JOURNAL OF MATERIALS SCIENCE 24 (1989) 402–408

Reactive sintering of manganese ferrite

F. J. C. M. TOOLENAAR, M. T. J. VAN LIEROP-VERHEES
Phillips Research Laboratories, PO Box 80000, 5600 JA Eindhoven, The Netherlands

The reactive sintering of manganese ferrite, i.e. the concurrence of a chemical reaction with densification during firing, has been studied using several raw materials. It was shown that the formation reaction from the raw materials is always accompanied by expansion and that such processing invariably results in a less dense end product. After calcining the powder, these phenomena did not occur. This was shown to be related to an improved initial homogeneity rather than to the degree of conversion. On the other hand, calcining increased the change of excessive grain growth, which was further influenced by the porosity, the firing temperature and the presence of impurities.

1. Introduction

In a previous paper [1] we described the effect of the formation reaction of zinc ferrite on a sumultaneously occurring sinter process. During the reactive (or "green") sintering the median pore size was increased prior to the densification step. As a consequence, the number of pores that could be removed in the sinter process was reduced, which lowered the final density. This increase of the pore size was thought to occur during the formation reaction by the solution of the zinc oxide particles into those of iron oxide.

In this paper we present an extension of the reactive sintering experiments to the manganese ferrite system. Besides its importance in many practical applications, this system has features that make it a suitable model system additional to zinc ferrite. Most important is the possibility of influencing the occurrence of the formation reaction, which is possible because the spinel structure can only exist with Mn^{2+}. Oxidation to Mn^{3+} will occur in air at intermediate temperatures (between 500 and 1000° C), while Mn^{2+} is the stable form in nitrogen.

The objective of this paper is limited to evaluating the effects of chemical reactions on the development of the microstructure during sintering. In order to identify side effects like those originating from impurities or inhomogeneities, we used three types of iron oxide and two types of manganese carbonate.

2. Experimental procedure

The iron oxides were, as before [1]: one from BASF, the same after calcining and a Ruthner type from Hoogovens; they are referred to as BASF, calcined BASF and Ruthner. We used two (commercial) manganese carbonates: one from GFE (Gesellschaft für Electrometallurgie mbH, Düsseldorf, West Germany) and one from Sedema (Tertre, Belgium). The powder characteristics and main impurities are collected in Table I. The processing was as follows. The reactants were first mixed by ball-milling for 4 h in isopropanol. The powder was then calcined by heating for 4 h at 900° C in nitrogen or air followed by ball-milling for 4 h in isopropanol. After consolidation the resultant tablet with a diameter of 26 mm was isostatically repressed at 100 MPa. Finally it was fired for 4 h at the top temperature in nitrogen air. With "green sintering" the calcining step was omitted, but the powder was in that case mixed twice in isopropanol to obtain the same homogenizing effect. Further details of processing and analysis have been published previously [1].

3. Results

The primary particle size of the GFE powder (as calculated from the specific surface area, see Table I) appeared to be smaller than that of the Sedema powder, but both powders showed a high degree of agglomeration (see Fig. 1). The mixtures calcined in nitrogen showed virtually full conversion into spinel, while those calcined in air contained only Fe_2O_3 and Mn_2O_3.

The conversion into spinel upon sintering pellets in nitrogen was hardly influenced by the type of iron oxide or manganese carbonate. The Ruthner iron oxide and the Sedema manganese carbonate seemed

TABLE I Raw materials

	$MnCO_3$*		Fe_2O_3†		
	(A)	(B)	(a)	(b)	(c)
A_N‡	80	16	20	2.5	3.0
D_N§	0.025	0.12	0.06	0.5	0.4
Purity	99.99	99.8	99.96	99.9	99.5
Na	< 0.06	0.1	< 0.01	< 0.01	0.02
Si	0.0006	0.0004	0.002	0.003	0.009¶
Ca	< 0.05	0.085	< 0.001	< 0.001	0.009
Cl¶	< 0.001	< 0.001	< 0.001	< 0.001	0.085

*(A): GFE manganese carbonate.
(B): Sedema manganese carbonate.
† (a): BASF iron oxide.
(b): *idem* calcined at 700° C in air.
(c): Ruthner iron oxide.
‡ Specific surface area from BET in $m^2 g^{-1}$.
§ Particle size from A_N in μm.
‖ By spectrochemical analysis in wt % (unless otherwise indicated).
¶ By chemical analysis in wt %.

