PREPARATION AND PROPERTIES OF THE SYSTEM $Cr_{2-x}Rh_xO_3(2 \ge x \ge 0)$

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Summary

Members of the system $\operatorname{Cr}_{2-x}\operatorname{Rh}_x O_3(2 \ge x \ge 0)$ were prepared by thermal decomposition of the nitrates. Magnetic measurements indicate that the chromium-rich members are antiferromagnetic and the spin-only moment, extrapolated from the high-temperature portion of the susceptibility curves, corresponds to Cr(III). Reduction studies indicate that the rhodium was stabilized in the solid solution and that at elevated temperatures between 1100 and 1200 °C the mixed oxides were reduced to either the elements or a rhodium-chromium alloy.

1. Introduction

Khanolkar [1] reported that rhodium metal and chromium(III) oxide react to form an ilmenite phase $CrRhO_3$ with a = 5.42 Å and $\alpha = 55^{\circ} 12'$. Shaplygin *et al.* [2] showed from differential thermal analysis (DTA) and X-ray studies that below 1210 °C, Cr_2O_3 and $CrRhO_3$ coexist at 0 - 50 mol.% Rh_2O_3 and below 1060 °C $CrRhO_3$ and Rh_2O_3 coexist at 50 - 100 mol.% Rh_2O_3 . The samples were prepared by heating mixtures of Cr_2O_3 and Rh_2O_3 at 900 - 1000 °C for 150 - 200 h.

There appears to be little else published concerning this system. Since both end-members crystallize with the corundum structure [3, 4], with cell parameters of a = 4.94 and 5.13 Å, and c = 13.58 and 13.85 Å for Cr_2O_3 and Rh_2O_3 , respectively, the re-examination of the earlier work using better synthetic methods was deemed advisable.

Furthermore, it was reported by Strater and Mantell [5] that hydrogen reduction of Cr_2O_3 to chromium was found to be feasible above 1130 °C at very low water concentrations. However, the presence of a small quantity of residual water vapor retarded the rate of reduction. This was confirmed by Hussein *et al.* [6] who succeeded in reducing Cr_2O_3 with hydrogen to chromium at 1200 °C. They also reported [7] that the addition of metallic iron markedly increases the extent of reduction. In this study, reduction studies of members of the system $Cr_{2-x}Rh_xO_3$ were carried out as a function of increased concentration of the rhodium to see if the results were similar to those found for the $Cr_{2-x}Fe_xO_3$ system.

2. Experimental procedure

Samples of $\operatorname{Cr}_{2-x}\operatorname{Rh}_x O_3(2 \ge x \ge 0)$ were prepared by codecomposition of rhodium nitrate and chromium nitrate. The calculated weights of $\operatorname{Cr}(\operatorname{NO}_3)_3 \cdot \operatorname{9H}_2O$ and $\operatorname{Rh}(\operatorname{NO}_3)_3 \cdot \operatorname{2H}_2O$ were dissolved in water and the solution was dried at 150 °C for 12 h, ground, and decomposed at 400 °C for 24 h. The sample was then ground and heated at 1000 °C for 48 h. Rhodium metal was prepared by reducing Rh_2O_3 with 15at.%H₂-85at.%Ar at 500 °C for 24 h in a horizontal tube furnace. The Rh_2O_3 was prepared by decomposing $\operatorname{Rh}(\operatorname{NO}_3)_3 \cdot \operatorname{2H}_2O$ at 800 °C in air for 20 h and Cr_2O_3 was prepared by decomposing $\operatorname{Cr}(\operatorname{NO}_3)_3 \cdot \operatorname{9H}_2O$ at 900 °C in air for 24 h.

Temperature-programmed reduction (TPR) studies were carried out on four compositions (x = 0.4, 1, 1.6 and 2) using a Cahn 113 thermal balance. These compositions were chosen to study the stabilization of rhodium(III) towards reduction in the solid solution series $Cr_{2-x}Rh_xO_3$. Each sample (of about 30 mg), after being placed in the balance, was purged with a stream of 15at.%H₂-85at.%Ar to obtain a constant initial weight. The H₂-Ar gas was pre-dried over a P₂O₅ trap and the flow rate was 60 cm³ min⁻¹. The temperature was then increased to 1000 °C at a rate of 50 °C h⁻¹.

To study the complete reduction of Cr(III), the end-member Cr_2O_3 was reduced in a Lindberg furnace at 1200 °C for 36 h in flowing hydrogen with a flow rate of 60 cm³ min⁻¹. The hydrogen was pre-dried over a P_2O_5 trap. For compositions with $2 \ge x \ge 1$, the reductions were carried out in a Lindberg furnace at 1100 °C. A sample weight of approximately 100 mg was put in a silica crucible. At the completion of the reduction, the furnace was turned off and the sample was allowed to cool to room temperature in the furnace.

X-ray powder diffraction patterns of all samples were obtained using a Philips diffractometer and monochromated high intensity Cu Ka1 radiation $(\lambda = 1.5405 \text{ Å})$. The diffraction patterns were taken in the range of $12^{\circ} < 2\theta < 80^{\circ}$ with a scan rate of $1^{\circ} 2\theta \text{ min}^{-1}$ and a chart speed of 30 in h⁻¹. To obtain the cell parameters, slow-scan X-ray patterns were obtained with a scan rate of $0.25^{\circ} 2\theta \text{ min}^{-1}$. Cell parameters were obtained from a least-squares refinement of the data with the aid of a computer program which corrected for the systematic experimental errors. The magnetic susceptibility of the oxide samples was measured using a Faraday balance [8] from liquid nitrogen temperatures to 763 K; a field strength of 10.4 kOe was used.

