

Distribution and Chemical Species of Chromium in the EAF Dust from Stainless Steel Plant



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Abstract Electric Arc Furnace (EAF) dust generated in the production process of stainless steel is a hazard to the environment and human health due to its large amounts of toxic substances, such as Cr(VI). Cr in the EAF dust is mainly in the form of a residue according to sequential extraction procedure test, and only small amounts of Cr are mobility. Although the formation mechanism of the EAF dust has been gradually understood, the distribution and chemical species of Cr in EAF dust are rarely studied. In this paper, the distribution and chemical species of Cr in EAF dust were studied. The results show that Cr(III) and Cr(VI) are mainly present in the small particles. After sputtering about 140 s with Ar⁺ ion beam, the Cr(VI) on the surface of dust particles disappears, and the content of Cr(III) reaches 100%, indicating the Cr(VI) in the EAF dust comes from the oxidation of lower valent Cr-containing substances and enrich on the surface of the dust particles.

Keywords EAF dust · Cr(VI) formation · Cr distribution · Stainless steel

Background

Chromium comes from chromium ore, which is widely used in metallurgy, refractories, and chemistry. The component of the chromium ore used in metallurgy industry contains Cr₂O₃ of more than 46% and Cr/Fe of 2, respectively [1]. Due to its corrosion resistance, chromium is widely used in the product of stainless steel in the form of

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Fe–Cr alloy. Stainless steel is classified into chromium stainless steel, chrome nickel stainless steel, chrome nickel molybdenum stainless steel and chromium manganese nitrogen stainless steel according to its chemical composition. In consideration of reducing production cost and the consumption of nickel, the chromium stainless steel becomes one of the most developed varieties. According to the corresponding standards [2–4], the content of chromium is higher than 10.5 wt% in chromium stainless steel.

In China, the production of stainless steel has increased from 7.3 million tons in 2001 to 24.93 million tons in 2016 [5]. With the increase of product of stainless steel, the environmental problems in the vicinity of the stainless steel plants have been concentrated. One of the concerns is the disposal of EAF dust, which is considered as one kind of carcinogenic materials as it contains 0.14–0.6 wt% Cr(VI). It exceeds the limit values of many countries [6]. Typically, 18–33 kg of dust generate per ton stainless steel produced [7]. The dust generated through the homogeneous or heterogeneous nucleation because of the splash of liquid steel and slags directly fly-off from the charge as well as volatilization of metals [8]. However, the distribution of Cr in the dust, especially Cr(VI), in different particle size has been rarely studied. As the hazards of waste depend on the concentrations of hazardous elements as well as its particle size since the small dust particles are easier to spread in air and dissolve in water [9], more attention should be paid to the control and collection of small particles of dust.

In consideration of the mobility of metals in the EAF dust, some regulations should be satisfied during the treatment process of EAF dust. Some researchers [10, 11] utilized TCLP to determine the toxicity of EAF dust and found that EAF dust is the hazardous waste due to exceeding the regulation limits of Cr. However, the mobility of the Cr-containing species and chemical fractionation are still required to study. To understand this, the sequential extraction method was adapted according to the procedure of Ma et al. [10], namely F1-soluble, F2-exchangeable species, F3-bound to carbonates, F4-bound to amorphous Fe–Mn oxides, F5-bound to crystallized Fe oxides, F6-associated to organic matter and sulfides, and F7-residual which bound to spinel group minerals and silicates.

In this paper, various techniques, such as Inductively Coupled Plasma (ICP), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), and thermodynamic calculation, have been used to study the distribution and chemical species of Cr in the EAF dust from stainless steel plant, in order to understand the formation of Cr(VI) in the EAF dust.

The Existence Form of Cr in EAF Dust

By studying the process of smelting Fe–Cr alloys, Ma [7] and Sedumedi et al. [12] reported that Cr(III) is hard to be oxidized since the smelting process is carried out in a reducing atmosphere and the oxygen partial pressure in the smelting furnace is less than 10^{-8} atm. However, while the oxygen partial pressure increases in the off-gas

duct, the oxidation of Cr(III) may occur. Compared with the total amount of Cr(VI) generated in acidic slag and alkaline slag [13], it indicates that alkaline media would promote the formation of Cr(VI).

