Corrosion mechanisms of magnesia-chrome refractories in copper slag and concurrent formation of hexavalent chromium

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A B S T R A C T

Magnesia-chrome refractories have been essential materials for application as wear lining in copper production furnaces for many years. Formation of hexavalent chromium (Cr(VI)) has been a major concern despite its admirable corrosion resistance in copper slag. Magnesia-chrome refractory specimens (9, 12, 15 and 18 wt% Cr2O3) with addition of Al2O3 and TiO2 were fabricated and subsequent corrosion tests using copper slag was conducted in air. The corrosion mechanism between magnesia-chrome refractories fabricated and synthetic copper slag were investigated by means of X-ray diffraction (XRD) and scanning electron microscope (SEM), and concurrent formations of Cr(VI) were assessed effectively by leaching test. All the magnesia-chrome specimens prepared are composed of periclase and composite spinel Mg(Al,Cr,Ti)2O4 phases after firing at 1700 °C. Densification of the specimens decreases with the increase in Cr2O3 content due to the increased volume expansion, while TiO2 addition can improve their densification as mass transfer is enhanced during the sintering process. The corrosion resistance of the specimens decreases slightly with the Cr2O3 content due to the increased apparent porosity, which would result in penetration of more corrosive slag at the initial stage of the corrosion test while a newly formed (Mg,Cu)(Cr,Fe)2O4 spinel dense layer between the slag and penetration layer effectively hinders further penetration of slag and well protects the specimens. The Cr(VI) in the specimens prepared increases obviously with the Cr2O3 added content, while the TiO2 addition can suppress the formation of Cr(VI) effectively and the copper slag can cause the formed Cr(VI) to be reduced further during the corrosion process. For all the specimens, concentrations of Cr(VI) in the leachates is much lower than the US-EPA limit of 100 mg/kg but exceeds the European limit of 2 mg/kg after the corrosion test.

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1. Introduction

In copper production, magnesia-chrome refractories have been widely used as highly corrosion resistance lining of smelting, converting and refining furnaces [1–7]. The high refractoriness and extremely low solubility of Cr2O3 into molten slag are responsible for their excellent corrosion resistance property [1,8,9]. However, recent environmental policies are providing a driving force for the development of chrome-free refractories [3]. The major concern of Cr2O3 containing materials is the potential formation of Cr(VI) compounds which are readily water soluble and can cause a wide array of negative impacts on the environment and human health since the Cr(VI) compounds are toxic and carcinogenic [10–13]. Unfortunately, there are no alternatives for Cr2O3 in terms of superior slag corrosion resistance. Therefore, magnesia-chrome refractories are still being widely used in copper production industry.

In order to predict the potential for Cr(VI) compounds formation in the Cr2O3 containing materials and develop appropriate countermeasures, many research works have been carried out to figure out how Cr(VI) formation is affected by the interaction between Cr2O3 and different substances. Several reports have proved that Cr(III) oxidation in the solid phase was dependent on the presence of alkali and alkaline earth metals at high temperatures [14–20].
and therefore, sodium, potassium, and calcium salts can cause the oxidation of Cr(III) easily. Recently, Mao et al. further confirmed that the formation of Cr(VI) for Cr₂O₃ containing materials was closely related to the basicity of other substances in the materials, while the acidic SiO₂ and phosphate could decrease the formation of Cr(VI) or even cause the formed Cr(VI) to be reduced [12,13]. High partial pressures of oxygen have also been proved to thermodynamically influence the oxidation of Cr(III). For example, Chen et al. [21] found that increasing the partial pressure of oxygen in flue gas favoured the oxidation of Cr(III) into Cr(VI) bearing species. In our previous work, we also observed that compared with reducing atmosphere, the formation of Cr(VI) was favoured by oxidizing atmosphere when corrosion tests of Al₂O₃-CaO-Cr₂O₃ refractory castables were performed in molten waste slag [22].

