High temperature reactions between Si_3N_4 bonded SiC materials and Cu, Cu_2O and matte

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ABSTRACT

Si_3N_4 bonded SiC (Si_3N_4-SiC) is a conventional refractory material and has broad applications. In the present study, Si_3N_4-SiC refractory materials were systematically investigated in the copper-making environment. Si_3N_4-SiC was reacted with Cu, Cu_2O, industrial matte, Cu_2S and FeS melts at 1200 °C in argon gas atmosphere, and all samples were directly quenched in water after the experiments. Phase changes and compositions of the phases were measured by electron probe X-ray microanalysis. The present investigations demonstrate that Cu and Cu_2S do not react with Si_3N_4-SiC at high temperatures and the wettability between this material and the melts is low. However, significant reactions occur between Si_3N_4-SiC and Cu_2O, industrial matte and FeS. The results imply that Si_3N_4-SiC material has limited oxidation-resistance and can only be used under reducing conditions.

1. Introduction

In copper-making industry, different types of furnaces are involved in the pyrometallurgical process including smelting furnace, converting furnace and refining furnace [1]. The melts in these furnaces include slag, matte (copper iron sulphide), blister copper (purity > 98 wt% Cu) and anode copper (purity > 99.5 wt% Cu). Matte tapping holes in smelting furnace and copper (blister copper and anode copper) tapping holes in the converting and refining furnaces are easy to be damaged due to frequent flushing by high-density molten liquids. Moreover, with the development of new copper making techniques, more and more continuous operations, such as Mitsubishi process [1] and two-step copper making process [2], are being used in the production, and the launders are used to transport molten matte or copper to the latter processes. Reliable launders become critical parts in maintaining continuous productions. The current materials used as matte and melting copper launders include steel trough with graphite, copper, steel brick or other refractory liners [3]. Magnesite-chrome materials are also used in some smelters [4]. These refractory materials used as launder linings are easily eroded and damaged by molten matte or copper flow at high temperatures even for a short period [3]. The service lives of the furnace linings and launder refractories determine the availability of the production line. The modern copper industry requires high productivities with continuous operation, which can be achieved by increasing service lives of all components on the production line. Short service lives of matte and copper tapping holes as well as launders are the key factors to cause operation shutdown, which will affect not only the furnaces but also other processes associated, such as acid plant and electrolytic refining.

In recent years, Si_3N_4 bonded SiC (Si_3N_4-SiC) material has been proposed for the copper making industry. The Si_3N_4-SiC material has been manufactured for more than 50 years, and many researchers have carried out the investigations on the synthesis of the material [5–12]. In the pyrometallurgical fields, Si_3N_4-SiC has already been widely used in the iron and steel industry [13–15]. The applications of Si_3N_4-SiC in the copper industry were also patented [16] and tested [17]. The Si_3N_4-SiC material was used in a cathode shaft furnace in contact with molten copper and slag and claimed to have a good resistance to these melts [17]. However, no systematic research was carried out to investigate the behaviors of Si_3N_4-SiC material with different melts encountered in the copper industry. In the present study, Si_3N_4-SiC material was tested at 1200 °C for 2 h with molten copper, Cu_2O, matte, Cu_2S and FeS respectively. The changes of microstructures and compositions of the samples after the reactions were analyzed in details.

2. Experimental

Commercial Si_3N_4 bonded SiC material was used in the present study. SiC content of the material is 75 wt%, and Si_3N_4 is 25 wt%. Bulk density was measured to be 2.60 g/cm^3, and porosity is around 18%.
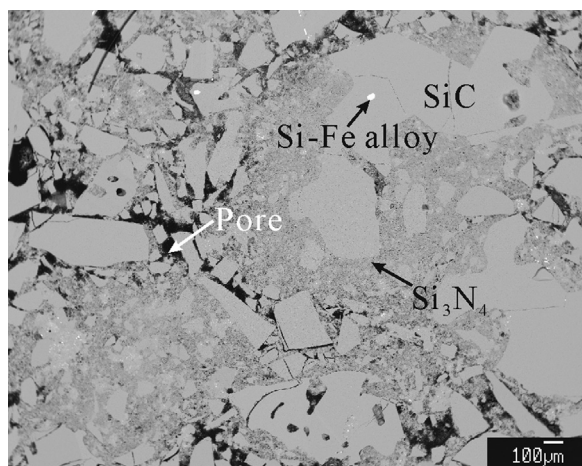
Fig. 1. Microstructure of the Si_3N_4 bonded SiC material.

