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01 Jan 1973

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Formation and Densification of Cadmium Manganese Ferrite

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FORMATION OF Ni-ferrite, Mn-ferrite,[1] NiZn-ferrite,[1,2] Zn-ferrite[3] and Mg-ferrite[4] have been investigated using X-ray diffraction analysis. Jander's diffusion equation described the data from these investigations over a portion of the temperature ranges studied. However, the reaction mechanisms and sequences involved in the formation of mixed ferrites have not been well defined in the literature. The purposes of this investigation were:

(1) To further the understanding of the formation of CdMn-ferrite by studying first the kinetics of the formation of Cd-ferrite and Cd-manganite, which provides a basis for understanding the details of the mixed CdMn-ferrite reaction and to obtain the optimum temperature-time cycle for calcination and sintering, along with the reaction sequence and densification behavior for polycrystalline CdMn-ferrite.

(2) To determine the magnetic properties of CdMn-ferrite as a function of composition, bulk density and grain size.[5]

Experimental

Sample Preparation

The powder materials used were reagent-grade CdO and α-Fe$_2$O$_3$* and reagent-grade MnCO$_3$.† The purity of each was >99.40%.

Samples for Reaction Kinetics of the Binary Oxides. Uncompacted 1:1 molar samples of CdO+α-Fe$_2$O$_3$ and CdO+Mn$_2$O$_3$ were heated in an electric furnace at 700°, 750° and 800°C for periods of 10, 30, 50, 70, 90 and 120 min and then air-quenched. The temperature was controlled to <±5°C and monitored with an 87% Pt+13% Rh vs Pt thermocouple. To quantify the phase analyses, a series of calibration samples were prepared by mechanically mixing various percentages of CdO, α-Fe$_2$O$_3$ and CdO·Fe$_2$O$_3$ and also CdO, Mn$_2$O$_3$ and CdO·Mn$_2$O$_3$. Quantitative X-ray diffraction calibration curves were made from those samples to determine the percent of each phase in the experimental samples.

Samples for Reaction Sequence of Mixed Ferrite Formation. Uncompacted 3-g 1:1 molar samples of CdO+α-Fe$_2$O$_3$ and of CdO+Mn$_2$O$_3$ and ½:½:1 molar ratios of CdO+MnCO$_3$+α-Fe$_2$O$_3$ in alumina crucibles were placed in a preheated furnace. After temperature equilibration for 1-2 min, the time count was initiated. Each sample was heated for 2 h at 650°, 700°, 750°, 800°, 850° and 900°C, and the phases were identified by X-ray diffraction analysis. Another set of uncompacted

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The formation kinetics of cadmium ferrite and cadmium manganite from the individual oxides were studied first to provide a basis for understanding the formation of the mixed ferrite Cd$_x$Mn$_{1-x}$Fe$_2$O$_4$. The reactions of CdO+α-Fe$_2$O$_3$→CdFe$_2$O$_4$ and CdO+Mn$_2$O$_3$→CdMn$_2$O$_4$ were both described by Jander's diffusion equation, $(1-\sqrt[3]{1-x})^2=Kt$, at 700°C and over a short time at 750° and also at 800°C in the ferrite case. The activation energies for the two reactions were 70±10 kcal/mole and 45±5 kcal/mole, respectively. The formation of Cd$_x$Mn$_{1-x}$Fe$_2$O$_4$ from CdO, MnCO$_3$ and α-Fe$_2$O$_3$ with mole ratios of $x:(1-x):1$ proceeded by first forming CdO·Fe$_2$O$_3$ and CdO·Mn$_2$O$_3$ followed by the dissolution of CdMn$_2$O$_4$ in the CdFe$_2$O$_4$ phase between 600° and 800°C. At 900°C, the cadmium manganite dissolution was complete forming the solid solution Cd(Mn,Fe)$_2$O$_4$ which coexisted with Mn$_3$O$_4$ and α-Fe$_2$O$_3$ for compositions of $0<x\leq0.5$ and with α-Fe$_2$O$_3$ only for $0.5<x<1.0$. A single phase of Cd$_x$Mn$_{1-x}$Fe$_2$O$_4$ formed for all compositions of $0.0<x<1.0$ at 1150°C. The densification rate Cd$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ at various temperatures was investigated and the most suitable sintering temperature for magnetic property characterization was 1150°C.

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samples with composition x CdO+$(1-x)$MnCO$_3$+α-Fe$_2$O$_3$, where $x=0.1$, 0.3, 0.5, 0.7 and 0.9, were calcined at 900°C for 2 h. Calcined samples were uniaxially pressed into disks at 600 psi and then isostatically pressed at 25,000 psi, sintered at 1150°C for 30 min, air-quenched and then ground to a fine powder. Both calcined and sintered specimens were used for X-ray phase identification and lattice parameter measurements to study the mixed CdMn-ferrite formation at 900° and 1150°C.

