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Binder burnout-material-process interaction during sintering of MnZn-ferrites

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Abstract

The binder burnout process step for MnZn-ferrite materials has been investigated in order to explain the origin of the binder burnout cracks that occur during the sintering of MnZn-ferrites. The binder burnout reaction extends to temperature regions where oxidation of the ferrite material (i.e. $Mn^{2+} \geqq Mn^{3+} \geqq Mn^{4+}$) occurs simultaneously. Under such conditions, the oxidation of the binder is favoured relative to that of the ferrite until the binder burn out oxidation has been completed. As a consequence, the ferrite oxidation occurs at higher temperatures and at higher reaction rates. The associated material shrinkage rates are therefore also increased, enhancing defect formation and eventual crack development within the products. When ferrite products of large dimensions are considered, the developed temperature gradients across the body provide a position dependency of these reactions, which results in the development of high stresses and ultimately in product cracking. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Binder burn-out; Ferrites; Failure analysis; (Mn,Zn)Fe_2O_4; Sintering

1. Introduction

MnZn-ferrites form the main category of soft-ferrite materials (the other being the NiZn-ferrites). They belong to the general category of ceramic magnetic materials. They are crystallised in the cubic structure of the mineral spinel. Their magnetic properties arise from interactions between metallic (magnetic) ions occupying particular positions relative to the oxygen ions in the crystal structure of the oxide.[1,2] They are used in devices that, in the broadest sense, may be described as inductors or transformers, and are recognised as essential elements in the electronic and telecommunication industry.[3,4] They can be found in virtually all types of broad consumption electronic equipment such as televisions, video-recorders, hi-fi equipment, and mobile phones.

Ferrite cores are most usually fabricated through conventional ceramic techniques by pressing a (prefired) mixture of powders containing the constituent raw-materials to obtain the required shape and then converting it into a ceramic component by firing.[5] For facilitating the pressing process as well as for enhancing the mechanical strength of the pressed but not yet sintered cores, certain amounts of binders are added to the powder. These organic binders are burned out during the initial stages of the final firing process and usually at temperatures up to 300–400°C. This is a very critical region since the elimination of the binder results in mechanically very weak products since strengthening due to neck growth and sintering has not yet taken place at these low temperatures. Industrial production lines of ferrite cores suffer quite often from cracks introduced into the products during this binder burn out process. These cracks may not be annihilated during the subsequent sintering and their appearance deteriorates both the mechanical and the magnetic quality of the final products.

The factors influencing crack generation in MnZn-ferrites during the binder burnout step form the subject of this study.

2. Materials and methods

MnZn-ferrites having the approximate formula $Mn_{0.7}Zn_{0.2}Fe_{2.1}O_4$ have been synthesised as follows. The appropriate amounts of Fe_2O_3, Mn_3O_4 and ZnO have been mixed and subsequently prefired at ca. 800°C in air. The oxidation degree of the samples has been

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varied by varying the ambient oxygen content during cooling from the prefiring top temperature. The prefired powders have been ball-milled for about 5 h, dried and finally granulated in a tumbling granulator using various amounts of polyvinyl alcohol binder. The granulate has been pressed into rod-shaped samples with a standard density of 2.8 g/cm^3 which have been subsequently examined for their binder burnout behaviour. X-ray studies (XRD) have been performed using a Philips APD1700 automated powder diffractometer with CuK_a-radiation. Temperature programmed dimensional analyses have been made with a BAHR DIL 802 dilatometer. A NETZSCH STA429 thermal analyser has been used for the thermal gravimetric studies (TGA).

3. Results and discussion

3.1. *The prefired powders*

Upon prefiring a reaction partly takes place during which the Mn-, Zn- and Fe- components are converted towards the final MnZn-ferrite product. However, because of the relatively short duration and the low temperatures of the prefiring step this reaction is never completed so that prefired MnZn-ferrite powders are not single phase. Even if the reaction had run to completion, the thermodynamic instability of the MnZn-ferrite (which contains Mn^{2+}) would have caused oxidation (i.e. $Mn^{2+} \geqq Mn^{3+}$) during cooling. So in general, MnZn-prefired powders consist of a mixture of Fe_2O_3, Mn_2O_3 (i.e. Mn^{3+}) and MnZn-ferrite cubic spinel phase. The relative amount of Fe_2O_3 to that of spinel reflects, for equal prefiring temperatures, the degree of oxidation upon cooling. In Fig. 1, the Fe_2O_3 /spinel peak area ratio is shown, as determined after profile fitting analysis of X-ray diffractograms, for four $(MnZn)Fe_2O_4$ powders of the same composition that have been prefired at various oxidation degrees. The oxidation during prefiring has been varied by varying the oxygen content of the atmosphere during cooling (i.e. the oxygen content of the atmosphere was increased in the order powder 1 to powder 4). As can be seen from Fig. 1, increased oxygen content during cooling reveals less spinel and more hematite (i.e. Fe_2O_3) phase in the end powder product.

