Journal of the European Ceramic Society **15** (1995) 265–269
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0955-2219/95/$9.50

Low Temperature Synthesis of Zinc Ferrite using Hydrazine Monohydrate

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(Received 18 May 1994; revised version received 28 July 1994; accepted 1 August 1994)

Abstract

Crystalline powder of zinc ferrite was synthesized from the mixed solution of $FeCl_2$ *and* $ZnCl_2$ *by adding hydrazine monohydrate solution and aging near room temperature from 30 to 60°C. The temperature condition for this synthesis was the same as that using aqueous ammonia reported previously. However, it was necessary to keep the concentration of metal chlorides below* 1×10^{-1} *mol* dm^{-3} *to obtain zinc ferrite, because hydrazine complexes with metal chlorides in solutions with high concentration. Zinc ferrite was also formed starting with* $FeCl_3$ *solution, probably because hydrazine reduces* Fe^{3+} *partly to* Fe^{2+}*.*

1 Introduction

Hydrazine (N_2H_4) is known to be complexing, strongly reducing and also a basic agent. In the first case, it behaves either as a unidentate ligand as in $BF_3N_2H_4$ or a bidentate bridging ligand as in $Zn(N_2H_4)_2Cl_2$. Its complexes with transition metal salts and lanthanide metal salts have been prepared[1,2] and characterized by infra-red absorption spectroscopy.[3-5] Thermogravimetric studies and magnetic moment measurements on the complexes with nickel salts have been carried out,[6] as has a structural analysis of $Zn(N_2H_4)_2Cl_2$ crystals.[7] As a reducing agent, hydrazine has been widely used for non-electrolytic plating (chemical plating) and for precipitation of metals from solution, e.g. fixing solution of photo films.

For the purpose of ceramic synthesis, however, only a few reports using hydrazine have been presented: hydrazine prevents the formation of ferric oxide on the synthesis of magnetite (Fe_3O_4),[8] and its complexes with metal nitrates are used as a precursor for the zinc nickel mixed ferrite.[9]

In a previous paper,[10] crystalline powder of zinc ferrite was synthesized using ammonia near room temperature. It was formed in the temperature range 30–80°C via an intermeditate phase of so-called green-rust which contains both Fe^{2+}, Fe^{3+} and possibly Zn^{2+}. For this synthesis, the use of Fe^{2+} solution was essential. Only amorphous product was formed from Fe^{3+} solution because of no formation of the green-rust phase.

The development of the synthesis of ceramics at such a low temperature is believed to be important in relation to energy conservation because most ceramic materials have been prepared at high temperatures. In the present work, the synthesis of zinc ferrite powder was attempted using hydrazine monohydrate ($N_2H_4{\cdot}H_2O$). The result was compared with a previous synthesis using ammonia in order to clarify the advantages and disadvantages of the present process.

2 Experimental

The experimental procedure is shown in Fig. 1, being almost the same as the one used previously,[10] except that hydrazine was used instead of ammonia. First, aqueous solutions of metal chlorides $FeCl_2$ and $ZnCl_2$ of reagent grade were prepared separately at a concentration of 5×10^{-2} mol dm^{-3}, and then mixed with each other to give a molar ratio of iron to zinc of 2. The flask containing this reaction solution was set in a temperature controlled water bath with a shaker. Hydrazine monohydrate of reagent grade diluted to a concentration of 4 mol dm^{-3} was added to the mixed solution of metal chlorides at a temperature ranging from 0 to 80°C. After aging of the solution for air oxidation and shaking at a constant speed, the precipitates were filtered, and washed with distilled water and acetone, followed by drying at room temperature.

In order to investigate the effect of the concentrations, metal chloride solutions in the range of 5×10^{-1}–5×10^{-3} mol dm^{-3} and hydrazine monohy-

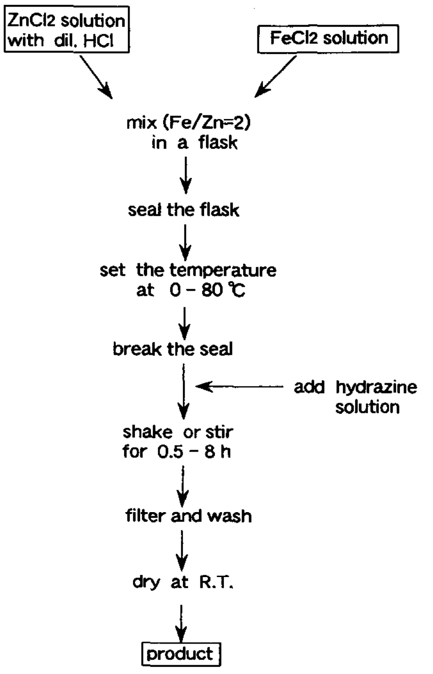

Fig. 1. Experimental procedure.

drate solution without dilution (20 mol dm^{-3}) were used. For the solution with high concentration, magnetic stirring was used in order to mix thick solutions.

