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INVESTIGATIONS OF THE THERMAL TRANSFORMATIONS OF PRECIPITATED MIXED TRANSITION METAL HYDROXIDES

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The thermal behaviour and phase composition of mixed oxides obtained by oxidation of iron(II) hydroxide in the presence of Mg, Zn, Co, Cu and Ni, is investigated by thermogravimetry, and conventional and high-temperature X-ray diffractometry.

Keywords: mixed oxides, thermal transition, TG, X-ray

Introduction

Methods based on thermal decomposition of hydrated oxide (hydroxide) mixtures as precursors often enable the spinel ferrite phase to be obtained at relatively low temperatures [1–3]. It is well known that oxidation by air of freshly precipitated iron(II) hydroxide at *pH* 5 to 10 leads to magnetite formation. This synthetic magnetite has the inverse spinel structure Fe(III)[Fe(II),Fe(III)]O_4. The aim of this work was to investigate the possibility of obtaining other spinel phases (ferrites) of some divalent metals by oxidation of iron(II) hydroxide in the presence of these metal cations in solution. The resulting mixed oxides of Mg, Zn, Co, Cu and Ni have been investigated by thermogravimetry and X-ray powder diffractometry. Some samples were investigated by high-temperature X-ray diffraction analysis.

Experimental

The mixed oxides were prepared by oxidation in air of freshly precipitated iron(II) hydroxide at $pH = 8$ and 80°C. The iron hydroxide was precipitated by ammonia from a solution stoichiometric to the spinel composition containing

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iron(II) (0.1 *M*) and the second divalent metal (0.05 *M*) sulphates. The materials were prepared in a U-tube reactor and circulation of the suspension was forced by an air stream. The *pH* during reaction was corrected by injecting small amounts of ammonia solution into the air stream. The extent of iron oxidation reaction was controlled by sampling the suspension and determining Fe(II) concentration.

The precipitated mixed oxides were filtered under vacuum, washed and then dried at 80°C. Part of each prepared sample was calcined at 950°C for 1 h in air. The calcined samples were finally milled in a vibratory ball mill.

Instrumental

To characterize the precipitates and calcined powders the following techniques were used.

1. Elemental chemical analysis: main components were determined by XRF spectrometry (Philips PW 1480 X-ray spectrometer); trace elements were determined by ICP spectrophotometry (Philips PV 8060 spectrometer).

2. Thermal transformations of prepared materials were investigated by thermogravimetric analysis (TG/DTG/DTA) under the following conditions: static air atmosphere, heating rate 10 deg·min^{-1}, sample weight 600 mg, reference sample Al_2O_3. Measurements were carried out using a MOM 1500 thermal analyzer.

3. Phase composition and phase transformations: X-ray diffractometry was performed using CuKα radiation (Philips PW 1710 diffractometer). Phases were identified from the strongest diffraction peaks on the patterns using the Philips

Table 1 Characteristic of precipitated mixed oxides

No	*M*(II)	*M(II)/Fe(III)* ratio	Weight losses to 500°C	Phase composition	
				Pecipitated sample	Calcined sample
1	Fe	0.4985	3.8	magnetite	hematite
2	Mg	0.4495	19.5	$MgFe_2O_4$ $(FeFe_2O_4)$	$MgFe_2O_4$ (Fe_2O_3)
3	Zn	0.2055	2.7	$FeFe_2O_4$ $(ZnFe_2O_4)$	Fe_2O_3,ZnO $(ZnFe_2O_4)$
4	Co	0.4766	7.3	$CoFe_2O_4$ $(FeFe_2O_4)$	$CoFe_2O_4$ (Fe_2O_3)
5	Cu	0.1551	–	$FeFe_2O_4$ $(CuFe_2O_4)$	$CuFe_2O_4$, Fe_2O_3,CuO
6	Ni	0.3563	16.5	$NiFe_2O_4$ $(FeFe_2O_4)$	$NiFe_2O_4$ (Fe_2O_3)

Total Access Diffraction Database (extended JCPDS system). Some samples were investigated by high-temperature X-ray diffraction analysis (high-temperature attachment Model HTK 10 for Philips PW 1710 diffractometer).

