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Effect of Al_4SiC_4 on the Al_2O_3–SiC–SiO_2–C refractory castables performance

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Abstract

Carbon-containing refractories are widely used in the steelmaking process due to their outstanding properties and, in order to improve their oxidation resistance, the so-called antioxidants have often been used. Al_4SiC_4 is pointed out as a novel additive that presents suitable properties such as Al, but without its drawbacks. Therefore, the effect of Al_4SiC_4 addition to Al_2O_3–SiC–SiO_2–C castables designed for lining blast furnace troughs was investigated in this work. Apparent porosity, oxidation, thermogravimetric, X-ray diffraction, hot elastic modulus tests and thermodynamic calculations were carried out in order to better understand the antioxidant effects and reaction mechanisms. Additionally, the collected results were compared with those from the compositions containing other commonly used antioxidants (Si, B_4C and sodium borosilicate glass). The performance of the novel additive proved to be limited as most of the carbon source used reacted earlier than the Al_4SiC_4 action. As a consequence, intense carbon oxidation, along with the thermal expansion mismatch among the phases during the cooling step, intensified the deterioration of the evaluated refractory material.

Keywords: D. Carbon; Al_4SiC_4; Antioxidant; Oxidation; Refractory castables

1. Introduction

High-carbon-containing refractory castables are widely used in blast furnace troughs due to their high refractoriness, thermal shock resistance and low wettability by molten slag [1–3]. Carbon presents many of the desired properties for the refractories, however the main drawback is its high susceptibility to oxidation. In recent years, numerous studies have been carried out to investigate the effect of metallic and non-metallic antioxidant additions on the oxidation resistance and mechanical properties of carbon-containing refractory castables [4–7]. Moreover, the use of both, single or multiple antioxidant sources has been widely discussed [8–11].

Aluminum (Al) is one of the most extensively used antioxidants in refractory compositions. However, its by-product can be Al_4C_3, which may lead to disintegration of castables due to the poor hydration resistance of this phase [12,13]. In addition, in the presence of cement, the Al–H_2O reaction during the castables mixing step takes place much earlier and faster, negatively affecting the performance of this additive to further decrease the carbon oxidation [14]. In order to overcome such effects, some efforts have been made to develop alternative antioxidants presenting suitable properties but with less drawbacks. In this sense, aluminum silicon carbide (Al_4SiC_4) is a promising material due to its low density (3.03 g cm^{-3}), high melting point (>2000 °C) and good oxidation and hydration resistances. Its action takes place above 750 °C leading to the formation of a protective coating comprised by Al_2O_3 and mullite (Eqs. (1)–(3)) on the refractory particles, which fills in the pores, preventing further carbon oxidation [15].

$$Al_4SiC_4 + 6O_2 \rightarrow 2Al_2O_3 + SiC + 3CO_2 \quad (1)$$

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2 \quad (2)$$

$$3Al_2O_3 + 2SiO_2 \rightarrow 2Al_6Si_2O_{13} \quad (3)$$

Various methods for synthesizing Al_4SiC_4 have been investigated by using metals (Al and Si), carbides (Al_4C_3

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and SiC) or oxides (Al_2O_3, SiO_2 and kaolin) as starting raw materials [12,13,15–17]. Barczak [18] prepared this complex carbide powder using a 4:1 molar ratio mixture of Al and Si with excess of carbon in a sealed container at 1620 °C for 10 min. Other authors [15,16] produced this compound by heating a mixture of Al, Si and C in argon atmosphere at 1700 °C. By mixing the starting materials (Al, Si and C) with $N(CH_2CH_2OH)$, Yamamoto et al. [19] managed to reduce the synthesis temperature to 1450 °C. Hot-pressing at 1750–1980 °C or sintering at 1600 °C using fine SiC and Al_4C_3 powders in argon atmosphere were also considered for this purpose [20,21]. In addition, Al_4SiC_4 was synthesized by heating a mixture of Al, Si, C and 3 wt% of Al_2O_3, Al, kaolin and C or Al_2O_3, SiO_2 and C at 1700 °C [13,15,16]. Various parameters can affect the efficiency of these methods, such as the mixture/contact of the raw materials (powder or pressed compact), heating temperature, heating time, chosen atmosphere and the component ratios.

Nevertheless, despite the various improvements in the Al_4SiC_4 synthesis procedures, to the best of our knowledge not much research has focused on evaluating this antioxidant performance in refractory compositions (mainly, MgO–C and Al_2O_3–C bricks) [12,22,23]. Therefore, there is a lack of studies concerning the analysis of this aluminum silicon carbide behavior in cement-bonded castables.