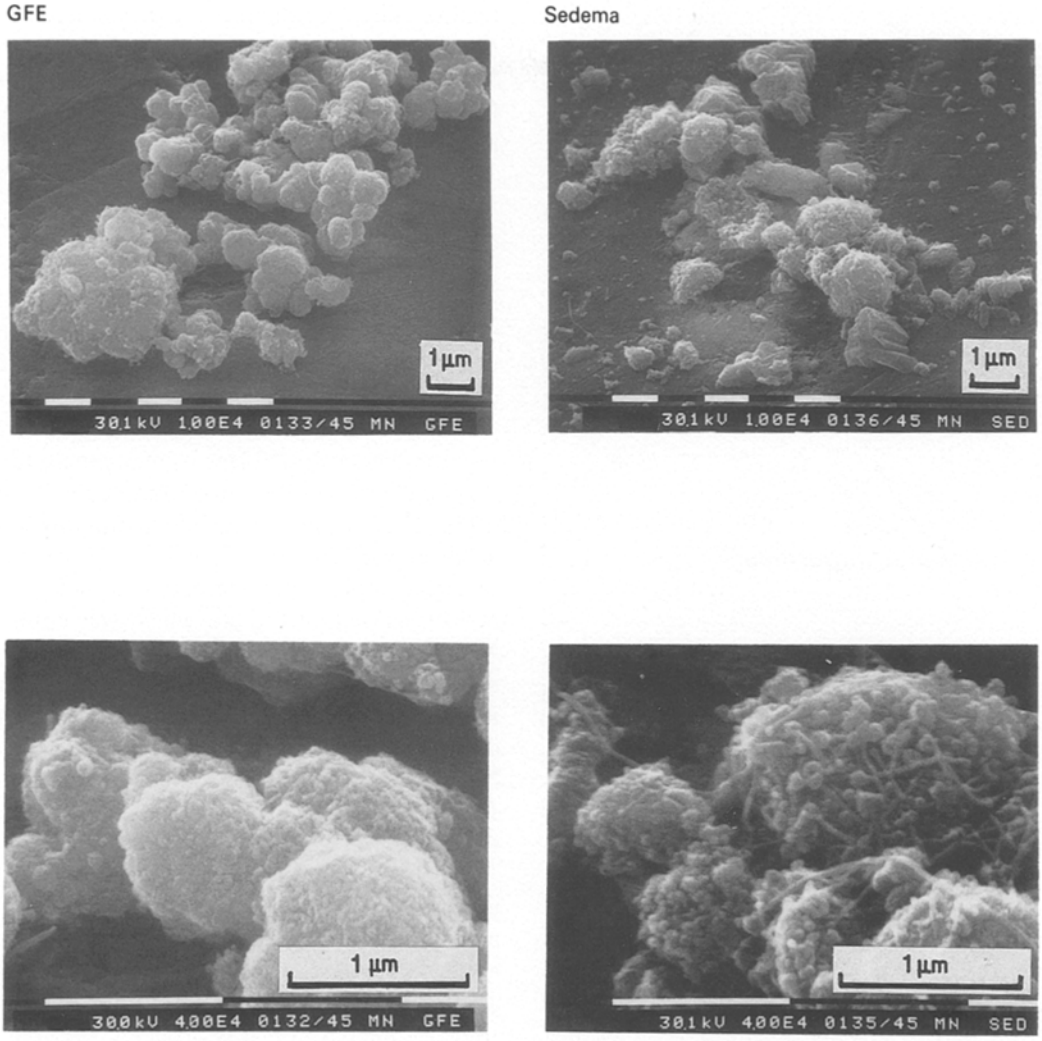

Figure 1 SEM pictures of the manganese carbonates.

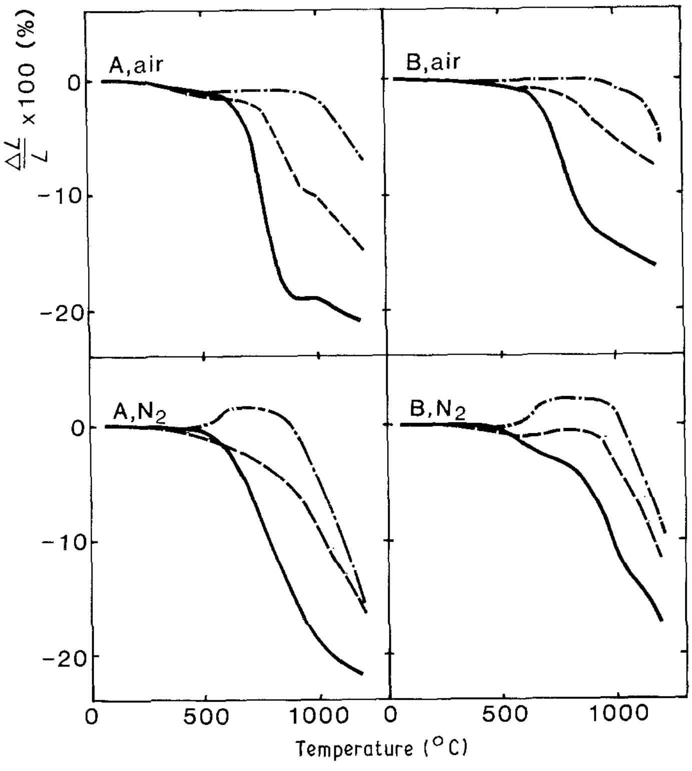

Figure 2 Densification of non-calcined mixtures. The type of manganese carbonate (A = GFE, B = Sedema) and the sinter atmosphere are indicated; the curves represent the various iron oxides: —— BASF, - - - calcined BASF, —·—·— Ruthner.

