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The Optimization of the Microstructure and Phase Assemblage of High Chromia Refractories

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Abstract

The effect of Al_2O_3 and ZrO_2 addition in chromia-based refractories was investigated. The strength of ZrO_2-bearing chromia refractories was greatly enhanced by 4–8 wt% Al_2O_3 additive. In the range of 0–12 wt% ZrO_2 addition, 6 wt% ZrO_2 was most beneficial to the improvement in thermal shock resistance. Corrosion resistance was compared by exposing to three kinds of coal slag with various CaO contents. As the substitution of ZrO_2 for Cr_2O_3 increased, slag penetration increased, particularly in the case of the slag containing ~16 wt% CaO. Considering the trade-offs between corrosion resistance, thermal shock resistance and mechanical properties, the optimum phase assemblage of high chromia refractories consists of the large granular Cr_2O_3 grains bonded by annular $(Cr, Al)_2O_3$ grains and well-distributed fine ZrO_2 grains. © 1998 Elsevier Science Limited. All rights reserved

Keywords: C. thermal shock resistance, C. corrosion, C. mechanical properties, C. ZrO_2, Cr_2O_3 refractories.

1 Introduction

A variety of dense high chromia refractories have demonstrated good performance in slagging coal gasifiers,[1] but potential problems still exist. The picrochromite ($MgCr_2O_4$) materials have low strength,[2] and chromia–alumina materials with or without the baddeleyite glassy phase usually possess poor thermal shock resistance.

For coal gasification vessels with operating temperatures higher than the ash fusion temperature, only refractories with high Cr_2O_3 content could be considered as the linings due to low solubility of Cr_2O_3 in coal slag. In order to improve their mechanical properties and thermal shock resistance, some supporting phases are needed. Therefore, addition of zirconia and alumina to chromia-based materials was investigated to optimize the microstructure and phase assemblage of high chromia refractories.

2 Experimental

The chromia used was high purity pigment-grade Cr_2O_3 ($\geq$99·0 wt%), and its grains that had apparent porosity 3·8% and bulk density 5·03 g cm^{-3} were synthesized by fusing. The dense chromia grains with maximum size 4·5 mm were used in the test. The other raw materials were $\geq$99·0 wt% Al_2O_3 ball mill powder of $< 20\,\mu$m and $\geq$99·0 wt% unstabilized zirconia powder of $< 3\,\mu$m, which was crushed by a jet mill. All the samples and crucibles were prepared by pressing under 200 MPa and firing at 1730°C for 10 h in a down draft kiln. Thermal shock tests were conducted as follows: each group of 25×25×125 mm test bars was heated respectively at 800, 1000 and 1200°C for 30 min, and then quenched into the running water at ambient temperature for 5 min. Cold modulus of rupture of the original and quenched samples was measured to evaluate the degradation.

Each type of 35 g slag, listed in Table 1, was packed into the Φ50 mm crucible that had a hole of 25 mm in diameter by 25 mm depth. They were heated at 1550°C for 10 h and 1600°C for 10 h. Once the test was completed, the crucibles were cut in two parts. The height of the residual slag in the crucibles showed a relative quantity of slag penetration. Some of the samples were examined by an optical microscope and a scanning electron microscope.

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Table 1. Slag compositions in corrosion test

Oxide (wt%)	*Slag A*	*Slag B*	*Slag C*
SiO_2	59·40	52·77	45·35
Al_2O_3	23·30	20·75	17·89
Fe_2O_3	7·13	6·33	5·39
CaO	6·09	16·48	27·13
MgO	1·63	1·64	2·34
K_2O	1·54	1·25	1·24
Na_2O	0·86	0·77	0·65

3 Results and Discussion

3.1 Characterization of samples

The effect of Al_2O_3 addition on strength of Cr_2O_3–ZrO_2 (6 wt%) materials is shown in Fig. 1. Their desired strength was achieved with 4 wt% Al_2O_3 addition. The sample without alumina had too low strength. It is important to point out that a suitable addition of alumina was also contributive to hot strength. Modulus of rupture at 1400°C was 15·8 MPa for 90 wt% Cr_2O_3 material with alumina and zirconia addition.

