SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 5, N° 5, 1997

CHARACTERIZATION OF SOME NODULAR CAST IRONS BY THERMAL ANALYSIS

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ABSTRACT

In this study thermal analysis has been used to characterize thermal behaviour and oxidation resistance of some nodular cast iron.

One has studied samples of nodular cast iron ,in several stages of elaboration, with different chemical compositions.The samples have been heated in air, in the temperature range : 18 - 1000°C and the thermal (TG,DTG an DTA) curves have been recorded.

A group of samples,with low silicon content,shows similar behaviour : a continuous increase of weight,some peaks and exothermal effect up to 850°C.The thermal peaks correspond to iron oxides (Fe_3O_4,FeO,Fe_2O_3) formation.At high temperatures (T>850°C) one can see a decrease of weight and an endothermal effect. A superficial decrease of carbon content by combustion ("decarburization" effect) takes place in the range of high temperatures The two effects : oxidation-decarburisation depend on the structural changes of cast iron,wich take place at high temperatures.

The decarburisation process has been modeled and the kinetical parameters have been determined (reaction order n=0.76;activation energy E=141.5 kJ).

Kinetical study of oxidation process has been achieved by nonisothermal methods using two mechanisms : bidimensional transport - for low temperatures and three-dimensional transport through a sphere - for high temperatures.The activation energies have been calculated : 67.7 kJ-for low temperatures and 122.5 kJ-for high temperatures.

RESUMO

O comportamento térmico de ferros fundidos foi estudado com análise térmica. Amostras de vários ferros fundidos foram aquecidas no intervalo de 18º - 1000ºC e curvas de termogravimetria, termogravimetria diferencial e análise térmica diferencial foram determinadas. Foram observados dois efeitos: um de oxidação e outro de decarburização que dependem de mudanças estruturais que acontecem a temperaturas elevadas. Estudos cinéticos do processo de oxidação foram também realizados. À temperaturas baixas foi usado o mecanismo de transporte bidimensional e à temperaturas mais elevadas o transporte tridimensional. A energia de ativação para decarburização é 141,5 kJ e para oxidação é 67.7 kJ para temperaturas baixas e 122.5 kJ para temperaturas altas.

DOI: 10.48141/SBJCHEM.v5.n5.1997.128_1997.pdf

Introduction

High mechanical properties,good casting properties and special oxidation resistance are the main features of nodular cast iron.Genarally nodular cast iron has a good oxidation resistance up to 650°C,higher than that of grey cast iron or low alloy steel[1].

The oxidation resistance of nodular cast iron is related to nodular shape of graphite and it is dependent on chemical composition and microstructural features of the material.

The nodular shape of graphite is the result of a special treatment of molten metal before casting.It consists of two processes : the addition of a (MgFeSi) alloy ("modification") and the addition of (FeSi) alloy ("postmodification" or "inoculation")[2,3]

One has studied nodular cast iron (F_1 - F_3) samples after modification process,without ferro-silicon addition and the F_4 sample,after modification and inoculation (final stage of elaboration).

The samples of nodular cast iron were powders,resulted by breaking some plates,with "white" structure,the particles having no more than 0,5 mm.These plates have a rapid solidification when cooling and therefore the structure is "white" (iron carbide Fe_3C = cementite is the main structural component).

Chemical composition of the samples is given in the table 1.

Table 1.Chemical composition of cast iron samples

Sample	C	Si	Mn	P	S	Cu	Mg	C.E.
F_1	3.78	0.74	1.20	0.020	0.026	0.026	0.027	4.03
F_2	3.79	0.88	1.25	0.021	0.024	0.370	0.028	4.09
F_3	3.94	1.45	1.00	0.021	0.034	0.046	0.026	4.43
F_4	3.50	2.80	0.50	0.021	0.032	0.450	0.050	4.44

C.E.= carbon equivalent = C % + 1/3 (Si + P)%

Primary solidification of hypoeutectic samples (F_2,F_3) has as its result austenitic dendrites and ledeburitic eutectic (with carbon content 4.3%),in accordance with Fe-Fe_3C diagram.When cooling goes on,the austenite turns into pearlite and secundar cementite.The microstructure of these samples consists of : acicular crystals of cementite and some pearlite.The microstructure of hypereutectic samples (F_3 ,F_4) consists of primary cementite and ledeburite[4].

