INCIPIENT FUSION STUDIES IN THE SYSTEM

CHROMITE - CaO - MgO - Al_2O_3 - SiO_2 - C

N. A. BAROZA

INCIPIENT FUSION STUDIES IN THE SYSTEM CHROMITE - CaO - MgO - Al_2O_3 - SiO_2 - C

A dissertation presented to the Faculty of Engineering, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering by Nicholas Adrian Barcza, B.Sc.(Eng.)(Rand).

This work was carried out in the Department of Metallurgy of the University of the Witwatersrand, under the supervision of Professor D.D. Howat, B.Sc.(Glas.), Ph.D., F.I.M., F.R.I.C., and Dr F.R. Jochens, B.Sc.(Rand), M.Sc., Ph.D.

UNDERTAKING

I hereby certify that this is my own work and has not been submitted for a Master's degree to any other University.

N.A. BARCZA

10.2.72.

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Due acknowledgement is made to the National Institute for Metallurgy for the bursary which enabled the research project to be undertaken.

Secondly the author wishes to record his appreciation of the assistance afforded him by his two supervisors, Professor D.D. Howat and Dr P.R. Jochens, throughout the course of the investigation.

SYNOPSIS

This project was concerned with an investigation into the reactions and interactions of various chromites with the fluxes used on a ferro-chromium plant as charged to the submerged arc furnace.

The first phase of the project involved the characterising of the fourteen selected chromite ores according to their behaviour on the thermal balance under atmospheric conditions. The importance of the gangue minerals in determining the shape of the TGA curve was established as well. It was in particular the hydrated gangue minerals which had this effect. The chromite spinel was found to oxidise up to 1200°C and then to undergo de-oxidation due to the instability of the iron oxides above this temperature.

Isothermal runs were subsequently carried out with the various Transvaal and Rhodesian chromites in order to establish their behaviour in the presence of solid carbon, CO gas, town gas, and with and without the appropriate fluxing additions. The thermal balance was used for these tests. The kinetics and mechanism for chromite reduction with solid carbon were established as well as the nature of the incipient fusion process. The latter aspect was studied using DTA.

It was shown conclusively that CO gas will not reduce chromite up to 1550°C, thereby eliminating it as the likely diffusing species when chromite is reduced by solid carbon. This means that carbon itself must be the diffusing species. This fact was confirmed by the result in which high carbon ferrochromium reduced a chromite sample at 1400°C where no free carbon was present.

INDEX

CHAPTER I

1.1 INTRODUCTION
1.2 THE OCCURRENCE OF CHROMITE IN THE TRANSVAAL
1.3 THE LOCALITY AND CHOICE OF THE SAMPLES
1.4 METHODS OF INVESTIGATION
1.5 LITERATURE SURVEY

1.5.1. The reduction behaviour of chromite ore in the smelting of high carbon ferrochromium

1.5.2. The behaviour of the Chrome-Spinel on heating at atmospheric condition

CHAPTER II

2. THE THERMAL BEHAVIOUR OF CHROMITES UNDER ATMOSPHERIC CONDITIONS

2.1 INTRODUCTION
2.2 EXPERIMENTAL METHODS

2.2.1. The Thermal Balance and Thermogravimetry

2.2.2. The Thermal Balance runs with Chromite under atmospheric conditions

2.3 RESULTS
2.4 DISCUSSION OF RESULTS

2.4.1. The theory of the Weight Loss Reactions from the hydrated Gangue Minerals

2.4.2. The theory of the Weight Gain Reaction due to Spinel Oxidation

2.5 CONCLUSION

CHAPTER III

3. THE BEHAVIOUR OF CHROMITE UNDER REDUCING CONDITIONS USING POWDERED CARBON AS A REDUCTANT WITH AN ARGON ATMOSPHERE

3.1 INTRODUCTION
3.2 EQUIPMENT

3.2.1. Modifications to the Stanton Thermal Balance for Gas Atmosphere Control

CHAPTER III (continued)

3.3 EXPERIMENTAL METHODS

3.3.1. Sample Preparation

3.3.2. Continuous Runs

3.4 DISCUSSION OF CONTINUOUS RUNS
3.5 STOICHIOMETRIC CARBON
3.6 ISOTHERMAL RUNS
3.7 THE RESULTS FOR THE ISOTHERMAL RUNS
3.8 EVALUATION OF THE MECHANISM AND KINETICS OF CHROMITE REDUCTION

3.8.1. Introduction

3.8.2. The Rate Equations

3.8.3. Kinetic Equation Table

3.8.4. The Rate Controlling Process

3.8.4.1. Introduction

3.8.4.2. Theory

3.9 THE ACTIVATION ENERGY VALUES FOR THE FOURTEEN CHROMITES

3.9.1. Introduction

3.9.2. Arrhenius Plots

3.9.3. The Analysis of the Kinetic Data

3.9.3.1. "Fitmec"

3.9.3.2. Subroutine "Fitlin"

3.9.4. Discussion of Results

3.10 THE REACTIONS ASSOCIATED WITH THE REDUCTION OF CHROMITE WITH SOLID CARBON

3.10.1. Introduction

3.10.2. The Reactions

3.10.3. The Diffusing Species

3.11 THE EFFECT OF FLUXING ADDITIONS ON THE REDUCTION MECHANISM AND KINETICS OF CHROMITE
3.12 USE OF A CORRELATION MATRIX TO ESTABLISH THE EFFECT OF VARIOUS PARAMETERS ON THE ACTIVATION ENERGY AND RATE CONSTANT

3.12.1. Introduction

3.12.2. The Correlation Matrix

3.12.3. The discussion of the Correlation Matrix Results

CHAPTER IV

4. THE BEHAVIOUR OF CHROMITE UNDER A CARBON MONOXIDE ATMOSPHERE

4.1 INTRODUCTION
4.2 EXPERIMENTAL METHODS
4.3 DISCUSSION
4.4 THEORY CONCERNING CARBON MONOXIDE

CHAPTER V

5. THE EFFECT OF PARTICLE SIZE OF CHROMITE F 533 ON ITS REDUCTION BEHAVIOUR

5.1 INTRODUCTION
5.2 EXPERIMENTAL METHODS
5.3 DISCUSSION OF THE RESULTS

CHAPTER VI

6. THE BEHAVIOUR OF CHROMITE AS STUDIED BY DIFFERENTIAL THERMAL ANALYSIS

6.1 INTRODUCTION
6.2 THE APPARATUS FOR DTA
6.3 EXPERIMENTAL METHODS

CHAPTER VII

7. DISCUSSION

CHAPTER VIII

8. CONCLUSION

CHAPTER IX

9. BIBLIOGRAPHY

APPENDIX

CHAPTER I

1. INTRODUCTION

The aim of this project was to define the reduction behaviour of chromite (and the incipient fusion behaviour of the chromite) with the associated fluxes in the submerged arc furnace producing high-carbon ferrochromium. This project was aimed at paving the way for subsequent projects relating to the behaviour of the components in the submerged arc furnace. The smelting and reduction processes occur as the charge approaches the arc zone of the furnace but may begin almost at the top of the furnace. It is at the top of the furnace that the initial reduction and incipient fusion processes begin, but these processes only become highly active as the temperature of the charge reaches (about) 1400°C to 1500°C.

There is a great lack of knowledge about these initial reactions, and it was therefore necessary to investigate the mechanisms and kinetics of the reactions of these components associated with the fusion and reduction processes. A study of this nature should thus assist in establishing a key between the solid charged burden at the very top of the furnace and the molten slag and metal at the bottom of the furnace. In other words this investigation should explain the initial solid-solid, solid-liquid, solid-gas, liquid-gas and liquid-liquid interactions which result in the formation of a suitable slag and the high-carbon ferro chromium. One first logical step in tackling this project was naturally to consider the raw materials, namely the chromite, the fluxes and the carbon. The chromites of greatest interest are of course the local Transvaal chromites, since these ores constitute over two-thirds of the known world reserves. Furthermore, relatively little is known about these chromites, both mineralogically and metallurgically. Pure components were chosen as the fluxing additions. This was done in order to minimize any complications in studying the fusion processes. The carbon was also used in a pure form since the essential goal was to investigate differences in the actual behaviour of various chromites rather than side-effects caused by impurities in the fluxes.

1. INTRODUCTION

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To investigate these differences between chromites, samples had to be collected over a wide area. As is commonly known, the Transvaal chromites occur in what is known as the Bushveld Igneous complex. This intrusive body of differentially crystallized magma extends from the Steelpoort area in the eastern belt and is to be found in the western belt in the Rustenburg area. The Zeerust area in the west is also considered to be part of this large formation. The only region in the Transvaal which is considered to be dissociated from this primary basin is the Potgietersrust area. This appears to be a basin, still within the BIC, but is isolated from the other formations.

1.2 THE OCCURRENCE OF CHROMITE IN THE TRANSVAAL

As was mentioned earlier, the chromites in the Transvaal are generally found in the Bushveld Igneous Complex (BIC). The chromite ore occurs in seams which vary in thickness from a few centimetres up to several metres. The overall shape of the BIC is that of a large oval dish or basin with its long axis lying east-west. The eastern perimeter is in the Lydenburg district and the western outcrop is found near Rustenburg. A secondary outcrop, believed to be associated with the primary basin, is found to the west of Rustenburg in the Zeerust area. Another chromite area is located just north of Potgietersrust in the Grasvally district.

The BIC has a relatively shallow dip over most areas. This dip varies from 9 to 15 degrees inwards. The BIC has been subdivided (ref. 1) into five distinct zones:-

1. Chill zone;
2. Basal zone;
3. Critical zone;
4. Main zone and
5. Upper zone.

The Critical zone contains the many bands of chromite ore. It comprises mainly pyroxene and pyroxene-plagioclase cumulates and lies below the Merensky Reef extending downwards to the Main Chromitite Seam. The depth of /...

depth of these beds is approximately 1 000 m. The widest zone in the above sequence is the Main Zone which is approximately 6 000 metres in width. The maximum measured thickness of these five zones is approximately 7 600 m.

Some 16 to 20 seams of chromite are present in many areas. These seams comprise thin sheets parallel to the igneous layers of silicate minerals. The lower bands are richer in MgO and contain less FeO than the upper bands. The $Cr/_{Fe}$ ratio also tends to decrease in successively higher beds. The deposit north of Zeerust is in the form of a basin with a 4° inwards slope. The Potgietersrust deposits are thought to be part of the Basal zone. They contain a high percentage of MgO and also have a high $Cr/_{Fe}$ ratio. This area is faulted and the chromite bands dip relatively steeply at 45°.

The eastern section of the BIC is divided into three sections. These are the western, central and southern sectors. The central and southern sectors are of importance while the western sector is of virtually no economic importance. A major fault separates the central and southern sectors. One of the most important seams in this area is the Steelpoort seam. It is about a metre in thickness and is separated from the Leader Seam by about ½ metre of pyroxenite. The Leader Seam itself is only ¼ m in thickness. Both these seams extend over nearly 60 kilometres in the central sector. There are only a few breaks along the whole length of these two important seams. These are caused by faults and dolerite dykes.

The deposit in the southern sector is quite different from that in the central sector. There is no evidence of the Leader Seam in this region. The seam of interest is called the "F" seam and it varies from 2 to 3 m across.

The seam of economic importance in the western belt just north of the Pilansberg is called the "Main" or "Magazine" Seam.

The BIC can thus be considered to be made up essentially of a layered sequence of sheetlike basin-shaped depressions. Its origin has led to much controversy, but one of the more generally accepted theories is that of Jackson[ref. 2]. He proposed that igneous layering took place. The chromite seams are thought to have resulted from the accumulation of chromite crystals on the floor of magma chambers. The nature and mode of occurrence of the chromites varies from area to area and so do the associated rock formations. Secondary alternation of the chromite in certain regions might explain some of these variations.

Although these chromites have been widely studied geologically, there is still a lack of fundamental information on certain aspects, especially the mineralogy. De Waal[ref. 3] in his report on these chromites of the BIC, points out that although several chemical analyses and partial analyses of chromites have been published in the literature, only a few are sufficiently comprehensive enough for detailed mineralogical studies. Thus the mode of occurrence of the chromites is well known but the chemical and physical properties of the chromites have been scantily studied. An evaluation of data published on the mineralogy of the BIC chromites is dealt with in De Waal's paper.

The series of tables (presented in the following section), however, is a guide as to many of the parameters relating to the twelve selected Transvaal chromites and the two Rhodesian chromites.

The various data from these tables were obtained from two internal NIM publications.[3,4].

1.3 THE LOCALITY AND CHOICE OF THE SAMPLES

All the chromite samples used were collected from the actual mines themselves, except for the two Rhodesian chromite ores. These two samples were collected by the mine personnel and railed down. The reason for collecting samples personally was to be able to

establish /...

establish the locality of the chosen sample within a particular mine. It was also necessary to note the sample type i.e. whether the sample was "hard lumpy", friable or just "run of mine". When choosing a locality in the mine, it was important to note whether the sample was taken from the top or bottom of a particular chromite band. All sampling points were chosen only after due consideration of all the aspects as discussed with the staff of each mine. Samples in excess of 50 kilograms were taken on mines which produce the "lumpy" type of chromite.

All the producing chromite mines in the Transvaal were visited and stockpiles of samples were assembled. From this stockpile twelve samples were selected (for examination) on a basis of usage on the various ferro-alloy plants and from an interest point of view as well. The chosen samples come from the mines listed below:-

1. The Eastern Belt:
   - Chrome Corporation
   - Winterveld
   - Lavino
   - Groothoek

2. The Western Belt:
   - Marble Lime
   - Ruighoek
   - Zwartkops
   - J.C.I. abnormal chromite

3. Far Western Belt:
   - Zeerust
   - Marico Minerals

4. Northern Transvaal:
   - Grasvally Chrome Mine

5. Rhodesia:
   Two samples were received - one was from the Rhodesia Chrome Mines - the other was supplied by The African Chrome Mines Ltd. Both these ores are Selukwe chromites.

TABLE 1

THE SOURCE, AREA, DESCRIPTION AND NUMBER FOR THE FOURTEEN SELECTED CHROMITES

Number	Source (Mine)	Description of Chromite Type	Area
F 524	Chrome Corp.	Selected hard lump	Eastern Transvaal
F 533	Winterveld (T.C.L.)	Lumpy ore	
F 539	Lavino	Metallurgical grade	
F 543	Groothoek	Hard lump	
F 582	Marble Lime	Hard lump	Western Transvaal
F 584	Ruighoek	Hard lump	
F 588	Zwartkops	Hard lump (Magazine seam)	Far West Transvaal
F 589	Zwartkops	Hard lump (Inter seam)	
F 596	J.C.I. sample	Abnormal Chromite	Rustenburg
F 602	Marico Minerals	Run of Mine	Far West Transvaal
F 604	Marico Minerals	Selected hard lump	
F 606	Grasvally C.M.	Hard lumpy	N.Transvaal
F 651, F 652	Rhodesian Chrome Mines	Lump ore	Rhodesian Dyke

TABLE 2

THE CHEMICAL ANALYSIS OF THE CHROMITES (Ref.5)

Number	Total Iron as % FeO	% FeO	% Cr_2O_3	% Al_2O_3	% SiO_2	% MgO
F 524	24,38	12,0	44,87	13,7	2,55	11,80
F 533	25,08	14,9	45,69	15,1	1,22	11,13
F 539	23,16	14,3	39,61	14,2	8,05	11,65
F 543	24,51	15,8	45,50	13,0	2,40	11,38
F 582	23,70	18,1	41,55	14,6	5,82	11,36
F 584	25,16	17,1	45,06	14,2	2,21	10,65
F 588	24,84	13,0	43,44	14,3	4,07	11,04
F 589	20,42	11,8	50,24	11,6	3,13	12,50
F 596	52,09	24,4	15,24	6,2	2,92	3,43
F 602	20,35	7,1	46,81	15,8	3,15	11,97
F 604	20,15	6,9	46,22	8,8	3,77	11,82
F 606	14,35	6,2	42,61	13,8	10,35	11,55
F 651	11,20	3,7	50,62	12,0	4,64	17,05
F 652	13,97	8,3	48,76	9,4	3,28	17,64

Less than ,005% CaO was found to be present in the chromite ores.

TABLE 3

CHEMICAL ANALYSES OF (A) BULK ORE, (B) GANGUE, (C) GANGUE RECALCULATED TO 100%, (D) PURIFIED CHROMITE, (E) RECALCULATED ANALYSES OF PURIFIED CHROMITE

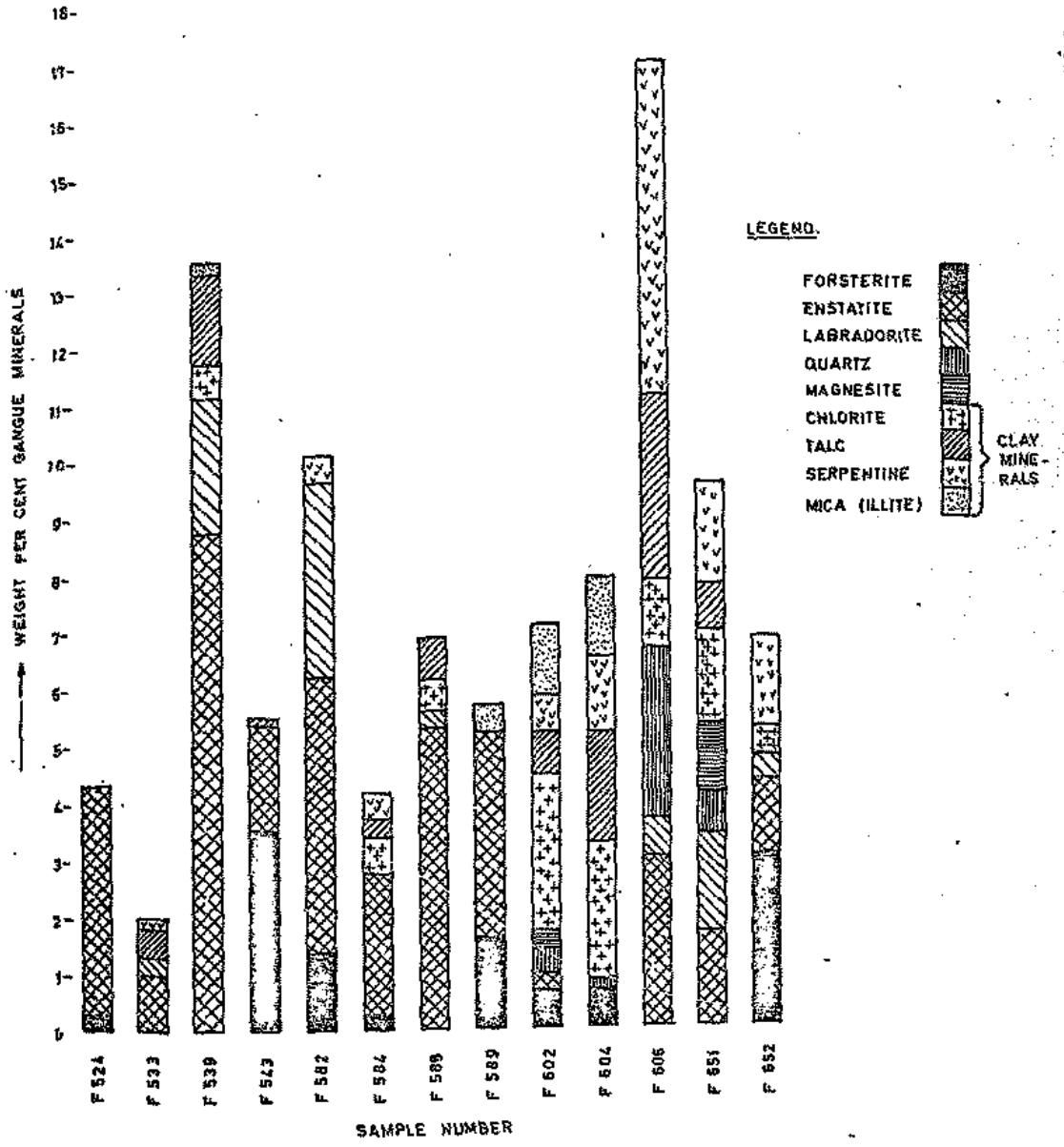
Sample No.		MgO	FeO	Recalculated FeO	Fe_2O_3	SiO_2	Na_2O	K_2O	CaO	Al_2O_3	Cr_2O_3	H_2O^+	CO_2	Wt % Gangue Minerals
F 624	A	11,80	24,38	-	-	2,55	-	-	Tr.	13,7	44,87	-	-	4,36
	B	1,81	-	-	-	2,55	-	-	-	-	-	-	-	
	C	41,5	-	-	-	58,5	-	-	-	-	-	-	-	
	D	9,98	24,38	-	-	-	-	-	-	13,7	44,87	-	-	
	E	10,9	26,2	18,0	7,6	-	-	-	-	14,8	46,3	-	-	
F 533	A	11,13	25,08	-	-	1,21	-	-	Tr.	15,1	45,69	-	-	2,31
	B	0,92	-	-	-	1,21	0,03	-	0,02	0,08	-	0,05	-	
	C	39,8	-	-	-	52,3	1,3	-	0,9	3,5	-	2,2	-	
	D	10,27	25,08	-	-	-	-	-	-	15,02	45,69	-	-	
	E	10,8	26,1	18,2	7,9	-	-	-	-	15,7	47,6	-	-	
F 539	A	11,65	23,16	-	-	8,05	-	-	-	14,2	39,61	-	-	13,61
	B	4,24	-	-	-	8,05	0,21	0,03	0,14	0,78	-	0,16	-	
	C	31,2	-	-	-	59,1	1,5	0,2	1,0	5,7	-	1,3	-	
	D	7,41	23,16	-	-	-	-	-	-	13,42	39,61	-	-	
	E	8,8	27,7	21,1	6,6	-	-	-	-	16,1	47,4	-	-	
F 543	A	11,38	24,51	-	-	2,40	-	-	-	13,0	45,5	-	-	5,66
	B	3,16	-	-	-	2,40	-	-	-	-	-	0,10	-	
	C	55,8	-	-	-	42,4	-	-	-	-	-	1,8	-	
	D	8,22	24,51	-	-	-	-	-	-	13,0	45,5	-	-	
	E	9,0	26,9	20,4	6,5	-	-	-	-	14,2	49,9	-	-	
F 582	A	11,38	23,70	-	-	5,80	-	-	-	14,6	41,55	-	-	10,09
	B	2,94	-	-	-	5,80	0,29	-	0,19	0,61	-	0,06	-	
	C	29,1	-	-	-	57,5	2,9	-	1,9	8,1	-	0,6	-	
	D	8,42	23,70	-	-	-	-	-	-	13,79	41,55	-	-	
	E	9,6	27,1	19,7	7,4	-	-	-	-	15,8	47,5	-	-	
F 584	A	10,65	25,16	-	-	2,21	-	-	-	14,2	45,06	-	-	4,74
	B	1,67	-	-	-	2,21	-	-	-	0,11	-	0,15	-	
	C	40,3	-	-	-	53,4	-	-	-	2,7	-	3,6	-	
	D	8,98	25,16	-	-	-	-	-	-	14,09	45,06	-	-	
	E	9,8	27,0	19,7	7,3	-	-	-	-	15,1	48,3	-	-	
F 588	A	11,04	24,84	-	-	4,07	-	-	-	14,3	43,44	-	-	6,97
	B	2,58	-	-	-	4,07	0,03	-	0,02	0,17	-	0,10	-	
	C	37,0	-	-	-	58,4	0,4	-	0,3	2,4	-	1,4	-	
	D	8,48	24,84	-	-	-	-	-	-	14,13	43,44	-	-	
	E	9,3	27,3	20,2	7,1	-	-	-	-	15,6	47,8	-	-	
F 589	A	12,50	20,42	-	-	-	-	-	-	11,8	50,24	-	-	6,20
	B	2,41	-	-	-	3,3	-	0,10	-	0,35	-	0,04	-	
	C	38,9	-	-	-	53,2	-	1,6	-	5,6	-	0,16	-	
	D	10,09	20,42	-	-	-	-	-	-	11,40	50,24	-	-	
	E	10,9	22,2	17,4	4,8	-	-	-	-	12,40	54,5	-	-	

TABLE 3 (continued)

Sample No.		MgO	ΣFeO	Recalculated FeO	Recalculated Fe_2O_3	SiO_2	Na_2O	K_2O	CaO	Al_2O_3	Cr_2O_3	H_2O^+	CO_2	Wt % Gangue Minerals
F 602	A	11,97	20,35	-	-	-	-	-	-	35,8	46,87	-	-	7,04
	B	2,12	-	-	-	3,15	-	0,16	-	0,87	-	0,48	0,16	
	C	30,1	-	-	-	44,7	-	2,3	-	13,8	-	6,8	2,3	
	D	20,35	-	-	-	-	-	-	-	14,83	46,81	-	-	
	E	10,7	22,2	16,2	4,0	-	-	-	-	16,1	51,0	-	-	
F 604	A	11,82	20,15	-	-	-	-	-	-	8,8	46,22	-	-	6,11
	B	2,47	-	-	-	3,77	-	0,18	-	1,06	-	0,64	-	
	C	30,3	-	-	-	46,5	-	2,2	-	13,1	-	7,9	-	
	D	9,36	20,15	-	-	-	-	-	-	7,74	46,22	-	-	
	E	11,2	24,1	16,3	7,8	-	-	-	-	9,3	55,4	-	-	
F 606	A	18,55	14,35	-	-	-	-	-	-	13,8	42,61	-	-	17,24
	B	5,30	-	-	-	10,35	0,08	-	0,04	0,4	-	1,09	-	
	C	30,7	-	-	-	60,0	0,4	-	0,2	2,3	-	6,4	-	
	D	13,25	14,35	-	-	-	-	-	-	13,4	42,61	-	-	
	E	15,8	17,2	10,4	5,8	-	-	-	-	16,0	51,0	-	-	
F 651	A	17,05	11,2	-	-	-	-	-	-	12,0	50,62	-	-	9,68
	B	2,85	-	-	-	4,64	0,17	-	0,11	0,81	-	0,47	0,63	
	C	29,4	-	-	-	43,9	1,8	-	1,1	8,4	-	4,9	6,5	
	D	14,20	11,2	-	-	-	-	-	-	11,19	50,62	-	-	
	E	16,3	12,8	9,1	3,7	-	-	-	-	12,8	58,1	-	-	
F 652	A	17,64	13,97	-	-	-	-	-	-	9,38	48,76	-	-	7,03
	B	3,19	-	-	-	3,28	0,04	-	0,03	0,22	-	0,28	-	
	C	45,2	-	-	-	46,7	0,8	-	0,4	3,1	-	4,0	-	
	D	14,46	13,97	-	-	-	-	-	-	9,16	48,76	-	-	
	E	16,8	13,2	7,8	8,3	-	-	-	-	10,0	56,4	-	-	

Figure 1 was received from D. Kotzè of the Mineralogy Division at N.I.M. through private communication. It has helped provide a great deal of discussibility relating to the thermal behaviour of the chromites, which is dealt with in a later section. Possible inaccuracies in this table can be attributed to the difficulty in separating the chromite from the gangue and the fact that the bulk sample might not be truly representative of the ore in a particular locality.

FIGURE 1: MODAL MINERALOGICAL COMPOSITION OF THE GANGUE MINERALS IN DIFFERENT CHROME ORES.
(CHROMITE WT % = 100 – GANGUE)



1. METHODS OF INVESTIGATION

The following are the methods of investigation that were considered when choosing which would be the most suitable for studying the thermal behaviour of the chromites and their associated fluxes under both oxidizing and reducing conditions:-

1. Thermogravimetric analysis (Thermogravimetry TG)
2. Differential Thermal analysis DTA
3. High temperature X-ray diffractometry
4. The Leitz Hot stage microscope
5. Room temperature X-ray diffractometry
6. Optical microscopy, using thin sections and slides
7. Electron microprobe studies of samples quenched out from elevated temperatures

1. Thermogravimetric data can prove very useful in following the course of reactions which involve weight changes. A Stanton Thermal Balance was available for immediate use in the department and this allowed preliminary tests to be carried out. This showed that a couple of the chromites, which were used for these preliminary tests, gained weight on being heated in an oxidizing environment.

   Modification could furthermore be made to the thermal balance to allow gas atmosphere control which could be extremely useful for studying chromites under conditions other than those of atmospheric conditions. It was considered that thermogravimetry could, very likely, provide many of the answers which were being sought in connection with the chromites.

2. It was hoped that the chosen chromites could be characterised by their behaviour in a differential thermal analyser. By adding the fluxes to the chromite in suitably chosen proportions it was also hoped to study the fusion process by the method of DTA. A correlation between these reactions and those noted using TG could be made in order to compare which reactions involved weight changes and which reactions involved only a free energy change.

3. The technique of high temperature X-ray diffraction analysis is a relatively new and also somewhat unproven tool in this field of research. Up to date only limited success has been achieved using this method. The role played by this form of X-ray analysis can be of great assistance if the reactions being studied are reversible, since the high temperature phases would be lost on quenching samples from these temperatures, rendering room temperature X-ray diffractometry unsuitable. Most of the reactions involved in the systems to be considered in this project are, however, non-reversible, making the use of high temperature X-ray diffractometry unnecessary.

4. The Leitz hot stage microscope can be very easily assembled to examine the melting processes optically as they occur. It is also possible to take photographs as the reactions take place. The use of this type of visual equipment depends very much on the degree to which the reactions taking place are capable of being followed using the naked eye. It was considered, after consulting the literature on this equipment, that all that the investigator would see was a melting process. It would be very difficult to spot reduction taking place since the metal and chromite look similar unless the surface is polished. The overall deciding factor, which resulted in abandoning ideas of using this hot stage microscope, was the fact that the answers would only be qualitative rather than quantitative. Techniques like TG and DTA lend themselves much more to obtaining quantitative answers.

5. 6. and 7. All three of these techniques, namely X-ray diffraction, optical microscopy and the electron microprobe are merely support methods of investigation in this project. Extensive use was made of the first two techniques to study the chromites both before and after they had been subjected to the tests on the TG and DTA apparatus.

1.5 LITERATURE SURVEY

The literature survey is subdivided into two main sections : the first dealing with the reduction behaviour and fluxing reactions and the second with the behaviour of chromite under oxidising conditions.

1.5.1. The reduction behaviour of chromite ore in the smelting of high carbon ferrochromium

The manufacture of high carbon ferrochromium necessitates a careful selection of the chromite ore since the technology and economics of the process largely depend on this choice. The reduction of the chromite takes place by the conversion and decomposition of the chromite spinel and the slag-forming oxides which can occur in both the chromite spinel and the gangue.(Ref. 6) The major consideration in the smelting of various grades of high-carbon ferrochromium is to obtain an alloy with the required carbon and silicon content. A chromium content of from 66 to 70 per cent has been found most suitable by steel makers.(Ref.7) There has been more recently, however, a tendency to develop a suitable process for steel-making where only 58 per cent Cr is required in the high-carbon ferrochromium. This possibility has increased the importance of the Transvaal chromites with their relatively low Cr/Fe ratio.

The silicon and carbon content of the alloy depends on the quantity and quality of the lump chromite ore as charged to the furnace and on the amount of reductant added. The choice of a suitable ore is complicated by the variation of chemical, mineralogical, and particle size compositions, and by the nature of the cementing rock(Ref.8). In the paper by Kh. N. Kadarmetov, the author compares results of smelting tests carried out on various Russian chromite ores to produce different grades of high-carbon ferrochromium. The author makes reference to two specific grades of chromite, namely: Chr 4 (4-6, 5 per cent carbon) and Chr 6 (6, 6-8 per cent carbon).

TABLE 4

Ore Number	1	2	3	4	5	6
Basic ore type	lump	lump	powder	lump	powder	lump
Charge composition (kg)						
Chromite Ore	500	1000	1000	1000	1000	1000
Quartzite	0- 30	-	-	30- 40	20- 60	20- 50
Coke Breeze	110-125	230-240	220-250	190-200	230-250	230-250
Texture of Lump Ore	dense	medium	medium	dense	medium	dense
Structure of Ore (Grain)	coarse	fine	fine	coarse	fine	coarse
Colour of ore	black	grey	grey	grey	red	red
Cementing Rock	siliceous	siliceous	siliceous	siliceous	ferruginous	
Composition of The Ore						
% Cr_2O_3	50-54	48-52	50-52	50-54	49-50	50-52
% SiO_2	4-6	6-8	4-8	5-7	4-8	4-7
Composition of The Slag						
% SiO_2	20-27	25-31	-	28-34	27-35	31-35
% MgO	55-39	30-43	-	24-38	-	-
% Al_2O_3	25-28	20-27	-	22-27	-	-
Composition of the Alloy %						
C	3,9-6,8	6,3-8,3	-	5,7-6,8	5,5-7,5	5,9-7,1
Si	0,8-1,0	0,4-0,9	-	0,5-0,8	0,7-1,4	0,6-1,1
Cr	70-76	70-76	-	68-71	67-71	70-73
Yield of Grade %						
CHR 4	83	17	1,2	70	5,0	85
CHR 6	17	83	98,8	30	95,0	15
% Cr Recovery	93	91,7	-	-	85,7	92,8

Table 4 shows the varying natures of the six different chromite ores. The author established that the Chr 4 grade could be produced from "lump and friable compact" and "dense coarse-crystalline" chromites as shown in groups 1, 4 and 6. He also showed that Chr 6 grade could be produced from the friable lump and powder ores. The reasons for these limitations of the chromite ores are discussed below.

The Chr 4 can be produced from lump ore because it has a high content of coarse chromite spinel grains (2 mm in diameter). The cementing binder occurs as fine veinlets. These ores have a low reducibility and their refractoriness means that these ores are capable of reacting in the furnace bath and forming a solid layer which favours the refining of the carbon from the alloy.

The quality of the chromite depends on the chromium oxide and silica content. Ores containing 61 - 63% Cr_2O_3 and very little silica are of a compact nature but as the degree of cementation increases, so the % Cr_2O_3 decreases and the % SiO_2 increases. The most common binder found in the Russian chromites is serpentine and various altered forms of this mineral. Thus the total serpentine content, and therefore the silica content, determines the quality of a particular chromite.

According to Kadarmetov(ref.8), the reduction process for powder ore begins at 1150°C to 1200°C and terminates at 1400°C to 1500°C. The incipient reduction of the Cr_2O_3 and FeO precedes slagging, but as the temperature increases, so the two reactions run concurrently and more intensively. Kadarmetov found that the reduction rate of lump ore is slower than that of powdered ore.

The tests carried out by Kadarmetov showed that the initiation of reduction and slagging and the progress of these reactions depended on the temperature and time of heating, texture and structure of the ore, concentration of Cr_2O_3 and Fe_2O_3 and FeO, as well as the nature of the cementing substance. The reduction of the iron oxides and the slagging reactions were shown to occur simultaneously and to initiate at the surface of the chromite and, to varying degrees, within the chromite itself. Chromites with a ferruginous binder reduce more readily than ores with a siliceous binder.

The beginning of intensive reduction was shown to coincide with intens e slagging. These reactions occurred at different temperatures for different ores. Thus lump chromite with 40 - 50% Cr_2O_3 and an open structure reduced and fluxed completely at 1450°C to 1550°C, while chromite with 58 - 62% Cr_2O_3 and a compact structure formed a fluid slag only at temperatures as high as 1850°C to 1950°C.

For suitable reduction and slagging of these ores at lower temperatures, quartz flux should be used. The efficiency of metal oxide reduction is greatly improved by the formation of the liquid phases of the metal and slag. A continuous flow of the liquid phases exposes the surface of the lumps to reduction and further fluxing. When the fluxes added come into contact with the surface of the chromite, they facilitate better fluxing by forming more fluxible and lower viscosity phases. In the lower grade ores these reactions take place without fluxes to a greater extent than in chromites which are high grade. This is due to the small amounts of gangue in high grade ores which make them non-self fluxing.

S.S. Lisniak and N.F. Evseev[Ref.9] have carried out research into the effect of various factors on the reducibility of different Russian chromite ores. The chemical analysis of these ores is shown in Table 5 and should be compared with the Transvaal chromites and the two Rhodesian ores. Tests were carried out in a carbon resistance furnace and CO atmosphere protection. Chromite ore 300, which was a purified ore, was used to establish the effect of temperature, reductant type and particle size. The remainder of the ores shown in Table 5 were used in a similar manner to ore 300 in order to determine the reduction behaviour at 1250°C after 3 hours. Kinetic curves for the reduction of ore 300 with graphite and charcoal at various temperatures are presented in the paper by S.S. Lisniak and N.F. Evseev together with other such curves for the remaining chromites.

TABLE 5

CHEMICAL COMPOSITION OF AKTIOBINSK CHROMITES

Ore	% Cr_2O_3	% Fe_2O_3	% FeO	% MgO	% Al_2O_3	% SiO_2	% CaO	Total %
300	60,1	15,7	-	13,4	9,0	0,8	0,6	100,1
301	57,5	14,9	-	14,0	10,0	1,2	trace	99,7
302	60,1	14,8	-	13,5	10,5	1,6	trace	100,7
315	53,6	21,7	0,8	11,4	8,5	1,5	2,0	100,4
308	52,8	4,8	6,7	20,1	7,8	5,8	trace	100,9
310	20,5	8,9	0,8	18,9	3,5	21,5	9,5	99,5
304	55,4	13,7	0,7	14,6	8,4	4,9	trace	98,5
309	30,8	5,5	3,6	8,1	3,5	47,5	trace	99,9
311	47,7	4,9	7,0	18,3	6,3	10,3	3,1	99,7
312	44,8	10,9	12,7	12,3	10,5	5,2	trace	96,8
313	59,8	5,9	7,8	13,0	10,8	1,6	trace	98,9

The findings of these two scientists are discussed below:-

Reduction was found to start at 1050°C and reached 10% within 40 minutes at this level. It virtually ceased at this point. At 1100°C and 1150°C, the same reduction value was reached within 5 - 10 minutes. At this point the reaction rate was observed to increase. At 1150°C the reduction ceased at 50% reduction after 160 minutes, while at the 1350°C level the rate of reduction was still more rapid. The tests showed that an increase in reduction rate occurred with decrease in particle size.

An important result was obtained. This is that despite their different chemical compositions the chromites from OBIENDINENNI had similar reducibility values. The reduction rate differed however in terms of time, although after a long enough time interval more or less the same degree of reduction resulted.

The reducibility of chromites 304 and 309 was found to be much higher than that for the other samples from the AKTIUBINSK deposit. A comprehensive study of chromite 300 revealed the following data:-

The lattice constant of the spinel phase = 8,25 Å
% Gangue = 2%
The iron was present in the Fe^{+++} form only.

The spinel formula was shown to be close to

$$Mg_{0,6}\ (Fe,\ Cr,\ Al)_2\quad O_{3,6}$$

The ferrochrome spinel is incomplete since there are points in the lattice which should be occupied by divalent Fe^{++} ions which are in fact vacant. It would appear that during reduction the Fe^{+++} is initially reduced to Fe^{++} and these divalent ions fill the vacant sites in the non-stoichiometric lattice of the original spinel. This results in a complete lattice.

The new spinel has the following formula:-

$(Mg, Fe)\ (Fe, Cr, Al)_2O_4$ and is called ferrochromepicotite.

On further reduction the remainder of the Fe^{+++} is reduced to Fe^{++} which is subsequently reduced to metallic iron. The remaining phase has this formula:-

$(Mg,Fe)\ (Cr, Al)_2\ O_4$ and is known as chromepicotite.

At higher temperatures the simultaneous reduction of Fe^{+++} and Fe^{++} to metallic iron and the Cr_2O_3 to Cr_7C_3 or some other chromium carbide take place. The formation of the $Mg\ (Cr, Al)_2\ O_4$ (chromespinel) results from this simultaneous reduction.

The final degree of reduction takes place at temperatures above 1250°C only, when the chrome spinel is reduced to form chromium carbide and $Mg\ Al_2O_4$ (alumomagnesium spinel).

Thus the whole reduction process can be summarised as shown in Table 6.

TABLE 6

THE VARIOUS STAGES OF REDUCTION OF CHROMITE ORE 300

Temp.	Stage of Reduction	% Reduction	Reaction Products
1050°C	Complete filling of the vacant divalent sites in the spinel lattice $Fe^{3+} \rightarrow Fe^{2+}$	5,7	$(Mg,Fe)(Fe,Cr,Al)_2O_4$ ferrochromepicotite
1100°C	Reduction of the remaining Fe^{+++}. The Fe^{++} tied up with Mg^{++} is not reduced at this temperature.	10,0	$(Mg,Fe)(Cr,Al)_2O_4$ chrome picotite +Fe metal
1150°C	Simultaneous reduction of Fe^{+++} and Cr^{+++} as well as the Fe^{++} associated with Mg^{++}	50,0	$(Mg,Fe)(Cr,Al)_2O_4$ reduced to give $Mg(CrAl)_2O_4$ (↑) + Fe metal (chrome-spinel) + Cr Carbide
1250°C	Reduction to completion but slowly	approaching 100	$MgAl_2O_4$ (alumomagnesium spinel) + MgO + Fe metal* + Cr carbide
1350°C	Rapid rate of reduction	100	same as above

* The Fe metal can completely dissolve in the Cr carbide so it is impossible to tell whether the metallic iron or iron carbide is the reduction product at the temperature level of 1250°C.

Lisniak and Evseev mention that the most prevalent point of view concerning the reduction of metal oxides is that gaseous phase reduction occurs. CO gas is suggested since its regeneration is rapid at elevated temperatures. They noted that, with decreasing size of graphite, the reaction rate increased, presumably due to better solid-solid contact. They considered that reduction was quicker in cases where the chromite ore reduces to chromepicotite with an abundance of metallic iron. This is substantiated by the fact that ores 304 and 309 have 3 - 5 times more metallic iron (based on calculation from the analysis) than the other ores. These are the ores showing most rapid reduction. Metallic iron apparently must catalyse the reduction of chromium to chromium carbide. The activity of the chromium would be lower in a mixed carbide of Fe and Cr). Lisniak and Evseev called this the explanation of the superior reducibility of samples 304 and 309. They did, however, feel that this factor alone was insufficient and recommended that close attention should be paid to the gangue. It is this observation that resulted in the necessity for the complete analysis of the gangue and chromite spinel in the Transvaal and Rhodesian chromite ores. (See Tables).

In a paper by S.S. Lisnyak, A.N. Belikov and A.N. Morosov(Ref.10), the kinetics and mechanism of chromite reduction are discussed at length. The important aspects they noted are as follows:-

The work of S.S. Lisnyak and N.F. Evseev(Ref.9) was confirmed in that in the initial stages of reduction of incomplete (i.e. non-stoichiometric) chromite spinels, the reduction of Fe^{+++} to Fe^{++} takes place. The Fe^{++} ions fill up available vacancies in a chrome spinel that is incomplete.

At temperatures from 1050°C to 1200°C, iron and chromium oxides in the spinel are reduced. The R_2O_3/RO ratio in the spinel approaches 1, and only when the iron oxide is totally reduced, does the chromium oxide start to reduce. At higher temperatures simultaneous reduction of iron and chromium oxides takes place.

Geld and Esin(Ref.11) point out, in their paper entitled "Kinetics of Reduction of Chromium Oxide and Iron Chromite", that in spite of the great technological importance of the process of reduction of Cr_2O_3 and chromite, their kinetics have been little studied. Prior to this time only Baukloh, Henkel(Ref.12) and Kaseev(Ref 13) had carried out research into this subject of Cr_2O_3 reduction by hydrogen. An examination by Kaseev of data for reduction rates of Cr_2O_3 led to the following empirical equation:-

$$\text{Log } A = \frac{30\,000}{4.575T} + b \quad \ldots\ldots\ldots (1)$$

where A = per cent reduction
b = coefficient
T = absolute temperature

Plots of this equation from data obtained by kinetic analysis were found to be both straight and parallel lines, indicating the absence of a relationship between activation energy and the degree of reduction. This result is similar to that for the reduction of iron oxide. Geld and Esin were able to put forward the following hypothesis based on the above data:-

The velocities of both the reduction of Cr_2O_3 and FeO by hydrogen are governed by a similar slow stage, namely that of crystallochemical transformations. This hypothesis is borne out by the fact that b, the coefficient in equation (1), changes with t according to the following equation:-

$$b = \log (177 \times 10^2 t - 4,575 \times 10^3 t^2 + 0,406 \times 10^3 t^3) \ldots (2)$$

This equation is very much like the expression for a topochemical reaction in which reaction takes place over the whole surface.

On combining equations (1) and (2) the following expression is obtained:-

$$A = 2.3e^{\frac{30\ 000}{4,575T}} \times (177 \times 10^3 t - 4,575 \times 10^3 t^2 + 0,406 \times 10^3 t^3) \ldots (3)$$

The research work carried out by Geld and Esin yielded several interesting facts about chromite ore and Cr_2O_3. A summary of their findings is dealt with below.

1. The authors found that reduction of pure Cr_2O_3 with carbon initiates at 1120°C to 1130°C, as compared with Greenwood's result of 1185°C.
2. They showed that carbon reduced Cr_2O_3 much more rapidly than hydrogen does.
3. These two scientists inferred that reduction of Cr_2O_3 by pure CO would be extremely slow.
4. The reduction rate of Aktyubinsk chromite ore by carbon was found to be substantially slower than that for pure Cr_2O_3 under identical conditions. This was explained by the fact that the Cr_2O_3 is not only combined with iron oxide but also with MgO and Al_2O_3. Thus not all of the Cr_2O_3 is in the free state and during the reduction of FeO part of the Cr_2O_3 remai..s tied up as magnesium chromite. This theory agrees with the postulations and results obtained by Lysniak and Eseev.
5. Some chromites have more dense crystalline structures than others, depending on the inert components, namely Al_2O_3 and MgO. This degree of compactness is a factor which

results in /...

results in the slowing down of the diffusion rate of the reacting substances in cases where the structure is dense.

