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THERMOCHEMICAL STUDIES IN THE SODIUM–CHROMIUM–OXYGEN SYSTEM

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ABSTRACT

The compound $NaCrO_2$ in the sodium–chromium–oxygen system is important from the point of view of corrosion of stainless steel by oxygen-contaminated sodium in fast reactors. Thermogravimetry, differential thermal analysis in different atmospheres, and X-ray powder diffraction studies on the products showed $NaCrO_2$ to be stable in argon up to 1200 °C. The compound was stable in a CO_2 atmosphere up to at least 900 °C, but in oxygen it was oxidised above 350 °C to a mixture of Na_2CrO_4 and Cr_2O_3. $NaCrO_2$ was found to be the only phase of chromium(III) which could be obtained from solid–solid reactions of Na_2CO_3 and Cr_2O_3.

Na_2CrO_4 showed a phase transition at 410 ± 5 °C with a heat of transition of 5.9 kJ mol^{-1}.

INTRODUCTION

In the sodium–chromium–oxygen system, $NaCrO_2$ has been reported to be the only stable double oxide phase in contact with chromium and liquid sodium [1]. This compound is thus important from the point of view of corrosion of stainless steel by sodium used as a coolant in fast reactors. The thermal stability of this compound has not been established [2]. $NaCrO_2$ has been reported to decompose reversibly at 795 °C to a mixture of Na_2O and Cr_2O_3 [3], but this observation needs confirmation, since it has been reported earlier that $NaCrO_2$ can be prepared by heating a mixture of Na_2CO_3 and Cr_2O_3 in vacuum at 800 °C [1]. The behaviour of $NaCrO_2$ at higher oxygen potentials has not been studied. Apart from Na_2CrO_4 and $Na_2Cr_2O_7$, a number of phases with chromium in the +4 and +5 oxidation states, such as Na_2CrO_3, Na_4CrO_4, $NaCr_3O_8$ and Na_3CrO_4, have been reported to exist at higher oxygen potentials [2,4].

The present work is a study on the thermal stability of $NaCrO_2$, both in argon and oxygen, from ambient temperature to 1200 °C by thermogravimetric (TG), differential thermal analysis (DTA) and X-ray powder diffraction (XRD) methods. In addition, thermal studies have been carried out on

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mixtures of Na_2CO_3 and Cr_2O_3 in different ratios, in both argon and oxygen, to establish the possibility of formation of other mixed oxides.

EXPERIMENTAL

Na_2CO_3 (GR) and Cr_2O_3 (Specpure) were mixed in ratios of 2 : 1 and 1 : 1, and 100 mg samples were heated in a Mettler Thermoanalyser up to a maximum temperature of 1200 °C, with simultaneous TG and DTA recording. The experiments were carried out at a heating rate of 6 °C min^{-1} with either pure argon or oxygen gas flowing at a rate of 100 ml min^{-1}. TG and DTA curves were also recorded under controlled cooling at a rate of 6 °C min^{-1}. The measured temperatures had an accuracy of ±5 °C.

Thermograms of $NaCrO_2$, $Na_2CrO_4 \cdot 0.5H_2O$ and $Na_2Cr_2O_7 \cdot 2H_2O$ were also recorded in an oxygen atmosphere. $NaCrO_2$ was prepared by heating a 1 : 1 mixture of Na_2CO_3 and Cr_2O_3 at 900 °C in argon. $Na_2CrO_4 \cdot 0.5H_2O$, a new hydrate, was obtained by evaporation, at 100 °C, of an aqueous solution containing Na_2CO_3 and CrO_3 in 1 : 1 ratio. $Na_2Cr_2O_7 \cdot 2H_2O$ was also prepared by evaporation of a solution containing Na_2CO_3 and CrO_3 in 1 : 2 ratio.

X-ray powder diffraction patterns of the products obtained at different temperatures were taken on a Siemens diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.541\,78$ Å).

RESULTS AND DISCUSSION

X-ray powder diffraction patterns of the various heated products are given in Fig. 1. X-ray data for $NaCrO_2$, Cr_2O_3 and Na_2CrO_4 taken from the literature are included for comparison. The results of thermal analysis are presented in Figs. 2, 3 and 4, and the observations are summarized in Table 1. Important features are discussed in the following sections.