Experimental

The powdered samples of cast iron have been heated from rom temperature to 1000°C with a linear heating rate of 10°C/min.The experimental conditions and total weight variation are given in the table 2.

The instrument used was a derivatograph MOM Paulik Paulik C Budapest with null thermobalance and air statical atmosphere of the sample chamber; reference material was Al_2O_3.

Fig.1 - 4 give the thermal curves for F_1 - F_4 cast iron samples.

Besides that ,the powders and the corresponding plates have been kept in a furnace,at the temperatures,which are peaks on thermal curves.Then the samples have been examined by a microscope.

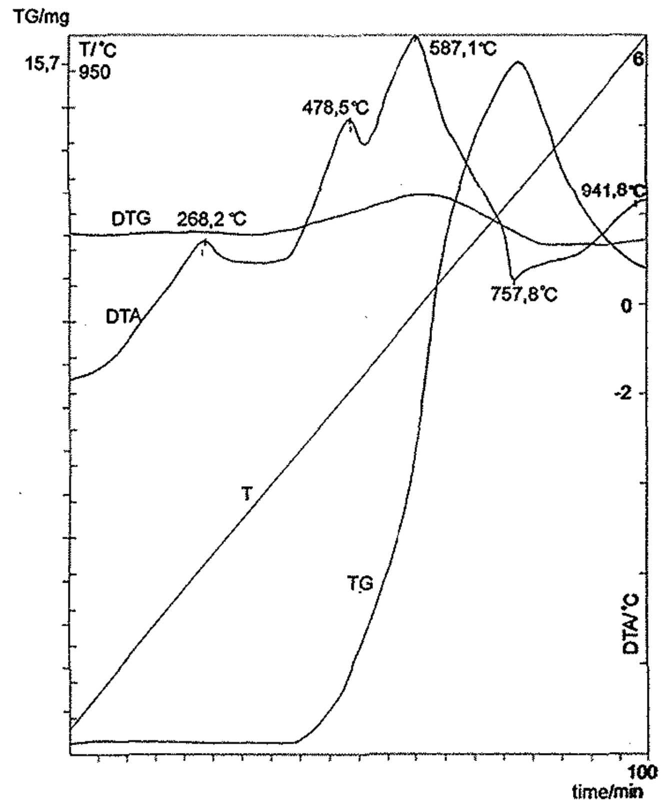

Fig.1.Thermal curves for F_1 sample

