JOURNAL OF MATERIALS SCIENCE 23 (1988) 3144–3150

Silica-induced exaggerated grain growth in MnZn ferrite

F. J. C. M. TOOLENAAR
Philips Reseach Laboratories, PO Box 80 000, 5600 JA Eindhoven, The Netherlands

It is shown that the effect of silica in inducing discontinuous or exaggerated grain growth in MnZn ferrites is not likely to be caused by the formation of a liquid phase, a change of the vacancy concentration of the ferrite matrix, or by diffusion-induced grain boundary migration (DIGM). The acceleration of the grain growth is rather connected with different intrinsic properties of the enriched grain boundary phase.

1. Introduction

The magnetic properties of ferrites are strongly influenced by their microstructure. With the growing demand for lower power losses, there is a particular need for more uniform fine grained materials. The grain growth kinetics during the sinter process are very sensitive to material and process variables, which require increasingly close control to meet the ever higher requirements. The presence of a foreign substance may also have a drastic influence on the development of the microstructure. Dopants may be added in order to increase the sinterability of the material, but the presence of impurities may also lead to discontinuous or excessive grain growth. The mechanism of the effect of an impurity (or dopant) on the grain growth kinetics is not straightforward and will be dependent on factors like charge, morphological nature and ability to react with or dissolve into the matrix material. A material which is not completely dissolved into the matrix may form a liquid phase which would drastically alter the experimentally observed grain growth kinetics.

Silica is a notorious impurity in MnZn ferrites; only a few hundredths weight percent is sufficient to induce discontinuous grain growth [1, 2]. On the other hand, the presence of silica in the grain boundary layers has been shown to increase the electrical resistivity of the material [3–6]. Giles and Westendorp [1] have reported that a silicon-rich second phase could be observed at a silica content of 0.04 wt %, so the solubility limit of SiO_2 in ferrites should be estimated to be below 0.04 wt %. The grain boundary may absorb much larger quantities, up to 8% in a layer of about 2 nm [7–8].

The occurrence of discontinuous grain growth is often ascribed to the presence of a liquid phase at the sinter temperature. A liquid phase is not to be expected in MnZn ferrites below 1350° C [9, 10]. The presence of Si, however, may lower this threshold temperature to 1200 [11–13] or even 1100° C [14].

Yan and Johnson [15] investigated the effect of 20 oxide dopants on the microstructural development of a MnZn ferrite with the help of diffusion couple experiments. Most dopants that induced discontinuous grain growth formed a liquid phase with the ferrite, but TiO_2 and SiO_2 caused exaggerated grain growth without showing a liquid phase after sintering. It was concluded that TiO_2 caused discontinuous grain growth by dissolving into the ferrite lattice. The mechanism proposed was that either other segregants were repelled from the grain boundaries by Ti^{4+} or that the pore mobility was increased by an induced excess of cation vacancies. On account of a similar microstructural development with the SiO_2 dopant, the same mechanism was suggested to be operative in that system too [15].

A different mechanism suggested by Kolar [16] to explain the experimentally observed phenomena was diffusion-induced grain boundary migration (DIGM). In this phenomenon the grain boundary along which a solute is continuously supplied, will migrate, leaving behind in its wake a solid solution [17–23]. DIGM allows alloying well below a temperature at which bulk diffusion would be possible, but it has also been reported upon demixing [18, 23]. The driving force appears to be connected with the transport of solutes along the grain boundary. So far, most papers have been concerned with metal-alloy systems [17, 18, 23–25] and it has been questioned if DIGM could occur in ionic systems because of the necessary prerequisite of equal anion and cation diffusion rate [26]. In spite of this, the effect has recently been reported in simple oxidic systems like CoO [27], NiO [28] and MgO [29–31] as well as in ceramic systems like (PbLa)(ZrTi)O_3(PLZT) [32] and $CaCo_3$ [33–34].

Another "dynamic" mechanism was introduced by Kools [35–36] to explain grain growth inhibition during the solution of silica into strontium hexaferrite. The observed phenomena could not be fully explained by mechanisms like pore drag, impurity drag or precipitate drag. As a qualitative explanation it was put forward that the rate of reduction of the Gibbs free enthalpy would be highest if the solution reaction were to precede grain growth.

The paper reports diffusion couple experiments analogous to those of Yan and Johnson [15] with SiO_2 on MnZn ferrite, but with one additional parameter.

