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Reaction Process between Cobalt Tungstate and Chlorine

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Synopsis. The reaction between $CoWO_4$ and chlorine proceeds above about 585 °C to form WO_2Cl_2 and $CoCl_2$. In the presence of carbon, the reaction proceeds above about 345 °C to form $CoCl_2$ and WO_3, the WO_3 subsequently reacts with chlorine to form WO_2Cl_2 and $WOCl_4$.

The development of the chlorine process for the recovery of tungsten and cobalt from the sludge generated in the electrochemical grinding of WC-Co cemented carbide is important for the future. The sludge consists of 69% $CoWO_4$, 20% Na_2WO_4, 10% WC, and 1% C. In order to obtain chlorides of tungsten and cobalt from the sludge by selective chlorination, it is necessary to clarify the chlorination processes of the constituents of the sludge.

Concerning the reaction between $CoWO_4$ and chlorine, no information is presently available. In this report, the reaction processes between $CoWO_4$ and chlorine, and between $CoWO_4$ and chlorine in the presence of carbon are examined.

The sample of $CoWO_4$ used was prepared by adding an aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution to an aqueous $Na_2WO_4 \cdot 2H_2O$ solution.[1] Both the salts used were guaranteed reagents. The resulting precipitate was washed with water, air-dried, and dehydrated at 400 °C. The sample obtained was confirmed to be $CoWO_4$[2] by X-ray analysis.

The weight change on the heating of 0.3 g of $CoWO_4$ placed in a quartz crucible in a dry chlorine stream was examined using a thermal balance with a quartz helix. The chlorine flow-rate was maintained at 50 ml/min. and a heating rate of 2.5 °C/min was employed. The sensitivity of the quartz helix was about 0.13 mg/0.01 mm. The results are shown in Fig. 1 (curve (a)).

The TG curve shows that the reaction between $CoWO_4$ and chlorine proceeds above about 585 °C.

The product formed by the chlorination of $CoWO_4$ was examined by heating 6 g of $CoWO_4$ in a quartz boat at a specified temperature and at a chlorine flow-rate of 350 ml/min for 1 h. The products obtained were examined by X-ray analysis[3] using Ni-filtered Cu radiation.

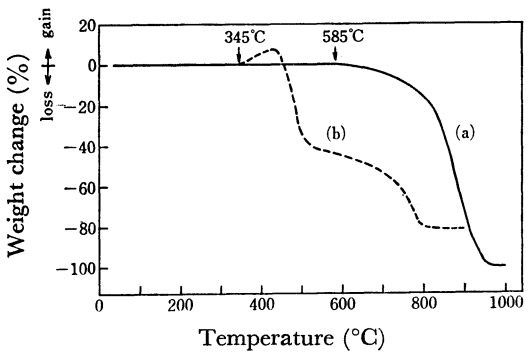

Fig. 1. TG curves of $CoWO_4$ (a), and a mixture of $CoWO_4$ and C(b) in a chlorine stream.

The volatile products obtained by the chlorination of $CoWO_4$ at 600—800 °C were WO_2Cl_2 and $CoCl_2$. No chlorination product was observed in the boat placed in the heating zone. From these experimental results, it was found that the reaction between $CoWO_4$ and chlorine proceeds above about 585 °C to form WO_2Cl_2 and $CoCl_2$.

The chlorination process of metal oxides was affected by the existence of carbon.[4,5] Thus, the effect of the existence of carbon on the reaction between $CoWO_4$ and chlorine was examined. The sample of carbon used was prepared by the pyrolysis of guaranteed reagent grape sugar.

The TG curve of a mixture of $CoWO_4$ and carbon ($CoWO_4$: C=1 : 8 by molar ratio) on heating in a chlorine stream is shown in Fig. 1 (curve (b)).

It is observed that the sample weight increased above about 345 °C, then decreased above about 430 °C, and reached a constant value above about 850 °C. The residue in the crucible, after heating the sample up to 900 °C, was carbon.

The products formed by chlorinating $CoWO_4$ in the presence of carbon at a specified temperature for 0.5 h were examined by X-ray analysis.[2,3,6] The results are shown in Table 1. The weight percentages of the chlorides in the volatile product obtained outside the heating zone were calculated from chemical analysis.[7] The values are shown in parenthesis in Table 1.

Table 1. Chlorination products of a mixture of $CoWO_4$ and C

Temp (°C)	In the boat	Outside the heating zone
380	$CoWO_4$, WO_3, $CoCl_2$	WO_2Cl_2
500	$CoWO_4$, $CoCl_2$	WO_2Cl_2 (>99.9%)
		$WOCl_4$ (<0.1%)
600	$CoWO_4$, $CoCl_2$	$WOCl_2$ (>99.9%)
		$WOCl_4$ (<0.1%)
		$CoCl_2$ (<0.1%)
700	$CoCl_2$	WO_2Cl_2 (95%)
		$WOCl_4$ (2%)
		$CoCl_2$ (3%)
800	$CoCl_2$	WO_2Cl_2 (53%)
		$WOCl_4$ (23%)
		$CoCl_2$ (24%)

At 380 °C, WO_3 and $CoCl_2$ were formed in the boat, and WO_2Cl_2 was obtained outside the heating zone. Above 500 °C, no WO_3 was observed in the boat. Considering the fact that the reaction between WO_3 and chlorine in the presence of carbon begins at about 330 °C and proceeds markedly above about 400 °C to form

volatile WO_2Cl_2 and $WOCl_4$,[4] it appears to be probable that above 500 °C, the WO_3 formed by the chlorination of $CoWO_4$ subsequently reacts with chlorine to form volatile WO_2Cl_2 and $WOCl_4$. Above 600 °C, $CoCl_2$ was obtained outside the heating zone, as well as in the boat. It may be considered that since the vapor pressure of $CoCl_2$ became appreciable above 600 °C,[8] the $CoCl_2$ formed by the chlorination of $CoWO_4$ vaporized and condensed outside the heating zone. Also, the ratio of $WOCl_4$ to WO_2Cl_2 in the volatile product increased with an increase in the reaction temperature. This fact was considered to support the above-mentioned estimate that WO_2Cl_2 and $WOCl_4$ were formed by the chlorination of the WO_3 formed by the chlorination of $CoWO_4$.[4] Furthermore, the weight gain observed at temperatures from 345 to 430 °C in Fig. 1 (curve (b)) was found to be due to the formation of non-volatile WO_3 and $CoCl_2$ by the chlorination of $CoWO_4$.

From these experimental results, the reaction between $CoWO_4$ and chlorine in the presence of carbon proceeds above about 345 °C to form $CoCl_2$ and WO_3, the WO_3 subsequently reacts with chlorine to form WO_2Cl_2 and $WOCl_4$.

In the absence of carbon, the reaction between $CoWO_4$ and chlorine proceeds above about 585 °C to form $CoCl_2$ and WO_2Cl_2, as described above. Considering the fact that the chlorination of WO_3 begins at about 680 °C to form WO_2Cl_2,[4] it appears probable that the WO_2Cl_2 was directly formed by the chlorination of $CoWO_4$ without passing through WO_3.

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