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ON THE POSSIBILITY OF FORMATION OF 3*d*-TRANSITION METAL MIXED OXIDES WITH SPINEL STRUCTURE

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ABSTRACT

A thermodynamic approach is used to predict the possibility of formation of 3*d*-transition metal mixed oxides with spinel structure on the basis of data on the thermodynamic stability of the single oxides. The temperature regions of the most probable formation of spinel chromites, ferrites, manganites and cobaltites were outlined. The theoretical considerations are compared with experimental results for copper and nickel cobaltites.

INTRODUCTION

Depending on the reaction conditions, transition metal oxides of different composition may be formed, i.e., with different oxygen contents, which are determined by the thermodynamic stability of the metal–oxygen system. It has been shown previously that the criterion for the thermodynamic stability of transition metal oxides must be the Gibbs free energy as calculated for a formula unit MO_x, i.e., related to one metal ion and to the oxygen anions corresponding to it [1]. In this manner it is possible to take into account the change in the energy of the system, including the stabilization of the metal ion in definite valence and coordination states. The determination of the thermodynamic possibility of formation of mixed oxides, depending on reaction conditions, principally offers no difficulties, it is just necessary to use initial data for the enthalpies and entropies of formation of the corresponding mixed oxide. However, in the case of spinels appropriate data can be found in the literature for only some of them, mostly for spinels containing iron, chromium and aluminium, in rather narrow ranges of temperature and oxygen pressure. The purpose of the present paper is to consider the experimental conditions for the preparation of mixed oxides containing two transition metal ions using data on the thermodynamic probabilities of the single oxides. The considerations concern spinel systems, although they can also be related to other types of binary metal oxides.

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GENERAL CONSIDERATION

The thermodynamic probability of formation of a mixture of two single oxides

$$A + 2B + (x/2 + y)O_2 = AO_x + 2BO_y \tag{1}$$

or a mixed spinel oxide

$$A + 2B + 2O_2 = AB_2O_4 \tag{2}$$

under given reaction conditions (temperature and oxygen pressure) is determined by the change in the corresponding Gibbs free energies: $\Delta G_T(1)$ and $\Delta G_T(2)$. (A and B are metals, x and y can take different values depending on the reaction conditions.) We assume that both reactions (1) and (2) are possible from a thermodynamic point of view, i.e., $\Delta G_T(1)$, $\Delta G_T(2) < 0$. The reaction of spinel formation will occur predominantly if

$$\Delta G_T(2) < \Delta G_T(1) \tag{i}$$

In the case when $\Delta G_T(1) < \Delta G_T(2)$, a mixture of single oxides is formed, AO_x and BO_y being the thermodynamically most stable oxides for the corresponding metal–oxygen system under the reaction conditions.

The formation of a mixed oxide with spinel structure can be presented as a sum of two consecutive processes

$$A + 2B + 2O_2 = AO + B_2O_3 \quad [\Delta G_T(3)] \tag{3}$$

$$AO + B_2O_3 = AB_2O_4 \quad [\Delta G_T(4)] \tag{4}$$

and

$$\Delta G_T(2) = \Delta G_T(3) + \Delta G_T(4) \tag{ii}$$

Using eqns, (i) and (ii) one obtains, for the reaction of spinel formation

$$\Delta G_T(4) < \Delta G_T(1) - \Delta G_T(3) \tag{5}$$

A minimal free energy of spinel formation, $\Delta G_T(4)$, from simple oxides will be obtained if the most favourable processes for the single metal–oxygen systems, A–O and B–O, considered separately, are the formation of the monoxide AO and of the sesquioxide B_2O_3 ($BO_{1.5}$), i.e., $\Delta G_T(1) = \Delta G_T(3)$.

Thus, our criterion takes the form: mixed spinel oxides may be obtained with greatest probability in those temperature and oxygen pressure intervals in which both AO and B_2O_3 are the thermodynamically stable oxides.