6. The authors found that direct proportionality between the macrosurface of the reactants and the rate of reaction does not exist in the case of chromite reduction with carbon. They found that the reduction rate was, as a first approximation, inversely proportional to the square root of the diameter of the particles. This statement indicates that the authors attempted to fit a kinetic equation to their data but they never in fact obtained a really suitable expression.

7. Reduction rate was shown to depend on both the chromite ore and carbon particle size - the chromite particle size having the more pronounced effect.

8. The addition of an alkali salt (potassium carbonate) to the chromite ore sample resulted in an acceleration of the reduction process. The authors explained this phenomenon by drawing a parallel with the calcining of dolomite. The salt facilitates the surface migration of metallic ions thereby lowering the energy required for this stage of the reaction.

9. Finally the authors put forward a very important idea. If the reduction rate of a particular chromite ore were to be increased, the Cr_2O_3 content of the resultant slag would be reduced and in turn the viscosity would be lower.

1.5.2. The Behaviour of the Chrome-Spinel on Heating at Atmospheric Conditions

It appears that it was as relatively recently as 1939 that it was noticed by Russian investigators that the FeO in the chromite spinel oxidises easily, though not completely to Fe_2O_3. The investigators Kariakin and Piatikop (Ref.14) mention several relevant findings concerned with this oxidation reaction. They identified both maematite and magnetite in their Russian Kempirsai ores which had been heated to 1400°K to 1700°K.

Kariakin and Piatikop (Ref.14) examined under the microscope mixtures of chromite and Fe_2O_3 (5% and 10% additions). On heating to 1400°K to 1700°K, the following was observed:-

1. During heating, all the Fe_2O_3 penetrated the chromite spinel structure in the form of a solid solution.

2. During slow cooling, excess iron oxide separated out partly from the chromite to form haematite needles.

3. On quenching after heating, above 1700°K, no precipitation of haematite took place.

Goncharov and Prokoféva (Ref.15) decided to undertake investigations into the behaviour of the heated chromite spinels in view of certain discrepancies which had been noted in prior research in this field. They mention the reaction in which Fe_2O_3 changes to Fe_3O_4 in air at atmospheric pressure. This transition point is at 1385°K (1112°C). The results obtained in this work are further discussed in the section dealing with the behaviour of the chromites under atmospheric conditions.

CHAPTER II

2. THE THERMAL BEHAVIOUR OF CHROMITES UNDER ATMOSPHERIC CONDITIONS

2.1 INTRODUCTION

The aim of this first phase of the project on incipient fusion studies of chromite was to characterise the fourteen chosen chromite ores by comparing their thermo-gravimetric behaviour with their mineralogical composition. The thermal balance, it was hoped, could be used to establish the nature of the chromites, both with respect to the gangue minerals present and to the nature of the chromite spinel itself.

2.2 EXPERIMENTAL METHODS

2.2.1. The Thermal Balance and Thermogravimetry

The first recorded step towards thermal balances was a quartz torsion microbalance which wa. constructed by Nernst in 1902. Since Nerst's experiments, several eminent research scientists have developed and improved on the simple apparatus used by scientists such as Brill (1905) and Honda (1915). The apparatus that Honda constructed was the first to be able to record weight changes continuously.

Thermogravimetry (TG) can be defined as a technique whereby the weight of a substance is recorded continuously as a function of time or temperature in an environment heated or cooled at a controlled rate, or soaked. Thermogravimetry is thus the field of investigation which is studied on a thermal balance. The heating, cooling or soaking of the furnace section of the thermal balance can be programmed through a chosen temperature or time interval.

Some of the typical reactions which can be followed by their weight change characteristics include: oxidation, reduction, dehydration, drying, decomposition and volatilization. The oxidation and dehydration type reactions are of most interest in this section on the behaviour of

chromites in /...

chromites in atmospheric conditions, whereas in the following sections, the reduction reaction will be of most interest.

2.2.1.1. The Thermal Balance

There are numerous devices whereby continuous weighings of a sample are recorded while the sample is being heated, cooled or soaked. The primary considerations in choosing the type of thermal balance required are the size of sample to be investigated and the overall amount of weight change likely to be incurred. Thermal balances vary from microbalances, in which changes of weight are measured in milligrams, to large thermal balances taking several kilograms of sample. The particular thermal balance used for this investigation was a STANTON THERMAL BALANCE which can be classed as a microbalance. The specifications of this particular balance are dealt with below.

The essential components of which a modern thermal balance is comprised are as follows:-

1. The balance section itself.
2. The furnace and its control section.
3. A reaction chamber.
4. A two-pen recorder, recording weight and temperature simultaneously.

There are basically two classes of thermal balance, namely beam-balances and balances other than beam-balances. The Stanton Thermal Balance is of the former kind. These various balances employ several techniques of weight reading and recording. Included in these balance types are the Null-Balance, the Force-Restored Balance, the Psuedo-Null Balance, the Displacement-Measurement Balance and Miscellaneous Beam Balances as mentioned by Garn(Ref.16).

In the Non-Beam Systems direct suspension of the sample can be used instead of a beam, e.g. a spring or a magnetic form of suspension. The mechanism of the Stanton Thermal Balance is discussed below.

2.2.1.2. The Stanton Thermal Balance

This instrument falls into the beam balance category. Movement of the beam is transmitted by means of a capacity following device. This allows the deflection of the balance beam to be followed without any mechanical contact between the beam section of the apparatus and the recording section. In this manner a relatively simple capacitance circuit can be used to measure the equilibrium point of the balance beam. This is an alternative method to the frequently used method whereby a L.V.D.T. (linear variable differential transformer) is used as an unbalance detector. The capacity following device on the Stanton balance is connected via a servo-motor directly to the weight recording pen of the two pen recorder. The temperature measuring section of the thermal balance was merely used as a guide. The actual temperature was accurately measured using a potentiometer.

2.2.1.3. Conclusion on Thermal Balances and Thermogravimetry

The description of a thermal balance has been dealt with and also the type of thermal balance which has been used for this project. It is important, however, to mention some valuable considerations put forward by Lukaszevski and Redfern (1961)(Ref.17) as to what they consider qualities of a good thermal balance should be:-

a) The thermal balance should be capable of continuously registering the weight and temperature on an X_1 - X_2 recorder.

b) The furnace should be capable of reaching the maximum temperature required to study a particular sample.

c) The heating and cooling rates should be uniform and, even more important, they should be reproducible.

d) The furnace should be able to attain and maintain a chosen isothermal temperature and should soak for considerable times at this temperature without varying by more than a few degrees centigrade.

e) The uniform temperature zone of the furnace should be as long as possible and the crucible and thermocouple should be located within this zone and within close proximity to each other.

f) The functioning of the balance should not be impaired by factors such as radiation, convection, induction or magnetic effects, nor by buoyance effects caused by upward gas flow.

g) There should be no interaction between the sample and the crucible or between the gas atmosphere and the crucible. The components of the thermal balance which are exposed to high temperatures or corrosive gases should also be protected or made of suitable materials which can withstand these destructive conditions.

h) The sensitivity of the balance should be chosen according to the expected weight change and to the size of sample to be tested. Thus microbalances must be much more sensitive than large thermal balances in which several kilograms are placed.

In most of these respects the Stanton Thermal Balance was found to be very satisfactory as far as microbalances are concerned. The only features of the balance which were not satisfactory were the non-linearity of its heating rate and the inaccuracy of the temperature scale. Both these drawbacks were suitably overcome and good results were achieved. The temperature was measured using a potentiometer and the heating rate was found to play only a small role over relatively limited temperature ranges. Furthermore, many runs were carried out at isothermal temperature levels so that heating rate was not involved.

2.2.2. <u>The Thermal Balance Runs with Chromite Under Atmospheric Conditions</u>

Each of the fourteen chromite ores was crushed to -325#. The description of this sample preparation is discussed below.

In preparing the chromite samples for use on the thermal balance several factors has to be considered. The lumps of chromite ore, as received, ranged in size from approximately 3 cm up to 30 cm across. This size range was obviously too large for the microbalance and furthermore the reaction kinetics of such large lumps would be difficult to study. Finer fractions were therefore prepared. The size grade chosen for these tests under atmospheric conditions was chosen as 95 per cent -325#.

A laborious but necessary procedure was used in the step-wise crushing down of the chromite lumps. The reason for the numerous stages of crushing was to produce the minimum amount of fines possible. It was also important to avoid introducing physical distortion of the sample either by introducing stresses of a severe nature during crushing, or by causing the sample to heat up considerably while

it was being /...

it was being crushed. These sources of distortion were minimised by using an agate grinder for the final stage of grinding.

The reason for this choice of particle size has been explained to some extent, but the most important reason was to obviate, at this stage of the project anyway, any surface effects and, hence, to make the only variable the actual difference in chromite ore types. The literature on this subject of particle fineness indicates that this mesh size will suffice in this respect. A second reason for this choice of fine particle size is that faster rates of reaction can be expected due to the greater surface area exposed, in this case, to oxidation. This approach would tend to highlight reactions, making them easier to spot. The reasons for this choice of particle size apply to the reducing conditions as well.

Consistent sample weights of 3,5000 grams were placed in a squat platinum dish-shaped crucible. Each sample was placed on the support rod of the balance and counter-balanced by placing weights on the counter-balance pan. The furnace was carefully lowered over the support rod on which the crucible containing the chromite sample was balanced (avoiding disturbance of the sample). The furnace was switched on and each of the fourteen chromites was heated from room temperature up to 1500°C. The runs were carried out in duplicate on the thermal balance in the Department of Metallurgy at the University of the Witwatersrand and also on the Stanton Massflow thermal balance at the Industrial Distributors Research Centre on Crown Mines. Use of this alternative thermal balance was made to check the reproducibility of the results from one piece of equipment to another. The heating rates of the two thermal balances were similar and thus a favourable comparison of answers could be made.

A flat crucible was chosen so that the bed of fine chromite could be fully exposed to the atmospheric conditions within the open furnace. A test run using a sample of calcium oxylate hydrate ($(COO)_2$ $Ca.H_2O$) was carried out to check both the reproducibility and the accuracy of the temperature measurements. A standard result for this substance was provided in the manual on the Stanton thermal balance. This test also helped to check that the weight change readings were accurate. The results of all these tests are given and discussed below.

2.3 RESULTS

As each run was carried out, both the temperature and the weight reading were recorded on the X_1 - X_2 two pen chart recorder. All the results were read off these charts and either tabulated or recalculated in order to allow representative thermogravimetric curves to be drawn. Use of a technique which yields the first derivative of the thermogravimetric curve with respect to either time or temperature can be made. Temperature intervals were chosen to calculate the DTG curve in this case.

The temperature was read from the TG curve at fifty degree intervals. The temperature was calibrated using a potentiometer which was connected to the thermocouple placed next to the sample. The thermocouple was a Pt/Pt-10% Rh type. The range over which the temperatures were read was from 300°C up to 1500°C. Corresponding to each temperature point chosen, a weight reading was taken. The weight was recorded in milligrams. An important consideration concerning these readings taken from these graphs is the accuracy to which they could be read. The precision and accuracy are both discussed in the appendix.

In this manner the temperature in °C and the corresponding weight reading in mg were recorded and read off from the TG curve. These results had now to be processed into a suitable form for graphical representation. This was done in the following way:-

Firstly the cumulative weight change was calculated from the sums of the differences between actual weight readings. Secondly the cumulative percent weight change based on the original 3,5000 grams of chromite ore was calculated. The cumulative percent weight change and temperature have been used to plot the lower graph in each case for the fourteen chromite ores. These are shown in Figures 2 to 15. In order to plot the DTG graph, the weight increments had to be calculated as a percentage. Then by dividing the percentage weight increment ΔW by the temperature increment ΔT, the rate of weight percent change with temperature was obtained. It is from these values that the graphs of $\Delta W/\Delta T$ versus the temperature have been plotted. These are represented as the upper graphs in Figures 2 to 15.

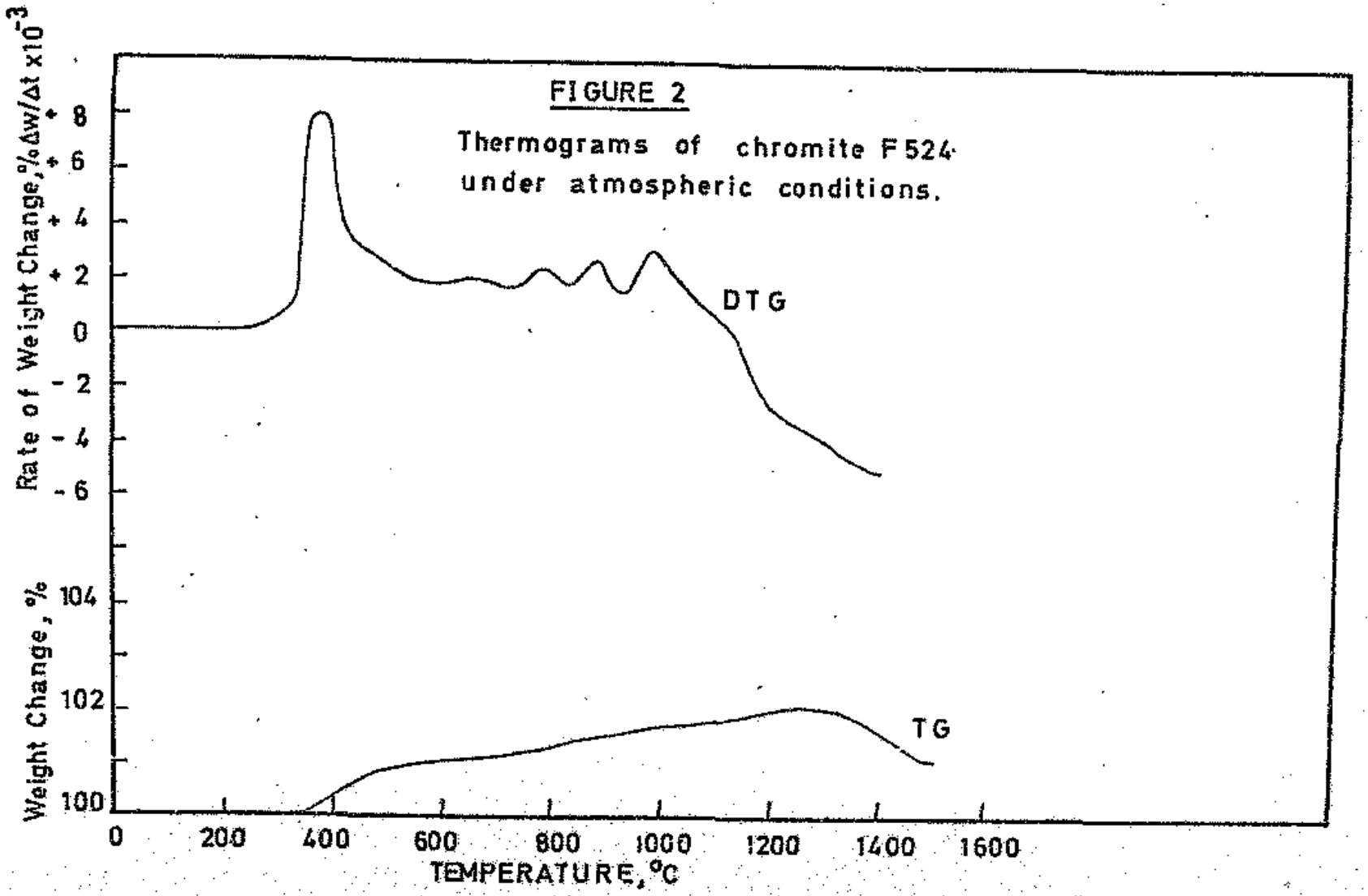


FIGURE 2

Thermograms of chromite F 524 under atmospheric conditions.

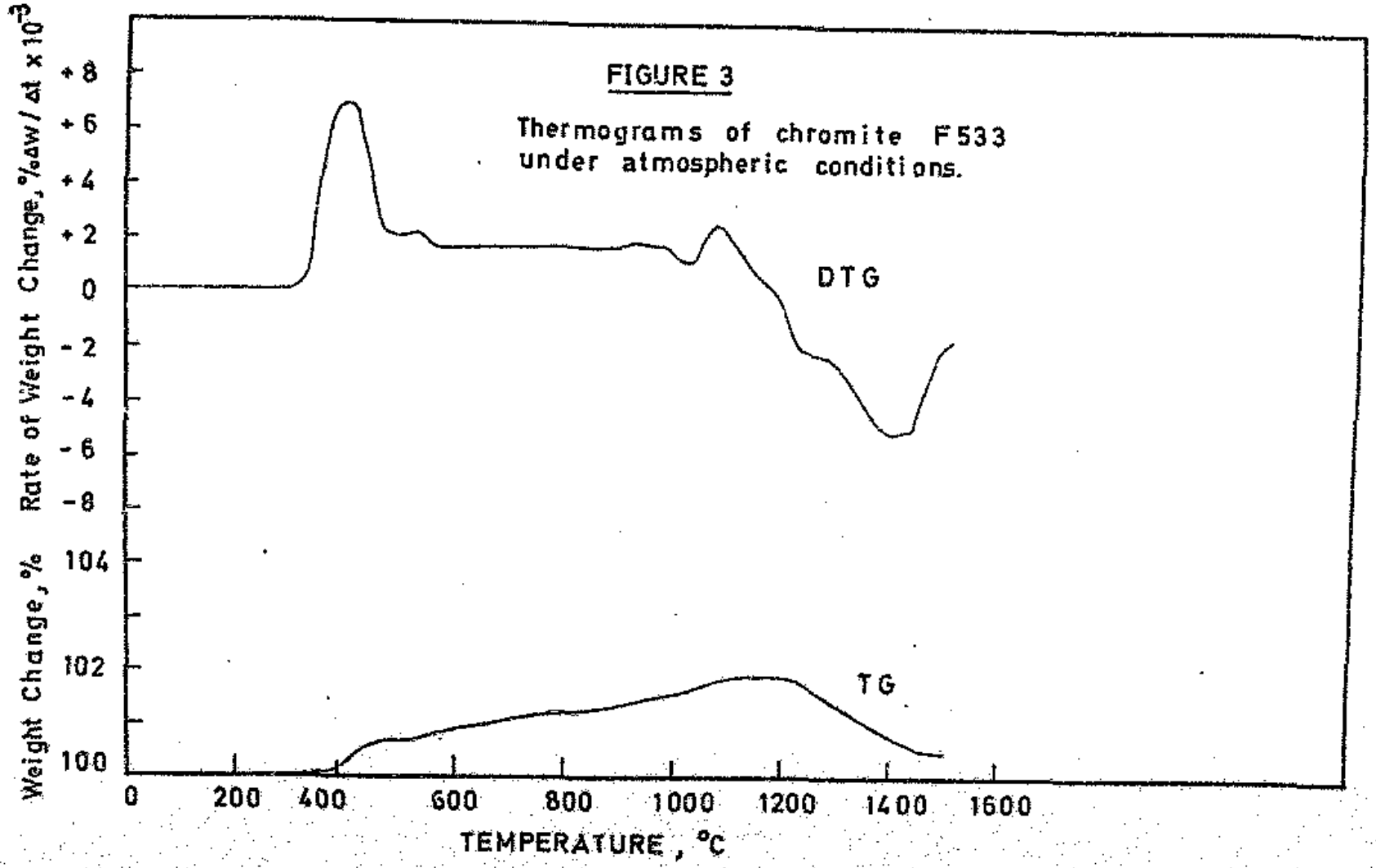


FIGURE 3

Thermograms of chromite F533 under atmospheric conditions.

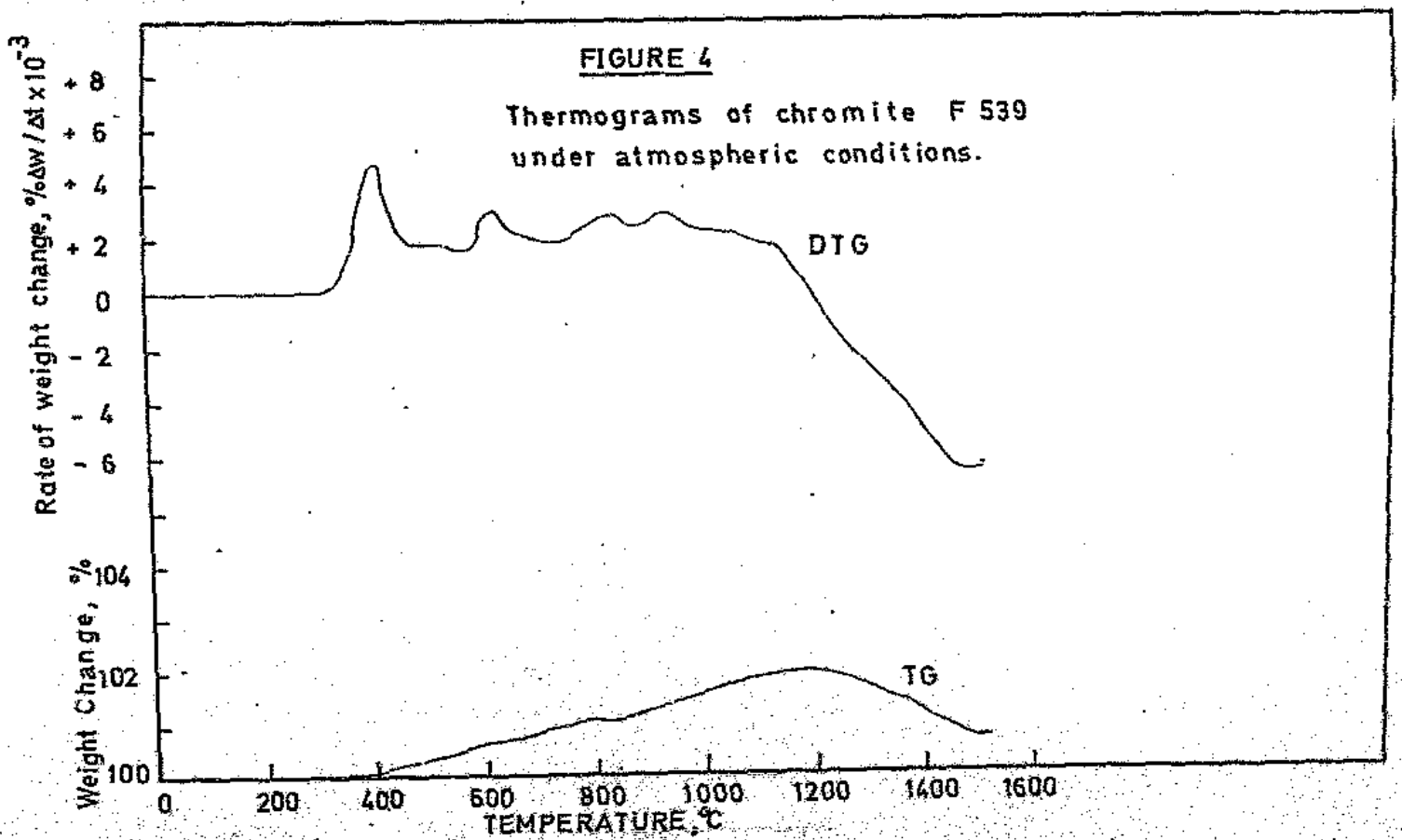


FIGURE 4

Thermograms of chromite F 539 under atmospheric conditions.

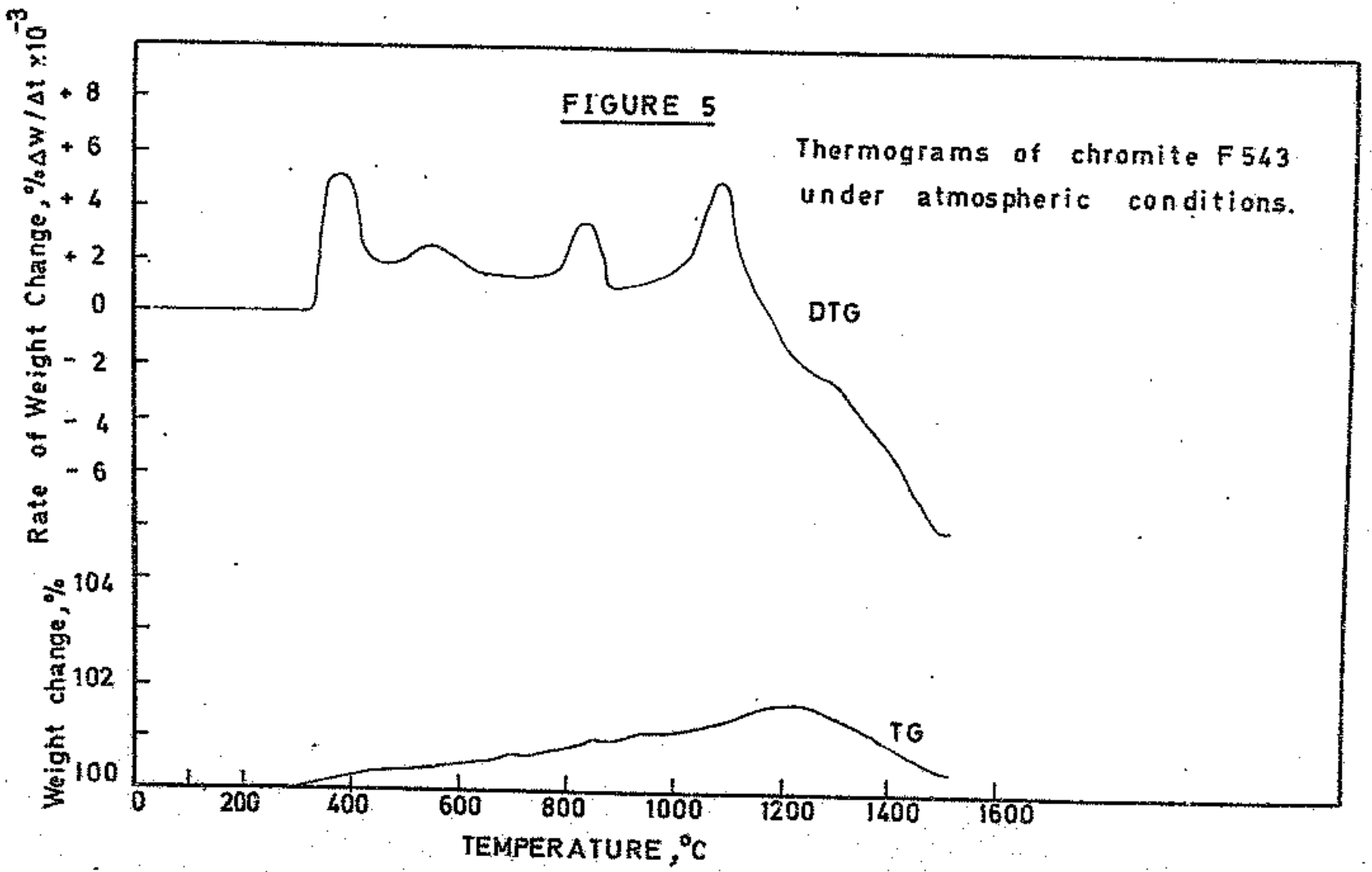


FIGURE 5

Thermograms of chromite F543 under atmospheric conditions.

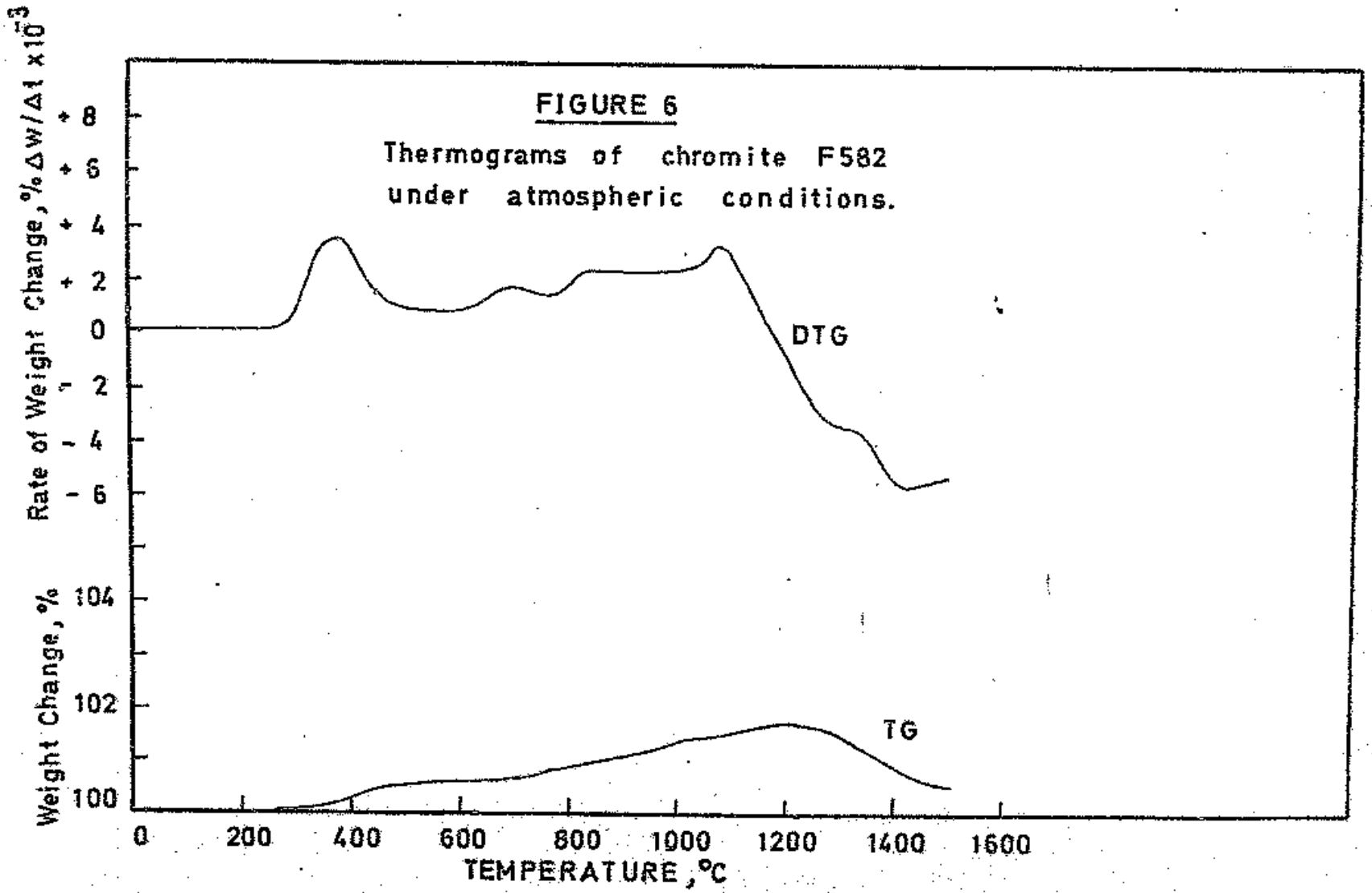


FIGURE 6

Thermograms of chromite F582 under atmospheric conditions.

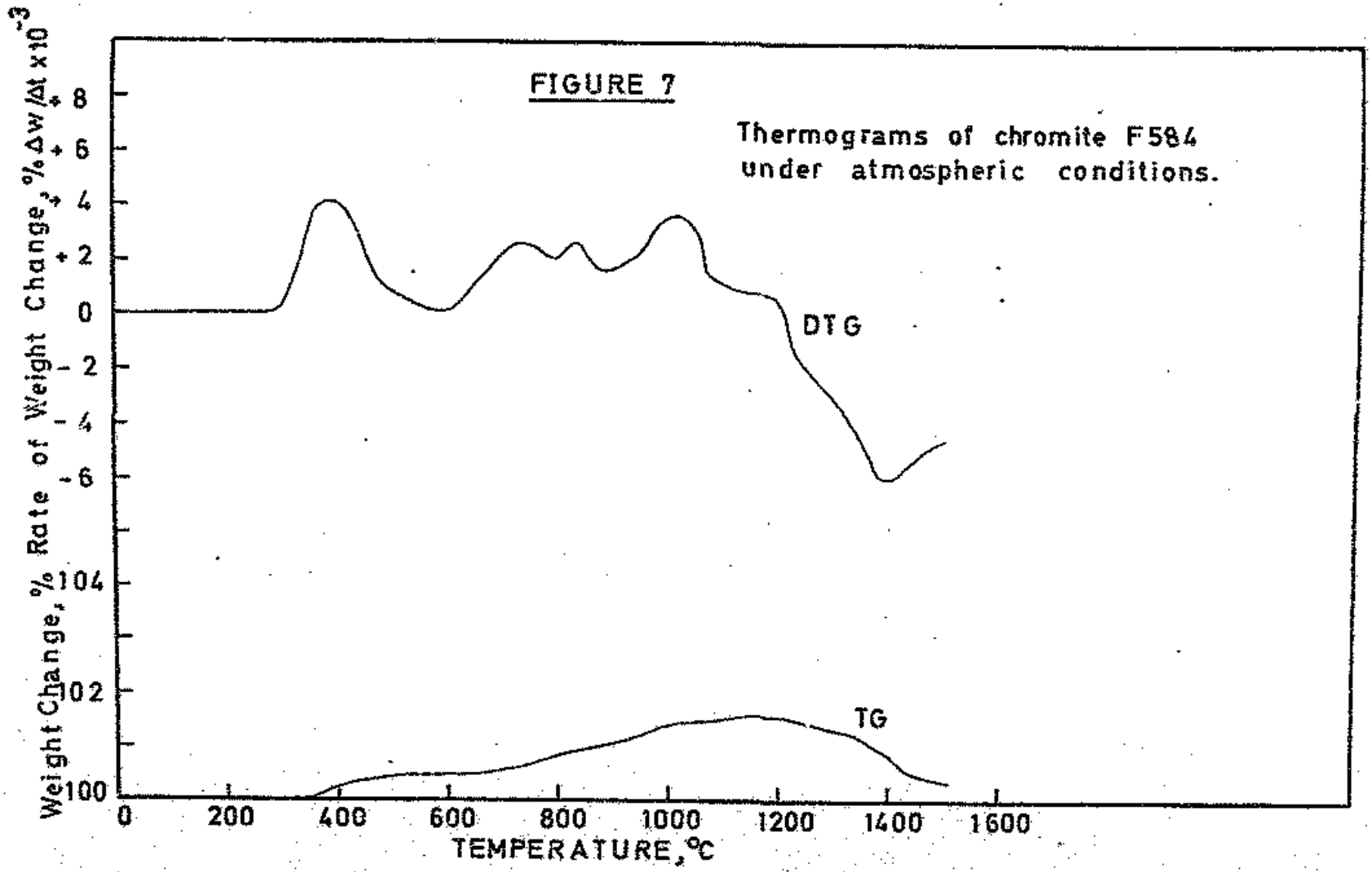


FIGURE 7

Thermograms of chromite F584 under atmospheric conditions.

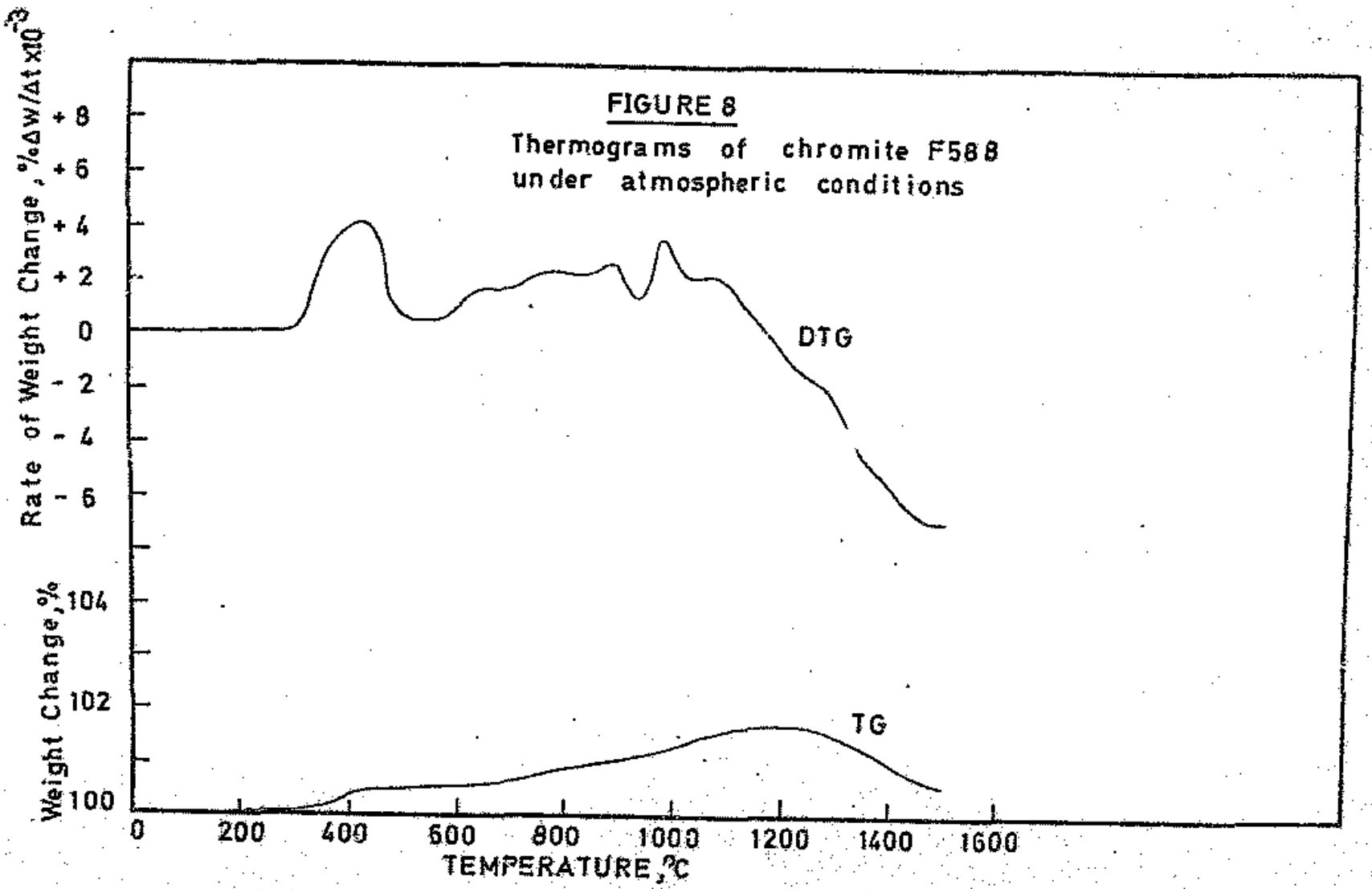


FIGURE 8
Thermograms of chromite F588 under atmospheric conditions

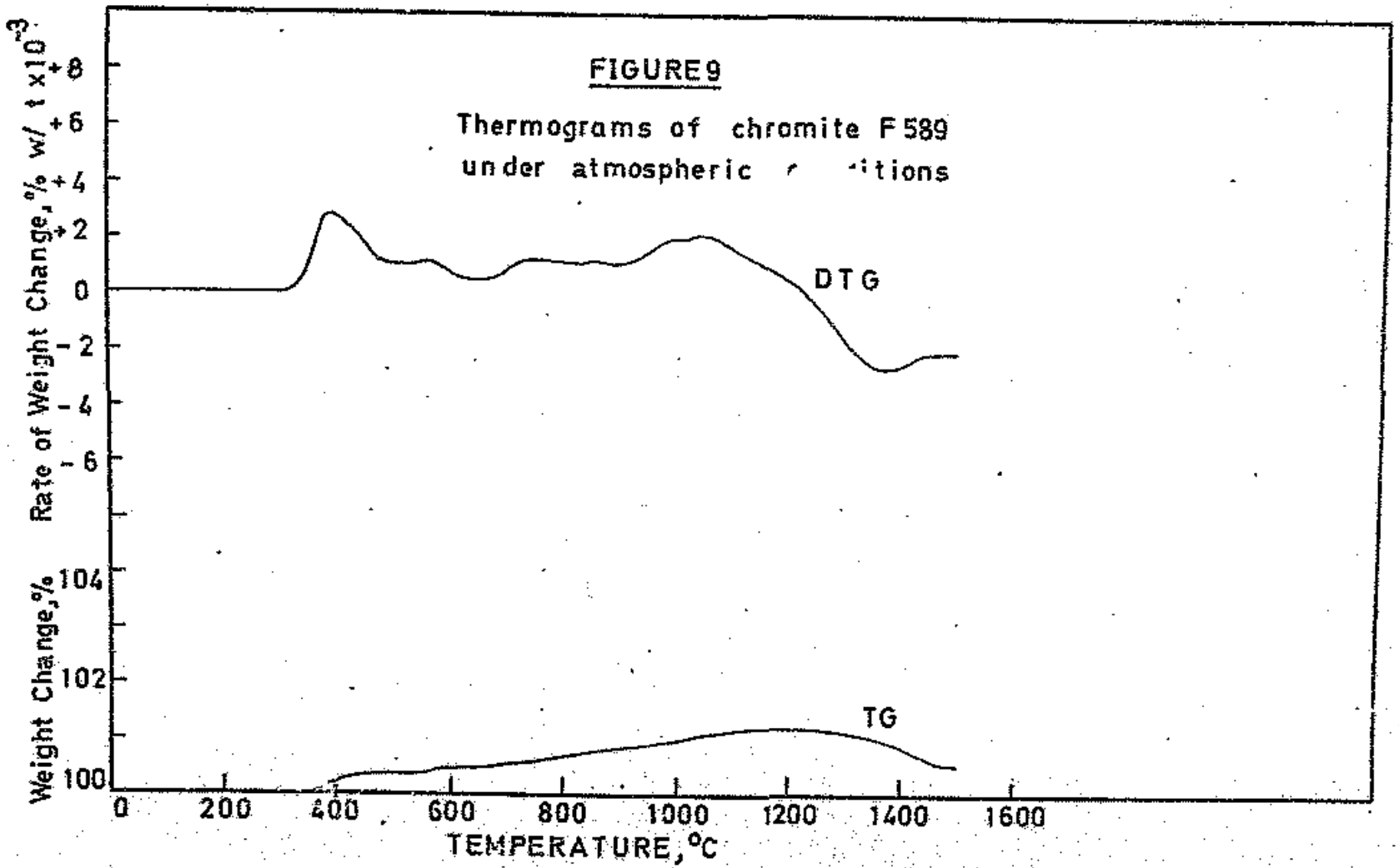


FIGURE 9

Thermograms of chromite F 589 under atmospheric conditions

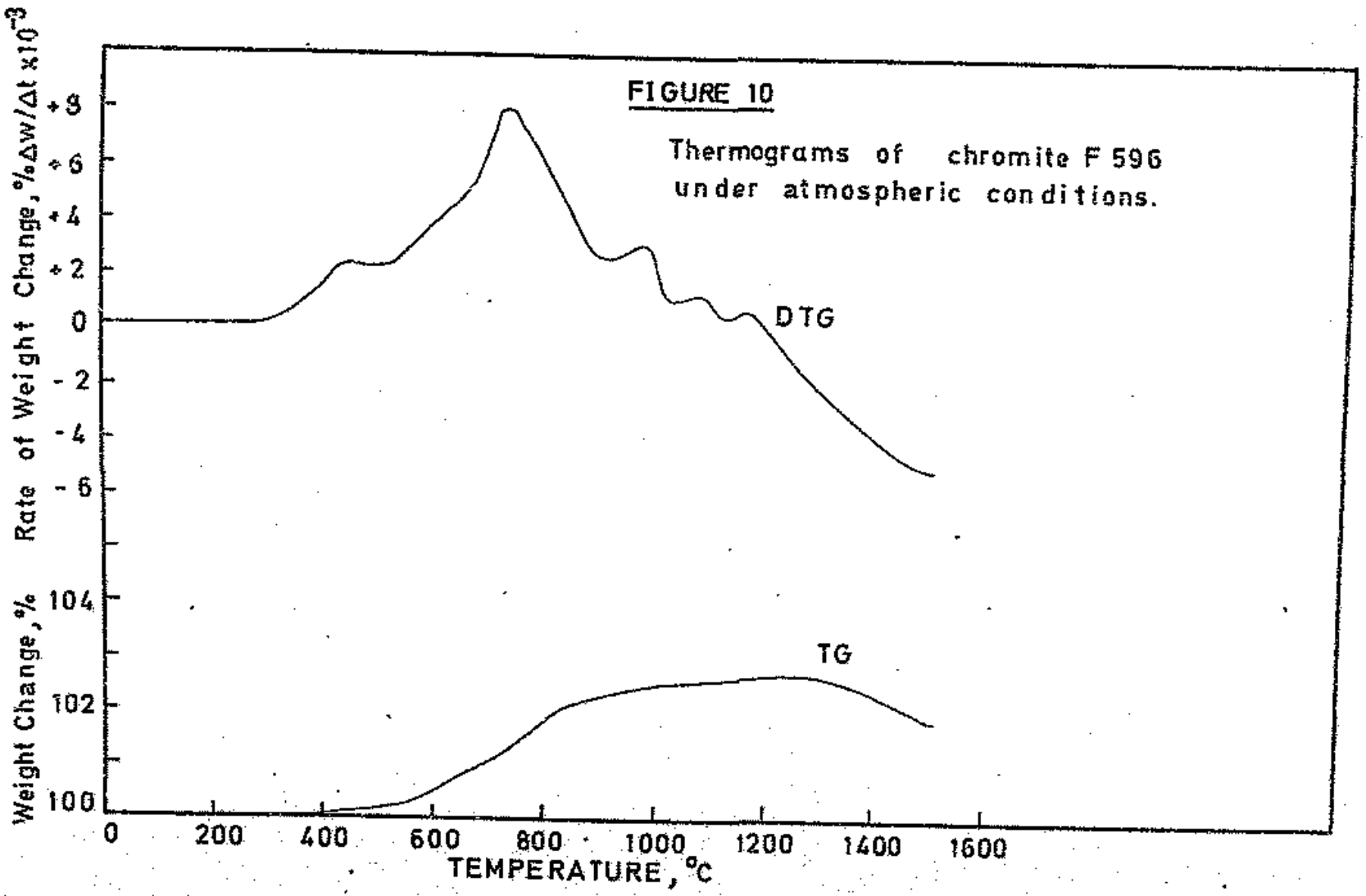


FIGURE 10

Thermograms of chromite F 596 under atmospheric conditions.

