

Dry Sintering of Refractory Oxides at Elevated Temperatures

J. Cameron and W.F. Caley

Recent efforts to explore the possibility of extending the service of alumina-based refractories into basic steelmaking operations have involved the application of a basic oxide veneer to both fireclay and high-alumina substrates. Because these investigations used a mineralogically complex system consisting of mixtures of commercial refractories and coatings, the nature of the chemical/mineralogical changes that occurred due to the presence of various metal oxides was often difficult to determine. Thus, the present work was undertaken to establish the extent of chemical/mineralogical reaction that might be expected when dissimilar pellets of high-purity single oxides were placed in pressureless contact for known reaction times at known temperatures. Results for the systems $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, and $\text{MgO-Fe}_2\text{O}_3$ showed significant diffusion of chromium into both Fe_2O_3 and Al_2O_3 , as well as iron into MgO after 3 h at 1450°C . Also, for mixtures of Al_2O_3 and MgO , over 29% spinel formation was evident, even at 1200°C for 3 h. However, because most couples in the solid state did not remain joined on cooling in spite of the extensive reaction, it would appear that to achieve good bonding, liquid or transient liquid sintering is a prerequisite to the formation of an adherent oxide veneer on a commercial refractory.

Keywords

Diffusion, refractory oxides, sintering, steelmaking

1. Introduction

Current slag practice in secondary steelmaking, or ladle metallurgy, generally involves use of a highly basic mixture of CaO and MgO , together with Al_2O_3 and residual amounts of SiO_2 and FeO .^[1,2] Although such slags are deemed to possess excellent refining characteristics, they are highly ionic in nature and thus provide a corrosive environment at elevated temperatures. As a result, both fireclay and, to a lesser extent, high-alumina refractories are incompatible with such slags and must be replaced by basic products such as periclase, dolomite, or mixtures of Cr_2O_3 and MgO , at least at the slag line. These products, although compatible with a basic slag, are both expensive and suffer from poor thermal shock resistance, necessitating a separate facility for preheating.

In an effort to extend the service of alumina-based refractories into secondary steelmaking, a series of investigations into the viability of applying a basic oxide veneer to the working face of these refractories was undertaken.^[3-5] In particular, various mixtures of Cr_2O_3 , MgO , and Al_2O_3 were applied as a veneer to both bloating fireclay and high-alumina products, and the resulting chemical and mineralogical changes that occurred both in the presence and absence of a basic slag at steelmaking temperatures were monitored.^[5]

From these studies, it was apparent that a significant reaction between various oxide couples occurred, even at low temperatures. For example a complete corundum solid solution series formed at the interface between high-alumina brick and a $\text{Cr}_2\text{O}_3\text{-MgO}$ coating after heating to 1450°C for only 1 h,

whereas one might expect this to occur only at temperatures approaching 2000°C . This is in accord with the expectations of the phase diagram.^[6]

As a result, the present work was undertaken principally to study the extent of the reaction between dissimilar pellets of high-purity single oxides when these are in pressureless contact at known reaction temperatures and times. Thus, the investigation was to simulate the extent of the chemical reaction that might occur on application of selected oxide veneers, possibly by gunning, to alumina-based refractories using pure oxide materials rather than commercial refractories and coating compounds.

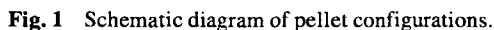
2. Experimental

2.1 Sample Preparation

The systems studied included the following oxide pairs: $\text{Cr}_2\text{O}_3\text{-MgO}$, $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{MgO-Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{-MgO}$, and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$. Reagent-grade pure, single-oxide powders of 200 mesh or finer were used to make the pellets, which were produced in green form using a standard three-piece die set of 1-cm internal diameter. Pressures varied from a low of 12,000 psi for MgO up to 24,000 psi for Al_2O_3 , generally for a time of 3 min. After removal from the die, the pellets were placed in a platinum mesh basket, using one of the three configurations shown in Fig. 1, and subsequently attached to the assemblage shown in Fig. 2 prior to thermal treatment. As shown in Fig. 1, thermocouples were placed either between oxide pairs (Fig. 1a and b) or within mixed oxides (Fig. 1c) in an attempt to measure any heat of reaction.

