Stability of Several Substituted Ferrites in a Reducing Atmosphere

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The stability of α-Fe_2O_3 and a number of ferrites were studied in a reducing atmosphere of 85%Ar/15%H_2. The reduction processes were followed by both thermogravimetric and X-ray analyses. These results allowed for the unambiguous characterization of the reduction processes. A relationship between the nature of the products and the reduction process is proposed.

Introduction

Qian et al. (1) have recently shown that reduction of the spinel $MgFe_2O_4$ results in the initial formation of the solid solution $Mg_{1-x}Fe_xO$ and that this phase persists even after 80 hr of heating at 450°C in a pure-hydrogen atmosphere. This is in contrast to the reduction of Fe_2O_3 under similar conditions. At the end of 12 hr they observed the presence of only iron peaks in X-ray diffraction patterns of the products. Thus, it appeared that the formation of an intermediate solid solution $Mg_{1-x}Fe_xO$ inhibits the reduction of the spinel to Fe and MgO.

Trivalent iron is present in a number of ferrites crystallizing with the spinel structure. In addition, a divalent ion is present either on tetrahedral or octahedral sites. The stability of Fe^{3+} in the structure should depend to a large degree on the reducibility of the divalent ion as well as on the stability

of any intermediate products formed by heating the spinel in a hydrogen atmosphere. The present study deals with the stability of the spinels MFe_2O_4 where M = Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}, as compared to the stability of Fe_3O_4.

Experimental

Preparation of samples. Copper diiron(III) oxide and cadmium diiron(III) oxide were prepared by grinding together the appropriate oxides and heating them to 800°C in porcelain crucibles (2). The other ferrites MFe_2O_4 (M = Co,Ni,Zn,Mg) were prepared according to the method of Wickham (3) by the addition of an oxalic acid solution to a solution containing appropriate quantities of the desired ions. The metal–oxalate solid solution is precipitated, and if decomposed in the presence of air, yields MFe_2O_4 according to the equation

$$MFe_2(C_2O_4)_3 \cdot 6H_2O + 2O_2 \rightarrow$$
$$MFe_2O_4 + 6H_2O + 6CO_2$$
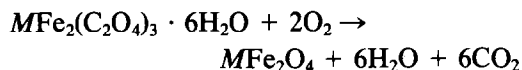
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TABLE I

REDUCTION MECHANISMS OF SOME FERRITES IN Ar/H$_2$ COMPARED WITH α-Fe$_2$O$_3$

Compound	Reduction temperature		Intermediate phase	Final phase
	A[a]	B[b]		
α-Fe$_2$O$_3$	270	470	Fe$_3$O$_4$	α-Fe
CuFe$_2$O$_4$	215	440	(Cu$_x$Fe$_{1-x}$)Fe$_2$O$_4$	α-Fe, Cu
CdFe$_2$O$_4$	365	465	Fe$_3$O$_4$	α-Fe
ZnFe$_2$O$_4$	370	690	ZnO	α-Fe
CoFe$_2$O$_4$	355	485	—	α-(Fe,Co)
NiFe$_2$O$_4$	360	490	α-Fe + γ-(Ni,Fe)	γ-(Ni,Fe)

[a] Reduction of compound starts.

[b] Final reduced phase.

X-Ray diffraction studies. Powder diffraction patterns of the samples were obtained with a Philips diffractometer using monochromated high-intensity CuKα_1 radiation (λ = 1.5405 Å). For qualitative identification of the phases present, the patterns were taken from 30° ≤ 2θ ≤ 80° with a scan rate of 1° 2θ/min and a chart speed of 30 in./hr.

