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Weight Losses from Zinc Ferrite and Nickel Ferrite During Sintering

C. J. RIGDEN
Department of Physics, Portsmouth College of Technology, Hants, UK

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The sintering in air of fully formed zinc ferrite and nickel ferrite is always accompanied by a loss of weight from the ferrite, caused by removal of some oxygen. Although the rate of weight loss from the ferrite has the same time and temperature dependence as the rate of shrinkage of the specimens, it is found that altering the loss of weight by changing the oxygen pressure has little effect on the sintering of fully formed ferrites. Criteria are established for the preparation of high density and high resistivity sintered ferrites.

1. Introduction

The production of dense ferrite suitable for electrical and microwave use requires the use of a high sintering temperature, usually above the temperature at which the ferrite begins to decompose. The electrical resistance of sintered nickel ferrite decreases as the sintering temperature is increased and this is attributed to a loss of oxygen from the specimen during sintering [1].

The temperature required to attain near X-ray density is such that the decomposition of the nickel ferrite causes the electrical resistance to fall to $\sim 10^2$ ohm cm (from a maximum resistance $\gtrsim 10^7$ ohm cm) even under high oxygen pressures during sintering.

The aim of the present investigation was to determine whether oxygen loss from ferrite during sintering is necessary for the sintering process to take place, by measuring the interdependence of densification and weight loss, and by observing the effect on the densification of suppressing the weight loss by using various oxygen pressures over the specimen during sintering.

These experiments must be performed with starting materials which are fully formed stoichiometric ferrite powders since (a) the rate of densification is influenced by the chemical reaction if this occurs concurrently, and (b) during the chemical reaction between simple oxides to form ferrite, oxygen is lost [2]. If sintering and chemical reaction occur together it is impossible to distinguish the weight loss due to sintering, if any, from that due to chemical reaction.

Thus for this investigation it is necessary to use a ferrite powder which can be fully formed chemically at a temperature below which appreciable sintering occurs.

It is found that zinc ferrite fulfils this condition. Zinc ferrite can be formed stoichiometrically from zinc oxide plus ferric oxide at 830° C in air, and little sintering occurs at this temperature. Hence the densification of fully formed ferrite can be studied, and in addition to information of weight losses during sintering, information on the kinetics of sintering of fully formed ferrite can be compared to the densification of unreacted mixtures of zinc oxide and ferric oxide compacts.

2. Experimental

The experiments were performed on materials prepared from "Specpure" grade zinc oxide and ferric oxide. These oxides were mixed in the ratio $ZnO : Fe_2O_3 = 1 : 1$ and ball-milled for 24 h. The grain-size after milling was ~ 2 μm diameter. The powders were reacted to form zinc ferrite after thermogravimetry and X-ray analysis had determined the optimum conditions for formation.

Cylindrical compacts, approximately 0.95 cm diameter and 0.7 cm length, of both reacted and unreacted powders, were pressed. The pressure used to compact the powders was below that at which pressure cones were formed, giving initial densities ~ 3.3 g/cm^3.

The specimens were placed on a platinum sheet and this was weighed with the specimens before and after each firing. The firing times at given temperatures varied from 5 min to 24 h. The platinum sheets did not change weight throughout a series of up to 20 firings. From the recorded weight losses δ is calculated where δ = number of oxygen atoms lost per $ZnFe_2O_4$ formula unit. The dimensions of the specimens were measured with a travelling microscope, and so the compacts were not handled between firings. The density, D, was calculated from the measured mass and dimensions of the specimens, and the relative shrinkage

$$\frac{\Delta V}{V_0} = \frac{V_0 - V}{V_0},$$

was calculated from

$$\frac{\Delta V}{V_0} = \frac{\Delta D}{D} = \frac{D - D_0}{D},$$

where V and D = volume and density of specimen after firing, and V_0 and D_0 = initial volume and density of specimen.

Experiment showed that for identical zinc ferrite powders, fired at the same temperature, the variation of $\Delta V/V_0$ with time was the same for compacts with initial densities ranging from 3.2 to 3.5 g/cm³.

3. Results

3.1. Kinetics of Sintering of Fully Formed Zinc Ferrite Compacts

Fig. 1 shows the variation of relative shrinkage, $\Delta V/V_0$, with time, t, for samples of fully formed zinc ferrite sintered in air. The shrinkage appears to tend to a maximum which is determined by the temperature, T, of firing.

