Brief Communications

Thermal decomposition of $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 3H_2O$ in inert and reductive atmospheres*

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The thermal decomposition of $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 3H_2O$ in hydrogen and helium atmospheres was studied. The thermal decomposition of the complex proceeds *via* the same four steps in a temperature range of 50–430 °C, regardless of the atmosphere. The thermolysis processes in inert and reductive atmospheres differ by the nature of the final solid products: a $Co_{0.5}Fe_{0.5}$ alloys is formed in a hydrogen atmosphere, and a mixture of iron and cobalt oxides is observed for an inert atmosphere. The major gaseous decomposition products are H₂O, NH₃, CO₂, and CO.

Key words: cobalt, iron, binary complex salts, oxalate complexes, thermal analysis.

The oxalate complexes as precursors in the preparation of ultradisperse metal powders provide high purity of the thermolysis products.¹ Since binary complex compounds (BCC) are proposed to be used for the preparation, for example, of bimetallic powders,^{2,3} BCC containing trioxalate anion are promising for the production of pure products. In order to study these possibilities, we developed the synthesis and studied the thermolysis of complexes $[CoA_6][M(C_2O_4)_3] \cdot nH_2O$, where $M = Fe^{III}$, Cr^{III} , $A = NH_3$ or $A_2 = en$ (see Ref. 4), in an atmosphere of air, argon, and hydrogen. The composition of the solid and gaseous solid thermolysis products in an oxidative medium are oxides of metals of complexing agents. Multiphase products containing oxides, metals, and carbon are

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formed in an inert atmosphere, whereas metals are formed in a hydrogen atmosphere. However, thermal analysis was possible up to now only in air and argon atmospheres, and experiments at particular temperatures were carried out in hydrogen. In this work, to supplement the earlier obtained data, the thermal analysis of compound $[Co(NH_3)_6]$ - $[Fe(C_2O_4)_3] \cdot 3H_2O$ (1) was carried out for the first time and the scheme of decomposition in a hydrogen atmosphere was constructed. The thermal analysis in a helium atmosphere was carried out for comparison.

Experimental

The synthesis of complex **1** was carried out by mixing aqueous solutions of equivalent amounts of $[Co(NH_3)_6]Cl_3$ and $K_3[Fe(C_2O_4)_3]$ prepared according to described procedures.⁵ The following reagents were used: $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $K_2C_2O_4 \cdot H_2O$, $H_2C_2O_4 \cdot 2H_2O$, and $KHCO_3$ (reagent grade), as well as a concentrated solution of ammonia. The synthesized compound was identified by X-ray phase analysis, chemical analysis, and IR spectroscopy.⁴ For analysis to metals, weighed samples of BCC were dissolved in a mixture of hydrochloric and nitric acids and the metal content in solutions was determined on an AAnalyst-400 spectrometer. Elemental analyses of the samples to the content of C, H, and N were carried out on a Euro EA 3000 instrument. Found (%): Co, 11.8; Fe, 10.3; C, 13.5; H, 4.6; N, 15.6. Calculated (%): Co, 11.0; Fe, 10.4; C, 13.5; H, 4.5; N, 15.7.

Thermogravimetric measurements were carried out in a reductive atmosphere (He + 5.8 vol.% H₂) using a TG 209 F1 Iris thermobalance (NETZSCH). The weight of the sample was 20 mg (Al₂O₃ crucible, flow rate 60 mL min⁻¹, heating rate 10 deg min⁻¹). Simultaneous thermal analysis (STA) was carried out for comparison in inert (He) and reductive (He + 5.8 vol.% H₂) atmospheres, including the simultaneous thermogravimetric (TG) determinations, differential scanning calorimetry (DSC), and mass spectrometric analysis (MS) of the isolated gas on an STA 449 F1 Jupiter instrument (NETZSCH) combined with a QMS 403DAëolos quadrupole mass spectrometer. The weight of the sample was 20 mg (Al₂O₃ crucible, gas flow rate 30 mL min⁻¹, heating rate 10 deg min⁻¹). Experimental data were processed using the Proteusanalysis standard program package.⁶

Point experiments were also carried out. Weighed samples of BCC placed in a quartz boat were heated in a hydrogen flow (15 L h⁻¹, GVCh-12 as a hydrogen source) in a quartz tubular reactor mounted into a SNOL-0.2/1250 tubular furnace. The reactor was taken from the furnace immediately after a required temperature was attained and cooled in the same atmosphere. Solid thermolysis products were analyzed to the content of metal and carbon and subjected to X-ray phase analysis. The JCPDS-ICDD database was used for the identification of the crystalline products.⁷ Gaseous thermolysis products were captured passing the outlet gas flow consequently through Drexel bottles with titrated solutions of HCl and NaOH. The amounts of evolved ammonia and CO_2 were determined in these solutions using titration by two indicators.⁸

