

Stability of Several Substituted Ferrites in a Reducing Atmosphere

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The stability of α -Fe₂O₃ and a number of ferrites were studied in a reducing atmosphere of 85%Ar/15%H₂. 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

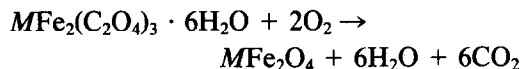
Qian *et al.* (1) have recently shown that reduction of the spinel MgFe₂O₄ results in the initial formation of the solid solution Mg_{1-x}Fe_xO and that this phase persists even after 80 hr of heating at 450°C in a pure-hydrogen atmosphere. This is in contrast to the reduction of Fe₂O₃ under similar 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 Fe³⁺ 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 MFe₂O₄ where M = Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺, and Co²⁺, as compared to the stability of Fe₃O₄.

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 MFe₂O₄ (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 MFe₂O₄ according to the equation



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TABLE I
REDUCTION MECHANISMS OF SOME FERRITES IN
Ar/H₂ COMPARED WITH α -Fe₂O₃

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 CuK α ₁ radiation ($\lambda = 1.5405 \text{ \AA}$). For qualitative identification of the phases present, the patterns were taken from $30^\circ \leq 2\theta \leq 80^\circ$ with a scan rate of $1^\circ 2\theta/\text{min}$ 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/H₂ was used in these studies. Both gases were predried through a P₂O₅ column before passing over the sample.

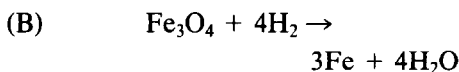
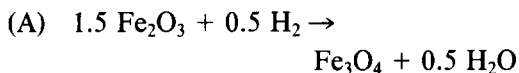
The TGA patterns obtained by reduction with pure hydrogen were used to determine the temperature for each step in the reduction process. Those obtained with Ar/H₂ as the reducing atmosphere were important in ascertaining quantitatively the phase relationships of the intermediate products formed during the reduction process.

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

Results and Discussion

The reduction of α -Fe₂O₃ and a number of iron spinels was carried out under the conditions given in Table I. A reducing atmosphere of 85%/15% Ar/H₂ 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 -Fe₂O₃ has been reported (4) as a two-step process and can be represented by the equations



In this study, the reduction process was carried out in an 85%/15% Ar/H₂ 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 -Fe₂O₃ is converted to Fe₃O₄ at 305°C . The reduction of the Fe₃O₄ to metallic iron is essentially complete at 470°C . Differences in the reported temperatures for the reduction of α -Fe₂O₃ 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 Fe₃O₄ began to be reduced to metallic iron before all of the α -Fe₂O₃ was completely converted to Fe₃O₄. In addition, the observed reduction temperatures were much lower than those reported for reductions carried out in an 85%/15% Ar/H₂ 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 -Fe₂O₃ to Fe₃O₄ and finally to iron (8 : 1) can be ob-

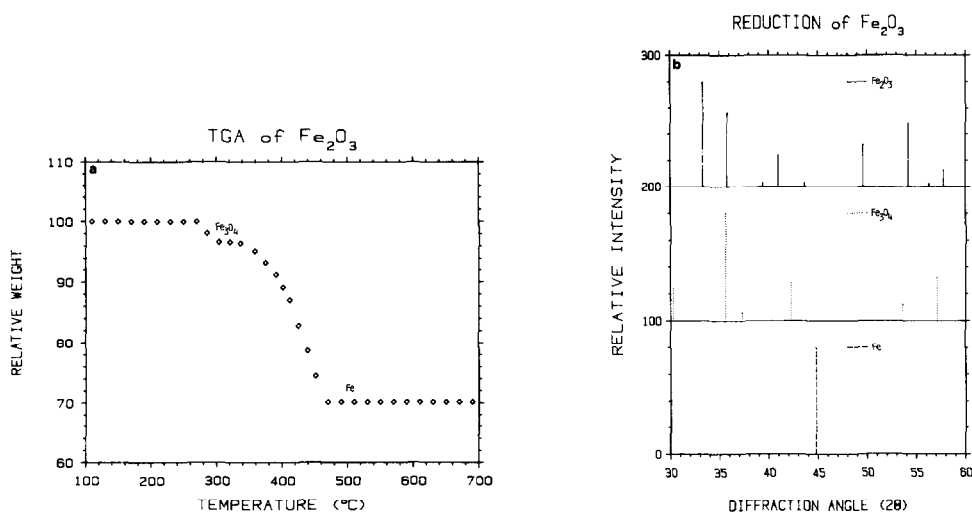


FIG. 1. (a) Relative weight versus temperature for Fe_2O_3 reduced in 85%/15% Ar/ H_2 . (b) X-Ray patterns of initial, intermediate, and final materials.

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 $^{\circ}\text{C}$ and at this temperature the Cu^{2+} was reduced to metallic copper; in addition, the tetragonal CuFe_2O_4 was transformed to a cubic spinel containing all of the iron. Further reduction re-