Up till now, plenty of research works have been carried out to investigate the physical, mechanical and corrosion resistance properties of magnesia-chrome refractories because of widespread adoption in copper production furnaces [3–7,23–28]. Ghosh et al. [25] investigated the effect of reactivity of magnesia and ZrO₂ addition on the properties of magnesia-chrome refractories. They found that introducing less reactive sintered magnesia could improve densification, hot modulus of rupture and the direct bonding of chrome grains, and ZrO₂ incorporation could improve the thermomechanical properties of magnesite-chrome refractories. As for slag corrosion of magnesia-chrome refractories, it was generally believed that the reactions of MgO with slag resulting in formation of forsterite (2MgO·SiO₂), magnesiowüstite ((Mg,Fe)O) and solid olivine (2(Mg,Fe)O·SiO₂) were the main chemical corrosion mechanisms [1,7,26]. Singh [27] performed corrosion tests on magnesia-chrome bricks in contact with copper slag containing 55% Fe₂O₃ and 35% SiO₂. According to this work, slag corrosion resistance of the bricks increased with increasing Cr₂O₃ content and to prevent slag penetration, 90% of the pores should have a diameter below about 20 μm. Nikoo [28] varied the FeO/SiO₂ ratio of copper slag from 1.5 to 2.6 to investigate the effect of basicity of the slag on the corrosion behavior of direct-bonded magnesia-chrome bricks. For slag with low basicity, it was concluded that a higher amount of spinel was interesting to resist slag attack as chromite spinels were not altered. On the other hand, for the high basicity slag, refractory corrosion took place both in the grains and in the bonding spinel phases, indicating that adding spinel was not particularly interesting to minimize slag attack in this case. However, though there are many literature focusing on the complex high temperature chemical corrosion mechanisms, the formation of Cr(VI) during preparation of magnesia-chrome refractories as well as during corrosion process in copper slag has not been studied by the researchers despite the potential threat to the environment and human health.

In the present study, magnesia-chrome refractory specimens with different amount of Cr₂O₃ were fabricated at high temperature. A certain amount of TiO₂ and reactive Al₂O₃ powders were added in order to enhance the densification of the specimens [29–31]. Then, the corrosion resistance of all specimens was evaluated in molten copper slag in air. Formation of various phases during the preparation of specimens and subsequent corrosion tests were studied by means of XRD and SEM. This study also focuses on concurrent Cr(VI) formation during the entire process which has been investigated by using the TRGS 613 standard method [32].

2. Experimental

2.1. Specimen preparation

Fused MgO (Tangshan Gejiatun Magnesia Factory, China), industrial grade Cr₂O₃ (Luoyang Yuda Refractory Co. Ltd, China), reactive Al₂O₃ powder (Kaifeng Special Refractory Co. Ltd, China) and reagent grade TiO₂ powder (98.6 wt% TiO₂, Shanghai Shandu Chemical Co., Ltd., Shanghai, China) were employed as raw materials. The chemical compositions of these raw materials are given in Table 1. The magnesia-chrome specimens were formulated (Table 2) with the addition of 9, 12, 15, 18 wt% Cr₂O₃ replacing the MgO since the Cr₂O₃ content in magnesia-chrome brick used in copper production furnaces was approximate 15 wt%. Sulphite wasteliquor (Linghai Liangxing Chemical Industry Co. Ltd, China) was added as binder (3 wt% in each). The fine powders for each formula were pre-mixed in intensive mixer (Eirich, R230261) for 10 min. Then, the aggregates with binder were mixed in Hobart’s mixers for 6 min. Finally, the pre-mixed powders were added and all the raw materials were mixed in Hobart’s mixers for 9 min. After kneading, specimens were pressed under 150 MPa into 50 × 50 mm cylindrical specimens and 50 × 50 mm cylindrical specimens with a groove of diameter 20 mm × 25 mm. The specimens were then dried at 110 °C for 24 h in an electric air oven. Lastly, dried specimens were heated to 1700 °C and maintained for 3 h in air. Heating rate of 5 °C/min up to 1000 °C, 3 °C/min up to 1400 °C, and then 2 °C/min until peak temperature was maintained, followed by natural cooling to room temperature.