The precipitates obtained were examined by X-ray diffraction (XRD) with Co Kα radiation, thermogravimetry coupled with differential thermal analysis (TG–DTA), infra-red spectrometry (IR) and atomic absorption spectrometry.

3 Results and Discussion

3.1 Formation of spinel phase of zinc ferrite

The phases formed in the mixed solutions of $FeCl_2$ and $ZnCl_2$ with a concentration of 5×10^{-2} mol dm^{-3} by adding hydrazine monohydrate solution with a concentration of 4 mol dm^{-3} are summarized in Fig. 2, as functions of temperature and time of aging. The resultant phases are green-rust, spinel and amorphous, as in the case where aqueous ammonia was used.[10]

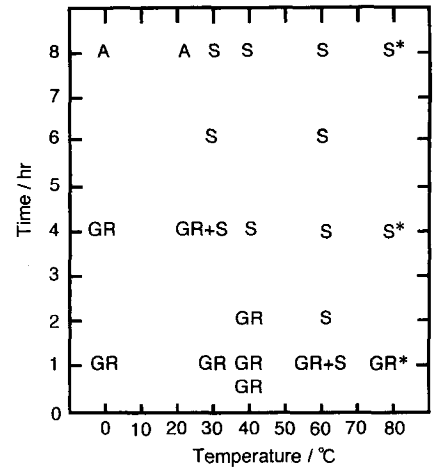

Fig. 2. Formation diagram of the phases as functions of temperature and time for aging. The symbol S stands for spinel-type $ZnFe_2O_4$, GR for green-rust and A for amorphous phase. S* and GR* indicate the coexistence of a small amount of unknown phase with S and GR, respectively. Metal chloride solutions of 5×10^{-2} mol dm^{-3} and hydrazine monohydrate solution of 4 mol dm^{-3} were used.

At the beginning of aging, the green-rust phase is formed at all temperatures. Its XRD pattern gave broad peaks at 13·70° and 27·60° in 2θ (0·75 and 0·375 nm in d-spacing, respectively).

By further aging, the formation of zinc ferrite spinel was observed above 30°C. The line profiles of XRD patterns for the spinel phase are rather broad, as shown in Fig. 3. The crystallinity of the spinel phase was improved with increasing aging temperature. The half-maximum breadth of 311 lines for the products at 30 (Fig. 3(a)), 40 and 60°C (Fig. 3(b)) after 8 h of aging were 1·3°, 0·91° and 0·74° in 2θ, respectively. At 80°C, another phase which cannot be