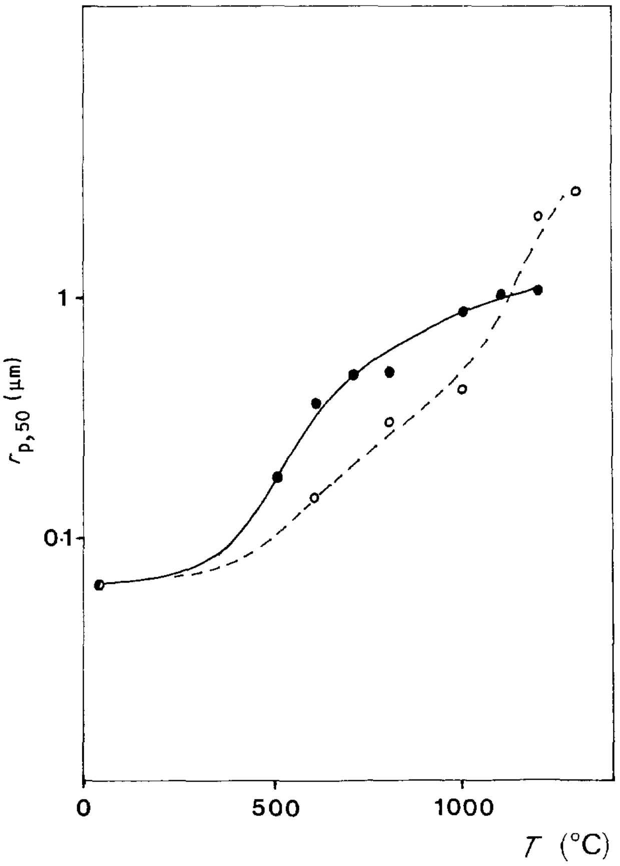

Figure 3 The median pore size $r_{p,50}$ as a function of the sinter temperature of samples of non-calcined mixtures of GFE-MnCO$_3$ and Ruthner-Fe$_2$O$_3$ after firing in: —●— nitrogen, – – -○- – – air.

to have a lower temperture of conversion, but any effect was only minor. The densification, on the other hand, was strongly influenced by the type of material. In Fig. 2 the densification of the various mixtures of the non-calcined materials is shown by their dilatometer curves in air and in nitrogen. The expansion which has been observed upon the formation of zinc ferrite when Ruthner iron oxide was applied is reproduced here with the formation of manganese ferrite, but only if nitrogen is used as a sinter atmosphere. Apart from this atmosphere effect, however, the results obtained before were confirmed. Also reproduced is the significantly higher temperature of densification when Ruthner iron oxide is used. The type of manganese carbonate was shown to have an additional influence on the temperature of densification: the GFE material with the smaller primary particle size induced a lower densification temperature.

To obtain more insight into the development of the microstructure during the first stages of densification, samples were analysed by means of mercury intrusion porosimetry. In Fig. 3 the median pore size is plotted against the sinter temperature. As can be seen, an extra increase of this pore size was observed after firing in nitrogen, i.e. when the formation reaction had occurred.

The final density that could be obtained after sintering non-calcined mixtures to manganese ferrite in air was much smaller than that obtained with zinc ferrite. Even after firing at 1350° C, the highest density achieved was not more than 85%. The microstructure of such samples often showed a second-phase pattern of iron oxide (see Fig. 4), which was confirmed with X-ray diffractograms of these samples. Yet this was not the cause of the high porosity. After sintering in nitrogen no second phase was observed, while X-ray diffractograms confirmed a full conversion into spinel. Nevertheless, the porosity still amounted to more than 10%, even after firing at the highest temperature (1350° C).

When sintering material that had been calcined in nitrogen (and thus almost fully converted into spinel) no expansion was observed in the dilatometer curves, either in air or in nitrogen (see Fig. 5). Yet also with air-calcined material, which did not contain any spinel, no expansion was observed (see Fig. 6).