Therefore, Al_2O_3 addition was fixed at 6 wt% to determine influence of the ZrO_2 content on high chromia materials. The formulae and properties of samples tested are listed in Table 2. As the zirconia content of samples increased, their apparent porosity increased and bulk density decreased. All the samples had high strength of more than 100 MPa,

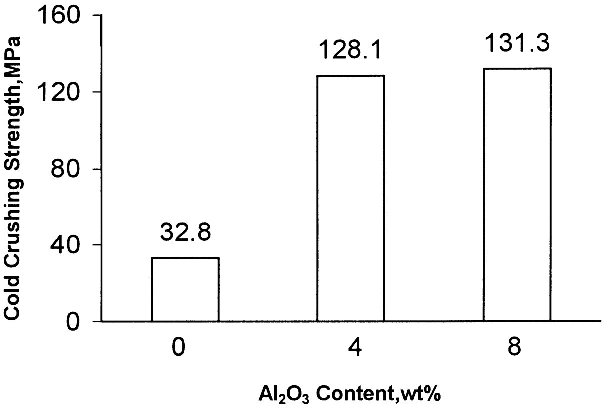


Fig. 1. Effect of Al_2O_3 addition on strength of Cr_2O_3–ZrO_2 materials.

Table 2. Properties of the tested samples

Sample no	*1*	*2*	*3*	*4*	*5*
Cr_2O_3 (wt%)	94	91	88	85	82
Al_2O_3 (wt%)	6	6	6	6	6
ZrO_2 (wt%)	0	3	6	9	12
Apparent porosity (%)	14	16	17	18	20
Bulk density ($g\,cm^{-3}$)	4·25	4·18	4·14	4·12	4·10
Cold crushing strength (MPa)	125·3	115·3	101·0	114·0	126·4
Cold modulus of rupture (MPa)	14·6	12·8	9·2	12·8	21·1

