FORMATION OF Na$_2$CrO$_4$-Na$_2$CO$_3$ MELT AND THE SPINODAL DECOMPOSITION OF NATURAL CHROMITE MINERALS DURING SODA-ASH ROASTING

V. D. Tathavadkar[**], M P Antony, and A. Jha,

Department of Materials,
School of Process, Environmental and Materials Engineering
University of Leeds, Leeds, LS2 9JT, UK.
Fax : +44 - 113 - 242 2531   Tel : +44 - 113 - 233 2342

Key words : Chromite, sodium chromate, soda-ash roasting

Abstract

Sodium chromate is produced via the soda-ash roasting reaction of chromite ore with sodium carbonate in air. The availability of oxygen at the reaction interface between sodium carbonate and chromite spinel is essential for the conversion of Cr^{3+} in the spinel lattice to Cr^{6+} in sodium chromate. The sodium chromate formed at the interface combines with the unreacted sodium carbonate melt and forms a liquid phase. In the present investigation, we have investigated the phase diagram of the sodium carbonate and chromate system by using the differential thermal analysis. From the measured liquidus temperatures, an evaluation of the thermodynamic mixing properties of sodium carbonate and chromate mixture was undertaken, and the mixing properties were determined from the shape of liquidus curve are discussed. The chromate-carbonate liquid plays an important role in determining the transport of O^{2-} ions.

The role of the chromate-carbonate liquid in promoting the spinodal decomposition in the chromite solid solution lattice is discussed with the help of energetic and crystal structure models.

The results obtained from the X-ray diffraction of phases formed after soda roasting and their scanning electron microscopic analysis help in explaining the mechanism and the conditions for spinodal decomposition. The research is aimed at improving the efficiency of extraction of chromium from chromite minerals and thereby reducing the amount of chromium lost in the waste stream during the extraction process.

INTRODUCTION

Soda-ash roasting process is most commonly used for extraction of reactive metals. The process has been exploited successfully over hundred years for extraction of chromium from chromite ore as a water-soluble sodium chromate phase. Chromium chemicals find applications in various fields e.g. for electro-plating, in lather and textile industries and as wood preservatives. The extent to which chromium compounds are used in the day-to-day life is quite astonishing, especially when one considers that they are ultimately derived from one chemical solution i.e. sodium chromate. Chromite is the only ore of the chromium, which is used for metallurgical, chemical and refractory applications. A very rich literature on various aspects of chromite ores and the production of ferro-chrome from chromite exit, however only limited literature is available on soda-ash roasting of the chromite (1 - 6). The importance of various process parameters and applications of various techniques such as pellet roasting has been studied for different ores (5 - 8).

During soda-ash roasting reaction, the chromium ions from chromite mineral diffuse out and react with sodium carbonate to form a water-soluble sodium chromate compound. The overall reaction can be represented as follows :

$$(Fe,Mg)[Cr,Al]_2O_4 + 2\,Na_2CO_3 + 3/2\,O_2 \;-->\; 2\,Na_2CrO_4 + (Mg)[Al,Fe]_2O_4 + 2\,CO_2 \qquad - (1)$$

The formation of liquid phase during soda-ash roasting is a common problem that results into product granulation, formation of rings on the kiln walls and lump formation. Thus, it is important to understand the formation of the liquid phase and its role in soda-ash roasting reaction, which will in turn help to adjust the process parameters to avoid above problems. The use of large quantities of process residues (50 - 80 % of chromite in the charge) or dolomite is recommended to solve the ring formation or granulation in the kiln during soda-ash roasting.

Present investigation is carried out to understand the role of sodium chromate - sodium carbonate liquid phase on soda-ash roasting and its effect on the phase transformation in the chromite spinel.

EXPERIMENTAL WORK

Materials :

The South African chromite ore, supplied by Elementis Chromium, UK, was used for this investigation. The physical and chemical properties of chromite ore used for the experimental work are given in table 1. Analytical grade reagents (AR) (sodium carbonate , sodium chromate) were used for determining the phase diagram.

Thermal analysis of Na_2CO_3 - Na_2CrO_4 system :

Differential thermal analysis was carried out using Stanton Redcroft model DTA- 673-4 system. Sodium carbonate and sodium chromate were weighed and mixed thoroughly using pestle and mortar. 50 mg of salt mixture in platinum crucible was used for analysis. Fine alumina powder was used as a reference material. Both the heating and cooling cycle data were recorded and processed using a personal computer. DTA experiments were carried out at an isochronal heating and cooling rate of $5^{o}C\ min^{-1}$.

