SOME EFFECTS OF MICROWAVE HEATING OF CHROMITE ORE FOR Fe-Cr-Al ALLOYS BY ALUMINOTHERMY

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ABSTRACT

Processes and prime materials involved in Fe-Cr-Al alloys production by aluminothermy are presented having in view new possibilities to produce them more ecological and more efficient, using energy of microwave field.

The capacity of heating pieces of chromite ore containing 56.52 %mass Cr_2O_3 and a ratio (% massCr_2O_3/ %massFeO)=2.622 in a domestic microwave oven is evaluated at the maximal power of the microwave field of 700W where a maximal temperature about 260^0C was obtained after 16minutes heating. A rapid cooling from this temperature to 20^0C, by water immersion induces an increasing of the internal voids due to new cracks and the development of pre-existing cracks of about 0.15-0.29 %, which helps to reduce the energy consumption in chromite comminution. The final heating temperatures show a low possible contribution to the reduction of energy consumptions in direct metallurgical processes on the account of chromite ore heating in microwave field.

KEYWORDS: chromite ore, microwave heating, internal voids, cracks

1. General aspects

Classical metallothermy is based on the thermal energy released by exothermic reactions of different oxides mainly that or those of the metal recuperated in ferroalloy, which spontaneously proceed after the ignition of an exothermic mixture. Igniting mixtures presents characteristics of a low ignition temperature and a high thermal effect. Around the ignition place a zone of important heat emission develops and the thermal energy contribution makes possible the development of the main metallothermic reactions related to the ferroalloy which is the object of this activity.

The main reaction could be generically written in the following form:

$$MeO +R \rightarrow Me+RO \qquad (1)$$

The condition for such reaction to take place in the direct sense, at a temperature T, is:

$$\Delta G^0_T<0 ,$$

where:

$\Delta G^0_T=\Delta H^0_{298}-T\Delta S^0_{298}$ is the standard variation of the free enthalpy.

According to basic papers [1][2], certain class of materials are necessary to compose an exothermic mixture of materials to obtain ferrochromium without carbon content, through the aluminothermic process. The sources of chromium are usually chromium concentrates containing 60% Cr_2O_3 and cca. 14% mass FeO. Chromite ore contain mainly the spinel of chromium $FeO \cdot Cr_2O_3$ and other oxides as magnesia (MgO), substituting for FeO and alumina (Al_2O_3) or the ferric oxide (Fe_2O_3), substituting for Cr_2O_3 are the main mineral materials used to obtain these concentrates. According to possibilities or requirements in the mixture are used partially materials bringing oxide as CrO_3 or oxy-salts $K_2Cr_2O_7$, instead of Cr_2O from chromite ore. Handling and storing by-products must be extremely controlled in the case of chromium trioxide CrO_3, due to carcinogenic potential of the Cr^{6+}. Chromates, dichromates, chlorates, perchlorates, nitrates, calcium permanganate, silicon permanganate, sodium permanganate are used as oxidizing materials. Aluminium, silicon, calcium, sometimes manganates are used as reducers. CaO as lime and CaF_2 as fluorine are used as fluxing agents. Mixtures, as barium peroxide and aluminium powder or sodium nitrate and magnesium powder, are used as igniting agents. In order to give a certain solid consistency to the column of granular and powder materials, cement, sodium silicate as aqueous solution or certain organic materials are used as binder.

2. Thermodynamic aspects of aluminothermy in obtaining chromium metal and alloys

Reduction of various oxides of chromium and other compounds containing chromium using aluminium as reducer are presented as chemical reactions in the Table 1.

The reasons of introducing of an oxidizing material, as mentioned before, consist in the energetic needs to ensure the progress of the reduction of the main chromium source. According to the data presented in the table 1., both two possible reactions of reducing Cr from Cr_2O_3 using aluminium as reducer are not enough exothermic to fulfill the necessary thermal energy.

In the case of metallic chromium and ferrochromium without carbon using the aluminothermy process, the main reduction reactions of chromium oxides with aluminium are not enough exothermic, compared to necessities. In the Table1 these effects are presented.

The bolded reactions are those making the object of aluminothermy.

The main problem of metallothermy, in general, is to ensure the necessities of thermal energy required in each volume where there are accomplished all the other conditions for reduction of oxides source of required metal in the ferroalloy.

According to ref. [2], the necessary unitary thermal effect which must develop to ensure the reduction reaction could be evaluated using the relation:

$$\Delta H = \frac{\Delta H^0_{298}}{M_{MeO} + M_R} , \quad kJ/kg$$

where:

M_{MeO} - is the molar mass of the oxide of the metal to be recuperated in the ferroalloy;

M_R- is the molar mass of the metal used as a reducer.