2.2. Characterization

Chemical analyses of the raw materials were carried out by using standard wet chemical methods. The apparent porosity and bulk density of all the fired specimens were determined according to Archimedes’ Principle with kerosene as medium. Phase composition was analyzed by X-ray diffraction (XRD, X’ pert Pro, Philips, using Ni-filtered, Cu Ka radiation at scanning speed of 2 deg/min at a temperature of 16 °C) using the powders from the milled specimens under 325 mesh sieve. The lattice parameter, plane interplanar spacing and 2θ values of the spinel phase in specimens were determined using X’ Pert Plus software and Philips Profile Fit 1.0 software. The microstructure was analyzed by means of scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (Nova 400 Nano-SEM, FEI Co., Philips, The Netherlands).

Static cup tests with 24 g synthetic copper slag (for chemical composition see Table 3) were performed at 1450 °C for 6 h in air. After static cup test, specimens were investigated in terms of Cr(VI) formation by leaching tests, phase evolution by XRD. For microstructure-morphology, a portion of slag-refractory interface was cut, polished and coated with Au to observe under SEM equipped with EDS.

The leaching test of Cr(VI) was carried out according to the German TRGS 613 standard method [32]. The specimens were milled and then 1.50 g of the milled specimens (<74 μm) were suspended in 30 ml of distilled water. The solutions were stirred for 15 min with a magnetic stirrer (stirrer bar 40 mm, 300 rpm) and then filtered through 0.45 μm membrane filters. The concentration of Cr(VI) in the leach solutions was estimated using 1,5-diphenylcarbazide method (UV–vis) and recording the absorbance at

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>MgO</td>
<td>1.73</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.73</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 1

The chemical compositions of raw materials.
540 nm using 722 Vis spectrophotometer.

3. Results and discussion

3.1. Reaction and sintering process

The phase compositions of all the magnesia-chrome specimens after firing at 1700°C were the same, and the X-ray diffraction patterns were shown in Fig. 1. It can be seen that, the initial Cr2O3, Al2O3 and TiO2 phases disappeared after firing at 1700°C while a composite spinel phase identified as Mg(Al,Cr,Ti)2O4 were generated and coexisted with MgO in all the specimens. The crystal structure of the Mg(Al,Cr,Ti)2O4 composite spinel formed varied with chemical composition of the specimens. As shown in Fig. 2, the 2θ value of the (311) peak of the Mg(Al,Cr,Ti)2O4 composite spinel in specimens decreased with the increase in Cr2O3 and TiO2 content; it was 36.080, 36.043, 35.963, 35.916 and 35.837 in specimens of M9, M12, M15, M18 and M18T4, respectively. To further investigate the crystal structure of the Mg(Al,Cr,Ti)2O4 composite spinel, the lattice parameter and (311) plane interplanar spacing of the composite spinel were calculated. As shown in Table 4, the lattice parameter and (311) plane interplanar spacing increased with both Cr2O3 and TiO2 content. Based on the above results, it can be deduced that when Al2O3, Cr2O3 and TiO2 were added into magnesia, a reactive sintering process took place at high temperatures, and led to the formation of the composite spinel. In this reactive sintering process, Al2O3 and Cr2O3 would react with MgO to form the MgAl2O4 and MgCr2O4 spinels [33,34]. And TiO2 would dissolve into the MgO lattices leading to increase of cation vacancy concentration. Above the solid solubility limit (about 0.3 wt%), Mg2TiO4 could be formed due to reaction of TiO2 with MgO [31,35,36]. Subsequently, the Mg(Al,Cr,Ti)2O4 composite spinel would generate as a substitutional solid solution by interdiffusion between MgAl2O4 (JCPDS: 96-900-2065, a = 8.1790), MgCr2O4 (JCPDS: 01-082-1529, a = 8.3341) and Mg2TiO4 (JCPDS: 00-025-1157, a = 8.4380) [37–39].

The micrographs of the specimens prepared had a similar morphology. Most of the composite spinel deposited in the matrix as a continuous phase while other composite spinel with a much finer size varying from 2 to 5 μm was precipitated in the small MgO particles or at the rim of larger MgO aggregates as intragranular spinel (Fig. 3(a)-(c)). The ruptured surfaces of specimen M18 (Fig. 3(d) and (e)) indicated that the particles of the composite spinel Mg(Al,Cr,Ti)2O4 had very regular octahedron crystal morphology with well crystallization.

