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Carbothermic reduction of ilmenite concentrate in semi-molten state by adding sodium sulfate

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ABSTRACT

The electric arc furnace (EAF) smelting process, which produces titanium slag, is the most popular method for utilizing Panzhihua ilmenite concentrate. However, the EAF process involves high energy consumption, high pollution, and low efficiency due to the high smelting temperature, the large amount of dust produced, and the long smelting period. An economical and clean method for semi-molten reduction followed by magnetic separation to produce titanium slag from Panzhihua ilmenite concentrate was presented. In this paper, the semi-molten reduction process was studied and the effect of reduction temperature, C/O molar ratio, and the addition dosage of Na_2SO_4 on the metallization ratio, phase transformation, and size of metallic iron grain was discussed. The results showed that Na_2SO_4 and its subsidiary products can function as fluxing agent for decreasing the melting point of metal and slag, thus promoting the growth of metal particles, and achieving high efficiency and clean reduction of ilmenite concentrate. The action mechanism of Na_2SO_4 addition is also discussed.

1. Introduction

Ilmenite is one of the most important raw materials to produce titanium pigments [1–3]. With the rapid development of the titanium industry, reserves of high grade titanium mineral have gradually been depleted all over the world, and it is, therefore, paramount that more attention is paid to relatively low grade titanium resources such as ilmenite concentrate [4]. The Panzhihua-Xichang area in the Sichuan province in China is home to about 35% of the titanium resources in the world, and about 92% in China [5,6]. However, the titanium resources in Panzhihua-Xichang area are mainly in the form of vanadium-titanium magnetite, and the ilmenite concentrate in this area benefits from the tailing of the first beneficiation process of vanadium-titanium magnetite. At present, about 300,000 tons of ilmenite concentrate is produced annually [7]. The carbothermic reduction of Panzhihua ilmenite concentrate is one of the most important techniques in the titanium industry for enriching titanium resources. However, the Panzhihua ilmenite concentrate contains relatively low-grade TiO_2, and has various impurity oxides of magnesium, calcium, and silicon, which are difficult to smelt [8–11].

As a result, electric arc furnace (EAF) smelting of Panzhihua ilmenite concentrate, which is widely used in the production of titanium slag, is employed and this consumes large amounts of electricity [1]. The EAF smelting of Panzhihua ilmenite concentrate is always kept at 1973 K (1700 °C) for around 8–10 h, and it contains 10–12 mass% FeO in slag in order to obtain high fluidity of slag to ensure the separation of liquid iron and liquid slag, which obviously decreases the grade of titanium slag. However, the EAF smelting process produces a lot of pollution, consumes a lot of energy, and has low efficiency, all of which have a negative impact on the environment. An alternative to the EAF smelting process, is the semi-molten reduction followed by magnetic separation, which produces titanium slag, and is proposed as a novel process for reducing iron oxide, decreasing the reaction temperature and time, and avoiding the high temperature melting separation of liquid iron from liquid slag, resulting in energy saving, high efficiency, and much reduced environmental pollution [12–14]. The flow chart in Fig. 1 compares the proposed process and the EAF smelting process.

During the past several decades, many studies have focused on the reduction of ilmenite [15–20]. El-Guindy et al. [21] found that the initial reaction temperature is near 1133 K (860 °C), and the reaction proceeded through CO as a gaseous intermediate at temperatures above 1293 K (1020 °C). Gupta et al. [22,23] found that it was difficult to nucleate iron during the reduction of ilmenite with carbon, but this could be overcome by the use of a catalyst. They also found that the addition of ferric chloride increased the reaction rate. Song et al. [24] reported the effect of $Na_2B_4O_7$ addition on carbothermic reduction of ilmenite concentrate. The reduction temperature decreased and the

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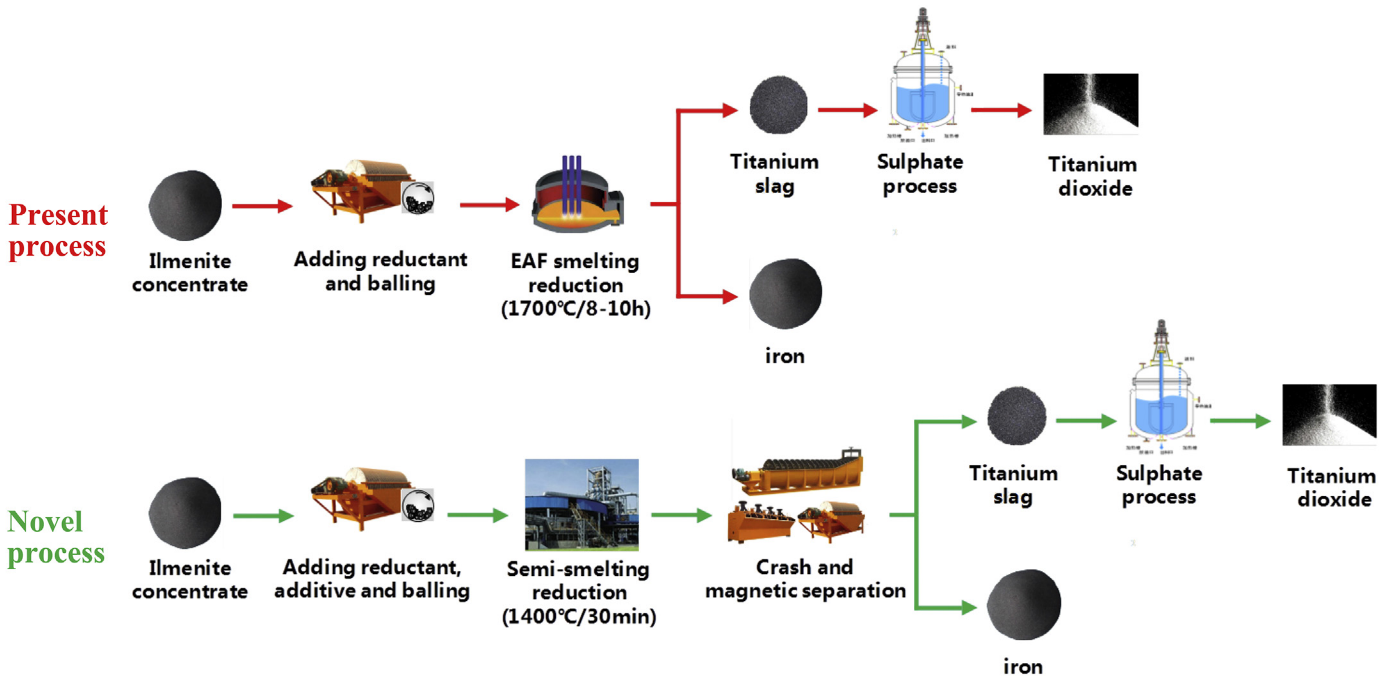