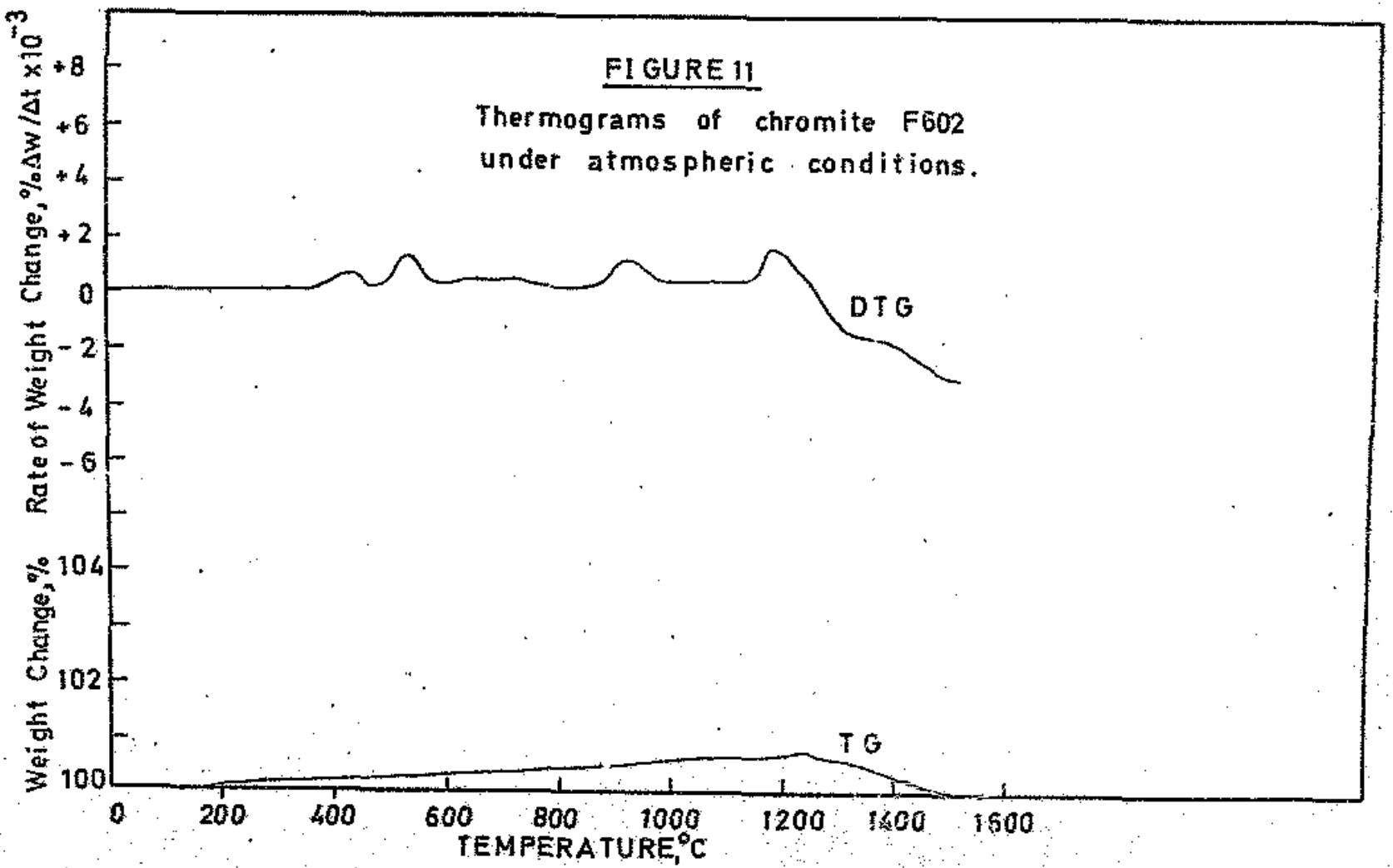


FIGURE 11

Thermograms of chromite F602 under atmospheric conditions.

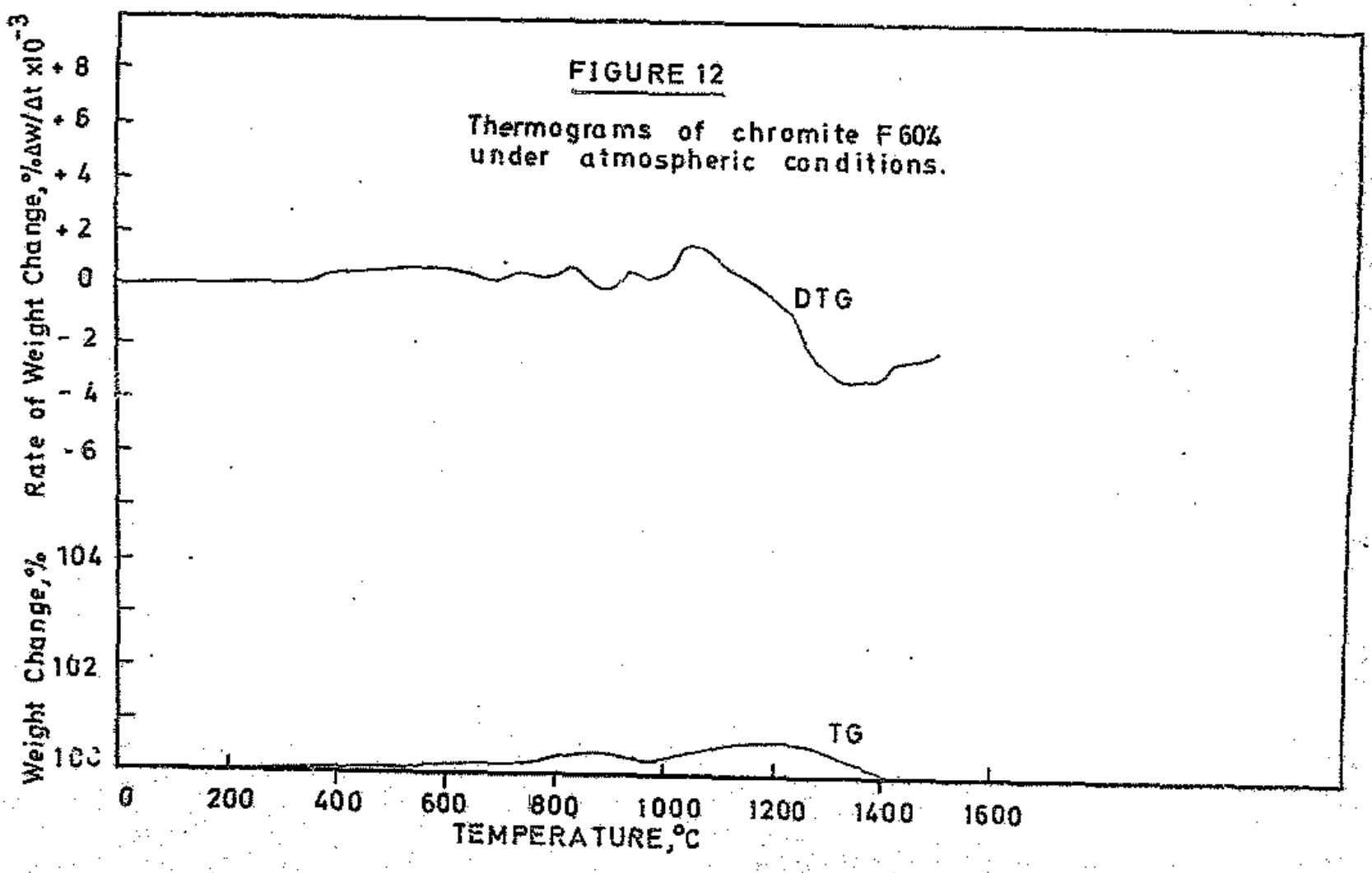


FIGURE 12

Thermograms of chromite F 60% under atmospheric conditions.

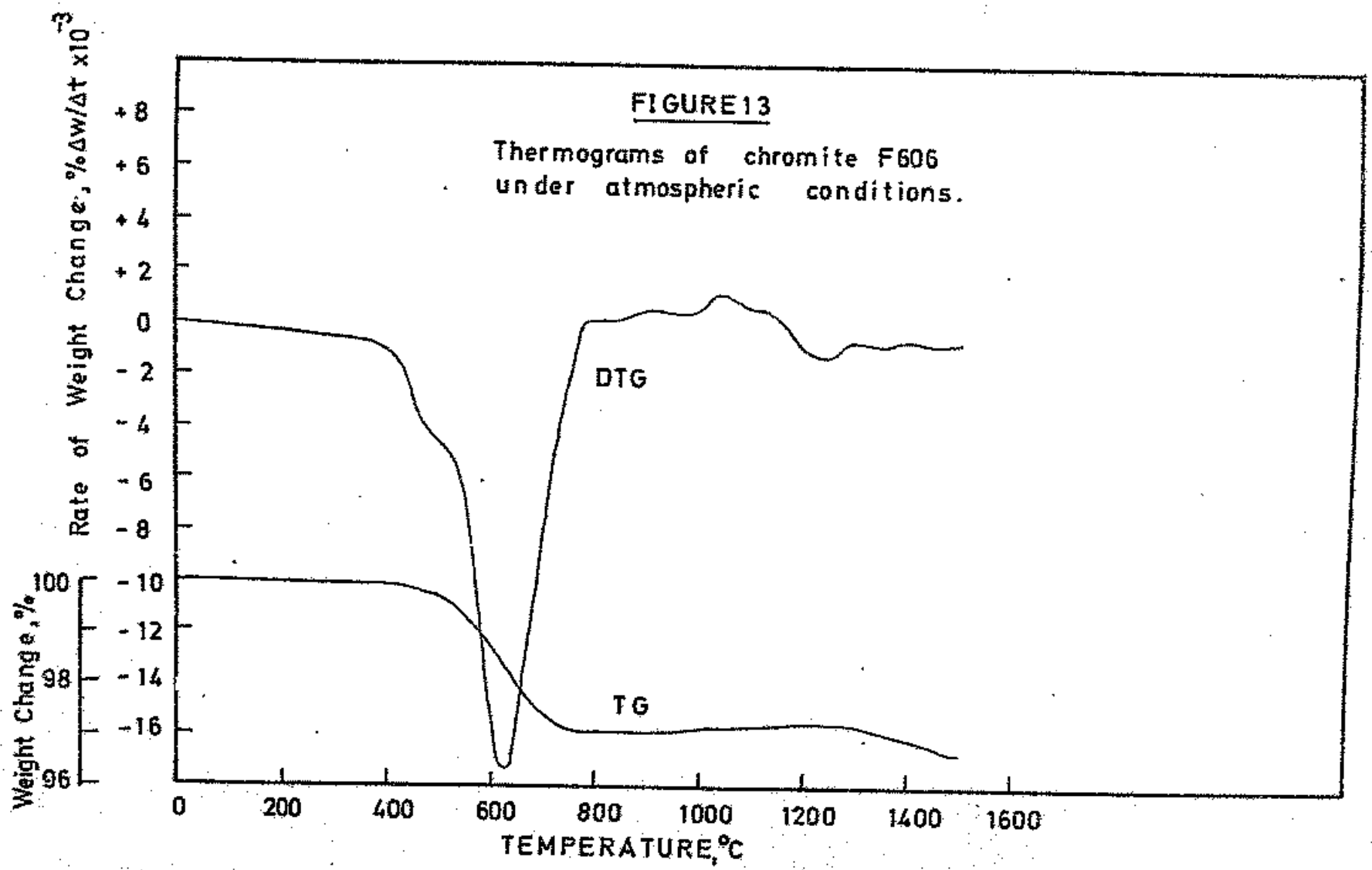


FIGURE 13

Thermograms of chromite F606 under atmospheric conditions.

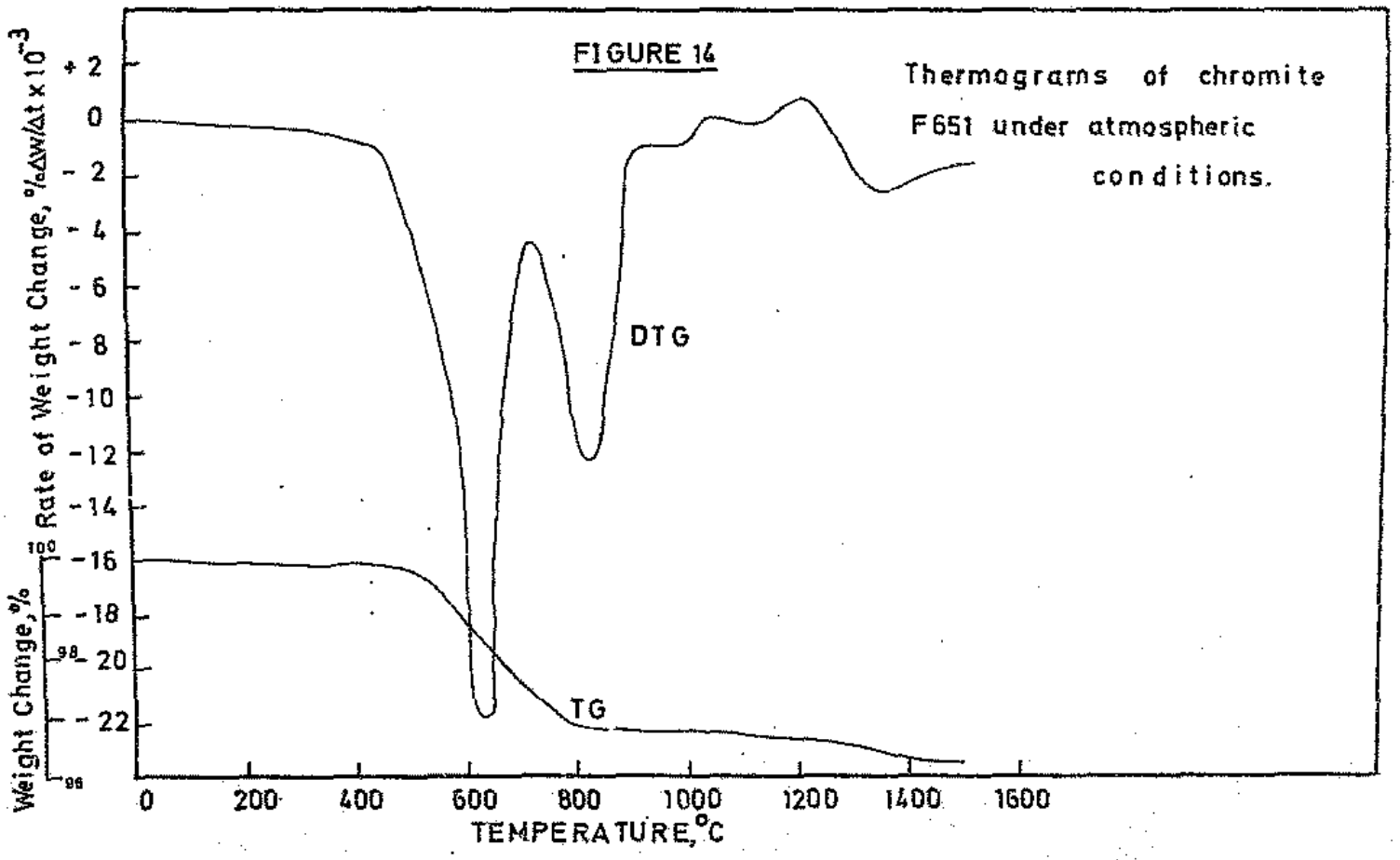


FIGURE 14

Thermograms of chromite F651 under atmospheric conditions.

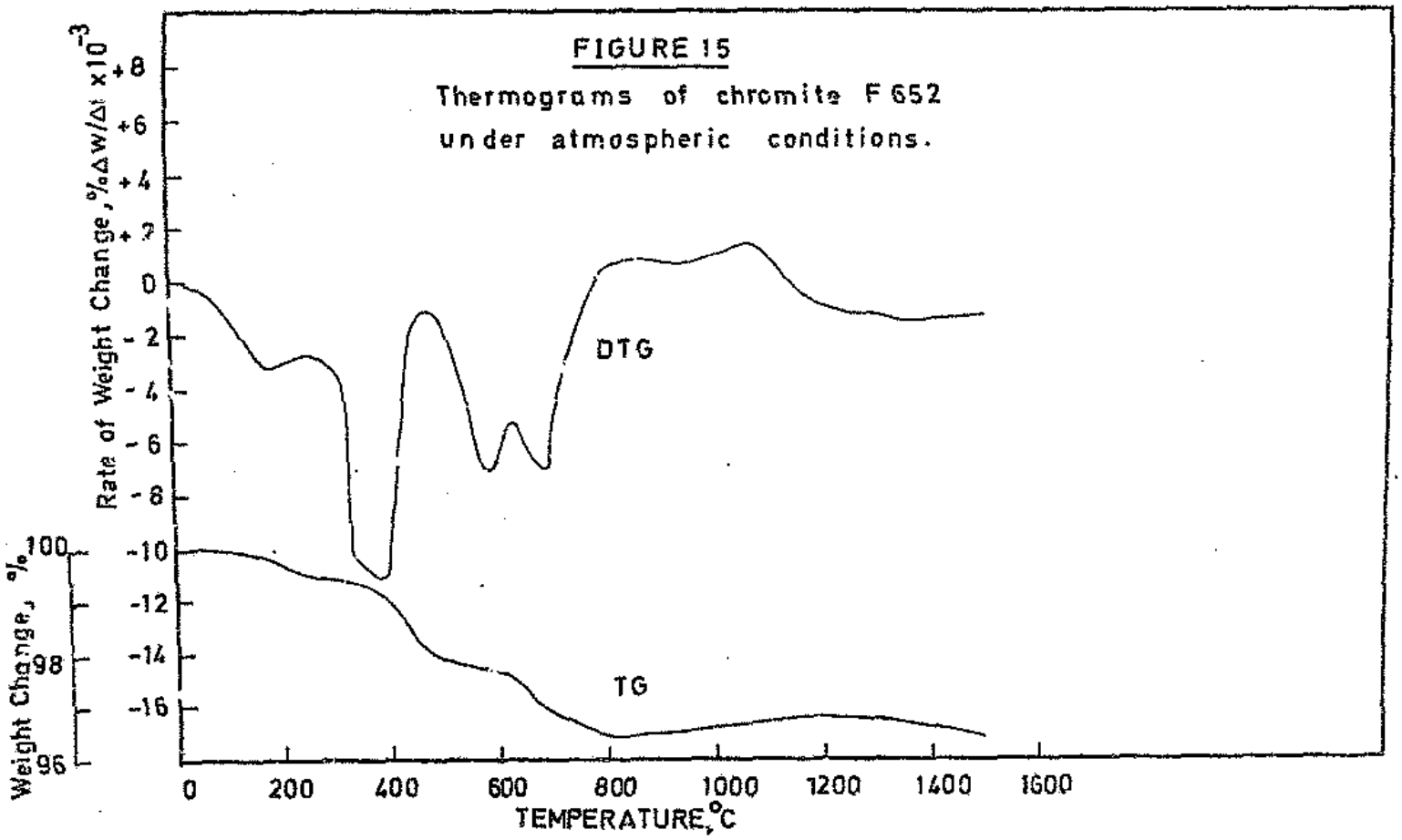


FIGURE 15

Thermograms of chromite F 652 under atmospheric conditions.

2.4 DISCUSSION OF TG RESULTS

The amounts of weight gained or lost by the various chromite ore samples can be tied up completely with the mineralogical nature of the chromite ore and moreover of the gangue in particular. Two comprehensive mineralogical reports covering South African chromites have been prepared by the Mineralogy Division of the National Institute for Metallurgy[3+4]. These results have been extremely helpful in characterising on the therm l balance each of the fourteen chromites with respect to its mineralogical nature.

Based on the data available, the fourteen selected chromites have been classed into four distinct groups:-

Group 1: Chromites which gain up to 2% weight and undergo no initial weight loss.

Group 2: Chromites which gain up to 1% weight and undergo no initial weight loss.

Group 3: The abnormal chromite which gains over 3% by weight and shows no initial weight loss.

Group 4: Chromites which have an initial overall weight loss at temperatures ranging from room temperature up to 1000°C.

A feature to be noted about all the chromite ores is that they showed a reversible weight loss reaction above 1200°C. The theory behind this reaction is discussed in a later section.

The reasons for the behaviour of these chromite ores and for their subsequent classification into these four groups can best be explained with the aid of the tables on the chromite ores given in the introduction. The abnormal chromite ore F596 is not shown in these tables since it was not investigated by the mineralogy division. It will, thus, be discussed separately since it is not actually a chromite ore but a magnetite rich in chromian sesqui oxide and ilmenite.

The overall controlling factor in the manner in which the various chromites behave can be attributed predominantly to the nature of the gangue minerals present in relation to the chromite spinel itself. Thus a high gangue/spinel ratio could indicate an overall weight loss if hydrated minerals, such as serpentines, chlorites and talcs, as well as micaceous minerals, are present. This weight loss is caused by the chemical water of hydration being driven off from the various gangue minerals in the temperature range 400°C up to 1000°C. Concurrently with this weight loss, however, it is noted that the spinel itself undergoes a gain in weight due to oxidation of the spinel.

These findings were all confirmed by carrying out tests on the thermal balance on separated fractions of gangue and chromite spinel.

The chromites which fall into the four groups are thus:-

<u>Group 1</u>: F524, F533, F539, F543, F582, F584, F588, F589
<u>Group 2</u>: F602, F604
<u>Group 3</u>: F596
<u>Group 4</u>: F606, F651, F652

The reasons for each of the chromites falling into one of these groups can be explained as follows:-

Group 1 chromites have relatively small amounts of hydrated minerals as can be seen in Table 3. Hence they show no overall weight loss in the temperature range 400°C up to 1000°C. They show, in fact, a weight gain due to the predominance of the oxidation reaction.

Group 2 chromites have a reasonably large content of hydrated minerals. Hence they show a relatively smaller weight gain than the chromites in Group 1.

The abnormal chromite ore of Group 3 behaves in a somewhat different manner from the above two groups. This behaviour of F596 ties in with the theory of the weight gain phenomenon of the chromite spinel in the temperature range 400°C up to 1200°C. The abnormal chromite ore undergoes the greatest weight gain. This results from the fact that it contains the largest proportion of FeO as can be seen from Table 2 of the analyses of the fourteen chromite ores. The abnormal chromite ore is not really a tightly bound spinel, since it is in fact not a chromite, and it can thus undergo oxidation more readily than the chromite spinel.

Group 4 chromite ores have large amounts of hydrated gangue minerals and this explains their tendency to show an initial overall weight loss in the temperature range 400°C to 1000°C.

The only feature, as was mentioned earlier, that is common to all the chromite ores is the weight loss reaction above 1200°C.

2.4.1. <u>The Theory of the Weight Loss Reactions from the Hydrated Gangue Minerals</u>

The chromite ores containing a reasonable amount of hydrated minerals are F602 and F604. The chromite ores containing large amounts of highly altered minerals are F606, F651 and F652. Peaks occurring in the range 630°C to 650°C, where no significant amount of carbonate are present, are indicative of serpentine. The behaviour of F602, which also contains serpentine, though in a lesser amount, is explained by the presence of talc. Chromite F651, according to the National Institute for Metallurgy mineralogical report, contains a large amount of carbonate in the form of magnesite and dolomite. This explains the broad peak in the temperature range 600°C to 700°C. The peaks shown in the temperature

range /...

range 410°C to 430°C and 780°C to 800°C in the graph for chromite F652 are most probably due to the chlorite minerals present. The small peaks superimposed on the weight gain parts of several of the TGA graphs are most probably due to the dehydroxylation of talc at temperatures around 1000°C.

Information relating to the thermal behaviour of the gangue minerals associated with the chromites, such as talc, chlorite and serpentine, is given in R.C. Mackenzie's book on differential thermal analysis(Ref.18). This information bears out the suggestion advanced above relating to dehydration (dehydroxylation) and evolution of CO_2.

2.4.2. <u>The Theory of the Weight Gain Reaction due to Spinel Oxidation</u>

It was determined in 1939 that, during the heating of chromite in air and oxygen, the FeO in the chrome spinel oxidises readily, though not completely, to Fe_2O_3(12) as described in section 1.5.2.

As mentioned earlier, Kariakin and Piatikop(Ref.14) identified both haematite and magnetite in the chromite spinel in Kempirsai chromite ores that had been heated up to 1400°K.

The South African chromites showed a weight gain starting from temperatures in the range 350°C to 400°C. They reached a peak in weight gain in the range 1150°C to 1200°C. This weight gain was shown by all fourteen chosen chromites once they had been separated from their gangues, and by the unseparated chromites as well in the cases where the gangue minerals did not undergo dehydration.

It can be concluded that these results for South African chromites indicate a reaction similar to those observed by Kariakin and Piatikop[Ref.14] in their Russian chromites.
In fact X-ray investigations of the heated chromites confirmed this conclusion by establishing the presence of free Fe_2O_3 in chromites which had been heated and slowly cooled, since these chromites have more Fe_2O_3 in their spinel structure than the Russian ores. This meant that no Fe_2O_3 needed to be added to observe similar results to those observed by the two Russian scientists.

A feature closely associated with this oxidation weight gain reaction is a weight loss reaction which commences at about 1150°C to 1200°C. This reaction is due to a de-oxidation of the iron oxide Fe_2O_3 due to its instability.

The partial pressure of oxygen in the environment of the spinel exceeds atmospheric pressure above this temperature (1150°C to 1200°C) and hence the Fe_2O_3 starts to lose oxygen.

V.V. Goncharov and E.A. Prokoféva[Ref.15] have drawn up a series of reactions to give a general idea of the phase changes occurring in a chromite in an oxidizing medium. These reactions are:-

Chrome Spinel $\xrightarrow{400^\circ C - 1100^\circ C}$ MgO Enriched Chromium Spinel $+R_2O_3$ phase $\underset{\longleftarrow}{\xrightarrow{1200^\circ C\ 1400^\circ C}}$ Solid solution of Chromium Spinel with R_2O_3 (in the presence of excess R_2O_3 with respect to $RO.R_2O_3$)

$\xrightarrow{1500^\circ C}$ Chrome Spinel approaching $RO.R_2O_3$

2.5 CONCLUSION

It is apparent that the gangue minerals in a particular chromite are a key factor in determining the shape of the thermogravimetric curve. The minerals such as serpentine, chlorite and carbonaceous minerals are the most important in determining the overall shape of the thermogravimetric curve. The iron oxide content can also play a role in determining the shape of the curve as shown especially by the abnormal chromite.

The fourteen chromite ores have thus been successfully classified into the four groups and, even if these groups seem arbitrary, it must be remembered that generally speaking the chromites would tend to move gradually from one group to another depending on their mineralogical composition. It is also gratifying to observe the complete tie-up between the mineralogical composition of a particular chromite and its behaviour on the thermal balance.

CHAPTER III

3. THE BEHAVIOUR OF CHROMITE UNDER REDUCING CONDITIONS USING POWDERED CARBON AS A REDUCTANT WITH AN ARGON ATMOSPHERE

3.1 INTRODUCTION

The study of the fourteen chromite ores under atmospheric conditions having been completed, the next logical step was the study of the fourteen chromites under reducing conditions. For the first phase of this investigation the reductant was chosen as solid powdered carbon. In the submerged arc furnace coke, or another form of carbon, is charged as a reducing agent. It is therefore of great interest to examine in what manner this carbon acts upon the chromite to form the mixed carbide of iron and chromium.

From work carried out in this field by Boericke and Bangert(Ref.20) a set of equations for chromite reduction has been established. The reduction of the ion oxides in the chromite was their primary concern. Consider the following equations where the chromite formula has been simplified to $FeO.Cr_2O_3$:-

$$FeO.Cr_2O_3 + C = Fe + Cr_2O_3 + CO \quad \ldots (1)$$
$$FeO.Cr_2O_3 + C = Fe + Cr_2O_3 + CO \quad \ldots (2)$$
$$FeO.Cr_2O_3 + {}^4/_3C = {}^1/_3Fe_cC + Cr_2O_3 + CO \quad \ldots (3)$$
$$FeO.Cr_2O_3 + CO = Fe + Cr_2O_3 + CO_2 \quad \ldots (4)$$

Reactions (1) - (3) show the reduction of $FeO.Cr_2O_3$ by solid carbon and reaction (4) shows the reduction by CO. Reactions (1), (2) and (3) have been evaluated on a thermodynamic basis and are potentially effective above 1220°K. Reaction (3), however, takes preference over (1) and (2) and the formation of iron carbide invariably occurs at temperatures about 1200°K.

Although it seems feasible that reaction (4) might be just as likely to occur as reactions (1), (2) and (3), this is not the case. This aspect is dealt with in the section dealing with CO reduction behaviour.

This iron oxide can form either the carbide or the metal th carbon. The carbide is known to form preferentially, however, from Cr_2O_3. Consider the two possible reactions:-

$$Cr_2O_3 + \frac{27}{7}\ C = \frac{2}{7}\ Cr_7C_3 + 3CO$$

$$\Delta G_T = 182,980 - 130,52\ T\ cal/mole$$

and

$$Cr_2O_3 + 3C = 2Cr + 3CO$$

$$\Delta G_T = 195,510 - 129,17\ T\ cal/mole$$

For thermodynamic considerations by putting $\Delta G_T = 0$ it can be seen that the carbide will form at a lower temperature than the metal. Its formation is therefore more favourable. (See Figure 5 in the final Chapter). The rates at which these reactions take place during the reduction of chromite ores and the kinetics and mechanism at various temperatures have not been investigated for the Transvaal chromites. It is this lack of fundamental knowledge that prompted this phase of the project.

The thermal balance was once more chosen as the most suitable apparatus for studying reaction rates with time and temperature as the variables. The thermal balance had firstly to be modified for gas atmosphere control. This was achieved using the Stanton gas attachment kit for upward gas flow.

One of the many reasons for deciding upon thermogravimetry was based upon the literature and especially on a paper on the "Kinetics and Mechanism of Ilmenite Reduction with Graphite"(Ref.21). A parallel was drawn between the approach used to study the reduction behaviour of ilmenite and the chromite ores. In this paper on Ilmenite reduction it is shown how, by using the thermal balance as the main instrument of research, a great deal of information about the kinetics and reduction mechanism can be found. Thus virtually the whole of this study is based on the thermogravimetric graphs and data obtained from the various chromites

under reducing /...

under reducing conditions, using an inert argon atmosphere for protection of the sample from oxidation.

3.2 EQUIPMENT

3.2.1. Modifications to the Stanton Thermal Balance for Gas Atmosphere Control

In order to carry out the tests involving the reduction of chromite ore, it was necessary to modify the thermal balance for atmosphere control. The new arrangement was designed for the upward flow of the gas to be used either as an inert blanket or as a reducing medium. The additional equipment required was a suitable sheath, a flow meter, a water-cooled gas flange and the necessary "O" ring seals. The whole gas attachment was purchased as a kit and assembled and installed once the runs under atmospheric conditions had been completed.

According to the manufacturers the kit could ensure a very good gas atmosphere control. It was quoted that with an argon gas flow in at the bottom entry port of about 500 ml/min, and from the top exit port of 300 ml/min, it is possible to reduce the oxidation of carbon from 7 mg/5 min to 0,1 mg/5 min for a sample weight of 100 mg at 800°C. Furthermore this arrangement was considered suitable for CO. The apparatus was tested for leaks and subsequently the runs were begun.

3.3 EXPERIMENTAL METHODS

3.3.1. Sample Preparation

The same mesh size (namely -325#) was chosen for this phase of the project as had been used for the runs under atmospheric conditions. A sample weight of 500 mg was used in all the runs concerned with chromite reduction. Runs were carried out with fluxing additions and solid powdered carbon. Pure components were chosen

in order /...

in order to minimize any possible complications that might have been incurred had the addition of the fluxes commonly used on a ferro-alloy plant been added. The reduction and fusion process was considered to go to completion for calculation purposes. The composition of this final slag was fixed at:-

30 per cent SiO_2	MgO/Al_2O_3	1 : 1
2,5 per cent CaO	Slag/metal	1 : 1

The resultant metal phase was fixed as well, namely 6 per cent carbon and 2 per cent silicon. These values for slag metal composition are representative of the reaction products from an average submerged arc furnace producing high-carbon ferrochromium. A model calculation for the necessary slag forming fluxing additions for chromite F 533 is given in the appendix.

3.3.2. Continuous Runs

Four chromites were selected for continuous runs on the thermal balance. These were F 524, F 533, F 602 and F 652. They were chosen to represent the three major groups as classified in the previous chapter. Two chromites, namely F 524 and F 533, were selected from the largest group. A -325# fraction of all four chromites was used for these continuous runs on the thermal balance. 500 mg of chromite was weighed into a mixing bottle and an excess of powdered carbon was added. The carbon used for all the experiments was Le Carbone spectrographic carbon of the following specifications:-

Code No. 207-16175 Ref. No. 9901
Mesh size = 75 per cent -200#
Ash - less than 20 ppm

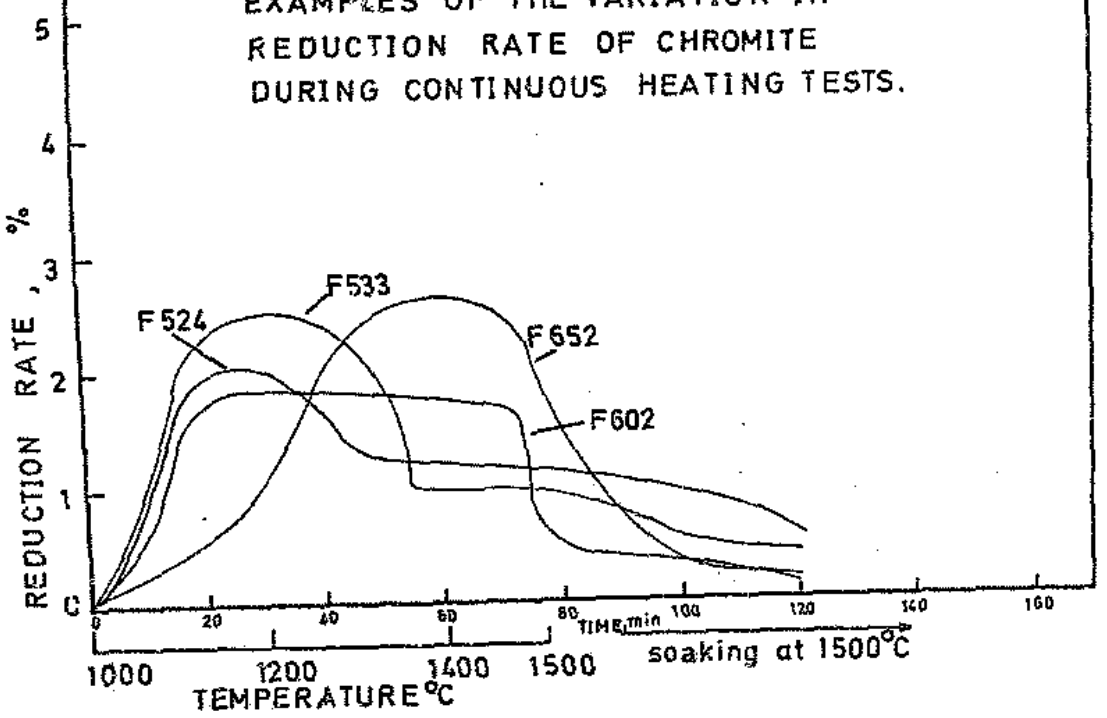
The excess carbon added amounted to fifty percent excess over the stoichiometric carbon requirement for complete reduction of the chromite to form the specified alloy.

After thorough mixing the sample was placed in a mini alumina crucible of the following dimensions: 17.0 mm in diameter and 17.5 mm in height. The crucible plus contents was then placed on the sample pedestal in the thermal balance. The furnace assembly was lowered over the sample and the heating cycle begun. The sample was heated at 6, 7°C/minute from room temperature up to 1550°C. This completed a continuous run. Tests were carried out with each of the four chromites plus excess carbon in the manner discussed above. Only one chromite was, however, chosen for runs with the fluxing additions as well as carbon. This was chromite F 533.

The resultant thermogravimetric graphs were read in the normal manner and are presented in Figures 16 and 17. A blank run with carbon only showed that the weight loss due to oxidation of the carbon was negligible.

FIGURE 16

EXAMPLES OF THE VARIATION IN REDUCTION RATE OF CHROMITE DURING CONTINUOUS HEATING TESTS.



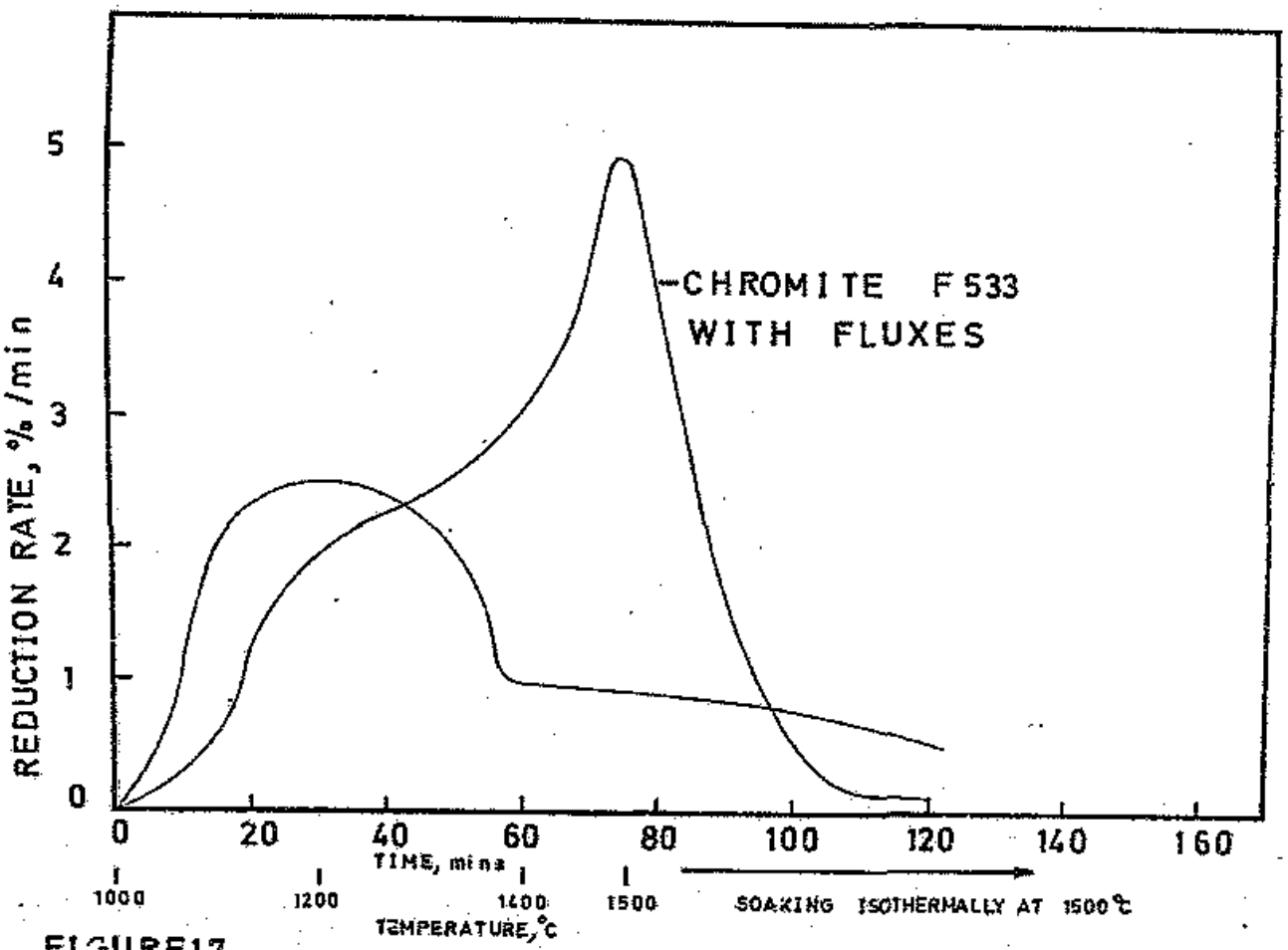


FIGURE17

The effect of fluxing additions on the reduction rate of chromite F 533 during continuous heating from room temperature to 1500 °C.

3.4 DISCUSSION OF THE CONTINUOUS RUNS

Figure 16 shows the various rates of reduction curves plotted for the four chosen chromite ores. The variation of rate of chromite reduction with time and temperature is illustrated by these graphs. The shift in the peak of the curves from left to right is attributable to an increase in the Cr/Fe ratio in the chromite ores. Since Cr_2O_3 is known to reduce at higher temperatures than the oxides of iron, this trend of maximum reduction rate to the higher temperatures is not at all surprising.

An important finding resulted from these continuous tests. This was the fact that reduction over the theoretical 100 per cent occurred. Percent reduction relates to the oxygen loss of the reducible oxides of Fe and Cr divided by the total theoretical oxygen content of these reducible oxides. Its definition is:-

$$\text{Present reduction} = \frac{\text{Weight loss of chromite at time t}}{\text{Possible weight loss for total reduction of Fe and Cr oxides}} \times 100$$

Rate of reduction is defined as:-

$$\frac{d(Cr_2O_3.FeO)}{dt} = \frac{\%(Cr_2O_3.FeO)\text{ reduced at time t} - \%(Cr_2O_3.FeO)\text{ reduced at time (t-n)}}{\text{n (mins)}}$$

The fact that the weight loss was greater than that for the theoretical 100 per cent reduction, when considering only the oxides of Cr and Fe as being reducible, was due to the fact that if excess carbon is present, SiO_2 will reduce as well. Where no fluxing additions were made, only slightly greater values than 100 per cent were noted. This must have been due to the small amounts of silica in the gangue, ranging from 1,2 up to 3,3 per cent, being reduced. Where fluxing additions were made, a much greater degree of reduction took place, 114 per cent as compared to 104 per cent where no fluxes were added. This increased degree in reduction can be explained by the fact that about 12 per cent extra SiO_2 was added as a fluxing component.

On reducing, the SiO_2 forms several products including SiO, Si and SiC.[22] If SiO is formed, it leaves the system in vapour form. Both Si and SiC, however, can dissolve in the alloy, giving a ferrochromium silicide rather than high-carbon ferrochromium as the reaction product.

It seems more likely that SiO was formed since the weight loss incurred reflects most of the SiO_2 leaving the system. The reactions involved are discussed as follows[Ref.23]:-

$$SiO_2\ (\alpha\ \text{quartz}) + C(S) = CO(g) + SiO(g)$$
$$\Delta G_T^{\circ} = +\ 160{,}230 - 78{,}27T\ \text{cal/g mole}$$

$$SiO_2\ (\alpha\ \text{quartz}) + 3C = SiC(s) + 2CO(g)$$
$$\Delta G_T^{\circ} = +\ 143{,}480 - 79{,}56T\ \text{cal/g mole}$$

Although the above thermodynamics show the formation of SiO to be more favourable, it is very possible that the kinetics and presence of other materials in the chromite might alter this thermodynamic viewpoint. It is quite possible therefore that SiO is formed.

A test run was carried out using pure SiO_2 excess carbon. The SiO_2 reduced quite rapidly in the temperature range 1450°C to 1550°C.

These findings necessitated a completely new approach to this whole question of carbon addition, since carbon in excess had been found to alter the process.

The graph, showing a comparison between the reduction rate during the continuous heating of chromite F 533 both with and without fluxes (see Figure 17), illustrates how the SiO_2 starts reducing near 1400°C, increasing the overall reduction rate. The slower start of the reduction process with fluxing additions is due to the fluxes reducing the effective ratio of the surface areas between chromite and carbon. This is, however, only a minor effect.

3.5 STOICHIOMETRIC CARBON

The amount of carbon added to a particular chromite can affect the nature of the reduction product. It has been shown how excess carbon will result in the reduction of SiO_2 to form SiO, SiC and Si. This tendency would result in an excess of Si in the metal, forming a ferrochromium silicide alloy instead of high carbon ferrochromium.