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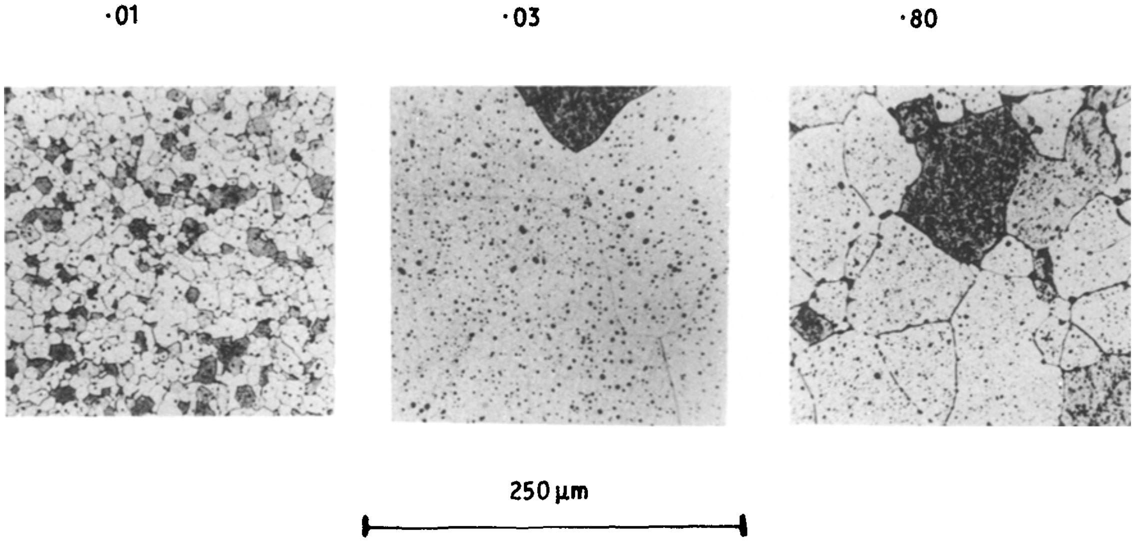

Figure 1 Etched microstructure of MnZn ferrites after sintering at 1300° C in an atmosphere with a temperature dependent oxygen content; the total silica content in weight percent is indicated above.

The ferrite material for the diffusion couples was predoped with different amounts of silica. In this way the effect of solid solution formation should become visible: samples with increased amounts of silica should experience an increasing resistance to the dissolution of SiO_2 from the diffusion couple.

2. Experimental details

The MnZn ferrite had the composition $Mn_{0.65}Zn_{0.25}$-$Fe_{2.10}O_4$ and was prepared by mixing and calcining $MnCO_3$, ZnO and Fe_2O_3 [37]. The reactants were fairly pure and contained about 0.005 wt % SiO_2 before processing. After processing this percentage increased to about 0.012 wt %, due to contamination from ball milling. By processing more carefully, this increased silica content could be reduced, but this proved to have no effect on the microstructure after sintering.

If SiO_2 was added in the form of a high surface-area aerosil (Degussa), scanning electron and X-ray electron diffraction analyses (SEM/EDAX) revealed large agglomerates (several microns) which contained only silicon. A better way of homogeneously distributing silica was by hydrolysing the corresponding amount of tetra-ethyl-orthosilicate during the first mixing step in isopropanol, according to:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$

The pH was adapted to obtain a full decomposition during this mixing step. SEM/EDAX investigations showed that this procedure resulted in a very homogeneous distribution of the silica. Again, however, the effect on the final microstructure was only minor.

The diffusion couples were made in accordance with the procedure described by Yan [15]. In order to let the SiO_2 stick to the ferrite it was necessary to add some binder (PVA) to the ferrite. After prepressing, the samples were isostatically repressed under 0.1 MPa. The binder was removed by heating in air at 600° C for 1 h; after this the amount of carbonaceous residue was equal to that of a sample without binder (about 0.004 wt % according to mass spectroscopic analysis). Sintering was then performed in an atmosphere containing a temperature dependent amount of oxygen, according to: $\log p_{O_2} = -13300/T + 8.475$ [38], with T in K.