In Fig. 2, the TGA results (in air) of the as previously described prefired powders are shown. In Fig. 3 the corresponding dilatometric (in air) results are shown. An initial weight increase can be distinguished which starts at about 250°C and which reaches a maximum at about 500°C. The weight increase is inversely proportional to the oxidation of the powder upon cooling during the prefiring step. This weight increase is associated with a volume shrinkage as can be seen from Fig. 3, which is partly covered by the thermal expansion but becomes clearly visible from about 300°C.

Both weight uptake and shrinkage phenomena are caused by the same reaction which is the oxidation of the Mn^{2+}-ions remaining in the spinel structure (and

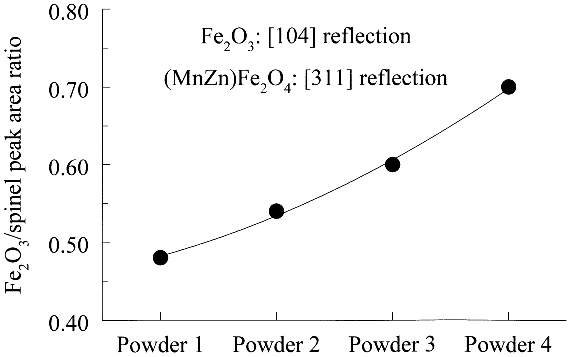

Fig. 1. The Fe_2O_3/spinel peak area ratio as determined by profile fitting analysis of X-ray diffractograms, for four equal composition (MnZn)-ferrite powders that have been cooled (during prefiring) at different oxygen partial pressures (the PO_2 during cooling was increasing in the order Powder 1–4).

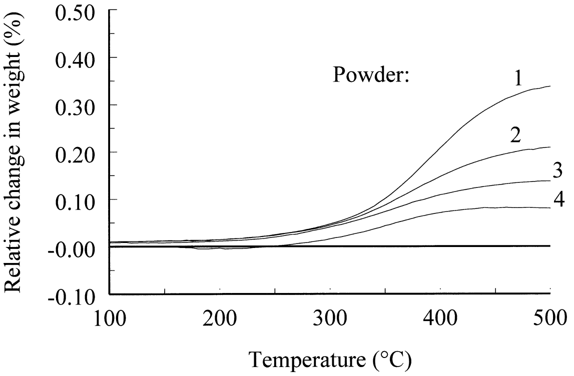

Fig. 2. TGA measurements in air of four equal composition (MnZn)-ferrite powders that have been cooled (during prefiring) at different oxygen partial pressures (the PO_2 during cooling was increasing in the order Powder 1–4).

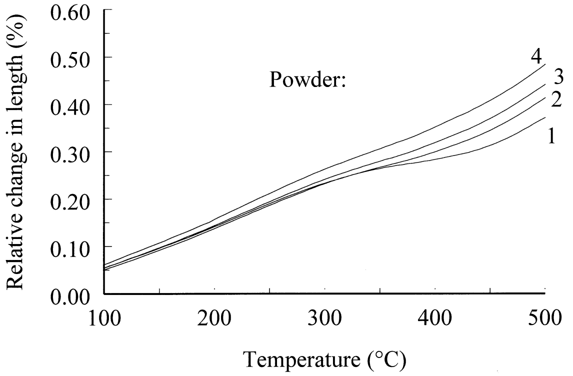

Fig. 3. Dilatometric measurements in air of four equal composition (MnZn)-ferrite compacts made of powders that have been cooled (during prefiring) at different oxygen partial pressures (the PO_2 during cooling was increasing in the order Powder 1–4).

perhaps also some Mn^{3+}-ions) to Mn^{4+} which is the thermodynamically stable form at these temperatures. Since the Mn^{2+}-content is inversely proportional to the oxygen content during cooling, it is expected that the weight uptake during subsequent firing in air will also follow the same trend, as shown in Fig. 2. Moreover, reduction of oxygen vacancies in the spinel structure is, for MnZn-ferrites, almost always associated with reduction in cubic lattice dimensions; therefore, volume shrinkage accompanies this reaction, as shown in Fig. 3.