$Na_2CO_3 + Cr_2O_3$ (1 : 1)

Figure 2 shows the TG and DTA curves in argon (C and D) and in oxygen atmospheres (E and F) obtained for a mixture of Na_2CO_3 and Cr_2O_3 taken in the ratio 1 : 1. TG and DTA curves of Na_2CO_3 are also given for comparison (A and B). In an argon atmosphere, although most of the weight loss occurs between 600 °C and 800 °C, the weight loss begins at ca. 400 °C. This weight loss is associated with an endothermic DTA peak with its maximum at 750 °C. Na_2CO_3, on the other hand, is found to be thermally stable up to 850 °C, its melting point. This shows that the interaction of Na_2CO_3 and Cr_2O_3 starts above 400 °C with the evolution of CO_2, and is

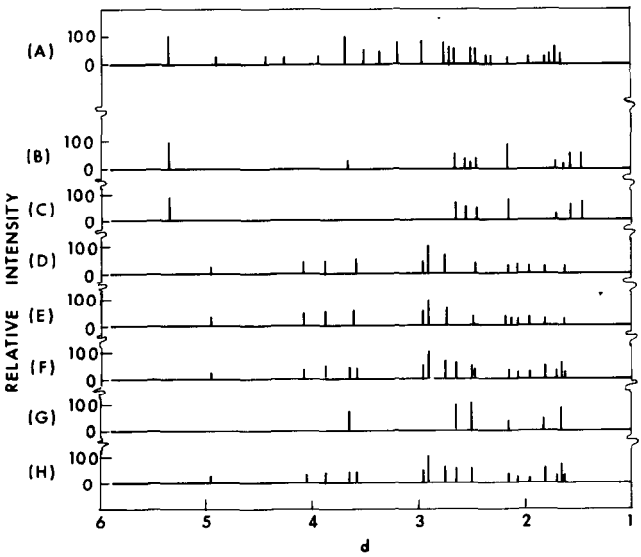

Fig. 1. X-ray powder patterns (Cu $K\alpha$). The heights of the lines indicate the relative diffraction peak intensities. A, $Na_2CrO_4 \cdot 0.5H_2O$; B, $Na_2CO_3 + Cr_2O_3$ heated to 900 °C in argon for 2 h; C, $NaCrO_2$; D, $2Na_2CO_3 + Cr_2O_3$ heated to 800 °C in oxygen for 2 h; E, Na_2CrO_4; F, $Na_2CO_3 + Cr_2O_3$ heated to 800 °C in oxygen for 2 h; G, Cr_2O_3; H, $NaCrO_2$ heated to 800 °C in oxygen for 2 h.

complete at 900 °C. The X-ray powder pattern of the green product obtained at 900 °C (Fig. 1B) shows mainly lines due to $NaCrO_2$ [2]. Additional weak lines observed in the pattern could be attributed to unreacted Cr_2O_3. The weight loss observed was 14%, as compared with the expected loss of 17% for the reaction

$$Na_2CO_3 + Cr_2O_3 \rightarrow 2NaCrO_2 + CO_2 \quad (1)$$

These results indicated that the reaction was not quantitative. Continued heating at 900 °C, however, led to disappearance of the X-ray lines due to Cr_2O_3, and pure $NaCrO_2$ remained as the final product. Earlier experimental studies by Knights and Phillips had suggested that $NaCrO_2$ remains a solid up to at least 790 °C [5]. However, Barker and Hooper found that $NaCrO_2$ decomposes reversibly at 795 °C to a mixture of Na_2O and Cr_2O_3 [3]. For the reaction

$$\tfrac{1}{2}Na_2O + \tfrac{1}{2}Cr_2O_3 \rightarrow NaCrO_2 \quad (2)$$

the reported ΔH value is -101.4 kJ mol^{-1} [1]. Hence the decomposition of $NaCrO_2$ to a mixture of Na_2O and Cr_2O_3 should show a significant DTA peak around 795 °C [6]. However, no DTA peak was observed on heating (or cooling) $NaCrO_2$ in argon in the range from ambient to 1200 °C. The present TG and DTA curves show that $NaCrO_2$ is stable and remains a solid up to 1200 °C. Thermogravimetric studies in a CO_2 atmosphere and