Graphs of log $\Delta V/V_0$ against log t at a given temperature and log $\Delta V/V_0$ against $1/T$ at a given time, both give straight line relationships, the slope of the former being independent of T and the latter of t. Hence it is concluded that

$$\frac{\Delta V}{V_0} = k\,e^{-Q/RT}\,t^n.$$

Fig. 2 shows the agreement between this equation and experiment. This equation is obeyed until 85% of X-ray density is reached.

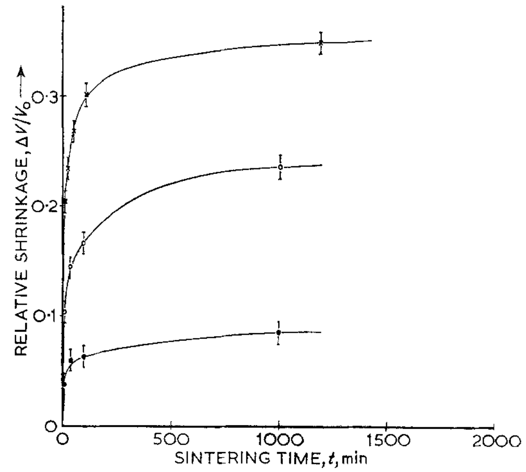

Figure 1 Graph of relative shrinkage, $\Delta V/V_0$, against time of sintering, t, for fully formed zinc ferrite. Temperatures of sintering: ● = 966° C, ○ = 1110° C, × = 1225° C.

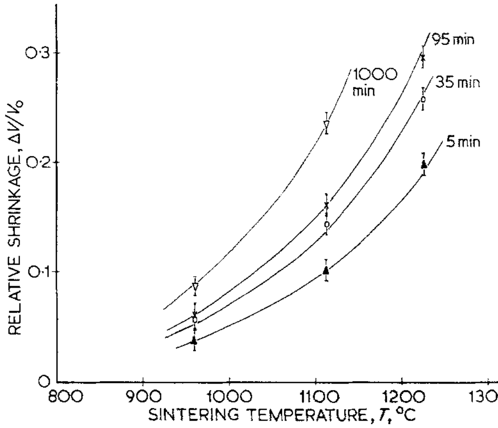

Figure 2 Graph of relative shrinkage, $\Delta V/V_0$, against temperature of sintering, T, after given times of sintering of fully formed zinc ferrite. The drawn lines represent the curve calculated from $\Delta V/V_0 = K\,e^{-Q/RT}\,t^n$ with $Q = 23$ Kcal/mol and $n = 1/6.3$, after 5, 35, 95 and 1000 min of sintering. Experimental points: ▲ = after 5 min sintering, ○ = after 35 min sintering, × = after 95 min sintering, ▽ = after 1000 min sintering.

3.2. Weight Losses from Fully Formed Zinc Ferrite during Sintering

Fully formed zinc ferrite begins to lose weight at temperatures above 850° C in air and since little sintering occurs below this temperature, sintering is always accompanied by a weight loss.

The relationship between relative shrinkage $\Delta V/V_0$ and oxygen loss, δ, is shown in fig. 3, at different temperatures. From fig. 3 a straight line relationship is found and the slope of the line is independent of the temperature of sintering, i.e. $\Delta V/V_0 = C\delta$, where C is a constant independent of temperature.

At the highest practical temperature of

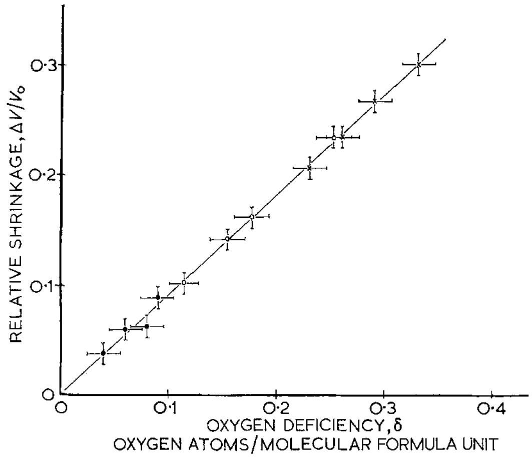

Figure 3 Graph of relative shrinkage, $\Delta V/V_0$, in air, against oxygen deficiency, δ, for fully formed zinc ferrite. All specimens mass = 1 g. Temperatures of sintering: ● = 966° C, ○ = 1110° C, × = 1225° C.

sintering (1230° C) the weight loss continued after the specimen had reached near X-ray density. Only weight changes after the first firing are meaningful since some handling of the specimens before the first firing is unavoidable.

