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Investigation on a postmortem resin-bonded Al-Si-Al_2O_3 sliding gate with functional gradient feature

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ABSTRACT

A resin-bonded Al-Si-Al_2O_3 sliding gate was designed on the basis of sintered alumina containing both Al and Si fine powders, and the sliding gate achieved good application results in the practical process of steel pouring. Moreover, the postmortem sliding gate was characterized and analysed by X-ray diffraction, scanning electron microscope, and energy dispersive X-ray spectroscopy. The results show that the postmortem sliding gate presents a functional gradient feature with a reinforcement zone–transition zone–plastic zone phase distribution, in which the phases in the reinforcement zone from 0 mm to 5 mm are Al_2O_3, Al_4O_4C, SiC, and Al_4C_3; i.e., the Al, Si, and carbon in the composite totally converted into non-oxide phases. Further, phases in the transition zone from 5 mm to 10 mm are Al_2O_3, SiC, and Al_4C_3, whereas phases in the plastic zone from 10 mm to 15 mm are Al_2O_3, SiC, Al_4C_3, Al and Si. The formation mechanism of the grade distribution of phases in the postmortem sliding gate is described as follows. During operation, Al and Si reacted with C so that Al_4C_3 and SiC formed in situ; then, Al_4C_3 further reacted with Al_2O_3, whereby Al_4O_4C was formed as the reinforcement phase at the 0–5-mm zone with a high temperature. As the temperature decreased from the hot face to interior, a part of the free Al and Si remained in the form of plastic phases.

1. Introduction

The Al_2O_3-C sliding gate has been widely used because of its good thermal conductivity, superior thermal shock resistance, and wear resistance [1,2]. However, it is not ideal for the Al_2O_3-C sliding gate to be applied in the clean and low-carbon steel-making industry because of the diffusion and dissolution of carbon into liquid steel. Therefore, low-carbon and even carbon-free refractories must be developed. Conversely, reducing the carbon content in the Al_2O_3-C sliding gate would deteriorate its application performance such as thermal shock resistance and corrosion resistance. In recent years, some effective ways to improve refractory performance have been proposed: (I) using additives to induce carbon graphitization in phenolic resin; (II) in-situ formation of non-metallic oxide reinforcement materials such as AlN, SiC, and Sialon; (III) the incorporation of nano-materials to compositions [3–7].

For the Al-Si-O-C quaternary system, Al_4O_4C and Al_4SiC_4 have many advantages, such as high melting point, excellent mechanical performance, good corrosion resistance, low thermal expansion coefficient, and good hydration resistance, which therefore are selected as promising reinforcement phases for Al_2O_3-based refractories. Al_4O_4C is an incongruent melting compound in the Al_4C_3-Al_2O_3 binary system; its decomposition temperature is approximately 1870 °C. Al_4O_4C can be formed at 1200 °C and higher temperatures. Al_4O_4C-reinforced Al-Al_2O_3 composite was successfully prepared by P Jiang et al. [8]. Al_4SiC_4 is a congruent melting compound with a melting point of approximately 2080 °C in the Al_4C_3-SiC binary system. Al_4SiC_4 can be synthesized at above 1300 °C using Al, Si, and C, or SiC and Al_4C_3 powders as raw materials [9,10]. Al (660 °C) and Si (1412 °C) can serve as both transient metal plastic phases and metal plastic phases when they are added to Al_2O_3-based refractories as raw materials ($W(Si+Al) \geq 9$ wt%); the advantages are: (I) the refractories' performance can be enhanced through the transformation of Al and Si into reinforcements such as Al_4O_4C, Al_2OC, or Al_4SiC_4 at high temperatures; (II) the remnant free Al and Si metal interior of the block maintain their original state, which is conducive to the thermal shock resistance of Al_2O_3-based refractories. Therefore, in this work, a resin-bonded Al-Si-Al_2O_3 sliding gate was designed in order to obtain an Al_4O_4C-, Al_2OC-, or Al_4SiC_4-bonded Al-Si-Al_2O_3 sliding gate with a functional gradient feature, i.e., reinforcement-transformation-plastic phase distribution during practical operation. The formation mechanism of this phase grade distribution in the postmortem sliding gate was investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS).

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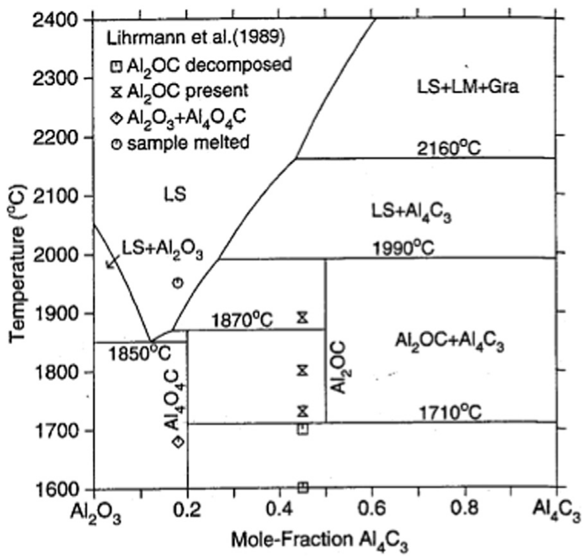

Fig. 1. Calculated phase diagram of the pseudo-binary Al_2O_3-Al_4C_3 system of Qiu and Metselaar [22] in comparison with experimental observation of Lihrmann et al. [23].

