THEORETICAL STUDY OF THE ALUMINOTHERMIC REDUCTION OF LEATHER INCINERATION ASHES FOR FeCr FERROALLOY PRODUCTION[1]

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Abstract

The tanning and leather goods industry produces residues that, because of the tanning method used, have Cr in their composition. The ashes from incineration retain Cr in the form of oxides. Obtaining a FeCr alloy by carbothermal reduction of the ashes has been successful, however, the process requires an electric reduction furnace and the produced alloy contains about 8 wt.% C This paper proposes the replacement of the carbothermic by aluminothermic reduction. That (i) eliminates the investment in an electric arc furnace and, simultaneously; (ii) lead to the production of an alloy with low C content (which would relieve the cost of C reduction in the production of stainless steel). Through computational thermodynamics, this work shows the determination of optimal conditions for preparation of FeCr alloy from the incineration ashes.

Key words: FeCr ferroalloy; Leather shavings; Aluminothermic reduction.

ESTUDO TEÓRICO DA REDUÇÃO ALUMINOTÉRMICA DAS CINZAS DA INCINERAÇÃO DE COURO PARA A PRODUÇÃO DE FERROLIGA Fe-Cr

Resumo

A indústria coureiro-calçadista produz aparas que, por causa do método de curtimento do couro, contêm Cr na sua composição. A sua incineração produz cinzas que retêm o Cr sob a forma de óxidos A obtenção de uma liga FeCr por redução carbotérmica das cinzas já obteve sucesso, contudo, o processo exige um forno elétrico de redução e a liga contém ~ 8% C. Este trabalho propõe a substituição da redução carbotérmica pela redução aluminotérmica. Isso (i) eliminaria o investimento em um forno elétrico e, ao mesmo tempo; e (ii) levaria à produção de uma liga com baixo teor de C (que aliviaria os custos com a redução de C na produção do aço inoxidável). Por meio da termodinâmica computacional, este trabalho mostra a determinação das condições ideais de elaboração da liga FeCr a partir das cinzas da incineração.

Palavras-chave: Ferroliga FeCr; Resíduos do couro; Redução aluminotérmica.

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1 INTRODUCTION

1.1 Waste Treatment *versus* Landfilling

There is an increasing interest in the productive sector to give their waste a different destination from the simple landfilling, because of pressure exerted by both (i) intense social awareness; and (ii) environmental law (blaming both the companies that produce waste as those that store).

This trend is also slowly becoming a reality in the leather and shoe industry. In this sector, a considerable fraction of the waste contains metal chromium in their chemical composition – something which, under certain conditions, is harmful to health and can not be discarded in the environment. In this case, the residuals are normally sent to landfills for hazardous waste, which, according to Brazilian law, represent an 'environmental liability' for this branch of industrial activity.

Thus, in the search for treatment processes for wastes containing chromium which prevent their disposal in landfills, incineration was considered an interesting alternative. It combines a drastic reduction in the volume with the use of the energy content of solid waste (with or without chromium), holding the role of fuel.

1.2 The Incineration Process

The overall process was adapted for the incineration of solid waste treatment of leather and footwear industry through a research project conducted specifically for this purpose.(1) A pilot plant was built for testing and is in operation in the city of Dois Irmãos, state of Rio Grande do Sul

The reactor is designed basically a unit which takes the destruction of organic waste (in two stages, combining gasification and combustion), added with a gas treatment system. This equipment, next to the off gas, produces a solid residue, the ash from the incineration of leather shavings, which is retained in the ash trays. The ashes collect all the chrome in waste, as predicted by an analysis based on chemical thermodynamics.(2)

Since it is not an ore, the chromium content of ashes is variable; depending on the mix which is placed in the waste incinerator. When the charge consists entirely of scraps of leather, ~ 50% of its mass consists of eskolaita, Cr_2O_3.

1.3 Chromium Recovery from Ashes

The use of chromium contained in the ash from incineration – the last step of the process of treating waste leather and footwear industry containing Cr – was purposely delayed so as not to stall the development of the incinerator.

Among the alternatives to the use of ashes may be cited: the refractory industry, ceramics, glass, chemical industry – especially leather tanning – and metallurgical industry.

Depending on the application, the metal may remain in the oxidized form or not. Depending on the application, chromium (neat compounds or forming) is present as the main material, pigment, reactant and alloying element capable of modifying the properties of the base material.