Soda-ash roasting experiments :

Thermogravimetric (TGA) and differential thermal analysis (DTA) experiments were carried out to study the soda-ash roasting reaction. The chromite ore and sodium carbonate powder were mixed in a stoichiometric ratio defined in reaction (1). For TGA experiments, pellets were prepared with 2 g powder mixture after pressing, each pellet was placed inside an alumina crucible, which was then hanged inside a silica reaction tube and connected to microbalance. The silica tube was used to maintain a chosen atmosphere inside the reaction chamber. The TGA experiments were carried out using heating rate of 5°C min^{-1} under air and argon. A part of TGA sample was then used for X-ray diffraction analysis and electron microscopic studies.

Effect of salt mixture on roasting reaction :

The chromite ore and the salt mixture of sodium carbonate - sodium chromate were mixed in the stoichiometric ratios. In the sodium chromate - sodium carbonate mixture, the ratio of carbonate to chromate was varied between 0 and 80 % with an increment of 20 %. Pellets were prepared using a 2 g powder mixture. The pellets were heated isothermally at 800°C in air for 1 hour. The roasted pellet was leached with hot water and filtered leach solution was used for chemical analysis of chromium.

RESULTS AND DISCUSSION

Na$_2$CO$_3$ - Na$_2$CrO$_4$ system :

The Na$_2$CO$_3$ - Na$_2$CrO$_4$ phase diagram was constructed using the fusion and liquidus temperatures obtained from DTA data and it is shown in figure - 1. It is evident from the figure that sodium carbonate - sodium chromate forms a eutectic at 655°C and 62.5 wt. % of sodium chromate. Similar observations were reported by Yil'nyanskii and co-workers (3). The activities of Na$_2$CO$_3$ and Na$_2$CrO$_4$ along the liquidus curves were calculated by using the Clausius - Claperyon equation and the enthalpy of fusion data (9, 10). The Clausius - Clapeyron relationship is :

$$- \ln a_x = \frac{\Delta H_f}{R} \cdot (\frac{1}{T} - \frac{1}{T_m})$$ ----- (2)

where a_x is the activity of component 'x' in the binary section and ΔH_f is the enthalpy of fusion of 'x' in Joules mol^{-1}, R is the universal gas constant (8.312 J mol^{-1} K^{-1}), T_m is the melting point of component 'x' and T is liquidus temperature in K. From the values of activities a_x along the liquidus curve, the heat of mixing was calculated using the regular solution model equation :

$$R T \ln (\gamma_x) = \Omega (1 - N_x)^2$$ ----- (3)

The heat of mixing was calculated by plotting $R.T.\ln (\gamma_x)$ against $(1-N_x)^2$, where N_x is the mole fraction of *x*. It was observed that plot of $R.T.\ln (\gamma_x)$ against $(1-N_x)^2$ is not linear and it varies with composition . The value of heat of mixing was 850 J mol-1 and 7019 J mol-1 for sodium

crabonate and sodium chromate respectively. Using the this activity coefficient data, the isothermal activities were calculated considering the regular solution model, equation (4) :

$$T_1 \ln(\gamma_1) = T_2 \ln(\gamma_2) \qquad \text{---- (4)}$$

The graph of activities against the molar concentrations of Na_2CO_3 in the binary mixture of Na_2CO_3 - Na_2CrO_4 at 1000^oC is shown in figure -2. From this figure it is evident that the activity of Na_2CO_3 exhibits a almost ideal / Raultian behaviour upto 0.50 mole %, whereas the activities of Na_2CrO_4 shows a positive departure from the ideal Raultian behaviour.

