

# KINETICS OF LOW TEMPERATURE HYDROGEN REDUCTION OF THE METASTABLE SPINELS Magnetite and solid solutions with Mn, Co, Ni and Cu

D. N. Drakshayani and R. M. Mallya

Department of Metallurgy, Indian Institute of Science, Bangalore-560012, India

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## Abstract

The kinetics of reduction at relatively low temperatures with hydrogen of pure and doped metastable non-stoichiometric magnetite with 1 at% Mn, Co, Ni and Cu and also with 5 at% Ni and Cu have been investigated by using isothermal thermogravimetry in the temperature range 300–400°C. With increase in the concentration of the dopant (5 at% Ni and Cu), the reactivity increases. The activation energies for pure magnetite varies from 7 to 9 kcal/mole with the preparation temperature of precursors  $\text{Fe}_2\text{O}_3$  (250–400°C), being the lowest for those prepared at the lowest temperatures. The corresponding activation energies for the reduction of doped samples  $(\text{Fe, M})_{3-2}\text{O}_4$ , it depends, apart from their porosity and surface areas, on the nature of the solute atom, amount of disorder, whether it occupies the tetrahedral (A) or octahedral (B) sites in the non-stoichiometric spinel and possibly on hydrogen 'Spill over' effects.

**Keywords:** kinetics, magnetite, metastable spinels, solid solutions, TG

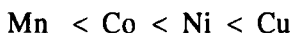
## Introduction

The hydrogen reduction of bulk metal oxides have attracted considerable attention in the past since such reductions form the basis of some metallurgical processes. If conducted at lower temperatures, it may be of use in preparation of some metallic and oxide catalysts. In addition, such reductions play a role in the operation of metal oxide gas sensors [1]. The kinetics of reduction of iron oxides are affected by the methods of preparation and presence of various additives in the precursor. The influence of preparation history of  $\text{Fe}_2\text{O}_3$  on its reactivity for hydrogen reduction was studied by Shimokawabe *et al.* [2]. The oxides prepared at lower temperature had higher reactivity. They have attributed the accelerating effect of the dopants  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Li}^+$  to the formation of solid solutions or of ferrites.

It was shown earlier by other workers that at higher temperatures [3, 4], the gas-phase reductions of bulk oxides usually proceed in three stages:

- i) metallic nuclei are generated,
- ii) the nuclei then grow until coalition occurs to produce metallic shells encasing cores of unreached oxide,
- iii) the reaction then proceeds at the metal/metal oxide interfaces until all the oxide in the cores is reduced.

An initial study on the low temperature reduction between 250–500°C by hydrogen of pure Fe<sub>2</sub>O<sub>3</sub> and doped (Fe, M)<sub>2</sub>O<sub>3</sub> (*M* = 1 at% Mn, Co, Ni and Cu) was investigated earlier [5] using dynamic TG in hydrogen. It was found that the reactivity of Fe<sub>2</sub>O<sub>3</sub> and the spinels derived from it in hydrogen increases with the decrease in preparation temperature of Fe<sub>2</sub>O<sub>3</sub> from 400 to 250°C. In case of 1 at% doped samples the reactivity is in the following order:



with Mn retarding the reaction, Co slightly affecting the reaction and Ni and Cu accelerating the reaction for the reduction of spinel solid solutions. The spinels containing 5 at% Ni and Cu were reduced at about 70°C lower temperature than the pure oxide prepared at the same temperature. The reduction of mixed oxides at low temperature (< 500°C) obtained from homogeneous precursors gave nanosized alloy particles [6].

In order to understand the effect of preparation conditions and dopants detailed isothermal studies were carried out on the pure and doped metastable non-stoichiometric magnetite (obtained from pure and doped Fe<sub>2</sub>O<sub>3</sub> respectively) by hydrogen reduction in the temperature range of 300–400°C.

## Experimental

Pure iron oxide and doped iron oxide precursors were prepared by thermal decomposition of ferric nitrate and of mixture of nitrates of iron and dopants in air. They were characterized by X-ray powder diffraction (XRD) and Mossbauer spectroscopic (MS) studies which indicated them to be pure oxide and its solid solutions with dopants as reported earlier [5]. The lattice parameters and crystallite sizes of Fe<sub>2</sub>O<sub>3</sub> and its solid solutions varies between 13.7–14.06 Å and 130–250 Å respectively. These samples were subjected to isothermal thermogravimetric (TG) studies in a hydrogen flow of 2.7 l/h at various temperatures in the range of 300 to 400°C. Isothermal boat experiments were also carried out to prepare larger quantities of the material by isothermal reduction for predetermined time intervals. Both methods are described in detail in our earlier work [7, 8].