Fig. 2. Schematic of vertical tube furnace used in the present study.

The microstructure of the Si_3N_4-SiC material is shown in Fig. 1. It can be seen that large SiC particles were connected by the Si_3N_4 phase. Small ferrous silicon alloy droplets were also found inside of the SiC particles, which indicates the incomplete carbothermic reaction during SiC production. The Fe content in the sample was measured to be lower than 0.5 wt%.

The Si_3N_4-SiC material was tested with pure chemicals (Cu, Cu_2O, Cu_2S and FeS) and industrial matte respectively. The composition of the matte analyzed from the XRF analysis is 72.1 wt% Cu, 6.0 wt% Fe, 21.9 wt% S. Around 0.5 g of Si_3N_4-SiC material (0.6*0.6*0.5 cm^3) was placed in an Al_2O_3 crucible with 2 g of testing chemical or matte in argon gas atmosphere. The details of the chemicals, gas and crucibles used in the experiments are listed in Table 1.

The reactions were carried out in a vertical reaction tube (impervious recrystallized alumina, 30 mm inner diameter) heated by lanthanum chromate ($LaCrO_3$) elements (Fig. 2). A working thermocouple inside a re-crystallized alumina sheath was placed inside the reaction tube adjacent to the samples to monitor the actual temperature of the samples. 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 °C.

All experiments were carried out under high purity argon gas atmosphere. The samples were introduced from the bottom of the reaction tube and left at the cold end of the reaction tube. The furnace was flushed with argon gas for 30 min to remove the air in the tube. The sample was then raised and kept in the hot zone of reaction tube by a platinum wire at 1200 °C for 2 h. The reaction temperature was selected to be 1200 °C as it is close to the operating temperatures in most of the copper smelting, converting and refining furnaces. At the end of the experiment, the bottom end of the reaction tube was immersed in water and the lower lid sealing the tube was removed. Then, the sample was dropped directly into the water and fast-quenched when pulling up the platinum wire. The specimen was dried, mounted in epoxy resin, and polished for examinations.

Table 1
Details of the chemicals, gas and crucible used in the current study.

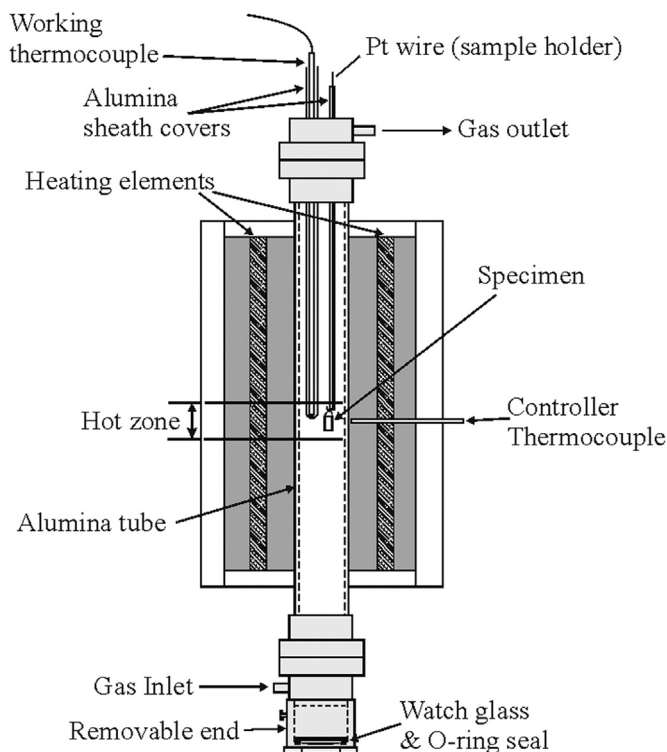| Chemicals	Purity (wt%)	Supplier
Copper (Cu)	99.7	Sigma - Aldrich, USA
Copper (I) oxide (Cu_2O)	99.9	Alfa Aesar, USA
Copper (I) sulphide (Cu_2S)	99.5	Alfa Aesar, USA
Iron (II) sulphide (FeS)	99.9	Alfa Aesar, USA
Argon gas (Ar)	99.999	BOC, Australia
Alumina crucible	99.5	Ceramic Oxide Fabricators, Australia

