Effect of Temperature on Hexavalent Chromium Formation in (Al,Cr)₂O₃ with Calcium Aluminate Cement in Air

Yingjiang WU, Shengqiang SONG, Zhengliang XUE, and Mithun NATH

1) The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, 430081 China.
2) Hubei Provincial Engineering Technology Research Center of Metallurgical Secondary Resources, Wuhan, 430081 China.
3) Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan, 430081 China.

(Received on October 17, 2018; accepted on January 28, 2019)

Cr₂O₃ containing refractories castables are widely used as linings of various furnaces because of its remarkable corrosion resistance. However, Cr₂O₃ can be oxidized to toxic Cr(VI) by calcium aluminate cement phases (CA and CA₂) which are used as hydraulic binder in castables. In the present research, one of the most stable Cr(III) phase viz., (Al,Cr)₂O₃ solid solution was synthesized and then reacted with cement phases in order to check the formation of Cr(VI). The (Al, Cr)₂O₃ solid solution and calcium aluminate cement (70% Al₂O₃) were mixed in the ratio 1:1 (mass%) and heated in the temperature range of 500–1500°C in air. The phase compositions and formation/leachability of Cr(VI) were investigated using XRD, XPS and the leaching tests. The (Al,Cr)₂O₃ solid solution didn’t react with calcium aluminate cement at 500–900°C, while it partially converted to a Cr(VI)-containing phase at 1100–1300°C. However, (Al,Cr)₂O₃ and cement phases react to form a ternary Cr(III) phase (Ca(Al,Cr)₁₂O₁₉) at 1500°C.

KEY WORDS: (Al, Cr)₂O₃ solid solution; calcium aluminate cement; Cr(VI); leaching.

1. Introduction

Cr₂O₃ has excellent corrosion resistance and thermal shock resistance, its use can reduce the materials consumption of any refractory system, and it was often used as linings of the glass tank, gasification, waste melting furnaces and pyrometallurgical processes. But the Cr₂O₃ (III)-containing refractories can be oxidized to toxic Cr(VI) by calcium aluminate cement phases (CA and CA₂) which are used as hydraulic binder in castables. In the present research, one of the most stable Cr(III) phase viz., (Al,Cr)₂O₃ solid solution was synthesized and then reacted with cement phases in order to check the formation of Cr(VI). The (Al, Cr)₂O₃ solid solution and calcium aluminate cement (70% Al₂O₃) were mixed in the ratio 1:1 (mass%) and heated in the temperature range of 500–1500°C in air. The phase compositions and formation/leachability of Cr(VI) were investigated using XRD, XPS and the leaching tests. The (Al,Cr)₂O₃ solid solution didn’t react with calcium aluminate cement at 500–900°C, while it partially converted to a Cr(VI)-containing phase at 1100–1300°C. However, (Al,Cr)₂O₃ and cement phases react to form a ternary Cr(III) phase (Ca(Al,Cr)₁₂O₁₉) at 1500°C.

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Therefore, this system finds its applicability in various types of high-temperature furnaces as an addition in refractories castables. Alumina and chromium oxide form substitutional solid solution over the entire composition range without formation of any eutectic at high temperature due to their similar crystal structure and nearer atomic radii of the cations.39,40) But data on the reaction of (Al,Cr)2O3 solid solution with calcium aluminate cement and whether form Cr(VI) during the serve at different temperature is not available in the literature. The objective of this study was therefore to investigate the reaction between the (Al,Cr)2O3 solid solution and the calcium aluminate cement which substitute of Cr2O3 in castables at different temperature in order to examine the possibility of Cr(VI) formation in (Al,Cr)2O3-containing castables. Since there is temperature gradient in the furnace lining, the sample was heat treated at different temperatures (500–1 500°C) in the air. The formation of various phases during the heat treatment of sample was studied using XPS. The generation of Cr(VI) was investigated by XPS and leaching tests.