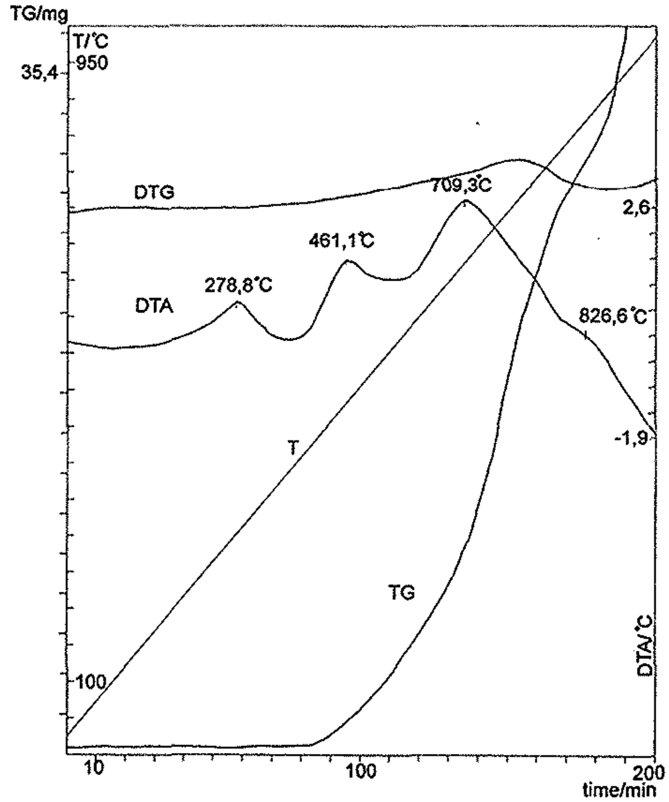

Fig.2.Thermal curves for F_2 sample

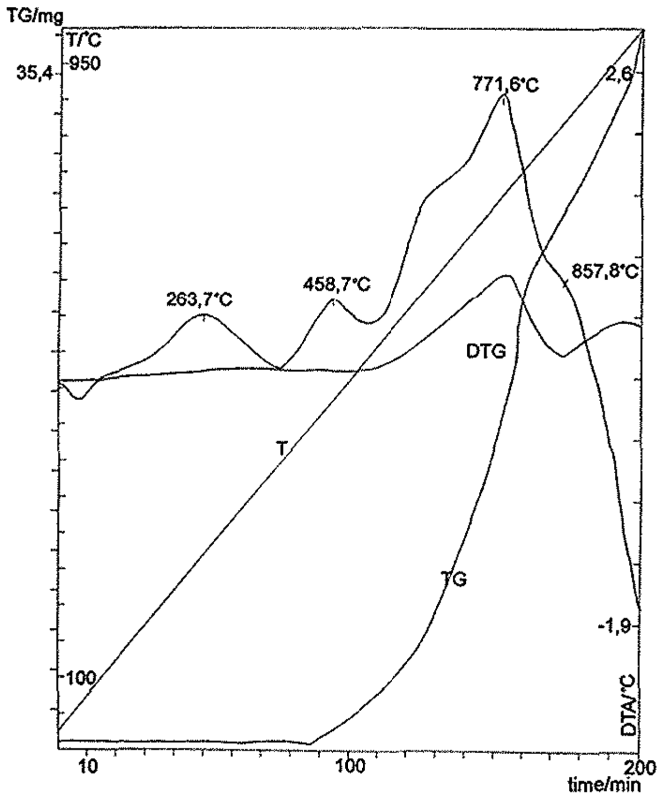

Fig.3.Thermal curves for F_3 sample

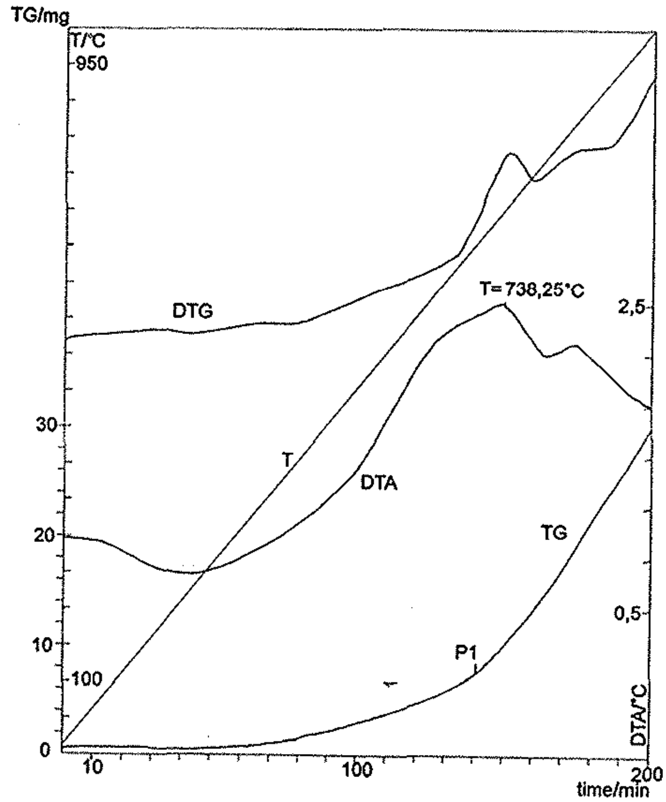

Fig.4.Thermal curves for F_4 sample

Results and Discussion

The F_1 - F_3 samples have a similar behaviour,while the F_4 sample shows a different behaviour.

Table 3 gives complete data from thermal curves : temperatures of interest,the weight variation Δm and the temperature variation ΔT.

A.The result of linear heating of F_1 - F_3 samples is a continuous increase of the weight up to 850 °C,then a decrease of the weight takes place.The DTA curves show an exothermal effect up to about 850°C and some thermal peaks.