Results and discussion

Characteristics of precipitated and calcined hydroxide and oxide mixtures are presented in Table 1. It is evident that under the experimental conditions used, coprecipitation of magnesium, cobalt and nickel hydroxides in the M(II) to iron ratio near to the spinel ferrite MFe_2O_4 composition occurs. X-ray patterns of the

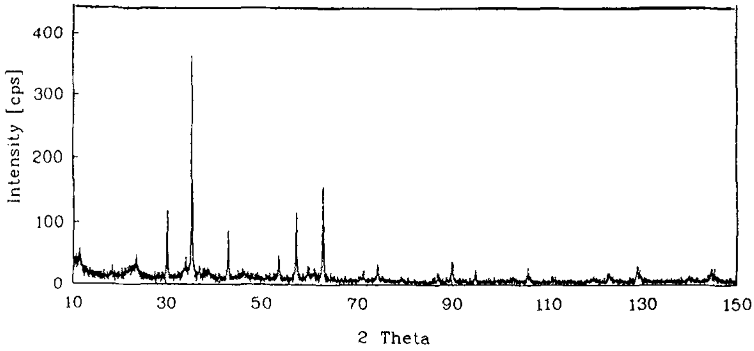

Fig. 1 Diffraction pattern of magnesium and iron precipitated oxide mixture

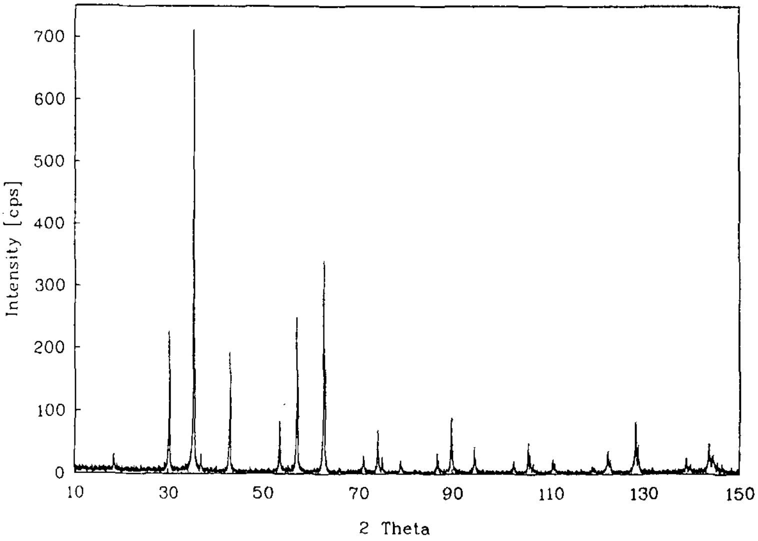

Fig. 2 Diffraction pattern of magnesium and iron calcined oxide mixture

precipitates reveal crystalline phases of major spinel ferrite and accompanying magnetite. X-ray patterns of precipitated and calcined materials are presented in Figs 1 to 4. Coprecipitation of zinc and copper occurs at a lower degree and magnetite is obtained as the dominant phase. During heating, magnesium-iron and nickel-iron oxides show three-step weight losses on TG/DTG curves. At temperatures up to 500°C the experimental weight loss is about 19.5% for magnesium-iron oxides and 16.5% for the nickel-iron mixture. Chemical analysis and thermal analysis results indicate that the prepared substances consist of a hydroxide (hydrated oxide) mixture. Iron(II)-iron(III) and cobalt-iron oxides are different and for these samples weight losses due to dehydration were only a few percent (3.8% for magnetite and 7.8% for cobalt-iron sample).