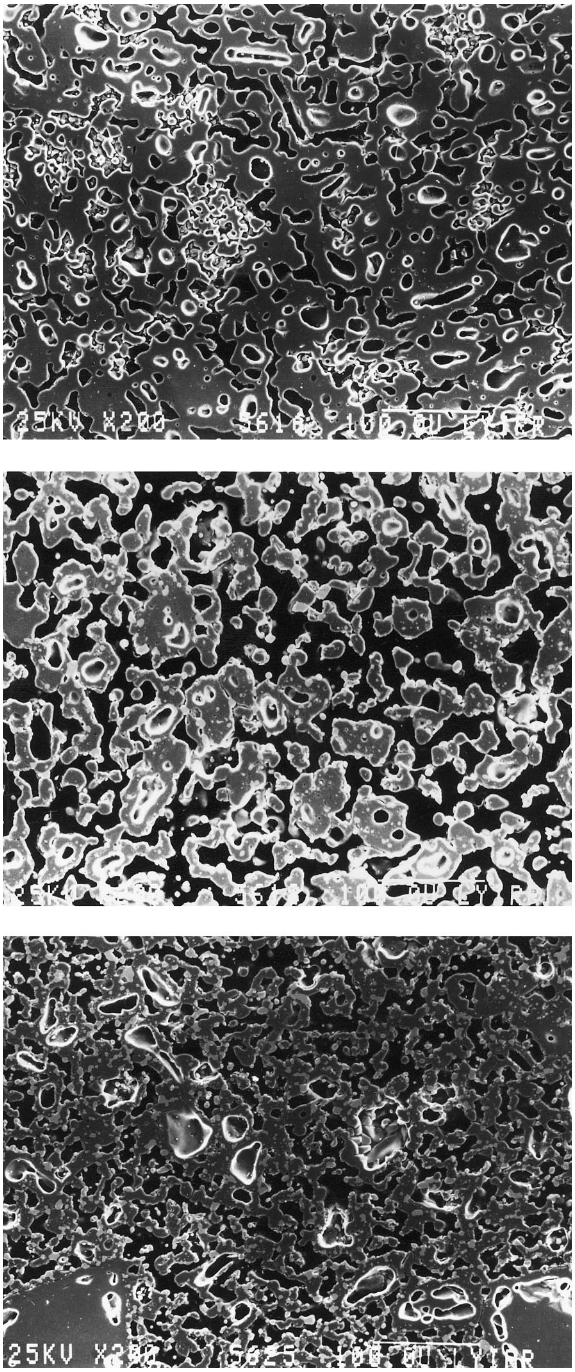


Fig. 2. SEI of nos 1, 3 and 5 samples (from top to bottom) ×200

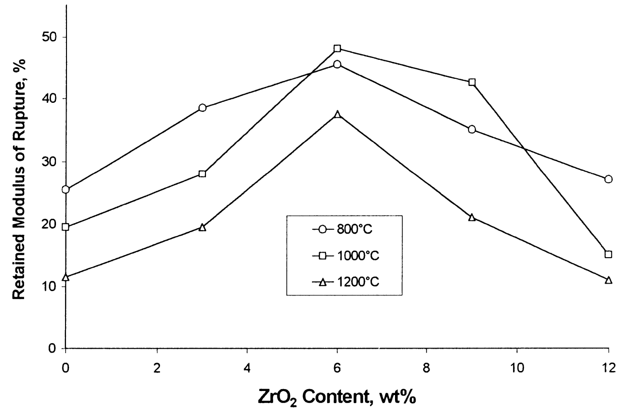
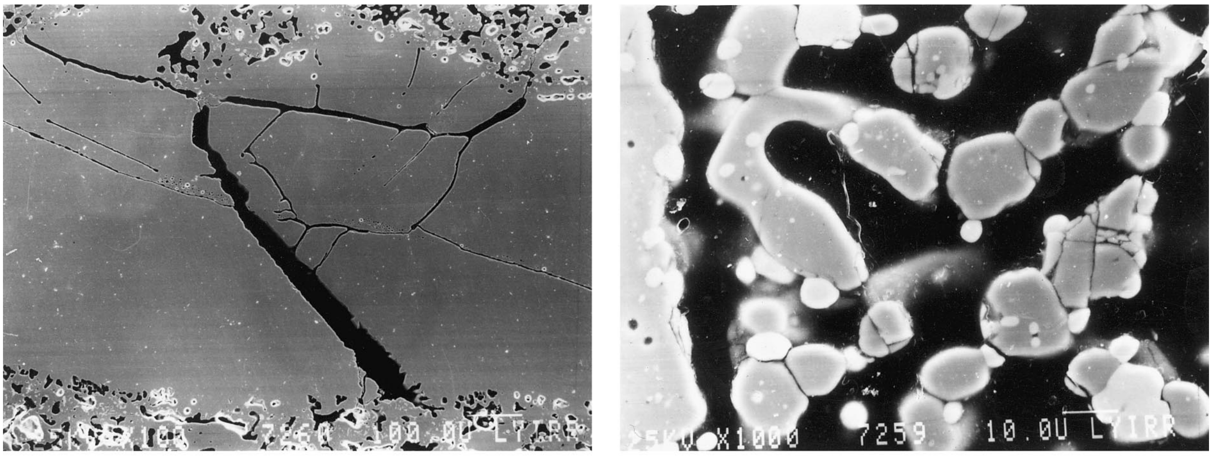


Fig. 3. Dependency of the retained strength on the ZrO_2 content of samples after quench test.



