Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 1191–1201

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Thermodynamic evaluation of spinel containing refractory castables corrosion by secondary metallurgy slag

A.P. Luz [a,*], A.G. Tomba Martinez [b], M.A.L. Braulio [a], V.C. Pandolfelli [a]

[a] Federal University of São Carlos – Materials Engineering Department, Rod. Washington Luiz, km 235, São Carlos – SP, C.P. 676, CEP 13565-905, Brazil

[b] Materials Science and Technology Research Institute (INTEMA), Ceramics Division, Av. Juan B. Justo 4302, (7600) Mar del Plata, Argentina

Received 24 July 2010; received in revised form 23 October 2010; accepted 28 November 2010

Available online 21 January 2011

Abstract

This work addresses the thermodynamic evaluation of different spinel-containing refractory castable compositions in contact with a basic steel ladle slag ($CaO/SiO_2 \sim 9$). The main differences among the castable compositions were the amount of silica fume (0 or 1 wt%), the binder source (calcium aluminate cement or hydratable alumina) and the spinel incorporation route (*in situ* or pre-formed). The interaction of the liquid slag with the refractory was carried out with the help of thermodynamic software (FactSage) and the applied methodology considered the changes in the slag composition due to the interaction with the castable. The theoretical results were compared with the experimental data attained by corrosion cup-tests, pointing out that the thermodynamic calculations were suitable for predicting various aspects observed in the corroded samples by SEM. Therefore, the equilibrium simulations led to parameters that indicated the corrosion resistance trends, complementing the experimental evaluation and reducing further experimental testing.

Keywords: C. Corrosion; Spinel containing castables; Thermodynamic simulation; Spinel

1. Introduction

Corrosion of spinel containing castables has been extensively studied [1–6]. Nevertheless, although work has been reported on the dissolution of Al_2O_3 into lime–alumina–silica slags [7–9], information regarding the reaction mechanisms and the characterization of the formed phases in the refractories microstructure at high temperatures is rather limited.

Al_2O_3–$MgAl_2O_4$ refractory castables present higher resistance to structural spalling than high alumina or basic castables due to their lower slag penetration. Refractory compositions in this system can be designed based on adding [9,10]: (a) coarse pre-formed spinel grains as aggregates, (b) fine pre-formed spinel as one of the constituents of the castable matrix, and (c) MgO and Al_2O_3 fines in order to generate the *in situ* spinel phase. Some authors [1,5] stated that fine spinel, formed *in situ* by the reaction of MgO and Al_2O_3 in the castable matrix, increases the slag penetration resistance when compared to pre-formed spinel containing ones. The positive effect of the *in situ* spinel formation on the refractory corrosion performance is still under discussion in the scientific literature. Sarpoolaky et al. [9] consider that the corrosion resistance of the spinel containing castables is mainly associated with the extensive interlocking between calcium hexaluminate ($CaO{\cdot}6Al_2O_3$ – formed due to the transformations and reactions of the calcium aluminate cement used as the bonding additive) and corundum or spinel grains in the matrix of the castables.

On the other hand, because the slag is the most reactive component in the melt, its composition has a critical effect on the corrosion mechanism of the Al_2O_3–$MgAl_2O_4$ refractories [1,10]. The current knowledge and understanding of the reaction sequences involved in the dissolution of alumina and spinel in the molten slags, particularly the nature of the various formed phases at the slag/castable interface and their stability regarding the slag composition and heat treatment temperature, are far from being complete [7,11].

Due to these aspects, an alternative to understand the reaction and corrosion mechanisms of the spinel containing castables and to predict their phase evolution at a high temperature is the thermodynamic calculations. The FactSage

* Corresponding author. Tel.: +55 16 33518253; fax: +55 16 33615404.
E-mail address: anapaula.light@gmail.com (A.P. Luz).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.11.043

software is an important tool to perform a wide range of thermochemical calculations. It provides information on the formed phases, their proportions and compositions, the chemical activities of individual components and the thermodynamic properties for the compositions at different partial pressures and temperatures [12].

Recently, some studies on the prediction of castable corrosion behavior were undertaken, considering the FactSage thermodynamic modeling [13,14]. Although very important insights could be attained in these works, some important factors, such as the saturation of the slag by the castable components and its chemical composition change after the reaction with the refractory, were not considered in these calculations [14]. Thus, some improvements in the thermodynamic modeling are still required to better fit the severe conditions that these refractories are exposed to during experimental tests and practical use.

