Thermochimica Acta, 92 (1985) 197-199
Elsevier Science Publishers B.V., Amsterdam

KINETIC ASPECTS OF THE Mn-Zn-Fe MIXED OXIDE FORMATION BY THERMAL DECOMPOSITION OF POLYNUCLEAR COORDINATION COMPOUNDS

Teodor Coseac*, Eugen Segal, Maria Brezeanu,
Polytechnical Institute of Bucarest, Bucarest, Romania

INTRODUCTION

Following our research (1) concerning thermal stability of polynuclear coordination compounds (pcc), this paper deals with the thermal decomposition of $Fe_2Mn_{0.5}Zn_{0.5}(C_2O_4)_4$, as well as with the crystallization of the cubic ferrite from the mixture of oxides generated through thermolysis of the parent pcc. The results of an attempt to limit the thermal stability temperature field of the cubic ferrite, considering the various oxidation states of manganese are equally discussed.

EXPERIMENTAL

Samples of powdered Fe-Mn-Zn oxalate have been isothermally heated between 200°C and 950°C. The X-ray diffraction analysis showed no crystalline structure between 200°C and 550°C and a cubic ferrite structure between 550°C and 700°C. The diffractograms of the samples heated over 700°C exhibit the cubic ferrite lines as well as the Fe_2O_3 lines. The (311) line of the cubic ferrite at temperatures near 500°C is verry broad and diffuse.

The derivatograms of the Fe-Mn-Zn oxalate have been recorded at the following heating rates: 2.5 K/min, 5 K/min and 10 K/min. According to the TG curves, the decomposition occurs in the following steps:

$$Fe_2Mn_{0.5}Zn_{0.5}(C_2O_4)_4(s) \xrightarrow{190°C} Fe_2Mn_{0.5}Zn_{0.5}(CO_3)_4(s)+CO(g) \quad (I)$$

$$Fe_2Mn_{0.5}Zn_{0.5}(CO_3)_4(s) \xrightarrow{235°C} Fe_2Mn_{0.5}Zn_{0.5}(CO_3)_3O(s)+CO_2(g) \quad (II)$$

$$Fe_2Mn_{0.5}Zn_{0.5}(CO_3)_3O(s) \xrightarrow{270°C} Fe_2Mn_{0.5}Zn_{0.5}O_4(s)+3CO_2(g) \quad (III)$$

The temperatures writen above the arrows correspond to the maxima of the decomposition rate.

Proceedings of ICTA 85, Bratislava

The kinetic parameters values of the reactions I, II and III, obtained according to the Coats-Redfern method (2) are given in table 1.

Table 1. Values of the kinetic parameters for the reactions I, II and III.

Reaction	I			II			III		
Kinetic parameters → / Heating rate ↓	E Kcal/mole	A (s^{-1})	n	E Kcal/mole	A (s^{-1})	n	E Kcal/mole	A (s^{-1})	n
2,5 K/min	36	$4.8.1o^{14}$	1	52	$4.2\ 1o^{19}$	1	53	$1\ 1o^{19}$	1
5 K/min	36,5	$3.8\ 1o^{14}$	1	57	$5.9\ 1o^{21}$	1	53	$9.7\ 1o^{18}$	1
1o K/min	34	$4.8\ 1o^{13}$	1	52	$3.6\ 1o^{19}$	1	49	$1.2\ 1o^{17}$	1

where: E = activation energy

A = preexponential factor

n = order of reaction

The quite satisfactory agreement between the values of the kinetic parameters for the three different heating rates shows no heat transfer limitations. The value n=1 actually means a particular case of the J-M-A-Y-K (3) equation, corresponding to instantaneous nucleation followed by one dimensional growth of the nuclei.

The DTA exothermic peak at 47o°C was assigned to the crystallization of the mixed Fe-Mn-Zn oxide. Using Sestaks(4) method the following values of the nonisothermal kinetic parameters have been obtained: E=68 Kcal/mole and m=1.13 (m being a parameter related to the mechanism of crystallization).

CONCLUSIONS

The stability temperatures field of the Fe-Mn-Zn mixed oxide is 55o°C-7oo°C. The crystallization of the Fe-Mn-Zn mixed oxide seems to be diffusion controlled, the nuclei being already present in the powder.

REFERENCES

1 Maria Brezeanu, Eugenia Tatu, Silvia Bocai, Oana Brezeanu, E.Segal, Luminita Patron, Thermochim.Acta, 78 (1984), 445
2 A.W.Coats, J.P.Redfern, Nature, 201 (1964),68
3 J.Sestak, Thermophysical properties of solids, Academia Prague, 1984, p.191
4 J.Sestak, Physics and Chemistry of Glasses, 15 (1974),177