The composition of the alloy to be produced was fixed at 6 per cent carbon and 2 per cent Si. Thus only enough carbon should be added to reduce the metal oxides and to form this chosen alloy. Hence for all further tests involving carbon, only the stoichiometric amount of carbon was to be added. A stoichiometric amount of carbon is defined in this case as the quantity of carbon needed to reduce the oxides of Fe and Cr completely and to form an alloy containing 6 per cent carbon and 2 per cent silicon.

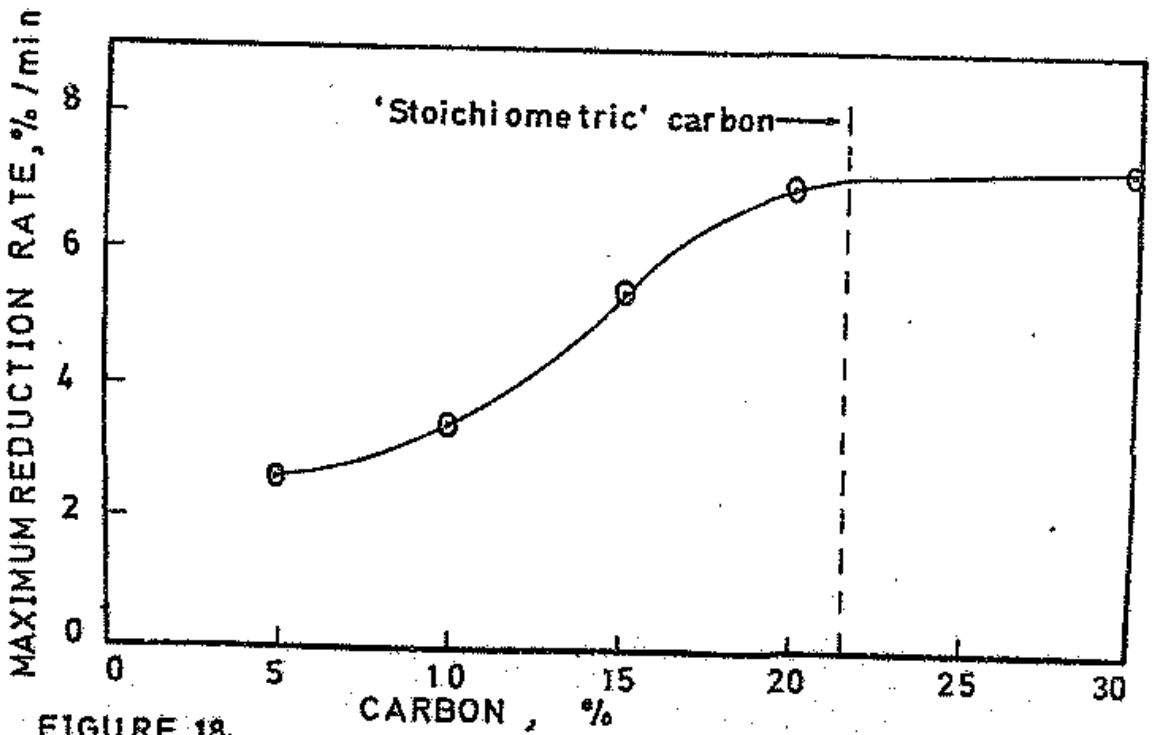


FIGURE 18

The effect of variations in the carbon additions on the reduction rate of chromite F533 at 1300°C.

3.6 ISOTHERMAL RUNS

Runs were carried out on all fourteen chromites at the -325 mesh size. These runs were done at four different isothermal levels, namely, 1200°C, 1300°C, 1400°C and 1500°C. Each chromite sample was weighed into a mixing bottle and the stoichiometric carbon addition was made. After thorough mixing the sample was placed in a mini alumina crucible which was placed on the sample pedestal in the thermal balance.

The furnace, which had been heated to the required temperature level, was subsequently lowered over the sample, which had previously been counter-balanced in the usual manner. In this way each of the runs was started. Blank runs using carbon powder only were also carried out in order to assess the rate of carbon oxidation. The temperature of the heating zone of the furnace was checked prior to lowering the furnace before each run in order to ensure that the zine in which the sample would rest was at the chosen temperature level.

Thus four thermogravimetric graphs were obtained for each of the fourteen chromites at the chosen isothermal levels. From these graphs the amount of weight lost in mg was read off at varying intervals of between five minutes and one minute.

The time interval chosen was dependent on the rate of weight loss. In other words chromites which underwent rapid weight losses were read off at minute intervals, whereas those chromites losing weight at slower rates were read off at five minute intervals.

A series of runs at four isothermal temperature levels was also carried out using chromite F 533 plus fluxes plus stoichiometric carbon. The temperatures used were 1280°C, 1300°C, 1400°C and 1500°C. The reason for using 1280°C instead of 1200°C is discussed at a later stage.

To ensure that as representative a study as possible could be carried out, several precautions were taken:-

1. Kinetic studies were carried out under identical conditions of heating rate, isothermal temperature level, argon flow rate and the method of mixing the powdered carbon and chromite.

2. The temperature was measured at the point in the furnace where the sample was placed, and, to minimize thermal gradients, the samples were heated at a slow rate for the continuous runs.

3.7 THE RESULTS FOR THE ISOTHERMAL RUNS

The method of evaluating the results was similar to that used for evaluating the results for the atmospheric conditions. The values of weight were read off from the thermal balance chart at various time intervals depending on the reduction rate. These weight readings were used to calculate the weight increments and hence the cumulative weight change. Finally the percent reduction was calculated from this cumulative weight change value. The results are to be found in Figures 19 to 32.

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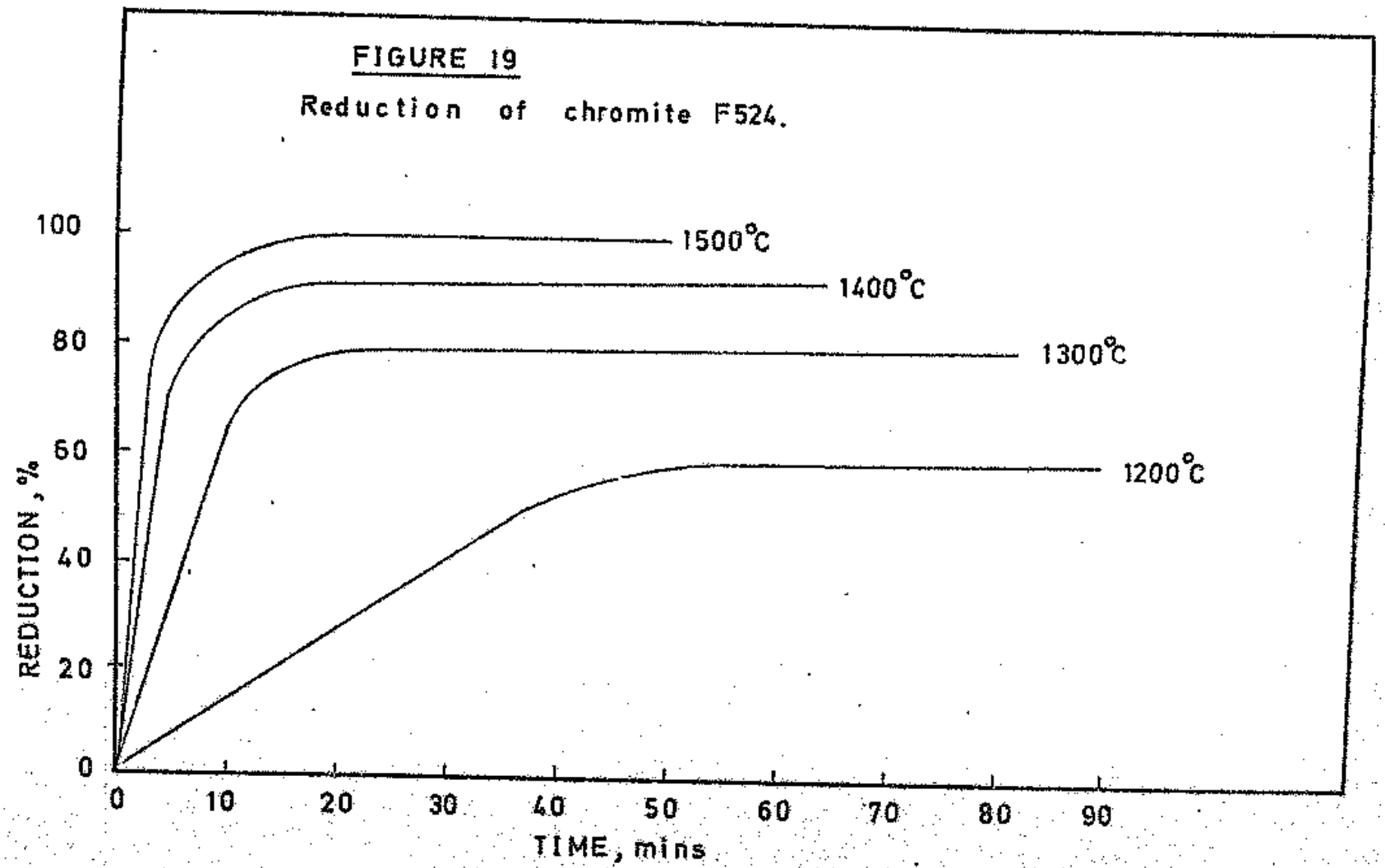


FIGURE 19

Reduction of chromite F524.

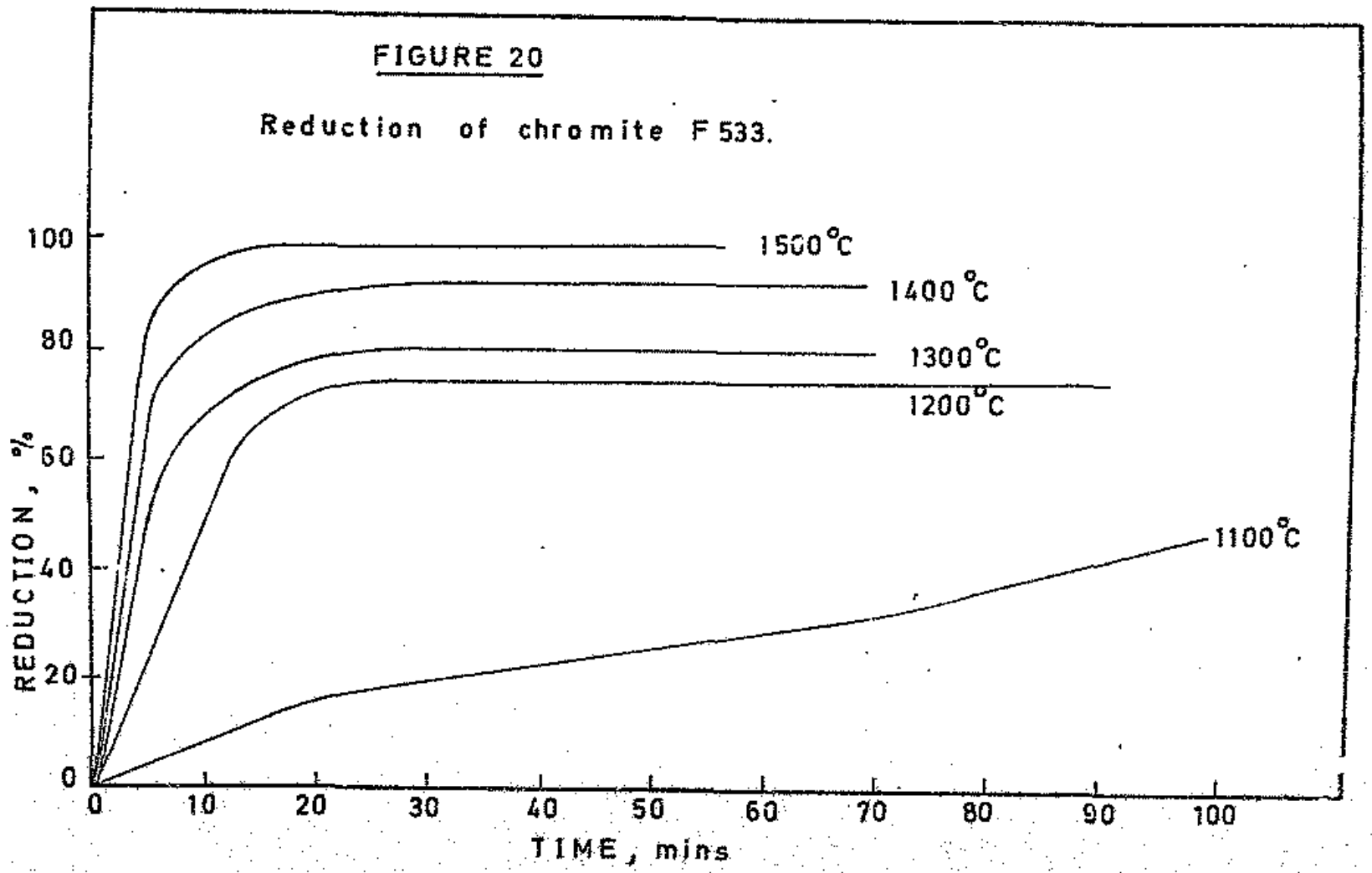


FIGURE 20
Reduction of chromite F 533.
1500°C
1400°C
1300°C
1200°C
1100°C
REDUCTION, %
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
100
TIME, mins

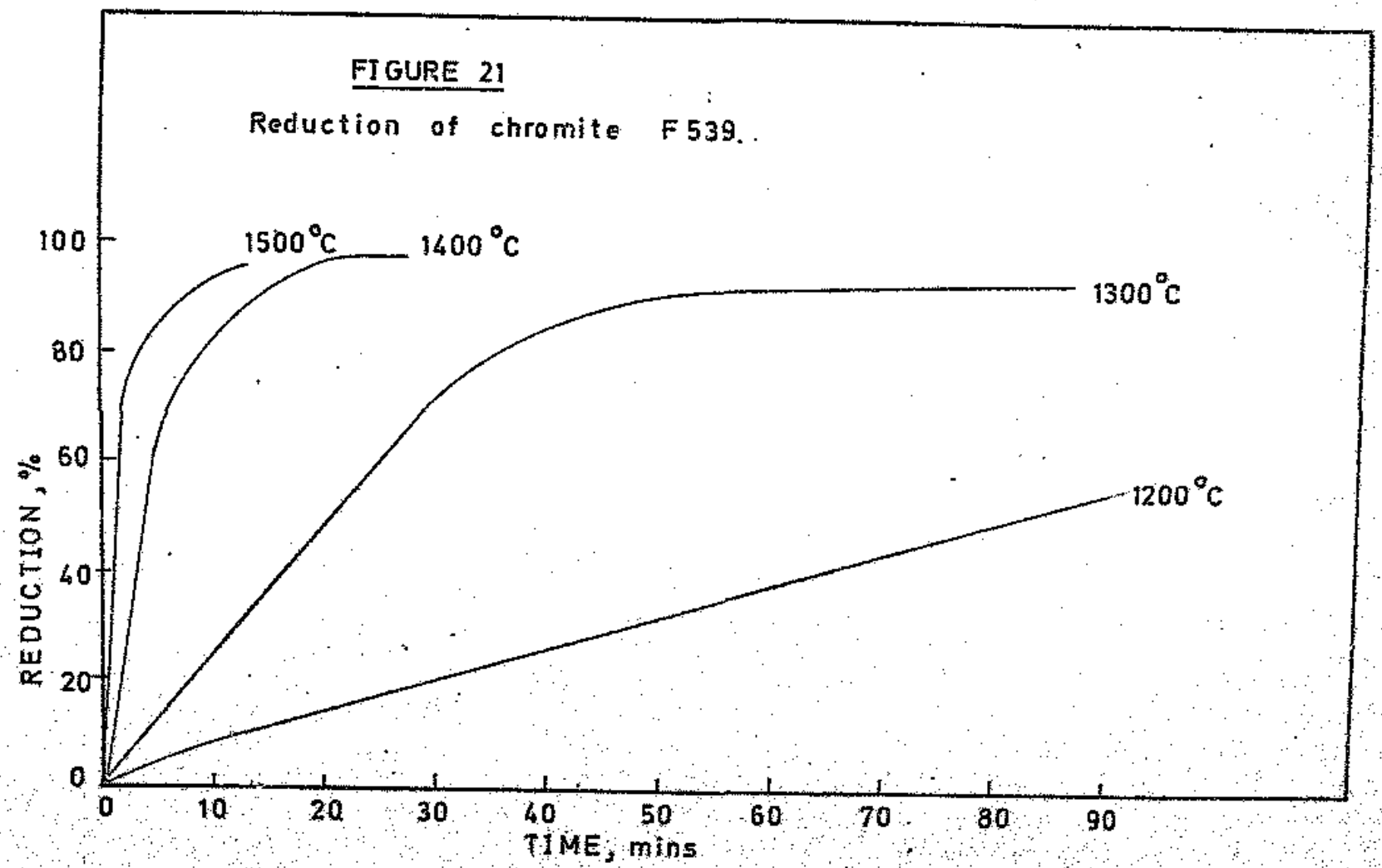


FIGURE 21

Reduction of chromite F 539.

FIGURE 22

Reduction of chromite F 543.

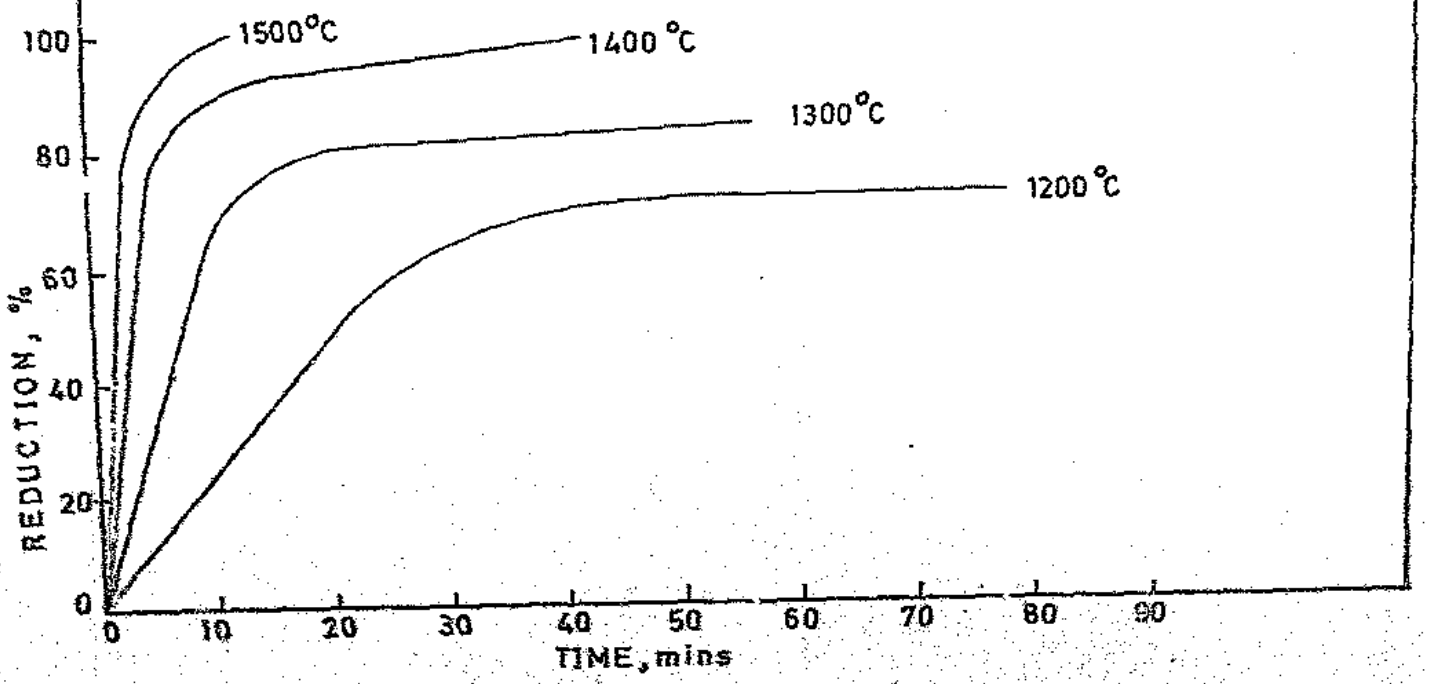
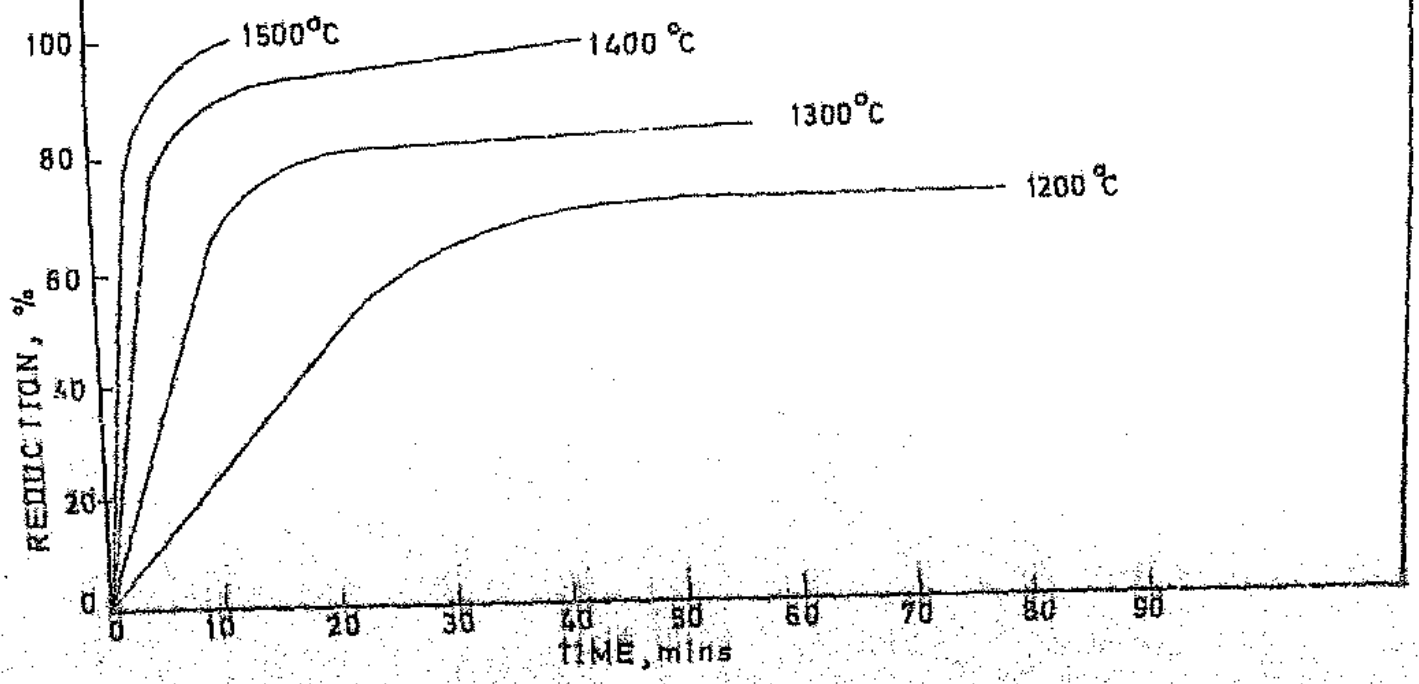


FIGURE 22

Reduction of chromite F 543.



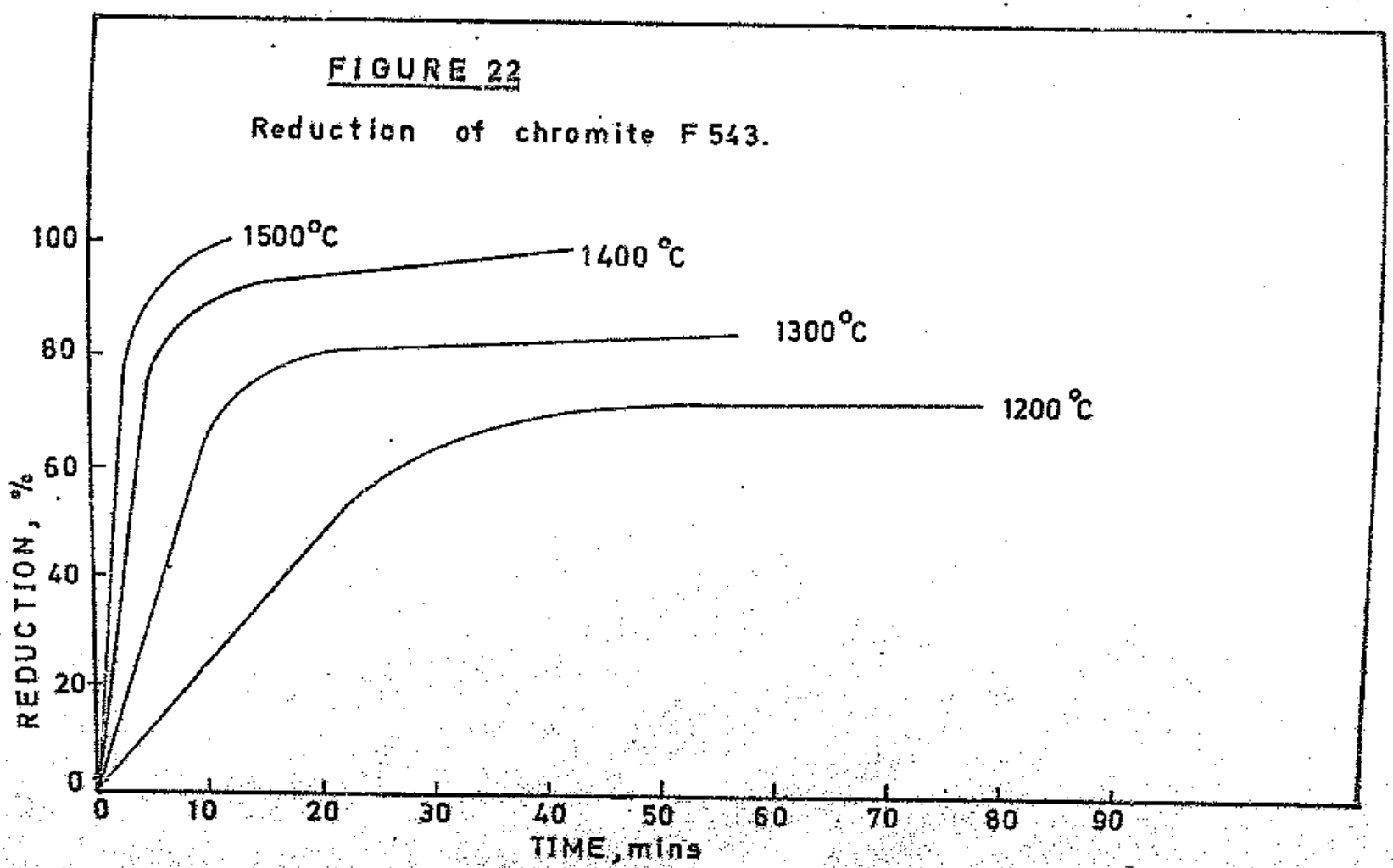


FIGURE 22

Reduction of chromite F 543.

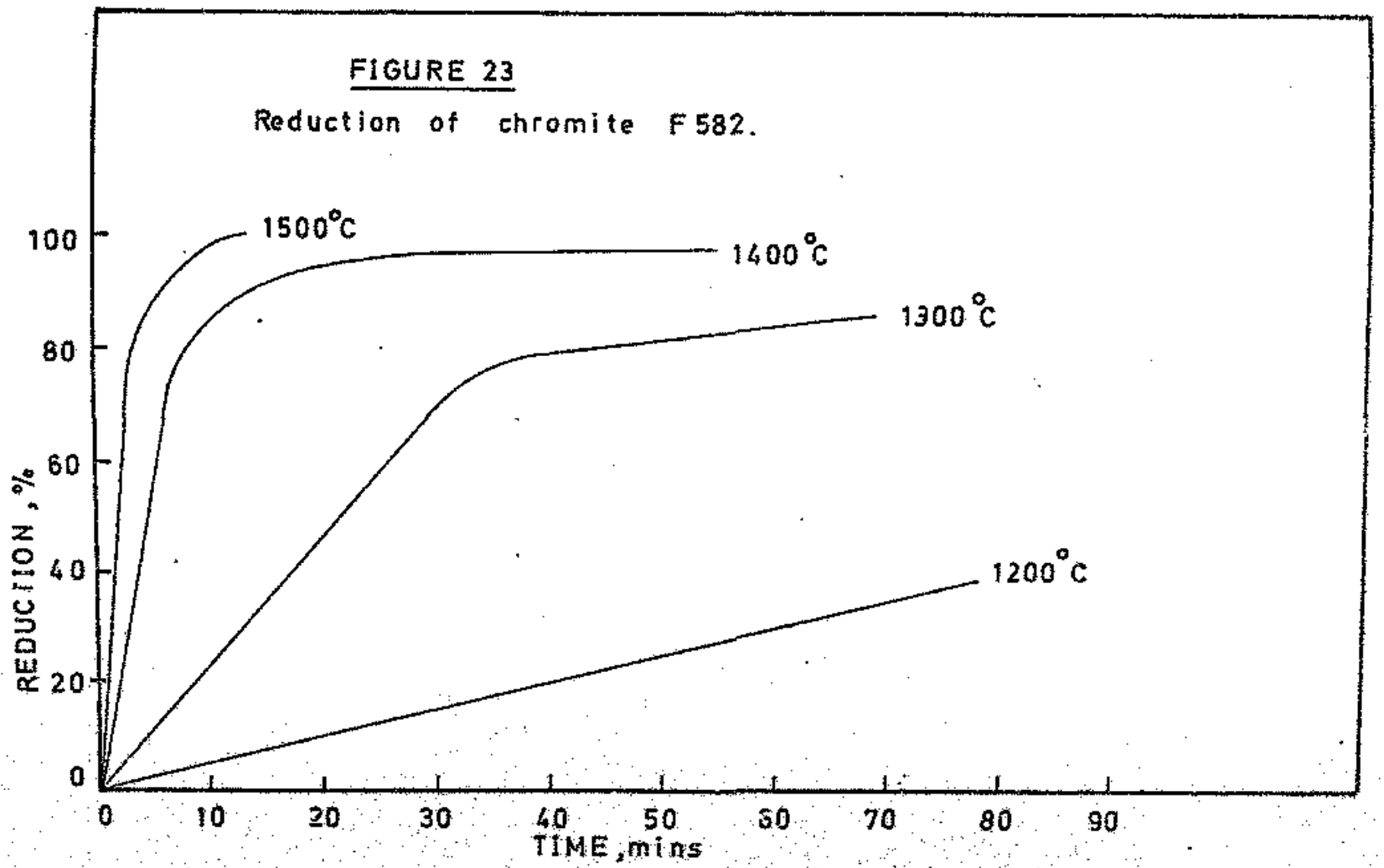


FIGURE 23

Reduction of chromite F 582.

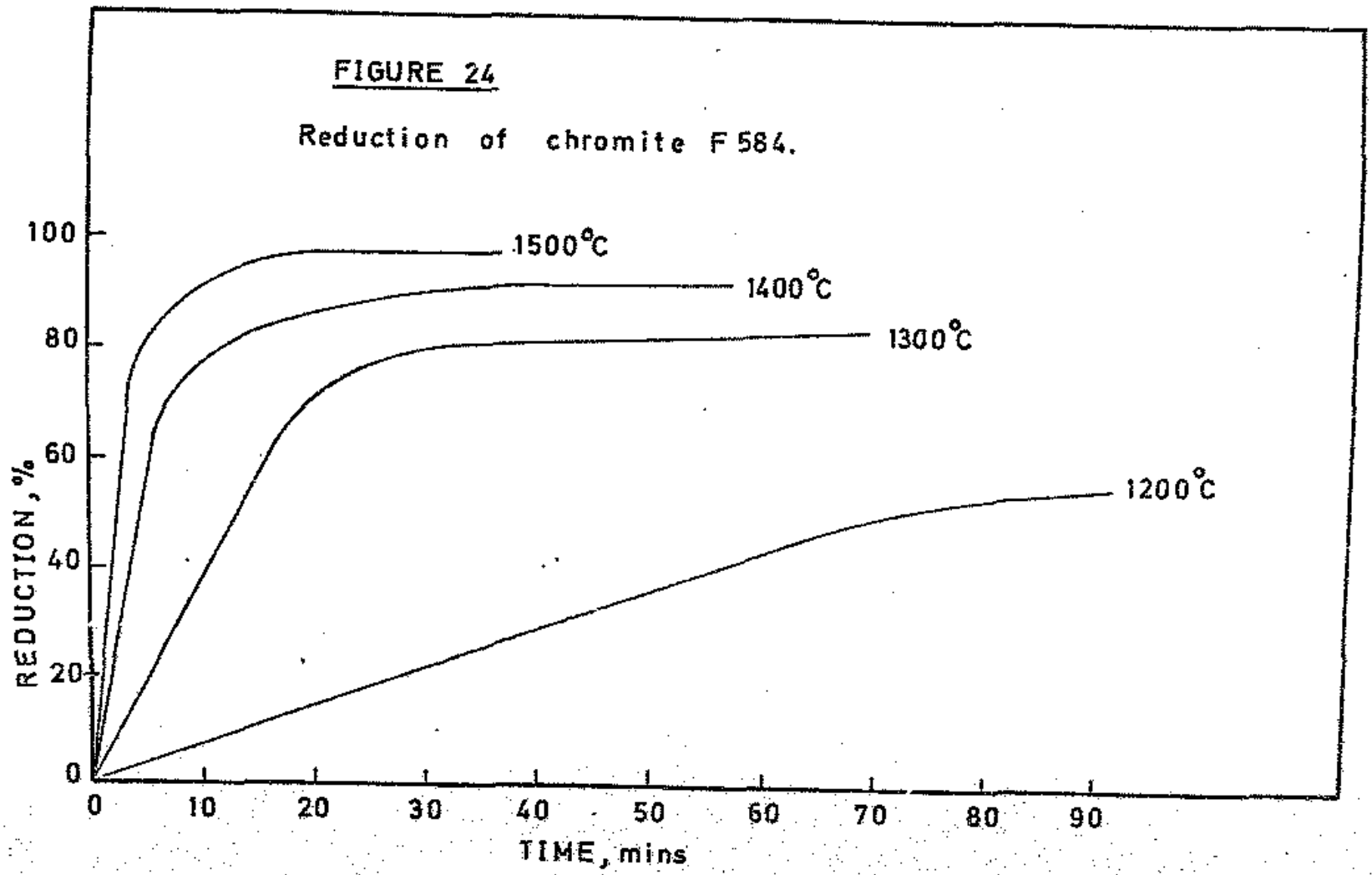


FIGURE 24

Reduction of chromite F 584.

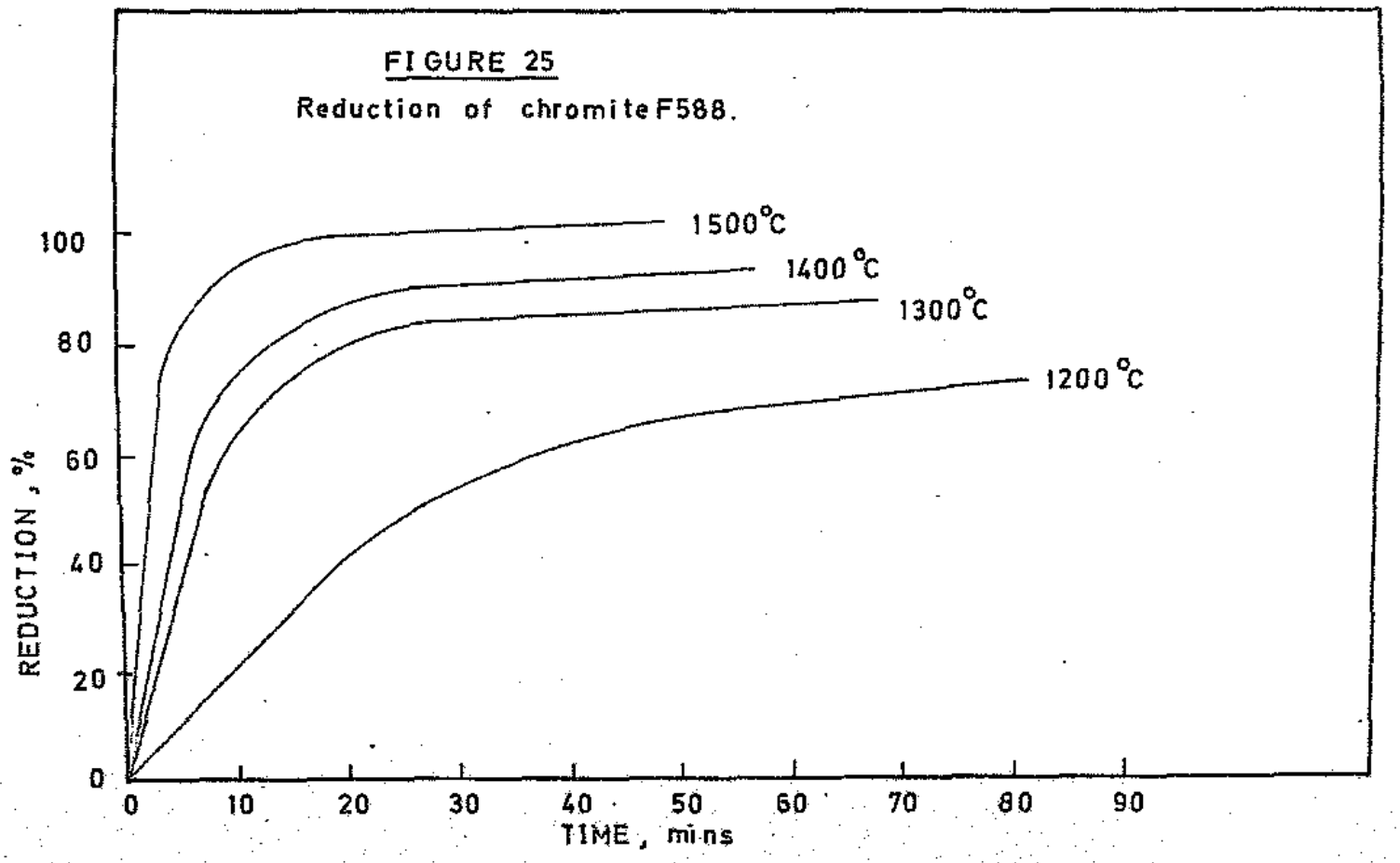


FIGURE 25

Reduction of chromite F588.

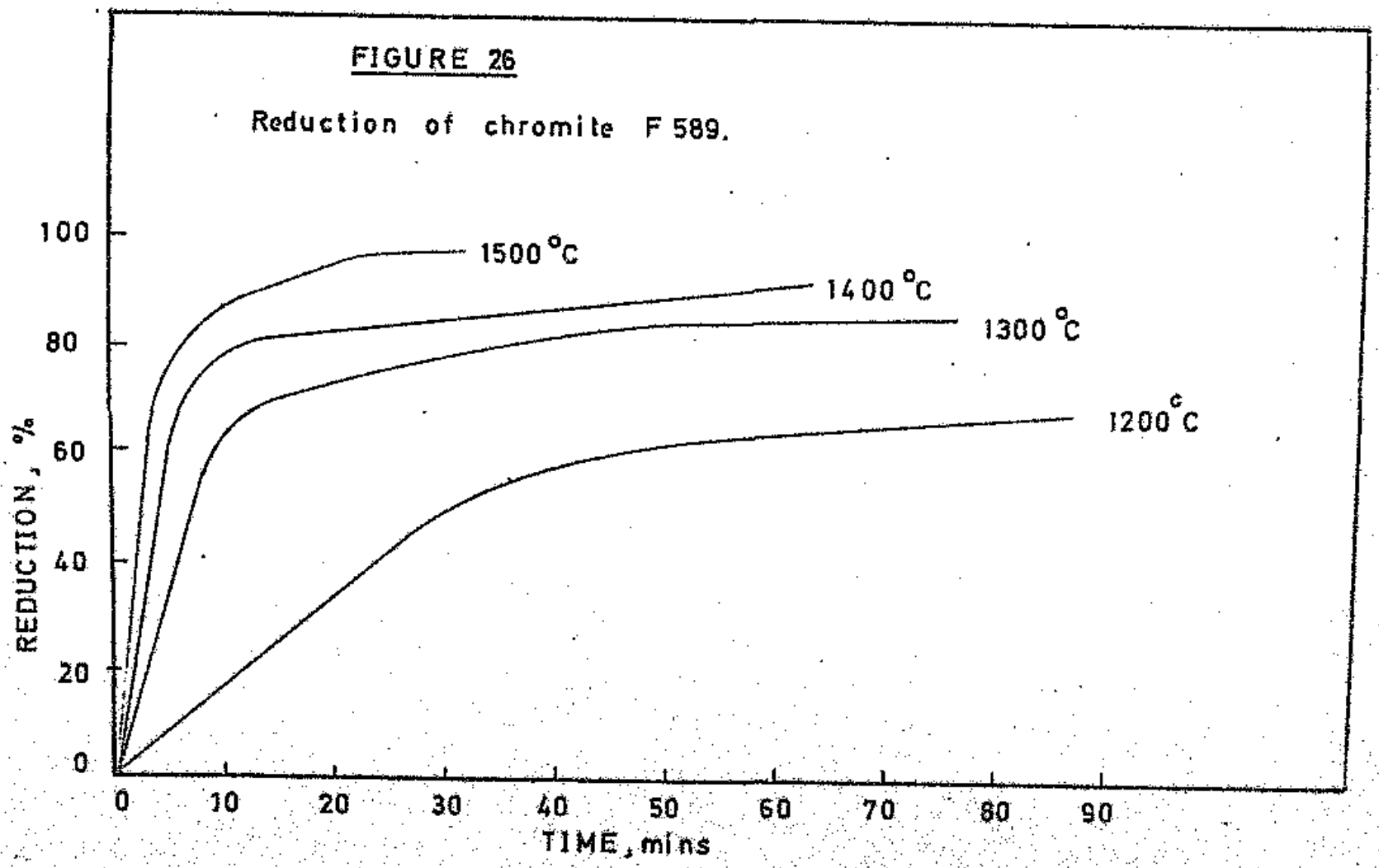


FIGURE 26

Reduction of chromite F 589.

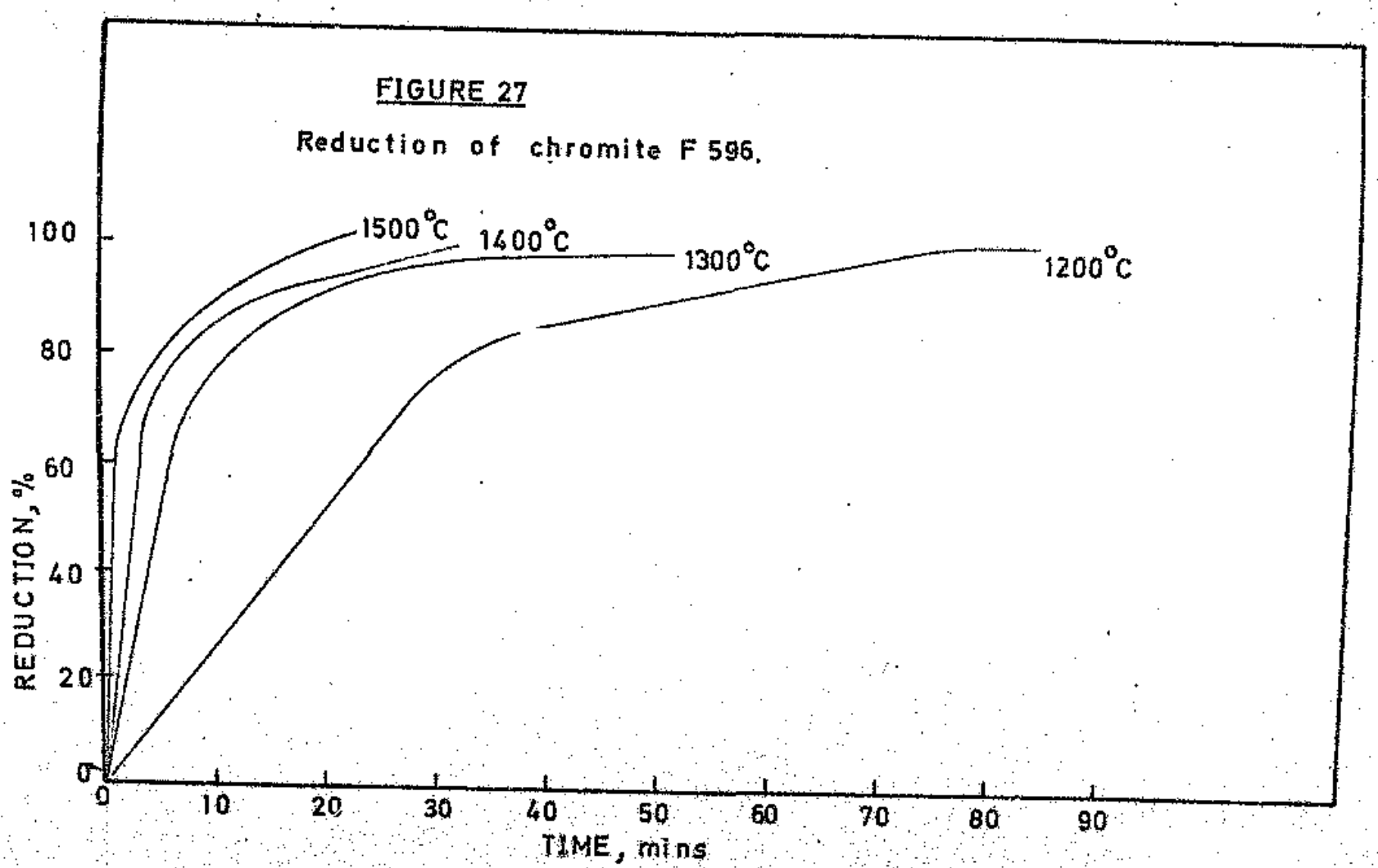


FIGURE 27

Reduction of chromite F 596.