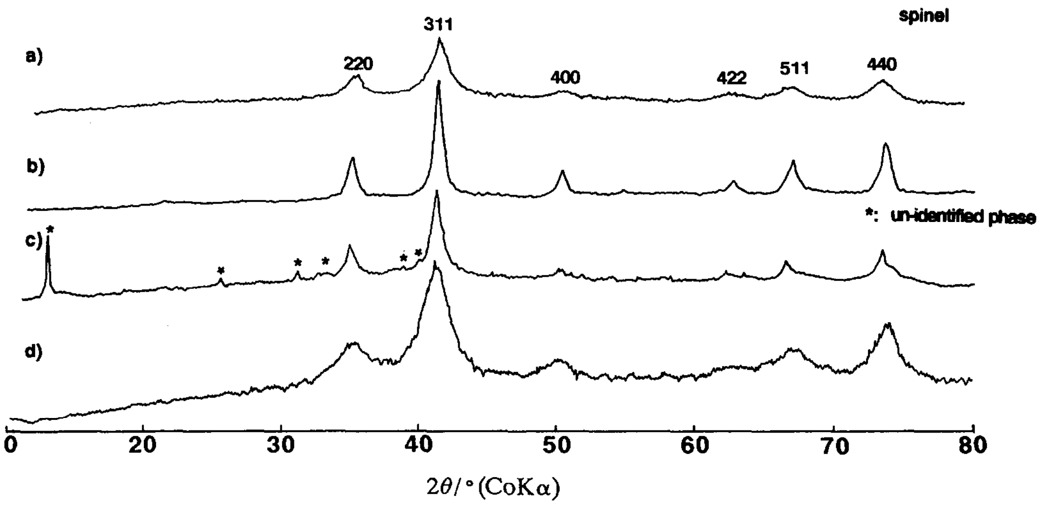

Fig. 3. X-ray powder patterns for the spinel phase synthesized from $FeCl_2$ solution at (a) 30°C, (b) 60°C, (c) 80°C and (d) that from $FeCl_3$ at 80°C.

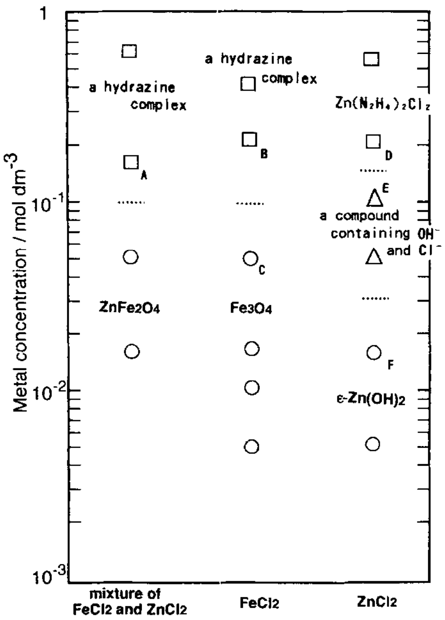

Fig. 4. The phases formed from the mixed solutions of $FeCl_2$ and $ZnCl_2$ (Fe/Zn = 2), $FeCl_2$ solutions and $ZnCl_2$ solutions with hydrazine monohydrate solution at 4 mol dm^{-3} by aging at 40°C for 4 h as a function of concentration of metal chloride solution.

identified from XRD powder patterns was formed in addition to the spinel phase (Fig. 3(c)). This seemed to be closely related to the fact that the evaporation of the reaction solution was remarkable at 80°C, suggesting that the concentration of metal ions and also anions were changed during aging, which brought considerable effect to the product phases. The relationship between the metal concentration of the solutions and products is discussed below.

The chemical analysis by atomic absorption spectrometry showed that the spinel obtained was zinc ferrite having the Fe/Zn ratio of 2·05–2·20.

Amorphous phase was formed by aging at 0°C for 8 h and it did not change to spinel phase without heating above 400°C.

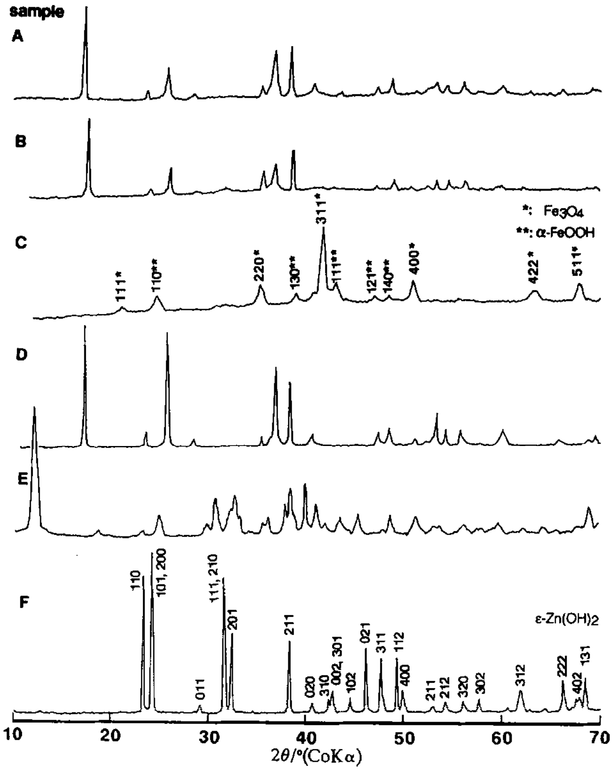

Fig. 5. X-ray powder patterns of the samples A to F of which the formation conditions are shown in Fig. 4.