Samples for Mixed Ferrite Densification Rate. 100-g batches of ½:½:1 molar ratios of CdO+MnCO$_3$+α-Fe$_2$O$_3$ were calcined at 900°C, soaked for 2 h and air-quenched. Distilled water slurries containing 60% solids with 1% PVA were steel ball-milled for 16 h. The dried and granulated powder was uniaxially pressed at 600 psi into 0.75 in. dia. disks $\approx$0.125 in. thick and then isostatically pressed to 25,000 psi. The green density reached 55% of the theoretical value for the mixed ferrite, Cd$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ($\rho_{th}=5.38$ g/cm^3). The pellets were sintered in air in tightly covered cylindrical alumina crucibles.

X-Ray Diffraction Analysis

CuKα diffraction patterns were made for each specimen. A 2θ range of 20° to 90° was covered for the majority of the specimens. These wide limits were used to check for new peaks that might have appeared as the reactions proceeded.

A scan rate of 0.2° 2θ/min was used for lattice parameter and kinetic studies. The CdO(200) peak area was used to measure the amount of cadmium oxide reacted. CdO(111)

Table I. Table of Activation Energies for the Formation of Different Spinels

Reaction eqs.	Activation energies (kcal/mole)
$CdO + \alpha\text{-}Fe_2O_3 \xrightarrow{700°\text{–}800°} CdFe_2O_4$	70 ± 10
$CdO + Mn_2O_3 \xrightarrow{700°\text{–}800°} CdMn_2O_4$	45 ± 5
$ZnO + Fe_2O_3 \xrightarrow{690°\text{–}760°} ZnFe_2O_4$	72 ± 10[*]
$MgO + Fe_2O_3 \xrightarrow{1000°\text{–}1300°} MgFe_2O_4$	117[†]

[*]Ref. 3.
[†]Ref. 4.

was used as the internal standard to calculate the d-spacing of the (311) planes for the mixed spinel solid solution which formed at the 900°C calcination and 1150°C sintering temperatures.

Density Measurement

The density measurements were made using the xylene displacement method. The precision of the density measurements was ± 0.02 g/cm³.

Results and Discussion

Kinetics of Formation of the Single Spinels

Ninety-five percent of the possible amounts of the CdFe₂O₄ and 88% of the CdMn₂O₄ had formed after 2 h at 800°C. The rates of spinel formation for cadmium ferrite and cadmium manganite were plotted according to Jander's diffusion equation, $(1 - \sqrt[3]{1-x})^2 = Kt$, and are shown in Fig. 1; x is the weight fraction of CdO reacted at time t and K is a rate constant. The activation energies for the reactions $CdO + \alpha\text{-}Fe_2O_3 \rightarrow CdFe_2O_4$ and $CdO + Mn_2O_3 \rightarrow CdMn_2O_4$ calculated from the K's obtained from the initial straight line part of Jander's equation plots are listed in Table I. They are compared to the reported activation energies for the formation of other spinels. Lower activation energies were found in this work for the formation of spinels containing cadmium.

Mixed Spinel Formation

The single spinel peaks of CdFe₂O₄ and CdMn₂O₄ were first observed at 700°C. The peaks of CdFe₂O₄ increased while the peaks of CdMn₂O₄ decreased as the temperature was raised from 700° to 900°C. The formation of the mixed spinel solid solution proceeded continuously as CdMn₂O₄ dissolved in the CdFe₂O₄. The mixed ferrite solid solution peaks were identified by a continuously changing diffraction angle. At 850°C, CdO had completely reacted. At 900°C, the single spinel, CdMn₂O₄, had almost completely dissolved in the CdFe₂O₄, forming the mixed spinel solid solution. At 1150°C, a single phase of Cd₀.₅Mn₀.₅Fe₂O₄ remained.

At 900°C, Mn₃O₄ was present for $x \leq 0.5$ while all manganese detected was in the form of $Cd(Mn,Fe)_2O_4$ for $x > 0.5$. This agrees with Hahn and Muan[6] who found that the transformation temperature of Mn₂O₃ to Mn₃O₄ in air atmosphere is 877° ± 8°C. Others[1] found that Fe₂O₃ will react with Mn₃O₄ above 1000°C to form Mn ferrite. A linear shift of the X-ray diffraction peaks to lower 2θ angles appeared in the mixed spinel solid solution as composition x increased in accordance with Vegard's Law. The 1150°C results indicate fairly good agreement with Vegard's Law, but the 900°C results, as indicated in Fig. 2, do not. Indeed, since there is still residual Fe₂O₃, and in some cases also Mn₃O₄, present at 900°C, the parameter x probably does not indicate the true composition of the spinel phase at this temperature.[1]

