



Thermal decomposition of chromite spinel with chlorite admixture

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ABSTRACT

The behaviour of minerals in a South African chromite ore during the increasing of the temperature has been studied. Firstly, the changes produced during the ignition process have been examined by means of thermal and differential analysis (TGA–DTA) until 1200 °C. The characterization of the initial mineral and those obtained after heating at several temperatures in room atmosphere has been performed by X-ray diffraction (XRD). Moreover, voltammetric analyses have allowed to determine the variation of the iron oxidation degree in the studied materials. Light microscopy was applied to find more information about the different phases by their colour. During the heating, a wide range of complex exothermic and endothermic transformations take place. Decomposition compounds were identified, which were produced by heat decomposition, loss of structural water, element substitutions and oxygen absorptions and desorptions, caused mainly by the variation of the iron oxidation degree. The spinels of the chromite ore decompose in other spinels, with a partial change of the iron oxidation degree. From nearly 800 °C, chrome oxide (Cr₂O₃) comes off from the chromite forming another phase, and almost at 1000 °C, a slow decrease of weight was detected, caused among others to the formation of a magnetite phase. Simultaneously, the silicates undergo strong modifications, including decompositions and incorporation of iron (II) in their structure and producing other silicates stable at high temperatures, which modify the behaviour of the pure spinels. Moreover, at 1200 °C these silicates decompose to cristobalite (SiO₂).

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1. Introduction

Pure chromite has a spinel crystalline structure and the theoretical chemical composition is FeCr₂O₄. Natural chromite structure is described as a cubic spinel with a formula unit (Mg,Fe²⁺)O·(Cr,Al,Fe³⁺)₂O₃, owing to the partial natural substitution of Fe(II) by Mg, Cr by Al and even by Fe(III) in lower proportion. These occurrences depend on the type of mineral which is usually found with the chromite, especially metha- and orthosilicates.

On the other hand, natural chromite minerals form extended solid solutions with binary spinels of FeCr₂O₄, MgCr₂O₄, FeAl₂O₄ and MgAl₂O₄. The decomposition of natural spinels strongly depends upon the chemical potential imposed in the forms of temperature, pressure and pH differences in aqueous media.

Some interesting studies have been realized about the viability of the use of chromites as chrome-diffusive covering materials in steel [1–5]. The introduction of chrome in the surface has

been made by the products from previously reduced refractory chromites with the addition of reducing agents.

Iron oxidation state in the chromites has been studied by means of solid-state electrochemistry. This methodology, which is based on the mechanical transference of solid microparticles to graphite electrodes in contact with a suitable electrolyte, was selected because of its ability to directly characterize the oxidation state of electroactive species [6–8]. This approach has been applied recently to characterize iron oxides [9–12]. Chemical and structural changes occurring as a result of thermal treatments were correlated with the variations in the electrocatalytic effect exerted by the studied materials on the reduction of dissolved oxygen and the oxidation of water to oxygen in alkaline aqueous solutions. This is based in the reported electrocatalytic ability of NiFe_{2–x}Cr_xO₄ spinel for promoting O₂ evolution in alkaline aqueous media [13] and the catalytic effect exerted by Fe₃O₄ cathodes on the electrochemical reduction of dissolved O₂ [14].

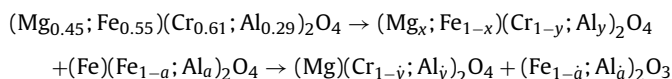
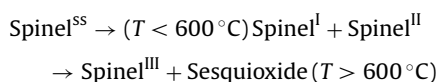
In the case of pure iron chromite, the phase reaction in spinels can be defined as the decomposition products at high temperatures [15], which are FeO and Cr₂O₃. The chemical strongly depends on the mineral composition and oxygen partial pressure, because the

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chromite mineral is a solid solution of pure spinel end members and the Fe(II) will oxidize to Fe(III) in the presence of an excess of oxygen.

Many investigations on chromite mineral phase equilibria have been undertaken [16,17]. However, the main focus of the previous research works was on the high temperature region (above 1300 °C) related to the production of ferrochrome alloys. By contrast, the literature on the phase transformation for oxidation conditions below 1200 °C, used for the extraction of sodium chromate from chromite spinels is rather limited [18,19]. Finally, Tathavadkar et al. used different techniques for the study of the decomposition of a refractory chromite with an amount of free silica less than 1% [20].

Hellwege and Hellwege [21] have proposed the following sequence for the decomposition of the spinel at low temperatures (less than 600 °C):



It means that the oxidation of Fe(II)–Fe(III) produces firstly maghemite ($\gamma\text{-Fe}_2\text{O}_3$), forming a metastable defective spinel, although the reported transition temperature of maghemite to hematite ($\alpha\text{-Fe}_2\text{O}_3$) is around 250 °C.

Moreover, some authors have studied the thermic behaviour of previously purified chlorites, providing interesting data about the temperature decomposition of the different analyzed specimens [22–24].

The aim of this paper was for determining the behaviour of a South African chromite ore during its heating. The study was carried out from a chrome spinel mineral with an appreciable amount of silicates. The mineralogical composition of the sample was as follows: magnesiochromite ferroan (spinel), labradorite, chlorite chromian and free silica. The chemical composition was: 42.88% Cr_2O_3 , 6.53% SiO_2 , 15.35% Al_2O_3 , 21.24% Fe_2O_3 , 0.48% CaO , 12.76% MgO , 0.16% Na_2O , 0.15% MnO and 0.44% others (TiO_2 , K_2O , etc.), where all the iron was as Fe(II) [25]. Different materials were obtained by ignition at several temperatures (450, 600, 800, 1000 and 1200 °C), from the initial chromite ore, and the modification of the weight was considered. The obtained samples were studied by XRD in order to characterize the formed compounds at each temperature. On the other hand, a TGA-DTA of the mineral was carried to 1200 °C. The study was completed by the observation by light microscopy of the most significant changes detected in the powder. Finally, solid-state voltammetry was used for determining the changes in the oxidation state in the samples using Fe(III) oxide and Fe(II) oxalate as reference compounds.