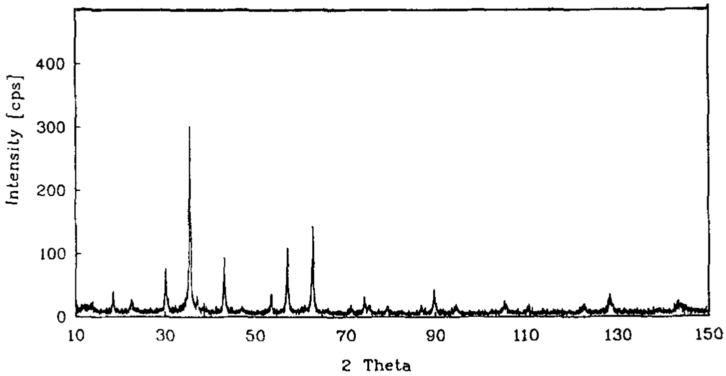

Fig. 3 Diffraction pattern of cobalt and iron precipitated oxide mixture

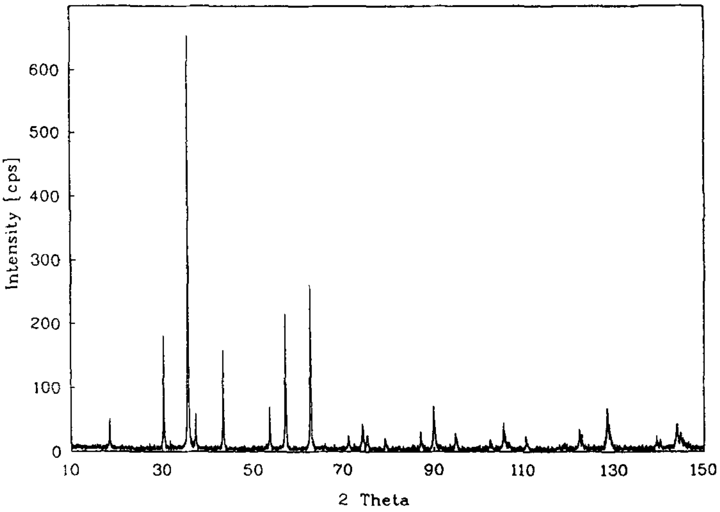

Fig. 4 Diffraction pattern of cobalt and iron calcined oxide mixture

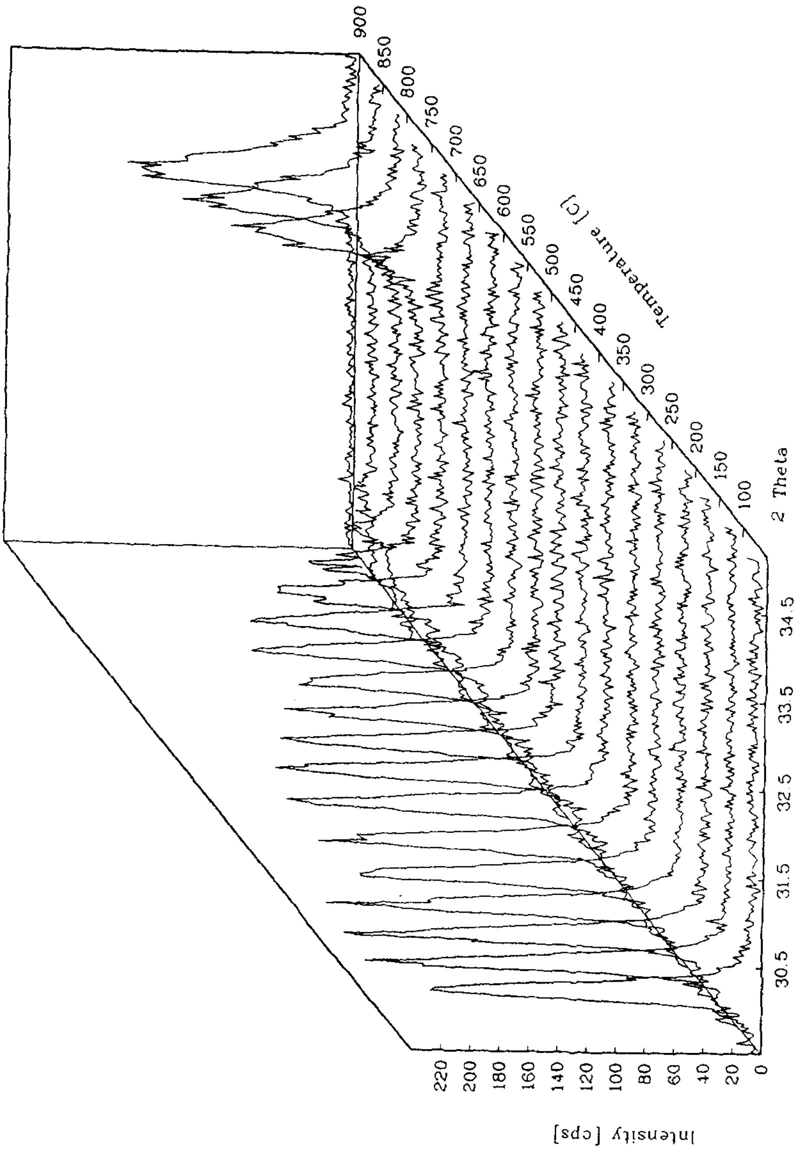

Fig. 5 High-temperature diffraction pattern of synthetic magnetite

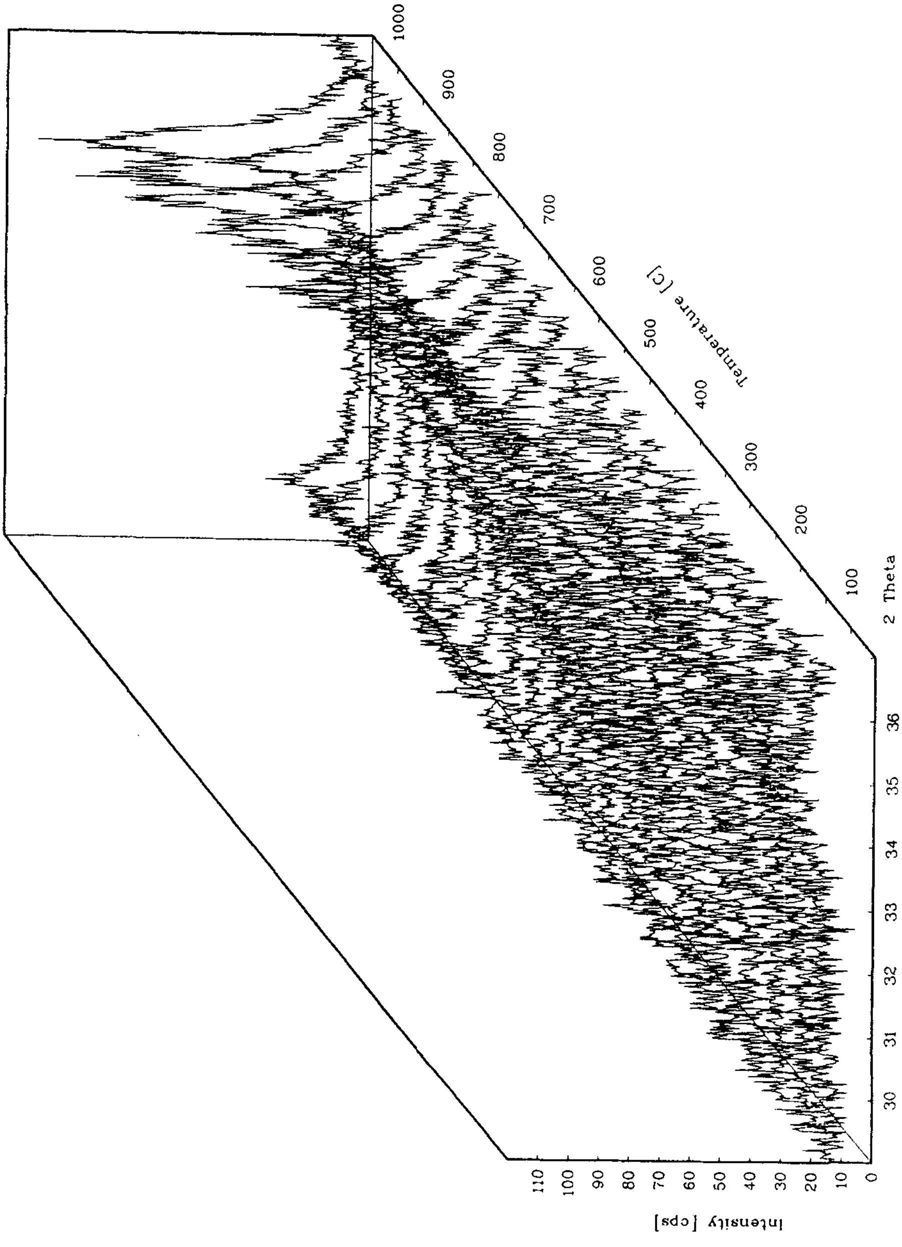

Fig. 6 High-temperature diffraction pattern of magnesium-iron oxide mixture

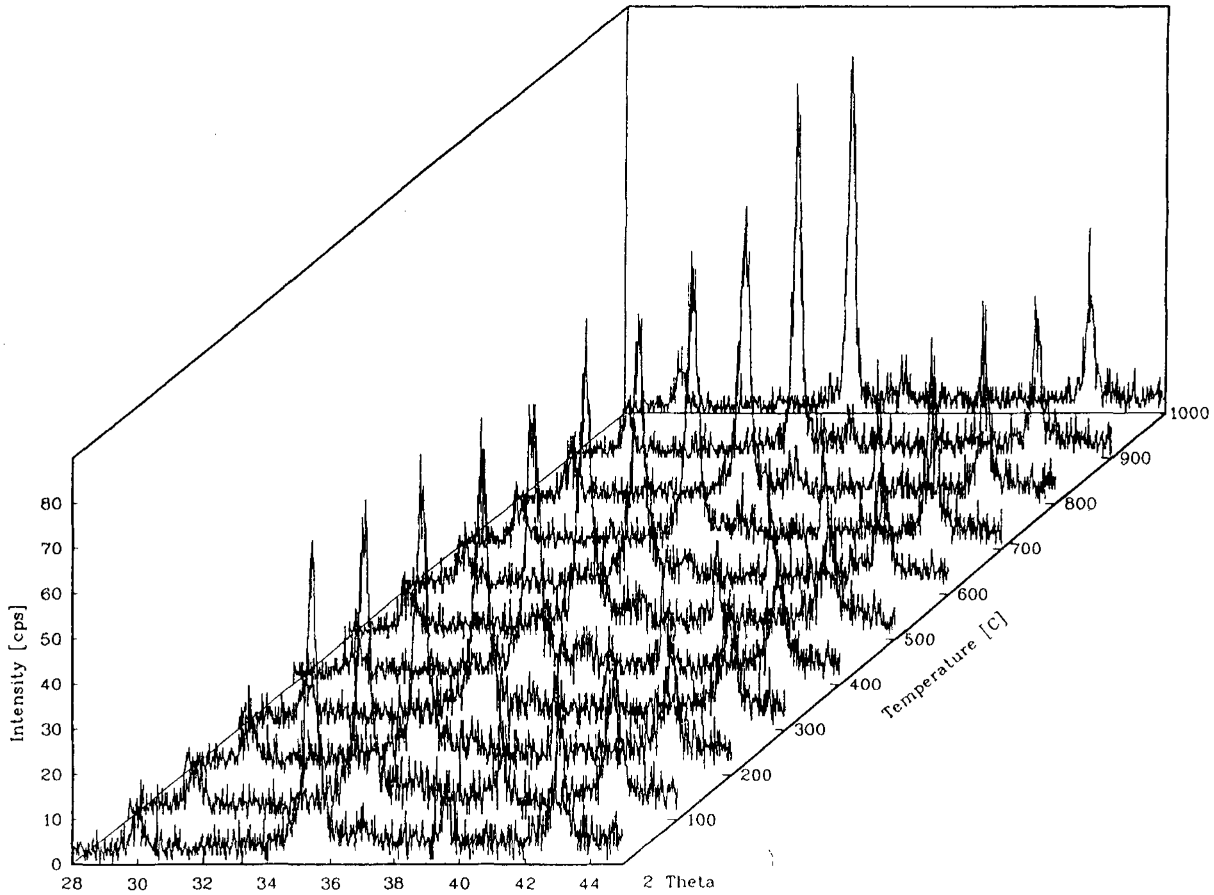

Fig. 7 High-temperature diffraction pattern of cobalt-iron oxide mixture

The investigated divalent cations can be divided into two groups. The first group consists of Mg, Co, Ni and Fe. These cations, prefering the octahedral sites in the spinel crystal structure form the inverse spinel $Fe(II)_{1-x}[Me(II)_xFe(III)_{1+x}]O_4$ or alternatively a continuous series of solid-solutions of magnetite and this spinel. Experimental results show that these cations can be precipitated almost quantitatively by the method