APPLICATION OF SiC-BASED REFRACTORIES IN COPPER INDUSTRY

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ABSTRACT

In the modern copper industry, it is important to achieve continuous operation to increase the productivity and reduce the environmental problems. Launder is one of the essential components to rapidly transfer molten matte and copper in different processes. In most of the copper-making plants, oxide refractories have been used as the launder materials. However, these refractories have certain amount of pores that slow down the flow rate and stick the freezed matte and metal when tapping is stopped. Removal of the heavy matte and metal stuck on the launder is time-consuming and often breaks the launder. Development of new launder materials for molten matte and copper is urgent for continuous operation of copper production.

SiC has some unique properties such as high hardness, toughness, chemical and thermal stability and, in particularly, low wettability to matte and copper metal. SiC-based materials have been proposed to be the alternative material for the launders and lining for refining furnace and ladle. However, SiC is hard to be sintered directly and suitable bonding phase is required to make strong and relatively cheaper refractories. In the present study, SiC-based refractories with different bonding phases were evaluated with molten matte, copper and cupric oxide respectively.

The silicates bonded SiC was prepared under controlled temperature and time in air. The pre-oxidised SiC powders that have a layer of SiO_2 on the surface were mixed with Al_2O_3 and heated under controlled temperature and time. The aluminosilicate formed acts as the bonding phase to join the SiC particles. The commercial Si_3N_4 bonded SiC materials was also used in the present study for comparison. Static corrosion tests were carried out to test the resistances of the new materials to molten matte, copper and cupric oxide. After reaction the material was quenched into water for electron probe X-ray microanalysis.

Keywords: Si_3N_4 bonded SiC material, aluminosilicate bonded SiC material, corrosion test, EPMA

INTRODUCTION

In copper-making industry, different types of furnaces are involved in the pyrometallurgical process including smelting furnace, converting furnace, and refining furnace. Launder is an essential component in modern copper making process to rapidly transfer molten matte and copper between different furnaces [1]. In the conventional copper making plants, the production of copper is a batch process, and launder is only used to transport the metallic copper melt to the casting wheels. With the development of new copper making techniques, for example, recently commercialised two-step copper making process [2] uses launders to transport high grade matte (>73% Cu) produced by the bottom blown smelting furnace to the next converting and refining furnace. The anode copper produced from second furnace is transferred to the casting wheel through the launder. Launder has become more and more important in the modern copper production to maintain continuous operation. Whole copper making process is integrated to a continuous process connected by the launders. Short service life of the current launder material causes frequent shut-down of the operation not only the furnace directly involved but also other processes associated such as acid plant and electrolytic refining.

In the continuous converting process liquid matte from the smelting furnace flows to the converting furnace through launder. Low flowrate of the matte flow will decrease it temperature even freeze to the solid. Nature gas burners may be required to maintain the temperature of the matte. The quality of the launder plays important role in rapid flow of the matte. The launder is usually open to air and the high temperature matte inside may react with oxygen to form copper metal or copper oxide. The lining materials used for launder should not react with matte, copper metal and copper oxide. The current lander is usually made from oxide refractories which has a large amount of pores. These pores on the surface of the launder significantly reduce the flowrate of the melt. When the tapping is stopped certain amount of heavy matte/metal can remain on the launder and it is practically difficult to remove these heavy residues from the launder. Cracks may be formed on the launder due to different thermal conductivities between oxide launder and matte/metal which penetrated inside the pores of the launder. The coarse surface of the launder will slows down the melt flow and result in even severe damage of the launder. The removal process for the solid matte and copper stuck on the launder will finally destroy it and new launder is required. The matte and copper stuck on the launder need to be treat also reduce the productivity of the smelter. Meanwhile, the refractory fragments from the launder transporting molten copper may come to the casting wheel and pollute the anode copper. It is urgent to develop new launder materials for copper industry to maximise the campaign life and minimise the production cost.