Additional runs were completed on all sets of pairs in which the two powders were intimately mixed prior to compaction. These pellets were given the same thermal treatments as the unmixed pairs discussed earlier. This was done to increase the area of contact and the degree of contact compared to those runs conducted by simply placing two dissimilar pellets to-

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2.2 Thermal Treatment

The principal study of the heated couples was carried out by examining the interface between all sets of the contacting pairs of oxides for evidence of reaction and interdiffusion. The original position of the interface was marked by use of 300-mesh molybdenum powder, which was sparingly applied between the pair layers during manufacture in the die pressing operation. This examination was done visually upon first removal of the reaction tray from the furnace, by optical microscopy, and finally by scanning electron microscopy (SEM) in both energy dispersive spectrometry (EDS) and X-ray mapping mode.

Both optical and scanning electron microscopy were used to assess the extent of reaction both between oxide pairs and between oxide grains in pellets containing two mixed oxides. Samples of all pairs of oxides were cold mounted and studied by SEM to determine the extent of reaction and to determine if solid solutions or interoxide compounds were formed at the interface. In addition, samples were studied by EDS to determine evidence of the codiffusion of species across the interface in the pairs. Samples that were made by mixing the powders prior to compaction were also studied for the extent of reaction.

Quantitative analyses by several X-ray diffraction methods were carried out using the Guinier-de-Wolff technique and the peak height and peak profile techniques using a 2-circle diffractometer.

3.1 Visual Observations

Diagram illustrating the experimental apparatus for the study of the Pt-Pt₁₃Rh system. The components are labeled as follows:

- transite cover
- Pt
- Pt-13%Rh
- Al₂O₃ support rod (8mm o.d.)
- Al₂O₃ reaction tube
- Al₂O₃ pin
- Al₂O₃ heat shield
- Al₂O₃ pin
- Al₂O₃ safety crucible (50cc)
- thermocouples
- oxide pellets
- Pt basket

Fig. 2 Schematic diagram of experimental assemblage.

In cases where the two pellets appeared to have bonded together, the strength of the bonding was very low, and easy separation occurred, sometimes even during gentle handling of the pellets. This led to the view that the extent of reaction across the interface was not significant, and only A-A and B-B sintering had taken place, with little reaction of the A-B type across the interface. Additionally, the mechanical strength of the separated pellets was low, and many specimens cracked and crumbled during handling.

All samples were studied under the light microscope at magnifications of 50 \times and 400 \times for evidence of reaction in the form of product layers, zones of liquefaction, or differences in porosity across the interface.

In some of the pairs containing Al_2O_3 , a product layer was evident on one side of the marked interface, but not on both sides. Al_2O_3 - Cr_2O_3 was such a pair.^[6]

Concentration profiles were detected for the $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3\text{-MgO}$ systems, as shown in Fig. 3. There was no measurable concentration profile detected in the $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Cr}_2\text{O}_3\text{-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{MgO-Al}_2\text{O}_3$, and