-At low twmperature (260-270°C) a change without weight variation takes place,perhaps an oxidation of nonmetallic components (S,P).

-At the temperature of about 460°C - the iron oxidation begins,the iron saturated with oxygen and Fe_3O_4 occur ,according with Fe-O diagram; the exothermal effect and the weight variation increase.

-At the temperature T > 570 °C,the iron FeO oxide occurs;

-The oxidation process proceeds,the next important temperature is 750°C; at this temperature a large amount of Fe_2O_3 occurs;

-The maximum oxidation effect is at the temperature T > 820°C- for F_2 and F_3 samples.

The differences between F_1 - F_3 samples are related to silicon element.So F_2 and F_3 samples,with higher silicon content,have the same peaks at higher temperatures;the end of the exothermal effect is also at higher temperatures : 826.6°C - for F_2 sample, 857.8°C - for F_3 sample and 757.8°C for F_1 sample.

On the other hand microscopical observations are given bellow :

-At low temperature - the samples do not show structural changes.

-At the temperature of 460°C one can see a thin oxide layer on the surface of the powders;no structural changes of the plates occur.

-For the temperature range 600-700°C : the amount of oxide enlarges; concerning microstructure of the plates-the particles of cementite become smaller.

-An important structural change of F_1 sample takes place at the temperature of 941°C (the cementite transformation)[5]- reaction (1) :

$$Fe_3C \rightarrow C\ (\text{graphite}) + Fe\gamma\ (\text{austenite}) \qquad (1)$$

The austenite phase is stable only at high temperatures;when cooling it will turn into pearlite and ferrite.The final microstructure of F_1 sample consists of : graphite (nodular shape) ,pearlite and ferrite.

-The F_2 plate, kept at the temperature of 830°C,shows some transformation concordant with reaction (1).The microstructure consists of : graphite and a few sections with pearlite and ferrite.

The powdered samples show an intensive tendency to sinter at high temperatures; the graphite appearence favours it.

At the same time we must take into account superficial decrease of carbon content produced by carbon combustion (for T > 870°C).This "decarburisation" effect leads to a loss of weight which can exceed the increase of weight resulted by iron oxidation.

Table 2.Experimental conditions for thermal analysis of nodular cast iron samples

Sample	Temperature range (°C)	Heating time (min)	Heating rate (°C/min)	Total weight variation (mg)
F_1	18 - 1000	100	10	15.25
F_2	18 - 1000	200	10	37.07
F_3	18 - 1000	200	10	36.34
F_4	17 - 1000	200	10	30.00

Table 3. Data from thermal curves

Sample							
Sample F_1	T (°C)	268.19	478.48	587.06	757.75	941.83	
	ΔT (°C)	+0.11	+3.93	+5.98	+1.50	-2.52	
	$\Delta m \cdot 10^3$ (g)	0	2.0	7.3	15.3	11.3	
Sample F_2	T (°C)	278.84	461.06	620.01	709.31	826.61	
	ΔT (°C)	+0.86	+1.41	+1.60	+2.46	+0.69	
	$\Delta m \cdot 10^3$ (g)	0	1.8	7.6	15.4	26.4	
Sample F_3	T (°C)	263.73	458.78	670.81	771.62	857.84	
	ΔT (°C)	+0.42	+0.59	+1.35	+1.83	+2.41	
	$\Delta m \cdot 10^3$ (g)	0	1.1	5.8	10.3	17.0	
Sample F_4	T (°C)	326.36	691.51	738.25	794.53	822.32	919.68
	ΔT (°C)	+0.02	+2.33	+2.51	+1.99	+2.14	+1.54
	$\Delta m \cdot 10^3$ (g)	0	6.0	9.3	13.7	15.8	24.0

Table 4.Thermal data for F_1 sample

T (°C)	$\Delta m \cdot 10^3$ (g)
749.1	15.25
758.4	15.23
767.2	15.16
777.3	15.03
786.6	14.87
796.0	14.70
806.6	14.51
816.1	14.30
825.2	14.07
834.8	13.86
844.2	13.62
854.2	13.37

863.6	13.12
873.1	12.82
882.9	12.51
893.1	12.20
902.3	11.89
911.8	11.60
921.1	11.37
931.1	11.20
939.4	11.06
950.5	10.99
959.6	10.95

The speed of decarburisation process of nodular cast iron depends on two factors: disolution of graphite into the matrix and carbon diffusion through the matrix to surface[1].