Transverse sections were polished and subsequently etched in boiling hydrochloric acid. Independently, experiments were performed with the ferrite materials (containing added amounts of silica between 0.01 and 0.80 wt %) without the silica caps. The microstructure of samples sintered in this way was quantitatively evaluated as follows. The percentage excessive grains was determined with a fully automatic image analysis (TAS plus, Leitz) system. The microstructure of the fine grained part of the material was analysed semi-automatically by the intercept method with an Apple graphics tablet. Assuming a log-normal distribution, the measured data were transformed and fitted by the linear least-squares regression method, resulting in a median grain size with standard deviation.

Silicon enrichment in sintered samples was detected by electron probe micro analysis (EPMA) using Si$K\alpha$ radiation on a Camebax microprobe. The bulk concentration of the matrix in these samples was estimated with secondary ion mass spectrometry (SIMS), using a Phi 550 (Perkin–Elmer) set-up with an Ar beam focused to about 5 μm.

3. Results

Below a temperature of 1200° C the presence of silica had no influence on the development of the fine grained microstructure. At higher temperatures however, after sintering under equilibrium conditions, silica induced excessive grain growth when present in amounts larger than about 0.03 wt % (Fig. 1). Increasing the amount of oxygen in the sinter atmosphere suppressed or even eliminated this effect.

If the silica was present as a cap on an undoped ferrite, the microstructure after sintering under equilibrium conditions showed large elongated grains perpendicular to the silica-ferrite interface (Fig. 2a) in agreement with the results of Yan *et al.* [cf. Fig. 3 in ref. 15]. However, when a ferrite material was used to which silica had been previously added homogeneously