The samples were coated with carbon using JEOL Carbon Coater for electron microscopic examination. Typical microstructures of the samples and compositions of the phases present were measured using a JEOL JXA-8200 electron probe X-ray microanalyzer (EPMA) with wavelength dispersive detectors. The analysis was conducted at an accelerating voltage of 15 kV and a probe current of 15 nA. The standards used for analysis were SiO_2 for Si, Fe_2O_3 for Fe, Al_2O_3 for Al, $CuFeS_2$ for Cu and S, BN for N. The Duncumb-Philibert ZAF correction procedure supplied with JEOL-8200 was applied. The average accuracy of EPMA measurements was estimated to be within 1 wt%. It should be noted that element C was not measured directly and the content of SiC is determined by the measured totals by EPMA comparing to the ratios of atomic weight of Si to the molecular weight of SiC.

3. Results

3.1. Reactions between Si_3N_4-SiC and Cu / Cu_2O

It was reported that the wear of Si_3N_4-SiC in flowing copper inside the cathode shaft furnace was limited [17]. In the present experiment, Si_3N_4-SiC was tested with molten copper at 1200 °C in Ar gas. The visual observation of the quenched sample showed that only a small area of solid copper metal adhered to the sample, and the copper metal could be easily separated from the sample. The quenched sample was then examined by EPMA, and the microstructure is shown in Fig. 3. It can be seen from the micrograph that no large copper droplet penetrated into the Si_3N_4-SiC sample after the reaction. Some fine copper droplets were scattered in the opening pores in the samples and attached to the SiC particles and Si_3N_4 bonding phase. EPMA line analyses were conducted to measure the compositions of SiC particles and Si_3N_4 phase contacting with Cu droplets. It was found that no reaction and phase change happened between the refractory material and Cu metal. The present phenomenon confirms that the wear of the refractory in molten copper mainly due to the physical flushing by the melt.

Metallic copper can easily react with oxygen from air to form copper oxides. As the tapping holes and the launders are exposed in air and
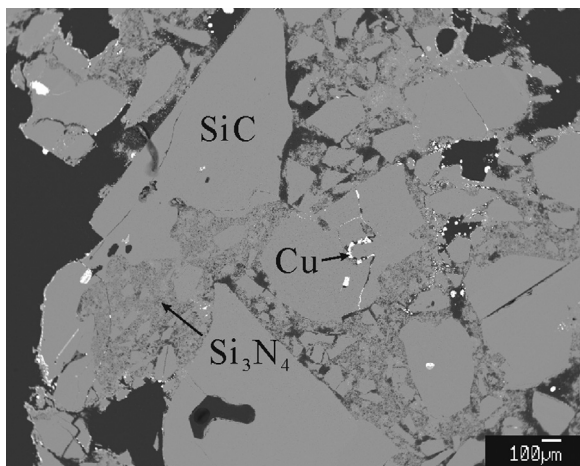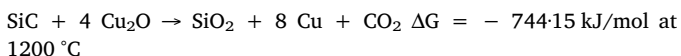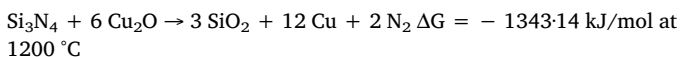
Fig. 3. Microstructure of quenched Si_3N_4-SiC refractory material after reaction with metallic copper.

heated by the melts repeatedly, the copper residues will be oxidized to form copper oxides. It is necessary to investigate the reactions between the Si_3N_4-SiC material and copper oxides. At high temperatures, copper oxide can be expressed as Cu_2O as the proportion of Cu^+ ions is much larger than Cu^{2+} ions [18]. Thermodynamically, both reactions Si_3N_4 – Cu_2O and SiC – Cu_2O can happen spontaneously at 1200 °C [19]:

$$Si_3N_4 + 6\,Cu_2O \rightarrow 3\,SiO_2 + 12\,Cu + 2\,N_2\ \Delta G = -1343{\cdot}14\ kJ/mol\ at\ 1200\ °C$$

$$SiC + 4\,Cu_2O \rightarrow SiO_2 + 8\,Cu + CO_2\ \Delta G = -744{\cdot}15\ kJ/mol\ at\ 1200\ °C$$

From the comparisons of free energies in these reactions, Si_3N_4 is more favorable to react with Cu_2O due to higher negative ΔG.