The bulk density, apparent porosity and linear expansion rate of the specimens after firing at 1700°C are illustrated in Fig. 4. It revealed that the bulk density decreased and the apparent porosity and linear expansion rate increased as the Cr2O3 content increased from 9 wt% to 18 wt%. From the theoretical calculations, it is known that the formation of the compound MgCr2O4 by reacting Cr2O3 with MgO is accompanied by approximate 3.6% volume expansion. Thus, too much MgCr2O4 formation would result in larger volume expansion, which is unfavorable for densification. However, compared with specimen M18, specimen M18T4 had lower linear expansion rate and higher densification. When TiO2 was added to magnesia materials, cation vacancy concentration increased due to

Table 2
The formulation of magnesia-chrome materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition (wt%)</th>
<th>MgO</th>
<th>Cr2O3</th>
<th>Al2O3</th>
<th>TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9</td>
<td>86</td>
<td>9</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>M12</td>
<td>83</td>
<td>12</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>M15</td>
<td>80</td>
<td>15</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>M18</td>
<td>77</td>
<td>18</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>M18T4</td>
<td>77</td>
<td>18</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3
The chemical composition of slag used for static corrosion test.

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Fe2O3</th>
<th>SiO2</th>
<th>CuO</th>
<th>CaO</th>
<th>MgO</th>
<th>Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>67</td>
<td>18</td>
<td>6</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of magnesia-chrome specimens fired at 1700°C.

Table 4
Lattice parameters of Mg(Al,Cr,Ti)2O4 composite spinel in specimens fired at 1700°C.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Lattice parameters a (Å)</th>
<th>(311) plane interplanar spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9</td>
<td>8.2469</td>
<td>2.4892</td>
</tr>
<tr>
<td>M12</td>
<td>8.2554</td>
<td>2.4918</td>
</tr>
<tr>
<td>M15</td>
<td>8.2737</td>
<td>2.4973</td>
</tr>
<tr>
<td>M18</td>
<td>8.2845</td>
<td>2.5006</td>
</tr>
<tr>
<td>M18T4</td>
<td>8.3028</td>
<td>2.5061</td>
</tr>
</tbody>
</table>

Fig. 2. The 2θ value of the (311) peak of the Mg(Al,Cr,Ti)2O4 composite spinel in specimens fired at 1700°C.
dissolution of TiO₂ in lattices of MgO, which could enhance mass transfer and densification of the specimens [40]. Besides, above the solid solubility limit of TiO₂ in MgO (about 0.3 wt%), Mg₂TiO₄ could occur and form solid solution with MgCr₂O₄ and MgAl₂O₄ spinels, which promoted diffusion sintering process and improved densification of the materials as well [40,41].

3.2. Corrosion test

Corrosion of refractories in copper slag is a very complex phenomenon, which generally involve physical (erosion or mechanical wear) and/or chemical (chemical wear, penetration and dissolution reactions) processes. Corrosion resistance can be defined in terms of depth of corrosion which is removal of refractory lining by slag and penetration which is permeation of liquid slag into the refractory lining [1,3,23]. Fig. 5 shows the images of the cross-section of the specimens (crucible) after static cup test for 6 h in air. A clear slag-refractory interface can be observed in all the specimens, indicating that the magnesia-chrome materials prepared possessed good corrosion resistance to the slag. The
average corrosion and penetration depth were measured from SEM images of the specimen cross-section, and the results are plotted in Fig. 6. It can be found that corrosion depth of the specimens increased slightly with increasing Cr₂O₃ content from 9 wt% (M9) to 18 wt% (M18) while decreased with increase in TiO₂ content from 2 wt% (M18) to 4 wt% (M18T4). The slag penetrations also increased
initially with Cr$_2$O$_3$ addition (up to 18 wt%, M18) then showed an obvious decrease. And combining the results of Fig. 4 with Fig. 6, it could be found that the corrosion resistance of the specimens was more dependent on the densification of the specimens despite the low solubility of Cr$_2$O$_3$ in copper slag. With a decrease in apparent porosity, available paths for infiltration of corrosive slag decreased [6, 23, 42], which was favorable for improving both penetration and corrosion resistance of the specimens.