2. Experimental

2.1. Experimental Procedure

High purity chemicals Al2O3 (99%), CaO (99%) and Cr2O3 (99.95%), supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), were employed as the starting materials. Before weighing the batches, Al2O3 and CaO powders were calcined at 1 000°C for 8 h in a muffle furnace in order to decompose any probable hydroxide and/or carbonate phases. Similarly, Cr2O3 powder was dried in an oven at 110°C for 8 h to remove any moisture. The samples were synthesized by conventional solid-oxide reaction route. The calcium aluminate cement (based on Secar 71) and (Al,Cr)2O3 solid solution compositions were formulated in Table 1. The composition of the cement is based on commercial Secar 71, Kerneos Aluminales Ltd., as it is one of the most widely used cement. The oxides were weighed in appropriate proportions, thoroughly mixed in a tungsten carbide mill and then pressed into pellets of 20 mm diameter. The calcium aluminate cement was simulated with a mixture of Al2O3 and CaO, heated to 1 550°C at a rate of 5°C/min and equilibrated for 6 h in a MoSi2-heated muffle furnace in air. The resulting pellets were then grounded and reheated again. The (Al,Cr)2O3 also was sintered at 1 550°C, and the detailed procedure was the same with cement.

XRD patterns of the synthesized (Al,Cr)2O3 solid solution was subsequently compared with the standard PDF cards and it confirmed that pure (Al,Cr)2O3 was successfully synthesized in the present experiments (Fig. 1). The synthesized cement also was confirmed with XRD (Fig. 1) and it exhibits CaAl2O4 (CA) and CaAl4O7 (CA2). As per Al2O3–CaO phase diagram (Fig. 2), the composition of the synthesized cement would produce the CA and CA2 phases. The XRD results of synthesized cements reveal a good agreement with the commercial Secar 7125) which has similar composition.

Samples were ground into powders, a mixed powder of composition in cement: (Al,Cr)2O3 was 1:1 (mass%) in a tungsten carbide mill, re-pelletized. At the second sintering step, the pellets were reacted in the air for 8 h (optimized from our previous studies27) in a tube furnace at 500, 700, 900, 1 100, 1 300 and 1 500°C, respectively, after that they were quenched by quickly immersing them into liquid nitrogen.

2.2. Analysis

The chemical valence state of chromium in the samples after heat treatment was analyzed by using X-ray photoelectron spectroscopy (XPS) which were carried out using an ESCA spectrometer (PHI 5000 VersaProbe, Ulvac-PHI, Physical Electronics), equipped with a non-monochromatic Al-Kα X-ray source. Samples were finely ground using a mortar and pestle. The results were acquired from the surface layers of powder samples with spot areas of 500 μm in diameter and penetration depth less than 5 nm. All the
spectra were obtained under CAE mode with 35 eV of pass energy and 0.05 eV of step size. The values are reported as the average of result of 15 times scanned of each sample.

The phase compositions of the quenched samples which were ground using a mortar and pestle were evaluated using X-ray diffraction (XRD; X’Pert Pro, Bruker, Germany), with copper radiation (Cu Kα, λ = 1.5418 Å) working at 40 kV and 40 mA. Scans were performed in continuous mode at a 2° min⁻¹ scan rate and 2θ scanning ranging from 5° to 90°. Phase identification was done by PANalytical X’Pert Highscore plus software. While the quantitative XRD analysis was performed using TOPAS V5 software.

Leach tests were carried out according to the TRGS 613 standard procedure to determine whether Cr(VI) formed during the heat treatment process. This method is used to determine water-soluble Cr(VI) compounds in cement and products that contain cement. Samples of 1.5 g which were ground using a tungsten carbide mill were weighed into leaching bottles, suspended in 30 ml of distilled water (DW), vigorously stirred for 15 min with a magnetic stirrer (stirrer bar 40 mm, 300 rpm) and then filtered through 0.45 μm membrane filter with a glass fiber filter by vacuum. The pH of the leach solution was determined using a PHS-3C Precision pH/mV Meter (Aolilong, China). The concentration of Cr(VI) in the leach solution was measured using a colorimetric method. The Cr(VI) can react in acid condition with the 1,5-diohenylcarbazide to form 1,5-diohenylcarbazone, which forms a red complex (0.01–0.5 mg/l chrome). Then the absorbance was recorded, using a 722 Vis spectrophotometer at 540 nm (Jinghua Instruments, China). In order to leach out all the Cr(VI) present in the samples, the solid residues were sequentially leached until the leach solution became colorless. For each leaching cycle, the solid residues were suspended in 150 ml of distilled water, stirred for 15 minutes using a magnetic stirrer, and then filtered through 0.45 μm membrane filters.