3. Results and discussion

Members of the system $\operatorname{Cr}_{2-x}\operatorname{Rh}_xO_3(2 \ge x \ge 0)$ were prepared by decomposition of the nitrates and cell parameters were measured and are shown as a function of increasing rhodium oxide concentration in Fig. 1. The magnetic susceptibility data are given in Table 1. The moments reported



Fig. 1. Cell parameters as functions of composition for the system $Cr_{2-x}Rh_xO_3$.

TABLE 1

Composition	Magnetic moment of Cr ³⁺ (µ _B)	Néel temperature T _N (K)	Weiss constant θ (K)
Cr_2O_3	4.0	315	-692
$Cr_{1.8}Rh_{0.2}O_{3}$	4.0	270	-546
$Cr_{1.6}Rh_{0.4}O_3$	4.0	205	-395
$Cr_{1.5}Rh_{0.5}O_3$	4.0	180	-331
$Cr_{14}Rh_{06}O_{3}$	4.0	150	-283
$Cr_{1,3}Rh_{0,7}O_3$	3.8	125	-194
CrRhO ₃	3.8	_	-102
$\operatorname{Cr}_{0.4}\operatorname{Rh}_{1.6}O_3$	3.8	—	-30

Magnetic properties of $\operatorname{Cr}_{2-x}\operatorname{Rh}_x\operatorname{O}_3$



Fig. 2. Temperature dependence of the inverse magnetic susceptibilities of members of the system $Cr_{2-x}Rh_xO_3$.

were extrapolated from the high-temperature portion of the susceptibility curves plotted in Fig. 2. The measured moment corresponds closely to the value $3.9 \mu_{\rm B}$ reported for Cr₂O₃.

The small observed variation in the observed moments (± 0.1) was due to the limited temperature range of the high-temperature measurements. The observed Néel temperatures for the chromium-rich members are consistent with the antiferromagnetic behavior of $3d^3$ chromium. Rhodium does not contribute to the observed moments but does reduce the strength of the antiferromagnetic interactions.

The results of the temperature-programmed reduction (TPR) studies for compositions where x = 0.4, 1, 1.6 and 2 are shown in Fig. 3. The shift in the initial sharp reduction step indicates the increased stabilization of Rh(4d⁶) from 90 °C for pure Rh₂O₃ to 900 °C for Cr_{1.6}Rh_{0.4}O₃. For the compositions CrRhO₃ and Cr_{0.4}Rh_{1.6}O₃, the total weight loss was greater than that calculated for the reduction of Rh(III) to Rh(0). Therefore, it was suspected that some of the chromium(III) was also being reduced. A mechanical mixture of Cr₂O₃ and rhodium to give a [Rh]/[Cr] ratio of 2:1 was reduced in pure hydrogen (60 cm³ min⁻¹) at 1000 °C for 24 h. The product was subjected to X-ray analysis and corresponded to the alloy Rh₂Cr (Fig. 4). From the TPR data shown in Fig. 5, the observed weight loss was found to correspond to that calculated for the complete reduction of Cr₂O₃. This is similar to the observation of Hussein *et al.* [7] for the influence of iron on the reduction of Cr₂O₃.

A series of solid solutions from Rh_2O_3 to $CrRhO_3$ were completely reduced under flowing hydrogen and complete reduction was achieved at



Fig. 3. Relative weight as functions of temperature for members of the system $Cr_{2-x}Rh_x$. O₃ heated at 50 °C h⁻¹ in 60 cm³ min⁻¹ of flowing 15at.%H₂-85at.%Ar.



Fig. 4. X-ray phase analysis of a mixture of rhodium and Cr_2O_3 before and after reduction in flowing H₂ for 24 h at 1000 °C.

1100 °C after 36 h. The results are given in Table 2 and indicate the formation of a pure (ϵ) alloy phase where [Cr] > 0.5. The reduction of Cr₂O₃ to chromium metal, as detected by X-ray analysis, was carried out in a flowing



Fig. 5. Time profiles of temperature and corresponding relative weight for a mixture of rhodium and Cr_2O_3 (Rh/Cr = 2/1) heated in flowing H₂.

TABLE 2

X-ray analysis of $\operatorname{Cr}_{2-x}\operatorname{Rh}_xO_3$ after reduction

Initial composition	Phases of reduction products	Cell parameters	
		a (Å)	с (Å)
Rh ₂ O ₃	cubic (γ -Rh)	3.803	
$Cr_0 ARh_1 O_3$	cubic (γ -Rh) + trace hexagonal (ϵ)	3.780^{a}	
$Cr_{0.48}Rh_{1.52}O_{3}$	hexagonal (ϵ) + trace cubic (γ)	2.685^{b}	4.290
$Cr_0 sRh_1 sO_3$	hexagonal (ϵ)	2.687	4.290
$Cr_{0.67}Rh_{1.33}O_{3}$	hexagonal (ϵ)	2.678	4.269
CrRhO ₃	hexagonal (ϵ)	2.665	4.251

^aCell parameter of cubic rhodium phase.

^bCell parameters of hexagonal phase.

hydrogen atmosphere (60 cm³ min⁻¹) for 36 h at 1200 °C. All the compositions between $CrRhO_3$ and Cr_2O_3 can be completely reduced under these conditions.

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