According to Cheng et al. [14], the Cr oxidation dynamics analysis indicates that Cr_2O_3 is the main oxidation product at low temperature, which will be decomposed to CrO and CrO_3 with the increase of temperature. At high temperature, CrO_3 is the main product. In the EAF dust, Cr mainly exists in the forms of Cr(III) and Cr(VI), and Cr(VI) is in the forms of CrO_3 , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} [15]. However, Peng and Peng [8] reported Cr exists in the form of CrO and FeCr_2O_4 by XRD analysis. Ma et al. [16] made a thermodynamic equilibrium calculation of Cr–Fe–Zn–Mn–Al–Ca–Ni–O–Cl system, which includes main components in the EAF stainless steel dust. The results indicated that Cr is in the form of FeCr_2O_4 with temperature higher than 1327 °C, and would transform into Cr_2O_3 when temperature is lower than 1327 °C. The evolutionary behavior of Cr in Cr– O_2 system with alkaline oxides was also simulated, demonstrating that CrO_4^{2-} is easily formed with the existence of alkaline oxides.

In order to further study the variation of Cr–Fe–C–O system with temperature, oxygen partial pressure and carbon content, the predominance area of Cr in the Cr–Fe–C–O system was calculated in Fig. 1. From the Fig. 1, the increase of temperature will make the predominance area more complex. In 1700 °C, CrO(l) is generated when $P(\text{O}_2) > 10^{-6.2}$ Pa, and $\text{Cr}_3\text{O}_4(\text{s})$ would be generated with the increase of the oxygen partial pressure. When the oxygen partial pressure continues to increase to $10^{-5.8}$ Pa, $\text{Cr}_2\text{O}_3(\text{s})$ is generated. The Cr is stable in the form of $\text{FeCr}_2\text{O}_4(\text{s})$ with the oxygen partial pressure more than $10^{-4.5}$ Pa. Cr(VI) would be produced when the oxygen partial pressure reaches 9.77 Pa. In the process of stainless steel smelting, the equilibrium oxygen potential of carbon is related to carbon content and temperature (Eq. 1) [17]:

$$\lg(\text{PO}_2/P^\theta) = -2\lg\omega[\text{C}] - 0.28\omega[\text{C}] - 14558/T - 3.6752 \quad (1)$$

The temperature of stainless steel smelting is about 1600 °C, and carbon content at the endpoint $\omega[\text{C}] = 0.04\text{--}0.08\%$ [18]. When the endpoint carbon content is controlled at 0.04%, the oxygen partial pressure is 2.23 Pa calculated by Eq. (1). Combined with Fig. 1, the Cr is mainly in the form of $\text{FeCr}_2\text{O}_4(\text{s})$ in the EAF dust.

Experimental

The EAF dust from a domestic stainless steel plant is rufous with small particles and easy to be accumulated. The chemical composition of the EAF dust was analyzed by Inductively Coupled Plasma (IRIS Advantage ER/S, Thermo Elemental, USA) shown in Table 1. It shows that the EAF dust has high levels of Cr, and more than 4 wt% alkaline oxides.

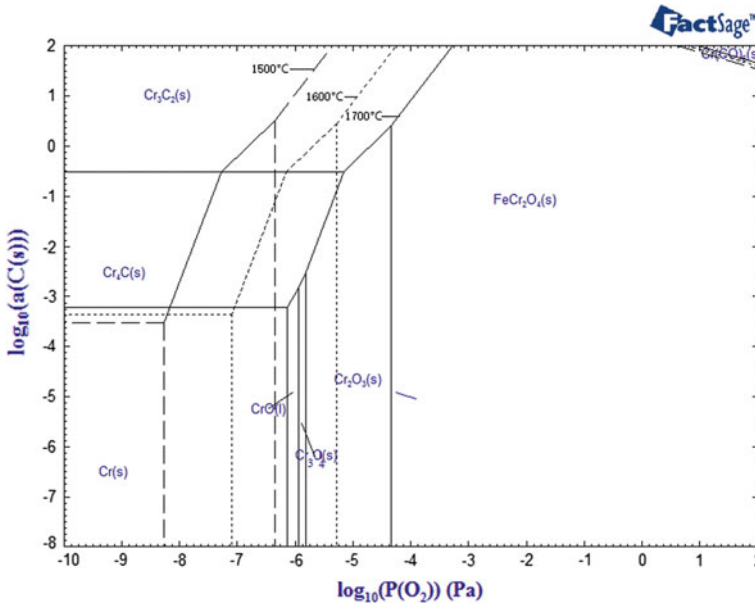


Fig. 1 Predominance area of Cr in the Cr–Fe–C–O system

Table 1 The chemical composition of EAF dust (wt%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	MnO	Cr	NiO	Zn	Cd	Pb
12.56	3.52	49.93	1.96	1.21	2.29	1.20	1.98	8.20	2.35	1.28	0.004	0.30

