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Selective metal cation concentration during the solidification of stainless steel EAF dust and slag mixtures from high temperatures for increased Cr recovery

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ABSTRACT

The selective concentration of valuable metal cations in Fe_tO-Cr_2O_3-NiO-MnO-containing stainless steel dust has been studied. The hazardous metal cations Fe, Cr, Ni and Mn could be locally concentrated during the solidification of a molten stainless steel slag and dust mixture from high temperatures by controlling the primary crystalline spinel phase. The nucleation and growth of the primary spinel phase could be controlled by varying the slag to dust mixing ratio and the cooling temperature. Significant redistribution between the primary spinel and amorphous phases could be observed, where the contents of Cr and Mn in the crystalline phase could be increased up to 40% and 10%, respectively, from their initial contents of 5% and 4% in the melt. Using the specified controlled cooling conditions, a primary spinel phase concentrated with Fe-Cr-Ni-Mn could be formed, which could be clearly distinguished and eventually separated from the amorphous matrix. The mixed stainless steel slag and dust samples were quenched at various cooling temperatures and with varying amounts of dust to identify and optimize the crystalline phases formed using SEM-EDS (scanning electron microscopy-energy dispersive spectroscopy) and XRD (X-ray diffraction) analyses.

1. Introduction

Stainless steel dusts containing metal oxides, including Cr_2O_3 and NiO, produced from the electric arc furnace (EAF) are classified as 'hazardous wastes' [1,2]. In the ferrous industry, the annual amount of stainless steel dust is increasing dramatically, and recycling this hazardous waste has become a critical issue for sustainable EAF stainless steel processing [1–5]. Through costly treatments by licensed recycling companies, the stainless steel by-product can ultimately be used as a feed material in ferro-alloy production, which can in turn be utilized in the typical carbon steel industry. Stainless steel dust is typically comprised of Fe_2O_3 (28–32%), Cr_2O_3 (9–11%), and NiO (2–4%) with additional major gangue materials of CaO, MgO, and SiO_2 [5–9]. To recycle stainless steel dust, the raw materials are briquetted with an appropriate reducing agent, such as carbon [3,10]. However, impurities such as CaO, SiO_2, Al_2O_3, MgO and ZnO in the recycled stainless steel dust can deteriorate the EAF process efficiency and consume unnecessary electricity by requiring an excess of binder such as bentonite or cement and increasing the slag volume [10,11]. Excessive dust accumulation wastes resources and generates additional costs due to its potentially adverse environmental impact in recycling [2,12]. Therefore, it is desirable to efficiently maximize the recovery of valuable metals from the stainless steel dust and minimize the amount of unnecessary gangue materials entering the EAF process. In particular, the pre-removal of CaO and SiO_2 before the briquetting process of the stainless steel dust can significantly reduce the power consumed in the EAF process, resulting in greater power efficiency and lower CO_2 emissions. Therefore, the effective utilization of stainless steel dust is needed for the concentration of the valuable components in the raw materials before the briquetting process.

Several studies have been dedicated to evaluating the possible applications of stainless steel slag and dust. Gravity separation and magnetic separation methods have been used to recover the Ni and Cr metals or alloys from stainless steel wastes in some commercial processes, but some of the metals present as metal oxides and in the silicate phase are difficult to recover by these methods [13]. Ma and Garbers-Craig reported the stabilization of Cr in stainless steel dust and investigated the possible mechanisms by mixing the dusts with clay [14,15]. Erdem et al. found that the rapid cooling of ferro-chromium slag with sprayed water can effectively inhibit the formation of Cr(VI), ensuring greater environmental safety for slag disposal [12]. It has been revealed that the addition of ferrosilicon decreases the Fe content of

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spinels in chromium slags, and calcium chromites form only in slags with high basicity in which the silicon content in the slag is low [16]. Additionally, several studies have determined that the spinel-type compounds present in stainless steel slag and dust are very resistant to oxidation and dissolution in acidic environments, and the leaching levels of hazardous elements such as Cr from stainless steel waste can be suppressed when these elements are contained in a spinel phase [17–22]. By incorporating chromium in spinel phases during the cooling of the slag, the reduction of the Cr released from the slag was observed, and the leaching levels of Cr are believed to be limited substantially due to the containment of Cr through spinel formation [17]. Cabrera-Real reported that low chromium levels of leaching are expected in MgO-modified slags, and the formation of $MgCr_2O_4$ spinel can suppress the formation of leachable chromium compounds [21]. In the case of a controlled cooling process of slag melts, specific metal cations can be locally concentrated in the primary crystalline phases, which can be further processed to selectively separate the primary crystalline phase from the amorphous phase in EAF slag mixtures [11,19,23].

In this study, the valuable and hazardous metal cations Fe, Cr, Mn and Ni present in slag melts and dust were locally concentrated into the primary crystalline phase during the solidification of stainless steel slag and dust mixtures from high temperatures. The controlled distribution of the elements in specific primary crystalline phases was observed and correlated to spinel phase formation, which was dependent on the slag/dust mixing ratio and the subsequent isothermal heat treatment and water quenching procedures. After rapid cooling, the solidified slag and dust mixtures were analyzed using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) for semi-quantitative analysis of the composition and distribution. In addition, the crystalline phase formed under controlled cooling was identified by X-ray diffraction (XRD) peak analysis.