3. Results and Discussion

3.1. XPS Analysis

XPS analysis was used to investigate the chemical valence variation in the samples with temperature as shown in Fig. 3. Gaussian curve fitting of the Cr 2p1/2 and Cr 2p3/2 photoelectron peaks were performed using CASA XPS software in order to deconvolute the peak position that associated with binding energies of 588.7, 586.5, 579.4 and 576.8 eV. Relating these values to standard spectra of various chromium species, it can be assumed that the binding energies of 586.5±0.2 eV (Cr 2p1/2) and 576.4±0.3 eV (Cr 2p3/2) are associated with Cr(III), while the binding energies of 588.7±0.2 eV (Cr 2p1/2) and 579.4±0.1 eV (Cr 2p3/2) are associated with Cr(VI). It is clear that the samples which were treated from 500°C to 900°C only Cr 2p1/2 and Cr 2p3/2 associated with Cr(III) could be observed. At 1 100°C, it has a maximum Cr(VI) content with a low concentration of Cr(III). With the temperature increased to 1 300°C, the intensity and the area covered by the peak associated with Cr(VI) decreased while that of Cr(III) increased. When the temperature was up to 1 500°C, only Cr 2p1/2 and Cr 2p3/2 associated with Cr(III) could be observed also, the peak associated with Cr(VI) totally disappeared. Thus, it is clear that the temperature plays an important role in the formation of Cr(VI)-containing compound.

3.2. Phase Evolution

XRD analysis was implemented to identify the presence of different crystalline phases in samples, with the results presented in Fig. 4. The XRD patterns of samples fired at 500°C, 700°C and 900°C was the same. (Al,Cr)2O3 is the major phase in the samples fired at 500°C, 700°C and 900°C while the secondary phases were CaAl2O4 and CaAl4O7. It means the cement and (Al,Cr)2O3 solid solution didn’t react from 500 to 900°C. In the case of sample fired at 1 100°C, (Al,Cr)2O3 still exists as the primary phase and CaAl2O4 was the secondary phase in the sample and also contains CaAl4O7 but the intensity of it decreased, while a minute amount of Cr(VI)-containing phase namely Ca3Al2CrO16 formed as well. The Ca3Al2CrO16 which has a cubic crystal structure belongs to the haüynite family (3CaO·3Al2O3·CaSO4, 3SrO·3Al2O3·SrSO4, and 3SrO·Al2O3·SrCrO4). In chrome-haüyne, the SO4²⁻ group is replaced by CrO4²⁻, and the chromium ion exists as the oxidation state of CrVI.44 As the temperature increased from 1 100 to 1 300°C, the amount of CaAl2O4 increased while the amount of (Al,Cr)2O3 solid solution and CaAl4O7 decreased, the Cr(VI)-containing phase Ca3Al2CrO16 also decreased with the temperature increased. But in the sample fired at 1 500°C, the peaks of CaAl2O4, CaAl4CrO16 and (Al,Cr)2O3 solid solution totally disappeared, leaving behind only cement phase CaAl2O4 and Ca(Al,Cr)12O19. The concentration of CaAl2O4 decreased compared with 1 300°C (Table 2). The Al2O3–CaO phase diagram (Fig. 2) also shows that CaAl12O19 is the intermediate phase between Al2O3 and CaAl2O4. Li and Medina reported that the CaAl12CrO19 (x = 0.5 - 3.5) solid solutions formed by solid state reactions through substitution of aluminum with chromium.45 The peaks of CaAl12O19 phase in the sample (fired at 1 500°C) were compared with standard CaAl2O19, all of them shifted towards lower 2θ angle which implies some Ca(Al, Cr)12O19 solid solution may be formed.
Amount of crystalline phases in all samples were determined using the Rietveld method (TOPAS V5) as shown in Table 2. It confirmed that just the samples treated at 1 100°C and 1 300°C have Cr(VI)-containing phase Ca₄Al₆CrO₁₆, and the concentrations of Ca₄Al₆CrO₁₆ are 4.92% and 2.57%, respectively. Combined with XPS analysis results, in the Ca₄Al₆CrO₁₆ phase chromium is present as +6 oxidation state, whereas in Ca(Al,Cr)₁₂O₁₉ and (Al,Cr)₂O₃ chromium are present as +3 oxidation state.