Soda-ash roasting of chromite :

The soda-ash roasting of chromite was studied using the thermal analysis techniques : namely TGA and DTA. In figure-3, the values of % reduction (% R), which is the ratio of actual weight change at a given time, *t* to the total stoichiometric weight loss, are plotted against the temperature for the reactions in air and argon atmosphere and they are compared in figure - 3. The corresponding DTA curve for the soda-ash roasting reaction in air is shown in figure - 4, from which it can be deduced that the first stage of weight loss in the TGA curve and the corresponding endothermic peak in DTA curve around 100^oC is due to the loss of moisture in the charge. The sample roasted in air shows a gain in weight over a temperature range of 350 to 525^oC. This gain in the weight is due to the oxidation of Fe^{2+} present in the chromite spinel to Fe^{3+} state. The oxidation of Fe^{2+} to Fe^{3+} is reflected by a small endothermic peaks in this temperature range. Above 600^oC temperature there is a gradual weight loss and the rate of weight loss increases near 850^oC. The endothermic peak, in the DTA curve, around 650^oC is due to the eutectic melting point in Na_2CO_3 - Na_2CrO_4 system reported above. The large endothermic peak around 850^oC is due to the melting of unreacted sodium carbonate. Above $950\ ^oC$, there is a considerable weight gain which is due to the oxidation of sodium chromite ($Na_2Cr_2O_4$) to Na_2CrO_4.

The observed difference in the reaction rates in argon and air, shown by TGA curves in figure -3, points out to the role of oxygen during the roasting reaction. The weight gain stage is not observed in the sample roasted in the argon atmosphere. Also the weight loss due to the decomposition of Na_2CO_3 is delayed by 150^oC and commences at around 800^oC compared to air roasted samples. The rate of weight loss is much higher in argon atmosphere than in air due to the absence of sodium chromate formation.

Effect of sodium carbonate - sodium chromate liquid phase :

The effect of sodium chromate- sodium carbonate liquid phase on soda-ash roasting was studied by roasting chromite ore at 800^oC for 1 hour in air using the Na_2CO_3 - Na_2CrO_4 binary mixture, in which the concentration of sodium chromate was varied between 0 to 80 wt. %. The results are compared in figure - 5. At 800^oC no liquid phase is present at the beginning of the reaction because the melting point of Na_2CO_3 is 858^oC. As the oxidation of chromite and the decoposition of sodium carbonate begin, the formation of liquid phase commences at the sodium carbonate / chromite mineral interface. The liquid volume progressively increases and the pore channels are filled by the binary Na_2CO_3 - Na_2CrO_4 liquid. The liquid as a result of the oxidation reaction (1), enriches itself with Na_2CrO_4. As the volume of the liquid continues to increase with the increasing concentration of Na_2CrO_4 at 800^oC, the oxygen transport through the pore channels become more difficult. The reaction rate decays rapidly as the liquid

composition crosses the eutectic point. The only means of oxygen transport is via the diffusion of O2- in the binary mixture, which is much slower than the oxygen gas diffusion across the solid -gas boundary layer.

The effect of the binary liquid phase formation is more apparent in the TGA experiment than in the DTA during the oxidation of chromite mineral. The formation of binary sodium chromate / carbonate mixture yields a carbonate-saturated mixture, in which the volume fraction of Na_2CO_3 is dependent on the temperature and time of the reaction. As explained above, the oxygen transport diminishes with the increasing proportion of liquid phase a given temperature. Above $900^{o}C$, the liquid viscosity appears to drop rapidly, which helps it to drain-off from the unreacted chromite ore. As a result, the barrier to oxygen diffusion through the liquid film reduces rapidly and a proportionate increase in the oxidation rate is observed.

The X-ray powder diffraction patterns of the chromite samples roasted in air and argon are compared in figure - 6. Sodium chromate and unreacted spinel are the major phases present in the air roasted sample while sodium chromite and unreacted spinel are present in the sample roasted in argon atmosphere. The SEM microstructure of chromite sample roasted in air and argon atmosphere are shown in figure - 7. The microstructure of reacted grains in air atmosphere confirms the formation of a liquid phase at the roasting temperature, the envelope of liquid (see area A in figure - 7 (a)) freezes on cooling. By comparison, in argon atmosphere there are only fewer areas where the chromite grains are surrounded by the liquid, see area A in figure - 7(b). It should be noted that as there was no sodium chromate present in the reaction product obtained from argon atmosphere roasting, the liquid present must have a different composition than one observed in air roasting.