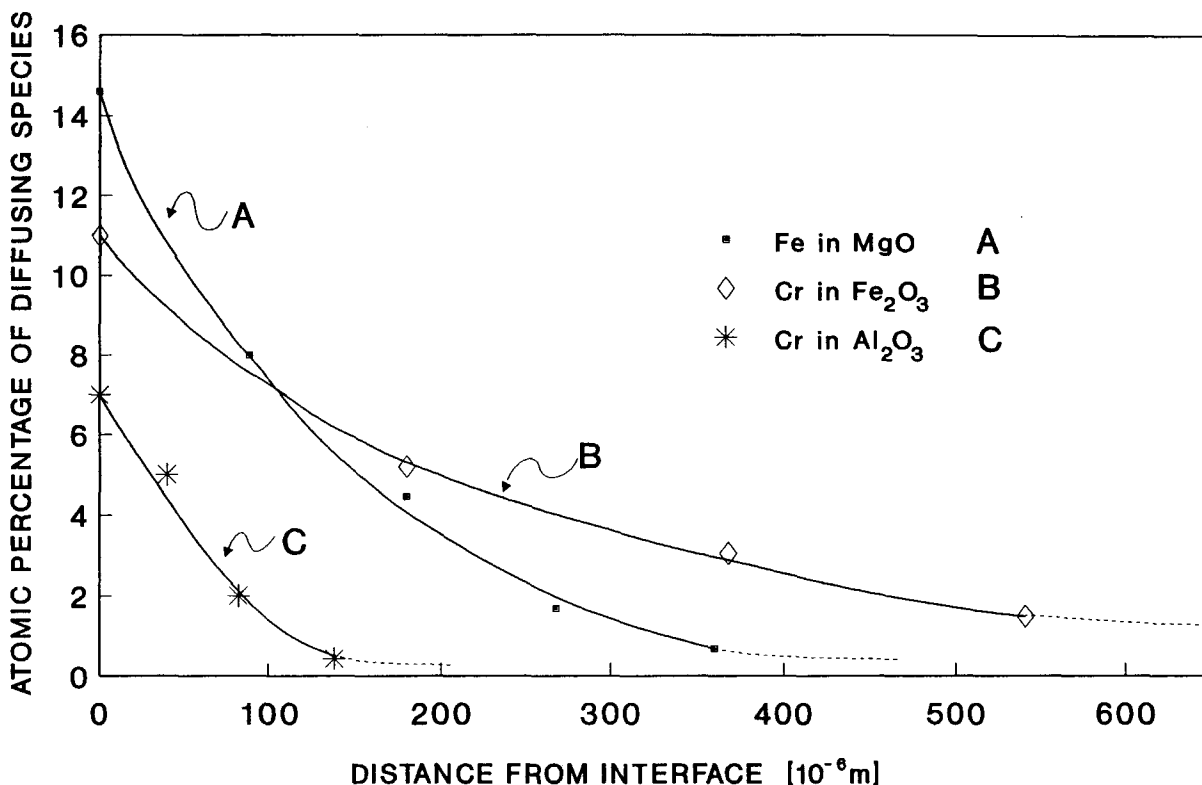


Fig. 3 Concentration profiles for the $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3\text{-MgO}$ systems.

Table 1 Concentration profiles of oxide couples

System	Temperature, °C	Time, h	Comment
$\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$	1450	3	Chromium diffused; >500 μm into hematite; almost no iron detected in chromia
$\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$	1450	3	Chromium diffused; >100 μm into alumina; almost no alumina detected in chromia
$\text{MgO-Fe}_2\text{O}_3$	1450	3	Iron diffused; >300 μm into magnesia
$\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$	1200	6	No measurable diffusion at 1200 °C after the long contact times at 1200 °C
$\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$	1200	5.75	
$\text{MgO-Fe}_2\text{O}_3$	1200	6	

$\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ systems. Additionally, micrographs were obtained for the oxide couples of interest, as an attempt to provide visual confirmation of any evidence of reaction provided by the EDS-generated concentration profiles. Table 1 provides a summary of the systems that exhibited measurable concentration profiles; an example of reaction product for the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system is given in Fig. 4(a) and (b).

3.4 X-Ray Diffraction

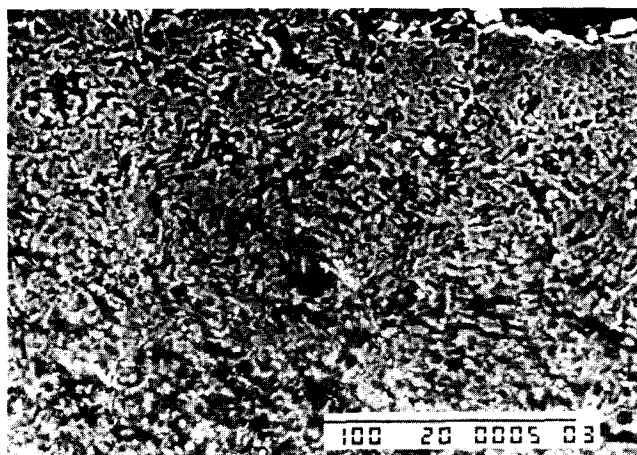
From the data generated for Al_2O_3 and MgO , it was evident that a very substantial reaction had, in fact, taken place. Even at

1200 °C for 3 h, for example, $34 \pm 3\%$ of the final pellet was converted to a spinel phase. Reaction at 1450 °C for 6 h yielded $64 \pm 3\%$ spinel formation. In these pellets, there was extensive reaction between the MgO and Al_2O_3 starting powders. The couple studied in this system, however, showed no joining at the interface, and scans for Mg atoms in the Al_2O_3 pellet and Al atoms in the MgO pellet away from the interface area were not successful. It was concluded that in this system compound formation takes place only at the interface and that all species that diffuse through the interface react with the other reactant. Table 2 summarizes these results.