TABLE 1

Summary of TG and DTA curves in the Na–Cr–O system

Reacting materials	Atmosphere	Temperature range (°C)	Weight change (%)	DTA peak temp. (°C), heating curve	Reaction products confirmed by XRD	DTA peak temp. (°C), cooling curve
Na_2CO_3 + Cr_2O_3	Argon	600–800	−14	750 endo	$NaCrO_2$	No peak
	O_2	350–800	−7	775 endo	Na_2CrO_4 + Cr_2O_3	775 exo 410 exo
$2Na_2CO_3$ + Cr_2O_3	Argon	700–900	−12	670 endo 810 endo	$NaCrO_2$ + Na_2CO_3	790 exo
	O_2	350–800	−10.5	800 endo	Na_2CrO_4	790 exo 390 exo
$NaCrO_2$	Argon	25–1200	0.0	No peak	$NaCrO_2$ stable up to 1200 °C	No peak
	CO_2	25–900	0.0	No peak	$NaCrO_2$ stable up to 900 °C	No peak
	O_2	300–700	+9	500 exo 775 endo	Na_2CrO_4 + Cr_2O_3	–
Na_2CrO_4 ·0.5H_2O	O_2	100–200	−4.5	120 endo	Na_2CrO_4	–
		200–900	0.0	450 endo 820 endo	Na_2CrO_4	
$Na_2Cr_2O_7$ ·2H_2O	O_2	100–250	−12	150 endo	$Na_2Cr_2O_7$	–
		250–500	0.0	390 endo	$Na_2Cr_2O_7$	
		> 500	slow loss		Na_2CrO_4 + Cr_2O_3	

exo, Exothermic; endo, endothermic.

the X-ray pattern of the product showed that $NaCrO_2$ is formed when a 1 : 1 mixture of Na_2CO_3 and Cr_2O_3 is heated at 900 °C. Similar studies with $NaCrO_2$ established its stability in a CO_2 atmosphere up to 900 °C. This ruled out the possibility of the reaction

$$2NaCrO_2 + CO_2 \rightarrow Na_2CO_3 + Cr_2O_3 \quad (3)$$

in the temperature range studied.

Thermogravimetric curves of a 1 : 1 mixture of Na_2CO_3 and Cr_2O_3 in oxygen (Figs. 2E and 2F) show that the weight loss starts above 250 °C and is complete at ca. 750 °C. The product was yellowish in colour, indicating the oxidation of Cr^{III}, and was also hygroscopic. The X-ray powder pattern (Fig. 1, F) indicated that the product was a mixture of Na_2CrO_4 and Cr_2O_3. However, no significant DTA peak could be observed in the temperature range 350–700 °C corresponding to the weight loss observed. This is probably because the heat absorbed during decomposition of Na_2CO_3 is com-

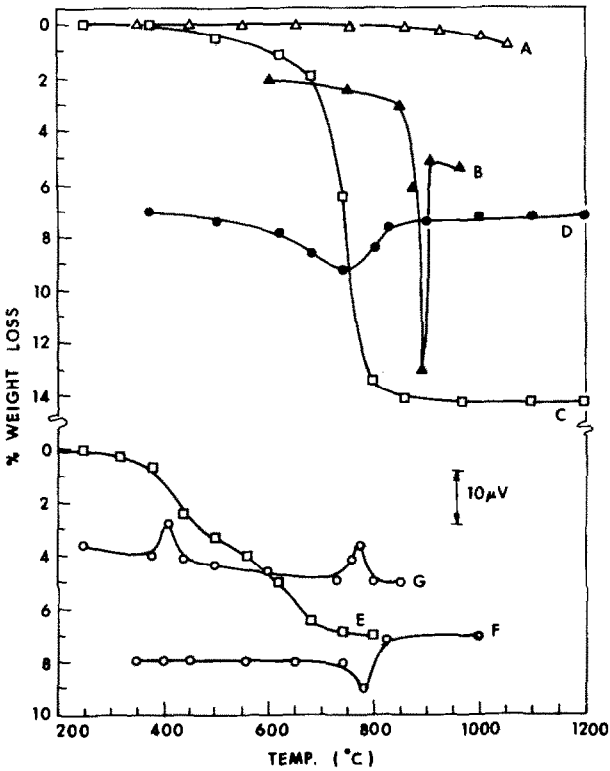

Fig. 2. TG and DTA plots: A, TG curve of Na_2CO_3 in argon; B, DTA curve of Na_2CO_3 in argon; C, TG curve of $Na_2CO_3 + Cr_2O_3$ in argon; D, DTA curve of $Na_2CO_3 + Cr_2O_3$ in argon; E, TG curve of $Na_2CO_3 + Cr_2O_3$ in oxygen; F, DTA heating curve of $Na_2CO_3 + Cr_2O_3$ in oxygen; G, DTA cooling curve of heated product of $Na_2CO_3 + Cr_2O_3$ in oxygen.

pensated by the heat evolved during oxidation of Cr^{III} to Cr^{VI} by oxygen. An endothermic peak was observed at 775 °C due to melting of Na_2CrO_4. The cooling DTA curve (Fig. 2G) showed two exothermic peaks, one at 775 °C and the other at 410 °C. The former could be attributed to solidification of the molten Na_2CrO_4 and the latter to a phase transition. Both the DTA peaks were reversible and were reproduced as endotherms on heating.