In our previous research, a Cr(VI)-containing compound CaCrO₄ can form from 500 to 1 100°C in Cr₂O₃-containing refractory castables where individual Cr₂O₃, Al₂O₃ and calcium aluminate cements (Secar 71) were subjected for reaction. But in the present research, cement phases (CA and CA₂) virtually didn’t react with (Al,Cr)₂O₃ solid solution from 500 to 900°C and almost no traces of any Cr(VI)-containing phases could be observed. It means that using (Al,Cr)₂O₃ solid solution instead of Cr₂O₃ can restrict the formation of Cr(VI)-containing phase CaCrO₄ at low temperature regime (500–900°C). But at 1 100 and 1 300°C the Cr(VI)-containing phase Ca₄Al₆CrO₁₆ still can be formed.

The activity of Cr₂O₃ in the (Al,Cr)₂O₃ has been investigated by Besman and Kulkarni. It was reported that the Cr₂O₃ activities increased with mole fraction of Cr₂O₃ in the (Al,Cr)₂O₃ solid solutions. At the treated chemical composition, the Cr₂O₃ is 0.04 mol%, the activity is ranged from 0.08 to 0.25, from 1 100°C to 1 500°C. The Cr₂O₃ activities in the (Al,Cr)₂O₃ solid solutions is much lower than that of pure Cr₂O₃ was used (where activity of Cr₂O₃ is equal to 1). And the chromium in (Al,Cr)₂O₃ solid solution is more stable and not to form Cr(VI)-containing compound comparing with that in pure Cr₂O₃.

### 3.3. Cr(VI) Leaching Tests of the Quenched Samples

The extraction of Cr(VI) was evaluated according to the TRGS 613 procedure. The leach solutions obtained from samples and Cr(VI) concentrations of these leach solutions are shown in Fig. 5. Yellow coloration of the leach solution is an indication of Cr(VI) in the leach solution. It indicated the leach solution from samples fired at 1 100 and 1 300°C contain a large amount of Cr(VI). While the leach solutions from samples fired at 500–900°C and 1 500°C was colorless.

The concentration of Cr(VI) leached from samples treated at 500–900°C and 1 500°C range from 0.29 mg/l to 2.08 mg/l. All of these were below the allowable EPA limit of 5 mg/l. However, the concentrations of Cr(VI) in the leach solutions from samples treated at 1 100°C and 1 300°C were up to 117.27 mg/l and 59.86 mg/l, respectively. The pH of the leach solution increased from pH 7.3 of the distilled water to range from 10.91 to 9.54. During the leaching process, Ca and Al containing cement phase presumably dissolved in water as Ca²⁺ and Al(OH)₃⁺, which increased the pH of the leach solution. And the amount of chromium ions in the leach solutions was also quantified with ICP. The Cr(VI) concentration leached out (measured from UV-vis) is close to that of Cr_total in leach solution (ICP). It means that most of the chromium present in the leach solutions as Cr(VI) only, on the contrary Cr(III) present in the (Al,Cr)₂O₃ and
Ca(Al,Cr)_{12}O_{19} phase didn’t leach out.

3.4. Repeat Leaching of the Solid Residues

The solid residues that remained after the TRGS 613 test procedure were repeatedly re-leached until the leach solution became colorless. In order to leach out all of Cr(VI) in the samples, leaching was done with an excess amount of distilled water (the solid residues was suspend in 150 ml of distilled water). Figure 6 shows the amount of Cr(VI) as a function of the number of times leached and corresponding leach solutions. The leach solution from samples treated at 500–900°C became colorless after just being leached one time. Similar is the case for samples treated at 1 500°C, just after one time leach, the leach solution became colorless. The samples fired at 1 100°C and 1 300°C became colorless after being leached for three times. It means that there were some water soluble Cr(VI) left in the solid residues of samples fired at 1 100°C and 1 300°C after the TRGS 613 leaching procedure. The amount of Cr(VI) in the leach solution decreases with number of leaching cycles.