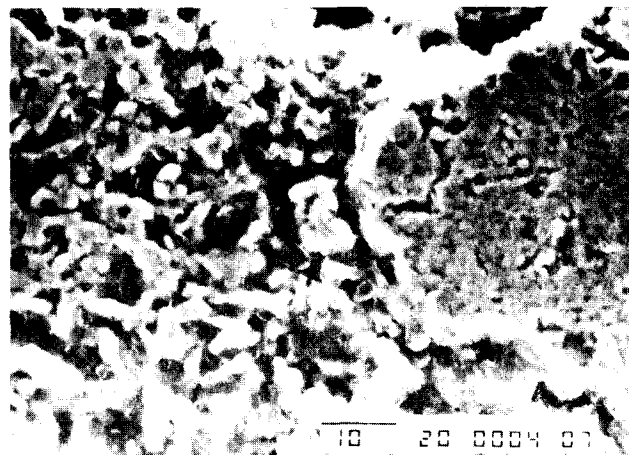
4. Discussion

4.1 Concentration Profiles

With respect to the concentration profiles generated using EDS, the $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ result at 1450 °C and 3 h, for example, is interesting and typical. Here, the two separate pellets were placed together and pressed prior to thermal treatment. After cooling and on removal from the furnace, the pellets were found to have both sintered by ~40% linear shrinkage, but they were not bonded or sintered together. The EDS line scans across the interface produced in the composition-distance plots shown in Fig. 3. Clearly, there are significant distances over which the two oxide species diffuse in a counter direction, with little evidence of a distinct product layer. This is expected from the phase diagram.^[7] Furthermore, no joining of the pellets occurred, even after substantial mass transfer occurs across the



(a)



(b)

Fig. 4 Micrographs of reaction product for the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ couple. (a) Representative region of reaction product. (b) Large sintered region.

Table 2 Percentage of spinel detected by X-ray diffraction in $\text{MgO-Al}_2\text{O}_3$ equimolar mixtures

Temperature, °C	Time, h	Spinel, %
1200.....	3	29
1200.....	6	34
1450.....	3	58
1450.....	6	64

interface. After 1450 °C, therefore, although the extent of solid solution that is formed near the interface is significant after 3 h, the quality of the bonding that results is not good and would not be conducive to the formation of a brick veneer when sesquioxide solid solutions or interdiffusion is the principal mode of joining.

In runs conducted with $\text{MgO-Al}_2\text{O}_3$, it was similarly found that the individual pellets did self-sinter, but that the extent of the reaction between the pellets was not significant. In this case, the primary mechanism of joining was through the formation of solid interoxide $\text{MgO} \cdot \text{Al}_2\text{O}_3$ -spinel. Visual and optical microscopy evidence pointed to the occurrence of only a small amount of reaction product, and the two sintered pellets were not bonded together strongly. The EDS line scans showed almost no counter diffusion through the two pellets, and although some interaction between the reactants was noted, in this all-solid diffusion test, no strong bonding occurred. This would be expected from consideration of the phase diagram.^[8,9]

During X-ray analysis, it was noted that the equimolar starting samples after the different thermal treatments exhibited widely scattered results when analyzed for the percentage of remaining unreacted single oxide. The magnesia/alumina molar ratios, for example, varied from 0.43 to 0.81. This is attributed to the considerable range of solid solution that the spinel phase is capable of assuming at these temperatures, as shown in the equilibrium phase diagram.^[8] During treatment, the equimolar mixtures will react and begin to dissolve the free oxides. The

solubility of MgO in the spinel is greater than that of Al_2O_3 , however. Locally, MgO will thus react and diffuse into the newly formed solid spinel at a faster rate than Al_2O_3 . Thus, depending on the time and temperature of the test, the molar ratio of the mixture will not remain at unity, but will assume a lower value.