X-Ray Lattice Parameters of Mixed Spinel Solid Solution

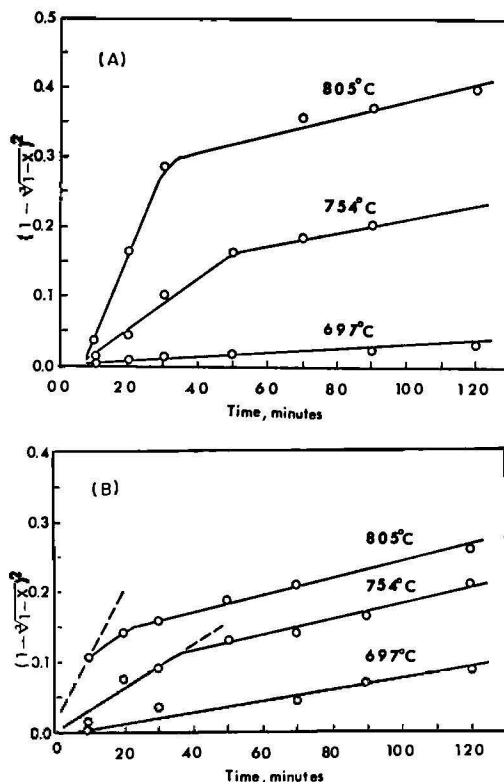It can be seen from Fig. 2 that the d-spacings decreased from 900° to 1150°C at a given composition. It appears that

Fig. 1. Plots of Jander's diffusion equation for the reaction (A) $CdO + \alpha\text{-}Fe_2O_3 \rightarrow CdFe_2O_4$, and (B) $CdO + Mn_2O_3 \rightarrow CdMn_2O_4$.
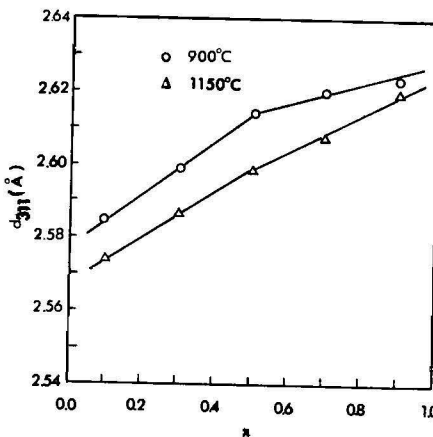
Fig. 2. Variation in (311) d-spacing with composition x for the mixed spinel solid solution $Cd_xMn_{1-x}Fe_2O_4$.

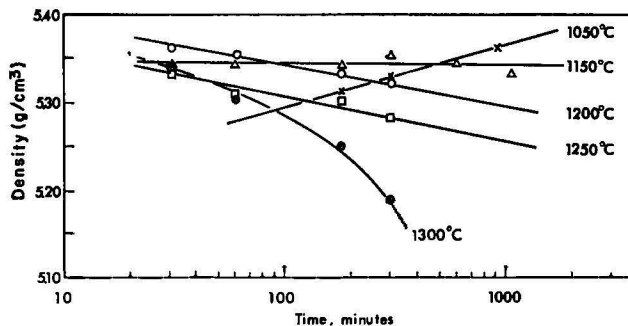Fig. 3. Density vs time for $Cd_{0.5}Mn_{0.5}Fe_2O_4$ sintered at various temperatures.

The Authors

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B. W. Jong is a research engineer in the High Temperature Materials Div. of the Engineering Experiment Station at Georgia Institute of Technology. He received a B.S. in chemical engineering in 1958 from the National Taiwan University and an M.S. in 1966 and a Ph.D. in 1972, in chemical and ceramic engineering, respectively, from the University of Missouri—Rolla. During 1961–64 he was with the Chinese Petroleum Corp.; he was with National Lead Co. during 1966–69. At the time this work was done, Dr. Jong was a research assistant at the Materials Research Center and Ceramic Engineering Dept. at UMR.