The combination of two effects : oxidation-decarburisation is more interesting in the case of F_1 sample.We have determined kinetical parameters of the process for the last section of TG curve (fig.1),where a loss of weight ,by carbon combustion ,took place (from 15,.5 mg at T= 755.5°C to 10.95 mg at T=958.08°C)

Table 4 gives the data from TG and T curves for F_1 sample.A program (in Basic language) allowed to determine kinetical parameters.The pattern of a sphere which contracts,based on the equation (2),has been used[6].

$$1 - (1 - \alpha)^{1/3} = kt \qquad (2)$$

$$\frac{d\alpha}{dt} = k\,(1 - \alpha)^{2/3} \qquad (3)$$

where α is the degree of reaction; t is time and k ,k are constant.

The following kinetical parameters have been obtained :

-activation energy - 141.5 kJ/mol;

-reaction order -0.76;

-preexponential factor - 199.5 s^{-1} .

B.The F_4 sample,with a typical chemical composition of nodular cast iron,has a particular oxidation resistance.

The DTA curve shows an important peak at T= 738.25°C; the oxidation practically begins at T= 525°C and it proceed slowly up to T= 715.6°C.The P1 point corresponding to T=715.6°C, delimits two sections on TG curve,which are characterized by different oxidation kinetics.

Nodular cast iron oxidation has been studied using nonisothermal kinetics of heterogeneous reactions,which involve solid phases.They are described by special equations (without reation order)[7,8].

Integral kinetical equation for noisothermal conditions ,using Coats-Redfern approximation,is :

$$\log \frac{F(\alpha)}{T^2} = \log \frac{AR}{aE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2{,}303R} \cdot \frac{1}{T} \qquad (4)$$

where $F(\alpha)$ is integral of conversion ,given by :

$$F(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \qquad (5)$$

where α is the degree of conversion ; $f(\alpha)$ is a function which shows the dependence of the reaction rate on the conversion degree;

A is preexponential factor ; E is activation energy;

a = dT/ dt is constant heating rate;

T is absolut temperature; R is perfect gas constant.

Table 5.Thermal data for F_4 sample - part I

No.	T (°C)	$(1/T).10^4(K^{-1})$	$\Delta m .10^4$ (g)	$-\log [F(\alpha)/T^2]$	α
1.	38.9	15.2	0.13		0.00044
2.	39.6	14.9	0.53		0.00176
3.	40.8	14.7	1.00		0.00334
4.	41.5	14.5	1.64		0.0055
5.	42.3	14.3	2.35		0.0078
6.	43.1	14.1	3.19		0.0106
7.	44.0	13.9	4.02		0.0130
8.	454.7	13.7	4.98		0.0170
9.	464.4	13.6	5.97		0.0200
10.	474.3	13.4	7.09		0.0240
11.	484.5	13.2	8.38		0.0280
12.	494.4	13.0	9.78		0.0325
13.	505.0	12.9	11.05	8.272	0.0370
14.	514.9	12.7	11.94	8.270	0.0400
15.	524.9	12.5	14.71	8.246	0.0490
16.	534.7	12.4	17.03	8.200	0.0570
17.	544.6	12.2	18.96	8.160	0.0632
18.	554.4	12.1	21.56	8.146	0.0718
19.	564.8	11.9	24.28	8.097	0.0809
20.	574.6	11.8	27.33	8.034	0.0910
21.	584.7	11.7	30.24	7.987	0.1010
22.	594.5	11.5	33.24	7.933	0.1110
23.	604.7	11.4	36.54	7.850	0.1220
24.	614.8	11.3	39.96	7.830	0.1330
25.	624.9	11.1	43.44	7.788	0.1450
26.	635.0	11.0	46.80	7.740	0.1560
27.	645.2	10.9	50.13	7.695	0.1670
28.	655.3	10.8	53.48	7.652	0.1780
29.	665.3	10.7	56.95	7.613	0.1900
30.	675.4	10.5	60.60	7.578	0.2020
31.	685.6	10.4	64.41	7.535	0.2150
32.	695.6	10.3	68.41	7.495	0.2280
33.	705.5	10.2	72.88	7.449	0.2430