Phase and Microstructure Analysis of EAF Dust

X-ray diffractometer (X’Pert PRO MPD) was used to analyze the crystalline phases of the EAF dust with Cu K α radiation, tube voltage 40 kV, tube current 40 mA, 2 θ scanning range 10°–70° and continuous scanning mode. The microstructures of EAF dust were observed by Scanning Electron Microscopy (PHILIPS XL30 TMP) with an energy dispersive spectrometer. Before sample preparation, the EAF dust particles was placed in the oven at 110 °C to dry for 2 h, and then it was placed on the conductive tape and observed after spraying gold.

Distribution of Cr in Different Particle Size

The EAF dust was sieved by the dry method with ultrasonic vibrating screen (ZD-250A). The sample was sieved into five different particle sizes of >40, 30–40, 10–30, 5–10, <5 μ m. The content of Cr was analyzed by ICP, and the content of Cr(VI)

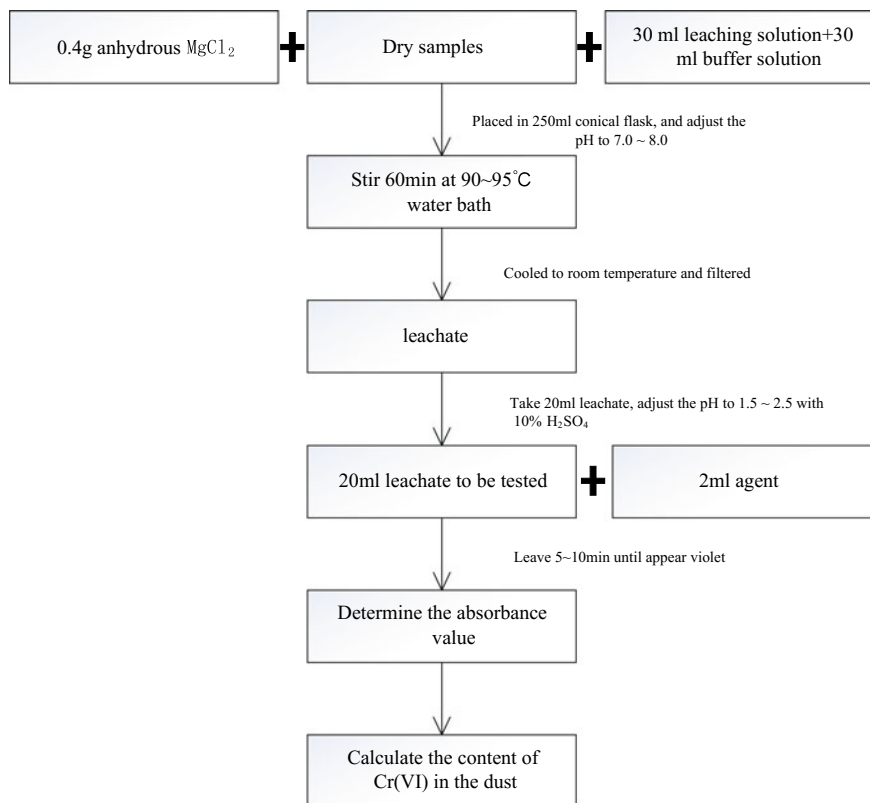


Fig. 2 The steps of determining the content of Cr(VI) in the EAF dust

in the dust of different particle size was analyzed by the EPA method 3060A. The specific steps of measurement of the content of Cr(VI) in the EAF dust are shown in Fig. 2. In this experiment, the standard curve equation is $y = 0.6974x + 0.001$, $R^2 = 0.9994$ (y is the concentration value of Cr(VI), x is the absorbance value).

Chemical Species of Cr in EAF Dust

Table 2 is the typical seven extraction procedure for residual elements. After each extraction step, the mixture was centrifuged at 2500 rpm for 10 min. The residual was then washed with 10 ml ultrapure water and centrifuged repeatedly. The supernate of each extraction step was used to determine the concentrations of heavy metals with ICP.