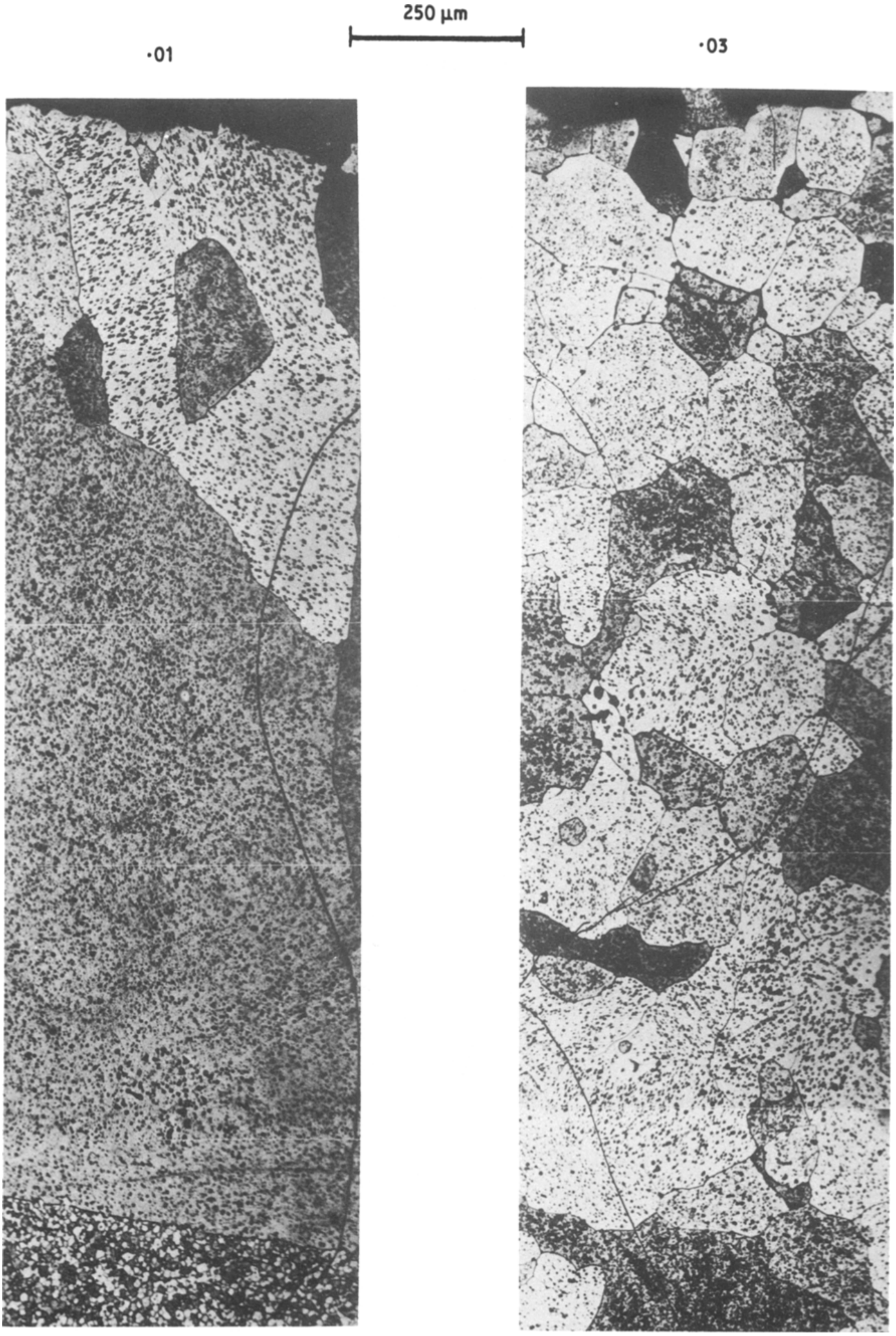

Figure 2 Etched microstructure of MnZn ferrites from diffusion couples with silica after sintering at 1300° C in an atmosphere with a temperature dependent oxygen content. The total silica content before the diffusion couple experiment is indicated above.

to any amount over 0.03 wt %, no effect of the silica cap was observed. This means that as little as about 0.03wt % SiO_2 in the ferrite is capable of inhibiting any additional effect of a large excess of silica.

An EMPA investigation of the diffusion couples shown in Fig. 2 revealed some additional information In Fig. 3 the silicon distribution is shown at the edge where the SiO_2 layer was located. In the first picture silicon-rich lines are shown, reaching about 700 μm into the sample, which coincide with grain boundaries of the large grains. These silicon-rich phases may well have been liquid at the sinter temperature. However,