described, forming a stable microcrystalline inverse spinel phase during heating and calcination with no evidence of magnetite. This is illustrated by the high-temperature X-ray patterns of magnesium-iron and cobalt-iron precipitated oxide shown in Figs 5 and 6, respectively.

The pure magnetite phase is thermally unstable and rapidly transforms into maghemite (below 200°C), which exists as an intermediate phase to about 700°C and then transforms to hematite (see high-temperature diagram in Fig. 7). Magnetite has the characteristic spinel cubic structure (space group $Fd3m$), maghemite the tetragonal structure (P), and hematite the rombohedral structure (R-$3c$). Due to the different crystallographic structures of these oxides the existence of magnetite in the sample can be easily detected by searching the intermediate diffraction patterns [4].

The second group consisting of Zn and Cu is not precipitated quantitatively under the conditions described. Zinc, prefering tetrahedral coordination, forms a probable spinel-structure phase, $Fe(III)_{1-x-y}Zn_y[Fe(II)_xFe(III)_{1+x+y}]O_4$, and coprecipitates to a lower degree. Although copper forms an inverse spinel, this phase is cubic only at high temperature and has tetragonal symmetry at room temperature (c:a = 1.06). For these cations, the products obtained contain mainly a magnetite phase with smaller amounts of a microcrystalline spinel phase, are amorphous and decompose at higher temperatures and form a separate oxide mixture. Above 800°C a spinel phase is observed.

The method described enables precursors for ferrite production with divalent cations to be obtained which form inverse spinel structures stable at room temperature.

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Zusammenfassung — Mittels TG sowie mit herkömmlicher und Hochtemperatur-Röntgendiffraktion wurde das thermische Verhalten und die Phasenzusammensetzung von Mischoxiden untersucht, die bei der Oxidation von Eisen(II)-hydroxid in Gegenwart von Mg, Zn, Co, Cu und Ni entstanden waren.