3.2. The role and influence of the binder

When an organic binder is introduced in the system, certain changes occur in the process development described in the previous paragraph.

In Fig. 4 the effect of the binder on the dimensions of the ferrite rod during firing in air is shown. Both curves correspond to the same (MnZn)-ferrite powder, and thus identical preparation and prefiring conditions are involved (i.e. identical oxidation degree). The binder burn out reaction causes an extra expansion of the ferrite cores which is subsequently followed by a shrinkage. As also indicated by the actual temperature curve, measured just above the sample (Fig. 4), the extra expansion is most probably caused by the exothermic effect of the burn out reaction (i.e. the expansion peak pattern corresponds well with the deviation of the actual temperature from the set temperature). Although, the magnitude of this effect depends on the amount of binder, it represents a rather general result and has been found to occur for other binder types as well. In Fig. 5 the corresponding TGA results are shown. The enhanced weight loss of the binder containing sample is because of the binder burn out reaction. The subsequent weight increase is because of the Mn^{2+} oxidation as described in a previous paragraph. It is worthwhile to notice that the TGA minimum point (i.e. completion of the binder burn out reaction) coincides rather well with the temperature peak maximum of Fig. 4.

3.3. The dynamics of the binder burn out reaction process

The binder burn out process involves a chemical reaction during which the organic binder is burnt with oxygen. As such, it is subject to an overall kinetic rate expression the development of which is beyond the scope of this paper. Ferrite compacted cores are fired, either in push-through kilns or in batch kilns, under continuous temperature profiles with certain heating-up rates. The temperature at which the binder burnout reaction is completed depends, therefore, on all the parameters that influence the overall kinetic rate expression. Such parameters include the binder type, the binder content, the oxygen concentration, the heating-up rate or even factors influencing the mass and heat transport rates between the products and their environment such as the density of the compacts. In Fig. 6, TGA results are shown during the firing in air of otherwise identical (MnZn)-ferrite powders which have been granulated with different binder contents. There is a clear shift of the temperature at which the binder burn out is completed, to higher temperatures at increasing binder content. Between 0.5 and 1.5 wt% binder content, temperature shifts in the order 70°C have been detected. Similar results are shown in Fig. 7 for identically prepared (MnZn)-ferrite powders that have been fired in air at two different heating rates. The real end temperature of the binder burn out reaction depends on the heating rate and is shifted to higher temperatures at higher heating rates. Analogous results have been achieved by varying the press density of the compacts which primarily affects the diffusion rate of oxygen from the environment to the interior of the core. On the basis of the previous

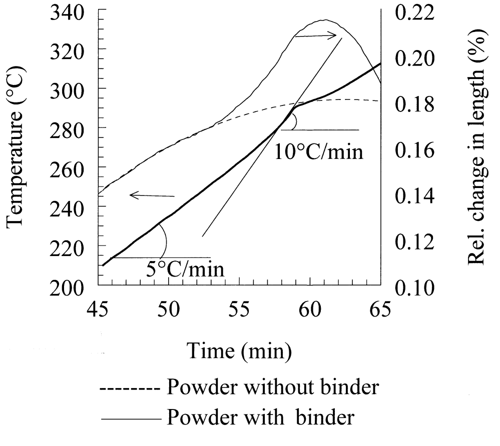

Fig. 4. Typical dilatometric measurements of a (MnZn)-ferrite compact with and without binder, indicating the effect of the binder on the development of the compact dimensions and the associated thermal effects.