2. Experimental

2.1. Instrumentation

TGA and DTA experiments were performed using a Universal V 3.0G TA instrument, with α -alumina powder as reference material. Throughout the experiment, the sample temperature and weight-heat flow changes were continuously monitored using a data logging device.

Glass discs for the XRF analyses were made from the samples using the following instrumentation: muffle furnace (GALLUR, max T 1300 °C with temperature ascent speed regulator, Valen-

cia, Spain); Wolfram Carbide disk mill (Fritsch Pulverisette 9, Idar-Oberstein, Germany); crucible (5% Au/Pt ZGS); glass discs conformator (Pt/Rh 30 mm diameter). XRF analyses were performed in an X-ray fluorescence spectrometer (Phillips PW with rhodium anticathode controlled by SuperQ/Quantitative software version 1.1, Eindhoven, Netherlands).

Studies by XRD were carried out with X-ray diffractometer Siemens D500 (using $\text{CuK}\alpha$) controlled by DIFFRACT/AT version 3 software. Munich, Germany) with DIFFRACTplus Evaluation Package Release 2001 and Powder Diffraction File (PDF) Release 1999 Database, provided by International Centre for Diffraction Data (ICDD).

Photographs were taken (144 \times) with a light microscope SZX12 Olympus (Milan, Italy) coupled to a digital camera Olympus 4.5 M.p. noise reduction system F 1.8.

Square wave voltammograms (SQWVs) were obtained with a CH 1420 equipment in a conventional three-electrode cell using well-deaerated HCl (Panreac, Barcelona, Spain) solutions at 298 K. A sample-modified composite electrode was used as a working electrode, a Pt-wire auxiliary electrode and a AgCl (3M NaCl)/Ag reference electrode completed the three-electrode cells after immersion of modified electrodes in suitable deaerated solutions at 298 K. The potential scan was routinely initiated at +1.0 V in the negative direction.

2.2. Electrochemical procedure

Experiments were performed in 1 M HCl with nanopure aqueous solutions. Paraffin-impregnated graphite electrodes (PIGEs) consist on cylindrical rods of 5 mm diameter of graphite impregnated under vacuum by paraffin. The samples (ca. 10–20 μg) were completely powdered in an agate mortar and pestle, and then placed on a glazed porcelain tile forming a spot of finely distributed material. Then, the lower end of the PIGE was gently rubbed over that spot of sample, and finally cleaned with a tissue paper to remove ill-adhered particles [6]. Iron (III) oxide (Fe_2O_3 , Aldrich) was used as reference material for electrochemical experiments. Electro-catalytic experiments were performed in O_2 -saturated aqueous solutions of NaOH (Panreac) using uniform deposits of the different chromites over PIGEs.

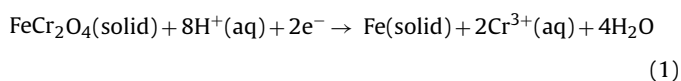
3. Results and discussion

The samples were obtained by heating of the natural chromite ore (3.5 g in a Pt crucible) at the following temperatures: 450, 600, 800, 1000, 1100 and 1200 °C in an oven, maintained during 30 min.

3.1. Voltammetric study

In order to determine the oxidation state of iron in the untreated natural chromite minerals and thermally treated specimens, solid-state voltammetric experiments were performed upon immersion of sample-modified graphite electrodes into 1.0 M HCl. The results for a) the untreated chromite ore and the specimens resulting from its ignition at (b) 600, and (c) 1100 °C are shown in Fig. 1. The voltammogram of chromite ore at room temperature (Fig. 1a) shows a unique cathodic peak at ca. –650 mV.

This peak is attributable to the electrochemical reductive dissolution of chromite Fe (II) to Fe metal, as suggested by comparison with the voltammetric response of iron (II) containing clays [9,10]. Following the literature data [6–12], the electrochemical process can be represented as:



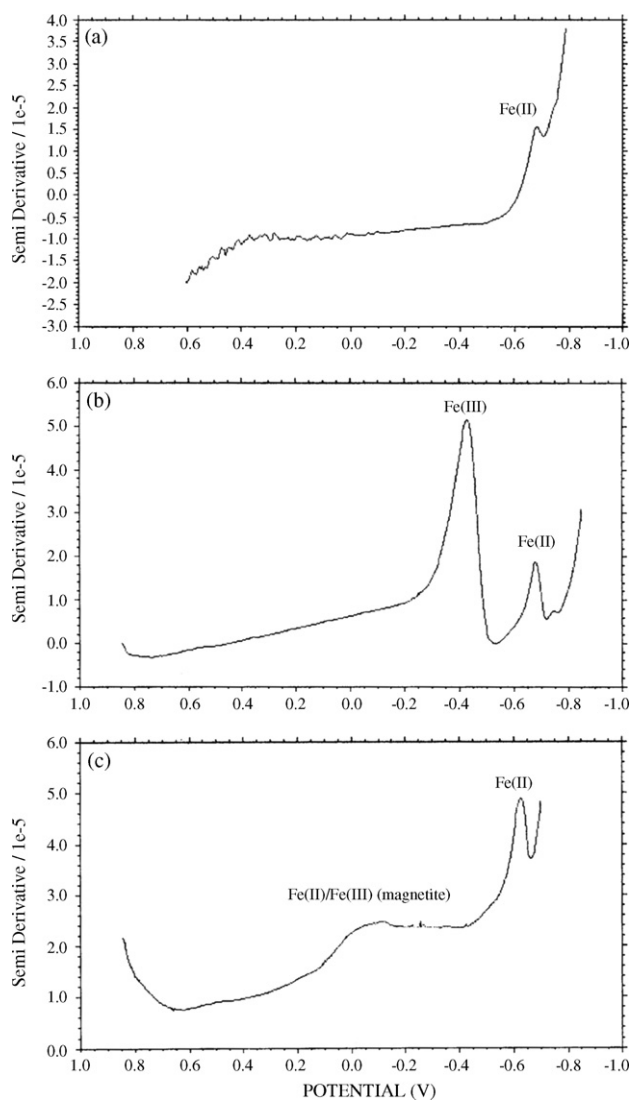
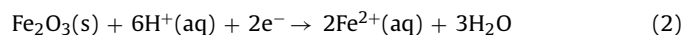