Thermogravimetric analysis. A thermogravimetric analysis was performed on each of the ferrites, using a Cahn electrobalance (Model RG). An atmosphere of either pure hydrogen (99% Linde) or 85%/15% Ar/H$_2$ was used in these studies. Both gases were predried through a P$_2$O$_5$ column before passing over the sample.
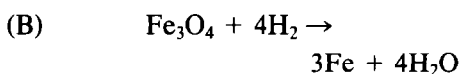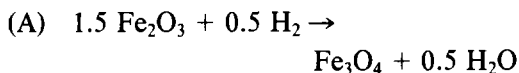
The TGA patterns obtained by reduction with pure hydrogen were used to determine the temperature for each step in the reduction process. Those obtained with Ar/H$_2$ as the reducing atmosphere were important in ascertaining quantitatively the phase relationships of the intermediate products formed during the reduction process.

Typical TGA experiments required 50 mg of the ferrite. The gases were passed over the sample at a flow rate of 50 cm^3/min and a maximum temperature of 700°C was reached at a heating rate of 30°C/hr.

Results and Discussion

The reduction of α-Fe$_2$O$_3$ and a number of iron spinels was carried out under the conditions given in Table I. A reducing atmosphere of 85%/15% Ar/H$_2$ was chosen because the use of this gas mixture allowed for clear identification of the intermediate step in the reduction process for several of the ferrites. With pure hydrogen gas, the reduction proceeded too rapidly and careful analysis of the reduction process could not be performed.

The reduction mechanism of α-Fe$_2$O$_3$ has been reported (4) as a two-step process and can be represented by the equations

$$\text{(A)} \quad 1.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ H}_2 \rightarrow \text{Fe}_3\text{O}_4 + 0.5 \text{ H}_2\text{O}$$

$$\text{(B)} \quad \text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}$$

In this study, the reduction process was carried out in an 85%/15% Ar/H$_2$ atmosphere, and the TGA pattern is shown in Fig. 1a. It is evident that under such conditions the reduction process begins at 270°C and all of the α-Fe$_2$O$_3$ is converted to Fe$_3$O$_4$ at 305°C. The reduction of the Fe$_3$O$_4$ to metallic iron is essentially complete at 470°C. Differences in the reported temperatures for the reduction of α-Fe$_2$O$_3$ are caused by different rates of heating as well as by the composition of the reducing atmosphere. In these studies when pure hydrogen was used the Fe$_3$O$_4$ began to be reduced to metallic iron before all of the α-Fe$_2$O$_3$ was completely converted to Fe$_3$O$_4$. In addition, the observed reduction temperatures were much lower than those reported for reductions carried out in an 85%/15% Ar/H$_2$ atmosphere.

It can be seen from Fig. 1 that the ratio of the weight loss for Step B to the loss for Step A is 7.97 : 1. The ratio of the calculated weight loss for the reduction of α-Fe$_2$O$_3$ to Fe$_3$O$_4$ and finally to iron (8 : 1) can be ob-
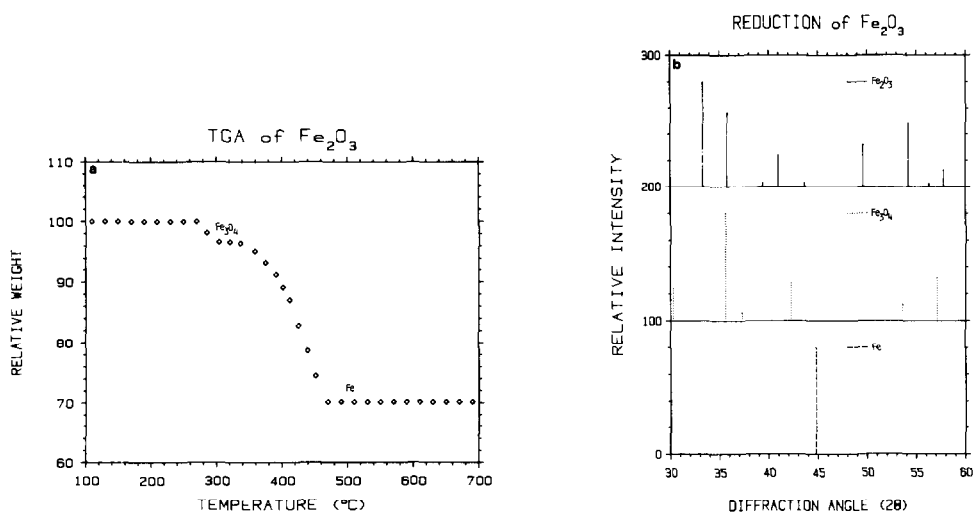
FIG. 1. (a) Relative weight versus temperature for Fe_2O_3 reduced in 85%/15% Ar/H_2. (b) X-Ray patterns of initial, intermediate, and final materials.