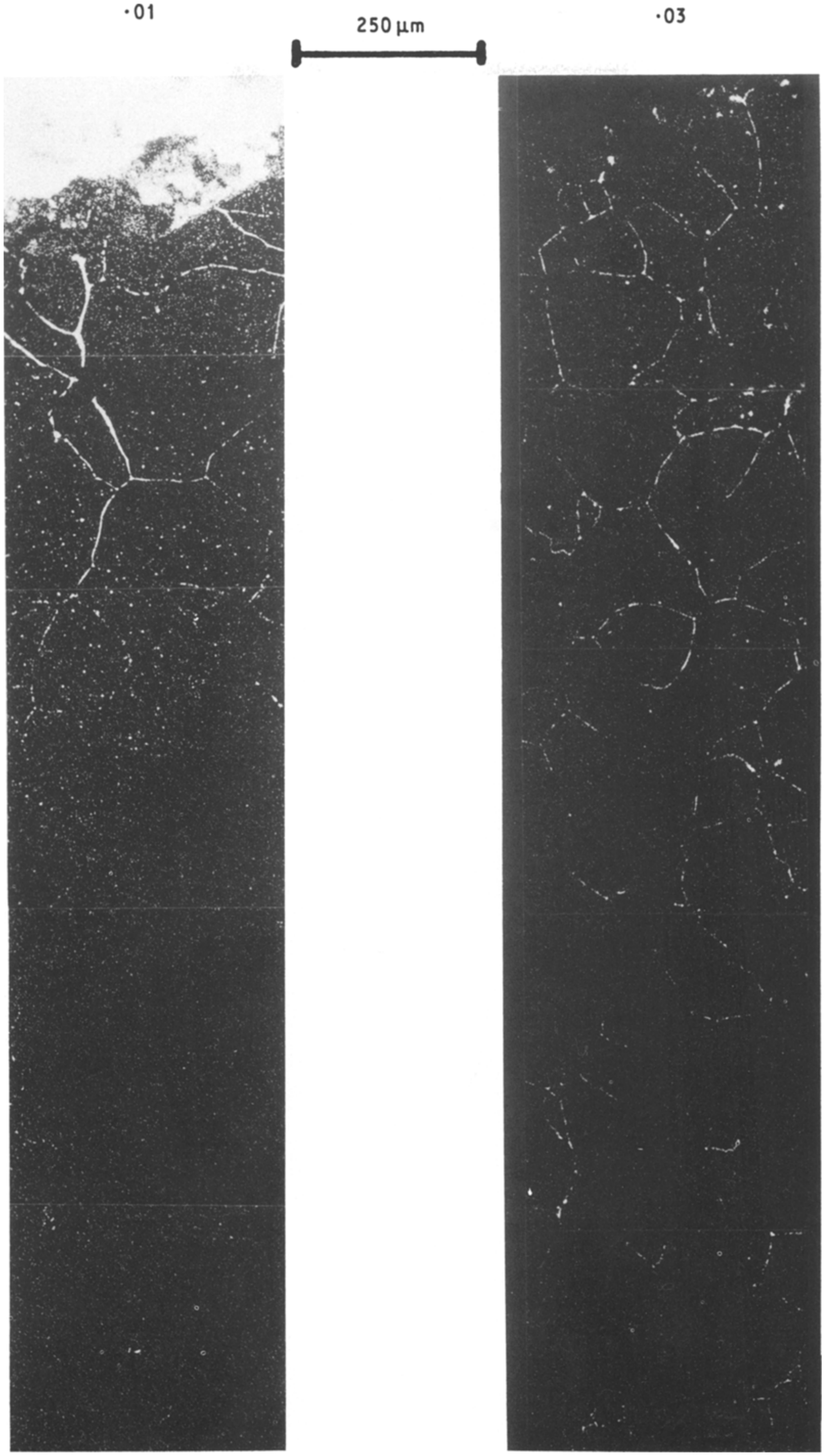

Figure 3 EPMA image of silicon in the same samples (with the same magnification) as in Fig. 2.

the extent of the large grains stretched further than this strong silicon enrichment (i.e. about 1500 μm: cf. Fig. 2), which disconnects this phenomenon from the development of the grain structure. In the second picture of Fig. 3 a comparable image is shown of the sample to which a small amount of SiO_2 had previously been added. The silicon-rich lines reach out even further into this sample, almost 2000 μm, or about one third of the sample. The microstructure, however, was uniformly coarse grained throughout the whole sample.

The silicon content of relatively small portions of the surface of sintered samples was analysed with SIMS. Within grains that had grown "excessively" a significantly larger amount of silicon (about three times, i.e. 0.04 wt %) was invariably found than in "normally" grown grains (e.g. above vs. below the change-over from large to small grains in Fig. 2a).

4. Discussion

All results obtained thus far indicate that the risk of discontinuous grain growth is strongly enhanced in the presence of SiO_2. The reason for this is a local strongly increased mobility of the grain boundaries. In these introduction a number of currently supported mechanisms were presented, which will now be evaluated in the light of the present results.

4.1. Defect structure

The sinter behaviour of a ferrite is strongly influenced by the defect structure of the material [39–41]. Yan [15] suggested that the effect of both SiO_2 and TiO_2 could be caused by their absorption into the bulk of the material. However, the effect of TiO_2 became manifest only after about 0.7 wt % had been incorporated in the ferrite lattice, while the solubility limit of SiO_2 is much lower. On the other hand, one could argue that titanium may be partly reduced upon introduction into the ferrite lattice, which is impossible for silicon. It is worthwhile, therefore, to take a closer look into the details of this mechanism.

When MnZn ferrite with an excess of iron oxide is sintered under equilibrium conditions all excess iron is bivalent. Usually, however, sintering is performed under more oxidizing circumstances to avoid local inhomogeneities in sinter behaviour through the presence of either anion or cation vacancies. Under oxidizing conditions the excess iron dissolves into the spinel lattice. The distribution over the spinel lattice leads to the formation of cation vacancies [39] $Fe_{8/3}[V_c]_{1/3}O_4$, (with V_c indicating a cation vacancy), i.e. one vacancy for every four molecules absorbed ($Fe_2[V_c]_{1/4}O_3$). The vacancies can be removed again through the redox equilibrium

$$\tfrac{3}{2}\, Fe_2O_3 + \tfrac{3}{8}\, [V_c] \rightleftarrows Fe_3O_4 + \tfrac{1}{4}\, O_2,$$

with the equilibrium constant:

$$K = \frac{[Fe^{2+}]}{[Fe^{3+}]}\, \frac{p_{O_2}^{1/4}}{[O^{2-}]^{1/2}}\, \frac{1}{[V_c]^{3/8}}$$