The reduced samples obtained from boat experiments were characterized by XRD and MS. XRD studies were done on a Philips powder diffractometer using

CoK $\alpha$  radiation ( $\lambda = 1.79021 \text{ \AA}$ ). A scanning rate of  $2^\circ/\text{min}$  was used. The broadening of the XRD peaks were used to calculate the apparent crystallite size of the spinels using the Scherrer formula. For the purpose of these calculations, it is assumed that the broadening of the diffraction peaks is only due to the variation in crystallite size, although additional contribution to line broadening is possible. The lattice parameters were calculated by least square methods and the error is  $\pm 0.002 \text{ \AA}$ . Mossbauer studies were carried out in the constant acceleration mode using  $^{57}\text{Co}$  source in rhodium matrix and the details are given elsewhere [9].

## Results

The isothermal TG of pure oxides and its solid solutions show two stages as the dynamic TG experiments reported earlier [5]. The results are given in Table 1. The first stage is the formation of pure magnetite (spinel) or its solid solutions from their precursors and the second stage is the subsequent reduction of these compounds to the metallic state. The  $t_{0.5}$  is the time required for 50% (at  $\alpha = 0.5$ ) and  $t_{0.75}$  (at  $\alpha = 0.75$ ) is the time for 75% of the reduction of magnetite or its solid solution to be achieved at  $340^\circ\text{C}$ .

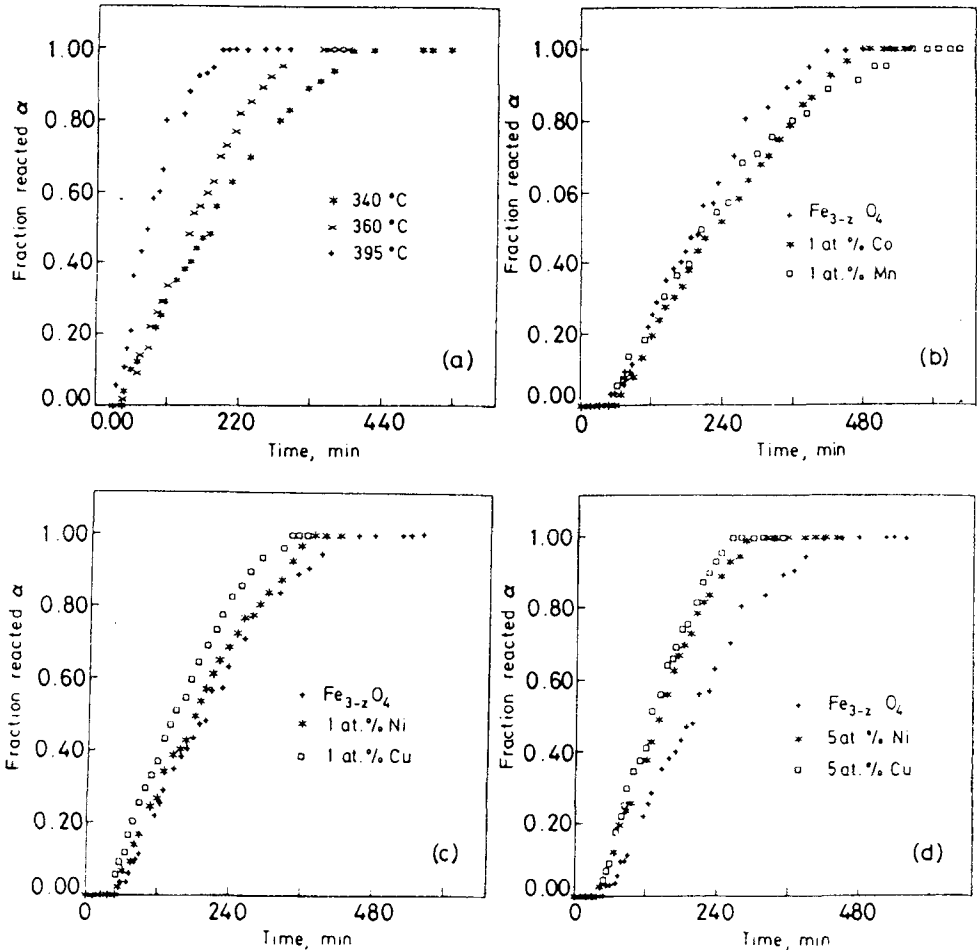
**Table 1** Isothermal reduction (TG) of pure magnetite and doped spinels at  $340^\circ\text{C}$  in hydrogen atmosphere