Effect of spinodal decomposition and precipitation of sesquoxide phase :

Natural chromite mineral has the general chemical formula $(Fe^{2+}, Mg) [Cr, Al, Fe^{3+}]_2O_4$, and it is a complex spinel structure, which is a solid solution based on the following spinels ; $FeCr_2O_4$, Fe_3O_4, $FeAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$ and $MgAl_2O_4$. When the chromite samples are heat treated in air, the strain energy component along with the chemical potential difference arising from the use of oxygen in air helps Fe^{2+} cations to diffuse and form a new coherent metastable spinel phase, maghemite at low temperatures in the region around $600^{o}C$. During the oxidation reaction, addition of one oxygen atom in the spinel lattice produces 3/4 vacant sites via the reaction (3) :

$$2 Fe^{2+} + 1/2 \ O_2 \ \text{-->} \ 2 Fe^{3+} + 2 O^{2-} + 3/4 \ V \qquad (3)$$

The formation of maghemite in iron-rich spinel system has been reported by many investigators (11) during the heat treatment of chromite in oxidising atmosphere. In the high temperature regions (> $600^{o}C$), this metastable phase transforms into a stable rhombohedral sesquioxide phase, hematite. The separation of sesquioxide from spinel takes place via the formation of oriented platelets in Widmannstatten structures. The microstructure of the heat treated chromite ore is shown in figure - 8. Both the spinel and the rhombohedral structures have nearly close-packed oxygen ion lattices, however different arrangement of cations produce a cubic structure for spinel and a hexagonal structure for sesquioxide. The orientation is such that the close packed {111} plane of oxygen in the spinel becomes the habit closed packed basal plane (0001) of hexagonal sesquioxide. Under these conditions, the new phase formed is coherent and can grow with a minimum interfacial energy corresponding to a change in the second co-ordination and its only requires a migration of cations. However, when the chromite

samples are heat treated in inert and partially reducing conditions, the change in the oxygen potential gradient is not sufficient to start the sesquioxide separation/ precipitation process.

The phase transformation in chromite during roasting in air reduces the incubation period, which is observed during roasting in argon atmosphere, under which the decomposition of Na_2CO_3 is delayed by 150°C. The phase transformation commences at 800°C. This behaviour is explained by the Hedvall effect (12), which states that reactivity enhances when the reacting material undergoes a simultaneous phase transition. Similar results are observed during magnetic roasting of hematite (13). The vacancies generated during the oxidation of Fe^{2+} aids the diffusion of Cr^{3+} towards the reaction interface, thereby increases the reactivity of the spinel phase during the roasting reaction. The oxidation of chromite in the temperature range from 250 to 600°C was observed. However, no separate sesquioxide phase was presented in the final products of the roasting. This may be due to the competition between two oxidation reactions namely the formation of sesquioxide and formation of sodium chromate, the later being more dominant of two. As a result at the end of the roasting reaction, the spinel phase shows an Fe-rich rim and Cr-rich core.

CONCLUSION

1)   Chromite mineral $(Fe^{2+},Mg)[Cr,Al,Fe^{3+}]_2O_4$ undergoes oxygen induced spinodal decomposition in the temperature range from 300 to 600°C in oxidising atmosphere.

2)   Mixture of sodium carbonate and sodium chromate forms a eutectic liquid containing 62.5 wt % Na_2CrO_4 at 655°C. The calculated phase diagram matches closely with experimental results.

3)   The formation of sodium chromate - sodium carbonate liquid phase during soda-ash roasting controls the diffusion of oxygen to reaction interface.

4)   The oxygen induced spinodal decomposition in spinel phase during roasting of chromite in air reduces the incubation period of the roasting reaction.

ACKNOWLEDGEMENT

REFERENCES

1)   Doerner, H A, U.S. Bureau of mines, Report of investigation, RI 2999, 1930

2)   Doerner, H A, U.S. Bureau of mines, Bulletin V Mining experiment station and state electro-metallurgical research laboratories, 1939.

3)   Yil'nyanskii Ya E and Pudovkin, O N, J. Appl. Chem, USSR, 20, 1947, 794 -799.

4)   Kireeva, M V and Klyukina E P, J. Appl. Chem. USSR, 34, 1961, 1280 - 1282.

5)   Krotov, Yu I and Vil'nyanskii, Ya E, J. Appl. Chem. USSR, 38, 1965, 1196 - 1200.

6)   Tel'pish, V V and Vil'nyanskii, Ya E, J. Appl. Chem, USSR, 42, 1969a, 1118-1120.

7)   El-Tawil, S.Z., Morsi, I.M., Shalabi, M E H and Mohamed, O.A., Neue Hutte, 36, 1991, 140 - 145.

