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THE PHASE ANALYSIS OF SYSTEMS CONSISTING OF MOLYBDENUM AND TUNGSTEN CHLORIDES AND OXOCHLORIDES BY THERMOGRAPHIC METHOD

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ABSTRACT

The differential thermal analysis have been established that during heating of equimolar mixtures of dioxodichloride molybdenum with tri-, tetra- and pentachlorides tungsten proceed complicated oxidation-reduction and exchange reactions. There were identificated intermediate and final products of these reactions.

INTRODUCTION

There are known chlorides and chloroxides of molybdenum and tungsten in oxidation degree from 2 and 3 to 6. Although the corresponding chlorides and oxochlorides have identical composition and have a similar structure sometimes, but their physico-chemical properties in most cases are very different. For example, a lower chlorides and chloroxides of tungsten are strong reductive agents in reactions with Cl-derivatives of Mo, reducting they to trichloride. At the same time the lower chlorides and chloroxides of Mo in corresponding processes are not all alike /1, 2/. The higher oxidation degree Cl-derivatives of Mo and W interact by exchange type /3, 4/. In most cases the interaction the lower Cl-derivatives of W with the higher oxidation degree Cl-derivatives of Mo results in the forming of combinations whiches can not separate. Hower by DTA can determine qualitatively proceeding of intermediate processes and the formed in results these processes products.

MEASURING METHODS

DTA studies have been done at 25-550°C interval by heating of equimolar mixtures of correspoding compounds in solder vessels of "Pirex" glass with the photorecording of a heating and cooling curves. The temperature was measured by chromel-alumel thermocouple with accuracy of graduating ± 3°C. The heating and cooling rate was 10°C/min. The standard was Al_2O_3. The total mass of components mixtures did not exceed 1 g.

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RESULTS AND DISCUSSION

The system MoO_2Cl_2 - WCl_3. The oxidation-reduction reaction proceeds at the first stage of interaction in this system:

$$MoO_2Cl_2 + WCl_3 = MoO_2Cl + WCl_4 \quad (1)$$

Then a formed compounds exchange by equation:

$$MoO_2Cl + WCl_4 = MoOCl_3 + WOCl_2 \quad (2)$$

At last upon a melting temperature of $MoOCl_3$ this compound interacts with $WOCl_2$ forming final products by equation:

$$MoOCl_3 + WOCl_2 = MoCl_3 + WO_2Cl_2 \quad (3)$$

Curve 1 in the figure shows that the interaction begins with exoeffect at 142°C. The following stage of interaction by equation (2) also with exoeffect begins at 191°C, in result of that process $MoOCl_3$ forms with a melting temperature of 283°C /5/ and at last stage WO_2Cl_2 forms with incongruent melting temperature of 463°C /6/. The endoeffect at 316°C corresponds to polimorphic transition of $\alpha MoCl_3 \rightarrow \beta MoCl_3$ /7/. In the cooling curve 2 have been marked the phase transitions of crystallization WO_2Cl_2 (432°C) and a therminal $MoOCl_3$ (275°C). In the heating-cooling thermograms 3, 4 of this mixture, standed in 3 hours at 450°C, have been observed only the phase transitions, corresponding to melting and crystallization of WO_2Cl_2 (462, 438°C) and also to polimorphic transition $\alpha MoCl_3 \rightarrow \beta MoCl_3$ at 306°C.

The system MoO_2Cl_2 - WCl_4. The final products of interaction are compounds: $WOCl_4$, WO_2Cl_2, $MoOCl_3$ and $MoCl_3$, whiches form across row of intermediate processes:

$$MoO_2Cl_2 + WCl_4 = MoOCl_4 + WOCl_2 \quad (4)$$

$$MoOCl_4 + WOCl_2 = MoOCl_3 + WOCl_3 \quad (5)$$

$$MoOCl_3 + WOCl_3 = MoCl_4 + WO_2Cl_2 \quad (6)$$

At temperature above 150°C $MoCl_4$ disproportionates by equation /8/:

$$2\ MoCl_4 = MoCl_5 + MoCl_3 \quad (7)$$

Forming by reaction (7) $MoCl_5$ interacts with a product of reaction WO_2Cl_2 by equation /3/:

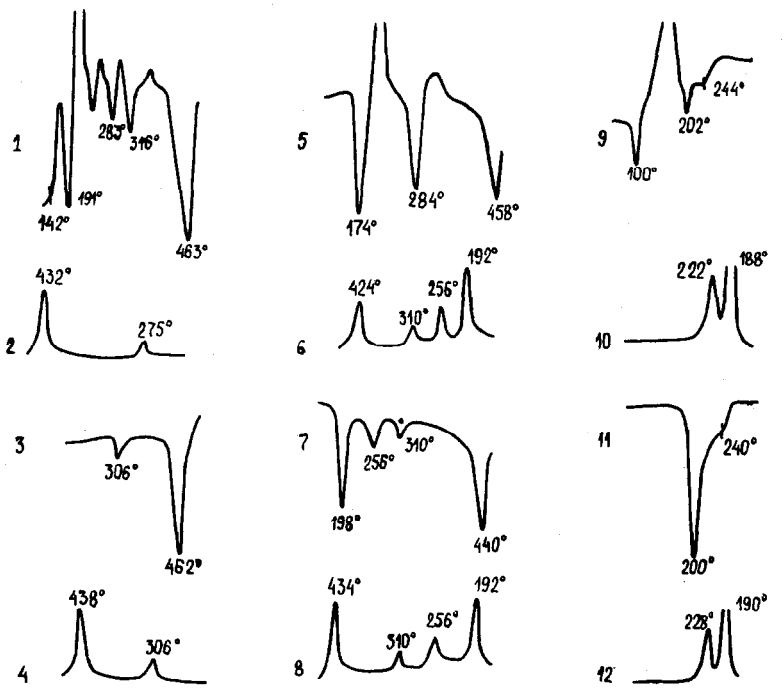
$$MoCl_5 + WO_2Cl_2 = MoOCl_3 + WOCl_4 \quad (8)$$

Hence, the interaction between MoO_2Cl_2 and WCl_4 proceeds by total equation:

$$2\ MoO_2Cl_2 + 2\ WCl_4 = MoOCl_3 + MoCl_3 + WOCl_4 + WO_2Cl_2 \quad (9)$$

In thermogram 5 of first heating of equimolar mixture of MoO_2Cl_2 with WCl_4 by equation (9) have been observed the total exoeffect of interaction at 174°C with forming of $MoOCl_3$, which has endoeffect of melting at 284°C, and WO_2Cl_2 with endoeffect of in-

congruent melting at 458°C. In the cooling thermogram 6 exoeffect at 424°C corresponds to crystallization of WO_2Cl_2, the exoeffect at 310°C - polimorphic transition $\alpha MoCl_3 \rightarrow \beta MoCl_3$, a exoeffects at 256°C and 192°C - crystallization of $MoOCl_3$ and $WOCl_4$ respectively. In the repeated heating and cooling thermograms 7, 8 of this mixture have been observed phase transitions corresponding to melting (crystallization) of $WOCl_4$ at 198 (192)°C, of $MoOCl_3$ at 256°C, of WO_2Cl_2 at 440(434)°C and to polimorphic transition $\alpha MoCl_3 \rightarrow \beta MoCl_3$ at 310°C, it is completely conformed with summary equation (9).



The system MoO_2Cl_2 - WCl_5. At the first stage of interaction proceeds a exchange reaction:

$$MoO_2Cl_2 + WCl_5 = MoOCl_4 + WOCl_3 \quad (10),$$

then - the oxidation-reduction reaction by equation:

$$MoOCl_4 + WOCl_3 = MoOCl_3 + WOCl_4 \quad (11)$$

In the first heating thermogram 9 have been observed the endo-

effect at 100°C corresponding to melting of formed $MoOCl_4$ /9/, it is evidence of interaction of compounds at low temperature. In the moment of melting of $MoOCl_4$ with exoeffect proceeds oxidation-reduction reaction (11), about this have been evidenced effects of melting $WOCl_4$ at 202°C /5/ and $MoOCl_3$ at 244°C. In the cooling thermogram 10 have been observed only 2 exoeffects of crystallization of $MoOCl_3$ (222°C) and $WOCl_4$ (188°C). In the repeated heating and cooling thermograms 11, 12 have been observed a phase transitions corresponding to melting and crystallization $WOCl_4$ (200, 190°C) and $MoOCl_3$ (240, 228°C) by equation (11).

CONCLUSIONS

The oxidation-reduction and exchange reactions proceed in systems MoO_2Cl_2 - WCl_3 (WCl_4, WCl_5), in result of whiches Mo (VI) transits to Mo (V) and Mo (III), at the same time W (III), W (IV), W (V) transite to W (VI). Under these conditions can be determine intermediate reactions and also formation of certain compounds and their groups on temperature phase transitions of chlorides and oxochlorides of molybdenum and tungsten by DTA method.

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