Another aspect observed with calcined materials was that the differences encountered upon applying the various oxides were strongly reduced (cf. Figs 2 and 5). The mixtures which had Ruthner iron oxide as a base material revealed even a shrinkage at a somewhat *lower* temperature than those with either type of BASF iron oxide, in complete contrast with the case of the non-calcined materials.

Figs 7 and 8 give some examples of the effect of the various parameters on the final microstructures. Fig. 7a shows a typical microstructure after "green

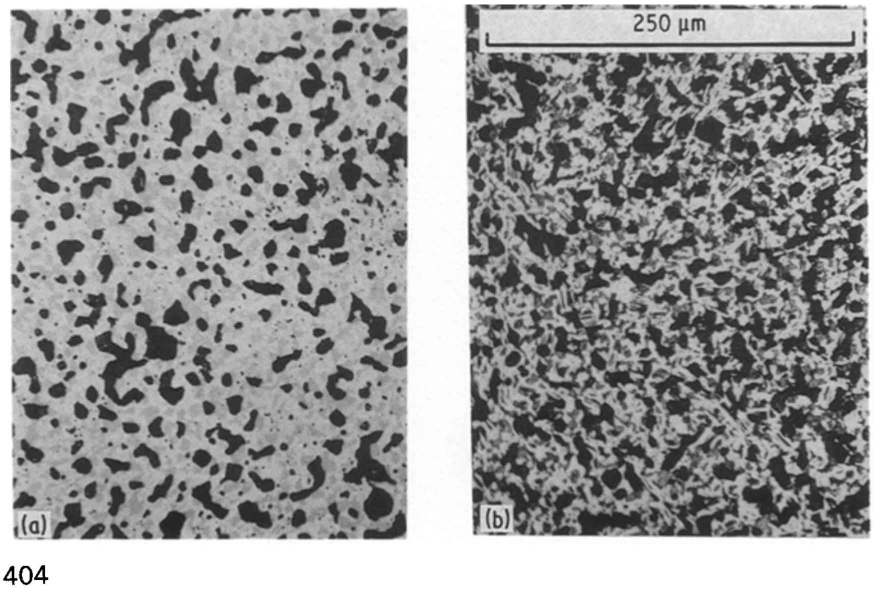

Figure 4 The microstructures (non-etched and etched) of a non-calcined mixture of GFE-MnCO$_3$ and BASF-Fe$_2$O$_3$ after firing at 1300° C in air (ϱ = 3.98 g cm^{-3}). The white spots indicate a second phase of iron oxide.

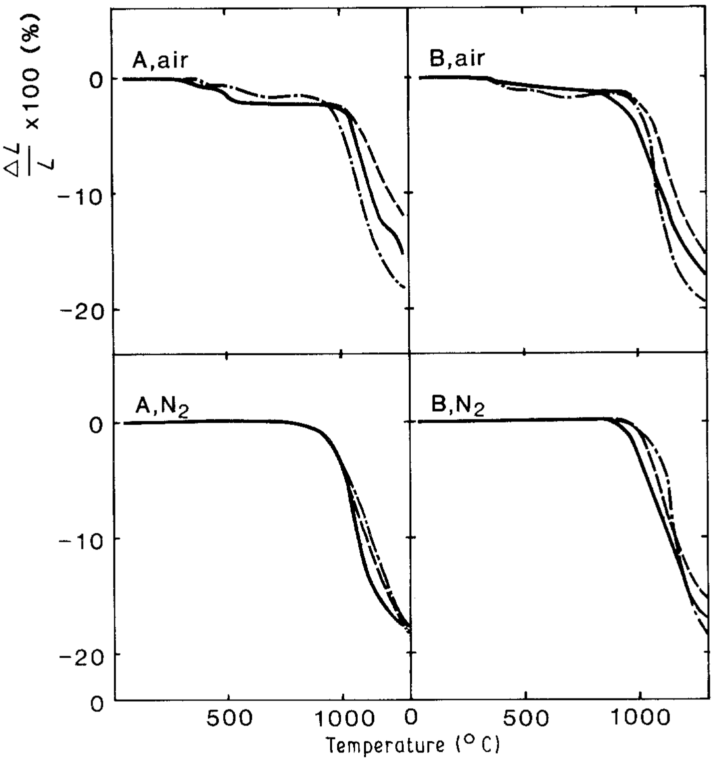

Figure 5 Densification of nitrogen-calcined samples. The type of manganese carbonate (A = GFE, B = Sedema) and the sinter atmosphere are indicated; the curves represent the various iron oxides: —— BASF, - - - calcined BASF, –·–·–·– Ruthner.

sintering": no excessive grain growth, but large pores with the size of the grains after sintering at 1350° C in nitrogen resulting in a density of 80%. Fig. 7b shows the effect of calcining: after firing at 1200° C a much higher density (93%) with even smaller grains is obtained. Fig 7c shows the occurrence of excessive grain growth: after sintering at 1300° C in air the same density is obtained, but in spite of the large pores excessive grain growth has occurred. Fig. 8 shows the effect of the raw materials: the microstructure of two different mixtures which had been treated identically (calcined and subsequently fired at 1300° C in nitrogen) resulted in equal overall densities of about 97% of the theoretical density. Yet only one material (with Ruthner iron oxide) showed the occurrence of excessive grain growth.