1.4 Metallurgy

In the metallurgical industry, the steel industry has been highlighted as a major consumer of this metal in the production of stainless steel (~ 18 wt.% Cr) or even some special steels. In the production of stainless steel typically the chromium metal is introduced in the form of ferroalloy (FeCr) with high content of Cr.

The production of FeCr-AC (variety of high-carbon) occurs in electric reduction furnaces (ERF) coated with magnesia refractory. According to Beneduce,(3) ore is typically chromite ($FeO{\cdot}Cr_2O_3$), with an aluminum-magnesian gangue, and the reduction is carried out by carbon. The slag produced during the industrial processing, has a composition similar to the quartzite gangue, adjusted so that the *liquidus* temperature be in the range 1,700°C-1,800°C.

The carbon contained in the ferroalloy, however, may cause a deleterious effect on the stainless steels, since it allows the precipitation of chromium carbides at grain boundaries. This effect apparently innocuous removes Cr from regions near grain boundaries and eliminates the ‘stainless property’ – given that the Cr is in the carbide. The stainless steel affected part, left without the protective effect conferred by chromium, behaves as common steel, undermining entirely the purpose of its employment. To address this drawback, the carbon is removed from the stainless steel by the use of vacuum or an equivalent effect (obtained by dispersion of argon bubbles in the metal). The oxidizing refining – standard procedure in common steels – can not be used here because it would eliminate the Cr.

This additional decarburization process increases the stainless steel production costs, but the production of ferroalloy LC-FeCr (variety of low-carbon) is complex,(4) which is reflected in its higher price, and does not constitute an alternative capable to eliminate the use of high-carbon ferroalloy.

The production of high chromium FeCr alloys in laboratory was the subject of recent work and the results are promising.(5) The elimination of phosphorus – a harmful element to the steel properties, which contaminates certain loads of waste – is currently under investigation.

1.5 Slag: The Last Residue

Concerning the recovery of chromium contained in the residue via metallurgy, one can say: (i) chromium can be effectively collected by the ferroalloy under strongly reducing conditions of the process; however, it is also true; (ii) the loss of Cr (from the ferroalloy) into the slag – the very last residue – is normal in the manufacture of stainless steel. This loss of course should be counted as a negative factor; however, an overall assessment of chromium reveals the positive aspects of this route, when some basic considerations are taken into account.

While chromium ore (chromite) comes from nature, Cr in the waste is being diverted from one route that certainly would lead to a landfill. If on one hand the chromium contained in the slag can be seen as the fraction of chromium which effectively ends in landfilling – a fact which reduces the treatment *yield* –, on the other it is a residue which is disposed in place of a precious raw material. Thus, it saves a similar amount of Cr provided by nature (non-renewable mineral resource) which is normally disposed with slag during production of stainless steel and now remains in the mineral deposit. Ultimately, the substitution of a mineral resource by a residue at least minimizes an adverse effect.

2 THE NEW APPROACH

2.1 Capital Costs

An analysis of the capital costs associated with the reduction process based on the carbothermic reduction may be more severe than originally estimated, and will be analyzed below.

The use of electric reduction furnace – in spite of the existence of alternative processes, which might have greater flexibility – is a path of proven success in the production of ferroalloy metal with low or even average reactive affinity by carbon.

The cost of the standardized product (in this case, the ferroalloy) can be seen in a simplified way, as the main factor of the driving forces behind industry – including the extractive metal industry. So, too, capacity and capacity utilization of the reactors of an industry stand out among many factors that contribute to good administrative practice.

In contrast, treatment of waste has another logic and moves for other reasons. Of course, not at any cost – once treatment or landfill costs end up contributing to the final product cost.

Thus, treatment of hazardous waste may be less efficient and produce products outside of industry standards.

Using an electric reduction furnace (solution given by carbothermic reduction of chromium contained in the ash) requires a substantial investment not only in the main reactor, but also with ancillary equipments such as transformers and transmission lines. To make matters worse, in view of the nature of the operation – the reduction of working time, pending the accumulation of ashes – the capacity utilization of the reactor would be low.

Finally, there is the direct use of electricity – one of the most important inputs and whose generation is limited and costly.