$Na_2CO_3 + Cr_2O_3$ (2 : 1)

The TG and DTA curves obtained for mixtures of Na_2CO_3 and Cr_2O_3 in the 2 : 1 ratio in argon and oxygen are shown in Fig. 3. In argon, the XRD analysis of the product obtained at 900 °C indicated it to be a mixture of $NaCrO_2$ and Na_2CO_3. No new phase of Cr^{III} containing a smaller proportion of chromium than that present in $NaCrO_2$ could be identified. The possibility of Na_3CrO_3 has been suggested by Gross et al. [1] in their studies on the Na–Cr–O system. The DTA curves show two endothermic peaks

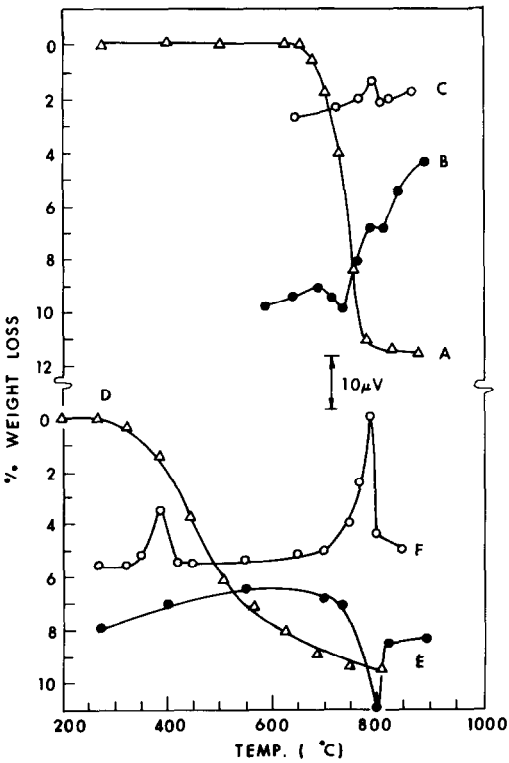

Fig. 3. TG and DTA curves of $2Na_2CO_3 + Cr_2O_3$. A, TG curve in argon; B, DTA heating curve in argon; C, DTA cooling curve of heated product in argon; D, TG curve in oxygen; E, DTA heating curve in oxygen; F, DTA cooling curve of heated product in oxygen.

with respective maxima at 670 °C and 810 °C. The former peak could be attributed to formation of $NaCrO_2$ from Na_2CO_3 and Cr_2O_3 and the latter to melting of excess Na_2CO_3. The lowering of the melting point of Na_2CO_3 from 850 °C is probably caused by the presence of $NaCrO_2$. The cooling curve (Fig. 3C) has an exothermic DTA peak at 790 °. Heating the mixture in oxygen gave Na_2CrO_4. The weight loss observed from 250–800 °C was 10.5%, as compared with the expected value of 11% for the formation of Na_2CrO_4 from $2Na_2CO_3 + Cr_2O_3$. The only sharp DTA peak observed was an endothermic peak at 800 °C caused by the melting of Na_2CrO_4. On cooling, however, two sharp exothermic peaks around 790 °C and 390 °C were observed, which were attributed, respectively, to the solidification and phase transition of Na_2CrO_4.

$NaCrO_2$, $Na_2CrO_4 \cdot 0.5H_2O$ and $Na_2Cr_2O_7 \cdot 2H_2O$

The thermograms recorded for $NaCrO_2$ (A and B), $Na_2CrO_4 \cdot 0.5H_2O$ (C and D) and $Na_2Cr_2O_7 \cdot 2H_2O$ (E and F) in an oxygen atmosphere are given