Silicon carbide (SiC), has been considered as a candidate material of refractory in high temperature process since 1893 [3]. The main technology to produce SiC is the Acheson process [4] by heating the silica sand and coke at a high temperature. SiC refractory shows outstanding features, such as high mechanical strength, good thermal conductivity, good shock resistance, and low wettability to matte and copper metal. As SiC is difficult to be sintered directly, the SiC based refractory is always made with additives to form the bonding phase to join the SiC particles strongly. SiC based refractory has been widely used in the iron- and steel-making industry. The uses of SiC refractories in the pyrometallurgical processes also found that it has a weak anti-oxidation characteristic. Well-controlled oxidation on the SiC particle will form a SiO_2 layer to cover the particle which will stop the further oxidation of SiC [5]. In the recent years, SiC based refractory has been considered in the copper making industry as launder [6]. In the present study, two types of SiC refractory materials, the silicon nitride (Si_3N_4) bonded SiC and silicate bonded SiC, were tested in liquid matte and copper metal to simulate the conditions used in the copper making industry. The present study is part of the comprehensive research program aiming to provide new generation refractory materials for modern copper industry.

EXPERIMENTAL

The Si_3N_4 bonded SiC refractory material was obtained from a commercial refractory making company. The SiC content of the material is ~75 wt% and Si_3N_4 is ~25 wt%. The bulk density is ~2.60 g/cm^3 and the porosity is ~18%.

The aluminosilicate bonded SiC was prepared in laboratory by the authors. The size of the SiC powder is 2 ~ 15 μm with purity 99%. The purity of the aluminium oxide used in the synthesis is 99.8 wt% from Alfa Aesar. The material was synthesized in a programmable muffle furnace. 5 wt% Al_2O_3 was mixed thoroughly with SiC powder and pelletised to a dense cylindrical shape (ϕ 10 * 8 mm). The pellet was then heated in air slowly to 1300 ºC (5 ºC/min) and kept for 2 hours followed by 1500 ºC for 2 hours.

The static corrosion tests of two SiC based refractory materials with different melts (matte/Cu/Cu_2O) were carried out under argon gas flow. The refractory material sample was placed in alumina crucible with solid matte/Cu/Cu_2O powder. The matte sample (Cu grade 72 wt%) used in the present study was provided by copper making industry.

The experiments were carried out in a vertical reaction tube (impervious recrystallized alumina, 30 mm inner diameter). A working thermocouple in a re-crystallised alumina sheath was placed inside the reaction tube to monitor the actual temperature of the sample. The working thermocouple was periodically calibrated against a standard thermocouple (supplied by the National Measurement Institute of Australia, NSW, Australia). The overall absolute temperature accuracy of the experiment was estimated to be ± 3 ºC. The sample was introduced from the bottom of the reaction tube, and then raised and kept in the hot zone of the reaction tube by platinum wire (0.5 mm diameter). After reaction for a predetermined period at a given temperature, the crucible will be directly dropped into water. This way the reactions between the refractory and the melt are stopped and the microstructure and compositions of the phases present are freezed. The retained microstructures and phase compositions of the refractory and melt can provide accurate information at high temperature.

The quenched sample was sectioned, mounted and polished for examinations using a JEOL JXA-8200 electron probe X-ray microanalyser (EPMA) with wavelength dispersive detectors. (JEOL is a trademark of Japan Electron Optics Ltd., Tokyo). An accelerating voltage of 15 KV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with EPMA was applied. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Al_2O_3 for Al, Fe_2O_3 for Fe, MgO for Mg, $CaSiO_3$ for Ca and Si, $CuFeS_2$ for Cu and S, NB for N. The average accuracy of the EPMA measurements is within 1 weight percent of element concentration; this is verified by comparison with standards as unknowns during analysis. Carbon concentration cannot be measured directly by EPMA.

The compressive strength of the refractory was measured by Instron Compression Tester 8031, which was obtained by the maximum load divided by the sample surface area. It is a combined measure of the refractory for the strength of the grains and also of the bonding system.

RESULTS

The Si_3N_4 bonded SiC refractory material

The Si_3N_4 bonded SiC material has been manufactured for more than 50 years and many researchers have carried out the investigations on the synthesis of the material [7-11] and effects of impurities [12]. Si_3N_4 bonded SiC material is produced by heating the mixture of SiC and Si powders at 1200 – 1400 ºC in N_2 gas atmosphere. Previous researches on the degradation of Si_3N_4 bonded SiC refractory were focused on the iron and steel making conditions [13-15]. However, limited information was found on the interactions between Si_3N_4 bonded SiC material and matte/copper melts.

The microstructure of the commercial Si_3N_4 bonded SiC material is shown in Fig. 1. It can be seen from the figure that large SiC particles are connected by the Si_3N_4 phase. Ferrous silicon alloy is also found on the centre of the SiC particle, which indicates the incomplete carbothermic reaction during SiC production.