In the present study, the experiment was conducted using Cu_2O with the Si_3N_4-SiC material at 1200 °C. The phases at different locations of the sample are shown in Fig. 4(a) and (b), and the compositions of the phases after the reaction are listed in Table 2. Both of Fig. 4(a) and (b) clearly show that Cu_2O has reacted with the Si_3N_4-SiC material at 1200 °C. Fig. 4(a) mainly demonstrates the reaction between Si_3N_4 and Cu_2O. It can be seen that a large amount of SiO_2 was present adjacent to Si_3N_4 phase and Cu droplets, which indicates that Cu_2O oxidized Si_3N_4 to form SiO_2 while Cu_2O was reduced to Cu. The fresh SiO_2 formed from the reaction continuously reacted with Cu_2O to form two immiscible liquid phases that were liquid 1 with high-SiO_2 and liquid 2 with high-Cu_2O (compositions are given in Table 2). A small amount of Al_2O_3 from the crucible was also present in the liquid phases. Clearly, liquid 1 was firstly formed and then it continuously reacted with Cu_2O to form liquid 2. Nitrogen was not detected in any of new phases formed during the reactions.

The reaction between SiC and Cu_2O can be also clearly demonstrated in Fig. 4(b). SiC particles reduced Cu_2O, and the product Cu droplets grew up from the SiC particles. Two immiscible liquid phases (liquid 2 and liquid 3 as shown in Table 2) were found in the areas closed to SiC particles. In this case, liquid 3 was first formed and it reacted with Cu_2O to form liquid 2. No SiO_2 particle was present in this area. This indicates that the reaction between SiC and Cu_2O is slower than the reaction between Si_3N_4 and Cu_2O. Note that liquid 2 was the continuous dominant phase present in the sample. Liquid 1 was only present locally between liquid 2 and Si_3N_4, and liquid 3 was also the phase locally present between liquid 2 and SiC.

Three liquid compositions are plotted in the phase diagram of the SiO_2-'Cu_2O'-Al_2O_3 system [20] in Fig. 5. It can be seen from the figure that the compositions of liquid 1 and liquid 2 lie at the 1200 °C isotherms and in equilibrium with SiO_2 and Cu_2O respectively. This indicates that the reaction between Si_3N_4 and Cu_2O was approaching
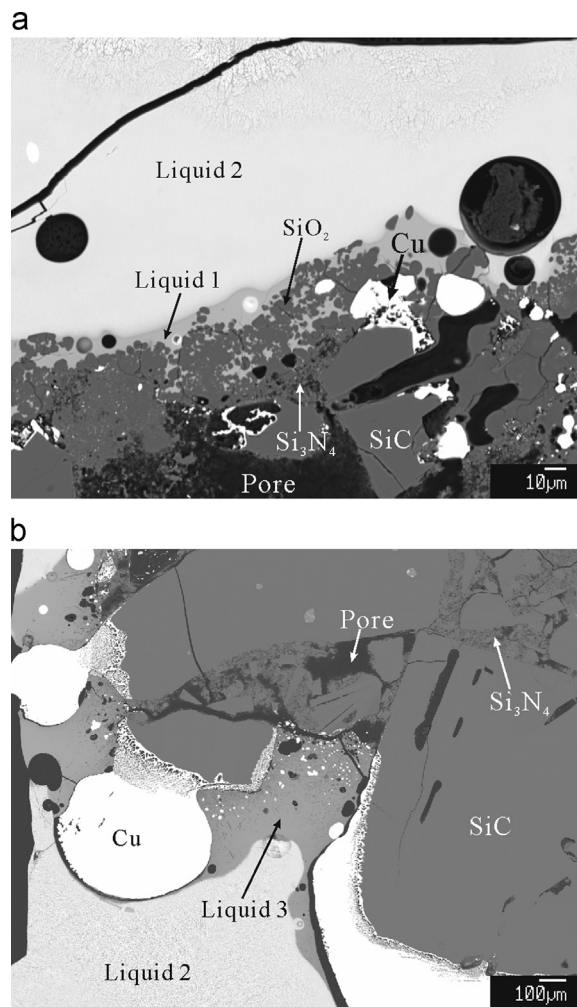
Fig. 4. Microstructures of quenched Si_3N_4-SiC refractory sample after reacted with Cu_2O at 1200 °C for 2 h: (a) Si_3N_4 dominant; (b) SiC dominant.