Upon absorption of e.g. Si^{4+} in the spinel matrix, the (Fe^{2+}/Fe^{3+}) ratio must be increased to compensate for the extra charge [6]. As K is constant this could indeed [15] be expected to increase the cation vacancy concentration. In fact, it is possible to derive the following expression:

$$[V_c]_{new} = [V_c]_{old} \left[\frac{[Fe^{2+}] + q}{[Fe^{3+}] - q}\, \frac{[Fe^{3+}]}{[Fe^{2+}]} \right]^{8/3},$$

in which 'old' and 'new' refer to the situation before and after the introduction of q Mol tetravalent ions. In this way the introduction of 0.01 wt % SiO_2 would already suffice to increase the number of cation vacancies by a factor of more than two.

However, it is questionable if this would promote the grain boundary mobility. Reijnen [40] showed that the material transport in a spinel is strongly decreased with an increasing cation vacancy concentration. The pores hold more strongly to the grain boundaries than in the case of anion vacancies, but this does not imply that the pore mobility is increased. It is much more likely that the grain boundary mobility is decreased: the large pores in ferrites sintered with an excess of cation vacancies are obviously not removed during the sinter process and hence the final density is lower than with an excess of anion vacancies. A further increase of the excess concentration of cation vacancies through the incorporation of Si^{4+} could then only be expected to reduce the sinterability still further. Reijnen has also shown [40] that the density of sintered Fe_2O_3 indeed decreased upon small TiO_2 additions; only larger amounts (above the solubility limit) promoted densification. The amount of SiO_2 that can be absorbed in the spinel matrix is unfortunately too low to expect equally clear results.

Moreover, increasing the amount of oxygen in the sinter atmosphere suppressed instead of intensified discontinuous grain growth by silica additions, probably just by increasing the amount of cation vacancies. If the addition of tetravalent ions had any effect on the defect structure of the matrix, one would expect an increase of the porosity and a suppression of the fast grain boundary movement. The introduction of Si^{4+} in the ferrite lattice should therefore be dismissed as an explanation of induced excessive grain growth.

4.2. Liquid phase

The occurrence of a liquid phase would explain the difference in behaviour between SiO_2 and TiO_2: a liquid phase can only be formed after the matrix has been saturated. However, a total silica content of 0.03 wt %, part of which will disappear by dissolving into the ferrite, would seem to be very small to account for such an effect.

Taking into account the EPMA results, it seems reasonable to assume that in the case of Fig. 2a the large grains are formed by a slowly progressing wave front of relatively low silica content leaving behind a 'saturated' material with very little if any second phase. In Fig. 2b many 'seeds' induce excessive grain growth at the same time. The strong silicon enrichment originating from the silica cap was apparently able to penetrate further here (Fig. 3b vs. 3a) possibly because of a more rapid accomplishment of the final coarse grained microstructure. In both cases the formation of the large grains themselves was not connected with this (possibly) liquid phase, as there is no difference in grain structure between spots with or without the strongly enriched boundary layers. The possibility of a (very small) liquid phase which is not detected with EPMA cannot be ruled out completely, as it is not known how much material is required to constitute an effective liquid phase. The solution to this problem might be found e.g. by transmission electron (TEM) analysis. Our impression at the moment, however, is that the occurrence of excessive grain growth is linked too strongly with the solubility limit to make a liquid phase mechanism likely.

4.3. Diffusion-induced grain boundary migration (DIGM)

Kolar [16] suggested a third mechanism as a possible explanation, viz. DIGM as discussed in the introduction. An interesting point would be that if this mechanism were valid, it would imply a dynamic one: only during the dissolution process of the grain boundary the motion would be accelerated. One prerequisite for DIGM would be that the area that had been swept by the boundary should contain the higher amount of solute. Within grains that had grown 'excessively' we did indeed invariably find (with SIMS) a significantly larger amount of silicon (about three times, i.e. 0.04 wt %). As the features essential to DIGM are still uncertain, it is hard to assess the probability of this mechanism here. The lack of 'undulating' grain boundaries or the very small amount of dissolving species that can be absorbed in the matrix (typically a hundred times smaller than in the metallic systems) are (as yet) not sufficient counter arguments. A weak point however, is that the dissolving process is obviously not influenced by the much larger amount of TiO_2 that can be absorbed.

In the mechanism suggested by Kools [35–36], the silica would be retarding grain growth while dissolving into the ferrite, i.e. an anti-DIGM mechanism. Discontinuous grain growth is then to be explained by locally different moments of saturation.