Table 2 The steps of the sequential extraction procedure

Chemical species	Description of extraction process
F1. Soluble	Place 2.00 g dust samples into 10 ml of water with horizontal shaking for 30 min at room temperature
F2. Exchangeable species	Add 10 ml 1 N $Mg(NO_3)_2$ into the residue from F1 for 1 h at room temperature
F3. Carbonate	Add 10 ml 1 N NaAc to the residue from F2 buffered to pH value is 5 with acetic acid for 5 h
F4. Amorphous iron manganese oxide	Add 10 ml 0.25 mol/l $NH_2OH \cdot HCl$ and 0.25 mol/l HCl to the residue from F3 for 30 min in a water bath at 50 °C
F5. Crystalline iron manganese oxide	Add 10 ml 4 mol/l HCl to the residue from F4 for 30 min in a water bath at 95 °C
F6. Organic matter and sulfides	Add 5 ml 30% H_2O_2 and 5 ml 0.02 mol/l HNO_3 to the residue from F5 for 6 h in a water bath at 85 °C
F7. Residue	The residue from F6 step is digested for the analysis of related heavy metals

Formation of Cr Species in EAF Dust

Peng and Peng [8] found that Fe and Si are unevenly distributed because the EAF dust particle grows by mechanical deposition. And Cr deposits on the surface of large dust particles by electrostatic interaction. However, electron probe can only analysis the bulk composition of the dust particles. A XPS (ESCALAB 250) was used to investigate the elements distribution on the surface of dust. The high kinetic energy Ar^+ ion beam was employed to sputter the surface of the dust particles continually, and then to analyze the surface elements of dust at interval.

Results and Discussion

Phase and Microstructure of EAF Dust

Figure 3 is the crystalline phases of EAF dust. It can be seen that Cr(III) is mainly in the form of $FeCr_2O_4$. This assists with the thermodynamic calculation on the predominance area of Cr species in the Cr–Fe–C–O system. In addition, Fe_3O_4 and NiO are also found in the EAF dust.

Figure 4a shows a typical spherical particle in EAF dust with a particle size of about 8 μm . The energy spectrum analysis shows that it is $CaO \cdot SiO_2$, which may be derived from the splash of the slag. In addition, a large number of well-crystallized particles (as shown in Fig. 4b) can be found in EAF dust. These particles are mainly composed of Fe, Cr, and O, which can be inferred to be $Fe(Fe, Cr)_2O_4$ by energy

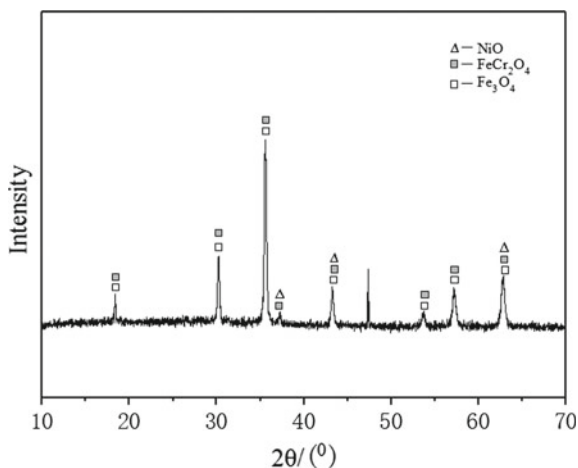


Fig. 3 Crystalline phases of EAF dust

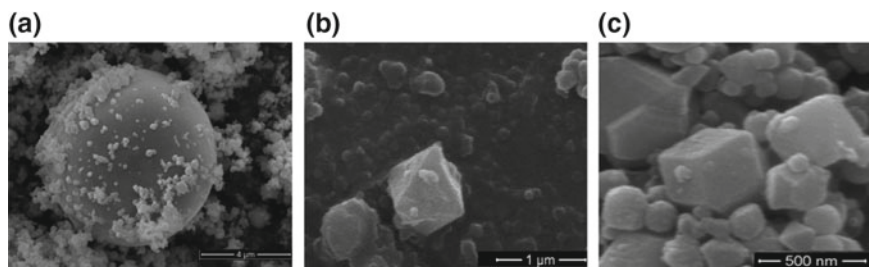
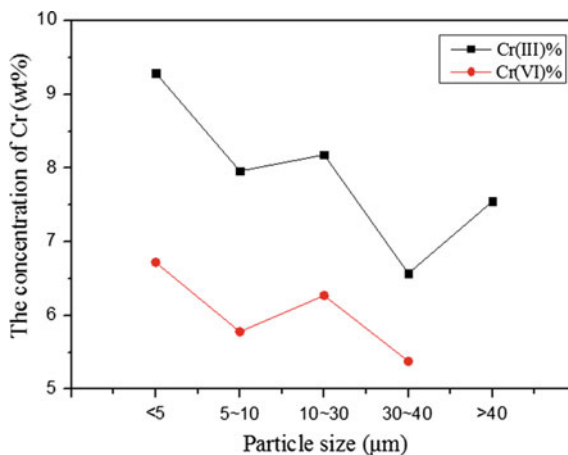