2.2 Aluminothermic Reduction

Thinking of minimizing the costs, the possibility of using the aluminothermic reduction process or *thermite* process – from Thermit, a trade name – will be suggested here, in view of reports in the literature of their successful application in reducing the chromium oxides.(6,7)

The aluminothermic reduction has a few features that make it very special and very appropriate for this case. Unlike the vast majority of the pyrometallurgical processes, it lacks a complex reactor. Uses, typically, instead, a cylinder coated with refractory material and, often, without cover and without a bottom, which rests on a bed of refractory material. The simplicity in this case can be taken as synonymous with low capital cost.

A simple low cost reactor can remain unused for a longer time (pending the accumulation of solid waste from incinerator) without pressing too much the overall costs of the company.

Little need for ancillary equipment would also relieve the pressure on capital investment needed for the ferroalloy production, and would add to the initial benefit given by the simplicity of the reduction reactor.

Because of the huge amounts of electricity used to produce aluminum it is very valued and therefore this reactant should be derived from discarded materials – though valuable – but of less interest for the Al recycling industry.

The absence of carbon in the ferroalloy thus obtained alleviates, to a great extent, the need for treatment of decarburization, relieving further the pressure on the cost of stainless steel production.

In order to study this hypothesis and to direct the conduct of future laboratory experiments, several simulations (based on computational thermodynamics) of the aluminothermic reduction of chromium oxide contained in the ash from the incineration of leather and shoe industry waste were performed in this work.

3 METHODOLOGY

3.1 Computacional Termodinamics

The application used in this work is called FactSage, version 6.2. It has been described in the literature by Bale.(8)

The following databases allow performing the simulation:

- Fact53 - FactSage compound database (2010);
- FToxid - Fact oxide compounds (2010);
- FSstel - FactSage steel intermetallic compound and alloy solutions (2010).

The phase liquid iron oxides includes the concept of ‘associates’.(9)

3.2 Ferroalloy Production Simulation

To simulate the ferroalloy production, two types of simulations were made. Initially, only eskolaite (Cr_2O_3) and hematite (Fe_2O_3) oxides constituted the load. Next, a more complex mixture of oxides is used. She tried to play the greater complexity of the real burden - the incinerator ash containing oxides of chromium.

Hematite acts as a sort of ‘fuel’, supplying the heat (from Al oxidation), which ultimately, because of adiabatic process mode of operation, will be perceived as a high temperature.

For both cases, the theoretical adiabatic temperature was determined, so that information could be taken into account in the evaluation process.

Apart from it, also the compositions of the alloy and slag – in its most significant components – and information about the oxidation state of the system, will be given in the results.

4 RESULTS AND DISCUSSION

4.1 Thermodynamic Analysis of the Pure Oxides Reduction

The production of a metal or metal alloy using the aluminothermic reduction involves reducing the metal oxide by aluminum and can be seen as a specific section of the metallothermic reduction.

The aluminothermic reduction of chromium oxide can be studied with the aid of the reaction:

$$Cr_2O_3(s) + 2\ Al(s) = 2\ Cr(s) + Al_2O_3(s)$$

The enthalpy change, measured at 25°C, is equal to -549.7 [kJ].

The production of pure chromium is not the objective of this research project. Chromium metal has a high melting point (1,907°C), much greater than the temperatures of the molten steel normally encountered in industrial processes – fact that hinders the formation of an alloy between them.

The aluminothermic reduction of iron oxide can be studied with the aid of the reaction:

$$Fe_2O_3(s) + 2\,Al(s) = 2\,Fe(s) + Al_2O_3(s)$$

The enthalpy change, measured at 25°C, is equal to -838.3 [kJ] – this figure is 50% above that of eskolaite reduction. Because of this, the adiabatic temperature for the hematite reduction is very high.

As mentioned earlier, the objective is to obtain a ferroalloy FeCr. Thus, the joint reduction of these oxides produces an increase in temperature of the system in relation to the aluminothermic reduction of chromium oxide alone – a fact that reflects the character of this synergistic association between Fe and Cr.

In order to obtain a molten slag and to facilitate the liquid-liquid separation between the alloy and the liquid oxide slag, it was decided by the addition of CaO to the load. The goal is to reach the eutectic composition of the CaO-Al_2O_3 slag, whose approximate composition is 35.4 at.% Al_2O_3. The addition of this material naturally leads to a reduction of the adiabatic temperature of the system – a fact that counteracts the previous effect.