(a) (b)

Fig. 4. SEI of no 3 sample after 1200°C-quench: (a) ×100; (b) ×1000

which showed a little reduction in the range of 0–6 wt% ZrO_2 and increase with ZrO_2 addition from 6 to 12 wt%.

There was a varying size of Cr_2O_3 grains in all the samples. But their matrixes were much different, as shown in Fig. 2. Comparison of the microstructure indicated that no. 3 sample had larger annular $(Cr, Al)_2O_3$ crystals and more pores than no. 5 sample. Approximately 5 μm granular ZrO_2 was situated in the intervals of Cr_2O_3 grains and annular $(Cr, Al)_2O_3$ crystals. In the matrix of no. 1 sample, crystals were closely connected and residual phosphorus from the binder was agglomerated, which was not completely volatilized during sintering due to its high densification. Too much ZrO_2 seemed to restrain growth of $(Cr, Al)_2O_3$ crystals in no. 5 sample.

3.2 Thermal shock resistance

The retained modulus of rupture for the quenched samples exhibited the convex curves with various zirconia contents, which is shown in Fig. 3. The maxima corresponded to the composition with 6 wt% ZrO_2 content after 800, 1000 and 1200°C-water quench, but nos 1 and 5 samples without

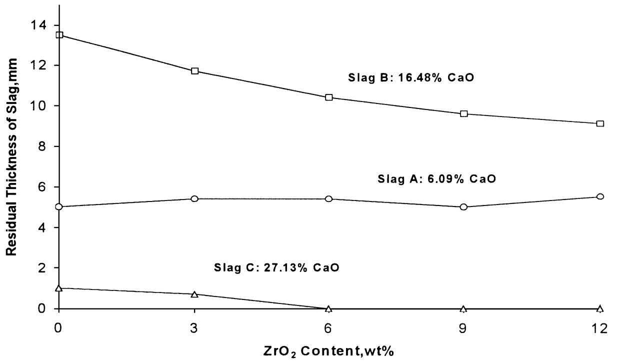


Fig. 5. Dependency of the residual amount of slag in the crucibles on the ZrO_2 content of samples.