Sample No.	Starting sample precursor	Spinel	Value of $t$ / min	
			at $\alpha = 0.5$	at $\alpha = 0.75$
I	Fe <sub>2</sub> O <sub>3</sub> prepared at			
	250°C	Fe <sub>3-z</sub> O <sub>4</sub>	152	220
	300°C	Fe <sub>3-z</sub> O <sub>4</sub>	170	252
	400°C	Fe <sub>3-z</sub> O <sub>4</sub>	209	310
II	Doped Fe <sub>2</sub> O <sub>3</sub> samples prepared at $300^\circ\text{C}$			
	1 atom % Mn	(Fe, Mn) <sub>3-z</sub> O <sub>4</sub>	200	316
	1 atom % Co	(Fe, Co) <sub>3-z</sub> O <sub>4</sub>	215	324
	1 atom % Ni	(Fe, Ni) <sub>3-z</sub> O <sub>4</sub>	168	244
	1 atom % Cu	(Fe, Cu) <sub>3-z</sub> O <sub>4</sub>	142	210
	5 atom % Ni	(Fe, Ni) <sub>3-z</sub> O <sub>4</sub>	134	188
	5 atom % Cu	(Fe, Cu) <sub>3-z</sub> O <sub>4</sub>	130	180

The fraction reacted,  $\alpha$ , from isothermal TG was plotted vs. time  $t$ . The value of  $\alpha$  was obtained by normalizing the measured weight at the end of the

first stage as 100% and corresponding to that weight,  $\alpha$  was taken as zero. The time  $t$  was calculated by taking  $t = 0$  when  $\alpha = 0$ . The  $\alpha$  vs.  $t$  curves are given in Fig. 1. Various equations such as Jander equation for diffusion controlled mechanism:

$$(1 - (1 - \alpha)^{1/3})^2 = kt$$



**Fig. 1** Plots of fraction reacted  $\alpha$  vs. time  $t$ , derived from isothermal reduction in hydrogen at various temperatures; (a) Pure magnetite  $\text{Fe}_{3-z}\text{O}_4$  obtained from  $\text{Fe}_2\text{O}_3$  prepared at  $300^\circ\text{C}$  and reduced at different temperatures; (b) Pure magnetite and spinel solid solutions with 1 at% Mn and Co reduced at  $340^\circ\text{C}$ ; (c) Pure magnetite and spinel solid solutions with 1 at% Ni and Co reduced at  $340^\circ\text{C}$ ; (d) Pure magnetite and spinel solid solutions  $(\text{Fe}, \text{M})_{3-z}\text{O}_4$  with 5 at% Ni and Cu reduced at  $340^\circ\text{C}$

Avrami-Erofeev equation for nucleation and growth:

$$-\ln(1 - \alpha)^{1/n} = kt$$

three dimensional phase boundary mechanism equations:

$$1 - (1 - \alpha)^{1/2} = kt \quad (\text{contracting area}),$$

$$1 - (1 - \alpha)^{1/3} = kt \quad (\text{contracting volume}),$$

Prout-Tompkins equation:

$$\ln\left(\frac{\alpha}{1 - \alpha}\right) = kt$$

and other equations were used to fit the experimental kinetic data and to calculate the activation energies ( $E_a$ ) for the hydrogen reduction of pure magnetite and its solid solutions to Fe/Fe-M alloys. But the best fit was obtained for the contracting area equation. This equation assumes that there is a rapid and dense nucleation, or initial rapid surface growth followed by advance of interface from the surface into bulk of crystallites. This type of behaviour can occur when the free activation energy for nucleus formation is comparable with that or subsequent growth ( $\Delta G_N \approx \Delta G_G$ ).

The Arrhenius plots used to calculate the activation energies for the reduction of  $\text{Fe}_{3-z}\text{O}_4$  and  $(\text{Fe}, \text{M})_{3-z}\text{O}_4$  by hydrogen using this equation are given in Fig. 2 and the  $E_a$ s at various stages ( $\alpha$ ) are given in Table 2.