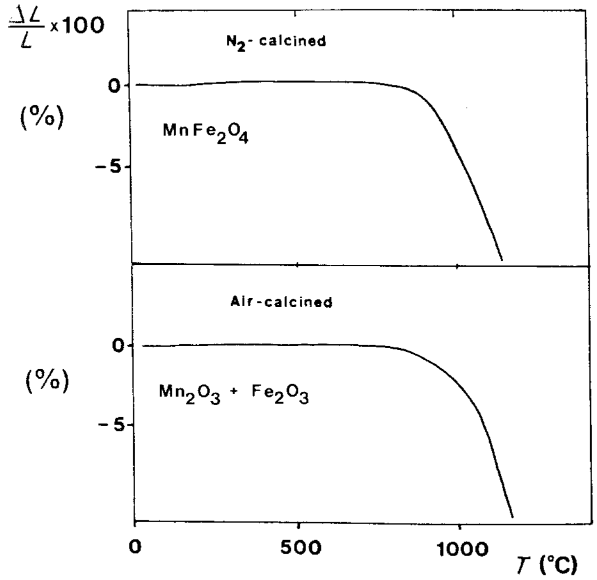

Figure 6 Densification in nitrogen of calcined mixtures of GFE-$MnCO_3$ and Ruthner-Fe_2O_3. The calcination atmosphere and the resulting chemical composition at the start of the experiment are indicated.

4. Discussion

4.1. Sintering during formation

The formation of manganese ferrite has been studied before [2–5], although less often than that of zinc ferrite. Diffusion of manganese is slower than that of zinc, but it is still considered the fastest diffusing species during ferrite deformation [4]. The spinel formation depends strongly upon the oxygen content of the sinter atmosphere. In air, Mn^{3+} is reduced to Mn^{2+} above a temperature of 900° C. Consequently, spinel can be formed only above this temperature. In practice, full conversion is not observed until above 1200° C. In nitrogen, Mn^{2+} is not oxidized and ferrite formation is observed above 650° C [5].

In Fig. 9 the most significant results are collected. Whenever conversion to spinel occurred in "green sintering", dilatometer experiments revealed an expansion. This was most clear when the formation reaction occurred before any significant densification had started, but even when they coincided and no macroscopic expansion was observed, the derivative curves of the dilatometer experiments showed clear maxima indicating that the expansion was only *seemingly* suppressed, just as before [1]. Likewise, the occurrence of extra pore growth was shown to coincide with the formation reaction. It is not surprising, then, that when a mixture of manganese carbonate and iron oxide was sintered in air, no expansion was observed. In that case the formation reaction does not occur until the temperature has been raised to well over 1000° C.

An analysis by comparing pore and particle size data, as performed with the reactive sintering of zinc ferrite [1], was not meaningful here because of the large surface areas and consequent low-temperature densification of the manganese reactants. In view of the other results, however, it does not seem far-fetched to assume that the same mechanism as with zinc ferrite is operative here. In that case it was shown that the stacking of the particles, as expressed by the

