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Journal of the European Ceramic Society 33 (2013) 95–103
www.elsevier.com/locate/jeurceramsoc

Inter-diffusion between NiCuZn-ferrite and LTCC and its influence on magnetic performance

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Received 20 May 2012; received in revised form 14 July 2012; accepted 23 July 2012
Available online 23 August 2012

Abstract

The present study investigated inter-diffusion between NiCuZn-ferrite and low-temperature-cofired ceramic (LTCC) during co-firing. The copper (Cu) ions in ferrite can diffuse into LTCC at a distance of 120 μm after sintering at 900 °C for 2 h, yielding a diffusion coefficient around 10^{-9} cm^2/s. The magnesium (Mg) and aluminum (Al) ions from LTCC also diffuse into ferrite for a shorter distance. Several new phases form through such inter-diffusion. For example, the inter-diffusion between alumina and ferrite induces the formation of hematite whose presence is detrimental to the saturation magnetization and permeability of ferrite. Additionally, inter-diffusion also induces changes in the lattice parameters of ferrite. We note a linear relationship between the lattice constant of ferrite and saturation magnetization, which demonstrates that magnetic properties are strongly tied to the crystalline structure of ferrite.

Keywords: A. Sintering; C. Diffusion; C. Magnetic properties; D. Ferrites; D. Glass

1. Introduction

Due to increased demand for miniaturized passive components, low-temperature-cofired ceramics (LTCC) have attracted considerable attention over the last two decades. Despite their small size, LTCC modules demonstrate excellent reliability and resilience in harsh environments. We have observed increasing demand for multi-functional LTCC modules, with magnetic performance especially desirable. Combining the dielectric and magnetic properties into one LTCC module, allows small LC filters, transformers, and other components to be manufactured.

The sintering temperature for manufacturing LTCC modules is inherently limited by the melting point of silver, 960 °C. Full densification of monolithic ferrite often requires a much higher sintering temperature and significant progress on the sinterability of ferrites has been made in the last several years.[1,2] Through particle size refinement and the addition of a liquid-phase sintering aid, Bi_2O_3, the densification of NiCuZn-ferrites is now possible at temperatures as low as 900 °C, thereby making the incorporation of NiCuZn-ferrite into a LTCC module a very real possibility. It is necessary to examine the co-firing behavior of LTCC and NiCuZn-ferrite.

Several research groups investigating this issue have discovered many defects within LTCC/ferrite laminates.[3–8] These defects can largely be attributed to physical mismatches such as differential shrinkage or a thermal expansion mismatch between LTCC and ferrite layers.[9] Unfortunately, relatively little research has focused on the chemical mismatch between ferrite and LTCC. Though Rabe et al. claimed that the inter-diffusion between LTCC and NiCuZn-ferrite is negligible, they also noticed a 50% loss on magnetic permeability after co-firing.[8] This loss was related to the refinement of ferrite grains near LTCC layer and can be attributed to shrinkage constraints imposed by the nearby LTCC layer. This study focuses on chemical reactions during the co-firing of ferrite and LTCC. Commercial LTCC powder is usually comprised of glass powder and alumina fillers; in order to distinguish the influence from glass or from alumina, the NiCuZn-ferrite powder was mixed with either glass or alumina powder. We then conducted phase analysis and microstructure characterization. Glass/ferrite and LTCC/ferrite laminates were also prepared to investigate the co-firing behavior.

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0955-2219/$ – see front matter
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.07.029

Table 1
Starting compositions for the powder compacts prepared in the present study.

Notation	Ferrite (wt%)	Glass (wt%)	Al_2O_3 (wt%)
F	100	0	0
G	0	100	0
A	0	0	100
GA[a]	0	60	40
FG	50	50	0
FA	50	0	50
FGA	50	30	20

[a] The composition of GA compact is similar to commercial LTCC.

2. Experimental

Two types of specimens were prepared for this study. The first is powder compacts, the second laminates.

The powder compacts are comprised of the powder mixtures of $Ni_{0.7}Cu_{0.12}Zn_{0.18}Fe_2O_4$ ferrite, borosilicate glass and/or alumina (99.5% Al_2O_3, ~0.5 μm, Sumitomo Co., Japan). Table 1 displays the compositions of the powder compacts prepared in the study. A small amount, 2.4 wt%, of Bi_2O_3 was pre-added to the ferrite powder to improve sinterability.[1] There was no inert ceramic filler in the glass. Instead, several cations, Al (~16 wt%, in terms of all cations %), Ca (~14 wt%), Mg (~2 wt%) and Zn (~6 wt%) were present in this borosilicate. The composition of GA powder compact (60 wt% glass and 40 wt% alumina) was similar to that of commercial LTCC. The powders were ball milled with zirconia media in alcohol for 4 h. After drying and sieving, the powders were die-pressed into pellets or toroids. The sintering was performed at 800 °C, 850 °C, 900 °C and 950 °C for 2 h in air.