The XRD of the precursors subjected to isothermal reduction studies at 300°C for 1 h in hydrogen indicate the presence of magnetite (Fig. 3) and a very small quantity of Fe as shown in Table 3. The Mossbauer studies also indicate non-stoichiometric magnetite and its disordered solid solutions are formed and the details of this study are reported elsewhere [9]. Representative spectra of the same are given in Fig. 4.

## Discussion

### *Pure oxides*

The activation energy for the reduction of  $\text{Fe}_{3-z}\text{O}_4$  derived from  $\text{Fe}_2\text{O}_3$  precursor prepared at lower temperatures (250°C) is lower (7.5 kcal/mole at  $\alpha=0.2$ ) than that prepared at higher temperatures as shown in Table 2 and this trend is continuous throughout the reduction process. The broadening of XRD peaks both in the starting  $\text{Fe}_2\text{O}_3$  [5] and the intermediate  $\text{Fe}_{3-z}\text{O}_4$  formed from

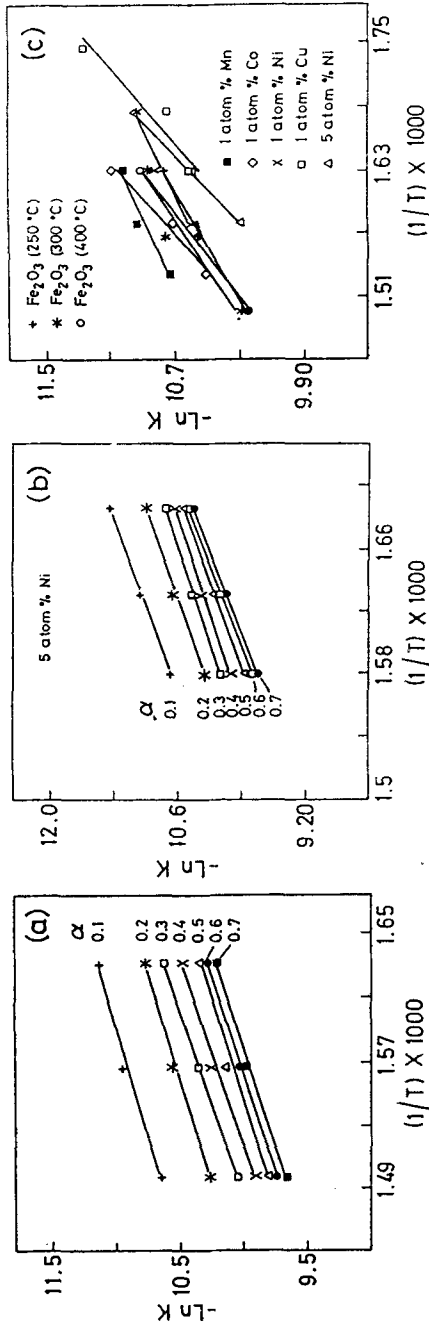


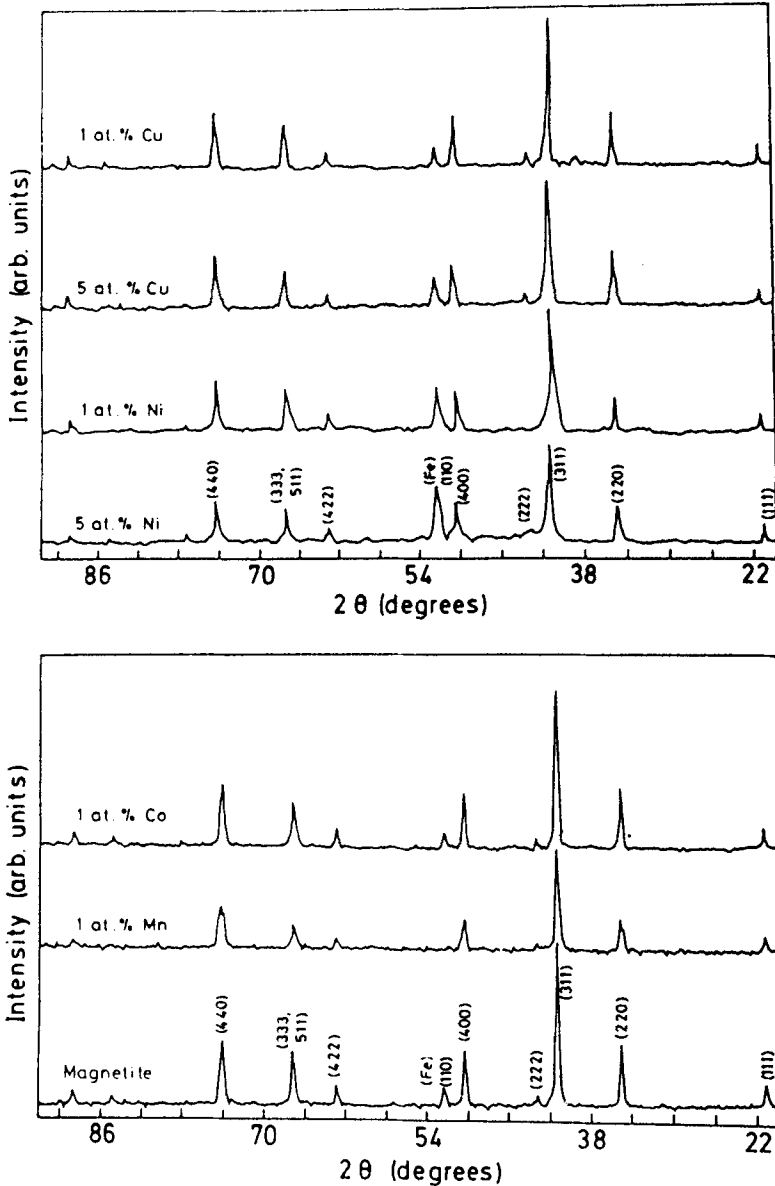
Fig. 2 Arrhenius plots for isothermal hydrogen reduction of spinels; (a)  $\text{Fe}_{3-x}\text{O}_4$  obtained from  $\text{Fe}_2\text{O}_3$  prepared at 250°C; (b)  $(\text{Fe}, \text{Ni})_{3-x}\text{O}_4$  (1 at % Ni) spinel obtained from doped  $\text{Fe}_2\text{O}_3$  sample prepared at 300°C; (c) Pure  $\text{Fe}_{3-x}\text{O}_4$  and spinel solid solutions  $(\text{Fe}, \text{M})_{3-x}\text{O}_4$  at  $\alpha = 0.2$