Fig. 1. Square wave voltammograms for: (a) pristine chromite specimen, (b) specimen after ignition at 600 °C, and (c) after heating at 1100 °C, attached to paraffin-impregnated graphite electrodes in contact with 1.0 M HCl. Potential scan initiated at +0.85 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

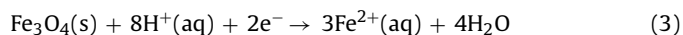
This was confirmed by the appearance of an oxidation peak at -0.30 V, displaying typical features for oxidative dissolution (stripping) processes, in voltammograms initiated at -850 mV in the positive direction. This peak corresponds to the oxidation of Fe solid to Fe^{2+} ions in solution phase [9,10].

Specimens prepared by heating chromite at 600 °C (Fig. 1b) show a prominent peak at -420 mV, and accompanied by a weaker peak at -650 mV. The peak at -420 mV can be described in terms of the electrochemical reductive dissolution of hematite, in agreement with extensive literature data [6–11,15], whereas the signal at -650 mV is attributable to the electrochemical reduction of remaining iron (II) in natural chromite minerals. This voltammetry indicates that hematite is formed from chromite ore during thermal turnovers. The electrochemical reduction of hematite can be described as:



Specimens prepared from natural chromite minerals by heating at 1100 °C show voltammograms consisting of a broad peak at

ca. -150 mV, accompanied by a sharp peak at -650 mV (Fig. 1c). This electrochemical response denotes that hematite turns to magnetite, whose presence is characterized by the reduction peak at -150 mV [27], which can be described as:



The peak at -650 mV is caused by the electrochemical reduction of the remaining iron (II) in the chromite ore heated at 1100 °C.

The remaining of Fe(II) in chromite ore sample for the whole ignition process has not been ever detected in previous works about the study of this kind of minerals and can be considered as a strong novelty. The peak corresponding to the electrochemical reduction of iron (II) appears in the voltammograms obtained by chromite ore in all the samples ignited at the considered temperatures. It may indicate the incorporation of the remaining iron (II) during the heating in a stable compound after the decomposition of chlorite. It might be also caused by a magnetite thermal reduction at the higher considered temperature.

In order to obtain additional information on structural changes accompanying thermal treatment of chromite ores, we introduce here a novel methodology based on the different catalytic ability of the studied systems, acting as electrode modifiers, with regard to selected electrochemical processes. Here, it is studied the variation of the catalytic effect exerted by chromite samples on the electrochemical reduction of dissolved oxygen and the oxidation of water in O_2 -saturated aqueous NaOH solutions.

This can be seen in Fig. 2, where cyclic voltammogram recorded at: (a) unmodified, and (b) chromite-modified PIGEs immersed into O_2 -saturated 0.10 M NaOH. A reduction peak appears ca. -0.45 V, corresponding to the reduction of dissolved O_2 . In the positive region of potentials, a prominent rising current was obtained, corresponding to the oxidation of water to O_2 . As can be seen on comparing Figs. 2a and b, both the current for O_2 reduction and the current for water oxidation recorded at chromite-modified electrode are significantly enhanced with respect to the currents at the bare graphite electrode. For our purposes, the relevant point to emphasize is that the chromites studied here exert a significantly different catalytic effect towards such electrochemical processes which can be reflected in changes in the peak current at -0.45 V and the maximum current at the extreme positive potential of the voltammograms ($+1.25$ V). The variation of the catalytic current for both processes, $i(\text{cat})$, with the temperature at which the chromite sample was treated, is shown in Fig. 3, expressed as the quotient between the actual current for a given sample, and the maximum current in the series, $i(\text{cat})/i_{\text{max}}(\text{cat})$.

As recently studied by Singh et al. [13], octahedrally coordinated surface Fe^{2+} ions are considered the active centres for the catalysis of electrochemical reduction of O_2 in alkaline aqueous media. According with the proposed reaction scheme for chromite ores, the catalytic effect on that process exerted by the studied chromite samples should decrease from the parent chromite to the sample treated at 450 °C, further increasing. This prediction agrees well with the observed results, as can be seen in Fig. 3 (squares).

In turn, the variation of the catalytic current for the reduction of dissolved oxygen in aqueous alkaline solution parallels the aforementioned pass from Fe^{2+} to Fe^{3+} at 450 °C and its subsequent re-formation of Fe^{2+} at temperatures above 800 °C. Eventually, this catalytic effect can be influenced by structural changes in the spinel structure and the formation of high-valence chromium species [14]. The variation of the catalytic current with temperature of thermal treatment agrees well with that observed for thermal analysis of samples (*vide infra*).

