PLASMA TRANSFERRED ARC REACTOR (P<40kW) TO STUDY THE CARBOTHERMIC REDUCTION OF OXIDIZED FeSi FINE PARTICLES

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ABSTRACT : the results of a study about the treatment of ferrosilicon dusts in a transferred arc plasma furnace are presented in this paper. To predict the reduction reactions, thermodynamic calculations were performed. The use of carbon allows to reduce the metallic oxides contained in the dusts and then to convert them in valuable metals (FeSi). The chemical and thermal treatment of the dusts in a graphite crucible have been studied, showing the formation of a metallic bath of pure ferrosilicon and a slag of silica.

INTRODUCTION

The steelmaking industry and the ferroalloy production by electric arc furnaces (EAF) generate large quantities of dusts composed principally of iron oxides with traces of metals (Cr,Mo,Ni,Pb,Zn,...) [1,2,3]. European and American environmental restrictions, more and more severe, allow no longer land filling, the dusts being entrained by rain-water and then polluting soils [4]. The encapsulation is an acceptable solution but the transport towards adapted dumps do not allow this solution to be economically attractive, compared to the recycling when recovered metals are valorized [5,6]. Since dust treatment cannot be made directly in the electric arc furnace, their introduction resulting in a drastic reduction of furnace efficiency, specific processes must be developed.

Arc plasma processes allow to achieve very high temperatures (up to 20000K), energy densities (up to $10^9 W/m^3$), heat fluxes (more than 10^8 W/m^2), and chemical reactivities together with a very low thermal inertia (<1s). They seem to be one of the most adapted solution for dust recovery.

In this paper, the results, obtained within the frame of a study about ferrosilicon dust treatment in a plasma furnace are presented. The work was devoted to the study of the treatment of the wastes in the molten bath.

EXPERIMENTAL SET-UP

Aim of the work :

The aim of this study was to recover ferrosilicon dusts in a transferred arc plasma reactor. For that a test powder of ferrosilicon was chosen, and iron and silicon oxides added. The calculation of carbothermic reduction of the dusts at equilibrium (computer codes), the formation of a molten bath in a graphite crucible and the reduction treatment in this bath have been studied.

Powders :

For this study, a commercial powder of ferrosilicon was chosen. Its composition is given in table 1. The grains are formed by a diphasic $FeSi_2$-Si (molar ratio $Si/FeSi_2$=2.33). The size distribution is very large (1-300μm), with an important part (90 nb%) of fine particles (<40μm). The grains are angular, with a shape factor of 0.6.

element	Si	Fe	O	Al	B	Pb	Hg	P	Te	Cd	Cr
wt%	63	29	5	0.95	0.35	0.10	0.09	0.08	0.08	0.06	0.04

table 1 : ferrosilicon commercial powder composition

To simulate the industrial dusts, this powder was mixed with iron and silicon oxides. Powders of carbon graphite as reducer, and calcite as slag former were added with different weight percentages, and the mixtures prepared by using a Turbula.

Reactor :

The experimental set-up (Fig. 1) was composed of a double-walled water-cooled controlled atmosphere chamber (internal diameter: 0.4m; height: 0.5m). At the top, a plasma torch system composed of a thoriated tungsten conically-shaped cathode (40° cone angle), was disposed. It could be moved vertically (v=0.75m/mn) in order to adjust the distance torch-crucible. At the bottom of the reactor, a water-cooled tube, in which off-gases were evacuated with the help of a primary pumping group, was used to support a graphite crucible which had an external diameter of 130mm, an internal diameter of 80mm and a height of 50mm. The bath temperature has been measured by using a bichromatic pyrometer (λ_1 varying between 0.7 and 1.08μm according to the considered temperature range and λ_2=1.08μm), disposed at 600mm from the crucible with a 45° angle (see Fig. 1). The temperature limit of the pyrometer was 1920K. The measurements have been performed after the stop of the arc, which unfortunately emitted in the pyrometer wavelengths range. As soon as the power was shut off, the bath temperature dropped rather rapidly and to extrapolate the cooling curve, three measurements per second were recorded. Knowing precisely the shut-off time of the power source this system allowed good extrapolations up to temperatures of 1950K.

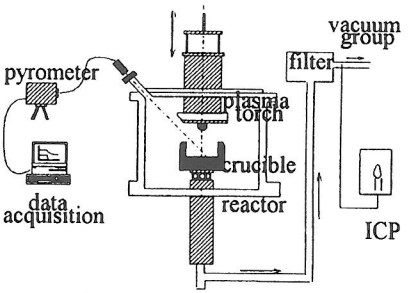


Fig. 1 : experimental set-up

Working conditions :

The tests have been performed in an argon atmosphere, at 0.102MPa, to avoid air penetration in the controlled atmosphere chamber. The electric arc was generated between the tungsten cathode and the anodic crucible, the distance between both being maintained constant at 100mm. The electric power used was then comprised between 12 and 30kW. Argon has been used as plasma gas and carrier gas. The ferrosilicon powder has been injected directly in the crucible, through a 3mm internal diameter water-cooled pipe, disposed at the border of the crucible with an angle of 45°, aiming the crucible centre. The working conditions are presented table 2 :