Table 2 Activation energies for the hydrogen reduction of Fe<sub>3</sub>O<sub>4</sub> and its solid solutions (Fe, M)<sub>3-2</sub>O<sub>4</sub>

Precursor	Spinel	Activation energies for various values of $\alpha$ / kcalmol <sup>-1</sup> ( $\pm 1$ )						
		0.1	0.2	0.3	0.4	0.5	0.7	
Fe <sub>2</sub> O <sub>3</sub> (250°C)	Fe <sub>3-2</sub> O <sub>4</sub>	7.1	7.5	8.5	8.5	8.1	8.0	
Fe <sub>2</sub> O <sub>3</sub> (300°C)	Fe <sub>3-2</sub> O <sub>4</sub>	7.4	8.5	9.4	9.5	10.0	10.3	
Fe <sub>2</sub> O <sub>3</sub> (400°C)	Fe <sub>3-2</sub> O <sub>4</sub>	8.5	9.7	9.8	10.0	10.2	11.5	
Fe <sub>2</sub> O <sub>3</sub> * + 1 at % Mn	(Fe, M) <sub>3-2</sub> O <sub>4</sub>	5.4	5.7	6.0	5.9	6.1	9.5	
Fe <sub>2</sub> O <sub>3</sub> + 1 at % Co	(Fe, M) <sub>3-2</sub> O <sub>4</sub>	10.3	11.5	12.7	13.3	14.0	15.3	
Fe <sub>2</sub> O <sub>3</sub> + 1 at % Ni	(Fe, M) <sub>3-2</sub> O <sub>4</sub>	6.2	6.2	6.9	7.0	7.7	8.6	
Fe <sub>2</sub> O <sub>3</sub> + 1 at % Cu	(Fe, M) <sub>3-2</sub> O <sub>4</sub>	10.7	11.3	12.0	11.8	11.7	12.3	
Fe <sub>2</sub> O <sub>3</sub> + 5 at % Ni	(Fe, M) <sub>3-2</sub> O <sub>4</sub>	12.3	11.9	11.1	11.0	12.2	13.0	
Fe <sub>2</sub> O <sub>3</sub> + 5 at % Cu	(Fe, M) <sub>3-2</sub> O <sub>4</sub>	8.9	9.9	11.6	12.0	12.7	13.5	

\*Doped Fe<sub>2</sub>O<sub>3</sub> samples with transition metal as solute atoms

