of particle size is pronounced.

The gap caused by the reduction reaction varied systematically as shown in Figure 9. The gap formation is schematized in Figure 10 which also illustrates a reaction layer depth. The reaction was modelled assuming spherical geometry of the MgO and the analysis yielded:

a) A linear dependency of Δw with time which relates in the early stages to a chemical reaction rate - determining step: $\Delta w = \text{KrSr-t}$ where

Kr is the rate constant

Sr is the reaction surface

b) A non-linear dependency of Δw with time which relates, in the later stages, to gaseous diffusion as the rate determining step: $\Delta w^2 = 2Kd \cdot t$ where Kd represents diffusion coefficients and geometrical influences.

Figure 11 is a more detailed schematic of the physical model. The reaction constant changed with particle size of the MgO in this study. Inflection in activation energies with temperature strongly support a shift of mechanisms described in a) and b).

Brezny and Semler⁽⁹⁾ have summarized the major chemical and thermophysical effects of carbon. They pointed to the important role of impurities in the MgO to explain required rates of vacancy diffusion to the interior of the grains during the reduction process. Figure 12 illustrates the effect of metal additive on MgO dense zone thickness.

Data from a typical engineering study underscore the role of physical and chemical parameters of the BOF refractory⁽¹⁰⁾. Penetration by slag is markedly reduced by combined improvements in particle sizing and pressing methods as shown in Figure 13. The effects of grain type and graphite content are shown in Figure 14. Gross factors such as brick dimension, long vs short brick, also played a role in affecting thermal gradients which relate to lining life in a major way.

III. Magnesia-Carbon-Metals

Yamaguchi⁽¹¹⁾, Smith, Liddle and White⁽¹²⁾ and Rymon-Lipinsky⁽¹³⁾ have considered the reactions between the magnesia-carbon and various metals from a equilibrium phase stability standpoint. The latter author has extrapolated a mechanism of protection from his complete thermodynamic analysis. It is not surprising that this mechanism is predicated on a number of kinetic and textural factors.

Lipinsky postulates a typical variation in atmospheric composition at the hot face of a BOF lining as illustrated in Figure 15 which shows a $\rm CO/CO_2$ ratio of 12.5 to 72.5 with 3.3 volume percent of $\rm H_2$ and 8.0 volume percent of $\rm N_2$ at the end of the "blow". Low levels of permeability are presumed to restrict inward flow of gases such that only CO and a small amount of $\rm N_2$ is present just below the surface; with depth only $\rm N_2$ is in contact with the refractory and finally a neutral atmosphere prevails.

The classical thermodynamic approach was used wherein all possible reactions were considered between refractory constituents and equilibrium gases throughout five zones depicted in Figure 16. Sets of reactions, particular for the metal additions, aluminum, magnesium and silicon were assumed and stability relationships determined for a broad range of temperature, bracketing all possible chemical reaction threshold temperatures. The results of these extensive calculations are illustrated in Table 2 which indicates the final reaction products in each zone for the respective metal additions. Only Al_2O_3 is calculated to be a stable product of the reactions between the hot face gases and the metal. Spinel is the obvious end product at the hot face. AlN and Al_4C_3 are predicted at depth in the refractory.

In the case of a Mg metal addition, only MgO is stable at the hot face; the nitride, Mg₃N₂ is stable below 1600°K (1327°C).

Silicon additions yield forsterite at the hot face and SiC and ${\rm Si}_3{\rm N}_4$ at depth into the refractory.

The oxides and the silicate which are predicted are to be found in a carbon free zone. In the next zone metal oxidation should be occurring together with the formation of secondary carbon (metals reducing CO). This secondary carbon could produce extremely low permeability and efficiently preclude gas penetration and slag incursion. The CO will be completely used up eventually such that only N₂ will be available to combine with AIN and Mg₃N₂, respectively. Only the carbides of AI and Si can form in the so-called neutral zone of the refractory.

The atmosphere demarcated zones (Lipinsky did not presume to illustrate the associated temperature intervals) are reminiscent of the zonal formation actually observed by Barthel and Kaltner however, their direct analysis reflected the chemical influence of the slags (omitted in the thermodynamic treatments by Lipinsky) and did not involve metal additions.