tained from the relative amounts of water formed as represented in the equations for Steps A and B. This ratio also represents the relative weight removal of oxygen from the iron oxides.

The TGA plot for the reduction of the ferrite $CuFe_2O_4$ with 85%/15% Ar/H_2 and the X-ray analysis of the reduction prod-

ucts which were formed for the two-step process are shown in Figs. 2a and b. These results indicate that the initial reduction step is complete at 270°C and at this temperature the Cu^{2+} was reduced to metallic copper; in addition, the tetragonal $CuFc_2O_4$ was transformed to a cubic spinel containing all of the iron. Further reduction re-
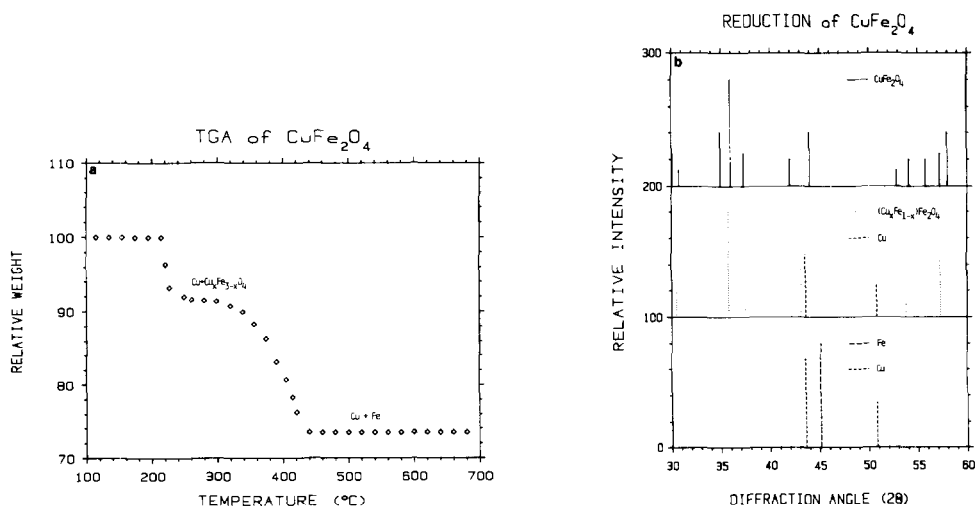

FIG. 2. (a) Relative weight versus temperature for $CuFe_2O_4$ reduced in 85%/15% Ar/H_2. (b) X-Ray patterns of initial, intermediate, and final materials.
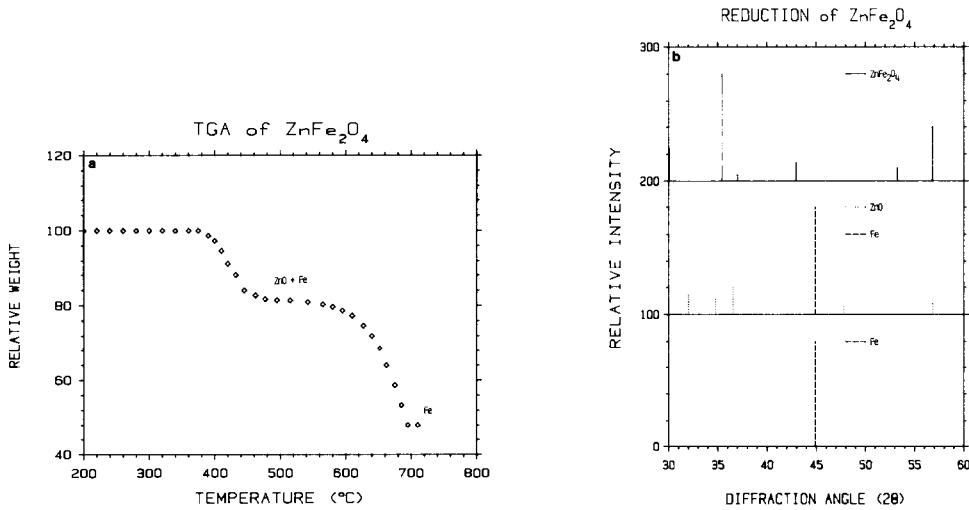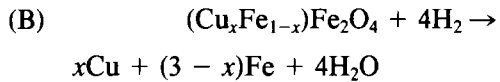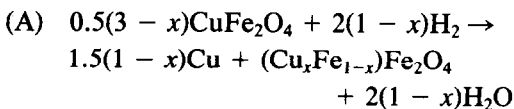
TGA of ZnFe$_2$O$_4$