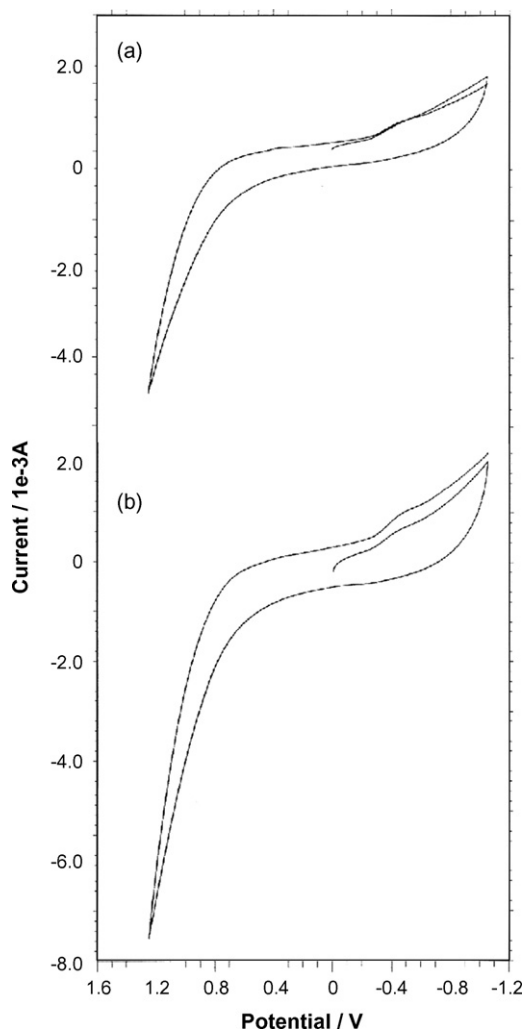


Fig. 2. Cyclic voltammograms for: (a) unmodified, (b) chromite-modified PIGEs immersed into O_2 -saturated 0.10 M NaOH. Potential scan initiated at 0.0 V in the negative direction; extreme potentials +1.25 and -0.85 V. Potential scan rate 50 mV/s.

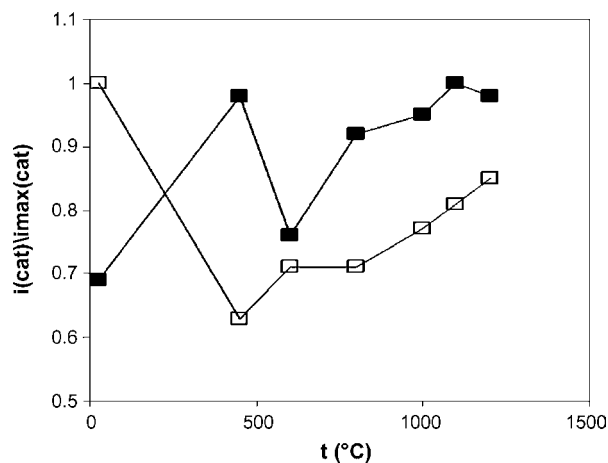


Fig. 3. Variation of the $i(\text{cat})/i_{\text{max}}(\text{cat})$ ratio with the temperature of thermal treatment for chromite samples studied here corresponding to the catalytic oxidation of water to oxygen (solid squares) and the catalytic reduction of dissolved oxygen (squares). From cyclic voltammograms using the conditions described in Fig. 2.

Table 1

Weight increment of the sample by heating at each temperature (compared with the initial)

T (°C)	450	600	800	1000	1100	1200
Weight increment (%)	+0.89	+0.66	+0.76	+1.10	+1.08	+0.99

Weight increment can be considered as negative LOI.

3.2. Ignition test

The variation of the weight at different temperature heating was studied. The results are shown in Table 1.

From these obtained data, it can be deduced that the weight of the sample get higher when heated at 450 °C, under the assay conditions. This increasing is minor at 600 °C, and then the slope returns to rise from 600 to 1000 °C, reaching the maximal value. Above this temperature, a progressive loss of weight was observed until 1200 °C.

In principle, it could be deduced from this assay that a global weight rising happens while the temperature reached 1000 °C. This can be caused by the increasing of the iron oxidation state by oxygen absorption. Between 450 and 800 °C, the increasing of weight would be partially hindered by mineral decomposition in the ore, with loss of several compounds and/or desorption of oxygen, caused by the lessening of the iron oxidation state at these temperatures. From 1000 °C, a continual process with loss of weight was observed.

3.3. Thermal analysis

Chromite ore sample was analyzed by thermogravimetric study until 1200 °C, with the aim to obtain more precise informations from the heating process of the mineral. Two temperature gradients, 10 and 20 °C min⁻¹, were tested. The obtained results were similar in both cases, so that the final assay was performed at 20 °C min⁻¹. Experimental data in the ignition test (Section 3.2) could differ from the thermogram (Fig. 4), because they were obtained from a continuous heating at a fixed temperature gradient. Therefore, specific results found by ignition at the several temperatures can be only used as basic information to propose hypotheses about the processes which can happen during the heating.

3.3.1. Thermogravimetric analysis

The following observations were extracted from the analysis of the obtained thermogram curves (Fig. 4):

In the TGA curve, the first interval points to a continuous increasing from the initial temperature to 180 °C (A), due to a low weight gain cause of the heating of oven atmosphere. The density decrease produces a rising of the sample weight with a similar effect to "Archimedes' Principle".

The slope of the TGA curve diminished between 180 and 400 °C (interval A-B) due to two simultaneous and opposed effects:

- a weight increasing by the initial oxidation $Fe^{2+} \rightarrow Fe^{3+}$ (as maghemite phase $\gamma\text{-Fe}_2\text{O}_3$ [28], which turns to hematite $\alpha\text{-Fe}_2\text{O}_3$ from 400 °C) [20]. However, this transition normally takes place at around 250 °C. This increase in transition temperature can be caused by the presence of Al(III), as they occupy holes in the maghemite structure [21].
- A low decrease of weight due to the loss of structural water (dehydroxylation stage) of the chlorites, which maintains the typical bilayer structure of chlorites and other similar minerals, and is normally removed at this temperature range.