After the corrosion test, the slag refractory interfaces of the specimens are very similar, and the micrograph of polished surface of the corroded specimen M9 is shown in Fig. 7. It can be seen that a dense ceramic layer was deposited between the slag layer and penetration layer. This layer could be regarded as the corrosion layer and it was much denser than the magnesia-chrome specimens themselves. The EDS analysis confirmed that the dense layer was composed of elements Mg, Fe, Cu, Cr and O (seen point 3 in Table 5), which was formed as a result of chemical reaction between slag (Fe$_2$O$_3$, CuO) and refractory (MgO, Cr$_2$O$_3$) components. The stable dense layer acted as a protection against further chemical interaction, blocking direct contact between the molten slag and the specimen. Therefore, all the specimens prepared obtained high corrosion resistance and the slight decrease of corrosion resistance with Cr$_2$O$_3$ content was attributed to the increased apparent porosity which would lead to penetration of more corrosive slag at the initial stage of the corrosion test. The increased Al content in the slag layer (point 1) indicated that Al$_2$O$_3$ from the surface of the specimen dissolved into the slag. Another remarkable feature was that monticellite (CaMgSiO$_4$, point 4) and forsterite (Mg$_2$SiO$_4$, point 6) formed in penetration layer as a consequence of reaction between SiO$_2$ and CaO (slag components) and MgO (refractory component). In addition, Fe$_2$O$_3$ from the slag dissolved into the Mg(Al,Cr,Ti)$_2$O$_4$ composite spinel at the hot face (point 5) and the Fe content in the composite spinel decreased continuously when going deeper into the refractory (point 7).

3.3. Leaching test for estimation of Cr(VI) formation

Since XRD analysis could not detect any Cr(VI) phases in the specimens during the preparation and corrosion test process, evidently due to its infinitesimal amount, therefore, it is necessary to perform leaching tests to assess the plausible formation of Cr (VI). Fig. 8 depicts the concentration of Cr(VI) in different stages of entire process for all the specimens. It was evident that the concentration of Cr(VI) increased with increase in Cr$_2$O$_3$ content (from 9 to 18 wt%) while the increase of TiO$_2$ (from 2 to 4 wt%) could lower the Cr(VI) concentration. The specimens before firing contained a significant level of Cr(VI) originating from chromium oxide (Cr$_2$O$_3$) raw material. During the Cr$_2$O$_3$ powders production process, some Cr$_2$O$_3$ can be easily oxidized into Cr(VI) compounds (mainly CaCrO$_4$ and Na$_2$CrO$_4$) at high temperature owing to the presence of CaO and Na$_2$O (Table 1) impurities [14, 16, 17]. However, after firing at 1700°C, the Cr(VI) leaching concentration decreased.

![Fig. 6. The average corrosion and penetration depth of the specimens after corrosion test.](image1)

![Fig. 7. The SEM micrographs of the polished surface of specimen M9 after corrosion test.](image2)

![Fig. 8. Concentration of Cr(VI) in mg/kg leached out from the specimens after different stages.](image3)