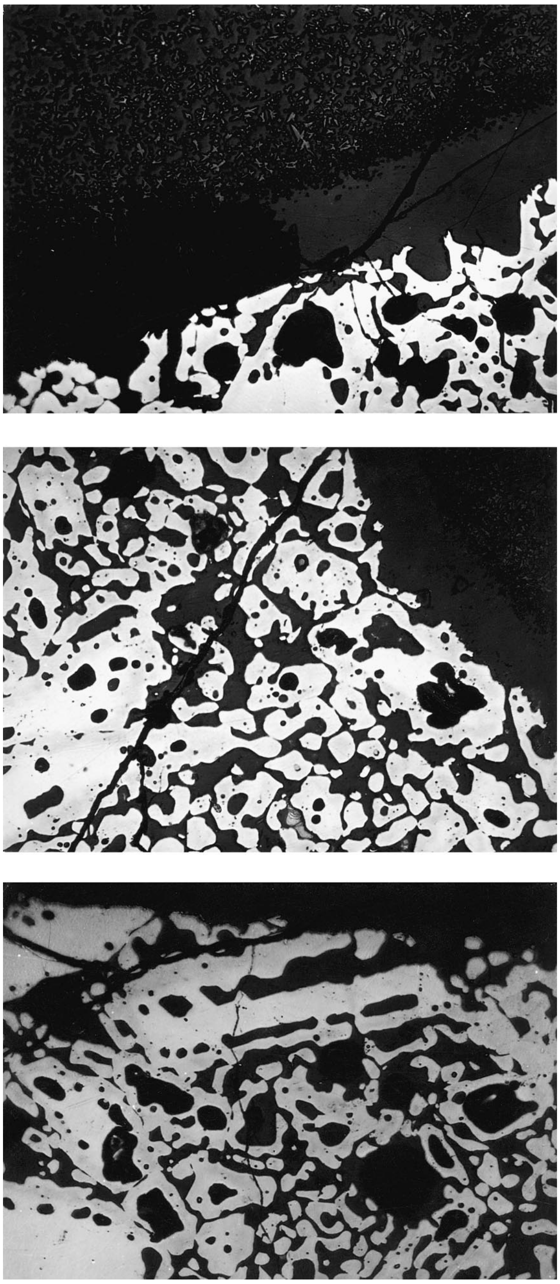


Fig. 6. Microstructure of the slag/refractory interface of nos 1, 3 and 5 samples exposed to Slag B. Reflected light ×250 (From top to bottom. nos 1, 3 and 5).

zirconia and with 12 wt% ZrO_2 lost the greatest strength.

The samples after 1200°C-quench showed the most strength loss. However, not all the samples retained the relatively high strength after 800°C-quench as expected. No matter how hot samples were once quenched into the running water, at least more than 50% strength was lost. Eventually, 6 wt% ZrO_2 was the optimum addition for high chromia materials to resist thermal shock.

According to the work of Hasselman,[3] the thermal-shock damage was hypothesized to be controlled by the propagation of long cracks. This hypothesis was supported by the strength degradation behavior of most of high chromia refractories in the water quench test.[4] The variation of retained strength with quench temperature difference is typical of stable propagation of large cracks. Figure 4 shows cracks in no. 3 sample after 1200°C-quench. Cracks in large grain are shown in Fig. 4(a) and cracks in fine grains of the matrix are observed as in Fig. 4(b). No. 3 sample had relatively long cracks and showed stable crack growth and strength degradation. Too close network structure in nos 1 and 5 samples was reasonably thought to be detrimental to thermal shock resistance.

3.3 Resistance to slag corrosion

All the samples listed in Table 2 were exposed to the molten Slag A, B and C, which had the result presented in Fig. 5. As the ZrO_2 content of samples increased, actually the Cr_2O_3 content was reduced from 94 to 82 wt%, the residual slag amount in the crucibles reduced in the case of ~16 wt% CaO slag and ~27 wt% CaO slag, but fluctuated a little for ~6 wt% CaO slag. ~27 wt% CaO slag had completely penetrated into the samples containing less than 90 wt% Cr_2O_3. A little of visible interaction was observed in no. 5 sample exposed to ~27 wt% CaO slag. It was again proved that relatively high Cr_2O_3 content in materials is very important for corrosion resistance to coal slag. Fortunately, there is less than 20 wt% CaO in most of the molten coal-slag. Such serious corrosion can be avoided.

A relatively great quantity of slag with high CaO content was expected to penetrate into refractories. It is really surprising that more slag with ~6 wt% CaO content penetrated into samples than ~16 wt% CaO slag. It can be explained by possibly lower viscosity of ~6 wt% CaO slag at high temperature.

The microphotographs in Fig. 6 show the slag/refractory interface of nos 1, 3 and 5 samples after exposure to Slag B. Gear-shaped or pillar $(Cr, Al, Fe)_2O_3$ grains were formed with penetration of slag. ZrO_2 grains disappeared in 700–870 μm zone from the interface of ZrO_2-containing samples and dissolved into penetrated slag. The microstructure of nos 3 and 5 samples deteriorated more than that of no. 1 sample due to ZrO_2 dissolution in slag.