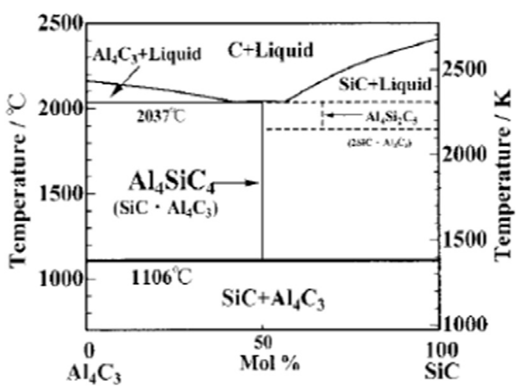

Fig. 2. Calculated phase diagram of the pseudo-binary Al_4C_3-SiC system [26,27].

2. Theoretical design for the resin bonded Al-Si-Al_2O_3 sliding gate

In the process of pouring steel, the temperature around the sliding gate casting hole rises rapidly to 1550 °C or above. The Al, Si, C, and Al_2O_3 in the resin-bonded Al-Si-Al_2O_3 sliding gate will initiate a series of reactions depending on the temperature gradient from hot face to interior during operation. It has been suggested [11–15] that Al and Si will react with C to form Al_4C_3 (~800 °C) and SiC (~1000 °C), respectively, in an environment with carbon existing.

$$4\mathrm{Al}(l) + 3C(s) = Al_4C_3(s) \tag{1}$$

$$\mathrm{Si}(s, l) + C(s) = SiC(s) \tag{2}$$

With reactions (1) and (2) progressing, the resin-bonded Al-Si-Al_2O_3 system finally transforms into an Al_2O_3-Al_4C_3-SiC system. The Al_2O_3-Al_4C_3 binary system was first constructed by Foster et al. [16], who identified two oxycarbide phases, Al_4O_4C and Al_2OC, on the basis of thermodynamic analysis and experiments. There has been extensive discussion and analysis since then [17–22]; the standard Gibbs free energies of formation of both aluminium oxycarbides, Al_4O_4C and Al_2OC, were determined by Lihrmann et al. [21]. The classical stability phase diagram deduced for Al_4C_3-Al_2O_3 was calculated by Qiu and Metselaar [22] as shown in its usual form in Fig. 1. As well, the Al-Si-C system was first calculated by Groebner et al. [24,25], with the phases of the Al-Si-C system all lying on the section between Al_4C_3 and SiC. The calculated phase diagrams of the pseudo-binary Al_4C_3-SiC system by Yokokawa et al. [26] is shown in Fig. 2. As shown in the Al_2O_3-Al_4C_3 and Al_4C_3-SiC binary phase diagram [22,26], Al_4C_3 will react with Al_2O_3 or SiC in-situ to form Al_4O_4C, Al_2OC, and Al_4SiC_4, among others, at specific temperatures.

In addition, according to the theoretical calculation, when the mass fraction of carbon in Al-Si-Al_2O_3 material is 3 wt%, a maximum of 46 wt% Al_4O_4C, 20 wt% Al_2OC, or 11 wt% Al_4SiC_4 can be formed, which indicates that even a small amount of carbon (such as residual carbon of phenolic resin binder) in the sample can still lead to the formation of several times its weight of Al_4O_4C, Al_2OC, or Al_4SiC_4, which can improve refractory performance. Therefore, the low-carbon resin-bonded Al-Si-Al_2O_3 sliding gate was designed on the basis of stoichiometry calculations.

3. Experimental procedures

Tabular alumina (2–1 mm, 1–0.5 mm, ≤ 0.5 mm, and 0.045 mm, W (Al_2O_3) > 99.31 wt%), SiC (≤ 0.074 mm, W(SiC) > 96 wt%), α-Al_2O_3 powders (99.28 wt%), metallic Al powders (99.07 wt%), Si powders (98.32 wt%), and flake graphite were used to prepare Al-Si-Al_2O_3 composite material. Phenolic resin was added as a binder. All raw materials were weighed stoichiometrically according to Table 1; after being ground for 40 min, the raw materials were shaped under a 630-t friction pressure to obtain the green sliding gate. After tempering at ambient conditions for 24 h, the green sliding gate was dried in a tunnel kiln for 12 h at a temperature of 200 °C in order to be applied in a practical process of steel pouring. In going from the hot face to the interior of the postmortem sliding gate, three representative samples recorded as B1 (0–5 mm), B2 (5–10 mm), and B3 (10–15 mm) with a temperature gradient were selected for investigation. The phases were identified by XRD (M21XVHF22, MAC Science, Japan) using Cu Kα radiation in the 10–80° angle range. The samples were ball-milled into powders for the XRD measurements. The morphology and composition of the samples were investigated using a field emission SEM (ΣIGMA HD, Germany) equipped with EDS (QUANTAX200-30, BRUKER, Germany). A gold coating was used to make the samples electrically conductive enough for SEM investigation after being polished.

Table 1
Initial raw material formula of Al-Si-Al_2O_3 composite sliding gate.

Material	Tabular alumina		96 SiC	α-Al_2O_3	Al powder	Si powder	Flake graphite	Phenolic resin (extra)
Particle size (mm)	0.5–2	≤ 0.045	≤ 0.074	≤ 0.088	≤ 0.088	≤ 0.088	/	/
Content (wt%)	62	16	5	5	8	2	2	3.5