REDUCTION of ZnFe$_2$O$_4$

FIG. 3. (a) Relative weight versus temperature for ZnFe$_2$O$_4$ reduced in 85%/15% Ar/H$_2$. (b) X-Ray patterns of initial, intermediate, and final materials.

sulted in the appearance of metallic iron in the product and, finally, the reduction end product consisted of iron and copper. The reduction was complete at 440°C.

If the product formed at the end of the first stage of the reduction process had been pure Fe$_3$O$_4$, then the equations

(A) $1.5 \, CuFe_2O_4 + 2H_2 \rightarrow$
$$1.5 \, Cu + Fe_3O_4 + 2H_2O$$

(B) $Fe_3O_4 + 4H_2 \rightarrow$
$$3Fe + 4H_2O$$
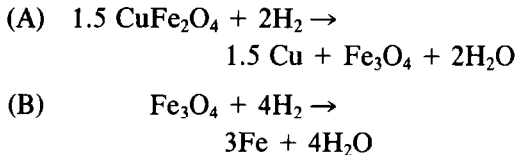
would indicate how the reaction proceeded. The calculated ratio of the weight loss for Step A to Step B is 1:2. From the TGA results plotted in Fig. 2, it can be seen that the ratio is actually 1:2.15. This discrepancy in the ratio of the observed weight loss to the calculated value is consistent with the reduction of copper ferrite to an intermediate phase which still contains copper. Accordingly, the reduction process can be represented by the equations

(A) $0.5(3 - x)CuFe_2O_4 + 2(1 - x)H_2 \rightarrow$
$$1.5(1 - x)Cu + (Cu_xFe_{1-x})Fe_2O_4$$
$$+ 2(1 - x)H_2O$$

(B) $(Cu_xFe_{1-x})Fe_2O_4 + 4H_2 \rightarrow$
$$xCu + (3 - x)Fe + 4H_2O$$

From the above equations, it can be seen that the weight loss which occurs in the reduction process is directly related to the amount of water formed. Hence, for the reduction products prepared at 270°C, the ratio of the weight loss in Step A to that in Step B is $2(1 - x):4$. From Fig. 2a, the ratio was determined to be 1:2.15, and therefore the value of $x = 0.07$.

The TGA plot for the reduction of the ferrite ZnFe$_2$O$_4$ with 85%/15% Ar/H$_2$ and the X-ray analysis of the reduction products are given in Figs. 3a and b. The reduction process of ZnFe$_2$O$_4$ takes place in two steps. The initial products formed at 495°C were identified as Fe and ZnO. The reduction process continued with the gradual loss in weight due to the formation of zinc and its volatilization at higher temperatures. The final reduction product at 690°C was identified as iron by X-ray diffraction analysis.