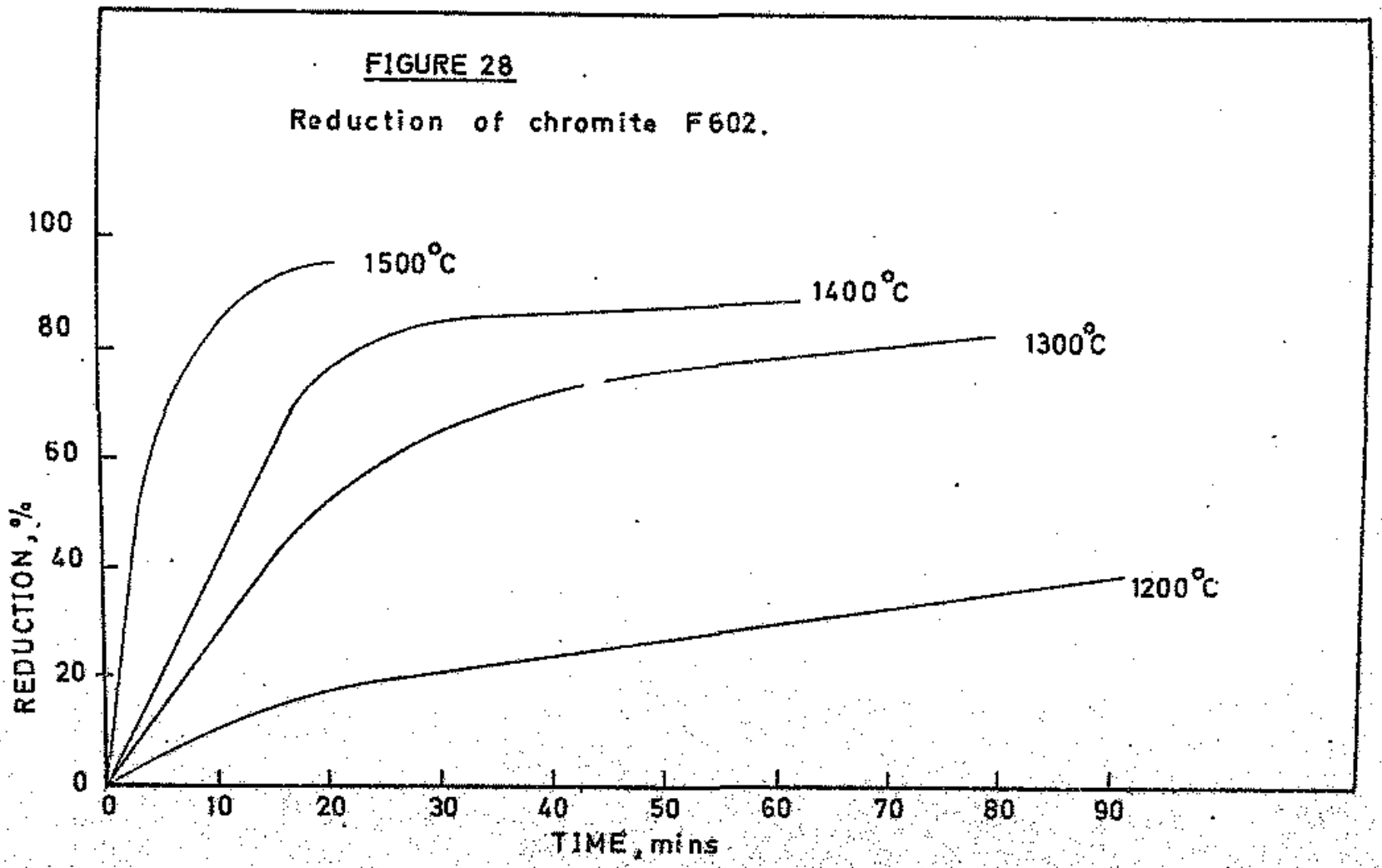


FIGURE 28

Reduction of chromite F602.

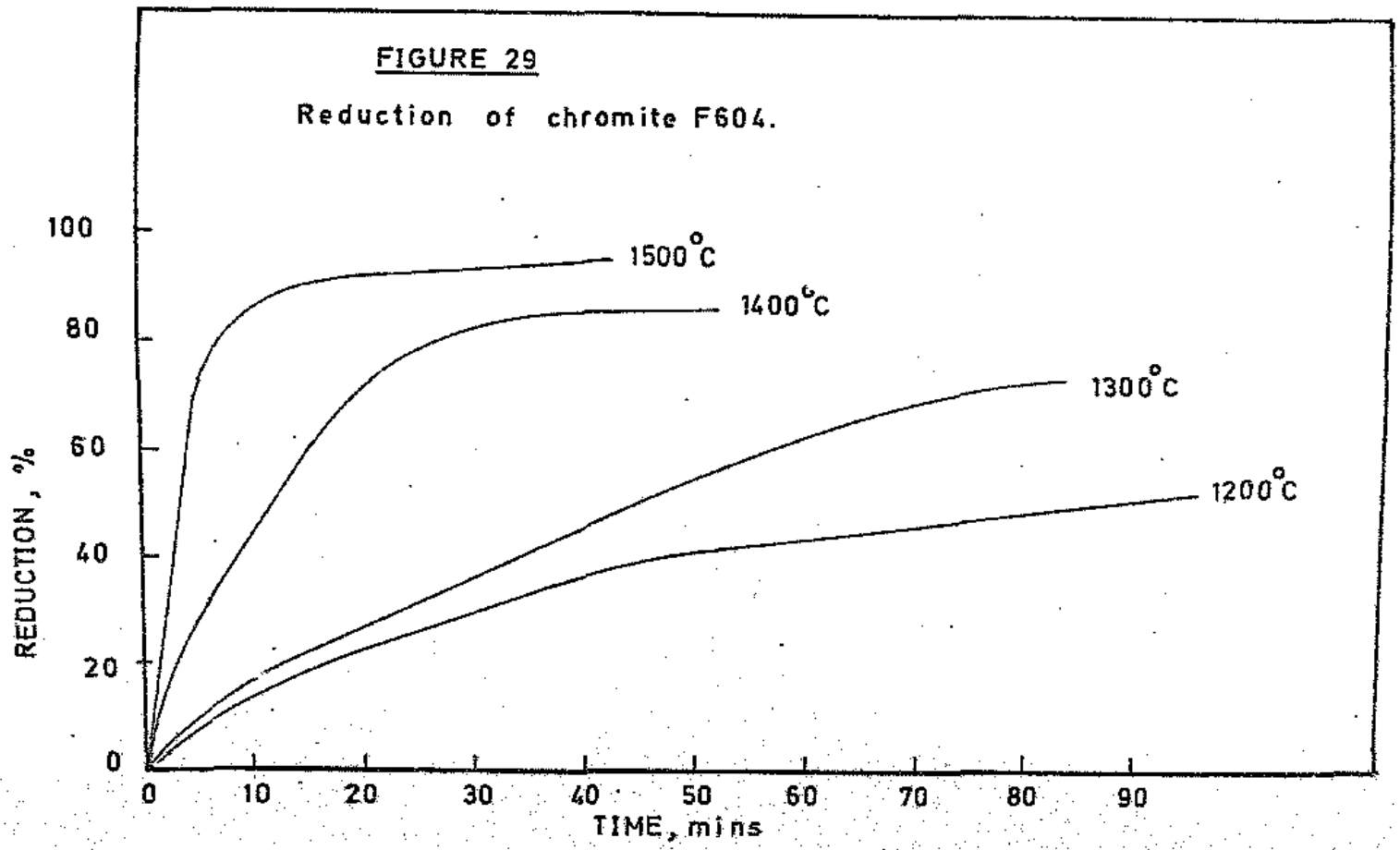


FIGURE 29

Reduction of chromite F604.

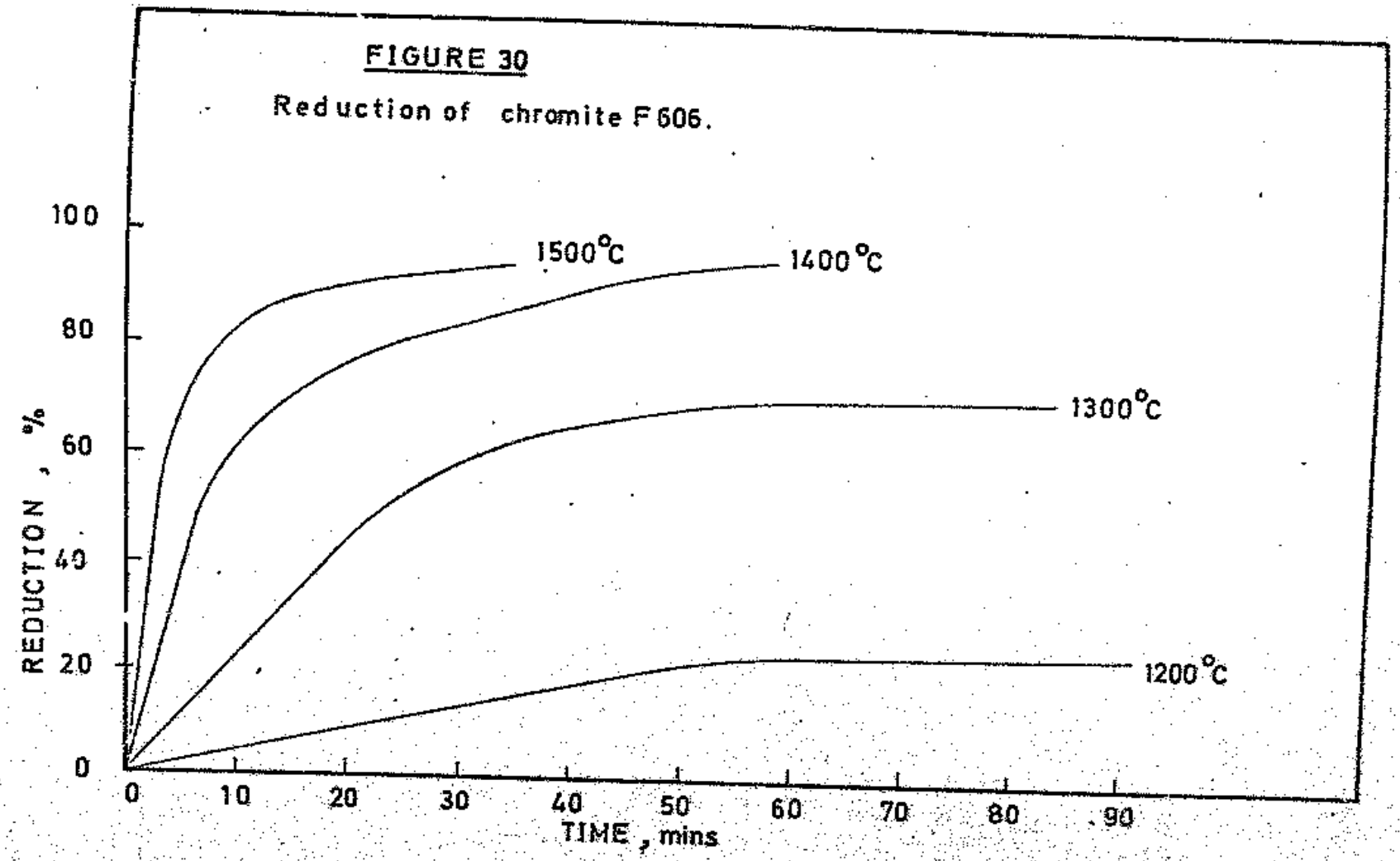


FIGURE 30

Reduction of chromite F 606.

FIGURE 31

Reduction of chromite F651.

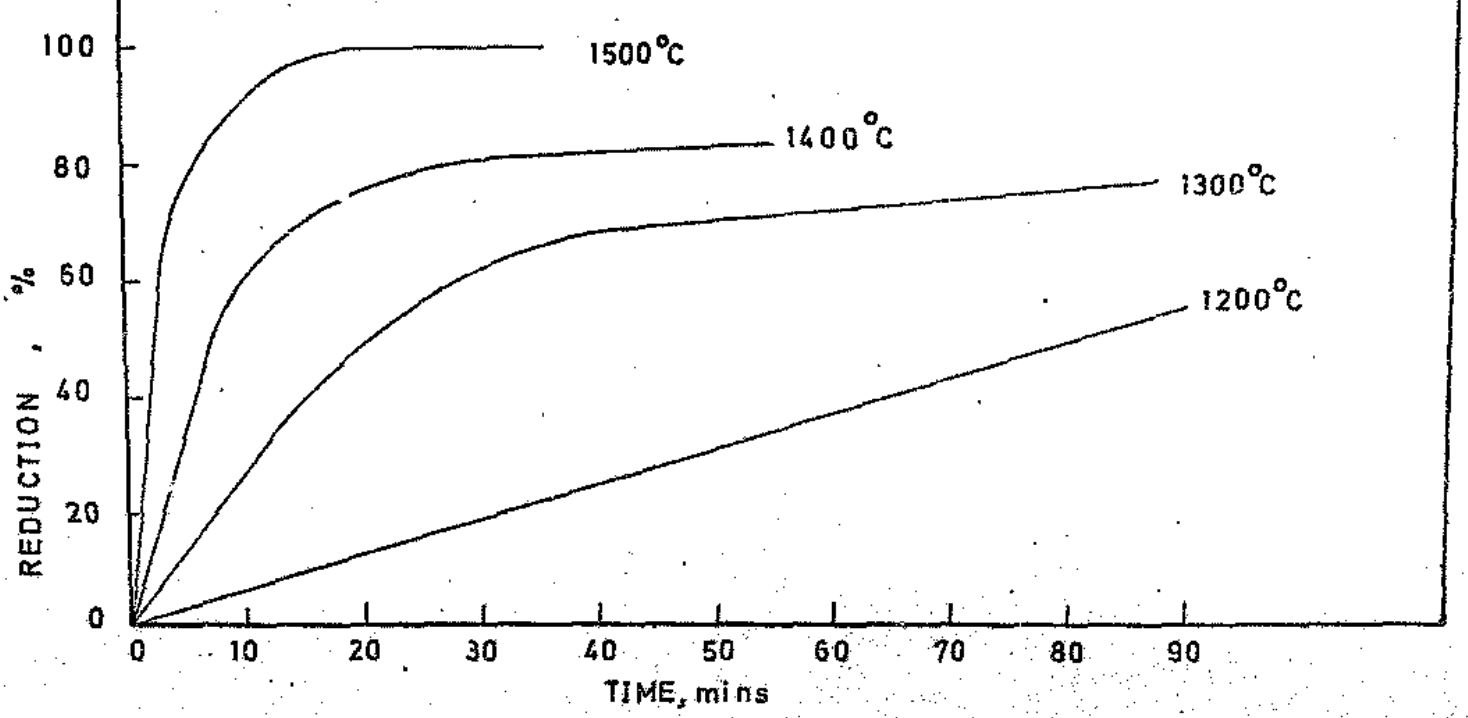
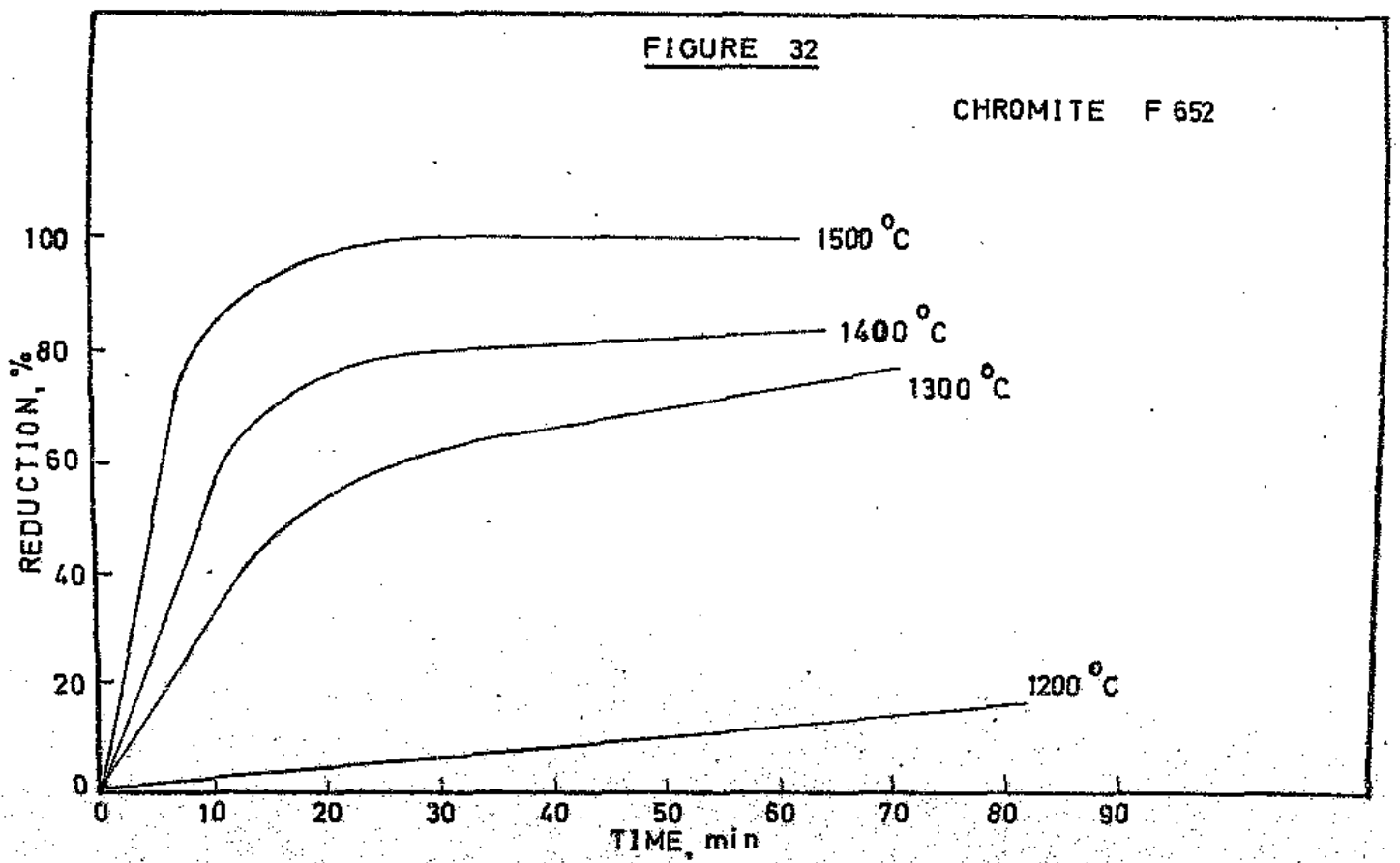


FIGURE 32


CHROMITE F 652
1500 °C
1400 °C
1300 °C
1200 °C
REDUCTION, %
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
TIME, min

3.8 EVALUATION OF THE MECHANISM AND KINETICS OF CHROMITE REDUCTION

3.8.1. Introduction

It has already been mentioned in the earlier parts of this report how mixtures of various chromites and powdered carbon were heated in an inert-argon atmosphere to temperatures ranging from 1100°C up to 1550°C. Since the reaction starts at about 1040°C for the -325 mesh size fraction, the study of the approach to equilibrium at temperatures above 1040°C might be obscured by the presence of varying amounts of reaction products in the sample. These reaction products could affect the reaction kinetics if there is any change in the reduction mechanism; however, at temperatures above 1040°C, if no change in the reduction mechanism takes place, the presence of these reaction products should not alter the reaction kinetics (Ref.21).

3.8.2. The Rate Equations

The whole crux of analysing the thermal data expressed as weight loss curves is based on the fact that these weight loss curves can be modelled according to a specific equation. According to this equation, which the data fits, a kinetic equation can be established and hence the mechanism or rate-controlling process can be found.

According to Doyle (Ref.24), the thermogravimetric curve of a decomposition reaction can be expressed as :-

$$\log g(x) - \log p(y) = B$$

(Where the variable y depends on the temperature T_x at which the fraction of the initial compound decomposed is x. Both functions $g(x)$ and $p(y)$ depend on temperature; however, B is independent of temperature. An empirical method can be used

to determine /...

to determine the g(x) and p(y) functions with the best fit to the curve, and thus an assessment of the probable mechanism can be made. Other kinetic parameters can thus be established, namely activation energy and frequency factor. Tables for the analysis of experimental data in the form log y(x) values for various mechanisms and - log p(y) vs temperature for activation energy values are to be found in the paper Satava and Skavara (Ref.25).

The method of studying thermal decomposition of solids is usually carried out by measuring the fraction, x, of material reacted as a function of time, t, at a constant temperature, T, and pressure P. In the case in hand, for the reduction of chromite the fraction x is measured as the weight loss converted back to a fraction of the reacting species under consideration, namely the chromite. It is assumed that only CO gas is formed and hence for a mass of CO evolved, say m mg, only $^{16}/28$ x m mg can be attributed to a weight loss from the chromite, the rest being from the powdered carbon. This value of $^{16}/28$ x m is the fraction x, the amount of reacted chromite, i.e. reduced material.

The probable reaction mechanism is determined by substituting the values for x and t i.e. the experimental data, in the various kinetic equations given in Table 21. The activation energy and frequency factors are obtained subsequently, using the suitable equation to draw up an Arrhenium plot of rate constant against the inverse of temperature. An alternative method of analysis does exist, however, in which the residual weight function is plotted against temperature for a sample heated at a constant rate. Thus from a single thermogravimetric curve the calculation for kinetic data can be made. This second method

was not considered /...

was not considered suitable as evaluation of the data is difficult and rather uncertain. It was therefore decided to adhere to the more familiar and proven method of analysis, namely isothermal runs at several temperature levels.

The mathematics can be set down as follows. Since no information about the mechanism of the reduction of chromite is well established, and none is available for South African chromites, the reaction was assumed to be able to be expressed in the formal kinetic equation(Ref.25):-

$$\frac{dx}{dt} = k\,(1 - x)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where x = fraction of reacted material
t = time
k = rate constant
n = apparent reaction order

However, in the case where the kinetics are more complex, an alternative more general kinetic equation can be used(Ref.25),

$$\frac{dx}{dt} = k\,x^{a}(1 - x)^{b} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where a and b are empirical constants. This is the Zsako(Ref.13) equation.

Under the chosen isothermal conditions the reduction can be expressed by the general equation.

$$\frac{dx}{dt} = k\,f(x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where $f(x)$ depends on the reaction mechanism, k is the rate constant, the temperature dependence of k can be expressed by the Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

Where E_a = activation energy
A = the frequency factor

Shap et al[Ref.26], prepared a table of kinetic equations. These are presented in Table 21, and are the equations into which the thermogravimetric data of x and t were substituted in order to establish the best fit equation. The Wits I.B.M. 360 model 50 computer was used to establish this best equation. The programmes used and the computer results are discussed in the following section.

According to Bridley et al[Ref.26] equation (1) is not suitable for heterogeneous solid state reactions. The variation of x with t cannot be expressed in the form of the equation if diffusion is the rate controlling process. Thus equation (2) is a more suitable basis for analysis of the data.

TABLE 21

KINETIC EQUATIONS

EQUATION	RATE-CONTROLLING PROCESS
$x^2 = kt$	One dimensional diffusion
$(1 - x)\ln(1-x) + x = kt$	Two dimensional diffusion, cylindrical symmetry
$(1(1-x)^{1/3})^2 = kt$	Three dimensional diffusion, spherical symmetry; Jander equation
$(1 - {}^2/_3x) - (1-x)^2/_3 = kt$	Three dimensional diffusion, spherical symmetry; Gunstling Brounshtein equation
$-\ln(1-x) = kt$	Random nucleation, one nucleus on each particle
$\sqrt{-\ln(1-x)} = kt$	Random nucleation Avrami equation
$\sqrt[3]{-\ln(1-x)} = kt$	Random nucleation Avrami equation
$1 - (1 - x)^{\frac{1}{2}} = kt$	Phase boundary reaction, cylindrical symmetry
$1 - (1 - x)^{1/3} = kt$	Phase boundary reaction, spherical symmetry

Thus the equation $1 - {}^{2}/_{3}x - (1 - x)^{2}/_{3} = kt$ was found to be the best fit equation.

So now in fact $y = a + bx$

is $f(x) = a + bx$

i.e. $1 - {}^{2}/_{3}\, x - (1-x)^{2}/_{3} = a + bx = Kt$

K = rate const. = $({}^{k}/_{r_o{}^2})$ r_o = initial radius

K = specific rate constant

i.e. $1 - {}^{2}/_{3}\, x - (1-x)^{2}/_{3} = ({}^{k}/_{r_o{}^2})\ t$

But r_o is considered the same for all the samples and can be neglected. Using the slopes at the various isothermal levels as computed by the above programmes, Arrhenius plots were constructed.

The best fit line through these points was obtained by using another programme called "Fita". The slope of the line is $\frac{E_a}{R}$ and the intercept A.

3.8.4. The Rate Controlling Process

3.8.4.1. Introduction

Having established the fact that the reduction of chromite takes place via the diffusion of the reacting species through a reaction product layer, it is now hoped to explain the part of theory behind this mechanism. Most of the theory is based on the findings of A.N. Ginstling and B.I. Brounshtein (Ref.27) and concerns the equation for three dimensional diffusion where spherical symmetry is considered.

A well known fact is that the diffusion process into a spherical particle often imposes serious limitations on many metallurgical processes of great importance to industry. Diffusion governs, in particular, the velocity of the bulk of such solid state reactions. Even today the knowledge of the theory behind such diffusion processes, and the step by step course of the chemical processes involved, is very limited.

Of all /...

Of all the fields concerning the metallurgist, the study of diffusion kinetics must surely rate as one of great theoretical and practical interest.

3.8.4.2. Theory

Consider a reaction where substance A reacts with substance B to form the product AB. The thickness of the product layer AB grows continuously as the reaction proceeds. During the course of this reaction A diffuses through this reaction product layer into B with a velocity immeasurably smaller than the velocity of the chemical reaction between A and B, if they were able to react without this barrier. Thus the diffusion through this product layer entirely controls the kinetics of the process.

From purely theoretical considerations of the above system for a spherical particle, the equation for the kinetics of reactions in these particles has been derived. The approximate solution of this equation is given as:-

$$1 - {}^{2}/_{3}x - (1 - x)^{2}/_{3} = k\left(\frac{1}{r_o^2}\right) t$$

where x is the degree of conversion of substance B in fractions of unity

t is the time

k is the constant

r_o is the initial radium of the particles of substance B.

The second kinetic equation arrived at is:-

$$a^2 \left(1 - \frac{2}{3} x \frac{a}{r_o}\right) = kt$$

(Where a is the thickness of the bed of the product AB, AB being the layer through which substance A diffuses to the surface of substance B).

The function k is a coefficient characterizing the physiochemical properties of the reacting species as well as the reaction conditions, e.g. temperature. Another important factor is that the growth of the bed of product AB is a function of a and t as well as of the ratio of the thickness of this bed to the initial radius of substance B. This growth is minimum when $a = 0,5\ r_o$.

The second equation concerning diffusion for spherical symmetry, namely the JANDER (Ref 28) equation is shown by Ginstling and Brounshtein to be suitable only for the kinetics of solid-state reactions when there is an extremely low degree of conversion of substance B. This error in Janders' equation increases with the degree of reaction, i.e. x.

Thus a very suitable expression has been arrived at by these two scientists, namely Ginstling and Brounshtein, and the use of this diffusion equation in this project has been of key importance in deriving values for the activation energy for reduction of the various chromite ores.

3.9 THE ACTIVATION ENERGY VALUES FOR THE FOURTEEN CHROMITES

3.9.1. Introduction

In 1889 Arrhenius showed that the rate constant increases in an exponential manner with the temperature. This empirical relation can be conveniently written as

$$k = Ae^{-E_a/RT}$$

where k = rate constant

A = frequency factor

E_a = activation energy

R = 8,314 joules/deg. mole (The gas constant)

T = temperature in ^oK i.e. degrees absolute.

The theory of Arrhenius and the Arrhenius plot have been used to obtain the E_a values for the fourteen selected chromite ores. The rate constants, however, could only be computed once a mechanism had been established.

3.9.2. Arrhenius Plots

Since it had been established that the rate controlling process in the reduction of all the chromites was diffusion and that the equation which was the best fit for the thermogravimetric data was the Ginstling-Brounshtein equation for three-dimensional symmetrical diffusion, it was possible to calculate the values of the rate constant at each isothermal level for each of the fourteen chromites.

The rate constant is found in fact from the computation of the best fit line to the data as plotted f(x) vs time. The slope of this line is k, the rate constant.

Now consider the Arrhenius equation:-

$$k = Ae^{-Ea/RT}$$

$$\ln k = \ln Ae^{-Ea/RT}$$

$$\ln k = \ln A - Ea/RT \ln e$$

$$\ln k = \ln A - Ea/RT \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Thus by plotting $\log_e k$ vs $1/T$, the Arrhenius plots were obtained. The computer was once again used to obtain the best fit line through the four points for the four isothermal temperatures. The slope of this line is equal to the following from equation (1):-

$$\text{slope} = \frac{-Ea}{R}$$

Thus $E_a = -R \times \text{slope}$

i.e. The slope of this line multiplied by R, the gas constant, gives the final answer, the activation energy in joules/mole since R is in joules/degree mole A, the frequency factor, is the intercept value.

Table 22 shows the E_a values, variances, correlation coefficients and frequency factors for all fourteen chromites.

These results were all obtained using computer analysis of the rate constants.

3.9.3. The Analysis of the Kinetic Data

The data was tabulated as shown in the section of results. This data consists of the values of x and the % reduction of the various times, t, chosen to suit the reduction rate. These two values were fed into the computer in a specific way according to the format statements in the programmes used. These programmes were then used to compute all the values needed to assess the mechanism, the activation energy, the frequency factor, the variance and the correlation coefficient.

The programmes used are discussed below:-

3.9.3.1. "Fitmec"

This is a main programme especially compiled to substitute the values of x and t into the nine possible rate equation and to calculate the corresponding fit of this function of x, i.e. f(x) and time t. The closer this plot of f(x) vs t approaches a straight line through the origin, the better the fit of the rate controlling equation. To obtain this straight line fit, a subroutine to the main programme "Fitmec" was used. This subroutine was called "Fitlin".

3.9.3.2. Subroutine "Fitlin"

The subroutine computes the straight line of the best fit kinetic equation. The line is of the form

$$y = ax + b$$

where a = intercept, b = slope, σ = variance, r = correlation coefficient

For the fit to be suitable, "a" should be as near to zero as possible, and "σ" (sigma) should have as small a value as possible. "b" is then taken t be the value of the rate constant at a specific temperature.

TABLE 22

THE COMPUTED RESULTS FOR ACTIVATION ENERGY OF THE FOURTEEN CHROMITES

	Chromite	Ea activation Energy K joules/mole	Variance	Correlation Coefficient	Frequency Factor A (min^{-1})
1	F 524	185,8	,14	- ,96	6,5
2	F 533	190,4	,20	- ,99	9,0
3	F 539	271,9	,16	- ,97	14,0
4	F 543	145,5	,14	- ,98	5,4
5	F 582	319,5	,25	- ,99	18,3
6	F 584	227,9	,09	- ,99	13,0
7	F 588	196,8	,07	- ,99	9,2
8	F 589	143,6	,07	- ,98	4,5
9	F 596	106,6	,09	- ,99	3,3
10	F 602	275,8	,15	- ,98	13,0
11	F 604	241,3	,02	- ,99	12,0
12	F 606	252,6	,16	- ,99	13,0
13	F 651	300,4	,08	- ,99	15,0
14	F 652	260,6	,15	- ,96	10,8

3.9.4. Discussion of Results

The chromite with the lowest E_a value is F 596. This is the abnormal chromite and is really a magnetite rich in chromium sesqui-oxide and some ilmenite, as has already been mentioned. The chromite with the highest E_a value is F 582 and by referring to the mineralogy tables, it can be seen that this chromite contains the most gangue. It would therefore be expected, looking at these two chromites on each end of the activation energy scale that factors relating to the varying proportions of Cr_2O_3, FeO and Fe_2O_3 in the chromite spinel and possibly to the differences in gangue composition, might play an important role in the value of the activation energy for a particular chromite.

Thus, broadly speaking, it would appear that the variation in activation energy values can be explained as follows:-

The overall compositions of the fourteen chromites are fairly similar but the amounts of non-reducible constituents occurring as gangue or as part of the spinel itself vary considerably, i.e. although the metal oxide content and slag forming components in the thirteen chromite ores are more or less the same, the gangue mineral contents vary. This gives rise to the suggestion that the spinel itself must vary in nature. Thus those chromites which have a large amount of gangue often have a small quantity of non-reducible components in their spinel structure. This leads to a difference, degree of molecular bonding in the spinel, which results in its being more difficult to reduce. It would thus have a higher activation energy than those chromites which have less gangue and by difference have more Al_2O_3 and MgO in their spinel structure due to the exclusion of the

balance of the /...

balance of the gangue components. (The words "non-reducible components" are used to refer to the components of the spinel which remain as metal oxides and are non-reducible in this metal/metal oxide/carbon system).

Thus chromites which are good examples of a high E_a value and high gangue content and contain lesser amounts of Al_2O_3 and MgO in their spinels are: F 539, F 582, F 606, F 651 and F 652. Examples of chromites with low E_a values and low gangue mi eral contents are F 543, i.e. containing a fair amount of Al_2O_3 and MgO in the spinel, F 589 and F 533. There are a few exceptions to this rule and the possible reasons for the discrepancies are discussed in the following section.

TABLE 23

	Chromite	E_a K Joules/mole	% Gangue	Note
1	F 524	185,8	4,4	
2	F 533	190,4	2,3	
3	F 539	271,9	13,6	High Gangue and E_a values
4	F 543	145,5	5,7	
5	F 582	319,5	10,1	High Gangue and E_a values
6	F 584	227,9	4,1	
7	F 588	196,8	7,0	
8	F 589	143,6	6,2	
9	F 596	106,6	±2,5	Low Gangue, low E_a values
10	F 602	275,8	7,0	
11	F 604	241,3	8,1	
12	F 606	252,6	17,2	High Gangue, high E_a values
13	F 651	300,4	9,7	High Gangue, high E_a values
14	F 652	260,6	7,0	

3.10 THE REACTIONS ASSOCIATED WITH THE REDUCTION OF CHROMITE WITH SOLID CARBON

3.10.1. Introduction

The computed results from the thermogravimetric date for the isothermal runs suggest that the reduction of chromite by solid carbon is controlled by the diffusion of the reactants through the reaction product layer. The nature of the diffusing species is the consideration which gives rise to the most uncertainty. The fact that the reduction process begins above 1000°C would suggest that CO is the diffusing species, but if it is CO that reduces the chromite in this system of chromite and solid carbon, then apparently so should CO gas on its own reduce chromite at temperatures near to 1500°C. It is this question that is the crux of the discussion on the reactions associated with the reduction of chromite with solid carbon.

3.10.2 The Reactions

The chemical reactions taking place during the reduction of chromite have been expressed as follows according to the two scientists S.S. Lisniak and N.F. Evseev(Ref.9). Here the reactions are shown in a schematic rather than a balanced chemical equation form. These equations show the reaction products likely to be formed at the various stages of reaction and hence likely to constitute the reaction product layer.

Reactions:-

A typical Russian chromite was used as an example:

NON STOICHIOMETRIC FERROCHROME SPINEL

$Mg_{0,6}\ (Fe, Cr, Al)_2\ O_{3,6}$

$\downarrow$ 1050°C

FERRO-CHROMEPICOTITE

$(Mg, Fe), (Fe, Cr, Al)_2O_4$

Metallic Iron Fe $\leftarrow$ $\downarrow$ 1100°C $\rightarrow$ Fe + Cr_xCy

CHROMESPINEL

$Mg\ (Cr, Al)_2O_4$

$\downarrow$ MgO (Periclase)

$\downarrow$ Cr_xCy (Chrome carbide)

$\downarrow$ 1150°C - 1350°C $MgAl_2O_4$ Spinel

The reaction products during the reduction process are thus:-

Iron, Chromium carbide, Periclase and Mg Al_2O_4 spinel. In the tests carried out on the samples obtained from the thermal balance work, the reaction products were found to be much the same as those found by the two investigators mentioned above. X-ray diffractometry was used to examine the reaction products. These tests are discussed in another section.

The products analysed by X-ray diffraction were chromium-iron carbide, periclase (Mg), aluminomagnesia spinel ($MgAl_2O_4$) and in some cases free carbon (i.e. where 100% reduction had not been attained). The reason for the fact that the presence of free iron was not established was most probably that the temperatures used for these tests were higher

than those /...

than those mentioned by Lisniak and Evseev, and hence the free iron and the chrome carbide, which form a solid solution, had dissolved in one another to form chromium iron carbide.

All these reaction products would thus be likely to form part of the reaction product layer at the temperatures used in the reduction tests and it is this layer that must act as the diffusion barrier to the reacting i.e. diffusing species.

The diffusing species must be the reductant and hence either solid carbon or carbon monoxide must diffuse through this product layer. The latter would seem the more likely for the reasons discussed below.

3.10.3. The Diffusing Species

The likelihood that CO is the diffusing species is based on the fact that the most prevalent point of view in the literature at present is that the reduction of metal oxides and ores with solid carbon occurs via the gaseous phase. Hence the easier the regeneration of CO, the more rapid is the reduction process.

If CO is considered to be the reducing species it must be formed by solid carbon interacting with some oxide. All possible reactions involving carbon, CO and the metal oxides are given below:-

Ref.	Reactions involving Carbon and FeO, Cr_2O_3 and CO	Temperature °C from start of reaction at which $\Delta G = 0$
1	$2\ FeO + {}^{8}/_{3}C = {}^{2}/_{3}\ Fe_3C + CO$	713
2	$2\ FeO + 2C = 2\ Fe + 2\ CO$	717
3	${}^{2}/_{3}\ Cr_2O_3 + {}^{54}/_{21}C = 2\ Fe + 2\ CO$	1201
4	${}^{2}/_{3}\ Cr_2O_3 + 2C = {}^{4}/_{3}\ Cr + 2\ CO$	1256
5	${}^{2}/_{3}\ Cr_2O_3 + 2\ Fe_3C = {}^{4}/_{3}\ Cr + 6Fe + 2\ CO$	1289
6	${}^{1}/_{3}\ Cr_2O_3 + {}^{1}/_{3}\ Cr_7C_3 = 3\ Cr + CO$	1430

Thus the formation of CO can begin at temperatures as low as 713°C, if only the thermodynamics are considered. Experimental results show clearly that the reaction only starts at somewhat higher temperature than 713°C, namely nearer 1050°C. Thus the FeO in the spinel is obviously more difficult to reduce that FeO on its own would be.

For the experimental conditions mentioned, i.e. solid carbon in contact with solid chromite, the reaction would be expected to initiate at the contact points between the reactants according to equations 1 and 2. After the initiation of the reaction, and as long as there remain contact points between the reactants, reaction 1 or reaction 2 must play an important role in the reduction process. The extent of the contribution of reduction by CO as shown now at higher temperatures, as in the equations given below, would depend on the regeneration of CO.

The possible reaction involving CO in the reducing species is as follows:-

7. $FeO\ Cr_2O_3 = Fe + Cr_2O_3 + CO2$

Kinetic studies of the regeneration reaction of CO, namely:-

$$CO_2 + C \rightleftarrows 2\ CO$$

indicate that it has a significant rate only above 1000°C. The activation energy for this reaction has been shown by Walker et al (Ref.29) to be 361,2 k joules/mole.

Thus it would appear that during the early stages of reduction (1050°C up to 1200°C and even higher temperatures) solid - solid interaction at the chromite/carbon contact points would seem to be the main contributor to the reduction process.

A chromite sample plus stoichrometric carbon held isothermally at 1100°C was found to react for about an hour and then the reaction tailed off. This is experimental verification of the fact that solid - solid interaction plays an important role at this temperature and the CO regeneration reaction is not predominant in reducing chromite at this temperature. At temperatures of 1200°C and higher the reactions become progressively faster as all the results indicate. The termination of the reaction at this temperature of 1100°C seems to be due probably to the formation of the products at the chromite/carbon interface, resulting in a decrease in the reaction rate and ultimately in its ceasing. At the higher temperatures the rate of regeneration of CO increases. This might possibly be the reason which causes this increase in reduction rate. Since, generally speaking, gas-solid reactions are much faster than solid - solid reactions, one would expect this overall increase in reaction rate. A second possibility was mentioned in the introduction. This is that the metallic iron which forms at higher temperatures acts as a catalyst for Cr_2O_3 reduction.

Initially the rate would increase slowly since the reaction due to solid - solid interaction would help for increasingly short times with increasing temperatures until temperatures are reached where the regeneration of CO predominates and the reduction proceeds mainly via the gaseous reduction process.

To establish the validity of the above postulations several tests were carried out. These are discussed in the section on reduction tests using CO

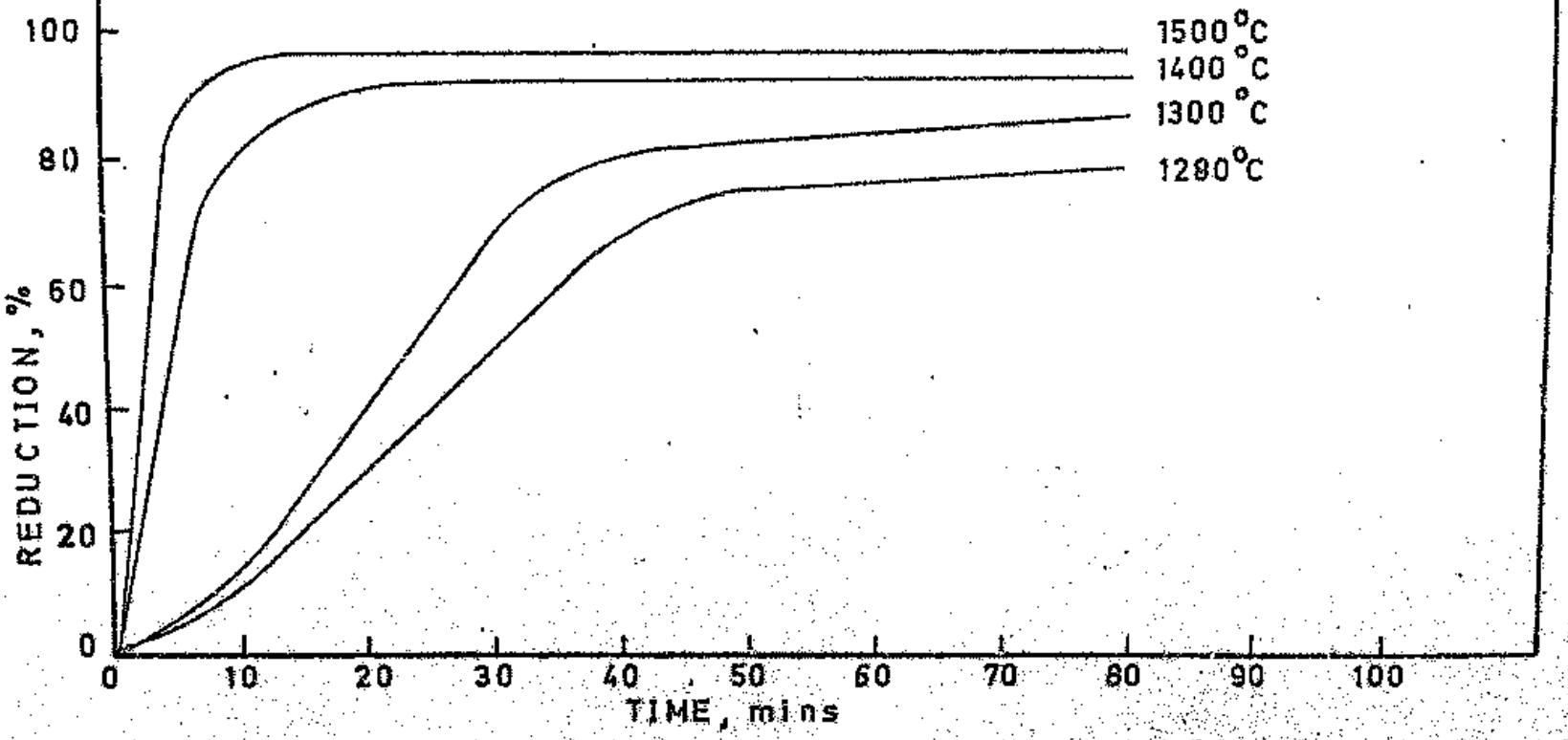
3.11 THE EFFECT OF FLUXING ADDITIONS ON THE REDUCTION MECHANISM AND KINETICS OF CHROMITE

The results for the isothermal runs at 1280°C, 1300°C, 1400°C and 1500°C are shown in Figure 33. Calculation using the computer showed the mechanism to be unaltered from that for chromite reduction without the presence of fluxing additions. The first temperature level for the isothermal run was taken as 1280°C, since the reduction behaviour at 1200°C and even up to 1275°C was inhibited by the presence of these fluxing additions due to poorer particle/particle contact between the chromite and the carbon. At 1280°C this effect had been over-ridden and it was therefore chosen as the first isothermal level.