In the interval B-C of TGA curve, the slope shows a higher value from 400 °C to nearly 550 °C. This is caused because of the

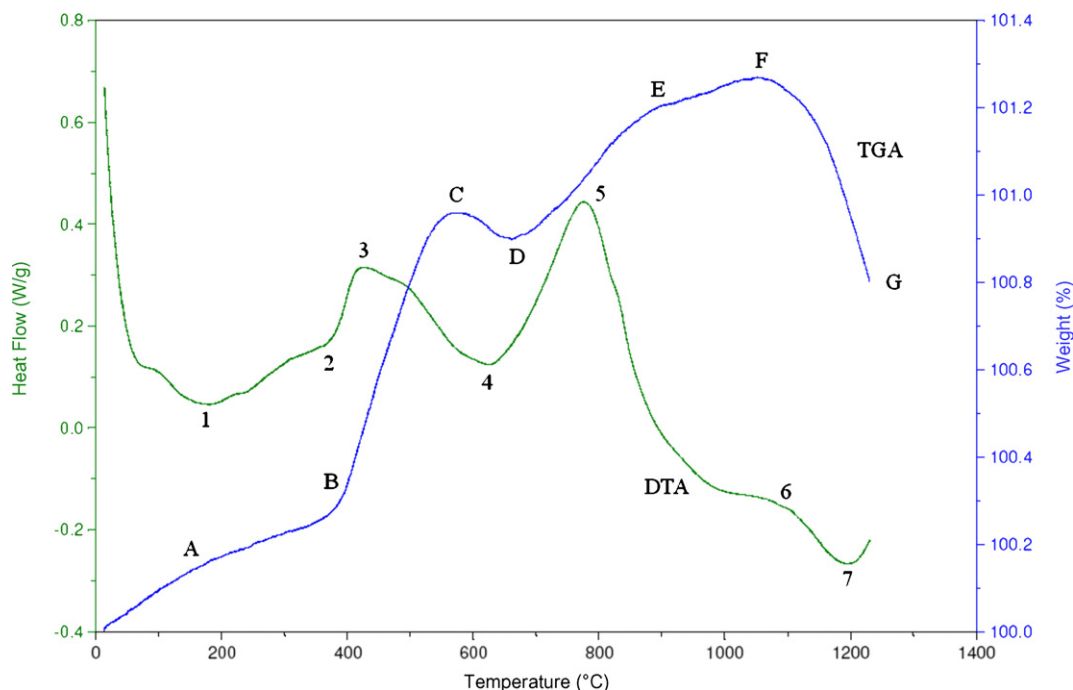


Fig. 4. DTA and TGA thermogram curves obtained by means of the ignition test applied to the South African chromite ore.

oxidation of from Fe(II) to Fe(III) happens without other effects, as the previously discussed elimination of water.

In the interval C–D (550–700 °C) of TGA curve, the thermogram shows a decrease of weight, owing to the loss of hydroxy ions (OH^-) from the structure of the chlorite (silicate phase of the mineral) during its decomposition. This process overcomes the sample weight by oxidation of Fe(II).

In the interval D–F of TGA curve, the increasing of the weight due to the exothermic oxidation of Fe(II), continues until nearly 1100 °C. The slope was smaller than in interval B–C, and this decrease was more marked for the interval E–F (850–1100 °C). This was caused by the minor amount of Fe(II) in the sample, probably together to iron (II) migration from the chromite spinel to the silicate, after chlorite decomposition. The formed iron (II) silicate is stable at these temperatures and do not undergo oxidation.

Finally from 1100 °C (point F) to higher temperatures, a strong fall of the weight was clearly observed in TGA curve. This effect is caused by the thermoreduction of iron (III) to lower oxidation degree, probably magnetite phase, among others. These deductions are in agreement to the results obtained by voltammetric studies (Section 3.1).

3.3.2. Differential thermal analysis

At the beginning of the analysis, the DTA curve indicates an endothermic process caused by the heating, which provokes an endothermic peak at 200 °C (peak 1).

The DTA curve shows an exothermic step (interval 1–3) with a slight and irregular slope to the peak 2, and an increasing of the slope to nearly 420 °C (peak 3), according to the proposed processes deduced from TGA for these temperature intervals (Section 3.3.1). From 420 °C, an endothermic process occurs with a peak at 650 °C (peak 4) and followed by an increasing of the heat-flow with an exothermic peak (5), related to the process described for this interval in TGA curve (Section 3.3.1), together with the decomposition of original pure chromite spinel in two other spinels [21]. From 800 °C (peak 5 of the TDA curve), the heat-flow showed a strong fall, due probably to the chromite segregation process (endothermic process), which ends nearly at 1100 °C (peak 6).

In the interval 6–7 of the DTA curve, the slope becomes more negative, which is attributed to the thermal reduction of the sesquioxide phase to ferrous-magnetite phase, according to the deductions taken from voltammetry analysis (Section 3.2). Furthermore, from 1200 °C (endothermic peak 7), the slope of the DTA curve turns strongly positive. This point to the occurrence of an exothermic process, owing possibly to decomposition of silicates to free SiO_2 and the incorporation of their elements to the spinels.

3.3.3. Extracted deductions from thermal analysis

As summary it can be deduced that the behaviour of the chromite spinel ore during the heating can be considered highly complex. Indeed, the following processes have been established by a series of phenomena: (i) overlapped changes of phases due to oxygen absorptions and desorptions, (ii) substitutions in the net of the cationic compounds, (iii) decompositions of the mineral and the siliceous gangue (which nature and amount is determinant in all the studied process), between others. The process can be considered as a global procedure, including a first oxidation of the iron in the mineral and followed by a thermic reduction of the iron oxidation state, process interfered by the chlorite behaviour.

Therefore, TGA and DTA curves are consequence of the behaviour and interaction between the three compounds present in the mineral sample. Although the main compound, the chromite spinel ($\text{Mg,Fe}^{2+}(\text{Cr,Al})_2\text{O}_4$) is responsible of the general behaviour of the curves. Also they are affected by the silicates in the sample, as labradorite ($\text{Na}_{2.84}\text{Ca}_{4.16}\text{Al}_{12}\text{Si}_{20}\text{O}_{64}$) and, specially, chromium chlorite ($\text{Mg}_{5.1}\text{Al}_{1.2}\text{Si}_3\text{Cr}_{0.7}\text{O}_{10}(\text{OH})_8$).