Table 2
Compositions of the new phases in quenched Si_3N_4-SiC sample after reacted with Cu_2O measured by EPMA (wt%).

	FeO	SiO_2	Cu_2O	Al_2O_3	N
Liquid 1	0.3	41.0	49.0	8.7	0
Liquid 2	0.1	11.5	83.3	4.6	0
Liquid 3	0.2	44.0	39.6	16.2	0
SiO_2	0	96.0	2.4	1.3	0

	Fe	Si	Cu	Al	N
Cu	0	0.8	99.2	0	0

equilibrium in two hours and the observed results agree well with the phase diagram. However, in Fig. 5, the composition of liquid 3 is not on the 1200 °C isotherm which indicates that it was not in equilibrium with the primary phase. This can be explained by the slow reaction between SiC and Cu_2O. There was no enough SiO_2 formed from the reaction. It is expected that longer time reaction will bring the composition of liquid 3 to the 1200 °C isotherm in the SiO_2 primary phase field.

The present study shows that copper oxide can react with the Si_3N_4-SiC material and the low melting point liquid phase could be formed. Si_3N_4 as the bonding phase reacts much faster with copper oxide than SiC which results in that SiC particles rapidly peel off from the body. In the refining furnace, the slag contains a high Cu_2O content which can
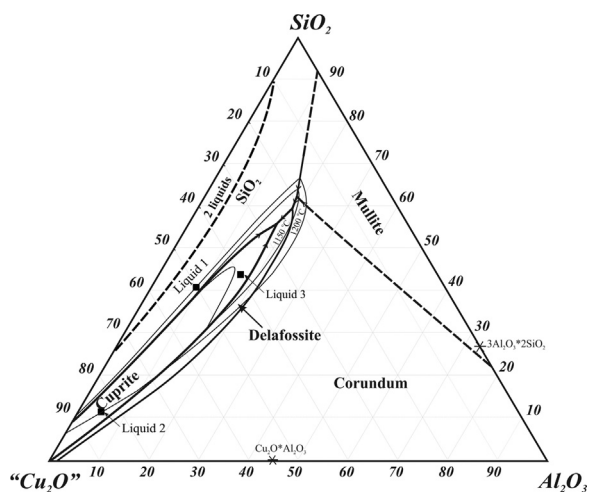
Fig. 5. The compositions of liquids plotted in the phase diagram of SiO_2-'Cu_2O'-Al_2O_3 system [19].

also react with Si_3N_4-SiC. Therefore, this material is not suitable for the lining of the refining furnace.

3.2. Reactions between Si_3N_4-SiC and matte

Matte, copper iron sulphide, is considered as an intermetallic alloy as it shares similar behaviors with alloys, such as high electric conductivities and low viscosities. In the present study, the industrial matte was used to investigate the reactions between matte and Si_3N_4-SiC at 1200 °C.

The visual observation at the cross-sections of the sample after the reaction revealed that the original morphology of the refectory sample was significantly changed and most parts of the material were reacted with the matte. The microstructure of the reacted sample is shown in Fig. 6, and the compositions of the phases measured by EPMA are listed in Table 3. It can be seen from Fig. 6 and Table 3 that matte, Fe-Cu alloy, metallic Fe, liquid slag and SiO_2 coexist with the original Si_3N_4-SiC material. The newly formed SiO_2 was found along the boundary between Si_3N_4-SiC and the Fe-Cu alloy. Metallic Fe and matte were also found inside the SiC particle as shown in the figure, and the presence of matte inside the SiC particles may result from the penetration through the existing pores. The microstructure of the sample clearly shows that both of Si_3N_4 and SiC can react with the industrial matte severely. Repeated experiments confirmed that the slag phases were always formed in the experiments, and the presence of FeO and SiO_2 in the slag
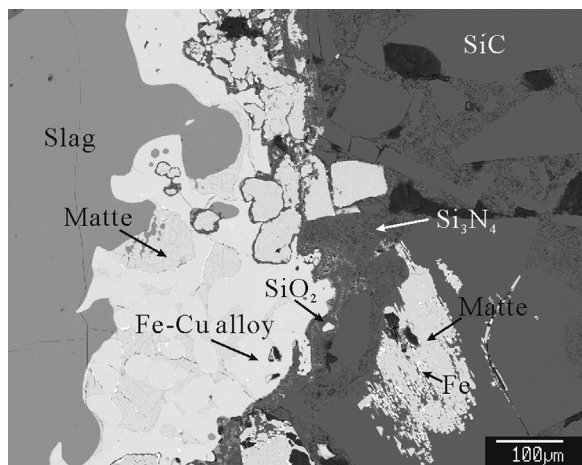