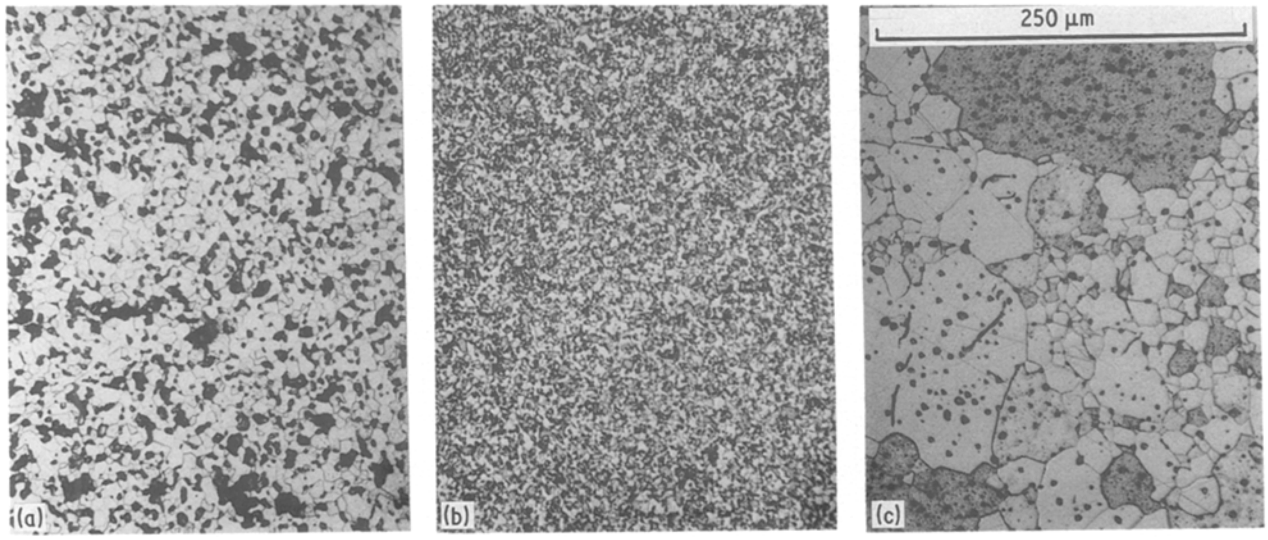

Figure 7 The etched microstructures of mixtures of GFE-$MnCO_3$ and Ruthner-Fe_2O_3: (a) non-calcined; firing: 1350° C in nitrogen ($\varrho = 3.98\,g\,cm^{-3}$). (b) calcined in nitrogen; firing: 1200° C in nitrogen ($\varrho = 4.61\,g\,cm^{-3}$). (c) calcined in nitrogen; firing: 1300° C in air ($\varrho = 4.62\,g\,cm^{-3}$).

$D_N/r_{p,50}$ ratio, was deteriorated by the solution of the zinc oxide particles into those of iron oxide during the formation reaction [1]. The agglomerates of manganese carbonate are to be considered now as large particles, which are solving into iron oxide during the formation reaction. As a result, pores of about the size of the original agglomerates are left behind, and cannot be removed during the subsequent densification process due to their too high coordination number [6]. The extra increase of the pore size during the formation reaction corroborates this picture. It is further supported by the observed expansion, just as with zinc ferrite: a less ideal packing evidently requires more volume. In view of the molecular volumes involved, this is even more striking here, as the formation of manganese ferrite from manganese carbonate and iron oxide should be accompanied by a volume *decrease* of more than 30%. Instead a (linear) *expansion* of a few per cent is observed. This confirms the conclusion of the previous paper [1] that the formation reaction deteriorates the starting position for the subsequent densification.

The final density that could be obtained with non-calcined mixtures of $MnCO_3$ and Fe_2O_3 was significantly lower than that with mixtures of ZnO and Fe_2O_3. This was caused in the first place by the evolution of CO_2 upon the decomposition of $MnCO_3$ below 500° C. This loss of material is necessarily accompanied by an increase of the initial porosity. Further, the effective particle size (i.e. of the agglomerates) of $MnCO_3$ is much larger that that of ZnO, leaving consequently larger pores after disappearance. Both effects may also be responsible for the considerable increase of the pore size even without a formation reaction.

From these data it appears that the results of "green sintering" might be improved by using a mixture with smaller particles of the reactant that is solving during the formation reaction. However, the space left in a close-packing of iron oxide particles is insufficient to contain the full amount of the other reactant. As a consequence, a certain deterioration of the final microstructure must always be expected with "green sintering". Furthermore, while the result would be at best comparable to that of the standard procedure, the effort of obtaining and controlling a really random