8)   Thompson S C and Lawson F, Proc. Australas. inst. min. met., 289, 1984, 247 - 251.

9)   Barin I, Knack O and Kuboschewsky O, Thermochemical properties of inorganic substances, Pub : Springer-verlag

10) Richardson, F.D., Physical chemistry of melts in metallurgy Vol. - 1 & 2, Publ. Academic Press, 1974.

11) Lindsley D H, (Ed.), Oxide Minerals, Reviews in Mineralogy Vol. 25, 1991.

12) Hedvall J.A., Solid state chemistry, Publ. Elsevier, 1966.

13) Sohn H.Y. and Wadsworth, M.E. (Ed.), Rate processes in extractive metallurgy, Publ. Plenium press, 1979.
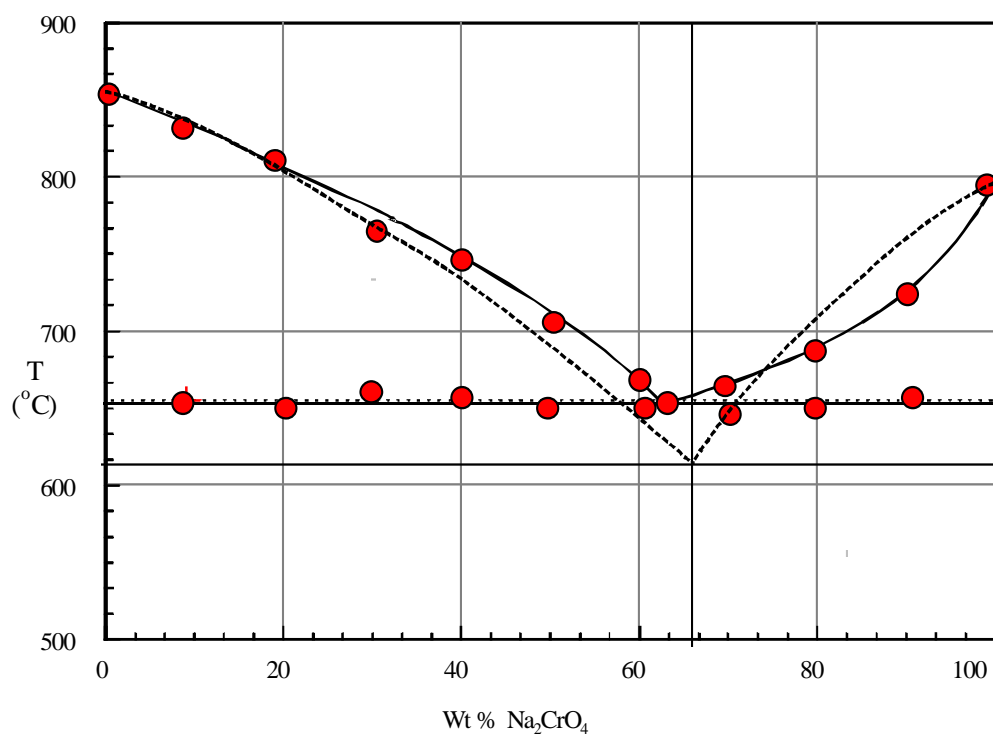
Figure - 1 : Sodium carbonate - sodium chromate phase diagram.
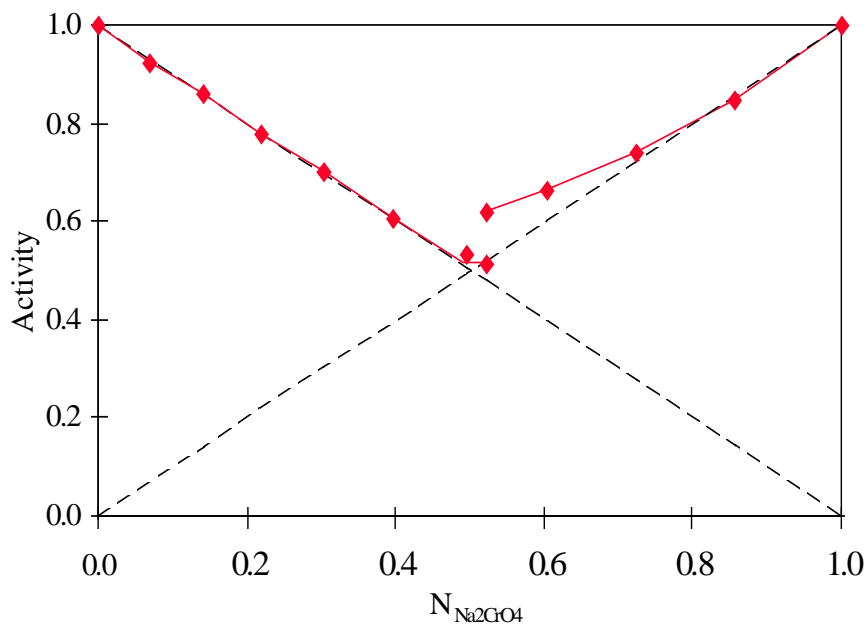Dotted line - Calculated using fusion data,   Solid line - DTA data

