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Note

THERMAL BEHAVIOUR OF CO-PRECIPITATED MIXTURES OF CHROMIUM(III) AND URANIUM(VI)

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In the chromium–uranium–oxygen system, earlier attempts to prepare chromium(III) triuranate by sealed tube, hydrothermal and high pressure methods have not been successful [1]. The present study describes the effect of heat treatment on co-precipitated mixtures of chromium(III) hydroxide and ammonium diuranate (ADU), in air, vacuum and hydrogen in the temperature range 500–1600°C.

Uranium and chromium were co-precipitated from uranium(VI) and chromium(III) solutions by ammonia. The uranium to chromium ratios chosen were in the range 3 : 1 to 1 :6. The precipitates were washed, dried and heated in air or hydrogen to temperatures ranging from 500 to 1600°C. Thermogravimetric studies of various mixtures and products were carried out using a Mettler thermoanalyser. X-Ray powder diffraction patterns of the products were obtained using Cu-K_α (1.5418 Å) radiation with Siemens X-ray diffractometer. IR Spectra of samples were taken in nujol mull in the region 4,000–650 cm^{-1} using a Perkin-Elmer spectrophotometer. The density was obtained by pyknometry using xylene.

RESULTS AND DISCUSSION

Table 1 summarises the data obtained in the uranium–chromium–oxygen system at different temperatures in reducing and oxidising atmospheres. It was found that $CrUO_4$ decomposes in vacuum or hydrogen above 1000°C to a mixture of Cr_2O_3 and UO_2. The presence of Cr_2O_3 in the reduced mixture could not be directly identified by X-ray powder diffraction, which gave lines for UO_2 only. However, on treatment with dilute HNO_3, uranium oxide dissolved completely and the green residue left was identified by X-ray and chemical methods to be Cr_2O_3. Reduction of 1 : 1 uranium and chromium co-precipitated mixtures in hydrogen at 1600°C gave UO_2 and Cr_2O_3 and no new phase could be identified. This is in contrast to the $CrPuO_3$ phase obtained in the chromium–plutonium–oxygen system by hydrogen reduction [2].

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TABLE 1

Behaviour of co-precipitated uranium and chromium mixtures on various heat treatments

No.	Uranium: chromium	Atmosphere	Temperature (°C)	Products identified by XRD
1	1 : 6	Air	1000	$CrUO_4 + Cr_2O_3$
		Hydrogen	1300	$UO_2 + Cr_2O_3$
2	1 : 3	Air	1000	$CrUO_4 + Cr_2O_3$
		Hydrogen	1600	$UO_2 + Cr_2O_3$
3	1 : 2	Air	1000	$CrUO_4 + Cr_2O_3$
4	1 : 1	Air	1000	$CrUO_4$
		Hydrogen	1600	$UO_2 + Cr_2O_3$
		Vacuum (10^{-4} torr)	1200	$UO_2 + Cr_2O_3$
5	2 : 1	Air	900	$CrUO_4 + U_3O_8$
6	3 : 1	Air	700	CrU_3O_{10-x}
			1000	$CrUO_4 + U_3O_8$
7	$CrUO_4$	Hydrogen	1000	$UO_2 + Cr_2O_3$
		Vacuum (10^{-4} torr)	1200	$UO_2 + Cr_2O_3$

TABLE 2

X-Ray powder diffraction data of chromium triuranate [CrU_3O_{10-x}]

I/I_0	d_{obs}	d_{calc}	hkl
80	4.148	4.144	004
5	3.780	7.785	111
5	3.540	3.542	112
90	3.405	3.393	200
5	3.110	3.148	202
5	3.030	2.979	105
90	2.628	2.625	024
30	2.071	2.072	008
60	1.959	1.959	220
100	1.770	1.771	224
20	1.695	1.697	400
5	1.632	1.635	315
60	1.569	1.570	404
5	1.521	1.527	308
5	1.481	1.481	410
40	1.423	1.423	228
10	1.382	1.381	0.0.12
15	1.313	1.313	408
50	1.281	1.281	2.0.12
20	1.224	1.225	244
40	1.126	1.129	2.2.12
25	1.091	1.091	428

Heating of co-precipitated mixtures of chromium and uranium in the ratio of 1:3 in air at 700°C gave a new product. The X-ray diffraction pattern of this product is given in Table 2. The pattern was indexable on a hexagonal lattice with lattice parameters $a = 7.835$ Å, $C = 16.575$ Å. The density determined by pyknometry was found to be 4.8 g cm^{-3}. The calculated number of molecules is 3 per unit cell. The X-ray pattern is quite similar to those of triuranates of zinc and magnesium [3].

The triuranate was dark in colour. On dissolution in phosphoric acid, it was found to reduce permanganate confirming the presence of a lower valent uranium. On heating in air the compound was found to lose oxygen slowly above 700°C as observed by thermogravimetry. The final product at 1000°C was found to be a mixture of $CrUO_4$ and U_3O_8 from X-ray powder patterns. The value of x in CrU_3O_{10-x} calculated on the basis of weight loss ($CrU_3O_{10-x} \rightarrow CrUO_4 + U_3O_8$) was found to be ~ 0.3. This was confirmed by dissolution of the compound in phosphoric acid and estimating uranium(IV) by titration against dichromate. A similar situation exists in triuranates of cobalt and manganese [1,4] which tend to remain oxygen deficient having compositions $MnU_3O_{9.57}$ and $CoU_3O_{9.46}$.

The chromium triuranate was found to have absorption maxima in IR at 700 cm^{-1} as compared with the peak at 550 cm^{-1} observed for $CrUO_4$. The 700 cm^{-1} peak is characteristic of asymmetric U–O stretching in the uranyl group and it is observed in other triuranates [1].

SUMMARY

In the Cr–U–O system, besides the phases reported earlier, a triuranate CrU_3O_{10-x} ($x \sim 0.3$) could be identified. It is unstable above 700°C and decomposes to a mixture of $CrUO_4$ and U_3O_8. Under reducing atmospheres up to 1600°C, the uranium–chromium–oxygen system gives a mixture of Cr_2O_3 and UO_2. No new phase could be identified. The compound $CrUO_4$ is unstable under reducing conditions and decomposes to a mixture of Cr_2O_3 and UO_2.

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