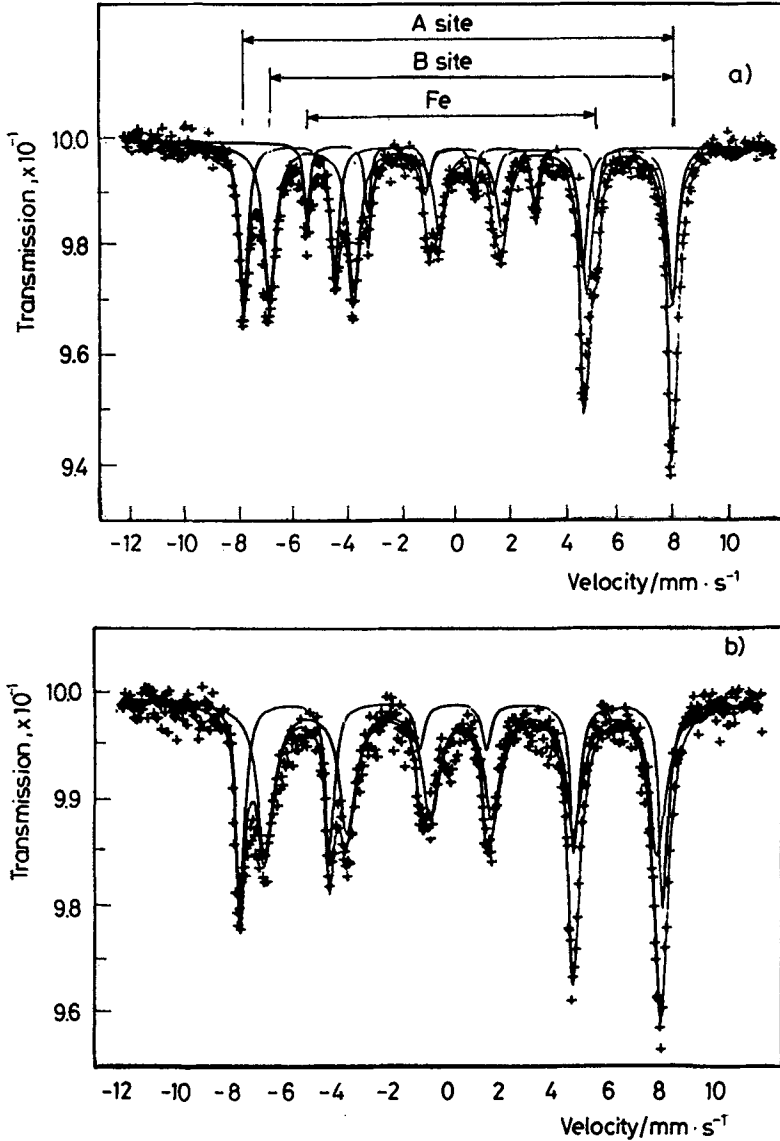
it as compared to the samples prepared at higher temperatures indicate that these oxides are highly defective. The XRD studies indicate that the lattice parameter of magnetite varies with preparation temperature of the precursor and



**Fig. 3** X-ray diffractograms of magnetite and spinel solid solution obtained after 1 h by isothermal reduction in hydrogen at 300°C from the precursors pure  $\text{Fe}_2\text{O}_3$  and doped  $\text{Fe}_2\text{O}_3$  samples respectively



the magnetite obtained is more disordered as the preparation temperature of the precursor decreases. The Mossbauer parameters indicate that non-stoichiometric magnetite is formed and the cation vacancies increase with the decrease in



**Fig. 4** Mossbauer spectra of spinels obtained from  $(\text{Fe}, \text{M})_2\text{O}_3$  precursors after 1 h in hydrogen atmosphere; (a) Spinel solid solution  $(\text{Fe}, \text{M})_{3-z}\text{O}_4$  with 1 at% Cu indicating the spectrum of A and B sites and some amount of, metallic Fe; (b) Spinel solid solution with 1 at% Mn with A and B site spectrum