RESULTS AND DISCUSSION

According to the previous section, the most probable formation of spinel chromites (ACr_2O_4), ferrites (AFe_2O_4), manganites (AMn_2O_4) and cobaltites (ACo_2O_4) should occur in the temperature intervals in which both B_2O_3

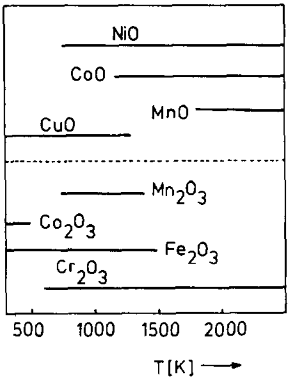

Fig. 1. Temperature regions of thermodynamic stability of B_2O_3 (B = Fe, Cr, Mn, Co) and AO (A = Ni, Co, Mn, Cu) at an oxygen pressure of 0.21 atm.

(B = Cr, Fe, Mn, Co) and AO are the thermodynamically most stable single oxide phases. Figure 1 illustrates the temperature intervals where B_2O_3 (B = Fe, Cr, Mn, Co) and AO (A = Ni, Co, Mn, Cu) are the thermodynamically most stable phases at an oxygen pressure of 0.21 atm [1]. However, we must take into account that the systems Co–O, Mn–O and Fe–O may form oxides of the type M_3O_4, which we can formally consider as a combination of a divalent and a tetravalent oxide. In this case we can present the reaction of spinel formation as the consequence of the following process

$$1/3A_3O_4 + 2/3B_3O_4 = AB_2O_4 \qquad (6)$$

i.e., the formation of spinel oxides is most probable at temperatures at which the thermodynamic stabilities of A_3O_4 and B_3O_4 overlap.

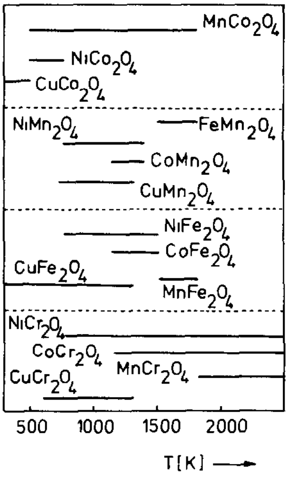

Fig. 2. Temperature regions of greatest thermodynamic probability of formation of spinel chromites, ferrites, manganites and cobaltites at an oxygen pressure of 0.21 atm.

Figure 2 illustrates the temperature regions with the greatest thermodynamic probability of formation of spinels containing iron, chromium, manganese and cobalt according to reaction schemes (4) and (6). It is evident that the formation of cobaltites is possible only at low temperatures while the formation of chromites, manganites and ferrites should be expected at much higher temperatures.

In the framework of our considerations the series of unsuccessful experiments on the synthesis of spinel copper cobaltite at normal pressure [2–4] could be explained by a very high reaction temperature. The formation of copper cobaltite, as can be seen from Fig. 2, is a thermodynamically favourable process up to a temperature of 500 K (the temperature of thermodynamic stability of both CuO and Co_2O_3). We realized the synthesis of a mixed copper–cobalt spinel at low temperatures by simultaneous decomposition of an initial nitrate mixture. The decomposition process, as monitored by thermogravimetric and in situ magnetic measurements, is completed at 490 K [5], the reaction product being a nearly stoichiometric copper–cobalt spinel [6].

The thermodynamic treatment of the system Ni–Co–O does not reveal temperature intervals in which the single oxide phases NiO (AO) and Co_2O_3 (B_2O_3) are simultaneously stable. In such a case the range of spinel formation would be confined between the highest temperature of Co_2O_3 existence and the lowest temperature of NiO existence (see Fig. 1). Indeed, nickel cobaltite is formed at 520 K as shown by thermogravimetric and magnetic investigations [7]. At a temperature above 750 K it becomes thermodynamically unstable and decomposes into Co_3O_4 and NiO, which agrees well with experimental results [8,9]. Similarly, the formation of $MnCo_2O_4$ is to be expected between 500 and 1800 K, the upper limit of Co_2O_3 and the lower limit of MnO stabilities, respectively.

Hence, we may point out that the thermodynamic approach, when used to predict the possibility of formation of 3*d*-transition metal mixed oxides with spinel structures on the basis of data on the thermodynamic stability of the single oxides, agrees well with experimental results and enables us to predict the reaction conditions for the synthesis of new spinel systems.

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