According to the results from computational thermodynamics, the joint reduction of 1 mole of Cr_2O_3 and 1 mole of Fe_2O_3 (added with 3.5 moles of CaO) using 4 moles of Al raises the system temperature adiabatically from 25°C to 2,064°C. Accordingly, the molar ratio of the oxides chosen produces a ferroalloy containing a Cr content of 47 wt.%. According to NBR 6837 ferrochrome (ABNT, 1989), the chromium content of the ferroalloy must be at least 50 wt.%.

To obtain higher levels of Cr in the ferroalloy, obviously the mole ratio Cr_2O_3/Fe_2O_3, must increase which, however, means the same as to lower the amount of 'fuel' available to provide an exothermic process and a high adiabatic temperature. Auxiliary measures, capable to 'activate' the reaction, such as: reagent heating, addition of substances which react exothermically with aluminum etc., may be used to counteract this tendency.

The effect of varying the quantity of hematite alone was also analyzed with the aid of thermodynamics. The amount of Al – a highly valuated substance – was kept constant in all cases, while the iron oxide varied by ± 0.2 moles.

As the amount of iron oxide in the load increases, the chromium content in the ferroalloy decreases dramatically. This is all in accordance with the more weakly reducing conditions – as indicated by the oxygen potential of the system, which increases in the same direction (Table 1).

The opposite effect occurs when the hematite amount decreases and there is an excess of Al in the system.

The system temperature is reduced by any of these actions (Figure 1).

The loss of chromium to the slag – an important factor because it means a loss in treatment efficiency – is growing strongly only in the direction of increasing hematite amount. This is because the oxidizing conditions of the system increase pronouncedly (Figure 2). A factor to worsen this effect is the increase in the amount of the slag itself, with the addition of iron oxide.

Table 1. Simulation results for aluminothermic reduction of the pure oxides as a function of Fe_2O_3 amount input; other reactants: 1 mole Cr_2O_3, 4 moles Al; initial temperature, 25ºC; (pO_2 in atm)

Fe_2O_3 [mol]	0.8	0.9	**1.0**	1.1	1.2
Adiab. temp. [ºC]	1,956	2,022	2,064	2,042	2,004
Slag					
X CaO	66	65	63	61	58
X Al_2O_3	34	35	36	35	33
Total	100	100	99	95	92
wt.% Cr	0.1	0.2	0.8	3.4	6.4
Mass [g]	379.4	389.9	401.5	418.9	437.9
FeCr					
wt.% Cr	50.7	49.2	47.0	42.1	36.2
wt.% Fe	43.7	47.8	52.1	57.6	63.6
wt.% Al	5.4	2.7	0.6	0.1	0.0
Total	99.8	99.8	99.7	99.7	99.8
Mass [g]	204.5	210.1	214.4	212.9	210.0
log(pO_2)	-13.8	-12.6	-11.1	-10.0	-9.7

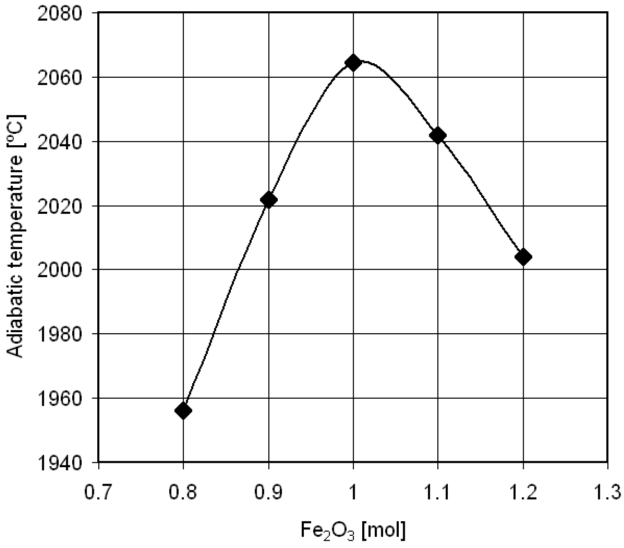

Figure 1. Adiabatic temperature of the system as a function of Fe_2O_3 input amount.