The rate constants at 1300°C, 1400°C and 1500°C have higher values than those for the runs without fluxes. The activation energy, however, is almost the same as can be seen in Figure 34. Thus the values of E_a are dependent only on the actual nature of the chromite, although the fluxes do have a diluent effect on the carbon chromite contact, causing an apparently lower rate of reduction i.e., lower rate constant at the four isothermal temperature levels. This is thought to be merely a pseudo effect on the rate constants, because if excess carbon were to be added, thereby increasing the carbon-chromite contact surface to the same value as was the case before the fluxing additions were made, then no deviation of the rate constant values would have been observed.

FIGURE 33

Reduction of chromite F533 + fluxes.



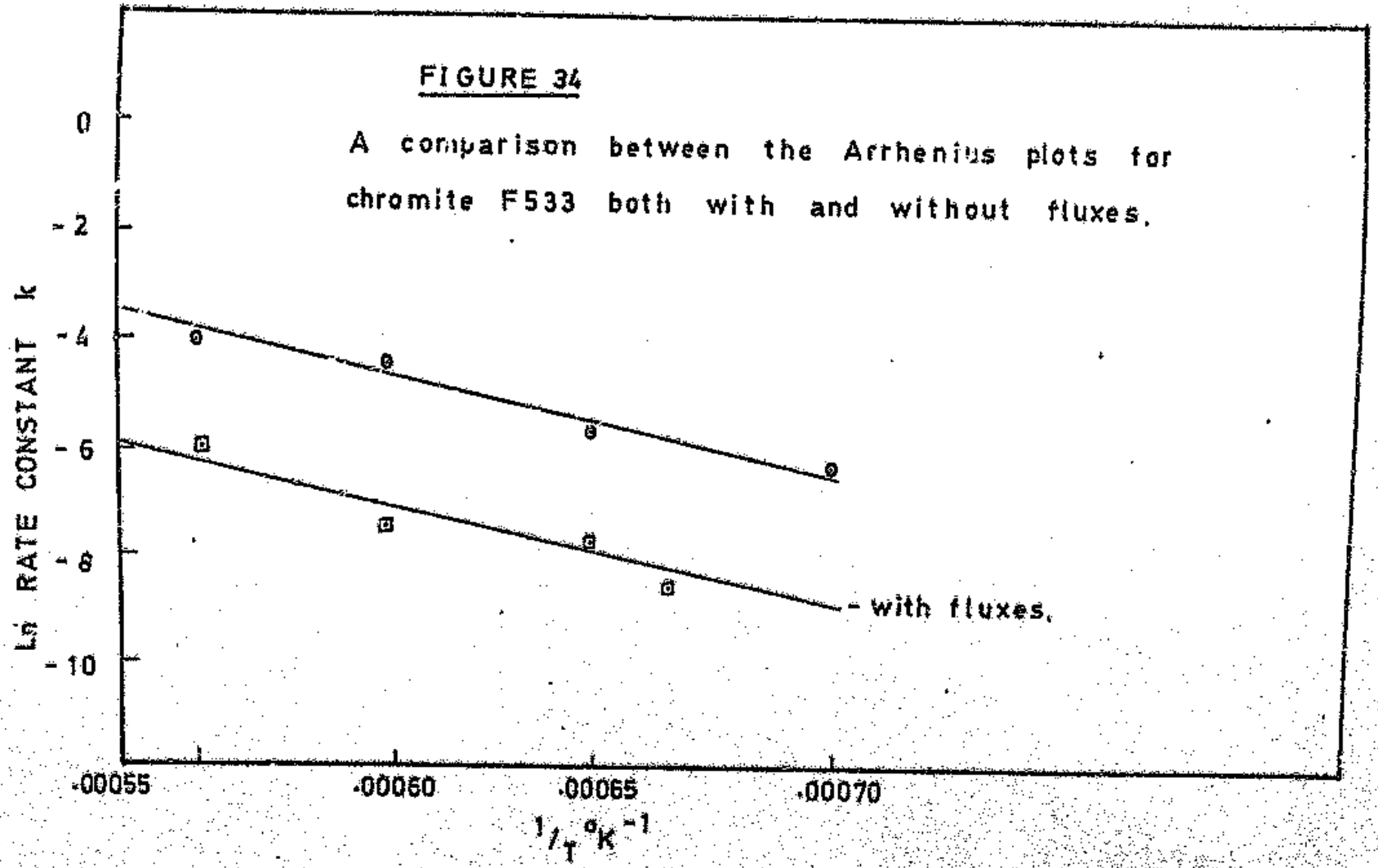


FIGURE 34

A comparison between the Arrhenius plots for chromite F533 both with and without fluxes.

3.12 USE OF A CORRELATION MATRIX TO ESTABLISH THE EFFECT OF VARIOUS PARAMETERS ON THE ACTIVATION ENERGY AND RATE CONSTANT

3.12.1. Introduction

A computer programme called "CORRE" was used to establish this matrix for data relating to E_a. This programme was used to calculate the means, standard deviation, sums of cross-products of the deviations from the means, and product moment correlation coefficients from the input data. If the input data is considered to be of the form X_{ij} where $i = 1,2, ----, n$ are observations and $j = 1,2, ----, m$ are variables, then the following equations can be used to calculate the above statistics:-

The sums of the cross-products of deviations

$$S_{jk} = \sum_{i=1}^{n} (X_{ij} - T_j)(X_{ik} - T_k) - \frac{\sum_{i=1}^{n} (X_{ij} - T_j) \sum_{i=1}^{n} (X_{ik} - T_k)}{n} \quad -----(1)$$

where $j = 1,2, ---, m$; $k = 1,2 ---, m$

The correlation coefficient $r_{jk} = \dfrac{S_{jk}}{\sqrt{S_{jk}} \times \sqrt{S_{kk}}}$

where $j = 1,2 ----, m$; $k = 1,2 ----, m$

In other words, this programme was used to find out what significance a variable such as composition might have on E_a and the rate constants. The use of such a matrix might help in assessing which variables have the most pronounced effect on E_a and what interactions these variables have on each other.

3.12.2. The Correlation Matrix

A table of all the variables to be considered is to be found in the appendix. The number of observations is in fact the same as the number of chromites, i.e. fourteen. This is because each set of /...

each set of data for each of the fourteen chromites is the actual observation for that particular chromite. The variables are given across the top of the table. Since there were only fourteen chromites, the maximum number of variables which can be considered is fourteen. Since there were more variables than observations, several matrices had to be completed to cover all the variables. These results are also given below in table form. Only thirteen variables are shown since these were found to be of most importance.

TABLE 24

THE CORRELATION MATRIX

Rate Constant at

	$Cr/_{Fe}$	A	E_a	1500°C	1400°C	1300°C	1200°C	% Gangue	% MgO	% SiO_2	% Al_2O_3	% Cr_2O_3	% FeO
% FeO	+ ,87	- ,37	- ,52	,33	+ ,81	+ ,83	+ ,73	- ,48	- ,83	- ,28	- ,18	- ,72	1,00
% Cr_2O_3	+ ,72	+ ,33	+ ,43	- ,21	- ,60	- ,80	- ,78	+ ,18	+ ,73	- ,06	+ ,49	1,00	
% Al_2O_3	+ ,11	+ ,42	+ ,39	+ ,29	- ,17	- ,27	- ,41	+ ,22	+ ,26	+ ,16	1,00		
% SiO_2	+ ,24	+ ,51	+ ,49	+ ,46	- ,18	- ,24	- ,27	+ ,98	+ ,45	1,00			
% MgO	+ ,89	+ ,46	+ ,59	- ,13	+ ,76	- ,78	- ,73	+ ,81	1,00				
% Gangue	+ ,44	+ ,60	+ ,61	+ ,40	- ,39	- ,44	- ,46	1,00					
1200°C	- ,69	- ,73	- ,82	+ ,006	+ ,87	+ ,89	1,00						
1300°C	- ,79	- ,63	- ,71	+ ,20	+ ,82	1,00							
1400°C	- ,75	- ,38	- ,54	+ ,25	1,00								
1500°C	- ,22	+ ,43	,36	1,00									
E_a	+ ,56	+ ,97	1,00										
A	+ ,43	1,00											
$Cr/_{Fe}$	1,00												

3.12.3. The discussion of the Correlation Matrix Results

The t=test for the significance of an observed correlation coefficient gives r = 0,55 for the 95% confidence level. (r = 0,48 at 90% confidence)(Ref.36). Thus any values below 0,55 do not have a sufficiently high correlation coefficient value to conclude that there is a relationship between the two variables under consideration.

Perhaps the most note-worthy aspect of the matrix is the relationship between the rate constants at the various isothermal temperature levels and the other variables such as % FeO, % Cr_2O_3, Cr/Fe and E_a. The reason for stressing the importance of these particular variables is that it is the rate constant, which is directly proportional to the reduction rate of the chromite, which can supply a good indication as to the reducibility of a particular chromite.

In looking at the actual values of the correlation coefficient (r) it can be seen that the % FeO has a positive r value with respect to k, the rate constant. The values at 1200°C, 1300°C and 1400°C show that the greater the % FeO, the higher the rate constant, i.e. reduction of the chromites with more % FeO is more rapid at a particular temperature than when the % FeO is low. At 1500°C, however, the value of r is only 0,33 indicating no correlation at all. This might be expected if the reduction rate is so fast that % FeO has no effect. It would thus appear that the compositional effect of % FeO is only of significance below 1500°C.

The relationship between % Cr_2O_3 and k is rather different in that the values of r are now

negative./...

negative. The greater the % Cr_2O_3, the slower the rate of reduction in the temperature range 1200°C up to 1400°C. Once again composition has little effect at 1500°C. The above two effects are borne out by the correlation of the $Cr/_{Fe}$ ratio. Thus it would seem that the actual composition of the chromite with respect to its metal oxides only plays a significant role below 1500°C in terms of reduction kinetics. This is also shown in that the k values for all chromite ores tend to approach one another at 1500°C. Only the pre-reduction would be affected by the variation in % FeO and % Cr_2O_3 but the rate of reduction at temperatures of 1500°C and higher would not be affected by any variations in the proportions of the two metal oxides. Furthermore, only the final composition of the high carbon-ferrochrome is affected by variations in the $Cr/_{Fe}$ ratio.

It is interesting to note that % MgO also shows good correlation with k, but this ties up with the fact that the composition of the actual chromite is inter-related in that as % FeO and % Cr_2O_3 vary, so must the % MgO. There are thus many obvious and some not so obvious correlations which result only from the interdependence of certain variables, e.g. $Cr/_{Fe}$ correlates well with % Cr_2O_3 and % FeO. It is therefore very important to consider not only the two variables at hand but how each of them fits into the whole picture before stating some irrelevant fact or even an incorrect one.

Other interesting significant correlations are shown between % SiO_2 and % gangue. This confirms the well known fact that no SiO_2 is found in the chromite spinel itself. % MgO also ties up well with the gangue but not to

the same degree /...

the same degree as the % SiO_2. This is exactly what one would expect since some MgO is found in the chromite spinel structure. The correlation between E_a and the % gangue is of fair interest.

Figure 35 has been plotted showing the variation between the E_a values and the gangue content for the various chromite ores. There are several possible reasons for this trend of E_a increasing with gangue content. Firstly the chromites with the greater gangue content tend to have gangue actually coating (partly and some even completely) some of the chromite grains. This tends to inhibit the reduction process via the solid phase resulting in an apparently high E_a value. The other possibility is that as the gangue percent varies, the percent of the non-reducible components in the spinel varies resulting in this variation of E_a. High gangue containing chromites have often low % MgO in the spinel. This fact can be gathered by studying Table 3 at the beginning of this report. Exceptions to this rule tend to cause the chromite to have a lower E_a value than might have been expected if only the gangue percent is considered.

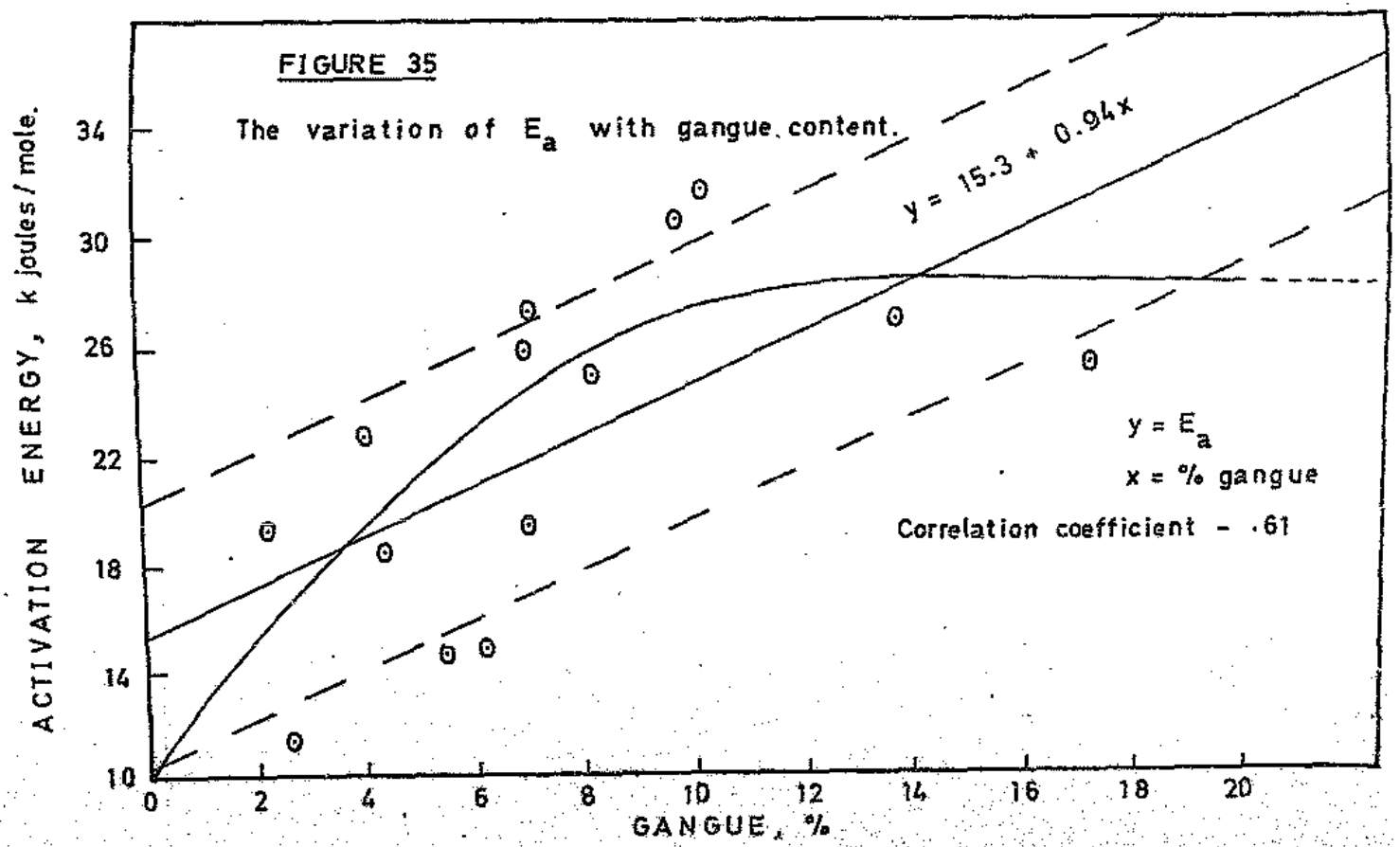


FIGURE 35

The variation of E_a with gangue content.

CHAPTER IV

THE BEHAVIOUR OF CHROMITE UNDER A CARBON MONOXIDE ATMOSPHERE

4.1 INTRODUCTION

It is a well known fact that hydrogen gas will reduce chromite[Ref.12]. The behaviour of chromite in a carbon monoxide atmosphere, however, is not well known. In spite of the great technological importance of the process of chromite reduction, very little work has been carried out in the field of the kinetics of reduction, especially where carbon monoxide is concerned. Thus this section of the project was devoted to finding out how chromite behaves in a carbon monoxide atmosphere in the temperature range 1200°C up to 1550°C.

In many reduction reactions CO is suggested as both the diffusing and reducing species. For example in the reduction of ilmenite[Ref.21], solid state reduction appears to be the main reaction mechanism up to 1020°C, while above this temperature a rate increase has been observed and has been attributed to a change in mechanism from solid state to gaseous reduction of ilmenite by regenerated CO gas.

One might therefore expect that CO could possibly play a role in the reduction of chromite, as it is suggested that it does for ilmenite, and certainly as it does play in the reduction of hematite. It is to be noted that nowhere in their paper dealing with ilmenite reduction do W.G. Davenport and El-Guindy[Ref.21] mention passing CO over an ilmenite sample. One would have expected that since they considered CO as the possible diffusing species, they would have carried out such an experiment.

As part of the introduction in Chapter I, it was considered appropriate to include a discussion of information concerning the reduction of Cr_2O_3 and chromite using hydrogen.

Geld and Esin[Ref.11] established that when hydrogen was used the reduction of chromium oxide proceeded much more slowly than when solid carbon was present. Furthermore they established that the Russian Aktyubinsk chromites reduce more slowly than pure Cr_2O_3. This difference in rates is ascribed to the structural characteristics of the chromite ore.

It is the lack of data for the possible reduction of chromite with CO gas as well as an attempt to justify the proposed mechanism that prompted the following series of tests. These tests were designed to establish what part CO might play in the reduction process in the submerged arc furnace producing high-carbon ferrochromium.

4.2 EXPERIMENTAL METHODS

The equipment used was once again the thermal balance with its modifications for gas atmosphere control. The CO gas was introduced in exactly the same manner as the argon was for the study of reduction by solid carbon. Suitable precautions were taken with this noxious gas.

Chromite F 533 was selected for the study under CO gas. A run was carried out using 0,5000 gram of chromite F 533 on a flat round alumina disc. This was in order to expose as much free surface to the CO as possible. The furnace was heated from room temperature up to 1550°C, while CO was continuously passed through the furnace at 500 cc/min. No reduction took place [illegible] after the sample had been held at 1500°C isothe[illegible] for several hours. Consequently it would appear that powdered chromite at -355 mesh is not reduced by CO gas at temperatures up to 1550°C.

It was decided, however, to check all the possibilities in the system under consideration to make quite sure that CO could not reduce the chromite. To ensure that the equipment was suitable for gaseous reduction town gas of the following composition was passed

through the /...

through the furnace sheath to establish whether a combination of CO, CO_2, H_2 and CH_4 could reduce the chromite as previously established.(Ref.37) The chromite started to reduce slowly and kept reducing at a steady rate of reduction up to 98% reduction, indicating that town gas will reduce chromite at 1500°C, even if it is considerably slower than solid carbon.

A 0,5000 gm sample of pure Fe_2O_3 was then placed in the furnace of the thermal balance at 1400°C. A flat disc of alumina was once more used as a container for the sample. CO gas was then introduced and the reduction of the Fe_2O_3 sample began at a reasonably rapid rate. It took about fifteen minutes to attain complete reduction. Thus in this manner, by substituting Fe_2O_3 for the chromite, in exactly the same system, it was shown definitely that no fault in the system itself could have been responsible for the fact that the chromite did not reduce. Both the substitution of the gaseous phase, namely to town gas, and the solid phase to Fe_2O_3 resulted in reduction. This confirmed the conclusion that CO will not reduce chromite at 1500°C under these conditions, at least when the CO is introduced as a bottled gas.

Further tests were performed, however, to eliminate any other possibilities that CO might act as a reducing agent for chromite. These tests were carried out at 1400°C and are summarised in Table 25.

TABLE 25

TEST	RESULT
1. Chromite plus 50% stoichiometric carbon under argon	Exactly 50% reduction took place
2. Chromite plus 50% stoichiometric carbon under CO gas	Exactly 50% reduction took place and the reduction rate was the same as 1.
3. Cr_2O_3 under CO gas	No reduction took place
4. Cr_2O_3 plus stoichiometric carbon under argon	Complete reduction took place at approximately the same rate as chromite
5. Cr_2O_3 plus stoichiometric carbon under CO gas	No increase in the reduction rate was noted compared with test 4.
6. Fe_2O_3 under CO gas	Complete reduction occurred at a moderate rate *
7. Fe_2O_3 plus stoichiometric carbon under argon	Complete reduction was achieved at a very rapid rate
8. 1/3 Fe_2O_3 plus 2/3 Cr_2O_3 under CO gas	Slow reduction of only the Fe_2O_3 took place
9. 1/3 FeO plus 2/3 Cr_2O_3 plus stoichiometric carbon under argon	Complete reduction of both the Cr and Fe oxide occurred

* This rate decreased after a short while due to sintering of the Fe_2O_3, causing less free surface to be exposed to the CO gas. It took therefore about one hour to reduce the Fe_2O_3 to iron.

4.3 DISCUSSION

Firstly it was established with a good deal of certainty that CO does not participate in the reduction of chromite. In announcing this fact, it is best firstly to consider what facts prompted the idea that CO might be a reducing agent. It is well known that CO can reduce hematite, namely Fe_2O_3. Fe_2O_3 is one of the major constituents of the spinel, but it is not the same as free Fe_2O_3, however, since it is tied up very closely with the other spinel components.

Novokhatski and Lenev(Ref.30) report that the free energy for spinel formation of iron chromite is extremely high. They postulate that the spinel could form either from the metals plus oxygen or from the metal oxides. In both cases the energy of formation is high as can be seen below.

Reactions:-

For temperatures between 1000 and 1500°C the metals plus oxygen react as follows:-

$$Fe + 2Cr + 2O_2 = FeO.Cr_2O_3$$

$$\Delta G_T = 348,100 + 78,66\ T\ (\pm 1200)\ \text{cal/mole}$$

whereas the high temperature formation of iron chromite from the oxides is as follows:-

$$FeO + Cr_2O_3 = FeO.Cr_2O_3$$

$$\Delta G_T = 15,800 + 2,60\ T\ (\pm 700)\ \text{cal/mole}$$

The reduction of the spinel would thus include the break up not only of bonds between the oxygen and the metal ions but of bonds formed within the spinel itself. These would include bonds between the Mg^{++} and Al^{+++} and their associated oxygen atoms since they are all part of the trivalent or divalent spinel network. This might possibly explain why the Fe_2O_3 tied up in the spinel does not reduce in the presence of CO, while Fe_2O_3 does. This was in fact confirmed by a rather simple test. Chromite F 533

from the /...

from the tests under atmospheric conditions was crushed to -325 mesh. The sample was introduced to a CO atmosphere at 1400°C. It reduced slightly and the amount by which it reduced was in fact the same amount that it gained under atmospheric conditions, showing that Fe_2O_3 which is liberated from the spinel will reduce under a CO atmosphere.

Secondly Cr_2O_3 does not even reduce with CO when it is in the pure form at 1400°C. It is thus even less likely to reduce when it is tied up as a spinel component. It seems even more than feasible then, that the Cr_2O_3 tied up with Fe_2O_3 would not be able to be reduced by CO. These facts seem to explain why CO does not work in this respect, but the reasons which explain why such favour has been given to CO as a possible reducing agent can be summarised as follows:-

1. The CO regeneration reaction, namely

$$CO_2 + C \rightleftharpoons 2\,CO$$

which takes place in several steps in fact:-

below 1000°C $\left\{ \begin{array}{l} C + (O) \rightleftharpoons C(O) \\ C(O) \longrightarrow CO \end{array} \right\}$ formation of original CO

above 1000°C $\left\{ CO_2 + C \rightleftharpoons 2CO \right\}$ C reaction with CO_2

has only a significant rate of formation at about 1000°C. The activation energy for this reaction has been shown by Walker et al (Ref.29) to be about 360 k joules per mole. The reduction of chromite begins only at about 1050°C at a stage when this regeneration reaction is more than feasible. This might easily lead the investigator to suppose that CO could contribute to the reduction process.

2. It is considered that the initiation of reduction occurs as a result of solid interaction at the chromite - carbon contact points. The reaction would thus be expected to terminate as a result of the formation of the reaction products at the interface /...

interface causing a break in the solid - solid contact between the chromite particles and the powdered carbon. This termination of the reaction, however, is found not to occur. This leads to the postulation that either CO gas must diffuse through this layer or in fact that solid carbon must diffuse from the outside of a chromite particle, which is surrounded by a product layer, into the unreacted zone. There has been a general reluctance to accept solid state diffusion as opposed to gaseous diffusion, as a possible mechanism for metal oxide reduction, since the data up to the present time on this subject indicates that gas - solid reactions are much faster than solid - solid reactions. Most of these reactions are in fact very rapid at elevated temperatures.

3. If CO is in fact the reducing species, despite the fact that CO in a pure form from a gas bottle has no effect on chromites at elevated temperatures, then one can only surmise that there are two forms of CO, namely bottled CO and a transition state CO. This latter form of CO might occur as an activated complex or merely as an activated form of CO. The possibilities of such a form of CO existing will be discussed in the theory on this section.

4. The possibility that carbon might act as a catalyst for the regeneration of CO was eliminated by the test carried out where only 50% stoichiometric carbon was added to the chromite. This fact is shown to be the case since the reaction went only to 50% completion in the presence of CO just as it had done when argon was used as a blanket gas. Furthermore even when this quantity of carbon had assisted in reducing the chromite to the 50% level, the spinel was not broken up so that CO /...

so that CO would reduce the remaining metal oxides. Alternatively the only remaining metal oxide could conceivably have been Cr_2O_3 which has already been shown not to be reducible under CO. Thus even in this instance CO proved ineffective.

5. It was noted that even when Fe_2O_3 was reduced with CO, the rate of reduction was very much slower than when solid carbon was used. It would appear then from all these tests that solid carbon is a far better reducing agent than CO and that CO does not in fact play any role in the reduction of chromite when it is introduced to the furnace as a pure gas.

6. A significant conclusion can be deduced from a comparison of the two curves in Figure 36. Both curves show the variation in rate of reduction in relation to the proportion of carbon added. In an earlier chapter the reduction of samples containing different amounts of graphite was dealt with. These results were used to draw the curve for chromite undergoing reduction at 1300°C. The maximum reduction rate at each different carbon content was chosen as the basis for comparison.

   For ilmenite reduction at 1075°C a maximum point is noted at 8,2 per cent carbon. While the increase in reduction rate with carbon content is due to an increase in the surface area of the carbon up to 8,2 per cent, the decrease above 8,2 per cent is due to a decrease in the surface area of ilmenite exposed to regenerated CO. In the case of the chromite, however, no such reversal in the slope of the curve is to be noted, since CO is not involved as a reducing species and therefore there is no diluent effect brought about by adding extra amounts of carbon.

Whereas /...

Whereas the shape of the ilmenite curve is attributable to changes in the relative surface areas of the reactants, no effect of surface area of carbon and chromite is found above the stoichiometric value. The slight upward slope of the chromite curve above stoichiometry is possibly due to small amounts of SiO_2 reducing even at 1300°C, since CO can reduce SiO_2 readily in the presence of carbon. Carbon lowers the activation energy for CO reduction of SiO_2 (Ref.22). The CO is present as the gaseous reaction product of the chromite.

7. A further point of interest is that whereas a decrease in the reduction rate was observed for ilmenite as the flow rate of the argon through the furnace was increased, no such trend was observed for the chromites. The dependence of the ilmenite reduction rate on argon flow rate suggests that at high flow rates, namely (20-30 cc/min), the argon dilutes the CO in the reaction zone, decreasing the partial pressure of CO and consequently the reduction rate. This result shows that no such effect on the reduction rate of chromite takes place, which further establishes the fact that CO gas plays no role as a reductant.

4.4 THEORY CONCERNING CARBON MONOXIDE

The part that CO definitely does play in the reduction of chromite is that it is the gaseous product of reduction when solid carbon is the reductant. Thus CO can be said to be a diffusing species, but it is not the reducing species. Boericke and Bangert (Ref.20) as mentioned earlier, established several reactions which indicate that CO is the gaseous product. The chromite formula has been simplified to $FeO.Cr_2O_3$.

Consider equation (4), namely

$$FeO.Cr_2O_3 + CO = Fe + Cr_2O_3 + CO_2$$

Thermodynamic calculations indicate that CO is definitely not an effective reducing agent in this system. The maximum calculated amount of CO that can react with a chromite at a temperature of 1700°K is close to 3 per cent. Thus for all practical purposes, the only gaseous product in the selective reduction of chromite with solid carbon is CO, this CO in turn is not a reductant.

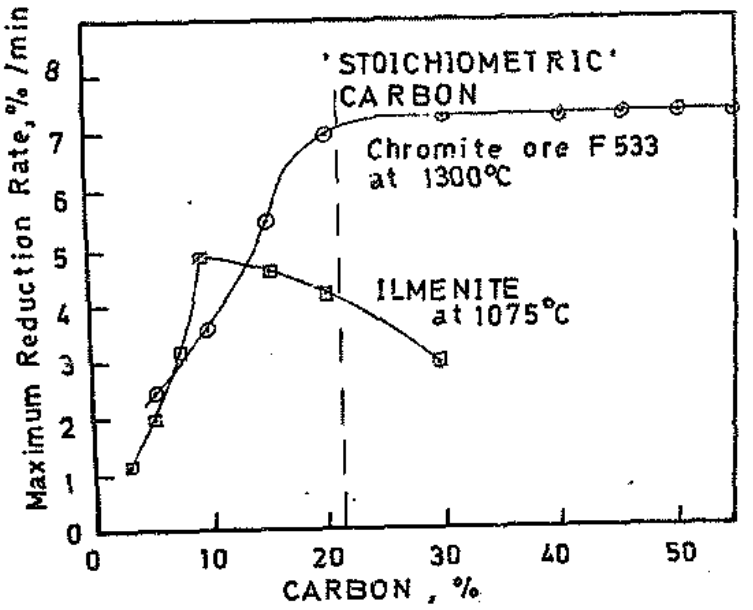


FIGURE 36 The effect of variations in the carbon additions on the reduction rates of chromite and ilmenite ores.

CHAPTER V

5. THE EFFECT OF PARTICLE SIZE OF CHROMITE F 533 ON ITS REDUCTION BEHAVIOUR

5.1 INTRODUCTION

The reason for this phase of the project was to establish what effects a variation in chromite particle size could have upon certain parameters such as the mechanism, the reduction rate and the activation energy. It might then be possible to extrapolate any possible trend associated with particle size from the small particles up to the large chunks of chromite actually used in the submerged arc furnace which produces the high-carbon ferrochromium.

Chromite F 533 was selected for this phase of the project as it contains the least quantity of gangue minerals, namely 2% by weight. This meant that on screening out several size fractions from a sample of the bulk crushed ore, there would be only a small variation in the distribution of the gangue minerals throughout the six size fractions which were chosen. This would ensure a relatively small difference in overall composition. The six size fractions chosen are given in the table below. The coarsest fraction was chosen to be just above the average grain size, namely -10# +14# . The in-between sizes were divided into four equally spaced groups thus:-

TABLE 26

TABLE OF SIX SIZE RANGES

	Mesh (Tyler)	Average Particle Size (mm) based on inbetween mesh size
1.	- 10# + 14#	1,397
2.	- 20# + 28#	0,701
3.	- 35# + 48#	0,351
4.	- 65# +100#	0,175
5.	-150# +200#	0,089
6.	-270# +400#	0,043

5.2 EXPERIMENTAL METHODS

Isothermal runs were carried out on the thermal balance at 1300°C, 1400°C, 1500°C and at 1550°C. This was a suitable temperature range for the larger size fractions since the rates of reduction of larger particles at temperatures of 1200°C and lower were found to be extremely slow. As in the previous thermal balance experiments when solid carbon was used as a reducing agent, 0,5000 gm of chromite was weighed out. The stoichiometric amount of carbon for chromite F 533 was added.

FIGURE 37

Reduction of chromite F 533 - Size 1.

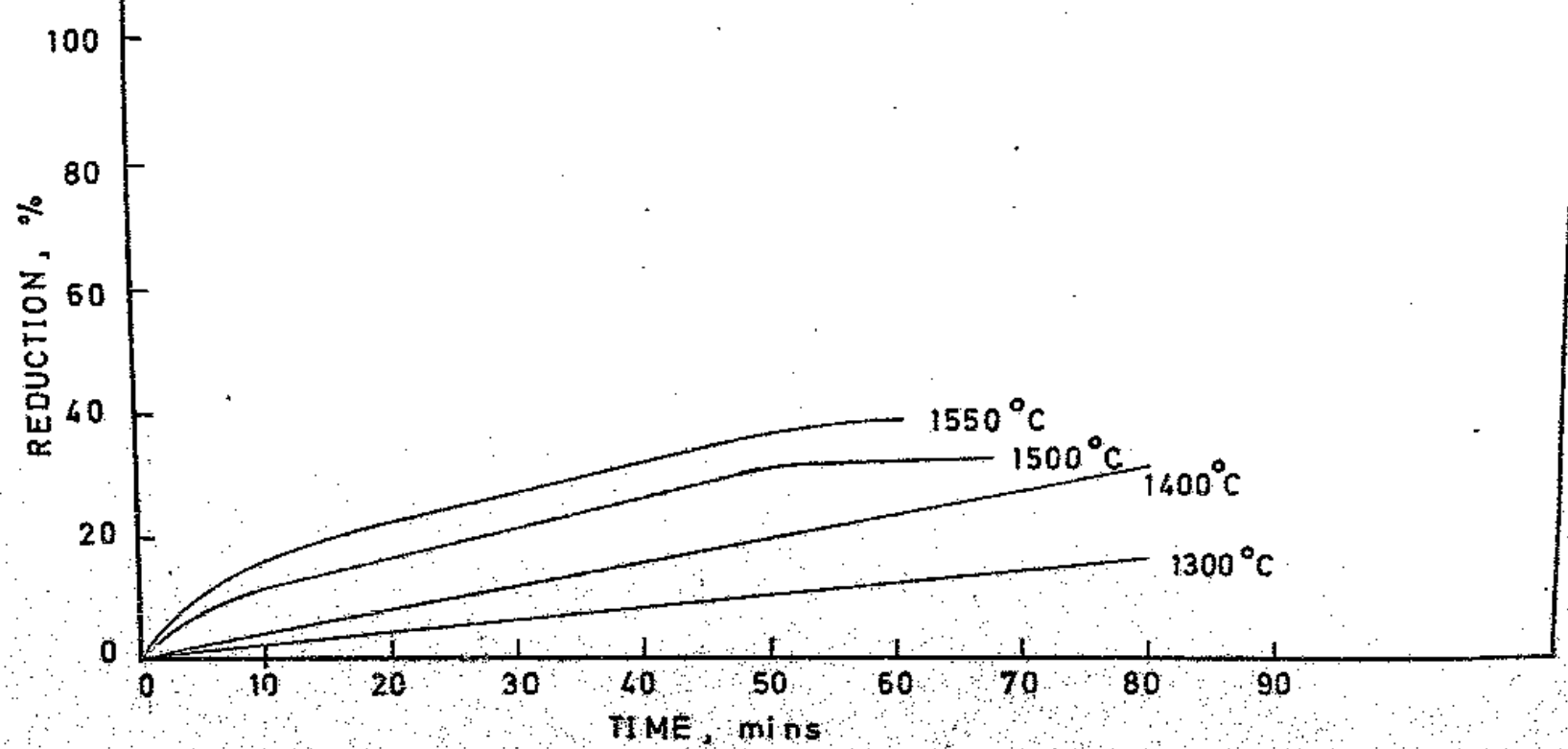


FIGURE 38

Reduction of chromite F 533 - Size 2.

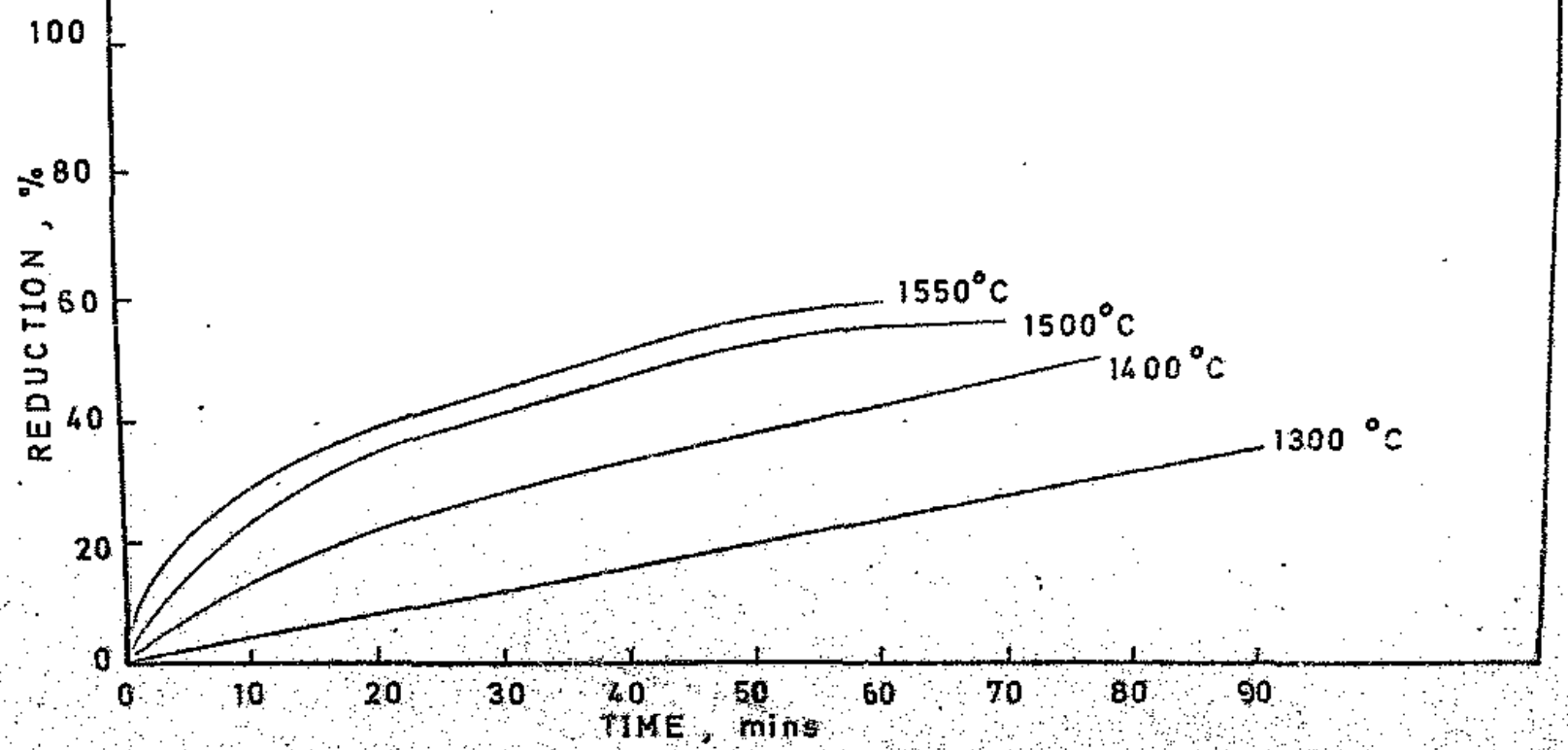


FIGURE 39

Reduction of chromite F 533 - Size 3.

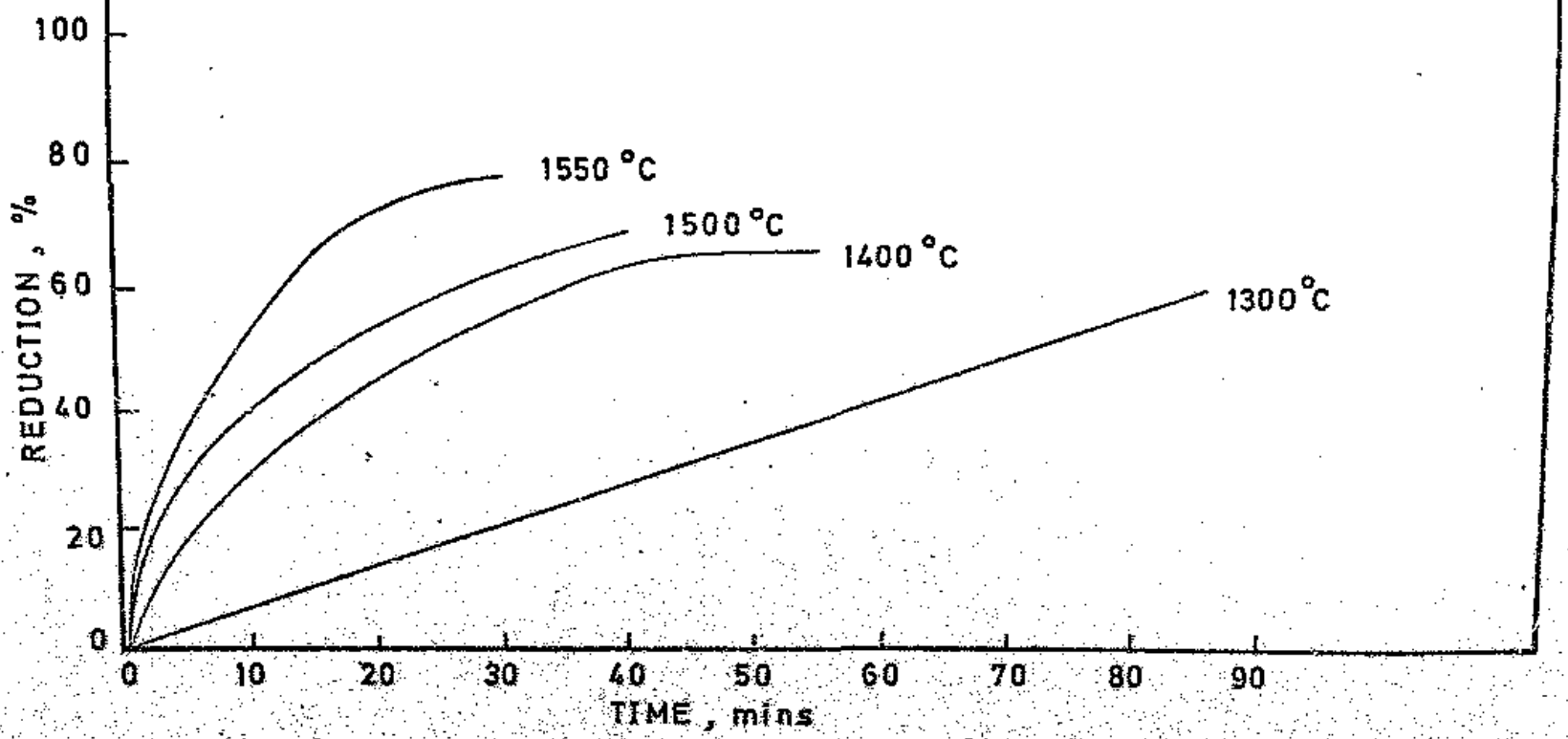


FIGURE 40

Reduction of chromite F 533 - Size 4.

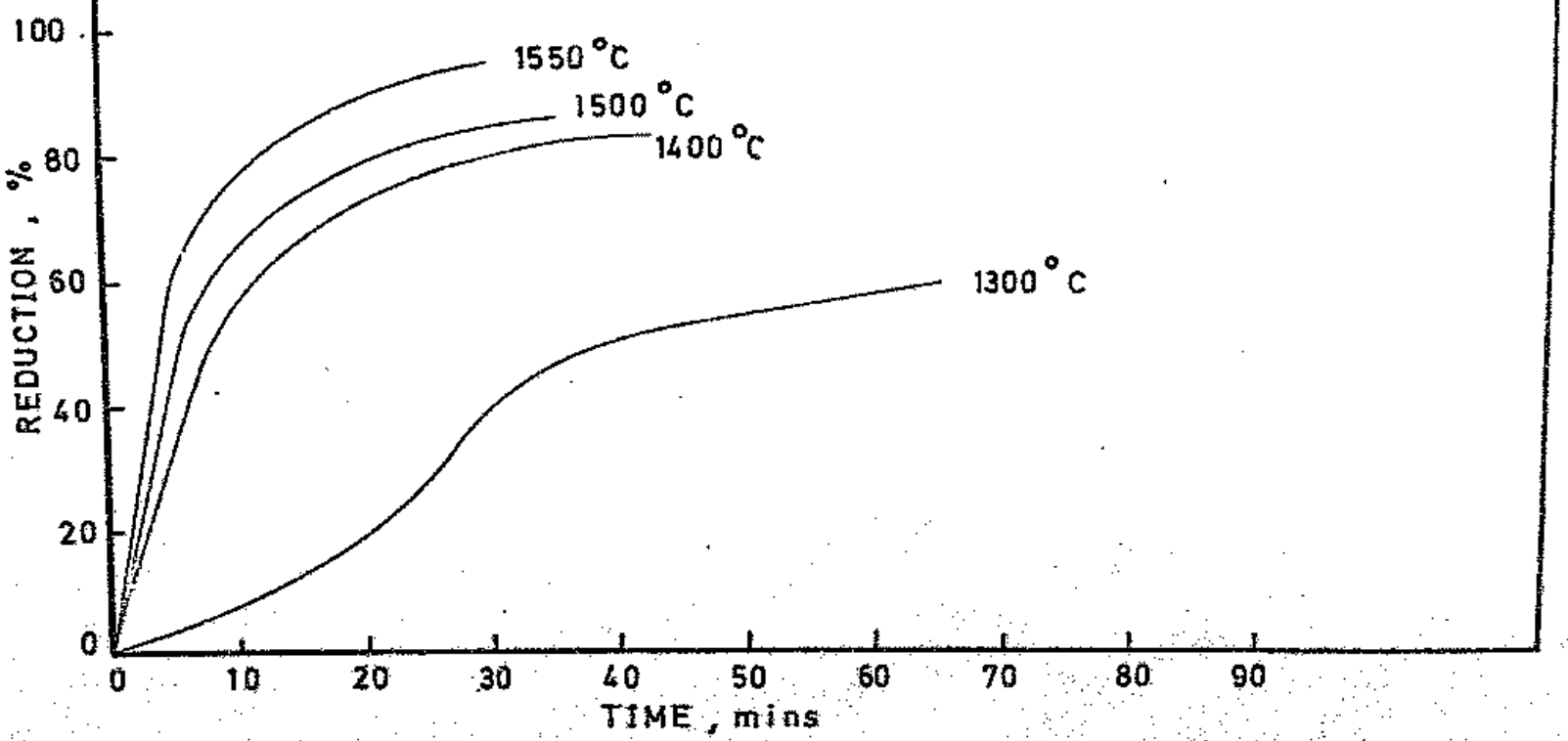


FIGURE 41

Reduction of chromite F 533 - Size 5.