Although C is independent of temperature it is affected by the partial pressure of oxygen over the specimen during firing, the value of C being larger for higher oxygen pressures. The shrinkage of fully formed ferrite is found to be independent of atmosphere. The value of C is dependent on the specimen size. The relative shrinkage with respect to time is independent of specimen size and δ is found to be proportional to the specimen surface area rather than the specimen mass.

It is concluded, therefore, that a loss of weight is not necessary for densification, although the process of weight loss is related to the process of sintering.

3.3 Shrinkage of Unreacted Compacts

The relative shrinkage with respect to time, of unreacted zinc oxide plus ferric oxide compacts is shown in fig. 4. The chemical reaction process appears to inhibit the densification process, there being an initial increase in dimensions. Also shown in fig. 4 is the variation of shrinkage under different oxygen pressures. In this case, the higher the oxygen pressure over the specimen during sintering the less is the shrinkage. The linear relationship between $\Delta V/V_0$ and δ is not observed for unreacted compacts, though weight is lost during firing (more than in the corresponding firing of fully reacted compacts).

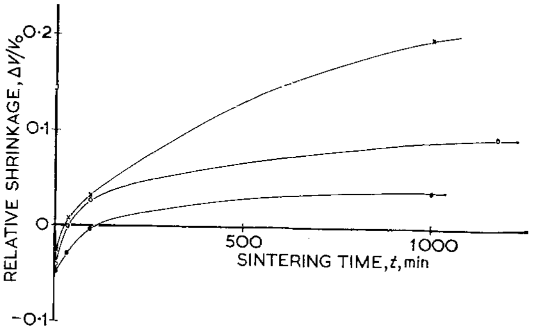

Figure 4 Graph of relative shrinkage, $\Delta V/V_0$, against time of sintering, t, for unreacted zinc oxide and ferric oxide compacts at 1100° C. Atmosphere over specimens during sintering: ● = oxygen flow, ○ = air, × = nitrogen flow.

3.4. Sintering of Nickel Ferrite

The sintering of fully formed nickel ferrite compacts is always accompanied by a weight loss in air, and as in the zinc ferrite case, a linear relationship between $\Delta V/V_0$ and δ is found, the constant of proportionality being independent of temperature. Changes in the oxygen pressure over the specimen during sintering, influence δ, but do not affect the shrinkage, unless the oxygen pressure is so low that δ becomes very large ($\delta > 0.05$ atoms of oxygen/molecular formula unit) and the nickel ferrite phase decomposes to two phases of nickel ferrous ferrite and nickel oxide and then shrinkage is enhanced.

Appreciable sintering takes place above 1050° C and at this temperature the chemical reaction $NiO + Fe_2O_3 \rightarrow NiFe_2O_4$ is not complete. Thus the true relationship describing the kinetics of sintering of fully formed nickel ferrite cannot be obtained.

4. Conclusion

The sintering of fully formed zinc ferrite, obeys the same kinetic equation as does the sintering of other oxides such as ZnO or Al_2O_3:

$$\frac{\Delta V}{V_0} = k\,e^{-Q/RT}\,t^n\,,$$

where n and k are independent of temperature. The activation energy $Q = 23$ kcal/mole.

Sintering of formed zinc ferrite and formed nickel ferrite in air is accompanied by a weight loss. Although the weight loss may be due to the material tending to an equilibrium composition phase at a given temperature, there appears to be a definite relationship between the relative shrinkage, $\Delta V/V_0$, and the weight loss, δ, from the specimen i.e. $\Delta V/V_0 = C\,\delta$, where C is independent of temperature. This implies the same time and temperature dependence of shrinkage and weight loss.

Reducing the weight loss by applying a higher partial pressure of oxygen does not hinder the sintering of fully formed zinc or nickel ferrites. However, application of a high oxygen pressure to unreacted compacts inhibits densification of these compacts, though this may be due to the effect of the higher oxygen pressure on the chemical reaction which affects the sintering.

To produce a dense stoichiometric zinc ferrite specimen, the ferrite should be fully formed at ~ 830° C in air and then sintered under as high an oxygen pressure as possible for a time just sufficient for maximum density to be attained at the temperature of sintering chosen ($T \gtrsim 1150\,^{\circ}$C).

Acknowledgement

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