The required value of the necessary released heat must be: $\Delta H > 2300 kJ/$ kg charge

According to the ref.[3] the required unitary thermal effect must be: $\Delta H > 2700 kJ/$ kg charge. In these conditions it was evaluated that a metallothermic process runs spontaneously, that means it is self–sustaining and ensures an adequate separation of metal product and slag, if the following condition is accomplished [3]:

$\Delta H^0_{298} < -302 kJ/gr.at$ Al According to the table 1[1-4] reduction reactions of chromium oxides with aluminum do not satisfy this conditions, also reduction of silicium dioxide with aluminium and reactions (2)(7)(8) are carcinogenic. Reduction of Fe_3O_4 with aluminium satisfies the required condition and the heat released is in an evident excess, compared to the condition. This physical evidence is not enough investigated and valorized, despite its high economical and ecological potential. In aluminothermy process applied to obtain chromium metal or alloys without carbon or silicon content, also in other metallothermic processes, other reactions mainly exothermic could be produced and also they have harmful effects being toxic, carcinogenic or present risks of strong inflammability and explosion.

Table 1. *Values of ΔH^0_{298}, [kJ/ mol Al] of different reactions possible to take place in metallothermic production of chromium alloys based on chromite, and of different associated reactions*

Crt no.	Reduction reaction	Variation standard enthalpy ΔH^0_{298}	Observations on reaction and on main reactant; [1]-[4]
1	$1/2Cr_2O_3+Al \rightarrow Cr+1/2Al_2O_3$	-272.2	deficit of heat
2	$1/2CrO_3+Al \rightarrow 1/2Cr+1/2Al_2O_3$	-547.2	Carcinogenic, deliquescent
3	$Cr_2O_3+2Al+CaO \rightarrow 2Cr+CaO \cdot Al_2O_3$	-275.8	deficit of heat
4	$Cr_2FeO4+8/3Al \rightarrow 2Cr+Fe+4/3Al_2O_3$	-290.6	deficit of heat
5	$Cr_2FeO4+8/3Al+4/3CaO \rightarrow 2Cr+Fe+ +4/3CaO \cdot Al_2O_3$	-298,6	deficit of heat
6	$CrO_3+2Al+CaO \rightarrow Cr+CaO \cdot Al_2O_3$	-550.8	Carcinogenic, deliquescent
7	$K_2Cr_2O_7+4Al \rightarrow 2Cr+2\ Al_2O_3+K_2O\uparrow$	-429.7	Carcinogenic
8	$Na_2Cr_2O_7+4Al \rightarrow 2Cr+2\ Al_2O_3+Na_2O\uparrow$	-449.3	Carcinogenic, hygroscopic
9	$3/8Fe_3O_4+Al \rightarrow 9/8Fe+1/2\ Al_2O_3$	-418.3	-
10	$3/4SiO_2+ Al \rightarrow 3/4Si+1/2\ Al_2O_3$	-158.7	deficit of heat

$\uparrow$- the compound vaporizes or it is a gas at reaction temperature.

3. Experimental trials

3.1. Composition of chromite ore

A piece of chromite ore obtained by cracking, taken into account in this research was analyzed visually.

On the surfaces of the chromite ore piece enough important zones contain thick filaments of silicates grown intimately with chromite. The chemical composition presented in the tab.2, was obtained on granular samples obtained by crushing using an X-rays spectroscopic device.

The result of the analysis of the average sample, obtained by quartation method, is not identical with the arithmetic average of the initial five samples, but enough close to this.

Table.2. *Chromite ore composition*

Crt. No.	Oxides, %mass						Cr_2O_3 /FeO
	Cr_2O_3	FeO	SiO_2	Al_2O_3	MnO	NiO	
1	59.231	19.2	18.97	2.097	0.605	0.693	3.098
2	55.74	20.884	22.267	-	-	1.108	2.669
3	57.281	23.796	16.816	-	0.721	1.386	2.407
4	52.24	20.69	25.71	-	-	1.36	2.525
5	55.48	21.852	21.0	-	-	1.668	2.539
6	59.332	23.157	16.177	-	0.30	1.034	2.562
*	56.52	21.56	20.21	0.23	0.27	1.121	2.622

* Average sample obtained by quartation method.

3.2. Heating of chromite ore in microwave field

Experiments have been performed in the laboratory "Alternative and Non-conventional Processes in Metallurgy" of the Faculty of Metallurgy, Materials Science and Environment of the "Dunarea de Jos "University of Galati.

Four samples of chromite ore of initial mass in the range 73.7-170.9 g measured after the exposure in free air at 20^0C for 24 hour, have been submitted to heating in a domestic microwave oven generating a microwave power of 700W.

Chromite samples have been placed inside of a central cavity (height H=80mm, inner diameter I.D=115mm) made in a refractory bond and covered by ceramic refractory wool (1250^0C) of 25mm thickness.