**Fig. 6.** Microstructure at the surface of Si_3N_4-SiC after reacted with industrial matte at 1200 °C for 2 h.

Table 3
Compositions of new phases in quenched Si_3N_4-SiC refractory sample after reacted with matte measured by EPMA (wt%).

	FeO	SiO_2	Cu_2O	Al_2O_3	S	N
Slag	47.1	41.9	0.3	9.9	0.7	0
SiO_2	0	98.6	1.4	0	0	0

	Fe	Si	Cu	S
Fe	99.9	0.1	0	0
Fe-Cu alloy	93.2	0	6.8	0

indicates that oxygen was introduced into the reaction system. Careful examination of the furnace conditions and the experiments with Cu metal and sulphides excluded the possibility of furnace leaking during the experiments. It has been reported that 1–3 wt% oxygen is present in the matte mainly in the form of FeO and Fe_2O_3 [21,22]. The dissolved oxygen in the matte actively participated in the reactions and provided the source of oxygen.

Fig. 6 shows the stepwise reactions between Si_3N_4-SiC and matte. The matte including metallic Fe was present inside the SiC particle indicating that iron in the matte was reduced by SiC to form metallic Fe. The matte and Fe phases were also found spreading all over the material, which demonstrates that matte penetrated into the Si_3N_4-SiC and corroded the material. At the surface of the material, the connected Fe-rich alloy phase was also found surrounding the Si_3N_4-SiC and in contact with the liquid slag and SiO_2. The presence of metallic Fe and large Fe-rich alloy demonstrates that SiC and Si_3N_4 can continuously react with matte to form metallic Fe. Cu in the Fe-Cu alloy may be due to the reaction between iron oxide in matte and Cu_2S:

$$Fe_2O_3 + Cu_2S \rightarrow 4\,FeO + 2\,Cu + SO_2$$
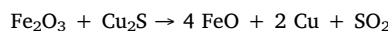
The composition of liquid slag in Table 3 indicates that SiO_2 and FeO were the major components, and Al_2O_3 from the crucible was also dissolved in the slag. Due to the different extents of the reaction and the matte phases separated by the other phases, the compositions of the matte phase containing low Fe varied from place to place.

From the reactions between Si_3N_4-SiC and industrial matte, it can be seen that copper and iron in the matte behave differently and iron oxides are shown to be more actively reacted with Si_3N_4-SiC. In order to clearly distinguish the different behaviors of copper and iron in matte with the Si_3N_4-SiC material at high temperatures, Cu_2S and FeS were applied in the reactions at 1200 °C for 2 h in argon gas. Using pure chemicals in the reactions can avoid the involvement of oxygen which is present in industrial matte. Fig. 7 represents the sample of Si_3N_4-SiC material after the reaction with Cu_2S (melting point 1130 °C). After quenching the sample into water, Cu_2S was easily separated from the refractory material and only tiny amount of Cu_2S droplets adhered to the surface of the refractory material. Careful EPMA analysis confirms that no reaction happened between the Cu_2S melt and Si_3N_4-SiC refractory. This indicates that Cu_2S melt has a low wettability to the Si_3N_4-SiC refractory material, and has a similar behavior as metallic copper. It is clear that both SiC and Si_3N_4 do not directly react with Cu_2S. It seems that Cu_2S is more difficult to penetrate inside the Si_3N_4-SiC material than copper metal.