Table 6.Thermal data for F_4 sample - part II

No.	T (°C)	$(1/T).10^4(K^{-1})$	$\Delta m .10^4(g)$	$-\log [F(\alpha)/T^2]$	α
34.	715.6	10.1	78.01	7.399	0.260
35.	725.7	10.0	84.16	7.801	0.281
36.	736.0	9.9	91.15	7.730	0.304
37.	746.2	9.8	98.96	7.630	0.329
38.	756.1	9.7	107.27	7.580	0.358
39.	766.2	9.6	115.32	7.510	0.384
40.	776.2	9.5	123.41	7.440	0.411
41.	786.3	9.4	131.00	7.400	0.437
42.	796.4	9.3	138.39	7.350	0.461
43.	806.7	9.25	146.03	7.280	0.487
44.	816.8	9.2	153.98	7.240	0.513
45.	826.9	9.1	162.30	7.200	0.541
46.	836.9	9.0	170.88	7.140	0.570
47.	847.1	8.9	179.58	7.085	0.598
48.	857.0	8.8	188.33	7.029	0.628
49.	867.2	8.75	196.89	6.977	0.656
50.	877.2	8.7	205.32	6.930	0.684
51.	887.6	8.6	213.56	6.890	0.712
52.	897.8	8.55	221.81	6.850	0.739
53.	908.1	8.5	230.12	6.800	0.767
54.	918.4	8.4	238.77	6.750	0.796
55.	928.4	8.3	248.11	6.680	0.827
56.	938.7	8.25	258.28	6.630	0.861
57.	949.0	8.2	269.42	6.545	0.898
58.	959.0	8.1	281.83	6.450	0.939
59.	969.3	8.0	295.41	6.263	0.985

Table 7.Kinetical parameters for F_4 sample

Temperature range (°C)	E (kJ/mol)	A (s^{-1})
385.9 - 715.6	67.7	3803.8
715.6 - 969.3	122.5	2913.3

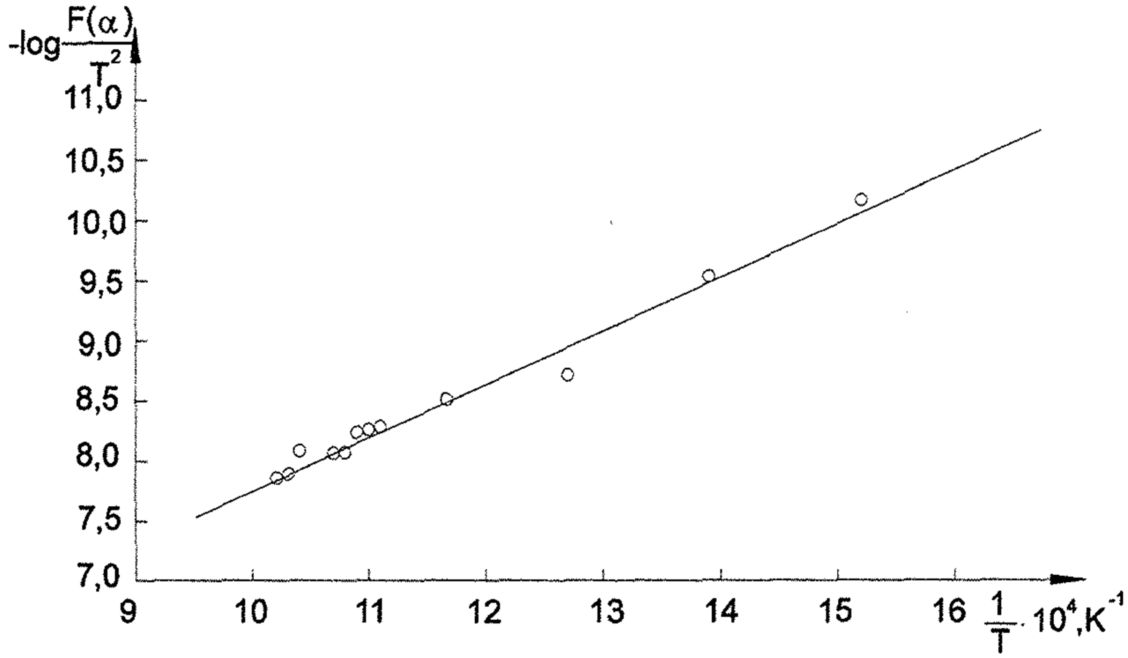

Fig.5.The dependence [log $\frac{F(\alpha)}{T^2}$, $\frac{1}{T}$] for low temperatures (Jander equation)