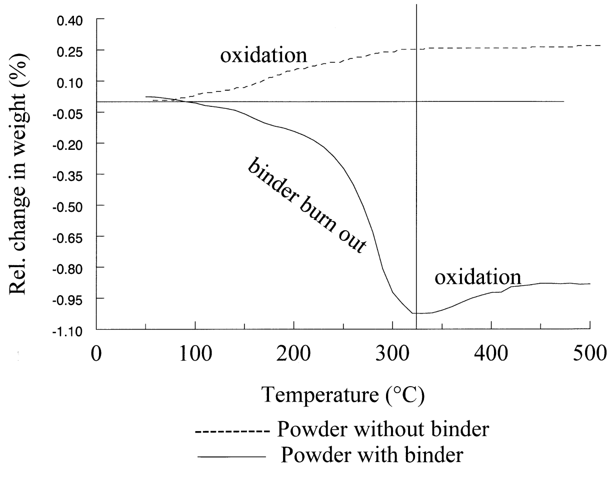

Fig. 5. TGA measurements of a (MnZn)-ferrite powder with and without binder, indicating the effect of the binder on the weight changes of the powder.

results it can be concluded that the temperature at which the binder burn out reaction is completed is not simply a binder property or parameter but rather a system parameter that depends on the choice of the operational parameters for the whole system.

3.4. Binder burn out and material oxidation reaction overlapping

By comparing the TGA curves of powders containing no binder with those containing binder in Figs. 5 and 6, it can be concluded that the burnout of the binder and the oxidation of the ferrite may proceed simultaneously in the same temperature region. However, as indicated by Fig. 6, where the magnitude of the relative weight loss at the curve minima is in good agreement with the initial binder content of the powders, while the binder is present in the system the ferrite oxidation is suppressed. This is also to be expected on the basis of thermodynamic considerations. The free Gibbs energy for the PVA oxidation (and also for other organic binder systems) is several orders of magnitude larger than for the Mn^{2+} oxidation.[2,6] Any available oxygen is, therefore, taken up by the binder and not by the ferrite (it has been reported that in oxygen deficient atmospheres the binder burn out proceeds even by taking oxygen from the spinel lattice which is hereby reduced).[7] The material oxidation, which is in this way suppressed, can proceed further as soon as the binder burn out reaction is completed, i.e. at a temperature that depends on the system parameters as described previously. The oxidation of the ferrite material is, in the presence of the binder, forced, therefore, to take place at higher temperatures and thus at higher reaction rates. This is shown in Fig. 8 where the rate of material oxidation is represented by the slope (i.e. the weight uptake rate) of the TGA curves just after they have reached their minimum. As can be seen the larger the temperature shift the higher the oxidation rate. The same result has been also obtained with the heating rate as variable parameter as shown in Fig. 9. As shown in a previous paragraph, the Mn^{2+} oxidation of the ferrite is associated with shrinkage. Higher and sharper oxidation rates will, therefore, result in fast and sharp dimensional changes within the ferrite cores, increasing, therefore, the possibility for defect formation and/or crack development. The effect of the material oxidation suppression on the shrinkage rate is shown in Figs. 10 and 11. Though the effect is here illustrated on basis of two selected parameters that have been found to cause material oxidation suppression, namely the binder content (Fig. 10) and heating rate (Fig. 11), the effect is essentially the same for all process parameters that may influence the effective binder burn out reaction rate.

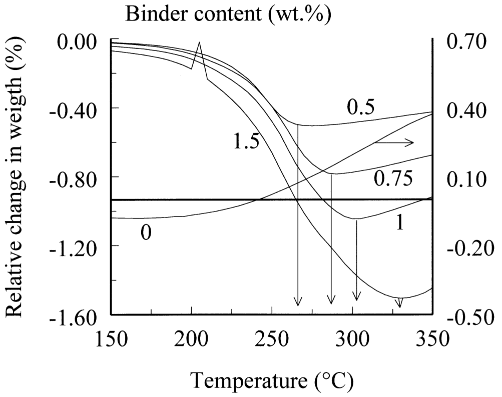

Fig. 6. TGA measurements in air of four (MnZn)-ferrite binder containing powders from the same basic composition and various binder contents, indicating the shift of the binder burn out reaction completion temperature to higher temperatures with increased binder content.

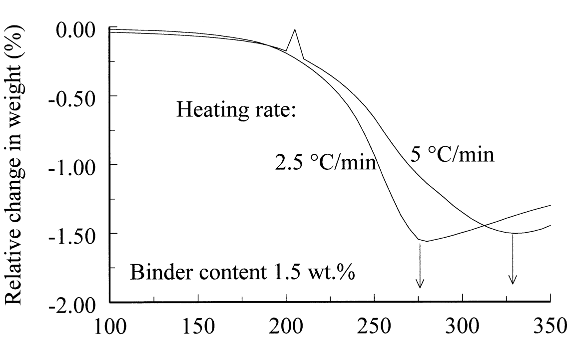

Fig. 7. TGA measurements in air of two (MnZn)-ferrite binder containing powders from the same basic composition and binder content, indicating the shift of the binder burn out reaction completion temperature to higher temperatures with increased heating rate.