Atmosphere (argon)	0.102 MPa
Plasma gas (argon)	10-20 Nl/mn
Current intensity	300-500 A
Arc voltage	40-60 V
Cathode/crucible distance	100 mm
Powder : carrier gas (argon) flowrate	5-20 Nl/mn 0.3-1.0 kg/h

table 2 : working conditions

CHEMICAL TREATMENT

Thermodynamic calculations :

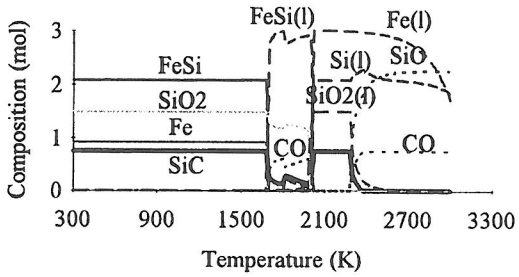
The carbothermic reduction of ferrosilicon dusts has been studied thermodynamically with the help of the Data and Calculations Base of Thermodynamic & Transport Properties [7], to determine the necessary quantity of reducer and the formation temperature range of the different products. The calculations are based on the minimization of the Gibbs free enthalpy. They were performed at atmospheric pressure and for a temperature range from 300 to 3000K. The considered species are presented in Appendix 1.

The quantity of carbon reducer has been determined for mixtures of ferrosilicon and Fe_2O_3, ferrosilicon and SiO_2, and ferrosilicon with both oxides, the different products being mixed in the same weight proportions. For example, the necessary carbon quantity for the molar mixture $1(FeSi_2 + 2.33Si) + 1Fe_2O_3$ is 0.75 moles.

The thermodynamic composition evolution with temperature of this mixture is presented Figure 2. A mixture of Si and FeSi, more stable than $FeSi_2$ was considered at room temperature. Si reduces Fe_2O_3 to form SiO_2 and Fe, and also reacts with all the C to form SiC. The mixture is then, between 300 and 1680K, composed of SiO_2 and SiC, very stable, and of Fe and FeSi. At 1680K, Fe reacts with SiC and SiO_2 and produces liquid FeSi and volatile CO. Then, $FeSi_{(l)}$ decomposes, at 2000K, in $Fe_{(l)}$ and $Si_{(l)}$ from wich a part is reoxidized as $SiO_{2(l)}$. Over 2280K, SiC and $SiO_{2(l)}$ decompose in volatile SiO and CO, the liquid mixture being then composed of $Fe_{(l)}$ and $Si_{(l)}$.

These calculations do not allow to predict the reactions that will occur in the crucible, because they do not account for the kinetic reactions and the diffusion of the species in the bath. But they give an indication about the minimum quantity of carbon necessary for each mixture to reduce the oxides and to limit the presence of carbides. It

allows too, to determine the temperature range in wich the experimentations have to be realized, i.e. 1680-2000K to obtain a molten bath of ferrosilicon ($FeSi_{(l)}$).



——— solid – – – – liquid ------- gas

Figure 2 : $(FeSi_2+2.33Si) + Fe_2O_3 + 0.75C$

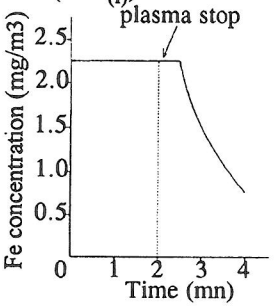


Figure 3 : Fe concentration

Off-gas concentrations :

The use of an ICP analysis system (see Figure 1) allowed to follow simultaneously and continuously the concentration of the major elements (Fe,Si) and metallic impurities (Al,B,Pb,Cr,Zn...) present in the off-gases. For example, measurements of the Fe concentrations, below the filter, have been performed during the melting of a ferrosilicon lump with a 8kW transferred plasma arc, the distance between the tungsten cathode and the anodic lump being 70mm. The values measured were below to $2.3mg/m^3$ (cf Figure 3). The delay between the modification of a plasma parameter (here, the arc stop) and the recording modification was about 30s. In the case of impurities, the concentrations (measurements realized with Cr) remained very low ($<10\mu g/m^3$), lower than the maximum allowable concentrations, but the powder quantity used for each experimentation was also low (<500gr).

Molten bath :

The chemical treatment of the dusts arose mainly in the molten bath on which the arc was transferred. A preheating of the crucible (~10mn) at temperatures up to 2150K was performed before particle injection directly inside the crucible (~15mn) and post heating of the molten bath to allow the migration of the species (~10mn).

The resulting compositions have been then characterized by XRD.