Results and Discussion

The thermal analysis curves for the BCC 1 obtained in the atmosphere consisting of helium (94.2 vol.%)and hydrogen (5.8 vol.%) are presented in Fig. 1. The first step of decomposition occurs in the temperature range 30-90 °C, is accompanied by an endotherm, and represents the removal of crystallization water molecules. The mass loss in this step is 10.0%, and the water content in the initial complex is 10.1%. Under the experimental conditions, the anhydrous product was stable up to 160 °C. The second step of mass loss occurs in a temperature range of 160-250 °C and is also accompanied by an endotherm. The third step occurs at 300-330 °C, results in an insignificant weight loss, and is accompanied by an exotherm. The overall mass loss in the second and third steps approximately corresponds to the removal of six ammonia molecules and one oxalate group. According to the X-ray phase analysis data, the product obtained at 300 °C is amorphous to X-rays (Fig. 2, curve 1). The completion of the thermolysis process at 350 °C followed by X-ray phase analysis of the cooled product showed an unidentified crystalline phase (see Fig. 2, curve 2). The similar unit cell parameters of the phases Co_3O_4 (JCPDS-ICDD No. 71-816)⁷ and Fe₃O₄ (JCPDS-ICDD No. 26-1136)⁷ do not allow one to determine unambiguously whether the M_3O_4 phase is a solid solution of cobalt and iron oxides or a mixture of oxides. The fourth step of thermal decomposition occurs in the temperature range 350-440 °C and is accompanied by an endotherm. The total mass loss is 78.6%, and the weight of the residue is 21.4%, which corresponds to stoichiometry of the CoFe residue (the calculated value is 21.45%). The refined parameter of the body-centered unit cell of the obtained phase (a = 2.861 Å) indicates the formation of a solid solution $Co_{0.5}Fe_{0.5}$ based on the crystalline lattice of iron. No su-



Fig. 1. Thermal analysis curves for complex 1 in a gas mixture of helium (94.2 vol.%) and hydrogen (5.8 vol.%): TG (I), DTG (2), and DTA (3).



Fig. 2. Diffraction patterns for the thermolysis of complex 1 in a gas mixture of helium (94.2 vol.%) and hydrogen (5.8 vol.%) at 300 (*I*), 350 (*2*), and 450 °C (*3*). Circles, asterisks, and triangles indicate oxide phases M_3O_4 , unidentified reflections, and a solid solution $Co_{0.5}F_{0.5}$, respectively.

perstructural reflections indicating the formation of intermetallic compound CoFe were revealed probably because of their low intensity. The comparison of the unit cell parameters of iron (a = 2.866 Å) and a solid solution CoFe (a = 2.857 Å, JCPDS-ICDD No. 44-1433) indicates the overestimated value of the unit cell parameter in the obtained solid solution, which is caused, most likely, by the presence of an insignificant amount of dissolved carbon. The thermal decomposition of the complex in the gas mixture consisting of 94.2 vol.% helium and 5.8 vol.% hydrogen is shown in Scheme 1.

The results of simultaneous thermal analysis of BCC 1 in a helium atmosphere accompanied by the mass spectrometric analysis of the gaseous products are presented in Fig. 3. The first, second, and third decomposition steps occur in the same temperature ranges, and the mass loss in these steps is close to the mass loss in a reductive atmosphere. The major gaseous product in the first step is water, and then ammonia and CO2 follow, which are detected in the mass spectra as ionic currents with m/z equal to 18, 17, and 44, respectively. The fourth step of thermolysis in an inert atmosphere occurs in a temperature range of 350-450 °C and is accompanied by an endotherm. The mass loss in this step is smaller than in the reductive atmosphere, since a portion of oxygen from the oxalate ions is consumed to the formation of oxides of central atoms. The major gaseous products in this step are CO and CO₂ with m/z equal to 28 and 44, respectively. The residue represents a mixture of a solid solution $Co_x Fe_{1-x}$ and oxide phase $CoFe_2O_4$ (JCPDS-ICDD, No. 3-864).⁷ As a whole, the course of the decomposition of the complex in a helium atmosphere coincides with that presented in Scheme 1, except for the composition of the residue.

Scheme 1



$$1 + 3 H_2$$

 $CoFe + 6 NH_3 + 4 CO_2 + 2 CO + 5 H_2O$

It should be indicated for comparison that the TG curve for this complex in an argon atmosphere⁴ also consists of four regions and the thermolysis ceases at approximately 410 °C. In an argon atmosphere, the weight of the final residue is 30% of the initial weighed sample and the phase composition of the residue is Co_xFe_{1-x} , Fe_3O_4 , CoFe₂O₄, which coincides with the residue composition in a helium atmosphere.



Fig. 3. Simultaneous thermal analysis curves for complex 1 in a helium atmosphere: TG (1), DTG (2), DSC (3), m/z = 15 (4), m/z = 17 (5), m/z = 18 (6), m/z = 28 (7), and m/z = 44 (8).

According to the results of point experiments in an atmosphere of pure hydrogen at 225 °C, the mass loss was 8.8%, 6.7% ammonia evolved, the composition of the residue was $CoN_{5.6}H_{16.8}FeC_{5.4}O_{11.6}$, and the residue contained 14.2% C. At 400 °C, the weight loss was 43.7%, 80% ammonia evolved, the composition of the residue was $CoN_{1.2}H_{3.6}FeC_4O_8$, and the residue contained 15.3% C. An almost pure solid solution $Co_{0.5}Fe_{0.5}$ is formed at 500 °C. An analysis of the evolved gases shows that 90–95% of the ammonia amount in the complex is evolved in the temperature range from 275 °C to 500 °C, and the amount of found CO_2 at 500 °C is only 64% of the carbon content in the complex. This is consistent with Scheme 1 taking into account that the evolved CO is partially oxidized.

The study of the thermolysis of BCC 1 in hydrogen, helium, and argon atmospheres showed that a powder of a solid solution $Co_{0.5}Fe_{0.5}$ containing no carbon can be obtained in a hydrogen-containing atmosphere. The products with oxygen contents (oxides) are formed in inert atmospheres.

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