3.5. Binder burn-out and powder oxidation degree

In the previous paragraphs it has been shown that the ferrite material oxidation rate during firing can be kept

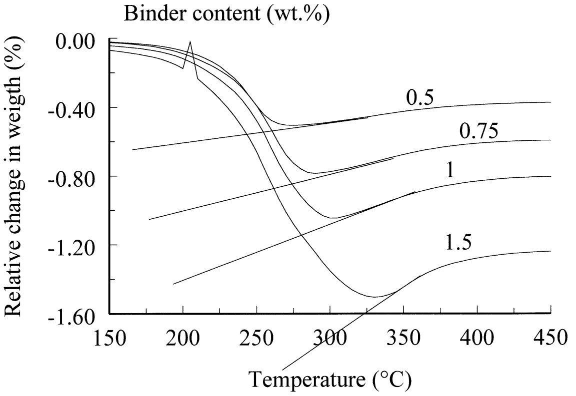

Fig. 8. TGA measurements in air of four (MnZn)-ferrite binder containing powders from the same basic composition and various binder contents, indicating the increased material oxidation rates (i.e. weight uptakes) at increased binder burn out reaction completion temperatures (through binder content).

under control by taking measures to restrict any prolonging of the binder burnout reaction. Another approach is to tackle the problem already during the prefiring step through the manufacturing of low Mn^{2+} content powders. As shown in a previous paragraph this can be done by varying the rate of oxidation during cooling. In Fig. 12 the TGA results are shown for equal binder content but for variable oxidation degree in the ferrite powders. Although the binder burnout kinetics can be considered identical and so also the extent of material oxidation suppression, the samples indicate variable oxidation rates because of their variable Mn^{2+} content. The oxidation rate decreases with decreasing Mn^{2+} content or with increasing oxidation upon prefiring. As a consequence the shrinkage ranges will be also reduced and the dimensional changes in the products will be smoother as shown in Fig. 13. The possibilities for crack-formation are, therefore, reduced.

3.6. Industrial sintering of large size cores

An additional problem arises when cores of large geometrical size are considered since sintering under industrial conditions can then generate profiles from the exterior to the interior of the core. Under these circumstances, it is anticipated that the binder burnout reaction starts at the exterior (which is at higher temperature) and gradually proceeds to the interior of the core. The exterior of the core (which becomes free of binder) can then be oxidised and can shrink while the interior of the core is still at the binder burnout stage and expanding. The exterior of the core is under tensile

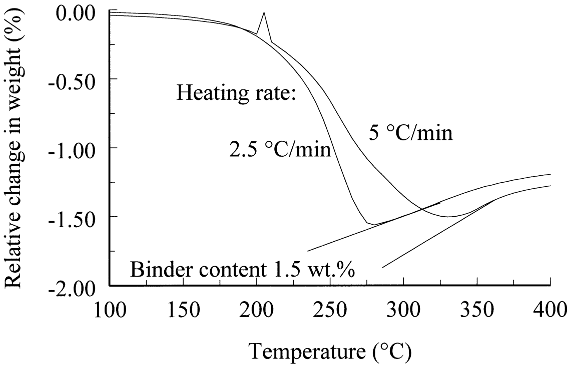

Fig. 9. TGA measurements in air of two (MnZn)-ferrite binder containing powders from the same basic composition and binder content, indicating the increased material oxidation rates (i.e. weight uptakes) at increased binder burn out reaction completion temperatures (through heating rate).