Fig. 1. Comparison of the novel process and present process of reduction of ilmenite concentrate.

reduction rate increased with the addition of the $Na_2B_4O_7$ as was expected. Huang et al. [1] investigated the effect of ferrosilicon on carbothermic reduction of ilmenite concentrate, and observed that the metallization ratio of iron in the reduced samples increased when increasing the ferrosilicon amount. El-Tawil et al. [25] found that the reduction efficiency increased by adding 30% Na_2CO_3 to the ilmenite. Huang et al. [26] observed that the vacuum carbothermic reduction of ilmenite concentrate can lead to both high titanium slag and ferrosilicon. Chen et al. [5] found that the metallization degree of titanomagnetite concentrates are improved by adding Na_2CO_3 additives. Geng et al. [27] and Li et al. [28] studied the effect of Na_2SO_4 on the reduction of titanomagnetite and nickeliferous laterite, and found that Na_2SO_4 can promote the reduction process.

According to the previous studies, it may be concluded that the additives are mainly $Na_2B_4O_7$, Na_2CO_3, Na_2SO_4, and Fe-Si, and they can function as reductants, activating agents, nucleating agents, exothermic agents, and catalysts, all of which are beneficial to the reduction of ilmenite concentrate. However, there are few reports on the semi-molten reduction of ilmenite concentrate followed by magnetic separation of iron and slag to produce titanium slag, which would not need a certain amount of FeO in the slag and would lead to energy conservation and reduce the environmental impact. The aim of this work is to investigate the semi-molten reduction behavior of ilmenite concentrate with a reductant and Na_2SO_4 additive. The effect of temperature, C/O molar ratio, and the addition dosage of Na_2SO_4 on the metallization ratio, phase transformation, and the size of metallic iron grain are studied.

2. Material and methods

2.1. Materials

The ilmenite concentrate powder was obtained from Panzhihua Iron and Steel Group, Sichuan province, China. The XRD pattern of the ilmenite concentrate is shown in Fig. 2, which indicates that the main phases in the ilmenite concentrate are $FeTiO_3$, Fe_3O_4, and $MgTiO_3$. The chemical composition analyses (as pure oxides) of the ilmenite concentrate powders are shown in Table 1, which indicates that the main impurities in the ilmenite concentrate are MgO, SiO_2, and Al_2O_3. The size of the sample particles are shown in Fig. 3, where the size of the ilmenite concentrate particles was approximately ~150 μm.

2.2. Experimental procedure

The ilmenite concentrate powder was mixed homogenously with the graphite powder (≥99.9% purity, <13 μm in particle size) and sodium

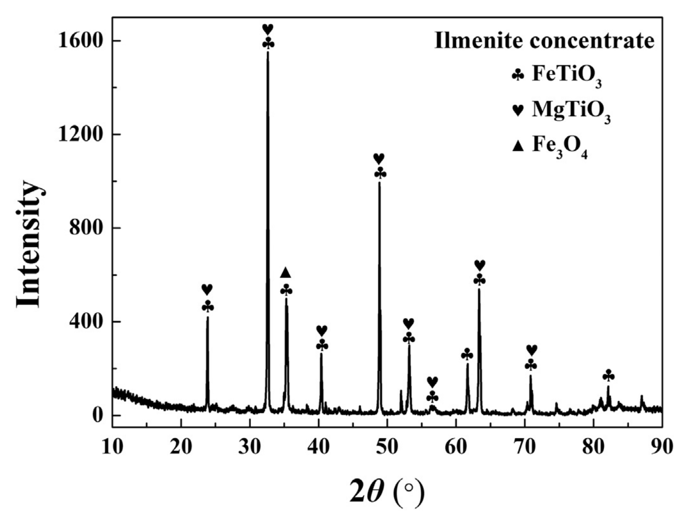

Fig. 2. XRD patterns of the Panzhihua ilmenite concentrate.

Table 1
Chemical composition of the Panzhihua ilmenite concentrate as pure oxides (wt%).

Compositions	TiO_2	FeO	Fe_3O_4	MgO	SiO_2	Al_2O_3	CaO	MnO	V_2O_5	S	P
Content	46.82	31.77	8.85	5.66	3.23	1.00	0.842	0.635	0.058	0.14	<0.005