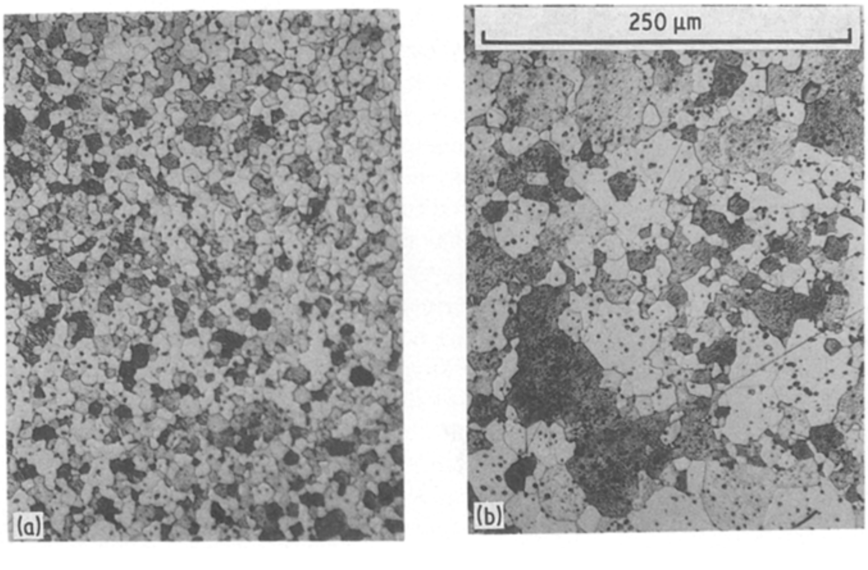

Figure 8 The etched microstructures of different nitrogen-calcined mixtures after firing at 1300° C in nitrogen: (a) GFE-$MnCO_3$ and calcined BASF-Fe_2O_3 ($\varrho = 4.84\,g\,cm^{-3}$). (b) GFE-$MnCO_3$ and Ruthner-Fe_2O_3 ($\varrho = 4.85\,g\,cm^{-3}$).

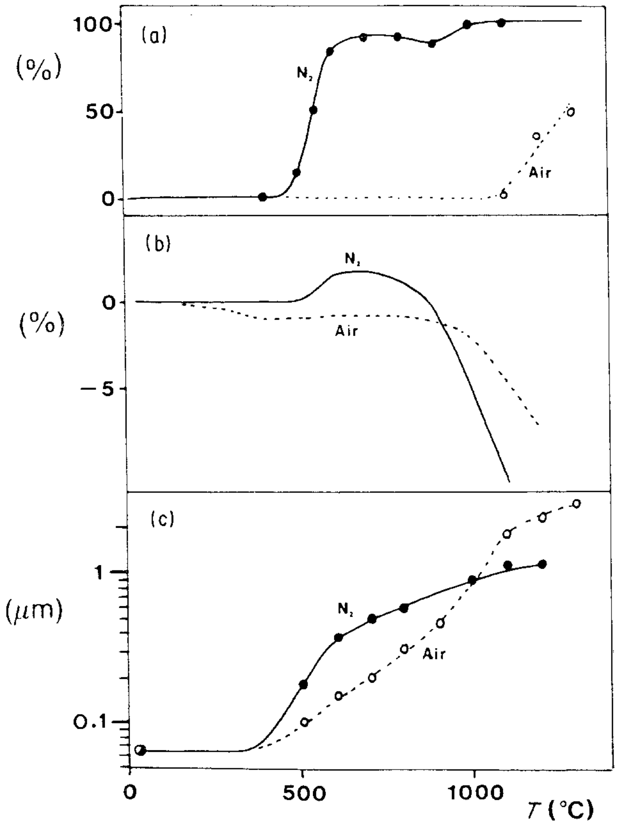

Figure 9 "Green sintering" of a mixture of GFE-$MnCO_3$ and BASF-Fe_2O_3 in N_2, showing the relation between (a) the conversion (α), (b) the expansion in the dilatometer experiment (L, or actually $\Delta L/L \times 100$) and (c) the extra pore growth ($r_{p,50}$).

mixture will probably be much higher than that of a calcining step. "Green sintering" does not appear to be a cheap alternative to the normal sintering procedures.

The type of reactant only had an influence on the temperature at which the phenomena described above occurred – not on their occurrence itself. In particular, the use of Ruthner iron oxide shifted the densification to very high temperatures. As this effect seems too large to be explained just by a coarser morphology, an additional chemical effect (of, for example, impurities) could be involved. Note, however, that the calcining procedure neutralized the difference in behaviour. This would imply that the impurities involved were highly volatile [7].

4.2. Sintering of calcined materials

In the previous section it has been shown that the formation reaction during "green sintering" causes a ferrite sample to expand. The question now is to what extent this expansion is linked with the formation reaction.

As can be seen in Figs 5 and 6, the expansion, which was characteristic of "green sintering", is absent when a calcined material is used. The decomposition of the ferrite by firing a nitrogen-calcined material in air is not accompanied by any change of volume (Fig. 5). Also during firing an air-calcined material in nitrogen, where conversion into spinel takes place between 600 and 1000° C, just as with "green sintering", no change of volume is observed (Fig. 6). Obviously, the formation reaction as such is *not* necessarily accompanied by expansion!

The deteriorating effect of "green sintering" appears to originate only from the fact that at the start of the process each particle consists of only one reactant. As ball-milling does not affect particles smaller than 1 μm, the mechanical homogenization prior to "green sintering" has no influence on the distribution of the reactants over the particles. However, after a calcining procedure in nitrogen, obviously an atomic mixing has occurred by the formation of the ferrite. As a result, no preferential solution of particles occurs during a subsequent sinter process and, consequently, neither expansion nor excessive pore growth are observed. However, these phenomena are not observed either after the powder has been calcined in air! Although a real atomic mixing cannot be confirmed in this case, any preferential solution is apparently suppressed in a comparable way. It must be concluded, therefore, that the effect of calcining is that of a homogenization on a sub-particle scale, even when no actual formation reaction is occurring. Any formation during a subsequent firing step will then leave the particle structure of the sample unaffected until densification. This homogenizing effect of calcining is further supported by the reduction of the differences in the densification behaviour (cf Figs 2 and 5).