Fig. 4 Microstructure of EAF dust (**a** spherical dust; **b** octahedron crystal; **c** cube crystal)

spectrum analysis. According to Peng and Peng [8], if there are not enough solid particles to agglomerate in a heterogeneous nucleation manner, the metal volatilized from the molten bath can form EAF dust by homogeneous nucleation, which means that volatilized substances collide and bond each other. When the particles grow into about 0.02–1.0 μm , they are heterogeneously nucleated and mechanically aggregated to form dust [8]. The formation of regular octahedral spinel particles in Fig. 4b may be formed by the vaporization of Fe and Cr elements at high-temperature zone of the smelting furnace and reaction in the off-gas pipe. Cube-shaped particles can also be observed (Fig. 4c). It is a Ni–Fe–Cr–K–Al–O based material (4.67% Ni, 39.12% Fe, 9.01% Cr, 6.85% K, 2.25% Al, and 38.10% O).

Table 3 The particle size distribution of EAF dust

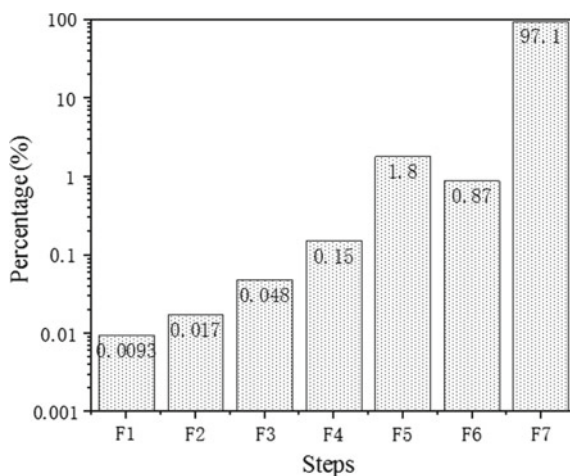
Particle size (μm)	<5	5–10	10–30	30–40	>40
Percent (wt%)	58.8	5.9	26.4	1.1	7.8

Fig. 5 The amount of Cr in different particle size

Distribution of Cr in Different Particle Size

The distribution of particle size is shown in Table 3. The particle size of EAF dust is mainly less than 5 μm (up to 58.8 wt%), there are only 8.8 wt% EAF dust of which the size is larger than 30 μm .

The result about the amounts of Cr(III) and Cr(VI) in different particle size is depicted in Fig. 5, interpreting the Cr(III) and Cr(VI) trend to accumulate in the small particles and they both have same tendency with the change of particle size. From the thermodynamics and dynamics analysis in the Cr–Fe–C–O system [13, 14], Cr(III) is easier to be oxidized while the oxygen partial pressure is higher than 9.77 Pa. When the EAF dust reaches into the off-gas pipe, the oxygen partial pressure would be higher than 9.77 Pa, indicating that the oxidation of Cr(III) would happen. From Table 1, there are alkaline media in the duct which can promote the oxidation of Cr(III) [16]. In addition, the smaller dust particle has larger specific surface area, which is easier to absorb Cr(III) and make the reaction between Cr(III) and oxygen to form Cr(VI). Therefore, Cr(VI) has the same tendency to accumulate in the small particles.

Fig. 6 Fractionation of Cr in EAF dust

Chemical Species of Cr in EAF Dust

Figure 6 shows the fractionation of Cr in EAF dust. It indicated that Cr tightly bound to stable phases extracted mainly in crystalline Fe–Mn oxide, sulfides and spinel group. More than 97% Cr are bound to spinel and there are only 0.0743% chromium extracted from F1 to F3 steps, which is mobile when EAF dust contacts with water or the pH value changes. This is further demonstrated that Cr is mainly presented in the spinel phase in the form of Cr(III). However, it is still paid more attention to that the Cr(III) species can transform into Cr(VI) species with the present of CaO and oxygen. It seems that the best way to treat these Cr-containing dusts is to recycle them back to the stainless steelmaking process through the existing technologies.