3.2 Starting with $FeCl_3$

Starting with $FeCl_3$ solution, broad peaks of zinc ferrite appeared on XRD patterns by the reaction at 80°C (Fig. 3(d)). At 40°C, however, they were too broad to be detected. This result is a distinct difference from the previous one[10] where only amorphous phase was obtained by the addition of ammonia to the solution of $FeCl_3$. Using hydrazine, however, spinel phase was obtained even from $FeCl_3$ solution, probably because Fe^{2+} was produced by the strong reducing action by hydrazine.

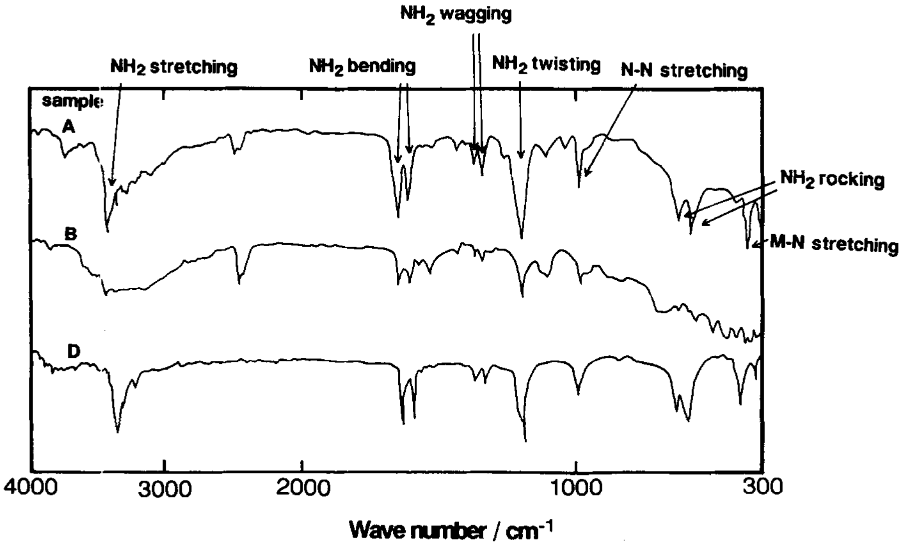

Fig. 6. IR spectra of samples A, B and D in Fig. 4.