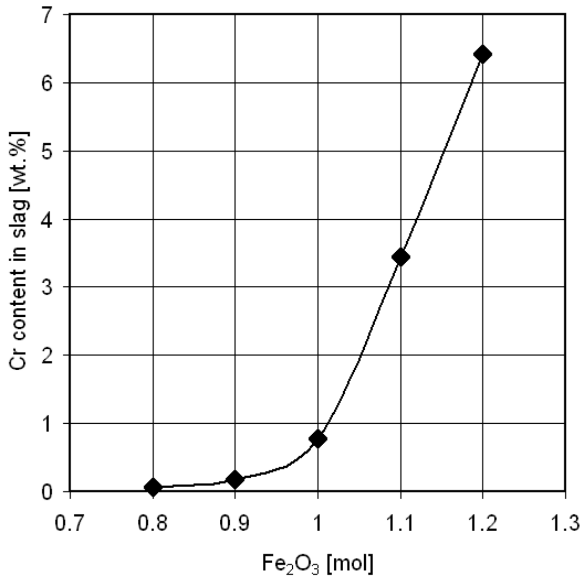

Figure 2. Cr content in slag as a function of Fe_2O_3 input amount.

4.2 Thermodynamic Analysis of Ash Reduction

The production of the ferroalloy with the use of incineration ash by aluminothermic reduction was performed in the sequence.

The composition of the hypothetical, synthetic, ash used is based on previously published works(1,5) and can be seen in Table 2. As already mentioned, since this row material is not an ore, its chromium content is variable, dependent on the mixture of waste which is placed in the incinerator.

Table 2. Hypothetical ash composition and the corresponding amounts in moles for all compounds relative to 1 mole Cr_2O_3

Compound	wt.%	Amount [mol]
SiO_2	15	0.70
Al_2O_3	10	0.27
TiO_2	13	0.45
CaO	7	0.34
Cr_2O_3	55	1.00

For the ferroalloy production, the 1:1 molar proportion of hematite to eskolaite could not be maintained, for the adiabatic temperature of the system has become too low. Thus, some new values were examined and, at 1.4:1, the temperature reached a reasonable level of 1,915°C. In this case, unlike the previous simulations, the amount of aluminum was raised together in a ratio indicated by the stoichiometry.

CaO was again added to the charge in such an amount that a total of 5.3 moles of CaO were present in the reactor load (the presence of CaO in ash was taken into account). No other fluxing agent was added, in order not to harm the exothermicity of reaction.

The chromium content – sacrificed due to the addition of hematite – dropped to 36.3 wt.%. However, as mentioned in the early part of this work, the treatment process of the ash has a purpose different from that which guides the commercial production of an alloy. Its goal is not to obtain a standardized product, but the recovery of the chromium contained in the ash, at a reasonable cost.

The chromium content in the slag was 2.5 wt.%. To attempt to lower this value, the already seen tendency, obtained with an excess of Al, was, again, explored. This (valuable) metal succeeded in the reduction of the chromium content in the slag.

Table 3. Simulation results for aluminothermic reduction of the ashes as a function of Al amount input; other reactants: 1 mole Cr_2O_3, 1.4 moles Fe_2O_3; initial temperature, 25ºC; (pO_2 in atm)

Al [mol]	**4.8**	5.0	5.2
Adiab. temp. [ºC]	1915	1961	1997
Slag			
X CaO	48	48	49
X Al_2O_3	36	38	40
X Ti_2O_3 + TiO_2	3	3	3
X SiO_2	9	8	7
Total	97	98	99
wt.% Cr	2.5	1.5	1.0
Mass [g]	559.4	556.3	555.1
FeCr			
wt.% Cr	36.3	37.4	37.6
wt.% Fe	63.1	61.0	59.5
wt.% Al	0.0	0.1	0.3
wt.% Si	0.5	1.4	2.4
Total	99.9	99.9	99.8
Mass [g]	247.4	255.8	262.3
log(pO_2)	-10.9	-11.0	-11.1

The simulation results show that fairly high amounts of Al can indeed reduce the Cr content up to 40% of the initial value. In support of this addition of reductant, it was found together: (i) a small reduction in the amount of slag; and (ii) a positive increase in system temperature (Table 3). The temperature increase is contrasting to the observed decrease in the case of pure oxides. This effect most likely is the result of aluminum oxidation by silica:

$$SiO_2(s) + 4/3\ Al(s) = Si(s) + 2/3\ Al_2O_3(s)$$

Which has $\Delta H_{298} = -206.4$ [kJ].

5 CONCLUSION

Based on thermodynamic simulations, it can be concluded that it is theoretically feasible to produce ferroalloy FeCr from the ashes of the waste leather incineration process by aluminothermic reduction.

This result consolidates new perspectives for the disposal of waste from tanning and leather goods industry, with the use of energy they contain.

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