### Table 5
Composition (in wt%) of the phases indicated in Fig. 7.

<table>
<thead>
<tr>
<th>Point</th>
<th>Al</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.32</td>
<td>30.33</td>
<td>–</td>
<td>3.80</td>
<td>–</td>
<td>–</td>
<td>1.24</td>
<td>4.99</td>
<td>12.16</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>4.12</td>
<td>–</td>
<td>–</td>
<td>4.70</td>
<td>–</td>
<td>1.30</td>
<td>66.32</td>
<td>3.98</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
<td>20.08</td>
<td>6.73</td>
<td>16.34</td>
<td>1.60</td>
<td>1.11</td>
<td>9.57</td>
<td>–</td>
<td>41.17</td>
</tr>
<tr>
<td>4</td>
<td>6.60</td>
<td>–</td>
<td>13.22</td>
<td>2.58</td>
<td>13.64</td>
<td>32.16</td>
<td>31.80</td>
<td>2.34</td>
<td>44.85</td>
</tr>
<tr>
<td>5</td>
<td>–</td>
<td>20.16</td>
<td>31.59</td>
<td>1.06</td>
<td>–</td>
<td>–</td>
<td>2.34</td>
<td>–</td>
<td>44.85</td>
</tr>
<tr>
<td>6</td>
<td>11.60</td>
<td>–</td>
<td>13.63</td>
<td>4.37</td>
<td>28.94</td>
<td>4.58</td>
<td>36.88</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
obviously in the specimens. It has been found that the potential of oxides causing Cr(VI) to be reduced was closely related to their acidity and oxides with more acidic had more potential to trigger the reduction of Cr(VI) \([12,13]\). Thus, the decreased Cr(VI) concentration in the specimens after firing was partly attributed to the presence of TiO₂, which exhibited strong acidic according to the ionic theory of molten slag and can trigger the reduction of Cr(VI) via chemical reaction (1). Besides, the formation of considerably stable Mg(Al,Cr,Ti)₂O₄ solid solution phase in which Cr exhibited as Cr(VI) concentration after implying that the molten slag can lead the Cr(VI) to being reduced. Concentration of Cr(VI) decreased further after the corrosion test, implying that the molten slag can lead the Cr(VI) to being reduced to Cr(III). Since the copper slag used mainly consisted of strong acidic oxides SiO₂ and Fe₂O₃, the reduction of CaCrO₄ and Na₂CrO₄ compounds could feasibly be triggered via the chemical reactions (2) and (3) \([12,17,20]\). After the corrosion test, concentrations of Cr(VI) from slag-refractory interface was much lower than the US-EPA limit of 100 mg/kg but exceeded the European limit of 2 mg/kg for all the specimens.

\[ \text{4CaCrO}_4(s) + 4\text{SiO}_2(s) = 4\text{CaTiO}_3(s) + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2(g) \]  

\[ \text{4CaCrO}_4(s) + 4\text{SiO}_2(s) = 4\text{CaSi}_2\text{O}_5(s) + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2(g) \]  

\[ \text{4Na}_2\text{CrO}_4(s) + 4\text{SiO}_2(s) = 4\text{Na}_2\text{SiO}_3(s) + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2(g) \]

4. Conclusions

Magna-chrome refractories were fabricated and subsequent corrosion tests were performed in air using copper slag. The whole process was monitored by XRD, SEM-EDS and leaching tests; and the following conclusions can be drawn:

(1) A reaction sintering occurs in the magnesia-chrome refractories during firing process. After firing at 1700°C, a composite spinel Mg(Al,Cr,Ti)(Cl)₂O₄ phase forms in all the specimens, whose lattice parameter increases with increasing Cr₂O₃ and TiO₂ content. Densification of the specimens decreases with the increase in the Cr₂O₃ addition due to the increased volume expansion, while TiO₂ addition can improve their densification as mass transfer is enhanced during the sintering process.

(2) The corrosion resistance of the specimens decreases slightly with the Cr₂O₃ content due to the increased apparent porosity, which results in penetration of more corrosive slag at the initial stage of the corrosion test. However, a dense (Mg,Cu)(Cr,Fe)₂O₄ spinel layer forms between the slag and penetration layer, which effectively hinders further penetration of slag and well protects the specimens. Thus, all the magnesia-chrome specimens prepared show good corrosion resistance to the slag.

(3) The Cr(VI) in the specimens prepared increases obviously with the Cr₂O₃ content, while TiO₂ addition can lower the concentrations of Cr(VI) effectively due to the fact that the acidic oxide TiO₂ can cause the formed Cr(VI) to be reduced and the chromium mainly exists in the form of Mg(Al,Cr,Ti)₂O₄. Moreover, the copper slag can cause the formed Cr(VI) to be reduced further, and after corrosion test, concentrations of Cr(VI) from slag-refractory interface was much lower than the US-EPA limit of 100 mg/kg but exceeded the European limit of 2 mg/kg for all the specimens.

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References