The molten baths obtained in the different experimentations, presenting the same morphology and composition, the results are presented for the case thermodynamically studied (see Figure 2), that of the mixture :

$FeSi_2$+2.33Si (49wt%) + Fe_2O_3 (45wt%) + C (3wt%) + CaO (3wt%)

The crucible pre-heating during 10mn, before powder injection was achieved by using a transferred arc plasma. The current intensity maintained at 400A and the argon plasma gas flow rate at 10 slm allowed to reach a crucible temperature of 2150K. During this pre-heating, the evaporation of carbon, from the crucible, has led to a 8% loss of arc voltage. The explanation of this loss remains complex, different phenomena occurring simultaneously in the transferred arc in presence of vapours (metal or carbon)

electrically conductive at temperatures below 7000K. The increase of the electrical conductivity, reducing the electric field, is often compensated by the arc cooling due to the enhanced radiation which increases it [8,9].

Then the particles were introduced in the crucible with a 0.5kg/h powder mass flow rate, during 15mn, the arc current intensity being maintained to 400A. Most of the particles were injected in the crucible centre, forming a molten bath. But a part of them were ejected outside the crucible, and, due to gas recirculation, a certain quantity of them was trapped on the torch shield forming a deposit of unmolten and untreated particles. The evaporation of the fines (<10μm), led to a perturbation of the arc equilibrium and a voltage decrease of 10%.

To allow the migration of the species within the bath, a 400A plasma arc was maintained, during 10mn, between the cathode and the molten bath, without powder injection. The evaporation of iron and silicon at the bath surface tended to decrease the arc voltage (7%).

The bath characterization has allowed to separate two phases :

- the metallic bath composed of iron silicide (FeSi and $FeSi_2$), in the hot arc striking area (centre of the crucible which diameter is about 40mm). It is produced by the melting of $FeSi_2$ present in the commercial ferrosilicon powder and the formation of FeSi. The metallic bath represent 45wt% of the injected powder (see Fig. 4).

- the slag, over and around the metallic bath, composed of amorphous silica with traces of $FeSi_2$ in the form of metallic grains which have probably not reached the metallic bath due to a too high viscosity of the slag. The slag and the untreated particles found in the crucible periphery represent 35wt% of the injected particles (see Fig. 4).

The other treated products (20wt%) are composed of iron condensates on the reactor walls and molten powder (XRD rays not identified) on the plasma torch shield.

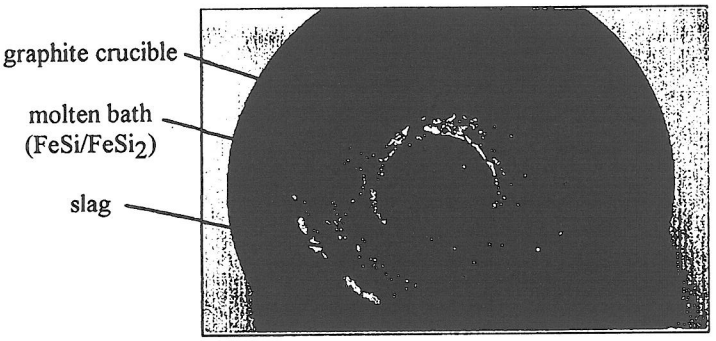


Figure 4 : molten bath

CONCLUSIONS

The treatment of ferrosilicon dusts in a molten bath heated by a plasma transferred arc has been studied, the powder (mixture of ferrosilicon, oxides, reducer and slag former) being injected directly into the crucible. The arc was transferred between a thoriated tungsten cathode with gas stabilization and an insulated carbon crucible. The reducer (carbon) quantity, necessary to treat chemically the ferrosilicon

dusts, has been determined by equilibrium thermodynamic calculations, for different mixture compositions. XRD characterization of the obtained products have allowed to determine two phases in the crucible : a metallic bath composed of pure FeSi and $FeSi_2$ (45wt% of the injected products), and a slag composed of amorphous silica and metallic traces (35wt%) provided a sufficient quantity (3wt%) of slag former (CaO) was added. The use of an ICP analysis system has allowed to follow continuously and simultaneously (delay of 30s) the evaporation of the elements Fe and Cr during experimentations.

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APPENDIX 1 : table of species considered in the thermodynamic calculations

$C_{(s)}$, $C_{(g)}$, $C_{2(g)}$, $C_{3(g)}$, $C_{4(g)}$, $C_{5(g)}$, $CO_{(g)}$, $CO_{2(g)}$, $C_2O_{(g)}$, $C_3O_{2(g)}$
$Fe_{(s)}$, $Fe_{(l)}$, $Fe_{(g)}$, $Fe_3C_{(s)}$, $Fe_3C_{(l)}$, $FeO_{(s)}$, $FeO_{(l)}$, $FeO_{(g)}$, $Fe_2O_{3(s)}$, $Fe_3O_{4(s)}$, $Fe_3O_{4(l)}$, $FeSi_{(s)}$, $FeSi_{(l)}$, $FeSi_{2(s)}$, $FeSi_{2.33(s)}$
$O_{(g)}$,$O_{2(g)}$,$O_{3(g)}$
$Si_{(s)}$, $Si_{(l)}$, $Si_{(g)}$, $Si_{2(g)}$, $Si_{3(g)}$, $SiC_{(s)}$, $SiC_{(g)}$, $Si_2C_{(g)}$, $SiC_{2(g)}$, $SiO_{(g)}$, $SiO_{2(s)}$, $SiO_{2(l)}$