2. Experimental procedure

2.1. Sample preparation and controlled cooling experiment

The stainless steel EAF slag and dust samples within the present work were supplied by a commercial stainless steel plant, and their chemical compositions are shown in Table 1. It should be noted that due to variations in the raw materials used and the specific products produced within a given time interval, additional compositional variations are likely. The composition of each sample was determined using X-ray fluorescence (XRF, S4 Explorer; Bruker AXS GmbH, Karlsruhe, Germany). The provided results represent the average value of the chemical composition of the bulk slag and dust. The EAF slag is calcium silicate-based and contains highly valuable metal oxides of 10.4 wt% Cr_2O_3 and 5.8 wt% MnO. The EAF dust has 45.2 wt% Fe_2O_3, 14.3 wt% Cr_2O_3, 3.3 wt% MnO and 4.3 wt% NiO. Fig. 1 shows the XRD (Ultima IV, Rigaku, Japan) patterns of the stainless steel slag and dust raw materials before the controlled cooling treatment. The phases found in the slag are melilite, $Ca_3Si_2O_7$ and spinel, while the dust has only the spinel phase. For the stainless steel slag containing large amounts of CaO and SiO_2, melilite and $CaSi_2O_7$ phase have been identified as the main phases.

The raw slag materials were crushed and ground to a fine powder with a particle size below 150 μm. Also, the stainless steel metal balls in the raw slag materials were previously removed. The slag and dust were mixed in ratios of 9 to 1, 8 to 2, and 7 to 3 at room temperature, and samples weighing approximately 5 g were inserted into a Pt-10 wt.% Rh cylindrical crucible (14 mm in diameter and 40 mm in height). The composition of each homogenously mixed sample with varying amounts of dust is summarized in Table 2. The slag and dust mixture was heated to 1823 K (1550 °C) for 2 h in a Kanthal resistance box furnace under a 2 slm flow of UHP Ar (99.9999 vol.%), which was maintained during the controlled cooling process. The samples were then either held or cooled to a target temperature of 1823 K (1550 °C), 1673 K (1400 °C), 1473 K (1200 °C) or 1273 K (1000 °C) at −5 K/min, held for 30 min, and subsequently quenched with water.

2.2. Analysis of the solidified samples

The as-quenched samples were physically removed from the crucible using a hammer and chisel. Fragments with an estimated circular diameter of 5 mm were obtained. The sample fragments were mounted in epoxy resin and polished below 1 μm using diamond paste. The polished cross-sections of the specimens were analyzed using a SEM (JSM-7001 F, JEOL, Japan) at a 15 keV accelerating voltage and a 10 mm working distance. Elemental information about the crystalline and amorphous phases was obtained with an EDS (Octane plus, AMETEK Inc., USA) for semi-quantitative compositional analysis. To evaluate the as-formed crystalline particle size distribution dispersed within an amorphous base, the average grain size of the crystalline phase was measured using the average Feret diameter in the image analysis software (Image-Pro Plus, Media-Cybernetics Inc., USA). As-formed spinel particles have a polygonal shape and can often be agglomerated. This agglomeration makes it difficult to determine the centroid of the particle for measuring a mean diameter. Therefore, in the particle size distribution analysis, the average Feret diameter, which is the average of the farthest measured distance between two parallel tangents on opposite sides of a randomly oriented particle over all directions within the periphery of the particle, was used through the image analysis software [24–26]. Since these values are dependent on the orientation of a randomly oriented faceted particle, a single measurement can result in significant error [27,28]. Thus, measurement of all the particles dispersed within the image, corresponding to more than 300 individual crystalline particles, was conducted in this particle size evaluation. Also it should be noted that the use of the average Feret diameter may not directly coincide with a 3-D particle, but considering the polygonal shape and the number of particles (> 300) analyzed within the image, a semi-quantitative trend can be obtained. In some cases, XRD analysis was performed on the fine powdered samples to confirm the existence of the observed phases. The XRD patterns were recorded at a scan rate of 4°/min and a step size of 0.02° using Cu Kα radiation at 40 kV and 40 mA.

3. Results and discussion

3.1. Thermodynamic equilibrium calculation of the phases in the slag and dust mixtures

The amounts of the solid and liquid phases in the slag and dust mixtures for each temperature were calculated by the thermochemical

Table 1
Compositions of the stainless steel EAF slag and dust measured using XRF.

	Contents (wt%)										
	CaO	SiO_2	Al_2O_3	MgO	Cr_2O_3	MnO	Fe_2O_3	TiO_2	NiO	ZnO	Na_2O
EAF Slag	36.0	32.0	7.9	4.4	10.4	5.8	1.6	1.9	–	–	–
EAF Dust	14.0	5.6	0.7	2.6	14.3	3.3	45.2	–	4.3	5.8	4.2