On this account, Tathavadkar et al. [20] have carried out a study about TGA and DTA curves from 130 °C. They used a chromite mineral spinel with less than 1% in silicates as impurities. The most important results were the apparent stability of the sample weight until 300 °C with a fast increasing of the weight, and an exothermic peak between 300 and 400 °C. That corresponds to the peak 3 of the DTA curve of the present study (Fig. 4), although slightly switched. The exothermic interval is even followed by a gain step until 637 °C, which is smaller than in the previous range. This was followed by an interval with a higher positive slope until

900 °C, exclusively corresponding to an endothermic process. The weight decrease due to the loss of dehydroxylation stage of the chlorite (explained by endothermic peak 4 and exothermic peak 5 of the present work) has not been observed by Tathavadkar et al. Moreover, the DTA curve shows stability from 750 to 930 °C. Those authors neither explain the evolution of the curve to 1100 °C [20]. It is important to indicate that in this work the thermal reduction of the iron (III) in the last step has been detected for the first time in the mineralogical study of this kind of materials.

On the other hand, Damodaran and Somasekar obtained pure chlorite from a chromite mineral. The chromium chlorite is separated from the remaining minerals by grinding to –200 mesh (B.S.S.) by hand picking using heavy liquids and a Frantz's Isodynamic Separator [22]. The purified fraction of the chromium chlorite was subjected to Differential Thermal Analysis. The curve has two endothermic peaks, one at 720 °C and the other at 850 °C, and another exothermic peak at 825 °C.

Other authors deal with different kinds of chromium chlorite, reducing the first endothermic peak even to 600 °C, and they proposed the presence of another exothermic point in the majority of the studied chromium chlorite, at 350 °C. This peak indicates a weak oxidation, suggesting the absence of oxidation during heating in chlorites which does not show this peak [24,26]. Those previously exposed are according to the TDA curve (Fig. 4). The mentioned peaks would correspond to the exothermic peaks 3, 5 and the endothermic peak 4 in the Fig. 4. The second exothermic peak was not visible in DTA.

On the other hand, the fact that the endothermic points found in this study appear at minor temperatures would have a justification. Laphman has correlated the percentage of Cr₂O₃ of the chlorite content with the temperature of the first endothermic peak and obtained a curve which shows a decrease on the decomposition temperature when the amount of Cr₂O₃ increases [24]. The oxide content in the chromium chlorite studied by these authors was 3–4%, whereas the chlorite of the mineral described was 9.3% in this work. Another interesting difference was the absence of iron in the composition of the chromium chlorite of the studied sample. However, the referred sample shows a little amount (total iron 0.4–1.8%).

3.4. Study by light microscopy

Powdered and sieved samples from the South African chromite ore, natural and obtained after heating to 450, 600, 800, 1000, 1100

and 1200 °C have been observed by light microscopy in order to identify the kind of chlorite.

From the observations of the samples, the following deductions were extracted:

The photography from the natural chromite ore shows particles with brown and especially orange colour, typical in chrome spinels with large amount of Fe(II), in several grey tones. Besides, other white and white-yellow particles, characteristic in silica and silicates, have been as well detected. However, the most interesting observation was the presence of numerous inclusions with violet colour, together marine blue interference colour (depending on the luminosity). These points to the presence of chromium chlorite, discarding the occurrence of antigorites and Fe–Mg chlorites, which can be characterized by their green colour [25].

In the 450 °C-heated mineral, an appreciable diminishing of the orange particles and the appearance of brown-red ones was observed. This can be explained by the partial oxidation of Fe(II) in the spinel and the formation of other spinels with Fe(II) and Fe(III).

In the 600 °C-heated sample, a small amount of green particles appear and the violet colour disappears. This indicates the decomposition of chlorite and formation of olivine (Fe and/or Mg silicate). Moreover, a gradual increasing of the green colour is observed in the 800 °C-heated sample.

In the 1000 °C–1200 °C-heated sample, the green colour strongly enlarge, owing to the separation of the formation of a Cr₂O₃ phase.

In all cases, white particles may be observed, due to the presence of other minority compounds, as silicates or several spinels, among others.

3.5. Study of the mineralogical composition of the materials obtained by ignition of the studied chromite ore by X-ray diffraction

In order to study the behaviour of the unknown sample during the heating process, the diffractograms of the samples obtained by ignition at the referred temperatures were measured, comparing them with that obtained for the original sample. The Fig. 5 displays the superposed diffractograms obtained from (below to above): original South African chromite ore sample [25], and those heated at 450, 600, 800, 1000, 1100 and 1200 °C.

The accurate chemical composition of the obtained minerals by the interpretation of the diffractograms shows a high difficulty, owing to, among others, to the similar values of the interplanar

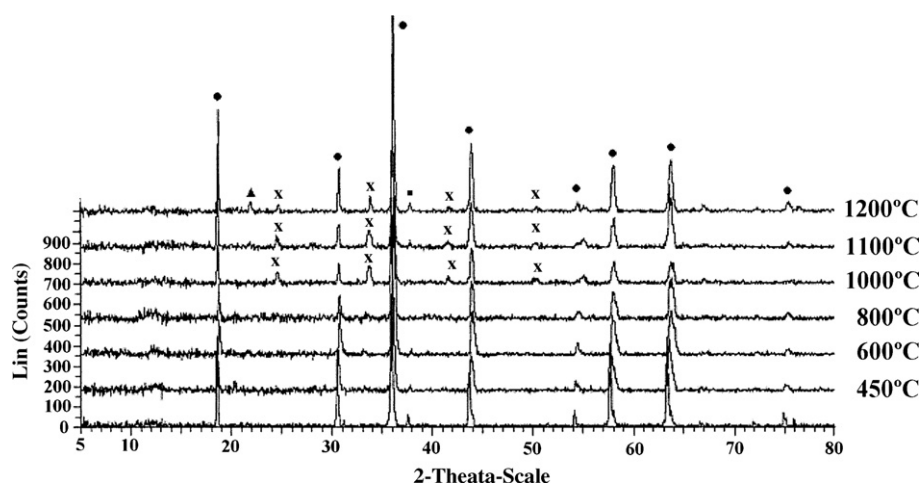


Fig. 5. Overlapped diffractograms obtained from the chromite ore and the materials obtained by the ignition at several temperatures. From below to above: original chromite ore, 450, 600, 800, 1000, 1100, and 1200 °C. The identified phases were: (●) spinels, (▲) cristobalite, (×) Cr₂O₃ and (■) chlorite.

distance characteristic of the different spinels, and even to several olivines, because the ignition at several temperatures produces specific minerals with different accurate elements ratio (Al/Cr, Fe(II)/Mg, Fe(III)/Al, Fe(II)/Fe(III), etc.), almost all not included in a database.