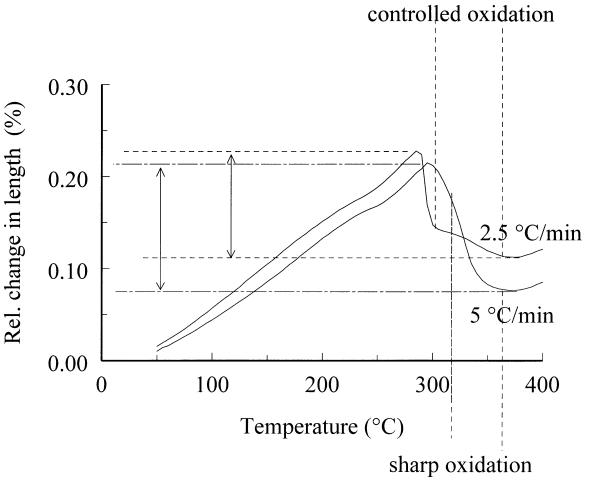

Fig. 11. Dilatometric measurements of two (MnZn)-ferrite compacts from the same basic composition and s binder content, indicating the increase of the expansion/shrinkage amplitude at higher heating rates (i.e. suppression of the material oxidation up to high temperatures).

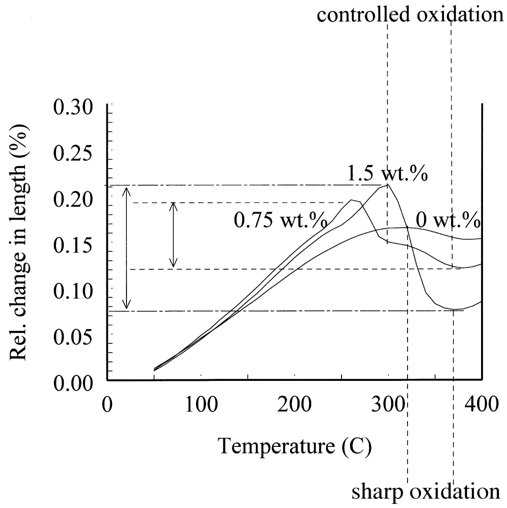

Fig. 10. Dilatometric measurements of three (MnZn)-ferrite compacts from the same basic composition and various binder contents, indicating the increase of the expansion/shrinkage amplitude at higher binder contents (i.e. suppression of the material oxidation up to high temperatures).

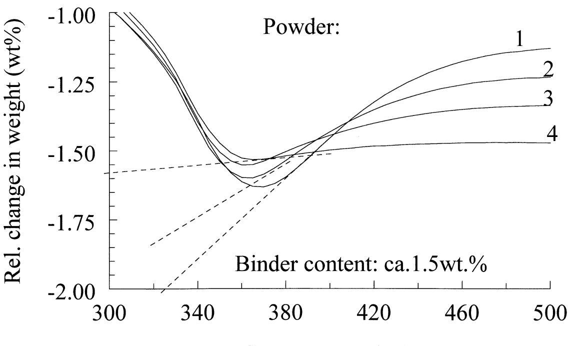

Fig. 12. TGA measurements of four (MnZn)-ferrite powders from the same basic composition and binder content that have been cooled (during prefiring) at different oxygen partial pressures (the PO_2 during cooling was increasing in the order Powder 1–4), indicating the change in material oxidation rate as a function of the powder oxidation degree.

stress while the interior is under suppression. Cracks can then develop at the surface of the core causing damage of the products. In order to prove experimentally this hypothesis, large cores have been pressed and during firing quenched at various stages of the material oxidation reaction process. Subsequently X-ray diffraction measurements have been made at the external surface, at the centre, and at an intermediate point of the core by successively polishing the material. The Mn^{3+} (detected as Mn_2O_3 to spinel ratio) has been determined by profile fitting based on the area of characteristic intensity peaks (i.e. [311] reflection for cubic spinel phase and [222] reflection for Mn_2O_3) and normalised to that of the external surface. The results are shown in Fig. 14. As can be seen for the sample quenched just after the binder burnout has reached completion, there is a gradient in the Mn_2O_3/spinel ratio when going from the surface to the interior of the sample. This gradient becomes smaller when the quenching occurs from higher temperatures. These results suggest that the binder burnout reaction front moves gradually from the exterior to the interior of the sample; the same then occurs for the ferrite oxidation reaction front. The simultaneous occurrence of these two reactions is the basis for the generation of stresses within the ferrite cores, which very often exceed the material strength and result in cracking.