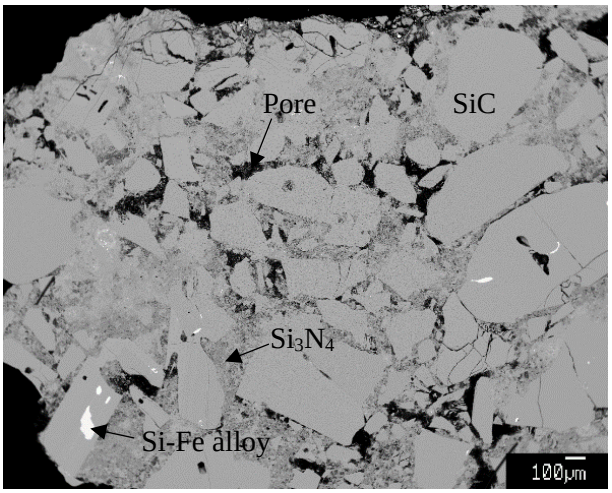

Fig. 1. Microstructure of the Si_3N_4 bonded SiC material

The static corrosion tests of the Si_3N_4 bonded SiC material with matte (Cu-Fe-S, 72 wt% Cu) was conducted in Ar at 1200 ºC for 2 hours. The observation of the cross-section of the sample after the reaction shows that most of the original material was reacted. The microstructure of the reacted material is shown in Fig. 2. From the microstructure and the compositional analysis of the phases, it was found that new phases were formed at the interface between the refractory and the melt: Fe-Cu alloy, new matte (Cu-Fe-S, 56 wt% Cu), metallic Cu, SiO_2 and slag. The formation of new phases demonstrates that oxidation-reduction happened between the Si_3N_4 bonded SiC material and matte. It also can be seen that both Si_3N_4 and SiC can react with matte and high Fe content Fe-Cu alloy (93% Fe) was transformed from the matte phase. Metallic copper droplets were found inside the matte. Due to the formation of Cu in the matte phase, the copper content has been decreased from 72 wt% to 56 wt% in the newly formed matte phase. The SiO_2 phase was seen in the sample from the oxidation of Si_3N_4 and SiC. SiO_2-"FeO"-Cu_2O slag was formed by the reaction between SiO_2 and FeO/Cu_2O which was formed from the matte.

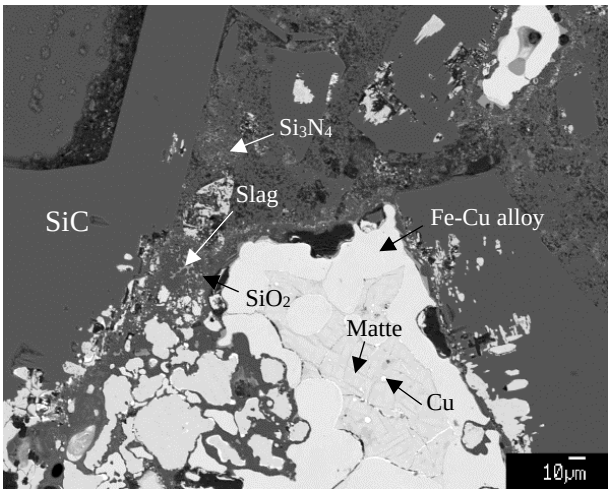

Fig. 2. Microstructure of the Si_3N_4 bonded SiC material after reaction with matte in Ar at 1200 ºC

The present investigation reveals that the direct reactions between matte and Si_3N_4/SiC are severe, and the Si_3N_4 bonded SiC material can be corroded by matte rapidly. High-grade matte always contains certain amount of oxygen which can react with Si_3N_4 and SiC. This material is clearly not suitable to be used as the launder material to transport matte at high temperature. It is speculated that when it is exposed in air, the oxygen will be more swiftly transported by the liquid slag and more iron and copper from the matte will be oxidised and reacted with SiO_2 to form the fluid liquid slag. The material will be peeled off quickly with the flow of matte at high temperatures.