4.3. Microstructures

The microstructure of a ferrite determines to a large extent its magnetic performance. Ideally the material should have a low porosity with small equi-sized grains. Above all, the occurrence of excessive grain growth should be avoided. Excessive grain growth occurs when the grain boundary mobility is increased. In general, four different mechanisms may be discerned.

(1) The mobility of a grain boundary is determined by the chemical composition: the accumulation of even (overall) minor amounts of impurities or dopes may completely change the nature of the grain boundary [8]. Also the oxygen content of the firing atmosphere can be expected to have a stong influence (through the valency of iron and manganese) on the chemical identity.

(2) The presence of separate phases on the grain boundary, whether pores or foreign substances, may retard the grain boundary mobility. When their number is reduced, e.g. by reducing the porosity, excessive grain growth may occur.

(3) The process of solution of a foreign substance may affect the grain boundary mobility. Various reports on diffusion induced grain boundary mobility (DIGM, see, e.g., [9]) assume that the mobility is increased, but Kools [10] has presented the alternative possibility of an inhibiting effect.

(4) Finally, a foreign substance may induce the occurrence of a liquid phase, through which the grain boundary mobility may be strongly increased.

In view of the relatively pure substances used in this investigation, we assume that the last two mechanisms are not involved here. The features observed in the microstructures after sintering can then be evaluated as follows. "Green sintering" causes excessive pore growth (e.g. Fig. 7a), as discussed above. These large pores are directly responsible for the relatively low density obtained, on the other hand they are probably dragging the grain boundaries to such an extent that excessive grain growth is never observed. Calcined materials are fired easily to a much higher density, but this entails the chance of excessive grain growth (Figs 7c and 8b). Comparing Figs 7b and c, it is obvious that firing in air at a higher temperature has led to a pore growth, in accordance with Reijnen [12]. At first sight it is strange that the large pores in Fig. 7c are apparently left behind more easily than the smaller ones in Fig. 7b. Most likely the intrinsic grain boundary mobility strongly increases with the sinter temperature.

A comparison of Figs 8a and b shows that the grain boundary mobility is obviously higher in the material containing Ruthner iron oxide, probably due to the presence of impurites. In this case therefore the material appears to have been "overfired". After sintering at a somewhat lower temperature a comparable density without excessive grain growth might have been obtained.

It is clear that the occurrence of excessive grain growth is determined not only by the temperature and the number and size of the pores, but notably also by the chemical composition of the grain boundaries of the various materials. A thorough investigation of the relationship between this composition and the tendency towards excessive grain growth would appear useful to gain a deeper insight into the development of ferrite microstructures during sintering.

5. Conclusions

(1) Reactive sintering of manganese ferrite from a mixture of commerically available reactants is always accompanied by expansion during firing and by a low final density and large pores. This confirms the earlier findings with zinc ferrite. The reason is a deterioration of the particle stacking of the compact by the formation reaction.

(2) The effect of calcining is not related to the degree of conversion. It is essentially a homogenizing effect on a sub-particle scale.

Acknowledgements

The authors would like to thank A. M. Romijnders for preparative assistance, C. Langereis *et al.* for X-ray diffraction analysis and T. P. M. Meeuwissen for use of the dilatometer.

References

1. F. J. C. M. TOOLENAAR and M. T. J. VERHEES, *J. Mater. Sci.* **23** (1988) 856.
2. G. CHOL, Y. GROS, J. C. PEBAY-PEYROULA and J. P. BARBE, *Mater. Res. Bull.* **2** (1967) 753.
3. S. A. MAZEN and B. A. SABRAH, *Thermochimica Acta* **105** (1986) 1.
4. P. Y. EVENO and M. P. PAULUS, *Reactivity of Solids* **8** (1977) 433.
5. G. CHOL and F. DAMAY, *Bull. Soc. Francaise Ceramique* **75** (1967) 61.
6. F. F. LANGE, *J. Amer. Ceram. Soc.* **67** (1984) 83.
7. F. KOOLS, private communications.
8. F. J. C. M. TOOLENAAR, *J. Mater. Sci.*, to be published.
9. F. J. A. DEN BROEDER, *Thin Solid Films* **124** (1985) 135.
10. F. KOOLS, *Sci. Sintering* **17** (1985) 49.
11. *Idem., Solid State Ionics* **16** (1985) 251.
12. P. J. L. REIJNEN, *Sci. Ceramics* **4** (1968) 169.

Recieved 18 January
and accepted 1 June 1988