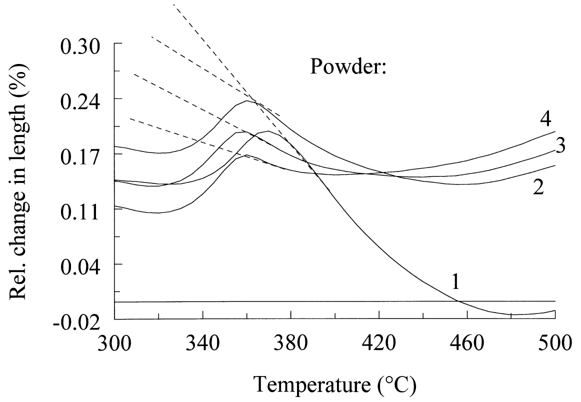

Fig. 13. Dilatometric measurements of four (MnZn)-ferrite compacts from the same basic composition and binder content that have been cooled (during prefiring) at different oxygen partial pressures (the PO_2 during cooling was increasing in the order Powder 1–4), indicating the change in material expansion/shrinkage amplitudes as a function of the powder oxidation degree.

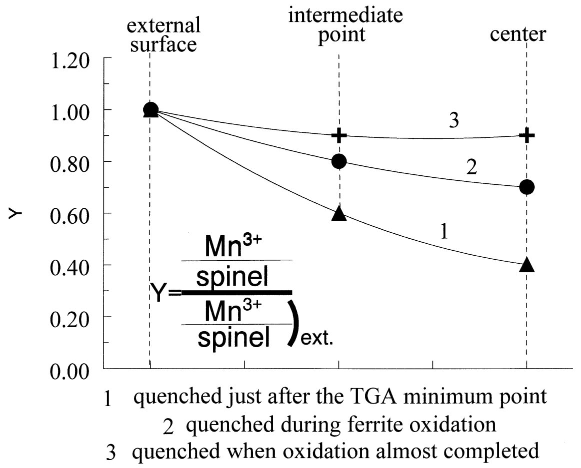

Fig. 14. X-ray diffraction profile fitting results of large ferrite cores quenched at different stadia of the binder burn-out and oxidation process indicating the dependence of the Y parameter (explained in the figure) on the position in the core as well as on the time of quenching.

4. Discussion

The model presented in this paper helps to explain a number of phenomena in the processing of ferrites. For example, the execution of the binder burnout under nitrogen atmospheres (in order to slow it down) and shifting to air when the binder has been burned off is a measure which is very often applied. The measure can now be seen to be problematic. Nitrogen atmospheres reduce the binder burnout reaction kinetics and prolong the burnout process to higher temperatures. When the atmosphere is then being changed to air, severe oxidation will happen with the risk of mechanical failure of the cores. In contrast, the incorporation of binders with low decomposition temperature makes sense since the binder will leave the cores at low temperatures where the ferrite oxidation rates are still acceptable; however, if this advantage is overcompensated by higher contents or faster heating rates or increased press densities, then it will disappear. Though not experimentally verified, it would be interesting to examine a process where the binder burnout reaction is prolonged up to ca. 500–550°C where the Mn^{4+} is not thermodynamically stable any more (then Mn^{3+} becomes the thermodynamically stable phase). The initial ferrite composition is also an important aspect since it is expected that low Mn-content recipes will lead to low oxidation rates. In any case, control of the prefiring process and the oxidation degree of the initial powders is also an important issue for the binder burnout process.

Though the ferrite material-binder burnout process interaction as described in this paper has been investigated for (MnZn)-ferrites, the essential points can be applied equally well to other types of ceramic component (either electronic, structural or technical) where there are ions in an oxidizable state [e.g. negative temperature coefficient (NTC) ceramics], and where the oxidation reaction is associated with lattice changes.

5. Conclusions

The simultaneous occurrence of the binder burnout reaction and the ferrite material oxidation reaction explains the generation of the “binder-burnout”-cracks.

The ferrite material oxidation is suppressed by the binder oxidation and forced to occur at higher temperatures and higher rates; this ultimately means sharp dimensional changes within the cores.

The extent of ferrite oxidation retardation can be controlled by controlling all those factors that influence the effective rate of the binder burnout reaction. Such factors can be binder specific (e.g. binder type), recipe specific (e.g. binder content) or process specific (e.g. oxygen content in atmosphere, press density, heating rate).

The rate of the ferrite oxidation is also influenced by controlling the prefiring process and in particular the oxidation degree of the prefired powders. Under industrial firing conditions, stress generation occurs since temperature gradients coupled with the two oxidation reactions cause simultaneous expansion and shrinkage in the same core.

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