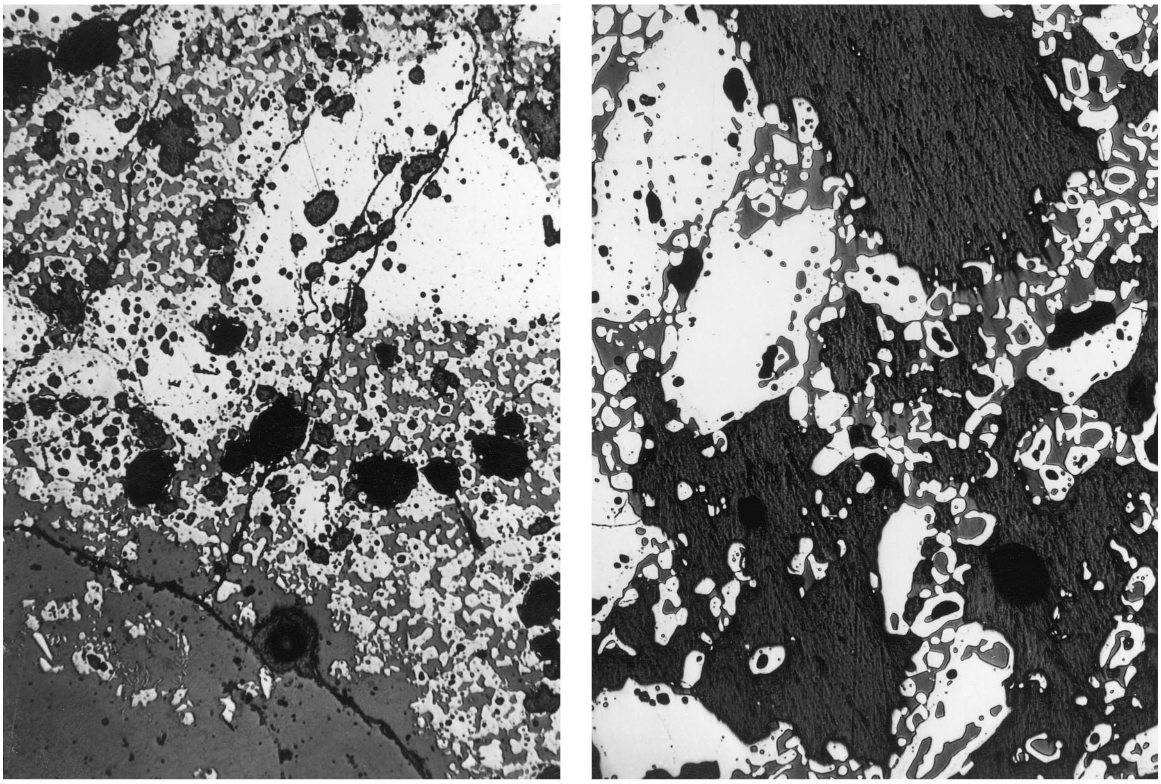

(a) (b)

Fig. 7. Microstructure of no. 3 sample exposed to Slag A (a) and (b) Slag C. Reflected light ×100.

Microstructure of no. 3 sample exposed to Slag A and C is shown in Fig. 7. After exposure to Slag A, no. 3 sample retained basically its original microstructure even though some Cr_2O_3 grains were found in the slag near the interface, as shown in Fig. 7(a). However, penetration of Slag C had changed the basic features of no. 3 sample. Porous layer with a width up to 1630 μm was formed from the interface, in which pores greater than 460 μm in diameter accounted for $\sim$50%, as shown in Fig. 7(b). Glass phase was not well distributed.

4 Conclusions

Investigation on Al_2O_3 and ZrO_2 addition to chromia-based refractories came to the conclusions that 4–8 wt% Al_2O_3 addition enhanced the strength of ZrO_2-containing chromia materials due to formation of annular (Cr, Al)$_2$O$_3$ crystals and cold crushing strength of more than 100 MPa could be reached. Slag penetration dissolved ZrO_2 near the slag/refractory interface, but 6 wt% ZrO_2 additive most improved thermal shock resistance. The trade-offs between corrosion resistance, thermal shock resistance and mechanical properties could be made by 4–8 wt% Al_2O_3 and 6 wt% ZrO_2 additives. Annular (Cr, Al)$_2$O$_3$ grains and well-distributed fine ZrO_2 grains bonding large granular Cr_2O_3 grains optimized the microstructure of high chromia refractories.

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