A different phenomenon was observed in the quenched sample of Si_3N_4-SiC reacted with FeS (melting point 1194 °C) at 1200 °C (Fig. 8). In Fig. 8, the refractory material was severely corroded by FeS melt although silicate slag was not formed. SiC particles were isolated inside the FeS melt as the Si_3N_4 bonding phase was destroyed by the melt. EPMA line analysis shows that up to 12 wt% Si was detected in the FeS melt as Fe-Si-S at the interface with Si_3N_4 and no nitrogen was detected in the same area. Thermodynamic calculations [19] confirm that liquid Fe-Si-S is stable in a wide composition range at 1200 °C. Clearly, FeS melt is much easy to react with Si_3N_4 than SiC.
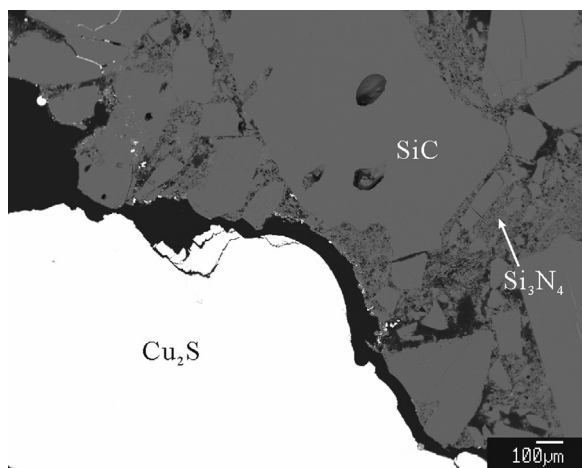
Fig. 7. Microstructure of quenched Si_3N_4-SiC after reacted with Cu_2S at 1200 °C for 2 h.
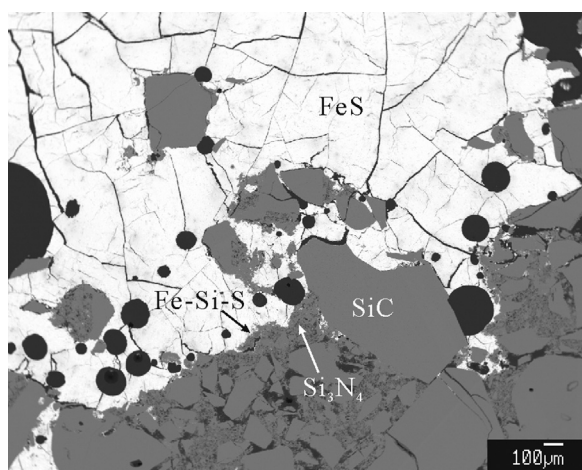
Fig. 8. Microstructures of quenched Si_3N_4-SiC sample reacted with FeS at 1200 °C for 2 h.

In summary, oxygen and FeS present in the industrial matte can react with Si_3N_4 to destroy the refractory structure, so the Si_3N_4-SiC material is not suitable for transportation of matte.

3.3. Implications in copper-making industry

In the present study, Si_3N_4-SiC refractory was tested with Cu, Cu_2O, industrial matte, Cu_2S and FeS, which cover most of the materials encountered in copper-making industry. It was found that no reaction happens between Cu / Cu_2S and Si_3N_4-SiC material, and the wettability was low. The Si_3N_4-SiC material may be suitable for copper tapping hole and copper launder if copper oxide is not formed. In addition, if the Si_3N_4-SiC refractory has a dense structure, copper melt can flow rapidly and smoothly on the surface of the refectory. However, the copper residues left inside the refractory can be oxidized to Cu_2O with time which reacts with Si_3N_4 and SiC to form liquid silicates at high temperatures. The SiC particles will be gradually washed away by flowing melt when the bonding phase Si_3N_4 is lost. The present investigations involving industrial matte and FeS show that significant corrosions will occur on the Si_3N_4-SiC material as both of SiC and Si_3N_4 can react with industrial matte due to the presence of iron oxides in the matte. Moreover, for matte launder and tapping holes, Si_3N_4-SiC refectory and matte are exposed in air, more dramatic reactions to form the low melting liquid phases may happen with sufficient oxygen and the structure will be quickly destroyed by the flowing melts.

4. Conclusions

In the present study, the Si_3N_4-SiC material was reacted with Cu, Cu_2O, industrial matte, Cu_2S and FeS at 1200 °C for 2 h in argon gas atmosphere. All samples were directly quenched in water after the experiments and the phase compositions were accurately measured by EPMA. The present investigation demonstrates that Cu and Cu_2S do not directly react with Si_3N_4 and SiC at high temperatures and the wettability is relatively low. However, Cu_2O, industrial matte and FeS can react with Si_3N_4-SiC material following different mechanisms. Applications of Si_3N_4-SiC refractory in the copper-making industry are limited according to the reaction mechanisms.

Acknowledgements

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