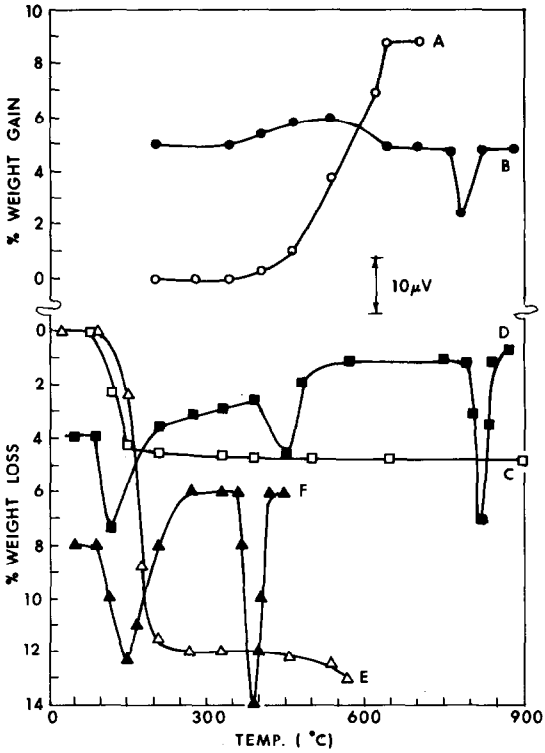

Fig. 4. TG and DTA curves in oxygen. A, TG curve of $NaCrO_2$; B, DTA curve of $NaCrO_2$; C, TG curve of $Na_2CrO_4 \cdot 0.5H_2O$; D, DTA curve of $Na_2CrO_4 \cdot 0.5H_2O$; E, TG curve of $Na_2Cr_2O_7 \cdot 2H_2O$; F, DTA curve of $Na_2Cr_2O_7 \cdot 2H_2O$.

in Fig. 4. It was found that $NaCrO_2$ was oxidised in oxygen above 350 °C, accompanied by a broad exothermic peak. The X-ray powder diffraction pattern of the product (Fig. 1H) showed it to be a mixture of Na_2CrO_4 and Cr_2O_3. The weight gain observed up to 700 °C was 9% against an expected value of 11.2%. The weight gain expected for oxidation of $NaCrO_2$ to $Na_2Cr_2O_7$ is 22.4%. The product gave an endothermic peak at 775 °C characteristic of the melting of Na_2CrO_4. These results established that $NaCrO_2$ is oxidised to a mixture of Na_2CrO_4 and Cr_2O_3 rather than to $Na_2Cr_2O_7$.

Thermogravimetry of the hydrate of sodium chromate (Fig. 4C) shows a weight loss of 4.5% due to water below 200 °C, and the product gave an X-ray pattern of Na_2CrO_4 that differed from that of the starting compound (Fig. 1A). On the basis of the weight loss at 200 °C, a composition of $Na_2CrO_4 \cdot 0.5H_2O$ could be assigned to the hydrate. This hemihydrate has not been reported in the literature, but it could also be prepared by heating $NaCrO_2$ or a mixture of Na_2CO_3 and Cr_2O_3 in air up to 900 °C and cooling the product. Na_2CrO_4 formed at 900 °C is converted to the hemihydrate on cooling when moisture is absorbed. Na_2CrO_4 is chemically stable in oxygen

up to 900 °C. It showed two endothermic peaks with maxima at 450 °C and 820 °C. Both peaks were reversible. The peak at 450 °C is probably due to a phase transition from an orthorhombic to a hexagonal phase. A reddish brown hexagonal phase of Na_2CrO_4 has been reported from high temperature X-ray patterns at 522 °C [7]. The peak at 820 °C is due to the melting of Na_2CrO_4. The transition and melting temperatures were accurately determined to be 410 °C and 795 °C, respectively, using $K_2Cr_2O_7$ as standard (melting point, 395 °C; heat of fusion, 36.6 kJ mol^{-1}) [8]. From DTA peak area measurements, the heat of transition and heat of fusion were calculated using the expression $\Delta H = KA/MW$, where K is a calibration constant, A is the peak area, M is the molecular weight and W is the weight of the sample. The values found were ΔH_T (transition) = 5.9 kJ mol^{-1} and ΔH_F (fusion) = 9.7 kJ mol^{-1}.

$Na_2Cr_2O_7 \cdot 2H_2O$ was found to lose its water of crystallisation below 200 °C, and was stable in oxygen up to 500 °C. A sharp DTA peak at 390 °C in the thermogram is caused by melting of the anhydrous dichromate, which was found to lose weight above 500 °C. Heating of $Na_2Cr_2O_7$ above 600 °C for a longer period gave a mixture of Na_2CrO_4 and Cr_2O_3, as was confirmed from XRD patterns.

The following conclusions can be inferred.

(i) $NaCrO_2$ is stable and remains a solid up to 1200 °C in argon. It is stable in a CO_2 atmosphere up to 900 °C. In oxygen, it is oxidised above 350 °C to a mixture of Na_2CrO_4 and Cr_2O_3 rather than to $Na_2Cr_2O_7$.

(ii) $NaCrO_2$ is the only phase of chromium(III) that can be obtained from solid–solid reactions of Na_2CO_3 and Cr_2O_3.

(iii) Na_2CrO_4 was found to undergo a phase transition at 410 °C with a heat of transition of 5.9 kJ mol^{-1}. The compound is stable up to 900 °C.

(iv) $Na_2Cr_2O_7$ decomposes to a mixture of Na_2CrO_4 and Cr_2O_3 above 600 °C in oxygen.

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