4.2 Friability/Sintering

The outcome of this study was to produce well-sintered pellets (40% linear shrinkage) that exhibited low crushing strength. Although the small samples were not tested in a quantitative manner for compressive strength, for example, it was clear that the resulting pellets were relatively friable and soft. Cracking was also evident, and under 400× optical microscopy, no evidence of extensive reaction or homogenization was noted. Thus, using this as a mechanism of attaching veneers to bricks will probably not produce acceptable, mechanically sound structural components within ladles and furnaces.

In cases where a third or more oxide species is added, as in commercial gunning mixes, a lesser degree of sintering is known to produce acceptable bonds between the lining and the added phase. In such cases, good mechanical bonding is only obtained when diffusion, reaction, and product formation takes place in the presence of a liquid phase. Even if this phase is transient, however, the resulting ceramic mass is usually well bonded, and the resulting structures are strong.

An obvious outcome from this present work is that, when the reactions take place in the dry state, with no liquid formation, the bonding between the masses is very poor. Although this may at first be attributed to a lack of significant reaction between the single oxides, in fact, the extent of reaction between the solids may be considerable. This was evident in the runs that exhibited reasonable concentration gradients, which reached >500 μm into the adjacent pellet, as well as in cases where the product is made by the formation of a solid solution, such as in Fig. 3, or in cases where the product is an interoxide.

The lack of strength is, in fact, not due to the absence of a reaction. Rather, it is the low mechanical strength and the defect-ridden nature of the interface material formed when two dissimilar oxides touch and react at high temperatures in the solid state when held in air for extended times. A review of the 30 runs involving up to 40 different interfaces, including the replicates, showed this to be a recurring outcome of the work in the seven systems where the potential to produce reactive solid-state sintered material is to be achieved by the formation of only solid-state products.

5. Conclusions

Although most of the oxide couples studied experienced shrinkage, and a measure of self-sintering, little evidence of chemical reaction was noted using semiquantitative scanning electron microscopy. In contrast, quantitative X-ray diffraction on the Al_2O_3 -MgO couple indicated substantial reaction, with spinel formation evident even at 1200 °C for 3 h.

From the results generated, it would appear that, although significant co-diffusion might take place between selected oxide couples at the reaction temperature (e.g., formation of mullite or spinel), the presence of a liquid phase, even if only transiently, is a prerequisite for the formation of an adherent oxide veneer on a commercial refractory. In almost all cases, the

samples studied here in the dry sintering state were not strong enough to remain joined upon cooling to room temperature.

References

1. R.J. Fruehan, *Ladle Metallurgy Principles and Practices*, *Iron Steel Soc.*, 1985, p 149
2. E.T. Turkdogan, *Slags and Fluxes for Ferrous Ladle Metallurgy*, *Ironmaking Steelmaking*, Vol 12 (No. 2), 1986, p 64-77
3. W.F. Caley, L.E. Kanary, and D.B. Clarke, Chemical and Mineralogical Examination of a $4\text{Cr}_2\text{O}_3$ -MgO Coating Applied to a Bloating Fireclay Brick, *Can. Metall. Quart.*, Vol 26 (No. 3), 1987, p 259-264
4. W.F. Caley, L.E. Kanary, D.B. Clarke, and S.H. Didyk, Reduction of Chemical Corrosion in Transfer Ladles by Application of an Oxide Ceramic Coating, in *Advances in Refractories for the Metallurgical Industries*, M.A.J. Rigaud, Ed., Pergamon Press, 1987, p 299-303
5. W.F. Caley, S.H. Didyk, and P.W. Kingston, "Reduction of Slag-Line Corrosion in Secondary Steelmaking Ladles," UNITECR '89 Proceedings, The American Ceramic Society, 1989, p 430-441
6. E.N. Bunting, *Bur. Stand. J. Res.*, Vol 6 (No. 6), 1931, p 317
7. A. Maun and S. Sōmiya, *J. Am. Ceram. Soc.*, Vol 43 (No. 4), 1960, p 207
8. A. Alper, R.N. McNally, P.G. Ribbe, and R.C. Coman, *J. Am. Ceram. Soc.*, Vol 45 (No. 6), 1962, p 264
9. D.M. Roy, R. Roy, and E.F. Osborn, *J. Am. Ceram. Soc.*, Vol 36 (No. 5), 1953, p 149