Figure - 2 : Activities of Sodium carbonate and sodium chromate at 1000 ^{o}C
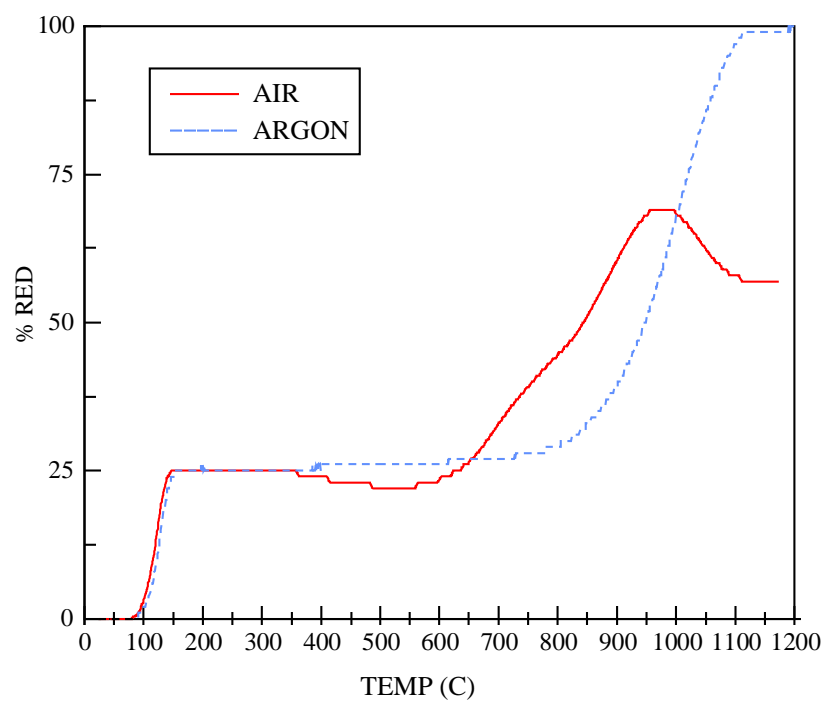calculated using data from phase diagram.

Figure - 3 : Thermogravimetric analysis results of soda-ash roasting of chromite under air and argon atmosphere
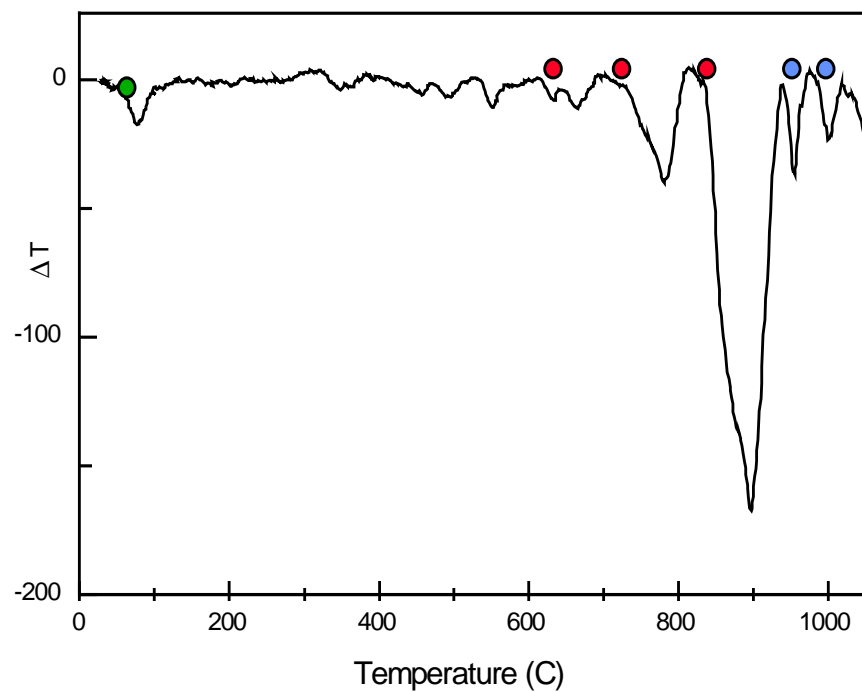