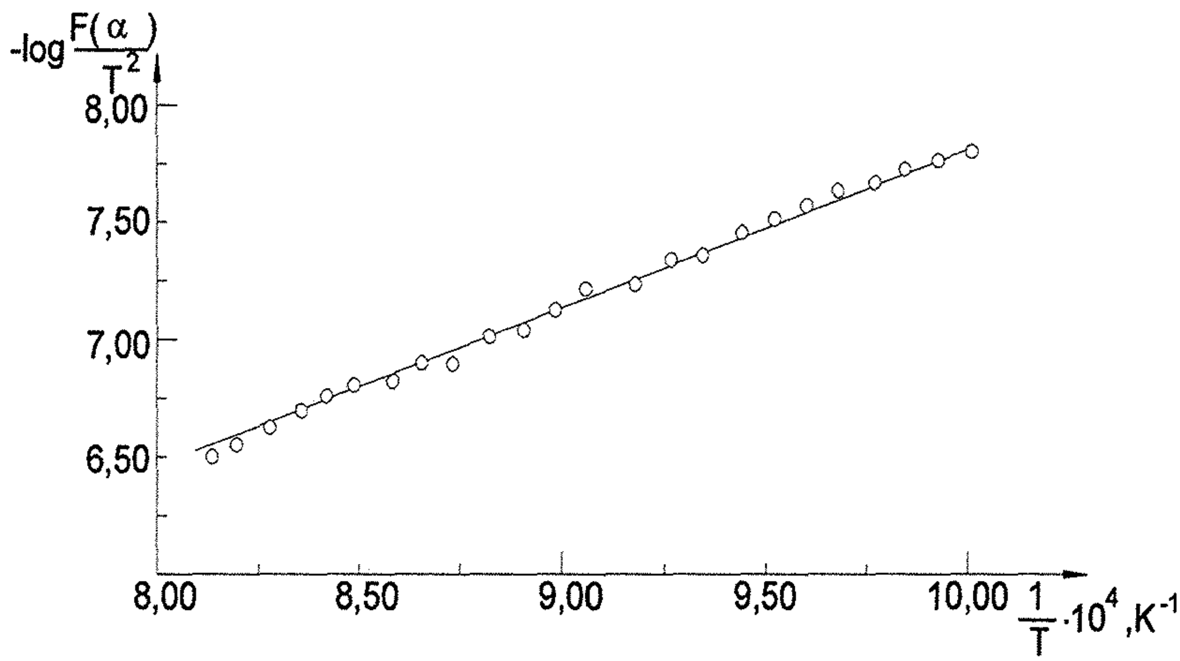

Fig.6.The dependence [log $\frac{F(\alpha)}{T^2}$,$\frac{1}{T}$] for high temperatures (Jander equation)

The plotting of the dependence $\left[\log \frac{F(\alpha)}{T^2}, \frac{1}{T}\right]$ is a straight line,wich gives Arrhenius parameters (A and E).

The model of reaction controlled by difusion and two mechanisms have been used :

a) Bidimensional transport ;

b)Threedimensional transport through a sphere.

The integral of conversion is:

a) $F(\alpha) = \alpha + (1 - \alpha) \ln (1-\alpha)$ – for bidimensional transport (6)

b) $F(\alpha) = 3\{ \frac{1}{2}[1 + (1 - \alpha)^{2/3}] - (1 - \alpha)^{1/3}\}$ (7)

-for threedimensional transport.

The corresponding equations are:

$$\text{a) } \log \frac{1}{T^2}[\alpha + (1 - \alpha)\ln(1 - \alpha)] = \log \frac{AR}{aE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2{,}303R} \cdot \frac{1}{T} \quad (8)$$

$$\text{b) } \log \frac{3}{T^2}\left\{\frac{1}{2}[1 + (1 - \alpha)^{2/3}] - (1 - \alpha)^{1/3}\right\} = \log \frac{AR}{aE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2{,}303R}\,\frac{1}{T} \quad (9)$$

Relation (9) is Jander equation.