Table 3 XRD analysis of samples reduced in hydrogen at 300°C for 1 h

Starting samples	End products with volume% of Fe $\pm 0.5$	Crystalline size / Å ( $\pm 20$ )		Lattice parameters / Å ( $\pm 0.002$ )	
		Fe <sub>3</sub> O <sub>4</sub>	Fe	Fe <sub>3</sub> O <sub>4</sub>	Fe
Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub> + Fe (6.0)	249	206	8.386	2.872
Fe <sub>2</sub> O <sub>3</sub> * + (1 at% Mn)	Fe <sub>3</sub> O <sub>4</sub>	224	—	8.415	—
Fe <sub>2</sub> O <sub>3</sub> + (1 at% Co)	Fe <sub>3</sub> O <sub>4</sub> + Fe (6.3)	283	206	8.408	2.872
Fe <sub>2</sub> O <sub>3</sub> + (1 at% Ni)	Fe <sub>3</sub> O <sub>4</sub> + Fe (8.5)	250	257	8.385	2.872
Fe <sub>2</sub> O <sub>3</sub> + (1 at% Cu)	Fe <sub>3</sub> O <sub>4</sub> + Fe (17)	239	228	8.393	2.872
Fe <sub>2</sub> O <sub>3</sub> + (5 at% Ni)	Fe <sub>3</sub> O <sub>4</sub> + Fe (11)	242	228	8.379	2.872
Fe <sub>2</sub> O <sub>3</sub> + (5 at% Cu)	Fe <sub>3</sub> O <sub>4</sub> + Fe (24)	249	206	8.383	2.872

\*Doped Fe<sub>2</sub>O<sub>3</sub> samples with transition metals as solute atoms

the preparation temperature of the precursor [9]. This could be ascribed to lower crystalline sizes and larger surface areas for  $\text{Fe}_2\text{O}_3$  prepared at  $250^\circ\text{C}$  and also higher defect concentration.

### *Doped oxides*

The spinels derived from doped  $\text{Fe}_2\text{O}_3$  samples show considerable differences in the activation energies calculated at different stages (values of  $\alpha$ ) of reduction. In all cases it increases with the increase in  $\alpha$ . The case of spinel solid solution containing Mn is different from the rest in that the final product is a lower oxide of Mn and not metallic alloy of Fe–Mn at these temperatures. The low  $E_a$ s in this system is for a different reaction leading to the formation of lower oxide of Mn and metallic Fe.

The Co spinel samples indicate the highest activation energies for the  $\text{H}_2$  reduction varying from 10.3 to 15.3 kcal/mole at  $\alpha = 0.1$  and at  $\alpha = 0.7$  respectively which reflects the difficulty of reduction of this spinel as compared to the pure magnetite prepared under similar conditions.

The 1 at% Ni spinel on the other hand clearly indicates low  $E_a$  for the reduction of doped spinel to metallic state with the  $E_a$  varying from 6.2 to 8.6 kcal/mole in the range of  $\alpha$  from 0.1 to 0.7. The corresponding values for the undoped spinel vary from 7.4 to 10.3 kcal/mole. The  $E_a$  are therefore lower by 1.2 to 1.7 kcal/mole in the 1 at% Ni spinel solid solution. The acceleration of the reduction reaction is therefore understandable.

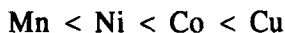
The 5 at% Ni spinel sample however reflects an overall activation energy obtained from kinetic data which are anomalously high ranging from 12 to 13 kcal/mole ( $\alpha = 0.1$  to 0.7). One might have expected a much lower  $E_a$  than for 1 at% Ni sample. This needs to be explained.

The 1 at% Cu spinel sample also similarly indicates anomalously high  $E_a$  varying from 10.7 to 12.3 kcal/mole in the range of  $\alpha = 0.1$  to 0.7. Whereas the 5 at% Cu spinel sample does so only to a smaller extent especially at low  $\alpha$  values (0.1 or 0.2). These need to be adequately explained. In case of 1 at% and 5 at% Cu spinel samples and also in case of 5 at% Ni case, it is possible that a significant part of the reduction of spinel is already over at the presumed start of the reaction when  $\alpha$  is taken equal to zero and therefore the kinetic parameters calculated could be for a later stage of the reduction reaction closer to the decay period. In these cases the initial reaction is very fast probably due to the formation of metallic Cu or Ni which could enable a hydrogen 'Spill over' over large distances making larger area of the reactant interface participate in the reaction with the activated hydrogen atoms. The role of metal additives in promoting bulk oxide reductions has been interpreted earlier in two ways. It has been postulated that the foreign metal forms sites for adsorption of hydrogen.

This leads to enhanced concentrations of surface hydrogen through a 'Spill over mechanism' [10]. Alternatively, or additively, it is thought [11] that the foreign metal atom may be responsible for the formation of extra nucleation sites by virtue of lattice or surface deformations. This fast progress of the reaction interface causes probably a porous layer to be formed which impedes the reaction and hence may be a cause to give high activation energies in the later stages of the reaction.