P. D. Ownby is associate professor of ceramic engineering and research associate at the Graduate Center for Materials Research at UMR. He received a B.S. from the University of Utah in 1961, an M.S. from UMR in 1962 and a Ph.D. from Ohio State University in 1967, all in ceramic engineering. Before joining the UMR faculty in 1968, he was a research ceramist at the Battelle Columbus Labs from 1963 to 1967.

at 900°C, as tetragonal $CdMn_2O_4$ dissolved in cubic $CdFe_2O_4$, a distorted cubic solid solution was formed while at 1150°C a true cubic solid solution was formed. The parameters a and c were calculated from the d-spacings of the (220) and (311) planes as follows:
at 900°C distorted cubic, $c > a$, $d_{900°C} = a/[(h^2+k^2)+(a/c)^2l^2]^{1/2}$,
yielding:

x	a(Å)	c(Å)
0.1	8.562	8.692
0.3	8.627	8.627
0.5	8.669	8.678
0.7	8.686	8.721
0.9	8.700	8.726

At 1150°C cubic, $c = a$, $d_{1150°C} = a/(h^2+k^2+l^2)^{1/2}$,
yielding:

x	a(Å)
0.1	8.528
0.3	8.576
0.5	8.621
0.7	8.655
0.9	8.686

Therefore, it can be seen that at 900°C, where $c \geq a$, d and a will both be larger than at 1150°C where $c = a$.

Densification Rate

The density vs the logarithm of the sintering times at 1050°, 1150°, 1200°, 1250° and 1300°C is shown in Fig. 3. At 1050°C, the sintered density increased with time according to the relation $\rho = K \ln t + C$. At 1150°C, no time dependence
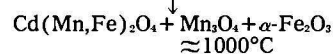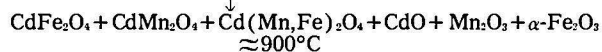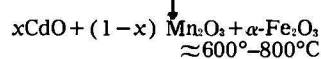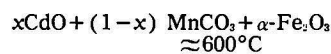
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was observed. The sintered density decreased at 1200°, 1250°, again showing a linear relation with the logarithm of time, but with a negative slope. The specimens were bloated when sintered at 1300°C, and show no linear portion. Once grain growth begins, it exaggerates rapidly, entrapping the remaining pores inside the grains. The sintered density decrease at the higher sintering temperatures appears to result from the volatilization of CdO which enlarges the pores. The results of Höschl et al.[7] on the loss of CdO alone, showed that the loss doubled from 1150° to 1200°C. In the present work, it appears that the densification rate by sintering is just balanced by the density decrease due to CdO loss at 1150°C. Above this temperature the loss mechanism predominates.
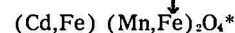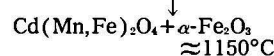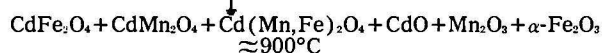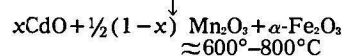
Summary

The reactions $CdO + \alpha\text{-}Fe_2O_3 \rightarrow CdFe_2O_4$ and $CdO + Mn_2O_3 \rightarrow CdMn_2O_4$ were described by Jander's diffusion equation. From this description, the determined activation energies were 70 ± 10 kcal/mole for the cadmium ferrite reaction and 45 ± 5 kcal/mole for the cadmium manganite reaction.

The reaction sequences for the formation of the mixed ferrite $Cd_xMn_{1-x}Fe_2O_4$ from CdO, $MnCO_3$ and $\alpha\text{-}Fe_2O_3$ with ratios of x: $(1-x)$:1 were:

(1) When $0.0 < x \leq 0.5$,

$$xCdO + (1-x) MnCO_3 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 600°C$$
$$xCdO + (1-x) Mn_2O_3 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 600°\text{–}800°C$$
$$CdFe_2O_4 + CdMn_2O_4 + Cd(Mn,Fe)_2O_4 + CdO + Mn_2O_3 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 900°C$$
$$Cd(Mn,Fe)_2O_4 + Mn_3O_4 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 1000°C$$
$$Cd(Mn,Fe)_2O_4 + (Mn,Fe)(Mn,Fe)_2O_4*$$
$$\downarrow \approx 1150°C$$
$$(Cd,Mn,Fe)(Mn,Fe)_2O_4*$$

(2) When $0.5 < x < 1.0$,

$$xCdO + (1-x) MnCO_3 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 600°C$$
$$xCdO + \tfrac{1}{2}(1-x) Mn_2O_3 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 600°\text{–}800°C$$
$$CdFe_2O_4 + CdMn_2O_4 + Cd(Mn,Fe)_2O_4 + CdO + Mn_2O_3 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 900°C$$
$$Cd(Mn,Fe)_2O_4 + \alpha\text{-}Fe_2O_3$$
$$\downarrow \approx 1150°C$$
$$(Cd,Fe)(Mn,Fe)_2O_4*$$
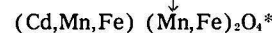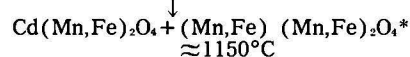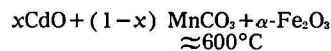
Optimum sintering temperature was 1150°C.

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*The cation distribution here is not yet known, however the last phase for $0.5 < x < 1.0$ was nonmagnetic.[5]