This work addresses the evaluation of the corrosion mechanisms and phase formation of four spinel containing refractory castables when in contact with a selected industrial secondary metallurgy slag composition. Additionally, the effect of silica fume, the binder source (in alumina–magnesia refractory castables) and also the spinel incorporation method (*in situ* versus pre-formed for CAC and silica fume-containing compositions) were analysed. A novel thermodynamic modeling was proposed and successive calculations were applied, considering the liquid composition changes during the interaction with solid phases at 1550 °C. Moreover, in order to point out the advantages and odds of the thermodynamic analyses, experimental corrosion cup tests were also carried out and these results were further compared with the calculated ones.

2. Experimental

2.1. Refractory castable compositions

Four vibratable castables were designed using the Alfred particle packing model ($q = 0.26$). Coarse tabular alumina was used as aggregate ($d \leq 6$ mm, Almatis, USA) and the castable matrix was comprised by dead-burnt magnesia ($d < 45$ μm, 95 wt% of MgO, $CaO/SiO_2 = 0.37$, Magnesita Refratários S.A., Brazil), silica fume (971U, Elkem, Norway), reactive alumina (CL370, Almatis, USA) and fine tabular alumina ($d < 200$ μm, Almatis, USA). General information regarding the compositions is presented in Table 1.

Two binders were selected and a total of 6 wt% of them was added to the castables: calcium aluminate cement CAC (Secar 71, Kerneos, France) or hydratable alumina HA (AlphaBond 300, Almatis, USA). An additional composition, PF-6C1S (Table 1), containing aggregates and fine particles of pre-formed $MgAl_2O_4$ spinel (78 wt% of Al_2O_3, $d < 1$ mm, Almatis, USA), was also evaluated. The addition of pre-formed spinel in this castable aimed to analyse the role and the resulting differences between this sort of spinel addition and the *in situ* spinel formation in the castable corrosion behavior.

2.2. Thermodynamic simulations

The calculations performed in this work were based on the minimization of the free energy of the system in order to find out the nature of the solid, liquid and gaseous phases, as well as their chemical composition and reaction rate at the thermodynamic equilibrium [12]. Simulations have been carried out using FactSage (version 6.1), a fully integrated database and software jointly developed between Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen). It consists of a series of modules that access and cross link thermodynamic databases and allow various calculations.

The databases used in this study were: Fact53 and SGTE (gaseous species, solid and liquid compound thermodynamic database) and FToxid (compounds and solutions for oxide databases). The equilibrium phases were predicted using the Equilib module, considering the following as possible phases: gas, slag or liquid and various solid-solutions (including spinel, mullite, etc.).

There are several procedures in the thermodynamic calculations that can be applied for evaluating the corrosion behavior of the refractory materials. A corrosion modeling proposed by Berjonneau et al. [14] includes the analysis of the refractory (R) and the slag (S) contact at a constant temperature and pressure, where all possible proportions (in mass) between these two materials are studied as a function of the reaction rate <A>, which is defined by the ratio: $(R)/[(S) + (R)]$ with

Table 1
General information of the castables compositions.

Designed compositions		IS-6C1S	IS-6C0S	IS-6H1S	PF-6C1S
Raw Materials	Tabular ($d < 3$ mm) and reactive alumina ($d_{50} = 4$ μm)	87	88	93	72
	Dead-burnt magnesia ($d < 45$ μm)	6	6	6	–
	Calcium aluminate cement	6	6	–	6
	Hydratable alumina	–	–	6	–
	Silica fume	1	–	1	1
	Pre-formed spinel ($d < 1$ mm)	–	–	–	21
Chemical composition	Al_2O_3	91.2	92.2	93.0	91.2
	MgO	6.0	6.0	6.0	6.0
	CaO	1.8	1.8	–	1.8
	SiO_2	1.0	–	1.0	1.0

IS: *in situ* spinel formation. 6C or 6H: 6 wt% calcium aluminate cement or hydratable alumina, respectively. 1S or 0S: 1 wt% or 0 wt% of silica fume, respectively.