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EROSION MECHANISM OF A SLAG GLASS-CERAMIC OF CaO-Al_2O_3-MgO-SiO_2 SYSTEM IN HYDROCHLORIC (HCl) ACID SOLUTION

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Abstract

The erosion mechanism of a slag derived glass ceramic in a hydrochloric acid (HCl) solution (ph=1) at 85°C was first revealed by visual, SEM, EDS and XRD examinations. The rod-like anorthite, one of two primary phases, is the only remaining crystalline phase within the corrosion layer of the sample after it has been etched for 5 days. Meanwhile, another original main phase, diopside particles, has been corroded out by dissolving with two minority phases: coesite and fluorite. This result suggests anorthite is more resistant to HCl erosion and more favourable than diopside in the future designs of a hydrochloric acid erosion resistive slag glass ceramic.

Introduction

To be used to fabricate glass-ceramic has been proved to be one of most effective ways to recycle large scale industrial solid wastes, such as fly ash[1], titanium slag[1], nickel slag[2], blast furnace slag[2], molten steel slag[3] and oil shale fly ash[4], *etc*. Besides of high hardness and bending strength, some of these wastes derived glass ceramics have also shown strong resistances to H_2SO_4 and NaOH errosion[5]. This may extends the application of the material from traditional field of construction[6] to that of conveying high corrosive liquids with high hardness particles in various chemical plants. In contrast to their two well explored chemical resistances mentioned above, little attention has been paid to the resistance of the material to HCl solution and the corresponding erosion mechanism. However, there do exist factorys, such as Zhun Neng alumina form, uses HCl solution as the working medium to extract alumina from fly ash. Therefore, we further investigated the erosion mechanism of our new glass ceramic within a hydrochloric acid (HCl) solution (PH=1) at 85°C in a five-day long test. This typical set of test conditions was chosen because it is the harshest working condition in the just mentioned firm, where conventional corrosion resistant materials, such as stainless steel, glass have all been proved to be not reliable. Our results would surly extend the appreciation and application of wastes derived glass ceramics.

Experimental Procedure

The compositions of the two main raw materials: refined Baiyanobo iron-rare earth (RE) ore tailing and fly ash, are listed in Table 1 respectively. They were identified by an inductively coupled plasmas atomic emission spectrometry (ICP-AES). The as-designed formula of the parent glass is given in Table 2. Industrial-grade $NaCO_3$, CaO, Al_2O_3, $BaSO_4$ and borax were used to compensate the composition gaps. The sample of around 2×2×6 cm in three dimensions was prepared at a pilot plant established by our research group at the campus of our University. Similar process consisting of melting, casting, and heat treatment was adopted as our previous study did[6]. The corrosion test of the sample was carried out in HCl solution at 85°C for 5 days. The morphology and the element distributions on the cross section of the sample were examined using a SEM (FEI Quanta 400) equipped with an EDS (Quest) operating in both second electron (SE) and back scattered electron (BSE) modes. The crystalline natures of the corrosion layer and remaining inner part of the sample were identified by an XRD (Bruker D8) respectively, using crushed powers from just mentioned two parts of the sample were used. A radiation of CuKα (λ=1. 54051×10^{-9}m) was used as the incident X-ray in our XRD examination.

Table 1: The compositions of the refined Banyan Obo ore tailing and fly ash used in current study (wt%)

	CaO	Al_2O_3	SiO_2	MgO	Na_2O	K_2O	CaF_2	FeO	Fe_2O_3	REO	Rest
Tailing	17.21	7.20	27.56	5.32	3.11	1.24	10.35	3.14	17.35	1.25	6.27
Fly Ash	8.47	20.35	53.44	3.15	1.11	1.15	—	1.02	3.25	—	8.06

Table 2: The composition of the parent glass used in current study (wt%)