Mass balance before and after the leaching for Cr(VI) in samples also has been done. The mass percentage of Cr(VI) in the leach test was calculated as per Eq. (1):

$$w_{\text{Cr(VI)}}[\%] = \frac{C_n V_n + (C_{\text{Cr(VI)}} + \ldots + C_{\text{Cr(VI)}}) \times V}{m} \times 100 \ldots \ (1)$$

where, $V_n$ is the volume of repeat leaching liquor of solid residue and $V_0$ is the volume of leaching liquor in TRGS 613, in L

$C_n$ is the concentration of Cr(VI) in repeat leach of solid residue and $C_0$ is the concentration of Cr(VI) in TRGS 613, in mg/L

$m$ is the weight of the synthesized sample used in leaching test, in mg

As predicted from earlier XRD quantitative using the TOPAS V5, in the sample treated at 1 100°C and 1 300°C, it has an amount of Cr(VI) while it was almost no Cr(VI) in other samples. During the repeat leaching test, the amount of Cr(VI) was the maximum in the sample treated at 1 100°C. The leachability of Cr(VI) in the sample fired at 1 100°C and 1 300°C during the repeat leaching is 0.398% and 0.203%, respectively. Moreover, XRD quantitative analysis of this two samples before leaching showed the mass percentage of Cr(VI) around 0.406% and 0.212%, which is consistent with the leaching result. Thus, all Cr(VI) in samples can be leached out.

The solid residues after multiple leaching were also analyzed by XRD to observe any changes in phase composition during the leach process (Fig. 7). After repeat leaching tests, the Cr(VI)-containing phase CaAl_{4}Cr_{6}O_{16} disappear completely in the samples treated at 1 100°C and 1 300°C, leaving behind only CaAl_{2}O_{4}, CaAl_{2}O_{4} and (Al,Cr)_{2}O_{3} solid solution. The XRD pattern of the sample treated at 700°C remained unchanged before and after multiple leaching.
Similar is the case for the samples treated at 1 500°C, with both CaAlO\(_2\) and Ca(Al,Cr)\(_2\)O\(_4\). It means that the Cr is in solid solution with CaAl\(_2\)O\(_4\)/Al\(_2\)O\(_3\) to form Ca(Al,Cr)\(_2\)O\(_4\)/ (Al,Cr)\(_2\)O\(_3\) and exists as Cr(III) which is very stable and insoluble in water. While all the Cr(VI)-containing phase Ca\(_3\)Al\(_4\)CrO\(_{16}\) can be leach out during the repeat leach tests.

4. Conclusion

It is clear that the temperature plays a very important role in the formation of Cr(VI) between the (Al,Cr)\(_2\)O\(_3\) solid solution and cement phases. The (Al, Cr)\(_2\)O\(_3\) solid solution didn’t react with cement (CA and CA\(_2\)) at 500–900°C. Thereafter, at 1 100°C and 1 300°C, the Cr(VI)-containing phase haüyne (Ca\(_4\)Al\(_6\)CrO\(_{16}\)) still can form. On the contrary, the sample treated at 1 500°C predominantly forms Ca(Al,Cr)\(_{12}\)O\(_{19}\) and CaAl\(_4\)O\(_7\), and there isn’t any other Cr(VI)-containing phase form. During the leaching test and quantitative XRD analysis, the sample treated at 1 100°C exhibit the highest concentrations of Cr(VI). However, all of the Cr(VI)-containing phase in the samples can be completely leach using distilled water through repeated leaching. So the spent (Al,Cr)\(_2\)O\(_3\)-containing refractory castables from 1 100°C to 1 300°C must be disposed very carefully.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51604203) and the Hubei Chutian Scholar Program.

REFERENCES