In this work, the diffractograms, together with the results obtained by voltammetry (Section 3.1), thermal analysis (Section 3.2) and light microscopy (Section 3.3), allow the approximate determination of the mineralogical and chemical composition of the sample to establish the process which happens during the heating.

3.5.1. General observations

From the analysis of the diffractograms of the Fig. 5, the following important generic observations have been stood out.

Until nearly 600 °C, a gradual displacement to the right side of the most representative peaks of the original chrome spinel ore. These effects may be caused (especially from 600 to 800 °C) by the formation of other chrome spinels, due to the progressive increasing of the oxidation state of the iron, or as consequence of partial or total substitution of the oxides of different cationic compounds. Indeed, the net parameters modify, providing different spinels stable at each temperature. In addition to these other spinels, anhydride silicates (essentially of iron) can be found, formed from the decomposition of the chromium chlorite, which occurs at that temperature. Iron (II) cations incorporate to the structure of the silicates and their peaks would superpose to those from spinels.

From 800 °C, new peaks corresponding to Cr₂O₃ appear, clearly visible in the Fig. 5, in the 1000 °C-heated sample diffractogram. This material partially segregates from the chrome spinels and the chromium chlorite during their decomposition.

Other effect clearly appreciable in the sample heated at 1200 °C is the appearance of free silica peaks as cristobalite, due to the decomposition of a part of the present silicates (especially the labradorite).

3.5.2. Mineral identification

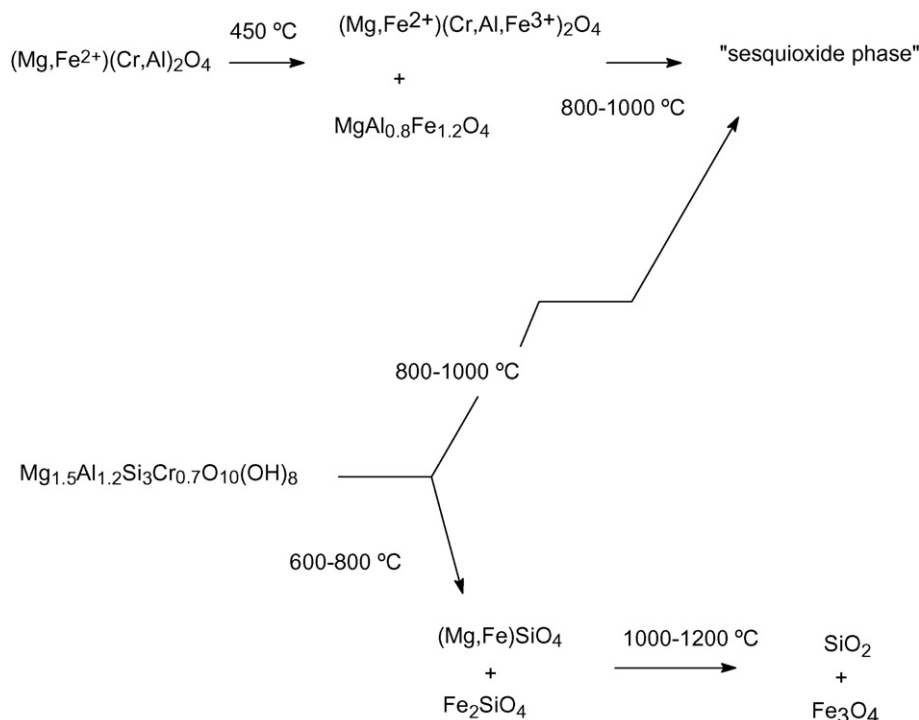
The identification of the mineralogical composition extracted from the X-ray diffraction study was summarized as follows:

As previously explained, the initial mineral is clearly composed by a chrome spinel, magnesiochromite ferroan. (PDF Card 09–0353, together with two silicates, chromium chlorite (magnesium aluminium chromium silicate hydrate PDF Card 72–1385), and, in lesser amount, labradorite (PDF Card 85–0878). The presence of a slow amount of free silica can be also envisaged [25].

In the diffractograms corresponding to the samples from 450 to 800 °C, the peaks of the initial chromite stabilize, matching to compounds which already have the generic formula of the natural chromium chromite (Mg,Fe²⁺)(Cr,Al,Fe³⁺)₂O₄. This spinel is formed by the partial substitution of Al(III) by Fe(III), which is obtained by the thermal oxidation of Fe(II) induced at these temperatures. This can also explain, in this range of temperatures, the presence of other spinels, as the standard magnesium aluminium iron oxide (PDF Card 71–1235) in the sample heated at 450 °C and magnesium iron aluminium oxide (PDF-Card 73–2159) in that ignited at 800 °C.