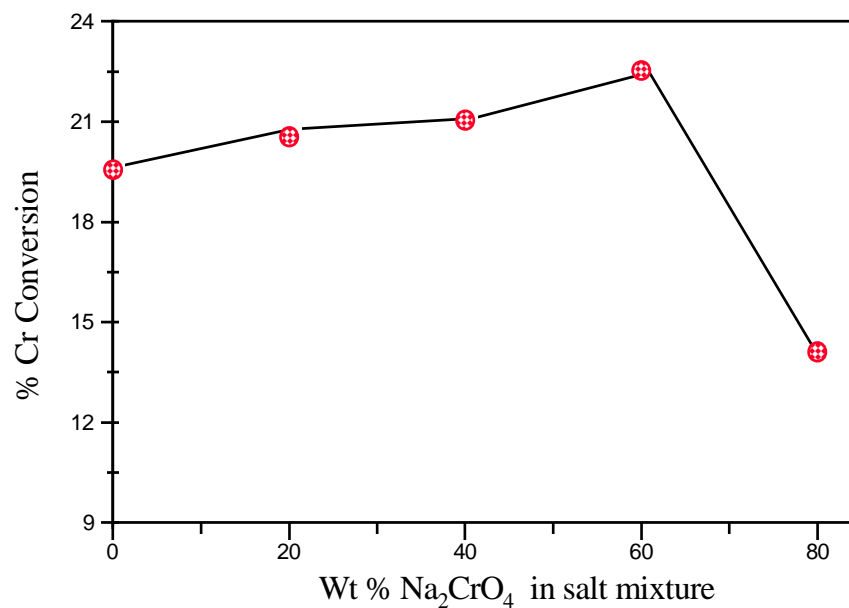Figure - 4 : Differential Thermal Analysis results of soda-ash roasting of chromite

Figure - 5 : The graph of % conversion of chromium against % sodium chromate in salt mixture
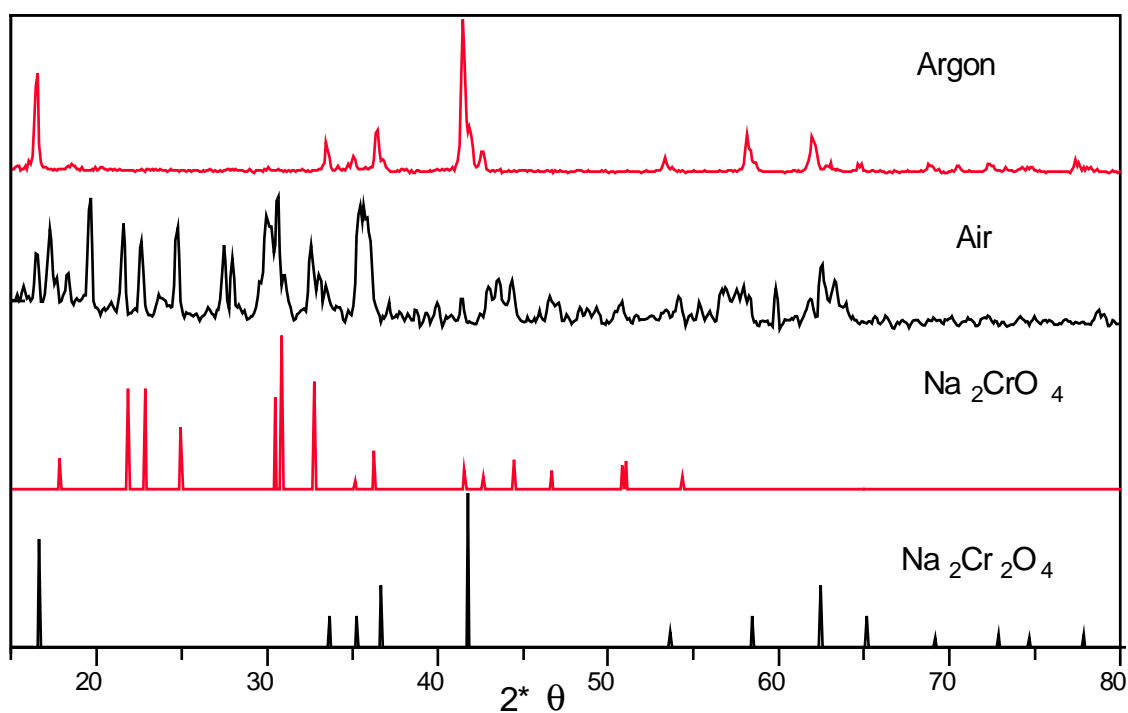