	Tailing	Fly Ash	CaO	Al_2O_3	$NaCO_3$	$BaSO_4$	Borax
Content	50	25	10	5	5	2	3

Results and Discussions

The results of surface morphology examination were present in Figure 1. It is clear from Figure 1a that the thickness of the corrosion layer is only about 0.5 mm, showing the material has a strong resistance to HCl solution etching. The BSE image present in Figure 1b shows both sides of the transition zone consist of considerable amount of rod structures scattering within the matrix. Those rod-like phases are more prominent than rest of the matrix within the corrosion region, indicating they are more resistant to HCl solution corrosion than the matrix. Figure 1c shows that both the rod-like phases and rest of the matrix contain numerous particle phase. These particles disappear after the erosion test forming as indicated by Figure 1d. The resultant voids are inter-connected, forming numerous tunnel-like passages within the corrosion layer. Considering the

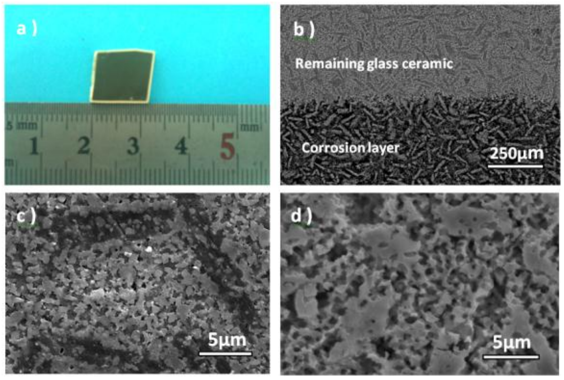

Figure 1: The macro and micro morphology pictures of the cross section surface of the sample after etched in HCl solution (pH=1) at 85°C for 5 days: a) Macro image of the cross section of the bar shaped sample; b) BSE photo of dilute HF etched cross section of the bar; c) SE image of the remaining glass ceramic and d) the corrosion layer

zigzag nature of these passages, the removal of these particles from the corrosion layer can be concluded as by dissolving. This is the main erosion mechanism of the sample in HCl solution.

The elemental and crystalline compositions were decided by means of EDS and XRD, and the results are shown in Figure 2. The characteristic x-ray peaks of Ca and Fe obtained from the remaining glass ceramic region (Figure 2a) are much higher than the corrosion layer (Figure 2b). This result indicates the remaining glass ceramic region generally contains more Ca and Fe elements than the corrosion layer. XRD patterns (Figure 2c) further reveals it is diopside (($Mg_{0.6}$ $Fe_{0.2}$ $Al_{0.2}$) Ca ($Si_{1.5}$ $Al_{0.5}$) O_6, 72-1379) instead of anorthite ($CaAl_2Si_2O_8$, 41-1486) which disappears from the corrosion layer.

Thus, our result in general suggests the resistance of anorthite to HCl erosion is much higher than diopside. And anorthite should be the target crystalline phase in the future development of HCl resistant glass ceramics, despite the fact that diopside, augite, and other varieties of pyroxene crystalline are generally preferred in the research field of slag glass ceramics because of the good mechanical properties they may offer to the resultant material[7,8].

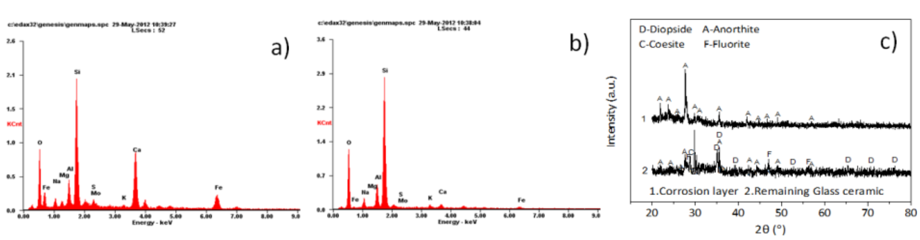

Figure 2: The average EDS examination results of the a) the remaining glass ceramic region; b) the corrosion layer of the sample and c) XRD patterns of these two regions

Conclusions

In the current study, we addressed the erosion mechanism of a glass ceramic previously fabricated by our research group using Banyan Obo tailing and fly ash as the main starting materials. Our result shows the glass ceramic contains rod-like anorthite and diopside particles as its main crystalline phases. Diopside particles dissolve away first from the corrosion layer along with those native secondary phases: coesite and fluorite. The anti-corrosion ability of anorthite phase to hydrochloric acid is much superior than diopside. Thus, anorthite phase should serve as a very promising candidate for the future design of a slag glass ceramic with good resistance to hydrochloric acid erosion.

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