While there is clear evidence from the value of  $t_{\alpha=0.5}$  and from analysis of 1 h reduced samples that Ni and Cu accelerate the reduction reactions, the contracting area model suggests that such features are indicative that the details regarding the kinetics are more complicated and two or more mechanisms may be involved during the reduction reactions.

The Mossbauer studies [9] indicate that the site occupancy in the metastable spinels obtained vary depending on the nature and concentration of dopant. Except in case of Mn which occupies predominantly A site, the site occupancy is mostly B site for all other dopants. In all cases there are cation vacancies and are increasing in the order:



However careful analysis of Mossbauer parameters indicate that in the metastable spinels formed there is considerable disorder in the site occupancy of solute atoms. As a consequence there should be anion vacancies for charge neutrality in case of Ni and Cu metastable spinels and it increases with the increase in concentration. It is likely that these factors are responsible for the discrepancies in the activation energies. Thus the nature of the low temperature  $\text{H}_2$  reduction of the solid doped oxides are more complicated and vary with the system. Further work is required in order to clarify several possibilities based on the nature of the intermediate metastable spinels formed during the course of these reduction reactions.

## Conclusions

The kinetics of low temperature (300–400°C) hydrogen reduction of magnetite obtained from  $\text{Fe}_2\text{O}_3$  prepared at 250, 300 and 400°C has been measured. The experimental data give a good fit with the equation  $1-(1-\alpha)^{1/2} = kt$ , for contracting area model for solid-gas reactions. The activation energies for the reduction of pure  $\text{Fe}_{3-z}\text{O}_4$  are in the range of 7–12 kcal/mole for early stages and is the least for the magnetite derived from  $\text{Fe}_2\text{O}_3$  prepared at the lowest temperature. This is ascribed to the lower crystallite sizes, higher surface areas and extent of disorder in the sample.

In case of doped spinels  $(\text{Fe}, \text{M})_{3-z}\text{O}_4$ , despite a good fit of experimental data to the contracting area model, the variation in activation energies indicate there are more complicated factors governing the kinetics of reduction. The spinel solid solution with Mn has a low  $E_a$  but follows a different reduction mechanism where Fe and lower oxide of Mn are obtained as products. In all other cases,  $(\text{Fe}, \text{M})_{3-z}\text{O}_4$  is reduced to give Fe–M alloy as the final product. The spinel with Co has high  $E_a$  of 10–15 kcal/mole and retards the reaction.

In the case of spinel solid solutions containing Ni and Cu the reduction reaction is initially accelerated but the calculated  $E_a$ s vary. The larger apparent activation energies may correspond to a later stage in the reduction process. It is likely that in samples containing Ni and Cu, the site disorder in their occupancies result in substantial vacancies in the oxygen sublattice decreasing the real activation energies for migration of cations. Possibly hydrogen 'Spill over' effects are responsible for the enhanced reduction. It is possible that more than one mechanism is contributing to the reduction reaction.

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**Zusammenfassung** — Mittels isothermer Thermogravimetrie wurde im Temperaturbereich 300–400°C die Kinetik der Reduktion von reinem und versetztem (1% Mn, Co, Ni, Cu sowie 5% Ni, Cu) metastabilem nichtstöchiometrischem Magnetit mit Wasserstoff bei relativ niedrigen Temperaturen untersucht. Durch ein Anhaben der Konzentration des zugesetzten Materiales (5% Ni und Cu) wird die Reaktivität erhöht. Die Aktivierungsenergie für reines Magnetit liegt je nach der Herstellungstemperatur des Präkursors  $\text{Fe}_2\text{O}_3$  (250–400°C) zwischen 7 und 9 kcal/mol, wobei der niedrigste Wert der niedrigsten Herstellungstemperatur entspricht. Die entsprechenden Aktivierungsenergien für die Reduktion versetzter Proben der Formel  $(\text{Fe}, \text{M})_{3-z}\text{O}_4$  (die wahrscheinlich mit Art und Konzentration des Zusatzstoffes variieren) hängen abgesehen von deren

Porosität und Oberflächengröße von der Art des gelösten Atomes, vom Grad der Ungeordnetheit, egal ob es im nichtstöchiometrischen Spinell die tetraedrischen (A) oder die oktaedrischen (B) Stellen besetzt, sowie weiterhin von Wasserstoff 'Spill over' Effekten.