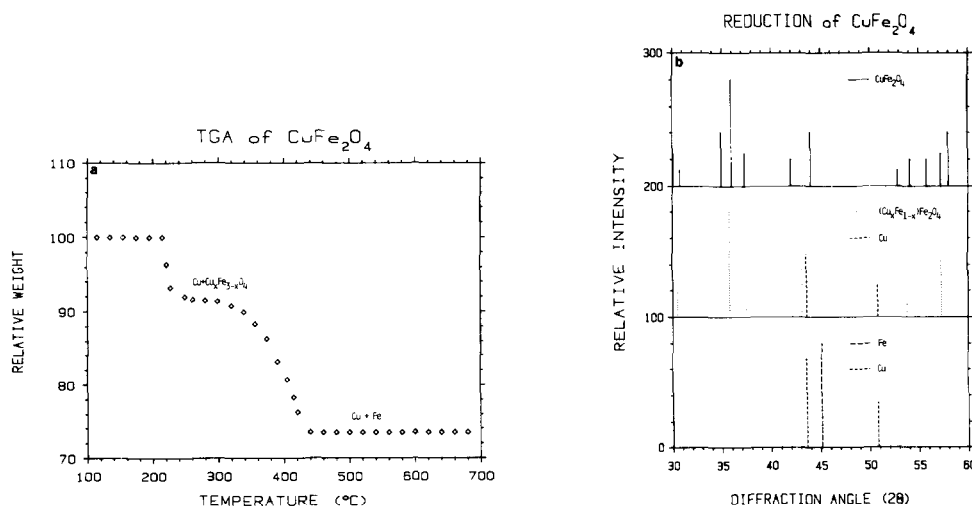


FIG. 2. (a) Relative weight versus temperature for CuFe_2O_4 reduced in 85%/15% Ar/ H_2 . (b) X-Ray patterns of initial, intermediate, and final materials.

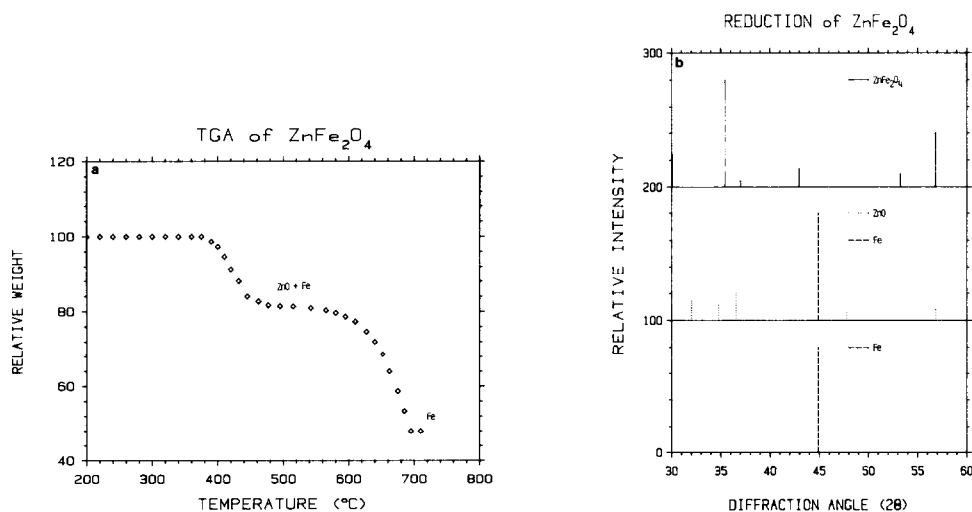
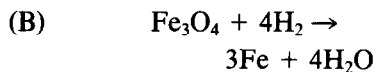
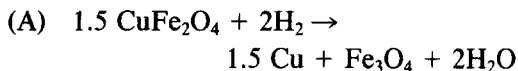


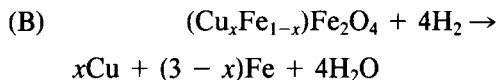
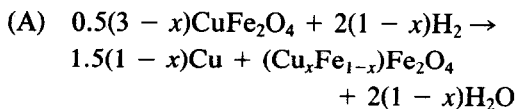
FIG. 3. (a) Relative weight versus temperature for ZnFe₂O₄ reduced in 85%/15% Ar/H₂. (b) X-Ray patterns of initial, intermediate, and final materials.

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 Fe₃O₄, then the equations



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



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 ZnFe₂O₄ with 85%/15% Ar/H₂ and the X-ray analysis of the reduction products are given in Figs. 3a and b. The reduction process of ZnFe₂O₄ 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 CdFe₂O₄ begins at 365°C and is complete at 465°C. As

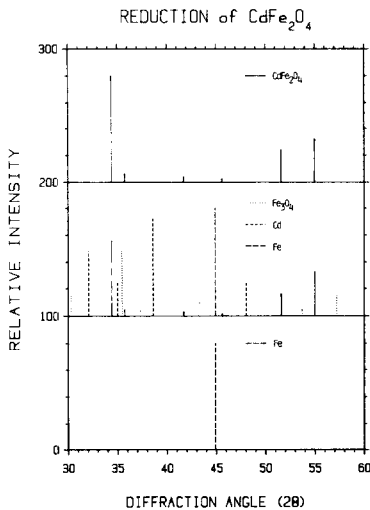


FIG. 4. X-Ray patterns of initial, intermediate, and final materials formed in the reduction of CdFe_2O_4 in 85%/15% Ar/H_2 .

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

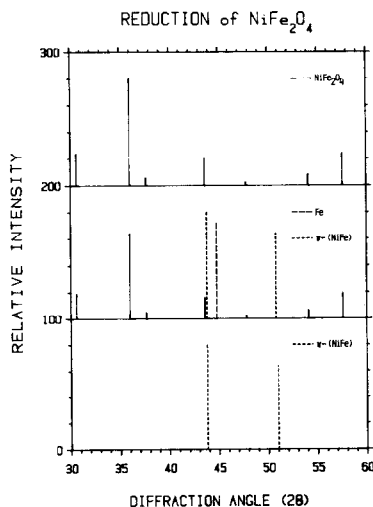


FIG. 5. X-Ray patterns of initial, intermediate, and final materials formed in the reduction of NiFe_2O_4 in 85%/15% Ar/H_2 .

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/H_2 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/H_2 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 $\text{Cu}_{0.07}\text{Fe}_{0.93}\text{Fe}_2\text{O}_4$. 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 NiFe_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.

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