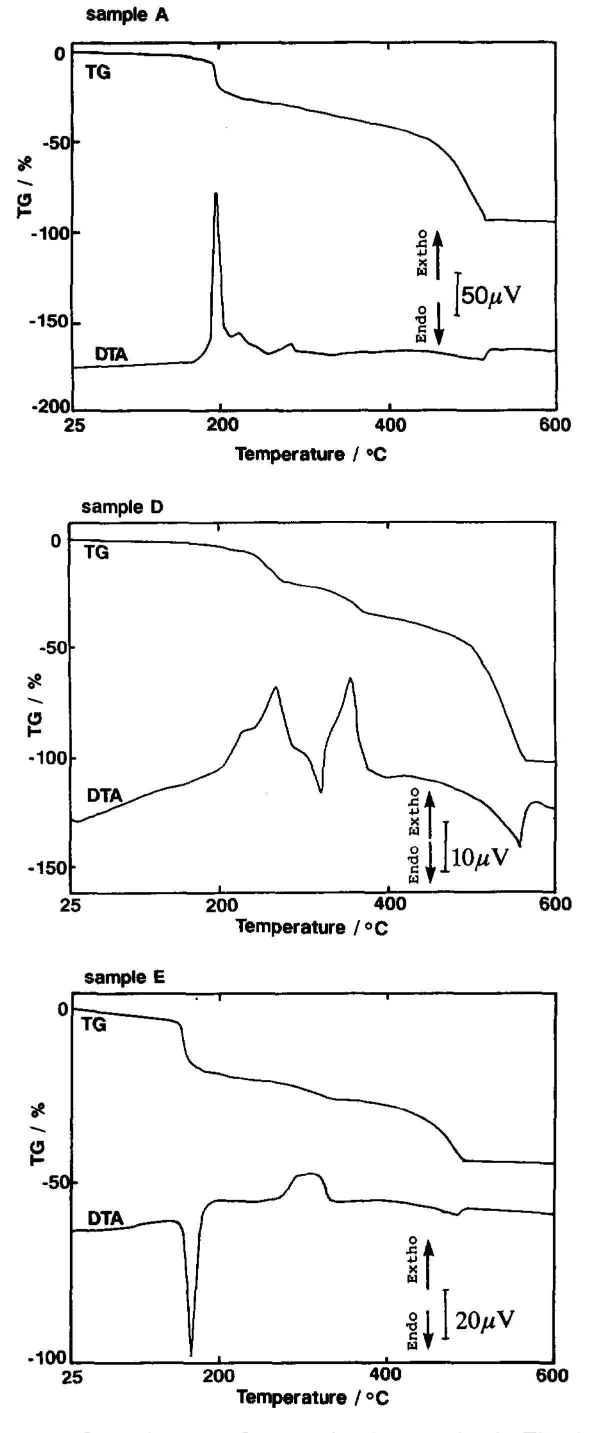

Fig. 7. TG-DTA curves for samples A, D and E in Fig. 4.

3.3 Effect of concentration

The relationship between the concentration of metal chloride solutions and the phases formed was investigated. The experimental results at 40°C after aging for 4 h are summarized as a function of metal chloride concentration in Fig. 4, by showing the concentration range for different phases which were deter mined from XRD, IR and TG–DTA studies.

It is clear that the products depend on the concentration of the starting solutions and that the borderlines are located around 1×10^{-1} mol dm^{-3} for the metal chloride solutions. Another line is present around 3×10^{-2} mol dm^{-3} for $ZnCl_2$ solution. The products shown by A to F in Fig. 4 were studied in detail in order to identify their phases.

The products formed in the solutions with low concentration are identified to be $ZnFe_2O_4$ (which has been described in Section 3.1), Fe_3O_4 (sample C) and ϵ-$Zn(OH)_2$ (sample F), respectively, from their XRD patterns (Fig. 5). The other products are not identified by XRD. Only sample D is considered to be a hydrazine complex because the d-spacings of diffraction peaks coincided with those reported for $Zn(N_2H_4)_2Cl_2$[7] though the relative intensities were different. In addition, samples A and B are also supposed to be complexes because the patterns obtained for samples A, B and D are all very similar.

For these products, IR and TG-DTA measurements were carried out and the results are shown in Figs 6 and 7, respectively.

Samples A, B and D give IR absorption peaks attributed to stretching, bending, wagging and twisting in the NH_2 group and stretching of N–N and metal–N bonds (Fig. 6), according to previous work.[6] These experimental results strongly suggest that they are the hydrazine complexes with respective metal chlorides. Characteristic sharp and strong exothermic peak, accompanying certain weight loss, observed in their TG–DTA curves also showed the existence of hydrazine in the products. TG–DTA curve of sample A is shown in Fig. 7. This exothermic peak has been considered to be due to the oxidation of liberated hydrazine to nitrogen oxides.[11] The result of sample B was very similar to that of sample A. Sample D in Fig. 7 shows slightly different behavior; the exothermic peaks are not so large and sharp. From this sample after heating above 550°C, nothing was left probably because the complexes released hydrazine to return to metal chloride which evaporated out above 500°C.

Sample E was not suggested to be a hydrazine complex, especially because of its IR spectrum which did not show any absorption peaks corresponding to the NH_2 group. On its TG–DTA curve (Fig. 7), a very strong endothermic peak, instead of an exothermic one on hydrazine complexes, is seen. This peak can be attributed to a dehydration reaction which had been observed in sample F. After heating up to 600°C, sample E gave ZnO powder, which was in contrast with sample D. As the common points among TG–DTA curves of samples D and E, a gradual weight loss above 400°C and an endothermic peak around 550°C are seen, suggesting the presence of $ZnCl_2$ component in sample E. These results suggest that the product E is the compound having both OH^- and Cl^-.

4 Concluding Remarks

Making use of a property of hydrazine as a base, crystalline powder of zinc ferrite was obtained after aging at a temperature between 30 and 60°C though the crystallinity was rather inferior to that prepared in the same temperature range by using aqueous ammonia.[10] The concentration of starting metal chloride solutions was required to be below 1×10^{-1} mol dm^{-3} to prevent the formation of hydrazine complexes, which did not change to zinc ferrite either by aging or by heat treatment at high temperatures.

By using the strong reducing ability of hydrazine, zinc ferrite was obtained even starting with $FeCl_3$ solution, which was very advantageous compared to the use of aqueous ammonia.

Acknowledgement

This work was partly supported by a Sasagawa Scientific Research Grant from The Japan Science Society, Tokyo.

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