Formation of Cr Species in EAF Dust

The change of content of surface element is depicted in Fig. 7. Except O(32 wt%), F(10 wt%) and Si(12 wt%), the contents of elements are lower than 4 wt% on the surface of EAF dust. With the increase of Ar⁺ sputtering time, the contents of Fe, Cr and O on the surface have an increasing trend, and other elements, such as Zn and Cl, do not change significantly. During the smelting process, the rupture of CO bubbles results in that the molten steel and slag are splashed to form the core of the dust particles. With the particles flowing up, the temperature decreases and the oxides with high smelting points would be condensed first. With the principle of nucleation, these oxides would become the crystallization nuclei. And then nuclei continue to grow through homogeneous or heterogeneous nucleation. Fe and Cr are mainly in the form of oxides with high smelting points, and they would become the nuclei of dust

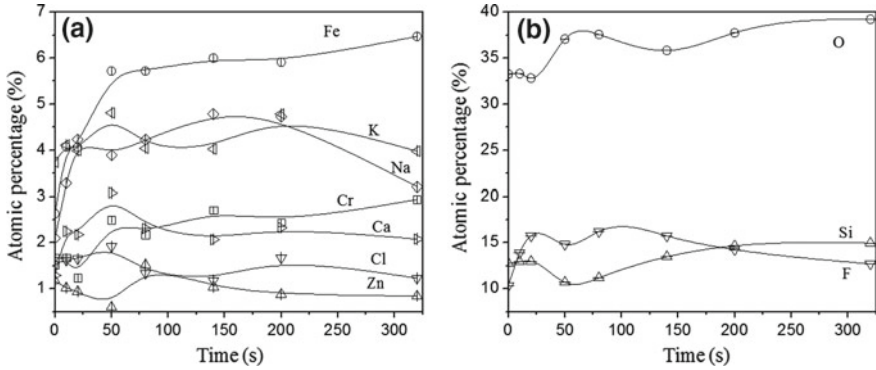
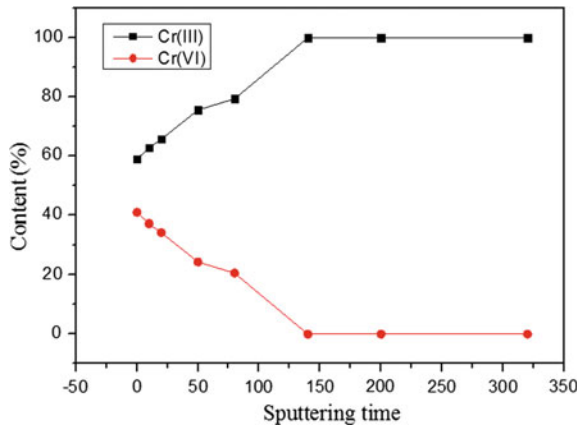


Fig. 7 The surface element concentration of EAF dust varies with Ar⁺ sputtering time

Fig. 8 The change of content of Cr at different sputtering times



causing the surface content of Fe and Cr is lower than the ones inside. The contents of Zn and Cl did not change much, indicating that they are evenly distributed during the whole process of grow of dust.

At different Ar⁺ sputtering time, the contents of Cr and Cr-containing compositions have been analyzed by XPS. Figure 8 is the change of content of Cr at different sputtering time, indicating that the content of Cr(VI) decreases gradually with the increase of the sputtering time, on the other hand, the content of Cr(III) increases. When the sputtering time is 140 s, the content of Cr(VI) on the surface is nearly zero.

As the smelting process of stainless steel requires decarburization reaction, the smelting furnace is mainly in high temperature and reduction atmosphere, Cr(III) is difficult to be oxidized. According to the thermodynamics calculation and dynamics analysis [13, 17], if the oxygen partial pressure is higher than 9.77 Pa at high temperature, the Cr(VI) would be generated. It proves that Cr(VI) would derive from the oxidization of Cr(III). Part of Cr form Cr₂O₃ or FeCr₂O₄ as the nuclei and grow

through homogeneous or heterogeneous nucleation. And while the particle size of Cr_2O_3 is large, the dust will be formed by mechanical deposition. With the oxygen partial pressure become high gradually in the off-gas duct, the Cr(III) on the surface is easier to be oxidized to Cr(VI). Thus, with the increase of sputtering time, the Cr(VI) on the surface disappears firstly, and the content of Cr(III), which is not oxidized inside, is getting higher and higher until content of Cr(III) is 100%.