Considering these aspects, this work aims to evaluate the Al_4SiC_4 performance in high carbon-containing castable compositions (Al_2O_3–SiC–SiO_2–C) designed for lining blast furnace troughs. Furthermore, a comparison among the collected results and the ones attained for other antioxidant additives commonly used in steelmaking refractory materials (Si, B_4C and sodium borosilicate glass) was also carried out. Apparent porosity, oxidation resistance, thermogravimetry, X-ray diffraction, hot elastic modulus tests and thermodynamic calculations were performed in order to better understand the phase transformations and the antioxidant effect in the castables properties.

2. Experimental

2.1. Al_4SiC_4 synthesis procedure

Aluminum (average particle size: 3 μm, purity: 99.9%), carbon (average particle size: 5 μm, purity: 99.9%) and SiC (average particle size: 2–3 μm, purity: 99%) powders by Kojundo Chemical Lab. Co. Ltd., Japan, were used as the starting raw materials. Al and C were firstly mixed in a 4:3 molar ratio, uniaxially pressed at 13 MPa, and the attained pellet was thermally treated in argon for 2 h at 1400 °C to give rise to the Al_4C_3 phase. The prepared Al_4C_3 was then mixed with SiC in an equimolar ratio and subjected to the same pressing procedure. After firing for 2 h at 1700 °C in a vacuum, the pellet consisting of pure Al_4SiC_4 was then crushed and ground to a material with an average particle size below 10 μm (Fig. 1).

2.2. Design, processing and evaluation of the carbon-containing castables

Four self-flow Al_2O_3–SiC–SiO_2–C refractory castable compositions with ultralow cement content were designed (Table 1), according to the Alfred packing model ($q = 0.21$) [24]. An antioxidant-free castable was prepared to be used as a reference material. Additionally, Al_4SiC_4, silicon powder (Si, Elkem Refractories, Norway, average particle size < 75 μm), boron carbide (B_4C, China Brasilis, China, average particle size = 32 μm) and sodium borosilicate glass (BS, Ferro Enamel, Brazil, BS – average particle size = 20 μm) were used as antioxidants in the other formulations listed in Table 1. According to previous studies [8,9], the addition of an antioxidant blend (Si + B_4C + BS) can protect the carbon sources in a broader temperature range, resulting in some beneficial effects, such as the increase in hot mechanical strength due to the in situ formation of SiC and mullite [9]. Therefore, refractory castables comprising this antioxidant blend (5SBC) or only boron carbide (2B) were also prepared and compared to the one containing Al_4SiC_4 (2A).

The dispersion of the castables was carried out using an electrosteric dispersant (0.2 wt%, Darvan-7S, R.T. Vanderbilt, Norwalk, Conn.) and a non-ionic surfactant (HLB = 8, 4.0 mg/m^2) as wetting agent for the carbon sources [25,26]. Before casting, the compositions were dry-homogenized for 1 min and mixed in a rheometer developed for refractory castables [27] for an additional 5 min, by adding 6.3 wt% of water to the antioxidant blend-containing castable and 5.4 wt% to the other ones.

Cylindrical samples ($d = 40$ mm and $h = 40$ mm) were prepared and cured at 50 °C for 12 h (relative humidity ~ 80%),

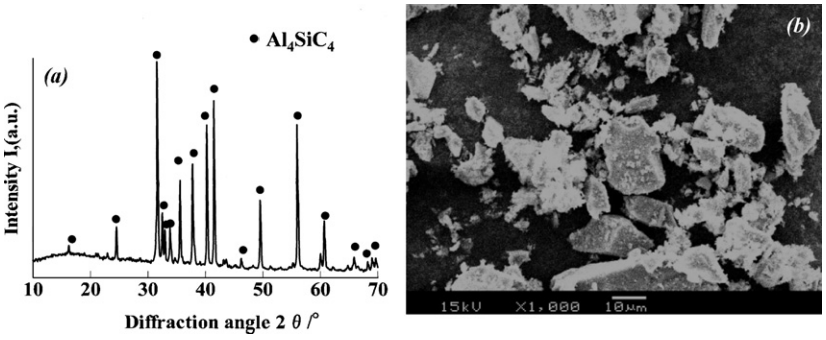

Fig. 1. (a) XRD pattern and (b) typical SEM image of the synthesized Al_4SiC_4 powder.