The static corrosion tests of the Si_3N_4 bonded SiC material with Cu_2O was also conducted in Ar at 1200 ºC for 2 hours. The microstructure of the sample after reaction is shown in Fig. 3. It can be seen from the figure that Cu_2O is acting as an oxidizing agent, and both of the SiC and Si_3N_4 were oxidated to form SiO_2 and metallic Cu was reduced from Cu_2O. The FactSage thermodynamic calculations [16] show that the two reactions can easily happen at 1200 ºC:

$$SiC + 4\,Cu_2O \rightarrow SiO_2 + 8\,Cu + CO_2$$
$$\Delta G = -\,744.15 \text{ kJ/mol at } 1200\ ^{o}C$$

$$Si_3N_4 + 6\,Cu_2O \rightarrow 3\,SiO_2 + 12\,Cu + 2\,N_2$$
$$\Delta G = -\,1343.14 \text{ kJ/mol at } 1200\ ^{o}C$$

The microstructure clearly demonstrates the reactions happened between SiC/Si_3N_4 and Cu_2O. In between the SiC particles and Cu_2O melt, metallic Cu phase and SiO_2 phase were present. The SiO_2 phase is also the oxidation product from the reactions between Si_3N_4 and Cu_2O. SiO_2 can further react with Cu_2O melt to form two immiscible slag liquid phases, high-SiO_2 liquid (42 wt% SiO_2, 50 wt% Cu_2O, 8 wt% Al_2O_3) and high Cu_2O liquid (12 wt% SiO_2, 83 wt% Cu_2O, 5 wt% Al_2O_3) (Al_2O_3 is from the alumina crucible).

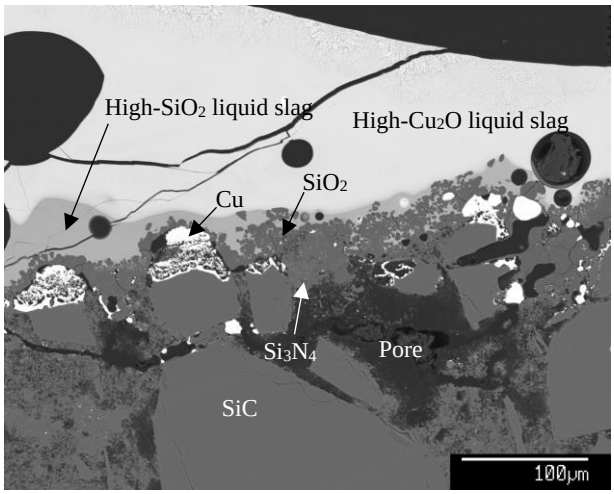

Fig. 3. Microstructure of the Si_3N_4 bonded SiC material after reaction with Cu_2O in Ar at 1200 ºC

Although matte and Cu have low wettability with SiC, the present investigations indicate that the Si_3N_4 bonded SiC material has a high reactivity with matte and Cu_2O. Both Si_3N_4 and SiC can be oxidised to form SiO_2 and then further reacted with oxides to form liquid slag, which will be flown away by the melts at high temperatures and the refractory will be worn out after a certain period.

The aluminosilicate bonded SiC refractory material

The silicate bonded SiC material is one of the common methods to manufacture the SiC-based refractory. The silicate is acting as the bonding phase to connect the SiC particles and also the silicate phase coats the SiC particle as a barrier to stop the direct reactions. The dense SiO_2 layers, formed to cover the SiC particles as anti-oxidation protective layer, can be prepared by controlled oxidation process [17-18]. Different additives [19-20], which is used to help the formation of liquid phase, were also added to obtain better sintering results. Al_2O_3 is one of the promising candidates with relatively low cost.

In the present study, the aluminosilicate bonded SiC material was prepared by firing process in air. The microstructure of the material after sintering is shown in Fig. 4. The EPMA analysis shows that the bonding phase is complex mixtures between SiO_2 and Al_2O_3. The porosity of the present material was measured to be ~ 20% and the compressive strength is ~ 120 MPa.

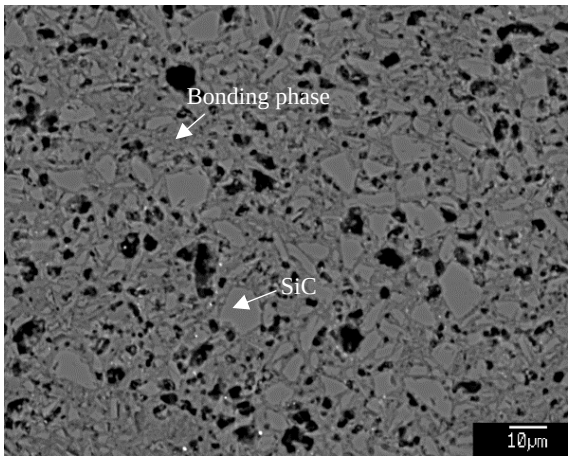

Fig. 4. Microstructure of the aluminosilicate bonded SiC material

The corrosion resistances of the aluminosilicate bonded SiC material to Cu_2O was tested at 1200 ºC in argon gas for 2 hours followed by direct quenching into the water. It was found that this material was easily to be separated from the melt and the thickness of the melt reminding on the aluminosilicate bonded SiC material sample is very limited (Fig. 5). The dimensional changes of the material were negligible after 2 hours corrosion test under high temperature. It can be seen from Fig 5 that there is clear boundary between the Cu_2O melt and refractory with little penetration.