Figure - 6 : The X-ray diffraction pattern of the chromite samples roasted in air and argon

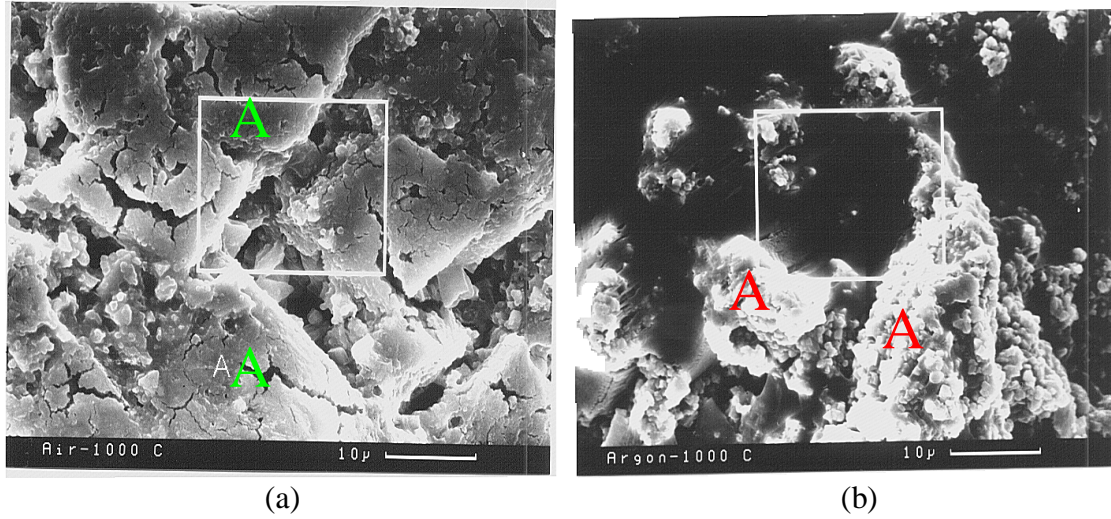(a)   (b)

Figure - 7 : SEM microstructure of chromite sample roasted under
a) Air   and   b) Argon atmosphere
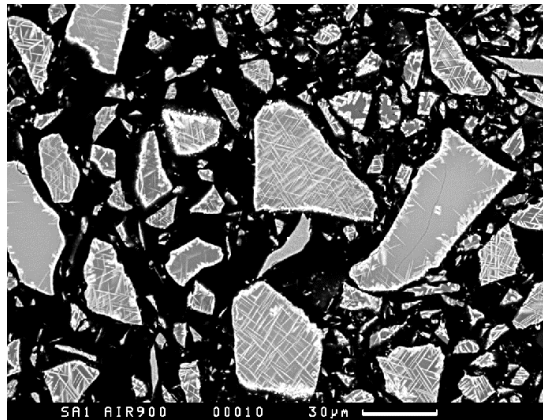A : Liquid phase regions

Figure - 8 : SEM microstructure of chromite ore heat treated in air
at 900 ^{o}C for 4 hrs.

Table I : Physical properties and chemical analysis of chromite ore

PROPERTY	UNIT	ORE
Physical properties :		
Density	g/cc	4.52
Av. particle size	μm	26
Sp. surface area	Sq.m/g	0.50
Lattice Parameter	Å	8.296
Chemical analysis :		
Cr_2O_3	Wt %	43.46
Al_2O_3	Wt %	13.81
MgO	Wt %	6.93
Total Fe	Wt %	21.21