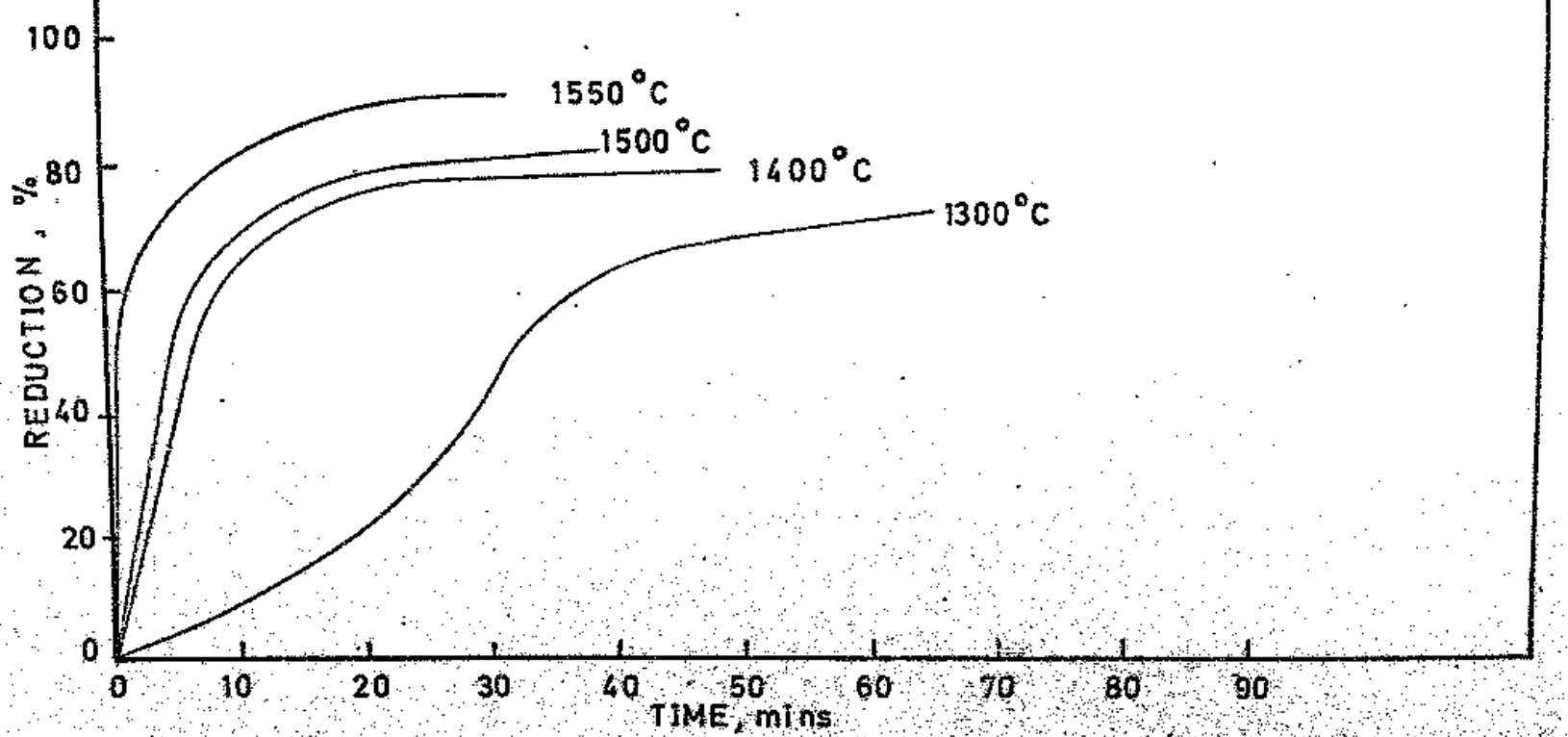
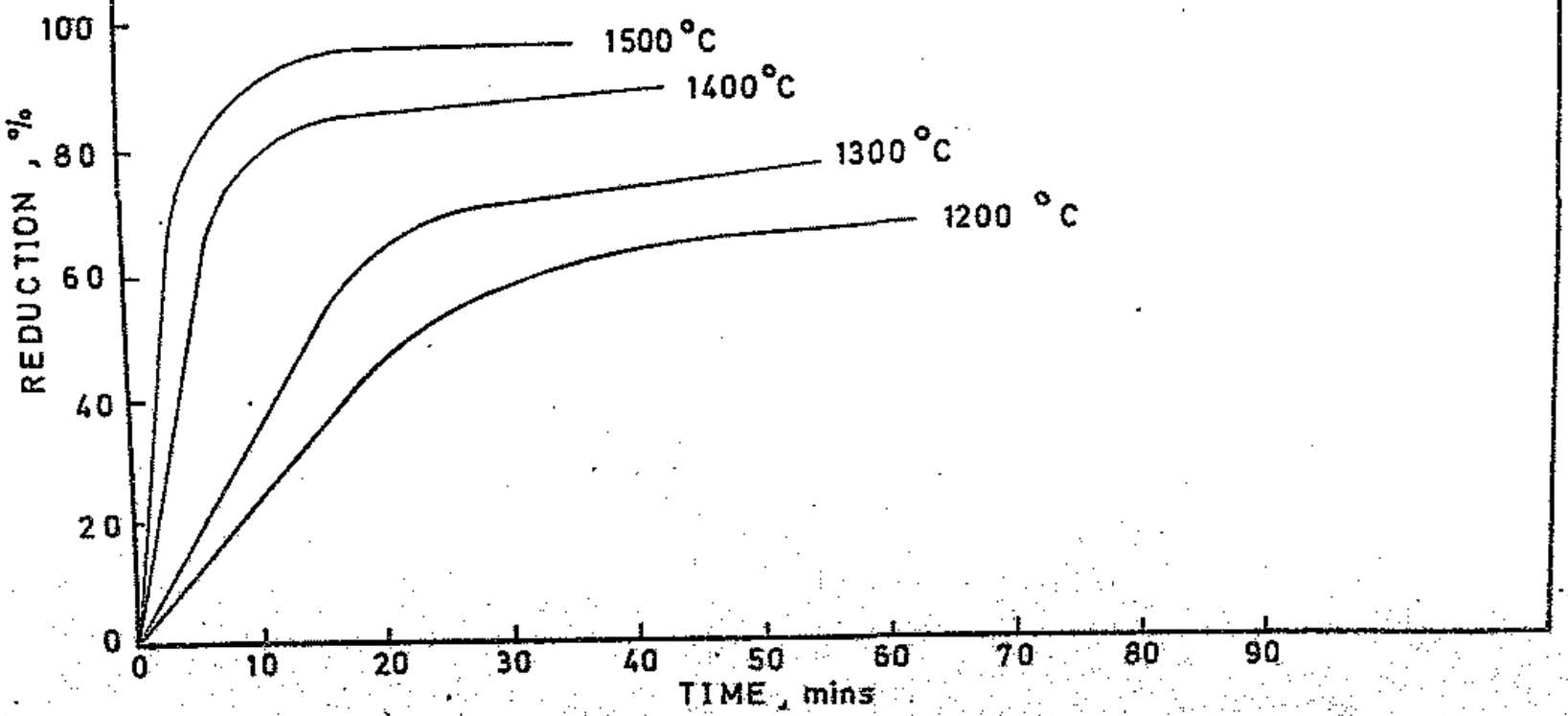


FIGURE 42

Reduction of chromite F533 - Size 6.



5.3 DISCUSSION OF THE RESULTS

5.4.1. Analysis of the Results

The computer was used to compute the data in exactly the same manner as described in section 3. The results from the computer analysis are presented in Table 27.

The mechanism for reduction which was found to hold for all sizes was the same as that which was found to hold for the results in section 3, namely diffusion through a reaction product layer according to th. Brounshtein-Ginstling equation.

In examining these results in Table 27 the first fact to be revealed about the various sizes is that the activation energy (E_a) values are of the same order of magnitude no matter what the particle size is. The six E_a values were fed into the computer and a mean value of 203.3 k joules/mole was obtained and the percentage deviation of the worst result from this mean was better than 5%. (Figure 43 shows this point). The activation energy appears to have a fundamental value for each of the chromites and it does not depend on the size of the particle.

The second fact to be noted is perhaps the more relevant from practical implications, and this is the fact that size has such a pronounced effect on the rate constant, i.e. reduction rate. The larger the particle size, the slower the reduction rate at a constant temperature.

The value of the rate constant decreases with increasing particle size but the E_a value is constant for all sizes.

TABLE 27

TABLE OF COMPUTED RESULTS FOR CHROMITE F 533 + STOICHIOMETRIC CARBON FOR THE SIZ SIZE RANGES CHOSEN

ee o.	Temp °C	Reduction k Rate f(x)/min	ln k	Slope b	E_a Value	r	σ	ln k = ln A - $E_a/_{RT}$ Equation
1	1300	,3889 x 10^{-4}	-10,1548	-,2598 E +04	216,0	,993	,115	y=6,45-,2598x10^4x
	1400	,1284 x 10^{-3}	- 8,9604					
	1500	,2922 x 10^{-3}	- 8,1381					
	1550	,3425 x 10^{-3}						
2	1300	,1386 x 10^{-3}	- 8,8839	-,2334 E +04	194,0	,986	,114	y=6,07-,2334x10^4x
	1400	,4669 x 10^{-3}	- 7,6694					
	1500	,8282 x 10^{-3}	- 7,0963					
	1550	,1037 x 10^{-2}	- 6,8714					
3	1300	,5014 x 10^{-3}	- 7,5981	-,2498 E +04	207,7	,989	,140	y=8,39-,2498x10^4x
	1400	,1763 x 10^{-2}	- 6,3407					
	1500	,3123 x 10^{-2}	- 5,7690					
	1550	,4503 x 10^{-2}	- 5,4030					
4	1300	,1139 x 10^{-2}	- 6,7776	-,2579 E +04	214,3	,961	,280	y=8,83-,2578x10^4x
	1400	,5690 x 10^{-2}	- 5,1690					
	1500	,8478 x 10^{-2}	- 4,7703					
	1550	,1114 x 10^{-1}	- 4,4972					
5	1300	,2053 x 10^{-2}	- 6,1885	-,2331 E +04	197,7	,950	,280	y=8,80-,2331x10^4x
	1400	,7946 x 10^{-2}	- 4,8351					
	1500	,9203 x 10^{-2}	- 4,6882					
	1550	,1961 x 10^{-1}	- 3,9317					
6	1200	,1961 x 10^{-2}	- 6,2343	-,2291 E +04	190,5	,991	,202	y=9,05-,2291x10^4x
	1300	,3533 x 10^{-2}	- 5,6456					
	1400	,1736 x 10^{-1}	- 4,4777					
	1500	,1891 x 10^{-1}	- 4,0069					

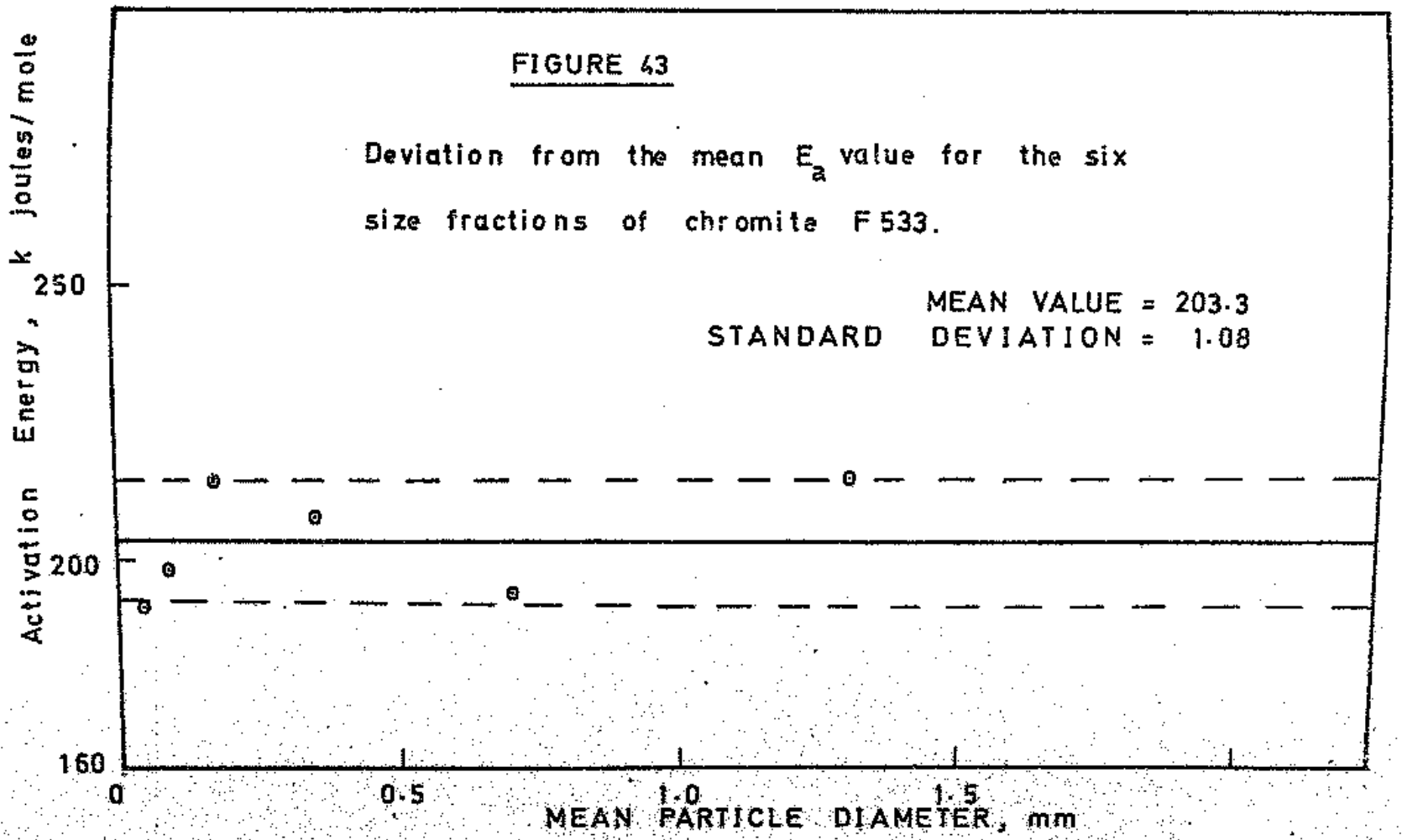


FIGURE 43

Deviation from the mean E_a value for the six size fractions of chromite F 533.

A fine particle size will result in a rapid rate of reduction, at say 1300°C, and in an even faster rate at say 1500°C, but nevertheless this increase in reduction rate is comparable to the rate of increase in rate of reduction for a coarse particle which reduces slowly at 1300°C and only somewhat faster at 1500°C.

The results obtained are satisfactory, since firstly the mechanism fit in the computer gives the same suitable equation throughout. The actual fit to this model equation, namely:-

$$1 - {}^{2}/_{3}\, x - (1 - x)^{2/3} = {}^{k}/_{r_o}{}^{2}.t$$

improves for the coarser size fractions. This observation has led to some interesting postulations about the effects of surface area and the diffusion process on the rate of reduction. Graph number 44 illustrates the point under consideration.

This graph of reduction rate against mean particle size (diameter) shows firstly that the lines are very nearly parallel as does Figure 43 which shows the Arrhenius plots for the various size ranges. The lines should be parallel in fact for similar E_a values. The slope of the lines in the former graph, however, changes rapidly in the diameter range 0 - 0,2 mm. After this 0,2 mm value the slope of the lines flattens out somewhat.

The feature could be explained as follows:-

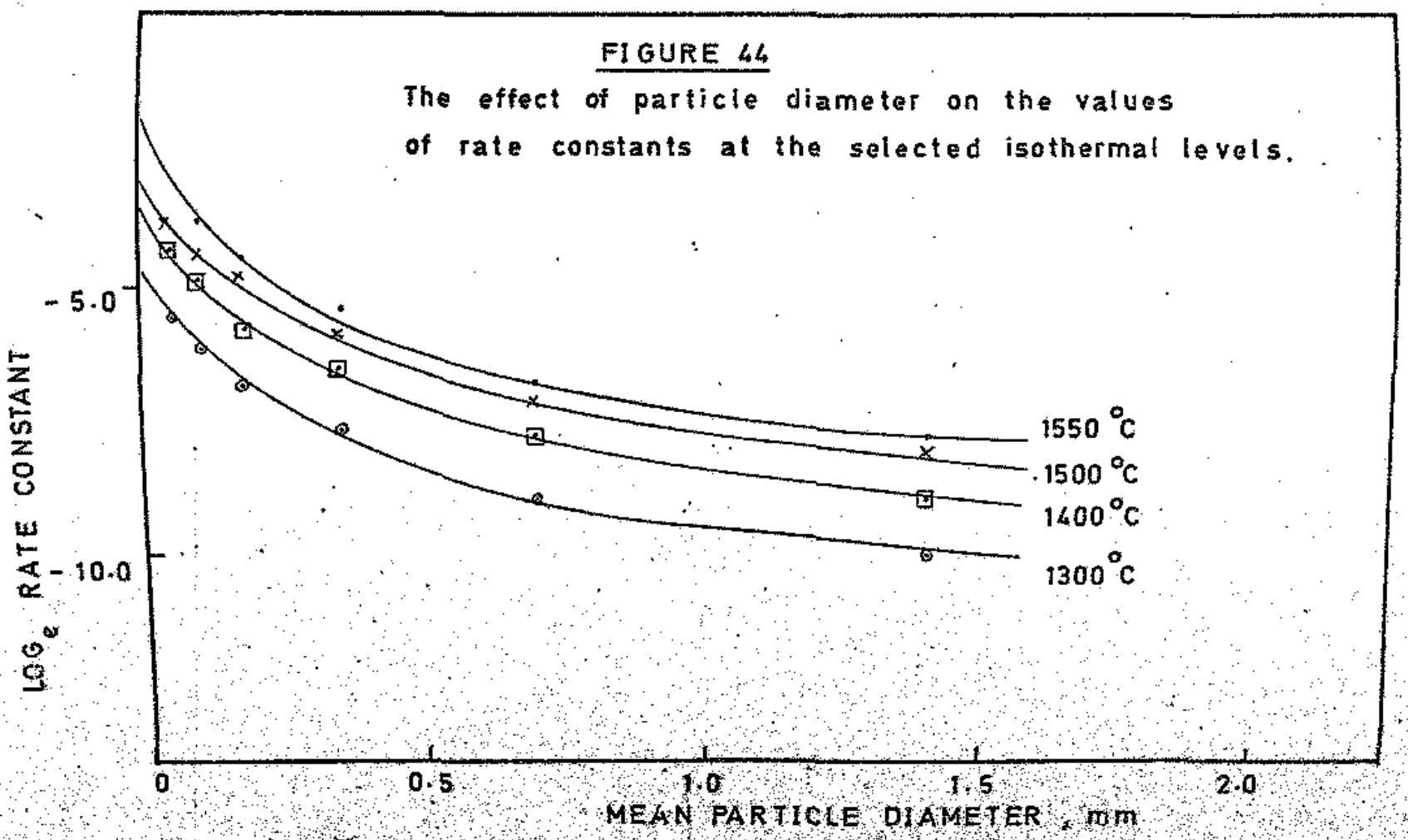


FIGURE 44

The effect of particle diameter on the values of rate constants at the selected isothermal levels.

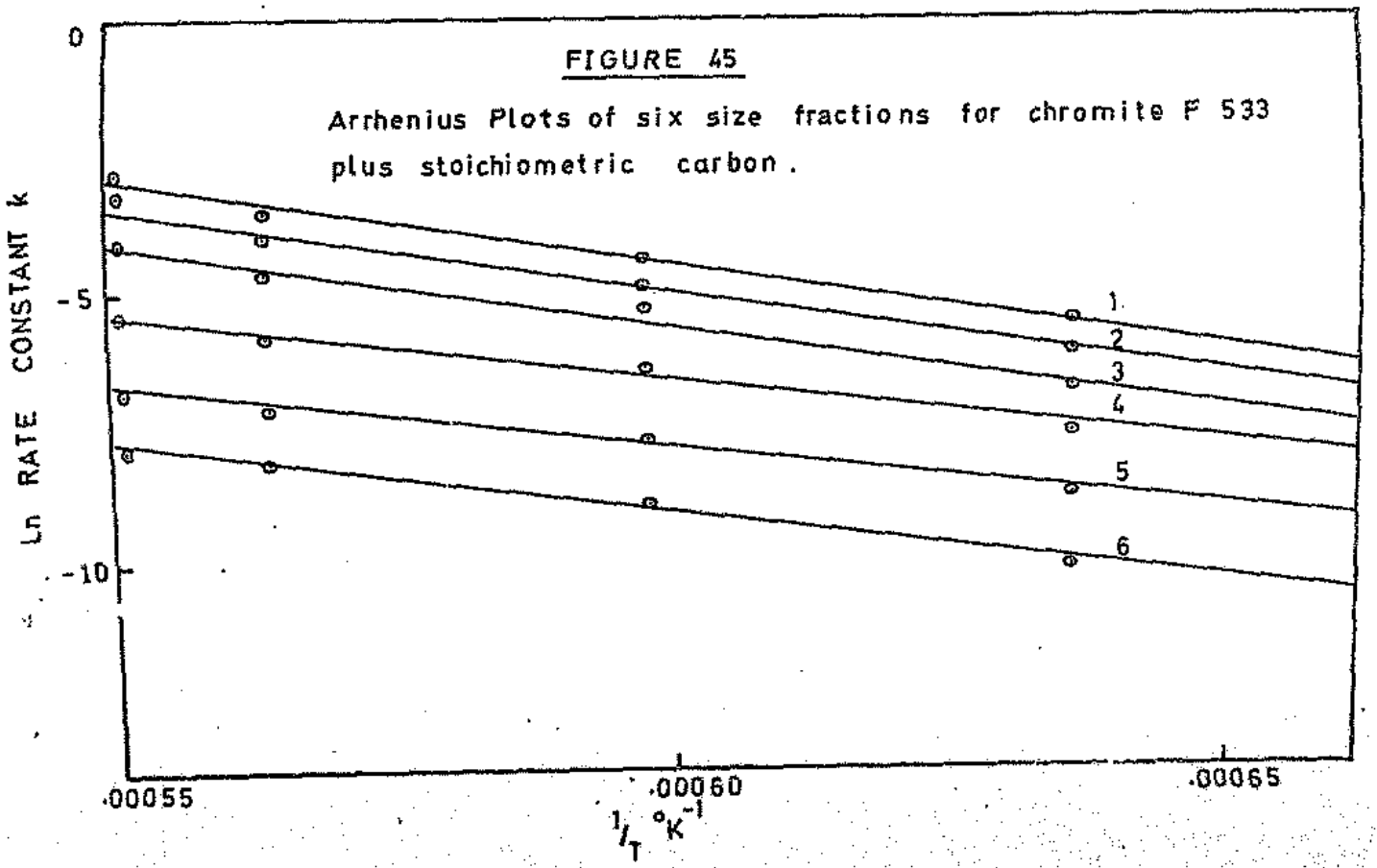


FIGURE 45

Arrhenius Plots of six size fractions for chromite F 533 plus stoichiometric carbon.

In the small particle size range, namely particles with diameters less than 0,2 mm, the effect of surface area is very marked. A small change in particle diameter results in a large change in the reduction rate. Therefore although surface contact is not a mechanism in the true sense of the word, it is a rate controlling process just as decreasing the carbon content or adding an inert diluent would be. The overall rate controlling process is not therefore simply diffusion, which must always take place, but actual particle contact between the chromite and the carbon. This is a surface area effect therefore. Once, however, the particles are greater than 0,2 mm in diameter, diffusion becomes a more and more important rate controlling process. Thus it does not matter whether a particle is say 0,4 mm or 1,5 mm in diameter - there is only a small decrease in the value of the rate constant, i.e. a small decrease in the rate of reduction at each of the temperature levels. In extrapolating the particle size up to chunks approximately 30 - 40 cm in diameter, diffusion can thus be seen to be an extremely important aspect of the reduction process in the submerged arc furnace. It is anticipated that the reduction rate would furthermore not be too different from particles 1,5 mm in diameter if extrapolation of the curves in Figure 43 is considered. One aspect must, however, be borne in mind. The largest particle size is about grain size whereas lump ore consists of many grains.

Another interesting point is that the value of the frequency factor "A", increases with decreasing particle size as can be seen in Table 27. This is related to the better

particle to /...

particle to particle contact for smaller particles and can be tied up with the point made above, namely, the surface area effect. Values of "A" from 10 - 8 indicate surface area dependency whereas values from 8 - 6 indicate diffusion dependency as the predominant rate controlling process.

CHAPTER VI

6. THE BEHAVIOUR OF CHROMITE AS STUDIED BY DIFFERENTIAL THERMAL ANALYSIS (DTA)

6.1 INTRODUCTION

Differential thermal analysis (commonly abbreviated to DTA) was considered as an alternative method to TGA, whereby the chosen chromites might be investigated. Since DTA is a well known method of studying heats of reactions as well as reaction kinetics, it was fairly likely that information gained using this method of investigation might help substantiate the TGA results relating to the kinetics of reduction by solid carbon. Furthermore tests carried out on the natural chromites under atmospheric conditions might help to confirm the effects that were noted when using TGA, namely the oxidation and dehydration reactions which should reveal endothermic peaks.

In introducing the subject of DTA, it is possibly best to discuss definitions relating to DTA. Differential thermal analysis is a technique whereby the difference in temperature between a substance and a reference material is recorded while the two specimens are in a region where an identical state of temperature prevails while the environment is heated or cooled under controlled conditions. The recorded graph is called the differential thermal curve (DTA curve). This curve should show a peak or series of peaks if the substance under consideration undergoes either phase changes or reactions with its environment. The peak areas are related to the energy of the reaction or phase change taking place.

In considering the behaviour of chromite under both atmospheric and reducing conditions, it was thought that DTA could be of assistance in finding out at what temperatures fusion takes place and the heats of reactions for the various chromites with their fluxes. To be able to study the chromites by DTA, suitable apparatus was assembled.

6.2 THE APPARATUS FOR DTA

6.2.1. The Furnace and DTA Head Assemblies

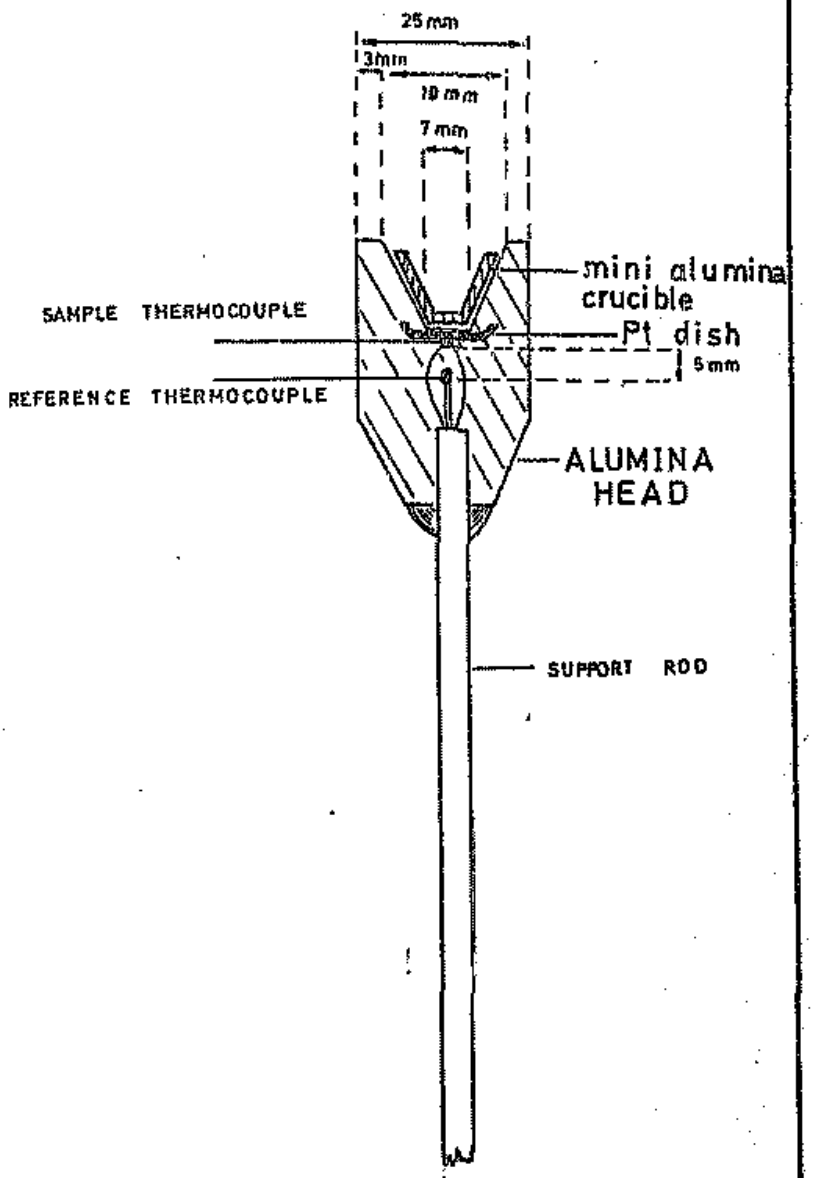
The furnace tube was supplied by Stanton. It was wound with platinum rhodium wire which allowed it to attain a temperature of 1700°C. This tube with its windings was mounted in a furnace shell. The material used to construct the inner and outer shells of the furnace was stainless steel. The inner packing was high purity alumina powder and the outer insulation was asbestos. The furnace end plates were made from Sindanyo board. The whole furnace assembly was mounted on a frame in such a way that it was suspended from a chain which passed over a series of cogs and was attached to a counter balance weight. The reason for mounting the furnace in this way was to enable it to be slid up and down over the DTA assembly. This facilitated easy loading and unloading of samples in the sample holder in the DTA head.

The DTA head was housed in a gas-tight sheath. This gas sheath was used to permit atmosphere control within the furnace. There was some difficulty in designing the most suitable DTA head since it had to conform to such small dimensions. The diameter inside the gas sheath was the limiting size.

The most suitable design for the alumina DTA head assembly was achieved by consulting the literature. To economise space the actual alumina head was made the reference sample as well, since Al_2O_3 does not undergo any phase changes in the temperature range in which the chromites were studied. An illustration of the DTA head is shown in Figure 46. The thermocouples used to measure both the reference and sample temperatures and the furnace temperature were all Pt-6% Rh/Pt-30%Rh.

FIGURE 46

DTA HEAD APPARATUS



6.2.2. The Control and Recording Systems

The control unit consisted of a "series 60 control using three action C.A.T. unit". Full details of this unit are to be found in the booklet put out by the Leeds and Northrup Company(Ref.31).

The major components may be summarised as follows:-

1. A primary element sensitive to the variable quantity to be controlled. In this case the variable to be controlled was the heating current to the furnace winding.
2. A recorder which measures the output of the primary element. This was in fact a dial graduated in millivolts from 0 to 7. This instrument, which also contains a control setting device, signals the control unit whenever the measured variable departs from the control point setting.
3. A control unit which automatically produces an output current proportional, in the range 0 to 5 milliamps, to the input requirements of the controlled process of either heating or cooling the furnace.
4. Equipment for translating the current output of the control unit into process input. The C.A.T. control unit can thus be adapted for use with a General Electric "REACTROL" system for the control of electrically heated processes. In this application, an IR drop produced by the control unit output current serves as the control voltage input to the "Reactrol" system. Another expression for "Reactrol" is a saturable core reactor. Thus by having the furnace temperature, as measured by a thermocouple,

(Pt-6%Rh/Pt - 30%Rh) as input to the C.A.T. control unit, and by using a cam, suitably graduated for the thermocouple over a certain temperature range, the heating of this furnace can be controlled very sensitively. Greater detail relating to the control unit is to be found in the relevant publication as mentioned earlier.

There were two recording units. One was simply a Leeds and Northrup Speedomax $bX_1 - X_2$ recorder and full details are found in the booklet on this apparatus (Ref. 31). The other was a recorder to follow the heating of the actual furnace windings.

6.3 EXPERIMENTAL METHODS

6.3.1. The Behaviour of Chromites using DTA under Atmospheric Conditions

Crushed samples of four of the chromites at -325 mesh were subjected to DTA runs from room temperature up to 1500°C. The four chromites chosen represented each of the groups chosen on a basis of their TGA behaviour under atmospheric conditions. The samples were placed in a mini alumina crucible in the DTA head but the gas sheath was left off the apparatus to allow free atmospheric conditions to prevail.

6.3.2. Results

The results were rather disappointing in that no sharp peaks were obtained. This is, however, not really surprising since the reactions taking place do so over a large temperature range and furthermore they do so gradually. The oxidation reaction of the FeO certainly takes place over a somewhat narrower range of temperature but the gangue percent is on an

average so low /...

average so low that the reaction heat is absorbed into the chromite mass as a whole. Thus little can be deduced from these results although in the discussion on this section a few points of interest are brought forward. A typical example is given in Figure 47.

6.3.3. Discussion of the Results

This discussion is based on the DTA and TG curves found in Figure 47. The theory behind the TG curve has already been discussed in Section 2. The endothermic curve on the DTA heating cycle ties up with this oxidation reaction of the chromite. The DTA curve switches to an exothermic trend at about 1250°C which corresponds to the reaction where oxygen is lost to the spinel structure, as mentioned in the section dealing with the theory of this weight loss reaction. Thus the shape of the DTA curve on the heating cycle can be very simply explained. As can be seen, however, there are no sharp peaks, merely endothermic or exothermic trends.

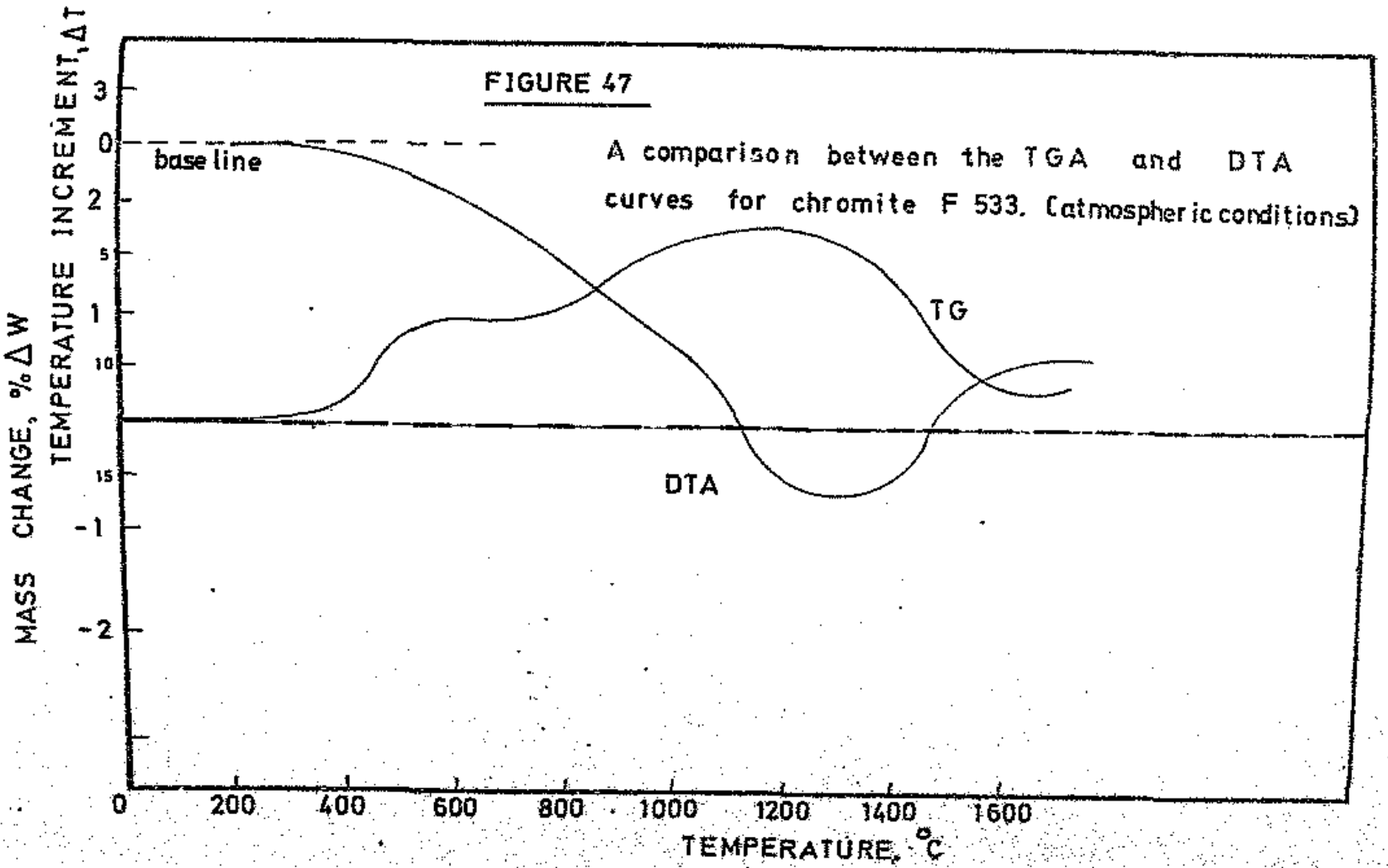


FIGURE 47

A comparison between the TGA and DTA curves for chromite F 533. (atmospheric conditions)

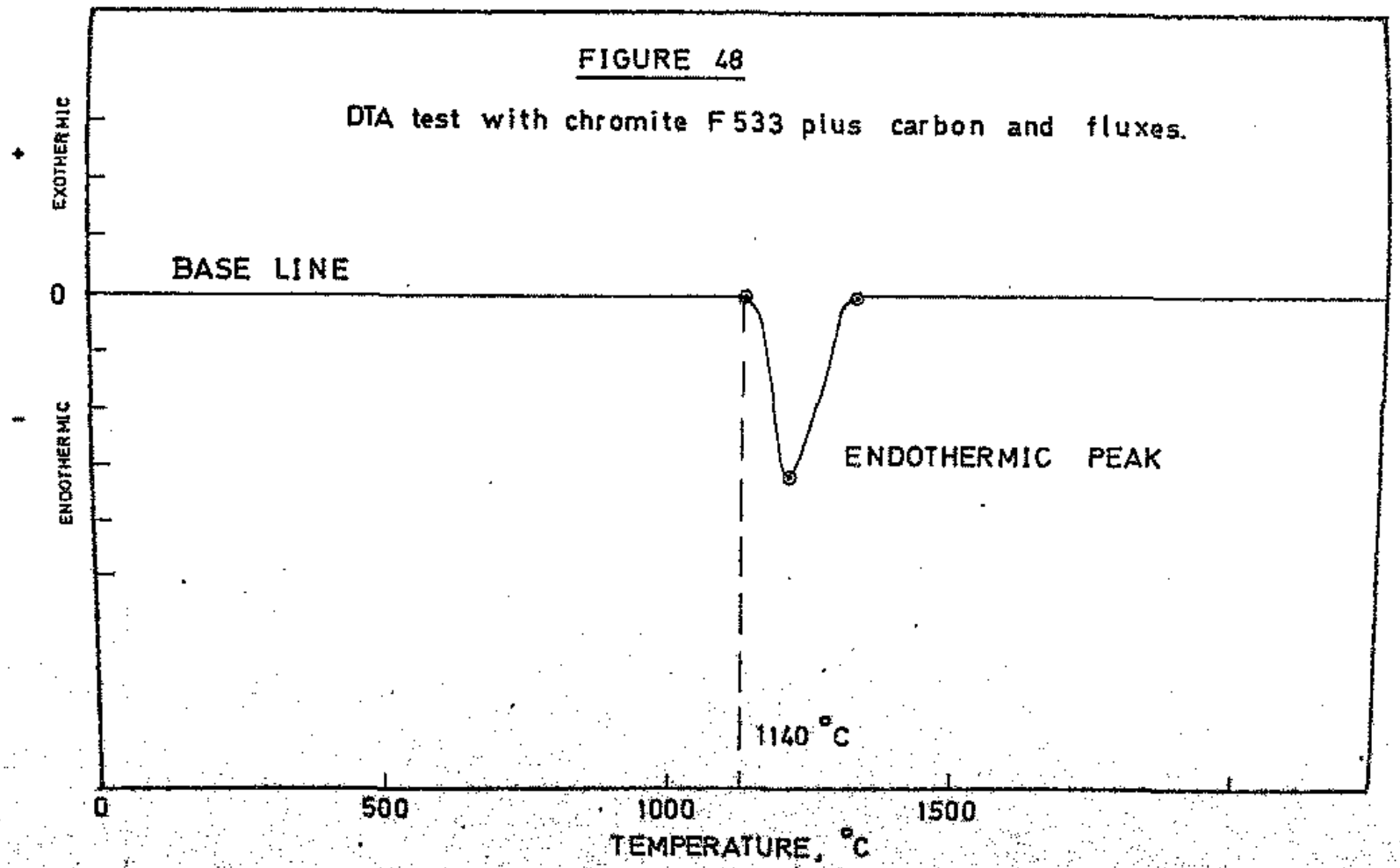


FIGURE 48

DTA test with chromite F 533 plus carbon and fluxes.

6.3.4. The Behaviour of the Chromites under Reducing Conditions with and without Fluxes as studied by DTA

6.3.4.1. Experimental Methods

The DTA apparatus was used in the same manner as discussed in the previous section. The results for the chromites with solid carbon gave an endothermic peak at 1200°C to 1250°C (see Figure 48). The addition of fluxes made no difference to this peak and neither did the chromite used. These results were therefore disappointing since it had been hoped to use DTA to confirm the characterisation as established by the TG results.

It was decided to use the DTA equipment, however, to prepare samples for optical analysis. The only chromite sample chosen for this phase of the project was chromite F 533. Samples of -325 mesh chromite were made up with the stoichiometric amount of carbon. A similar procedure was followed to that which was used when the samples were tested using TG. The fluxing additions were also carried out in exactly the same way as dealt with in an earlier section.

Twenty runs were carried out in all. The samples were heated from room temperature up to 1100°C, 1200°C, 1300°C, 1400°C and 1500°C. At each of these temperature levels the samples were cooled after times varying from 0 to 4 hours at the zero, one, two and four hour intervals. The samples were cooled at the same rate as they had been heated. The answers obtained are displayed diagrammatically in Figure 49.

Simultaneously with the DTA runs, twenty TG runs were carried out by heating the chromite plus fluxes plus carbon to each of the five temperature le els and soaking isothermally at these temperatures. The percentage reduction values were read from the TG curves at the 0, 1, 2 and 4 hour intervals (see Figure 49).

6.3.4.2. Results

A typical DTA curve is presented as Figure 48. No secondary calculations were made because it was felt nothing could be gained in analysing the DTA results since they reflected no differences between the various chromites. Thus this curve is merely a reproduction of the endothermic peak which occurs in the temperature range 1100°C to 1200°C. This peak appears to be due to the sintering of the sample.

6.3.4.3. Discussion of the Results

On consulting Figure 49 it can be seen that reduction really only commences after 2 hours at 1200°C or after the sample reaches 1300°C. The values for the percent reduction were read off TG curves for the runs carried out in parallel with the DTA runs. The photographs merely illustrate the formation of the metal phase, which is most clearly shown in the series at 1400°C and the fusion process at 1500°C resulting in the coalescence of the metal as shown in the photograph for the same at 1500°C for four hours. This photograph thus illustrates visually the process of incipient fusion.