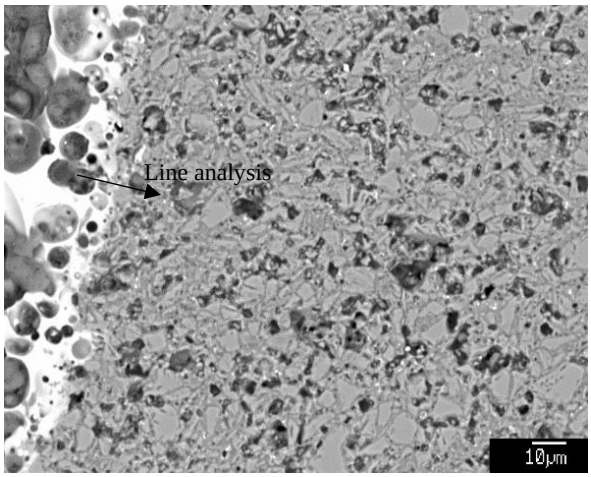

Fig. 5. Microstructure of the aluminosilicate bonded SiC material after reacted with Cu_2O in Ar at 1200 ºC

The EPMA line analysis was conducted on the interface after the corrosion test (Fig. 5). It was found that a very thin layer of liquid slag was covered on the surface of the refractory material. The slag contains mainly SiO_2, Cu_2O and Al_2O_3. The liquidus temperature of the slag is approximately 1200 ºC according to the

phase equilibrium in SiO_2-Cu_2O-Al_2O_3 system [21]. The thickness of the interface layer is around 10 μm which can be determined from the results of EPMA line analysis (Fig. 6). Note that SiO_2 is not present in the refractory and the concentration in the refractory is indicative only. It can be seen that the composition of the slag formed in the interface is not uniform. High-SiO_2 slag near the refractory is very viscus and difficult to penetrate inside the refractory. Copper metal was not observed in the interface area indicating that Cu_2O and slag did not react with SiC directly. SiO_2 formed on the surface of the SiC during the pre-oxidation well protected SiC particles.

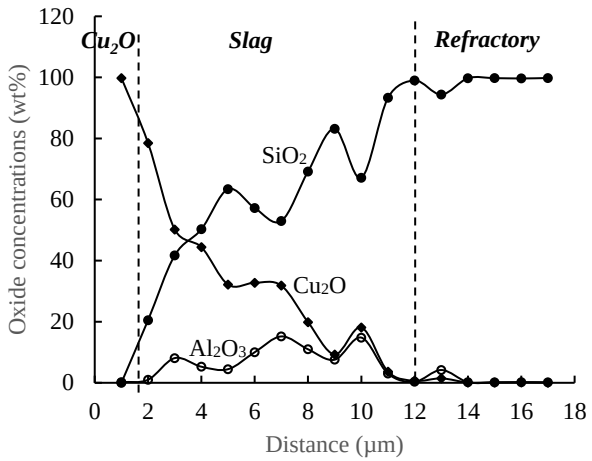

Fig. 6. EPMA line analysis results

The investigations imply that the aluminosilicate bonded SiC material has the potential to be used as the launder material for liquid copper transportation. Further experiments will be carried out to optimise the sintering process and obtain a better material with less porosities.

CONCLUSIONS

In order to find a suitable material to be used as launder material in copper making industry to transport molten matte and copper, Si_3N_4 bonded SiC material and aluminosilicate bonded SiC material were tested at high temperature. The static corrosion tests were conducted between the refractory and matte/Cu_2O melts. It was found that both Si_3N_4 and SiC in the Si_3N_4 bonded SiC material can react with matte and Cu_2O to form silicate slag. The aluminosilicate bonded SiC material behaves a relatively better corrosion resistance to the matte, Cu_2O and Cu, and may have the potential to be used as the launder material.

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