Two types of laminates, glass/ferrite and LTCC/ferrite, were also prepared and laminate structure can be seen in Fig. 1. The LTCC was prepared by mixing 60 wt% glass and 40 wt% alumina powders together. The glass, LTCC and ferrite tapes with a thickness of 20 μm were prepared through tape casting. Laminating different numbers of green tapes created the laminate structure and the laminates were then punched to produce discs with the dimensions of 2.5 mm × 2.0 mm × 1.0 mm. The binders were removed by firing the laminated specimens from room temperature to 450 °C at a heating rate of 1 °C/min in air. The sintering was carried out at 900 °C in air for 2 h.

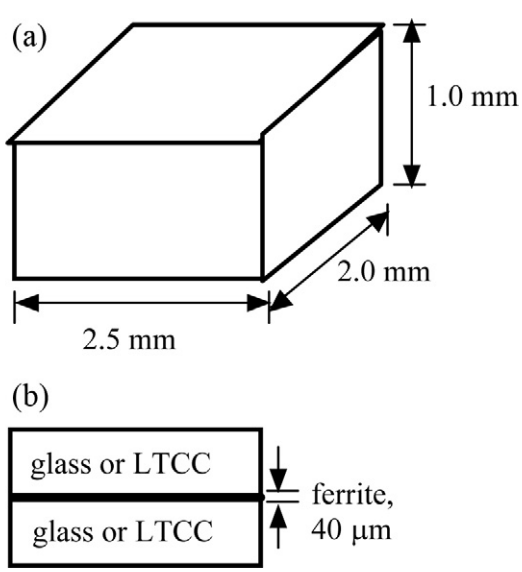

Fig. 1. (a) Dimensions and (b) cross-section of green glass/ferrite and LTCC/ferrite laminates. The thickness of ferrite (middle) layer is 40 μm.

Phase analysis was conducted using X-ray diffractometry (XRD, TTRAX III, Rikagu Co., Japan). A Rietveld software MAUD 2.14[10] was adopted to estimate crystalline phase levels within the sintered powder compacts. The microstructure was observed through scanning electron microscopy (SEM, TM-1000, Hitachi Co., Japan). The magnetic hysteresis loop was measured with a superconducting quantum interference device (SQUID, MPMS7, Quantum Design Co., USA). The magnetic permeability was determined with an impedance analyzer (Model 4291A, Agilent, Palo Alto, USA). The measured frequency varied from 1 MHz to 800 MHz. The composition variation within the laminates was analyzed using an electron-probe microanalysis (EPMA, JXA-8200, JEOL Co., Japan).

3. Results

3.1. Powder compacts

Fig. 2 shows typical micrographs for powder compacts after sintering at 900 °C for 2 h. There were few pores in the monolithic NiCuZn-ferrite (powder compact F) specimen and the relative density estimated from the micrograph is >95%. Also, the size of ferrite grains in the powder compact F was around 4 μm after sintering, Fig. 2a. The white phase at the boundaries of the ferrite grains, as identified by the EPMA, is a Bi_2O_3-rich phase. There were many spherical pores in the monolithic glass (compact G) and glass + alumina (compact GA) specimens, Fig. 2b and c. This indicates that the densification of the G and GA compacts has reached the final sintering stage. The density of the ferrite + alumina (compact FA) specimen is low, Fig. 2d and the size of ferrite grains small. Though the ferrite + glass (compact FG) specimen is dense, the size of ferrite grains within the glass matrix is small, Fig. 2e. The pores in the ferrite + glass + alumina (compact FGA) specimen have a spherical shape. The FGA sintering was carried out at 900 °C and reached the final stage. Similar to the FA and FG compacts, the size of ferrite grains in the FGA compact is small.

Fig. 3 shows XRD patterns for the powder compacts after 2 h of sintering at 900 °C. In addition to the spinel phase for the monolithic NiCuZn-ferrite specimen (F), a very small amount of Bi_2O_3 was found. No crystalline phase was found in the monolithic glass compact (G) and only corundum phase (α-Al_2O_3) was found in the monolithic alumina compact. In addition to the α-Al_2O_3 phase in the sintered GA (LTCC) compact, two reaction phases, anorthite ($CaAl_2Si_2O_8$) and gahnite ($ZnAl_2O_4$), were observed. However, these two reaction phases were not observed in the GA compacts after sintering at 800 °C and 850 °C for 2 h (not shown). A reaction phase, hematite (α-Fe_2O_3), was observed in the sintered FA compact. In the sintered FG compact, cristobalite (SiO_2) phase was found. In the sintered FGA