In the samples heated at 1000, 1100 and 1200 °C, a large amount of peaks, corresponding to chromium oxide PDF-card 85–0730, appear. This oxide comes from the segregation of two sources. The first one is chromium chlorite (magnesium aluminium chromium silicate hydrate, Mg_{5.1}Al_{1.2}Si₃Cr_{0.7}O₁₀(OH)₈), which shows higher content of chrome than other chlorites and has decomposed at minor temperatures. The other source is the chromite spinel. The intensity of the peaks of Cr₂O₃ remains constant until 1200 °C without a significant increasing of the peak intensity, so probably the segregation of this last one is almost total about 1100 °C in both cases. As consequence, the chrome spinel would disappear, forming a unique phase, in which the standard which better fit the peaks is magnesium aluminium iron oxide, PDF Card. However, probably Fe(III) would lessen the oxidation degree, by transformation of the hematite phase into magnetite.

On the other hand, iron silicate (PDF-CARD 29–0722), a compound highly thermostable, was detected in the mineral ignited



Scheme 1. Schematic summary of main processes produced during the heating process of natural chromite spinel ore.

at 800 °C. This indicates that the iron incorporates as Fe²⁺ in a silicate after the decomposition of the chromium chlorite, and partially remains with this oxidation state in the whole process, including in the sample at 1200 °C. However, it can also oxidize since 1000 °C. From this temperature, the wollastonite (PDF-Card 76–1948) was clearly detected. This phase probably comes from the gehlenite, SiO₂·Al₂O₃·2CaO, which has been formed after the decomposition of the silicates by a loss of aluminium (maybe incorporated to the spinel).

Finally, new peaks, already described and corresponding to the standard cristobalite low (PDF-Card 76–0941), a silicon oxide obtained by partial decomposition of the silicates, appear at 1200 °C. This material would be found together with tridymite low, (PDF-CARD 76–0894), which also appears in the materials obtained at 1000 and 1100 °C, and is considered as a source of cristobalite. In the case of the labradorite and the iron silicate, segregated Fe(II) would move during the thermal reduction to the spinel, consequently increase the amount in this cation.

3.6. Global processes during heating

The initial compounds in the natural chromite spinel ore are magnesiochromite ferroan [(Mg,Fe²⁺)(Cr,Al)₂O₄], chlorite chromian (magnesium aluminium chromium silicate hydrate Mg_{5.1}Al_{1.2}Si₃Cr₇O₁₀(OH)₈), labradorite (Na_{2.84}Ca_{4.16}Al₁₂Si₂₀O₆₄) and quartz (SiO₂). During the heating process, they undergo several decomposition and sintering processes, together with elements exchanges and substitutions, forming new compounds stable at each temperature (Scheme 1). From the results found in this work, these processes can be summarized as follows:

- Until 450 °C, the magnesiochromite ferroan decomposes in other two spinels, a chromite spinel (Mg,Fe²⁺)(Cr,Al,Fe³⁺)₂O₃ and magnesium aluminium iron oxide (MgAl_{0.8}Fe_{1.2}O₄). Iron (II) gradually oxidizes to iron(III). The other minerals do not undergo modifications.
- From 600 °C to nearly 800 °C, the decomposition of the chlorite begins to affect the process, to form olivines, iron (II) and/or magnesium silicates (green and red), and iron silicate (very stable at these temperatures), where the Fe (II) incorporated from chromite. Therefore, in the chromite the Fe(III)/Fe(II) ratio grows up and the magnesium aluminium iron oxide increases its proportion in the spinels. Moreover, olivines stable at these temperatures are formed.
- From 800 °C to nearly 1000 °C, these processes continue, and the segregation of the chromium from chromium oxide (green Cr₂O₃) is produced, which ends at this temperatures. Therefore, the original chromite spinel disappears, whereas the amount of the other sesquioxide phase rises. The Al₂O₃ and MgO incorporated from the silicates to the sesquioxide phase, whereas the iron (II) remains in the silicates.
- From 1000 to 1200 °C, a magnetite phase is formed by thermal reduction. The silicates decompose to cristobalite, and part of the iron (II) incorporate to the spinel.

4. Conclusions

The ignition of the chromite spinel mineral provokes a complex process consisting of several different transformations, as changes in the oxidation degree in the iron, cations substitutions, decompositions, chemical reactions between the compounds, etc., producing other spinels and more stable at each temperature. These processes become more complex if the mineral contain an appreciable amount of silicates, because their own transformation interferes and strongly modifies the generic behaviour in the spinel.

Thermal analysis showed a gradual and unsteady increasing of the weight, mainly caused by the oxidation of FeO, originally found in the chromite spinel. However, near 950–1000 °C, a gradual and abrupt loss of weight due to the formation of a ferrous-magnetite phase was observed. This process is stopped by the decomposition of the chromium chlorite, which takes place in two steps: firstly the dehydroxylation stage between 200 and 400 °C, and the second by the decomposition of the silicates provoked by the loss of hydroxy groups near 600 °C.

Analyses by X-ray diffraction, light microscopy and voltammetry indicate that the primary chromite spinel ((Mg,Fe²⁺)(Cr,Al)₂O₄) decomposes at low temperatures in other two spinels: another chromite spinel with a progressive introduction of iron (II) in the structure (Mg,Fe²⁺)O·(Cr,Al,Fe³⁺)₂O₃ and Magnesium aluminium Iron Oxide, MgAl_{0.8}Fe_{1.2}O₄, which relative amount in each element can vary depending on the oxidation degree of the iron by the increasing of the temperature. On the other hand, after the chromium chlorite decomposition, part of the Fe(II) would incorporate to the silicates forming a stable Iron Silicate (Fe₂SiO₄). From 800 to 900 °C, the Cr₂O₃ segregates as a differentiable compound, being removed from the chromite spinel and remaining only in spinels as magnesium, aluminium and iron oxides. Finally, a reduction process of the iron takes place, provoking the formation of a ferrous-magnetite phase, and the silicates decompose near 1100–1200 °C, producing as cristobalite low and tridymite low (SiO₂), which normally turns into the other one at high temperature. The occurrence of Fe(II) in the chromite ore sample for the whole ignition process is considered as a strong novelty, as it has been never detected in previous studies about chromite ores. The influence of the chlore chromite over the heating process have been found very important in the entire heating process.

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