Conclusions

- (1) The Cr contained in EAF dust is mainly in the form of FeCr_2O_4 . The amount of Cr(VI) would decrease with the increase of size of EAF dust particle because the smaller dust particle has larger specific surface area, which is easier to make the oxidation reaction of Cr(III) to form Cr(VI).
- (2) Cr in EAF dust is mainly in the form of Cr(III) existing in spinel residual.
- (3) The contents of Cr(VI) and Cr(III) have opposite trend, with the increase of Ar^+ sputtering time. The former would decrease from 40 to 0%, and the latter would increase from 60 to 100%. Since the oxygen partial pressure becomes higher and higher from smelting bath to off-gas duct, the Cr(III) on the surface would be oxidized to Cr(VI).

References

1. Yan YF, Chen JX, Hu L (2007) Chromium metallurgy. Metallurgical Industry Press, Beijing
2. GB/T 12230, General purpose industrial valves-Specification of stainless steel castings
3. ASTM A351, Standard specification for castings, austenitic, for pressure-containing parts
4. JIS G5121, Corrosion-resistant cast steels for general application
5. International Stainless Steel Forum (ISSF). Meltshop production statistics 2001 to 2006. http://www.worldstainless.org/crude_steel_production/meltshop_production_2001_2016
6. Vargas ASD, Ângela B, Masuero, Vilela ACF (2006) Investigations on the use of electric-arc furnace dust (EAFD) in Pozzolan-modified Portland cement I (MP) pastes. *Cem Concr Res* 36(10):1833–1841
7. Ma GJ (2005) Cr(VI)-containing electric furnace dust and filter cake: characteristics, formation, leachability and stabilization. University of Pretoria, Pretoria, South Africa, pp 25–98
8. Peng B, Peng J (2003) Stainless steel electric arc furnace dust physical and chemical properties and formation mechanism. *North China Univ Technol* 15(1):34–40
9. Davis A, Ruby MV, Bergstrom PD (1992) Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district. *Environ Sci Technol* 26(3):461–468
10. Ma GJ, Fan W, Xue ZL, Wang W, Tang H (2010) Leachability and fractionation of heavy metals in stainless steelmaking plant dusts. *Acta Metallurgica Sinica (English Letters)* 3(4):267–276
11. Laforest G, Duchesne J (2006) Characterization and leachability of electric arc furnace dust made from remelting of stainless steel. *J Hazard Mater* 135(1):156–164
12. Sedumedi HN, Mandiwana KL, Ngobeni P, Panichev N (2009) Speciation of Cr(VI) in environmental samples in the vicinity of the ferrochrome smelter. *J Hazard Mater* 172(2):1686–1689
13. Beukes JP, Dawson NF, Zyl PGV (2010) Theoretical and practical aspects of Cr(VI) in the South African ferrochrome industry. *J S Afr Inst Min Metall* 110(12):743–750

14. Fan W, Ma GJ, Xue ZL, Yang F, Fang Y (2012) Formation of Cr(VI)-bearing phases in the EAF dust from stainless steel plant. *J Mater Metall*
15. Cheng JF, Xu MH, Zeng HC, Feng R, Qiao Y (2002) The study of oxidation dynamic of Cr at high temperature. *Chin J Electr Eng* 22(8):135–138
16. Ma GJ, Su WH, Xue ZL, Xu ZH (2009) Microstructure and occurrence of chromium of the stainless steel plant dusts. China Iron and Steel Association, Beijing, China, 12 Nov 2009
17. Wu YJ, Jiang ZH, Liang LK, Jiang MF, Huang ZZ, Chen ZP (2003) Analysis of correlative thermodynamic problems in stainless steel smelting process(II)-dephosphorization of chromium-containing hot metal. *J Iron Steel Res* 15(4):12–17
18. Zhang JY, Xing XR, Song B (2004) Metallurgical physical chemistry. Metallurgical Industry Press, Beijing, pp 317–318