Different in principle and effect though these mechanisms may be, both assume that a secondary solution phase has had an effect on the grain growth kinetics. In order to investigate the occurrence of such an effect, the microstructures of ferrite materials with silica levels around the solubility limit were examined more closely. The results of these experiments are collated in Table I. As can be seen, the percentage of excessive grains is not related with the density, but it does increase with the percentage of silica. This effect is enhanced by increasing the sinter temperature. The microstructure of the small grains showed in all cases a log-normal distribution. The thus determined median grain sizes showed some spread, but no clear trend with the silica percentage. The increasing average amount of SiO_2 increases the number of 'seeds' for discontinuous grain growth, but does not alter the process of normal grain growth. Consequently, no 'dynamic' mechanism of whatever nature appears to be effective here.

Summarizing, the effect of silica in inducing excessive grain growth in MnZn ferrites is unlikely to be explained by a liquid phase mechanism and is definitely not caused by effects on the defect structure of the material or by the dissolution process. The answer to this problem should rather be found in the following way.

TABLE I Microstructure characteristics

T*	% SiO_2†	ϱ‡	D_{50}§	Σ¶	% disc.**
1250	0.026	4.76	6.1	1.9	0.5
	0.034	4.67	4.8	2.0	2.7
	0.036	4.69	4.6	1.9	36
	0.045	4.76	–	–	100
1300	0.026	4.87	6.0	1.9	0
	0.034	4.81	7.9	1.8	6.1
	0.036	4.83	6.4	2.0	66
	0.045	4.86	–	–	100

* The temperature (in ° C) at which the sample was sintered for 4 h. † The titrimetrically determined weight percentage of SiO_2. Accuracy: ± 0.002 wt %. ‡ The density in $g\,cm^{-3}$; the theoretical density is 5.10 $g\,cm^{-3}$. § The median grain size (in μm) determined from the log-normal curve. ¶ The standard deviation of the grain size distribution. ** The percentage of discontinuously grown grains.

4.4. Intrinsic grain boundary mobility

With increasing amounts of silica in a MnZn ferrite, the dopant is absorbed up to an amount of about 0.03 wt %; too little to have any effect on bulk diffusion characteristics. When the material is fully saturated, a silicon-rich phase has accumulated at the grain boundaries up to several percent silica [7]. The grain boundary mobility is then strongly increased.

The most likely reason for this is that the newly formed species have different properties. Although the repelling of grain boundary movement inhibitors as suggested by Yan [15] cannot be precluded. Experiments with very pure ferrite materials or identification of these 'inhibitors' may provide the answer. The grain boundary no longer has the mobility of the ferrite, and this may be affected in either direction. It is true that the solution reprecipitation of silicon, a prerequisite for the grain boundary to move, may have a retarding (precipitate drag) effect, but the net effect may still be in either direction. Most likely impeding or synergic effects of e.g. the oxygen content of the sinter atmosphere or of other impurities like calcium oxide could be explained in the same way. It is important to note that in this explanation the driving force for grain boundary movement is not changed in magnitude or direction; only the resistance towards its motion is affected.

Contrary to the other mechanisms described above, this model is supported by all the experimental evidence obtained so far:

1. SiO_2 has no effect until a certain threshold concentration (around 0.03 wt %) has been reached: the different grain boundary mobility occurs only after the different species has been formed.

2. The discontinuously grown grains are largest near the threshold concentration of SiO_2: when only a few grain boundaries have obtained the high mobility state, they are not likely to impinge upon each other. Note that this will also occur when the silica is distributed inhomogeneously, like in the diffusion couple experiments.

3. The absence of any additional diffusion couple effects when the ferrite contains more than the threshold concentration of silica: the different mobility is caused by the different grain boundary compositions which will not change above the saturation level. Any additional effect originates from the distribution of changed grain boundaries, not from further inherent changes.

Acknowledgements

The author would like to thank A. M. Romijnders and W. Horden for preparative assistance, M. T. J. Verhees for TAS analyses, J. T. Hengst for EPMA analyses, A. D. van Langeveld (University of Technology, Eindhoven) for SIMS experiments and F. J. A. den Broeder and Professor. G. de With for stimulating discussions.

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Received 26 June
and accepted 22 September 1987