A K-thermocouple (1200^0C) places in a refractory shell with diameter D=3mm, length L=145mm, coupled to a measuring device Digitron 2751-K was placed centrally through a hole drilled in the roof of the microwave oven, inside of this as closed as possible to the chromite sample. The evolution of temperature is shown in fig. 1
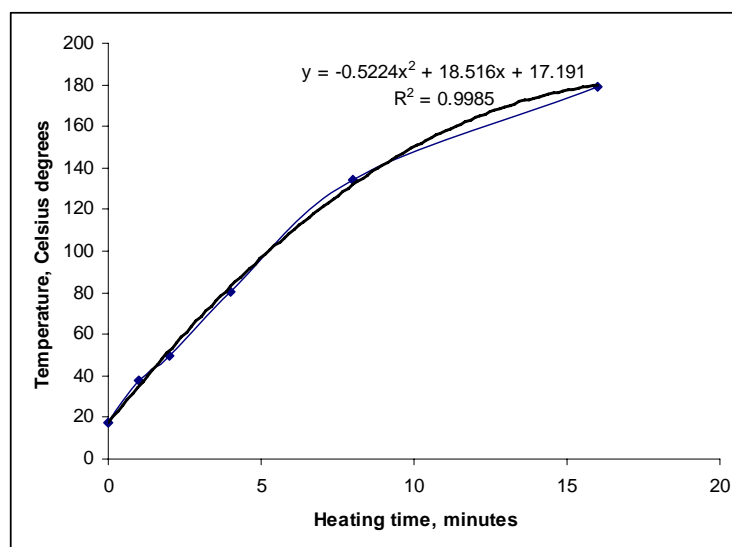

$$y = -0.5224x^2 + 18.516x + 17.191$$
$$R^2 = 0.9985$$

Fig.1. *Evolution of temperature (contact) on the heating time in microwave oven at maximal power 700 W of chromite ore samples no1 and 2 together. Temperature measured after heating pause cycle 1min./pause/1min./pause/2min/pause/4min./pause/8min./final. Total heating time: 16 minutes.*

The registered temperatures upon the heating time (excepting pauses) are presented in the figure 1. The samples at their final temperatures have been cooled in water (20^0C) by rapid immersion and weighted mainly in order to evaluate the contribution of the rapid heating and cooling to the cracks development. They have been weighted again after an exposure of 16 hours in a free air at 20^0C The distance between the thermocouple and the sample influence much the displayed value of the temperature because of the inertia in heating transmission by different mechanisms, mainly by convection and radiation, but which is desired to take place by direct contact, from sample to the shell of thermocouple and further, inside of this through the thin refractory protection layer, to the junction point chromel–alumel. These aspects could lead to differences of instant temperature of several tenths of degrees, not enough evaluated in the present experimental trials.

Therefore, only in the case of the first two samples of chromite, a heating curve could be established, without to take into account the pauses durations, separated or summated.

The maximal performance of heating is better represented by the samples no.3 and no.4. The experimental results in table 2 after 16 minutes at 100% power show a temperature about 259^0C by heating of chromite samples in microwave oven and an induced porosity and cracks of samples by cooling in water, of 0.15% (sample no.3) and 0.29% (sample no.4). The total volume of internal voids, concentrated or as active cracks, by the treatment consisting in microwave heating and freezing by immersion in water seems to double, compared to the initial state. These results show the necessity to determine better on more systematic bases the tendency to cracking by heating in microwave oven, followed or not by cooling, commonly in water.

Table 3. Results of microwave heating applied to samples of chromite ore

Sample No.	Mass, [g]				Temp.[^{0}C], after heating 16 minutes in microwave oven at 100% power
	Initial	After heating	After cooling in Water [20^0C] for 25 minutes and 25 minutes drying at 20^0C	After 16 hours at 20^0C	
1*	-	73.7	75.2	74.7	179.3**
2*	-	120.6	123.6	122.3	179.3**
3	130.2	129.3	131.9	130.4	259
4	170.9	169.6	172.4	171.4	255

* samples no.1 and 2 have been heated together.

** temperature according to the explanations in the Figure1.

4. Commentaries and conclusions

Thermodynamic data on the specific reactions show an important potential to use iron ores as an oxidizing material and iron source in the final alloys especially when technical alloys Fe-Cr-Al are produced. This could be better exploited by applying a preliminary heating of the oxides mixtures before processing by aluminothermy. Direct heating using microwave field energy is full of benefits because of its fastness and direct mass heating effects resulting from the energy transfer particularities offered by this energetic field. Eventual limitations in extending this process, due to the limitations of power of magnetrons, used to generate microwave field, are not prohibitive in industrial practice, when introduction of preliminary heated amounts of reactants in the aluminothermic process could be done gradually but relative continously in a certain time period, until the whole programmed amount is consumed. In case of a bigger industrial aluminothermic facility several lines for microwave heating working simultaneously at a maximal capacity could use for heating reactant mixtures. In this way, the general classical problem of metallurgical plant consisting in an extremely limited flexibility around initial designed capacity is largely avoided in the case of using heating energy by microwave field for aluminotherhic production of chromium alloys without carbon, not only for alloying steels but also including those containing high contents of iron as basic materials for technical Fe-Cr-Al alloys.

It is expected that heating in microwave even at important rates of temperature increasing due to the particularities of microwave energy transfer from the generated field and the samples of chromite, taken separated or coupled with a relative high cooling rate by immersion in water, induces inner mechanical tensions of dilatation and compression, which locally could exceed the internal mechanical resistance and

further lead to new cracks and to the development in length and/or width of the already existent cracks. In this way the implementation of the microwave heating technology could be useful in decreasing of energy consumptions during different comminution operations applied to chromite ore.

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