Tables 5,6 give data from thermal curves : the weight variation and the degree of conversion.

First we have tried to describe oxidation kinetics using Jander equation for the two temperature range (fig.5,6).One can see that Jander equation better describe the oxidation kinetics for the second temperature range (T= 715,6....1000°C). This equation is not appropiate for the first temperature range,where small oxidation takes place.

The model of bidimensional transport is better for the first temperature range (T<715,6°C) - fig.7.

Kinetical parameters calculated using the two mechanisms are given in the table 7

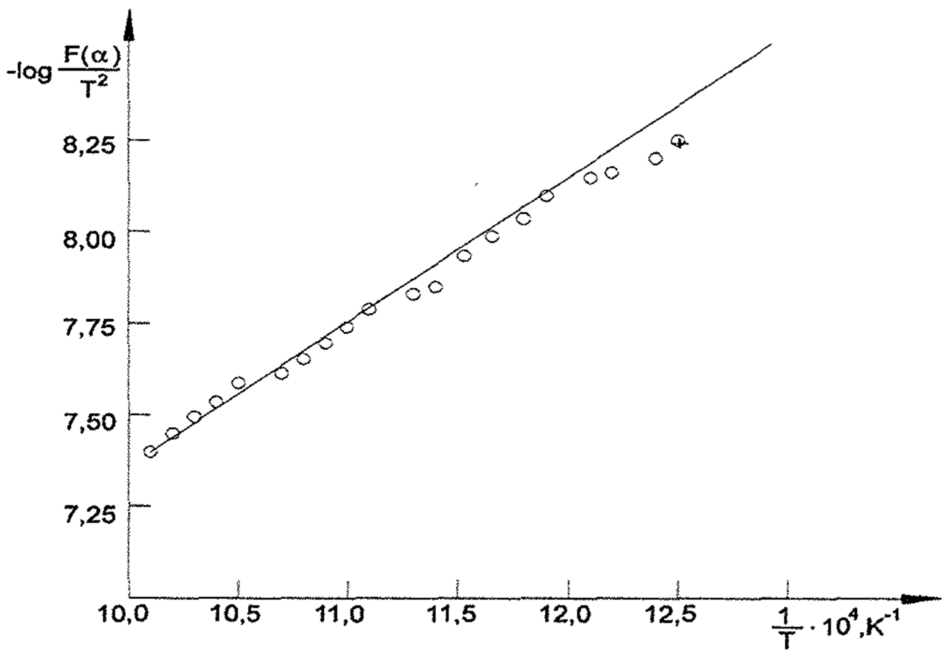

Fig.7.The dependence $\left[\log \frac{F(\alpha)}{T^2}, \frac{1}{T}\right]$ for low temperatures (bidimensional transport)

Conclusions

1.Thermal methods of analysis and microscopical obsevations have been used to characterize some less studied features of nodular cast iron : thermal behaviour and oxidation resistance.

The study is an application of thermal analysis based on heating curves ; usually cooling curves are recorded for metallurgical studies of iron-base alloys.

2.Generally all the samples (which are nodular cast iron melts) have a good oxidation resistance up to 600-670°C.This property depends on silicon content.The (F_1 - F_3) samples,modified with magnesium alloy and without ferro-silicon addition,show similar features on thermal curves: some thermal peaks,corresponding to iron(Fe_3O_4,FeO,Fe_2O_3) oxides.The F_1 sample (with lower silicon content) has smaller oxidation resistance.

The F_4 sample,having specific nodular cast iron composition,shows a good oxidation resistance up to 715,6°C.

3.The decarburisation process must be take into account at high temperature (T>870 °C) It is correlated with phase transformation (reaction 1).

4.The kinetics of decarburisation and oxidation have been modeled and the kinetical parameters of these processes have been calculated.

The model of a sphere which contracts has been used for decarburisation process; two mechanisms (bidimensional transport and threedimensional transport through a sphere) have been used to describe oxidation kinetics of nodular cast iron ,as of a function of temperature.

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The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com.
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