Reduction at 1200°C is very slow compared with the rate at 1400°C. It takes only 40 minutes

heating /...

heating continuously up to 1400°C to reach 90 per cent reduction, whereas it takes four hours at 1200°C to reach only 80 per cent reduction. A further point to notice is that no separation of the slag and metal phases takes place at 1200°C. At 1300°C the metal starts to coalesce and in the 1400°C temperature range complete coalescence takes place. True slag metal separation takes place after one hour at 1500°C. The metal phase remains trapped in the slags of samples shown in Figure 49 for times of 1, 2 and 4 hours at 1500°C. The metal has a much higher density than the slag, so it is somewhat strange that the metal does not collect in the bottom of the crucible, but this fact might be explained by the small amount of metal being held in suspension in small globules. The crucible geometry might also be a contributory factor.

Holding the sample isothermally at 1200°C results in reduction from 0 to 80 per cent in 4 hours, whereas at 1300°C, reduction increases from 19 per cent to nearly 90 per cent in four hours. At 1400°C, reduction in the four hours increases from 91 per cent only to 100 per cent. By the time the temperature reaches 1500°C, nearly 100 per cent reduction has already been achieved where the heating rate is 7°C per minute.

These photographs merely show the sintering metalization and melting processes and do not really assist in giving any quantitative answers. The reason for not using the Leitz hot stage microscope, as mentioned at the beginning of this report, are her-by substantiated.

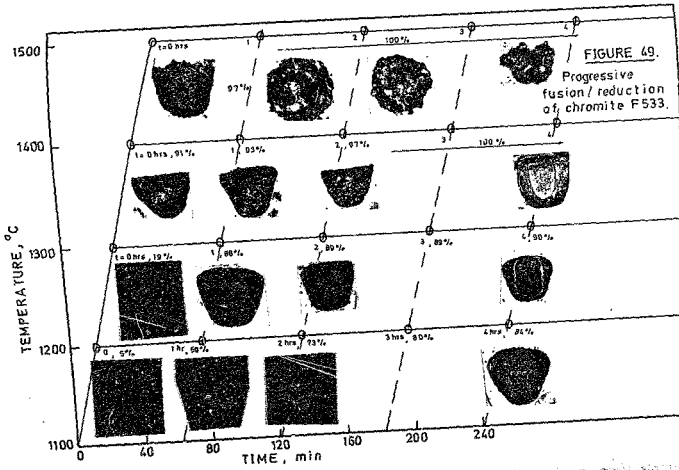


FIGURE 49.
Progressive fusion/reduction of chromite F533.

CHAPTER VII

7. DISCUSSION

The chromite ores were found to undergo several reactions under atmospheric conditions. Some chromite ores underwent weight losses of up to four percent in the temperature range 400°C to 1000°C. The weight loss reactions were attributed either to hydrated minerals, e.g. serpentine, or to carbonataceous minerals, e.g. magnesite. Therefore these two weight loss reactions can be seen to be a property only of the gangue and not of the actual chromite spinel. It was mainly this weight losing characteristic of the gangue of some of the chromites that enabled the four groups in Chapter II to be drawn up.

The original structure of the chromite spinel is unbalanced in that the Fe^{2+} and Mg^{2+} ratio is non-stoichiometric, and neither are the Fe^{3+}, Al^{3+} and Cr^{3+} ratios stoichiometric. The spinel structure consists of both tetrahedral and octahedral co-ordinations in the lattice - the tetrahedral sites being the smaller(Ref.32). The spinel has an inverted type of structure since the larger divalent cations of Fe^{2+} and Mg^{2+} occupy these smaller tetrahedral positions, whereas the smaller trivalent cations of Fe^{3+}, Al^{3+} and Cr^{3+} occur in the larger octahedral positions.

When the chromites are heated in the temperature range 300°C to 1200°C under atmospheric conditions, the Fe^{2+} oxidises partially to Fe^{3+}(Ref.12). This causes a partial reconstitution of the spinel, since the divalent cations from the tetrahedral positions move to the octahedral sites, while the trivalent cations move to the tetrahedral localities(Ref.31). The reconstitution leads to a more stable spinel structure. If, however, pure oxygen is introduced during heating, the Fe^{2+} all tends to oxidise to Fe^{3+}, leaving no divalent cations to balance the

Mg^{2+} /...

Mg^{2+}. This would result in a complete breakdown of the spinel.

Under reducing conditions (obtained in the submerged arc furnace), naturally, no oxidation of the spinel is expected, so that the chromite would be expected to reach temperatures around 1100°C, where reduction begins, without having undergone this reconstitution, and only the gangue will have altered. (See Figure 56). The chromite ore contains oxides of Al, Mg, Fe and Cr, but only those of Fe and Cr are thermodynamically reducible in the system with carbon as a reductant and at the temperatures associated with the submerged arc furnace. The temperatures at which FeO and Cr_2O_3 in the spinel are reducible are above 1050°C and 1130°C to 1185°C for the two oxides respectively. The FeO is reduced to the metal or the carbide thus:-

$$FeO + C = Fe + CO$$

or

$$2FeO + {}^{8}/_{3}C = {}^{2}/_{3}Fe_3C + CO$$

while the Cr_2O_3 preferentially forms the carbide only. (See Figure 50).

$${}^{2}/_{3}Cr_2O_3 + {}^{18}/_{7}C = {}^{4}/_{21}Cr_7C_3 + 2\,CO$$

From thermodynamic considerations it can be seen that the formation of metallic iron and Fe_3C precedes the formation of chromium carbide. Once the temperature reaches about 1200°C, the chromium carbide and Fe_3C are preferentially formed. Both of these components dissolve in the iron to give a mixed carbide of iron and chromium.

Unlike the laws of thermodynamics, however, the theory of reaction rates is far from being rigorous. Both homogeneous and heterogeneous reactions can take place. Almost all metallurgical reactions are heterogeneous in that they involve two, three or even more stages. The method used to study the kinetics was to /...

was to measure the reduction rate at several temperature levels. The reduction step which has the highest activation energy is the rate controlling stage. There can, however, often be more than one slow stage controlling the overall observed reaction rate. The approach used in this project enabled an overall mechanism to be established from the reaction rates at the various isothermal temperatures. The reduction of chromite was shown to be diffusion controlled, but this statement is in fact a generalization.

The process of diffusion is an involved study. Some doubt still existed as to whether carbon was definitely the diffusing reductant species. A final test was design[illegible] establish whether carbon was the most feasibl[illegible] [illegible]using species. A sample of chromite F 533 weighing 0,5000 gm was mixed with a specially prepared sample of high-carbon ferrochromium weighing 2,000 g. The composition of the high carbon-ferrochromium was:-

58 per cent Cr
34 per cent Fe
8 per cent C

This sample made up from the chromite ore and the high-carbon ferrochromium was run on the thermal balance, isothermally, at 1400°C. Reduction of the chromite took place at a reasonably rapid rate at this temperature. A blank was also carried out using the high-carbon ferrochromium on its own. The rate of weight loss was negligible. Both these tests were carried out with an argon atmosphere for protection of the sample from possible oxidation.

This very important result indicates that the reaction product of the reduction of chromite, namely, high-carbon ferrochromium, can itself act as a reducing agent. Since this carbide is in fact the major constituent of the reaction product layer, it is easy to understand how the reduction of a particle of

chromite can go to completion even though there is no actual contact between the centre of the chromite particle and the carbon powder at the surface of the particle.

It would appear, thus, that the carbide can itself act as a reductant and can also act as a vehicle for the ready diffusion of carbon. This can be explained by considering Figure 53. At t = 0 no reduction has taken place. After x minutes a reaction product layer has formed. This layer has been shown to consist of the mixed carbon of iron and chromium at temperatures above 1200°C.

The above result shows that this actual layer can act as a reductant in that the carbon, both substitutionally dissolved and chemically combined as a mixed carbide, can move into the unreduced chromite via diffusion across the interface. Thus this carbon does the actual reduction so in this case the carbide is the carbon source. Furthermore this reaction product layer will allow the passage of carbon from the carbon/carbide interface to the carbide/chromite interface. In this manner carbon will be continuously replenished at the reaction zone. At t = y minutes, the progressive nature of the reduction process is illustrated. The carbon now reaches the carbide-chromite denuded zone before it reaches completely unreacted chromite. The carbon has thus to react with and diffuse through this intermediate layer. That a gradual transition of composition from carbon-saturated carbide at the surface through to completely unreduced chromite exists in this area is probably closest to the truth. The results obtained during this test are shown in Table 30.

The diffusion of the carbon through the reaction product layer was shown to be represented by the kinetic equation of Brounshtein and Ginstling (Ref.27). This equation relates to spherical symmetry and has the following approximate solution for a spherical particle:-

FIGURE 50

Free energy diagram.

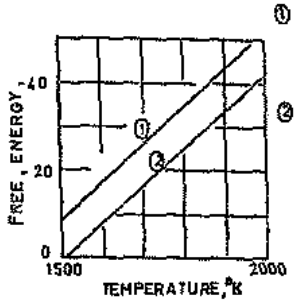
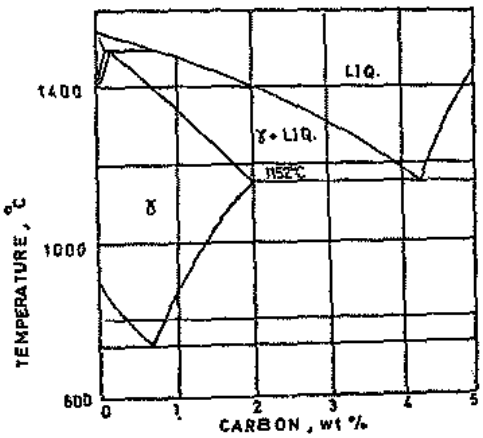


FIGURE 51



Fe–C Phase Diagram.

FIGURE 52 Diffusion of carbon in iron at 1150°C.

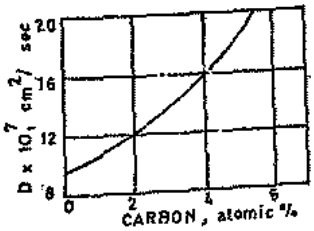


TABLE 30

THE REDUCTION OF CHROMITE F 533 BY HIGH-CARBON FERROCHROME

:- 0,5000 gm Chromite + 2,0000gm $(Fe,Cr)_7C_3$

Time mins	Percent Reduction
0	
5	18,4
10	23,6
15	26,8
20	28,9
30	32,0
40	34,6
50	36,2
60	37,8
70	39,3
80	40,9
90	42,5
100	44,1
120	47,2
140	50,4
160	53,5
180	56,7
200	58,8
220	60,9
240	63,0
260	65,1
280	67,2
300	69,2
400	76,6
500	80,8

$$(1 - {}^{2}/_{3}x) - (1 - x)^{2}/_{3} = kt$$

where x = degree of reduction
k = rate constant
t = time

The Brounshtein-Ginstling[Ref.27] equation was derived from the second FICK Law for non steady state diffusion.

Second FICK Law:

$$\frac{\partial c}{\partial t} = \mathcal{D} \frac{\partial^2 c}{\partial x^2}$$

where c = the amount of substance per unit volume
x = distance in the direction of diffusion
t = time
$\mathcal{D}$ = diffusivity or diffusion coefficient (cm^2/sec)

There is unfortunately a lack of experimental data on the diffusion coefficients of carbon into chromite and carbon into high-carbon ferrochromium. If, however, the mechanism of diffusion is not affected by temperature then variation of the diffusion coefficient can be represented by an Arrhenius expression:-

$$\mathcal{D} = \mathcal{D}_o \, e^{\left(-\frac{\Delta H}{RT}\right)}$$

where $\mathcal{D}_o$ = constant
ΔH = heat of activation for diffusion
R = gas constant
T = absolute temperature

With the above background on diffusion, the following discussion can now be dealt with:-

Consider a small particle of a chromite ore containing several grains. This particle reaches the zone in the submerged arc furnace where the temperature is about 1100°C. Up to this point no reduction of the chromite has taken place, even though the

particle is in/...

particle is in contact with carbon. See Figures 54 and 56 Some of the carbon has already started to diffuse into the chromite particle below 1100°C, but it is only at above this temperature that the reduction of the iron oxide in the chromite is thermodynamically feasible.

The diffusion of the carbon into the chromite occurs via three processes. These are surface, grain boundary and volume diffusion(Ref.34). Diffusion along the surface and along grain boundaries is more rapid than volumetric diffusion, since there are a greater number of dislocations at surfaces and at grain boundaries. All three rates of diffusion are affected by temperature and show a rapid rate of increase as the temperature is increased. Thus in Figure 57 the surface of the chromite particle is seen to be undergoing reduction. The metal forms at the surface and in the grain boundary zones. In these positions the metallic iron at 1100°C can substitutionally dissolve carbon. As the temperature increases above 1150°C and up to 1200°C, and as the carbon content of the metallic iron increases, so the liquidus of the metal phase drops - see Figure 51, i.e. as shown in the iron-carbon phase diagram. Once the carbon content of the iron reaches 4,27 per cent, a completely liquid phase exists above 1152°C. Thus at 1200°C even if the carbon content is lower than 4,27 per cent, some liquid phase is present. If the carbon content is below 4,27 per cent, this liquid phase consists of γ Fe (which is solid) and liquid iron, both phases containing carbon. The diffusion of carbon through this liquid iron, in which some carbon has dissolved substitutionally, varies with the carbon content of the metal. See Figure 52(Ref.32). Diffusion of carbon is very rapid - 14×10^7 cm^2/sec in an alloy containing 2,5 per cent carbon(Ref.32) at 1150°C in the solid state.

The iron-carbon alloy flows and collects in small pools and rivers, in cracks, dislocation planes and at the surface as well as at grain boundaries. See Figures 54, 57 and 58. A metal denuded zone is left behind.

So initially the overall reduction rate is governed by volume diffusion into the bulk of the chromite grain. The activation energy for diffusion through a structure with low atomic packing is lower than for a more dense packing (Ref. 32). This fact can explain the variation in the activation energy values for different chromites. Once these interconnecting streams of metal liquid form, these act as channels along which rapid transportation of the carbon can take place by diffusion. Furthermore, the formation of these liquid metal rivers sub-divides the grain so that the distances over which volumetric diffusion has to take place are drastically reduced. See Figures 58 and 59. This results in the rapid increase in the rate of reduction, which was found experimentally to occur at 1200°C.

When the isothermal run at 1100°C for chromite F 533 was carried out on the thermal balance, the resultant rate was much slower than one might have predicted by extrapolating the Arrhenius plot from the 1500°C, 1400°C, 1300°C and 1200°C values back to 1100°C. See Figure 55. If the point at 1100°C were to be included, an apparently higher activation energy would result. There would seem to be an overall change in mechanism for chromite F 533, i.e. from 1100°C to 1200°C. This is borne out by the theory relating to the change in the rate controlling step from volume diffusion to diffusion of carbon via a liquid phase.

On further heating to 1300°C, the Cr_2O_3 becomes readily reducible to form the carbide and a mixed carbide of iron and chromium results.

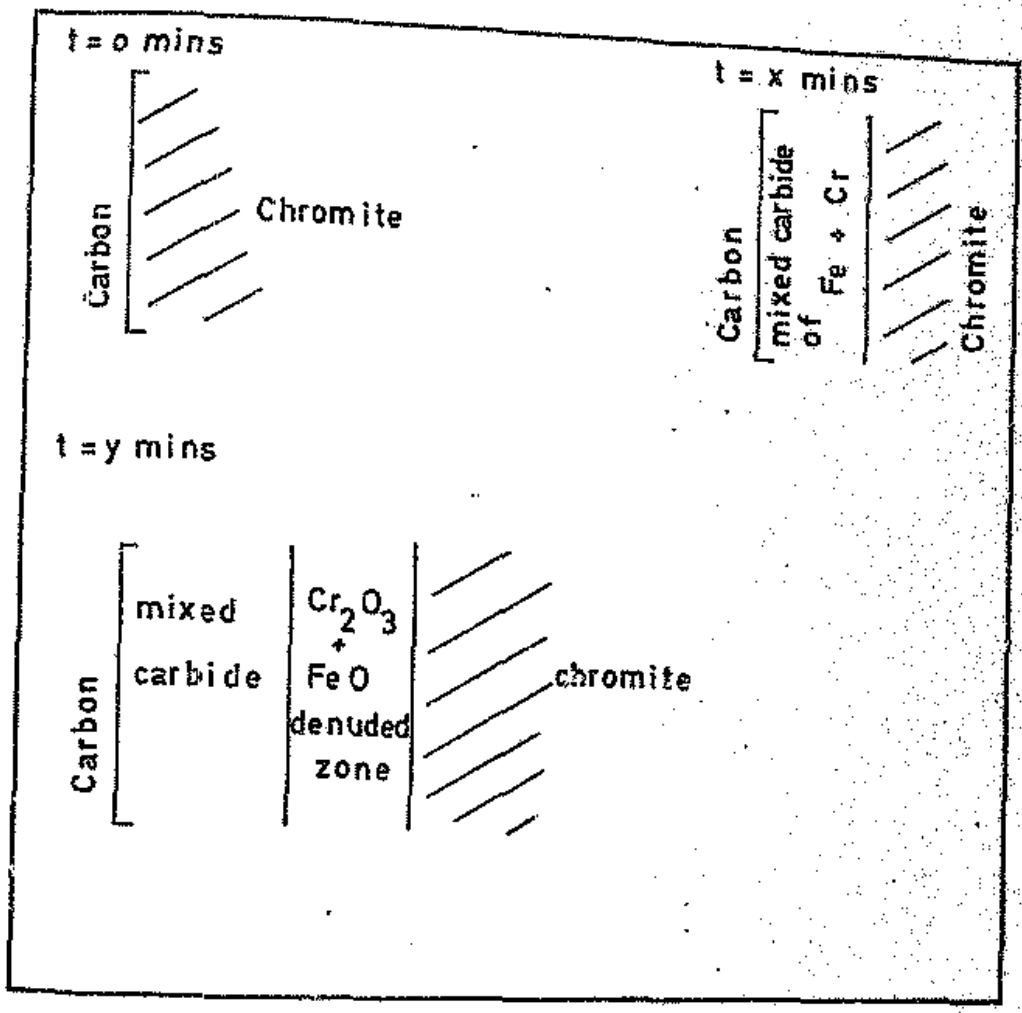


FIGURE 53

Reduction stages illustrating reaction product layer formation.

The two scientists, Lisniak and Evsesv (Ref.9) mentioned that they considered the presence of metallic iron catalysed the reduction of Cr_2O_3. This is in fact true up to a point, in that the liquid iron plus substitutionally dissolved carbon, the Fe and the Fe_3C all can act as carbon carriers which facilitates the rapid reduction of Cr_2O_3. The Cr_7C_3 can dissolve in the iron and carbon liquid to form many phases which will vary both with the amount of Cr_7O_3 dissolving and the amount of carbon already present in the iron. Hence the activity of the Cr is reduced and reduction proceeds more readily. A detailed study of the relevant phase diagrams is needed if the possible phases are to be established.

A great deal relating to the mechanism has been answered but several important aspects still remain unanswered.

It has already been shown how gangue minerals in a particular chromite can affect its TG curve. This characteristic of the chromites showed that there were substantial differences between the chromites. One would therefore expect that the chromites in the various groups would behave differently not only as far as their reducing behaviour is concerned, but also, and perhaps even more important, as far as their fluxing behaviour is concerned. In the submerged arc furnace producing high-carbon ferro-chromium, it can be stated positively that the gangue minerals in a particular chromite can play as important a role, and possibly an even more important role, than the actual chromite spinel. The gangue minerals can therefore act in several detrimental ways to upset the operation of the furnace.

Thus for example if a chromite contains gangue occurring interstitially as a matrix coating the grains, as is the case for many of the chromites containing hydrated minerals, the following sequence of events could well result:-

As the burden descends into the furnace, the pre-reduction of the chromite should begin initially at about 1100°C. Depending on the gangue mineral composition of the chromite, these minerals may start to melt very early on during this pre-reduction stage. Temperatures in this zone would range from 1100°C to 1400°C. This melting of the gangue prematurely can result in several important occurrences.

1. The fusion of the gangue minerals could result in wetting of the individual chromite grains. This could inhibit reduction, since carbon would be unable to reach the reaction interface.

2. This fusion process near the top of the furnace would tend to decrease the electrical resistance between the three carbon electrodes. The electrodes would tend to 'ride out' of the furnace moving the heat zone upwards and creating a 'hot top' which is most unfavourable for good furnace operation.

3. The chromite could dissolve in its own molten gangue, causing heavy Cr_2O_3 losses in the slag. The Cr_2O_3 raises the viscosity of the slag as well (Ref. 35).

   An ideal chromite, therefore, would contain preferably no low melting point gangue minerals and as little gangue as possible.

A further two projects in the Department of Metallurgy are at present dealing with various aspects of chromite reduction and fluxing behaviour. The first project deals with the fundamental behaviour of the chromite, especially with reference to the kinetics and mechanism of reduction. This project should, it is hoped, confirm and extend the results dealt with in this report. One aspect warrants special mention. It is well known that CO gas is the product of

chromite reduction./...

chromite reduction. What is not so well known is to what degree the liberation of CO from a reducing interface through the reaction product layer participates as a rate controlling step. Tests on the variation of reduction rate with various imposed pressures of CO gas could help to answer this question. Another field of interest which should be dealt with is the diffusion of the reduced species of Fe and Cr_7C_3 from the localities at which they were first formed to their new positions at the surface of the particle or at the grain boundary or even at dislocation or planes of weakness within an actual grain. This diffusion process would not be a primary rate controlling step, but it would affect the time interval for the formation of the liquid rivers of metal. It is most likely, from observed data for reduction rates above 1200°C, that this diffusion of the reaction products is very rapid.

All the reduction and fluxing behaviour studies carried out in this report are concerned with fine fractions of chromite. This was done in order to minimize complications caused by particle size. Tests were, however, carried out with six different size grades to show what effect size had on the kinetics of reduction. All these particle sizes were relatively fine, however, and when the chromite was being crushed down to these fine particle sizes, the gangue or at least the greater part of the gangue must have been dislodged from the chromite grains. The whole chromite grain-gangue mineral contact surface would thereby have been disrupted. Any tests carried out with these fine fractions would tend to give an incorrect picture of the fluxing behaviour of the ore.

This statement leads to the discussion of the second project being carried out in this field of research. Samples of chromite F533 have been crushed into relatively large chunks. A burden of this chromite with char and quartz as fluxes is made up and placed in a graphite crucible - the total burden weight being approximately 4 kg. An induction furnace is being used to heat these charges to selected temperatures (as high as 1800°C) for various lengths of time. The results from this project (which really investigates elements of furnace charge) should answer many of the problems associated with the fluxing nature of chromite F 533.

A third project investigating the fluxing behaviour of some of the other chromite ores would go a long way towards establishing a method of assessing the suitability of an ore from a metallurgist's viewpoint.

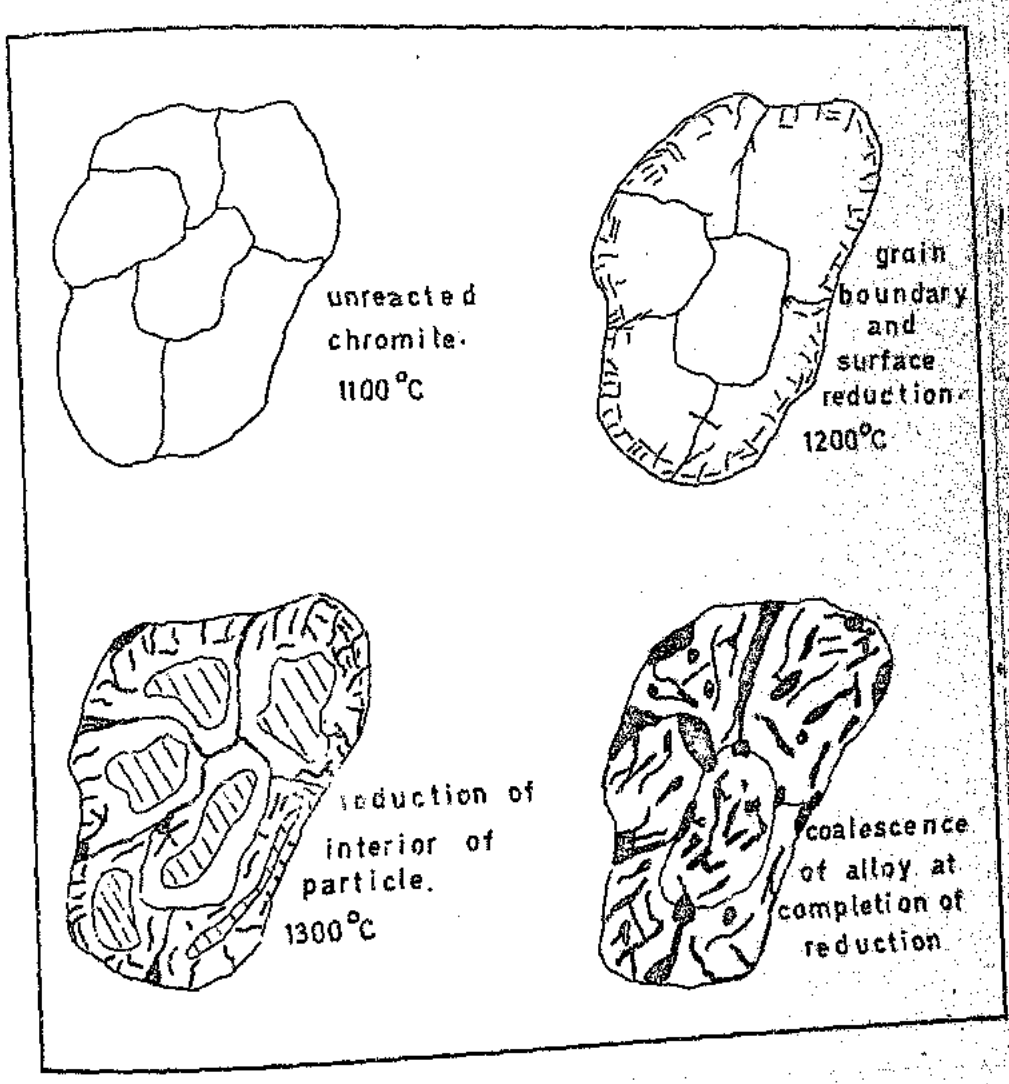


FIGURE 54 The progressive reduction of a chromite particle.

FIGURE 55

Arrhenius Plots for E_a including and excluding the rate constant at 1100 °C, illustrating a change in mechanism.

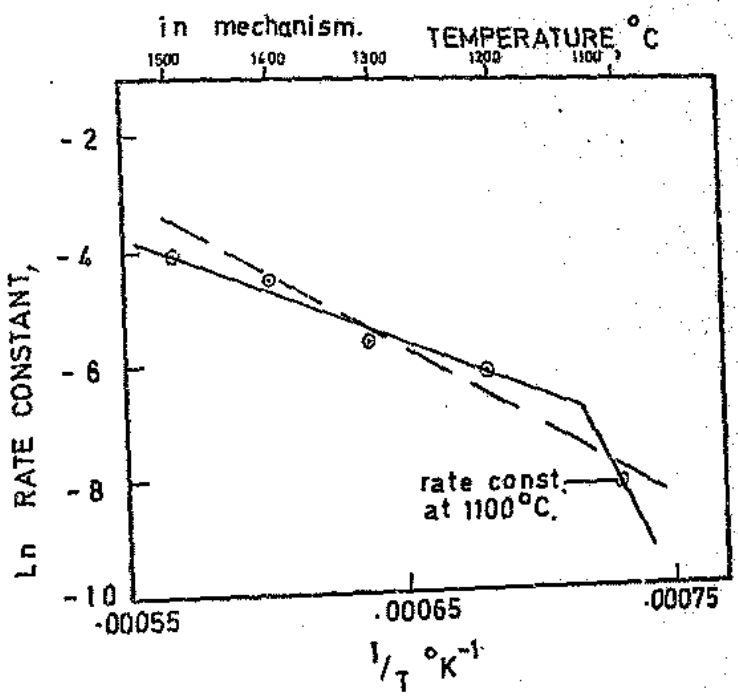
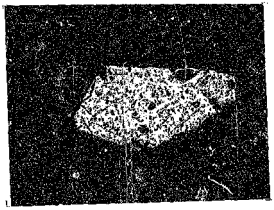


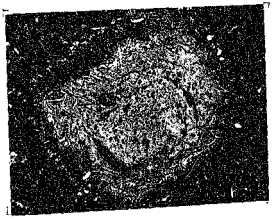
FIGURE 56



Unreacted chromite grain heated to 1000°C in the presence of powdered carbon.

MAGNIFICATION 90X.

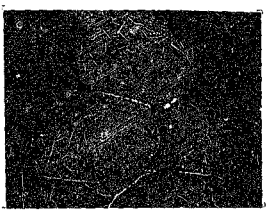
FIGURE 57



Start of reduction at the surface, with unreacted chromite in the centre.
(a reaction time of 30 mins at 1200°C).

MAGNIFICATION 90X.

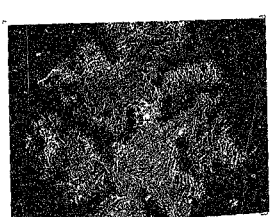
FIGURE 58



The formation of liquid alloy and its collection at the grain boundaries.
(a reaction time of 30 mins. at 1300°C)

MAGNIFICATION 90X

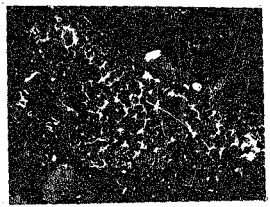
FIGURE 59



Extensive reduction has occurred.
(a reaction time of 60 mins. at 1300°C)

MAGNIFICATION 90X.

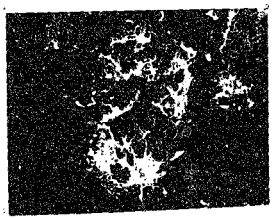
FIGURE 60



Complete reduction has occurred and the alloy has started to coalesce. (a reaction time of 30 mins at 1400°C).

MAGNIFACTION 90 X.

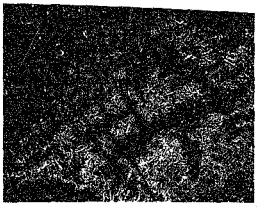
FIGURE 61



Coalescence of the alloy at the completi[illegible] reduction. (a reaction time of 30 mins at 1500°C).

MAGNIFICATION 90 X.

FIGURE 62

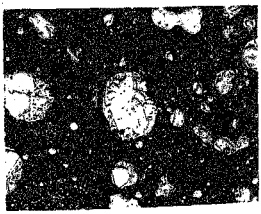


Reduction of a chromite particle showing the remnant cubic structure.

(a reduction time of 30 mins at 1400°C).

MAGNIFICATION 180X.

FIGURE 63



Chromite F 533 reduced completely in the presence of fluxing additions.

(a reaction time of 30 mins at 1500°C).

MAGNIFICATION 90X.

CHAPTER VIII

8. CONCLUSION

Thermogravimetry was found to be a most suitable method of studying the thermal behaviour of the twelve selected Transvaal and two Rhodesian chromite ores. It was shown that the gangue was the predominant factor in controlling the shape of the thermogravimetric curve when the chromites were heated in atmospheric conditions. Hydrated minerals in the gangue of some of the chromite ores resulted in weight losses on heating, while oxidation of FeO to Fe_2O_3 occurred in all the chromites.

The kinetics and mechanism of the reduction of chromite by solid carbon were dealt with in some detail. It has been shown conclusively that CO gas will not reduce chromite, thereby discounting CO as the reductant diffusing species. Carbon was shown, by a series of tests, to be the diffusing species. The transport of carbon into the chromite was shown to be volume diffusion controlled at the lower reducing temperatures, i.e. less than 1150°C and to be controlled at the lower reducing temperatures i.e. less than 1150°C and to be controlled to a much lesser degree by volume diffusion above 1150°C. The explanation of the decrease in volume diffusion is based on the observed fact that liquid iron with substantionally dissolved carbon facilitates the rapid transportation of carbon into the interior of the chromite grains. Thus the mechanism of reduction was shown to be controlled by diffusion of carbon through the reaction product.

The increase in particle size was shown to have a marked effect on the reaction rate up to grain size. On increasing the particle size above grain size, only a small decrease in reaction rate was observed.

Fluxes had only a minor effect on the reduction process. Thus the overall mechanism has been shown to remain the same, irrespective of both particle size and fluxing additions. Only the kinetics are slightly altered.

CHAPTER IX

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APPENDIX I

FLUXING ADDITION CALCULATION

Consider chromite F 533

(i) Composition of chromite ore

	Cr_2O_3	:	44,1 per cent		
Total	FeO	:	25,1 per cent	FeO	: 14,9 per cent
				Fe_2O_3	: 10,2 per cent
	CaO	:	0,5 per cent		
	MgO	:	11,6 per cent		
	Al_2O_3	:	15,2 per cent		
	SiO_2	:	3,1 per cent		
	Total %		99,6		

(ii) Fixed parameters relating to the slag and metal composition. (The slag is formed from the MgO and Al_2O_3 from the spinel and from the gangue minerals. The CaO and SiO_2 come only from the gangue). The following slag composition is based on an average slag composition as would be suitable in the production of high-carbon ferrochromium. It was considered for calculation purposes that the reduction and slagging processes would go to completion to give this final slag composition.

SLAG			METAL
MgO/Al_2O_3	=	1:1	6 per cent Carbon
SiO_2	=	30 per cent	2 per cent Silicon
CaO	=	2,5 per cent	Balance iron and chromium
Slag/Metal	=	1:1	

(iii) The percentage /...

(iii) The percentage metal formed from reducible components of the spinel

$$= \frac{104}{152} \times 44,1 + \frac{56}{72} \times 14,9 + \frac{112}{160} \times 10,2$$

$$= 48,9 \text{ per cent METAL}$$

From 100 grams of chromite, 48,9 grams of metal will be formed.

To this metal 6 per cent carbon and 2 per cent Si must be added to allow for the amounts of each of these components that dissolve in the slag.

Thus total metal weight = 48,9 + 8 per cent extra wt.
= 54,9 gm

(iv) The non-reducible components of the 100 grams of chromite come from the spinel and the gangue. MgO and Al_2O_3 come from the spinel, while the gangue can contribute MgO, Al_2O_3, CaO and SiO_2.

The non-reducible fraction of the chromite amounts to 100 - 54,9 gm = 51,1 gm.

The loss of oxygen from the total weight must, however, be accounted for. This equals 20,8 per cent for chromite F 533. Thus 51,1 - 20,8 = 30,3 gm, i.e., CaO + MgO + Al_2O_3 + SiO_2 in chromite = 30,3 gm.

(v) The quantities of each of the non-reducible components from the chromite ore (100 gm) are:-

0,5 gm CaO
11,6 gm MgO
15,2 gm Al_2O_3
3,1 gm SiO_2

In the total slag weight of 54,9 gm these amount to the following percentages:-

$\frac{0,5}{54,9} \times 100$ = % CaO

$\frac{11,6}{54,9} \times 100$ = % MgO

$\frac{15,2}{54,9} \times 100$ = % MgO

$\frac{3,1}{54,9} \times 100$ = % SiO_2

To contain 2,5% Cao in the final slag of 54,9 gm

$$\frac{2,5 \times 54,9}{100} = 1,37 \text{ gm is needed}$$

Addition is therefore 1,37 - 0,5 gm = <u>0,87 gm CaO</u>

Similarly for 30% SiO_2 16,47 - 3,1 gm = <u>13,37 gm SiO_2</u>

For MgO and Al_2O_3 ratio of 1:1

Remaining slag addition = 24,60 - 0,87 - 13,47 = 10,36 gm

Since MgO = 11,6 per cent
Al_2O_3 = 15,2 per cent i.e. 11,6 and 15,2 grams respectively

Al_2O_3 + MgO total = 37,16 gm (26,80 + 10,36)

But MgO = Al_2O_3 = $\frac{37,16}{2}$ = 18,58 gm

Thus additions to be made for

MgO = 18,58 - 11,60 = 7,02 gm
Al_2O_3 = 18,58 - 15,20 = 3,38 gm

(vi) To 100 gm of chromite the following amounts of fluxing additions have to be made:-

CaO	=	0,87 gm	FLUXING ADDITIONS
MgO	=	7,02 gm	
Al_2O_3	=	3,38 gm	
SiO_2	=	13,37 gm	

To 0,5000 gm 4,4 mg CaO 35,1 mg MgO
16,9 mg Al_2O_3 66,9 mg SiO_2 have to be added.

APPENDIX II

STOICHIOMETRIC CARBON CALCULATION

(i) Carbon required to reduce the metal oxides:-

say % Cr_2O_3 = x
% Fe_2O_3 = y
% FeO = z

then the total oxygen content of the metal oxides is:-

$$x \times \frac{48}{152} + y \times \frac{48}{160} + z \times \frac{16}{72} = [O]$$

Thus the amount of carbon required to reduce the total amount of oxygen is:-

$$\frac{12}{16} \times [O] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1.$$

The above is only true if CO is the only gaseous product.

Now for the chosen weight of chromite of 500 mg, the amount of carbon necessary is:-

$$500 \times \frac{12}{16} \times [O]$$

$$= 375 \; [O] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.$$

(ii) Carbon to bring alloy up to specification:-

The alloy must contain 6% C and 2% Si. Thus for this quantity for each chromite to be calculated the alloy weight must be known. The alloy weight from 500 mg of a particular chromite is:-

$$500 \left(\frac{104x}{152} + \frac{112y}{160} + \frac{56z}{72} \right)$$

(This was approximately 270 mg on an average).
The % carbon required for the carbon content of the alloy is thus:-

$$\frac{6}{100} \times 500 \left(x \times \frac{104}{152} + y \times \frac{112}{160} + z \times \frac{56}{72} \right)$$

Let $\left(x \times \frac{104}{152} + y \times \frac{112}{160} + z \times \frac{56}{72} \right) = [M]$

Thus $\% \ C = \frac{6}{100} \times 500 \times [M]$

$= 30 \times [M]$ ..... 3.

The % Carbon required for the reduction of SiO_2 can be calculated by considering the following equation:-

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Thus $\% \ C = \frac{24}{64} \times \frac{2}{100} \times 3[O][M]$ ..... 4.

The Total Stoichiometric Carbon = 2. + 3. + 4.

TABLE 1

TABLE OF STOICHIOMETRIC CARBON VALUES FOR THE FOURTEEN CHROMITES

Sample weight of 500 mg Chromite

Chromite	Composition			% Oxygen			Total % Oxygen	Stoichiometric Carbon=(Total Oxygen + Carbon for Alloy) mg
	Cr_2O_3	FeO	Fe_2O_3	Cr_2O_3	FeO	Fe_2O_3		
F 524	44,9	12,0	12,4	14,2	2,7	3,8	20,7	95,1
F 533	45,7	14,9	10,2	14,4	3,3	3,1	20,8	95,5
F 539	39,6	14,3	8,9	12,5	3,2	2,7	18,4	86,4
F 543	45,5	15,8	8,7	14,4	3,5	2,6	20,5	94,4
F 582	41,6	18,1	5,6	13,1	4,0	1,7	18,8	88,1
F 584	45,1	17,1	8,1	14,2	3,8	2,4	20,5	94,2
F 588	43,4	13,0	11,8	13,7	2,9	3,6	20,2	93,2
F 589	50,2	11,8	8,6	15,9	2,6	2,6	21,1	96,6
F 596	15,2	24,4	27,7	4,8	5,4	8,3	18,5	87,0
F 602	46,8	7,1	13,3	14,8	1,6	3,9	20,3	93,8
F 604	46,2	6,9	13,3	14,8	1,5	3,9	20,2	93,7
F 606	42,6	6,2	8,2	13,5	1,4	2,5	17,4	82,4
F 651	50,6	11,2	-	16,0	3,6	-	19,5	90,8
F 652	48,8	14,0	-	15,4	3,4	-	18,8	88,1

APPENDIX III

THE CALCULATION FOR THE PERCENT REDUCTION

Definition

The percent reduction at any time t is defined as follows:-

$$\frac{\text{Weight loss of chromite at time } t}{\text{The theoretical weight loss for total reduction}} \times 100$$

The weight loss of the chromite at this time t can be calculated from the total weight loss from the system of chromite plus carbon. This weight loss is attributed to CO gas. Thus the fraction of weight lost by the chromite is only $^{16}/28$ of the total weight loss.

Say M is the total weight loss at this time t.

Thus $M \times \frac{16}{28}$ is the fraction lost by the chromite.

The total theoretical weight loss can be found by calculating the total oxygen content of a particular chromite. Say this is [O] then for 500 mg the total theoretical oxygen content is

$500 \times [O]$ Where [O] is in fact $\left(x \times \frac{48}{152} + y \times \frac{48}{160} + z \times \frac{16}{72} \right)$ as a percentage

$$\text{Thus \% reduction} = \frac{M \times \frac{16}{28} \times 100}{500 \times [O]}$$

$$= \frac{M \times 0{,}1143}{[O]}$$

Example For chromite F 533

% Oxides [O] = 21,8

$$\text{\% reduction} = \frac{m \times ,1143}{\frac{21{,}8}{100}}$$

$$= 0{,}525 \times m$$

(Where 0,525 is the factor)

TABLE 2

TABLE OF CONVERSION FACTORS FROM CUMULATIVE WEIGHT CHANGE IN MILLIGRAMS TO PERCENTAGE REDUCTION OF 100 PERCENT THEORETICAL REDUCTION

Chromite	Percent Metal Oxides	Plus O_2 from SiO_2 %	Total Oxide Percent	Factor
F 524	20,7	1	21,7	0,527
F 533	20,8	1	21,8	0,525
F 539	18,4	1	19,4	0,591
F 543	20,5	1	21,5	0,532
F 582	18,8	1	19,8	0,577
F 584	20,5	1	21,5	0,533
F 588	20,2	1	21,2	0,540
F 589	21,1	1	22,1	0,518
F 596	18,5	1	19,5	0,586
F 602	20,3	1	21,3	0,536
F 604	20,3	1	21,3	0,536
F 606	17,3	1	18,3	0,625
F 651	19,5	1	20,5	0,557
F 652	18,8	1	19,8	0,577

APPENDIX IV

EXAMPLE CALCULATION FOR ACTIVATION ENERGY FOR CHROMITE F 533

To the data for percent reduction namely x, and for time t, the following best fit lines were obtained using the computer programmes "FITMEC" and "FITLIN":-

at 1200°C

$$y = 1,961 \times 10^{-3}x - 8,535 \times 10^{-3}$$
$$\sigma = 2,17 \times 10^{-3}$$
$$r = ,9925$$

at 1300°C

$$y = 3,533 \times 10^{-3}x - 8,004 \times 10^{-3}$$
$$\sigma = 2,54 \times 10^{-3}$$
$$r = ,9968$$

at 1400°C

$$y = 1,136 \times 10^{-2}x - 1,985 \times 10^{-3}$$
$$\sigma = 9,600 \times 10^{-3}$$
$$r = ,9736$$

at 1500°C

$$y = 1,819 \times 10^{-2}x - 4,681 \times 10^{-3}$$
$$\sigma = 1,18 \times 10^{-2}$$
$$r = ,9841$$

Thus the rate constants at each temperature level as given by the slopes of the lines are:-

At 1200°C	$1,961 \times 10^{-3}$
At 1300°C	$3,533 \times 10^{-3}$
At 1400°C	$1,136 \times 10^{-2}$
At 1500°C	$1,819 \times 10^{-2}$

The Arrhenius plot is the $\log_e$ of the rate constants versus $1/T\ {}^{o}K^{-1}$

The following table is used:-

TABLE 3

Temp °C	Temp °K	1/T °K^{-1}	k Rate Constant	$\log_e$ K
1200	1473	,000679	$1,961 \times 10^{-3}$	-6,2343
1300	1573	,000636	$3,533 \times 10^{-3}$	-5,6456
1400	1673	,000598	$1,136 \times 10^{-2}$	-4,4777
1500	1773	,000564	$1,819 \times 10^{-2}$	-4,0069

The slope of the Arrhenius plot is given by the best fit line through the above points. The computer programme "FITA" was used.

$$y = 2{,}291 \times 10^4 x + 9{,}054$$

Thus slope $= 2{,}291 \times 10^4$

Since $E_a = -R \times \text{slope}$

$= -8{,}314 \times (-2{,}291) \times 10^4$

$= 190{,}5$ k joules/mole

From the intercept at $x = 0$

The frequency factor $A = \underline{9{,}054}$ →

APPENDIX V

THE ACCURACY OF THE NUMERICAL RESULTS

The only numerical results were obtained from the TG curves. The first error in obtaining quantitative answers could thus have arisen from inaccuracies within the instrument itself. A test run with calcium hydrate oxylate showed the apparatus to be reproducible. Duplicate tests showed an error of less than 2%. A comparison between the Stanton thermal balance and a second balance of the same make gave reproducibility of just better than 5%.

A second error could have been introduced from the actual reading of the thermal balance chart, especially where the rates of reduction were extremely rapid. Checks on several graphs showed that errors of up to 5% could be made on reading such curves. Use of higher chart speed helped to minimize this error. The overall error within the thermal balance and the reading of the TG curves could result in an error of not more than 7%.

In calculating values such as the rate constant and the activation energy, the error which could have been introduced was the closeness of the mechanism fit to the model equation of A.M. Girstling and B.I. Brounshtein. As can be seen the fit of the data to the equation for diffusion in a three dimensional direction through the reaction product layer is extremely good. The fit of the Arrhenius plot to the four points is also good and the average variations are about 3% to 5%. The rate constant values are thus better than 7% while the activation energy values are better than 12% and mostly better than 10%. Several checks on repeated thermal balance runs show the precision to be in fact much better than 10%.

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