The reduction process for CdFe$_2$O$_4$ begins at 365°C and is complete at 465°C. As
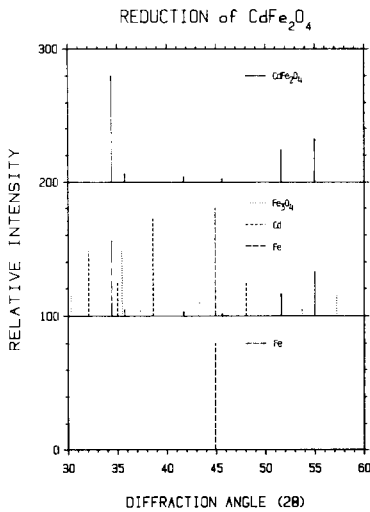
REDUCTION of CdFe₂O₄

FIG. 4. X-Ray patterns of initial, intermediate, and final materials formed in the reduction of CdFe₂O₄ in 85%/15% Ar/H₂.

the temperature is increased to 380°C there is a continual separation and volatilization of metallic cadmium as well as the formation of magnetite and metallic iron. At 465°C the reduction process was complete and only iron remained. The cadmium was
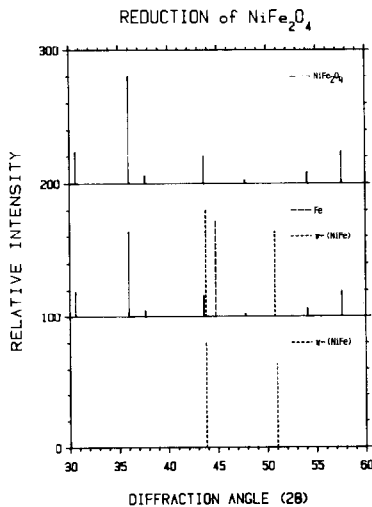
REDUCTION of NiFe₂O₄

FIG. 5. X-Ray patterns of initial, intermediate, and final materials formed in the reduction of NiFe₂O₄ in 85%/15% Ar/H₂.

completely volatilized at this temperature. The results of X-ray diffraction analyses are shown in Fig. 4.

The TGA data for $CoFe_2O_4$ indicate that the reduction in 85%/15% Ar/H₂ is continuous and begins at 355°C and is complete at 485°C. The X-ray diffraction pattern for the product indicates the presence of an alloy which crystallizes with the α-Fe structure and contains both α-Fe and cobalt.

The reduction of $NiFe_2O_4$ begins at 360°C and is complete at 490°C. The X-ray diffraction data are shown in Fig. 5. It can be seen that metallic iron and an alloy of iron and nickel crystallizing with the γ-(Ni,Fe) structure are formed at 400°C. At 500°C, only the γ-(Ni,Fe) alloy can be identified in X-ray diffraction patterns of the product.

Conclusions

The stability of iron(III) oxide and five ferrite spinels, where the divalent ion was Cu,Zn,Cd,Co,Ni, was studied under an 85%/15% Ar/H₂ atmosphere. The thermogravimetric studies indicated that for Fe_2O_3, $CuFe_2O_4$, and $ZnFe_2O_4$, the loss of oxygen occurred in two distinct stages. Fe_3O_4 was formed as the intermediate product in the reduction of Fe_2O_3 to Fe. Reduction of $CuFe_2O_4$ gave initially a mixture of metallic copper and an iron-rich copper ferrite with the stoichiometry $Cu_{0.07}Fe_{0.93}$ Fe_2O_4. The final reduction product was a mixture of copper and iron. The reduction of $ZnFe_2O_4$ first gave iron and ZnO. However, by 690°C the ZnO was reduced to metallic zinc, which was volatilized. On reduction, the spinel $CdFe_2O_4$ first forms volatile cadmium as well as magnetite and iron. The final end product of the process was metallic iron since all of the cadmium volatilized at 465°C.

The inverse spinels $CoFe_2O_4$ and Ni Fe_2O_4 showed a continuous loss of oxygen on reduction and the final products were α-(Fe,Co) and γ-(Ni,Fe) alloys, respectively.

Thus it can be seen that for each of the compounds studied, the reduction proceeds by a different mechanism depending on the nature of the reduction products.

Acknowledgments

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