Development of a New Sealing Material for PDP

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Abstract
Glass frit was selected to be a Bi_2O_3-RO-R_2O_3 system as a sealing material to replace the current PbO system in PDP. Fillers such as a zircon, cordierite and β-eucryptite were added for the control of thermal expansion coefficient (CTE), flowability and strength for sealing. At 450-500 ℃, reaction of frit and filler and interface were evaluated by a flow button test and SEM observation. The composite (frit and filler) showed CTE in the range of 70-83 x 10^{-7}/K and flowability of 14-20mm. It can be a candidate for the replacement of PbO system.

1. Introduction
In information industry, a sealing glass is applied to junction of glass substrate which has reasonably close expansion match with glass substrate [1]. To use as a sealing material for PDP process, it needs to be fired below 500℃, thermal expansion coefficient in the range of 70-83 x 10^{-7}/K. Most of the sealing materials used are the lead oxide system which has a long history in CRT. However, PbO system adversely affects the health of workers handling the glass powder as well as environmental pollution caused by glass waste.

Recently, environment protection issues restrict the wide use of PbO system for example, the regulation of RoHS and WEEE in European society. From this circumstance, the demand for the development of Pb-free material is urgent [2, 3].

It is our purpose to get fundamental data for developing a lead free new sealing material for PDP. In this work, Bi_2O_3-RO-R_2O_3 system was used as a frit which had the thermal expansion coefficient in the range of 100-115 x 10^{-7}/℃. Fillers (zircon and cordierite, ß-eucryptite) were added to the glass to reduce high CTE of glass. After firing, we have evaluated the relationship of glass frit and filler as a function of filler types and their content.

2. Experimental procedures
Bi_2O_3-RO-R_2O_3 glass was prepared by mixing appropriate amount of each powder (Aldrich, USA) with a reagent grade. The batch was melted in an alumina crucible at 1000℃ for 2h. The glass melt was quickly poured and quenched on a ribbon roller. The glass cullet was pulverized by using a sieve (D_{50}: 106㎛). For the preparation of bulk specimens, the melts from the furnace were poured into a graphite mold and heated to the temperature of 10℃ above T_g of glass. The particle size (D_{50}) of fillers was 16㎛ (zircon), 45㎛ (ß-eucryptite), and 45㎛ (cordierite). The matrix frit [M] and fillers [zircon (Z), ß-eucryptite (E), cordierite (C)] were mixing by ball mill for 24h and then dried for making pellets (12.65mm in diameter) by a uniaxial pressing method (70㎏/㎠) that is, flow button test (F/B test). The pellets were sintered in the temperature range of 470℃ for 10min on PD200 glass substrate under a heating rate of 3.3℃/min.

The glass transition temperature (T_g) were determined with a differential thermal analyzer (TG-DTA, Rigaku, Japan) under 10℃/min of heating rate. Glass bulk was made of 3 x 3 x 2mm in size for the test of T_s (Softening Point). The CTE of samples were measured using a vertical type of thermal mechanical analyzer (TMA, Rhometric, UK) with a heating rate of 5℃/min. The flowability was determined by samples diameter after sintering on PD200 glass substrate. The interface between matrix frit and filler was evaluated using a scanning electron microscope (SEM, HITACHI, Japan) and energy dispersive X-ray microanalysis system (EDAX, Phoenix60).

3. Results and Discussion
The differential thermal analysis results of the frit in Fig. 1, the graph shows the glass transition temperature (T_g) at 362℃. The softening point (T_s, $\eta=10^{7.6}$ dPas) of frit is 430℃ that suggests the

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properties of low melting glass.

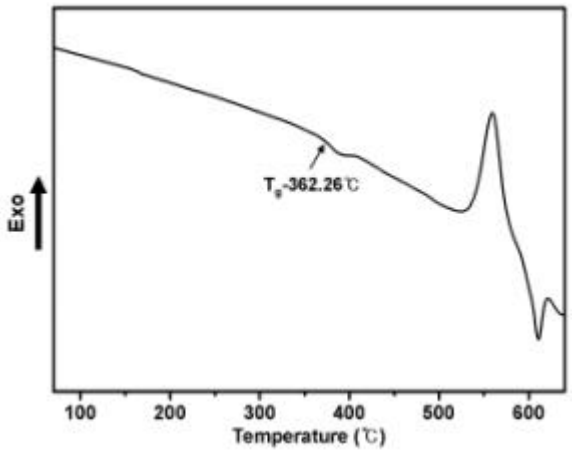


Fig. 1 Differential thermal analysis of frit

As shown in Fig. 2, with increasing the filler content, the diameter of composites were decreased. When the filler content was over 10wt%, the composites indicate inappropriate flowability of below 15mm with the exception of zircon. It seems that particle size have an effect on flowability. In addition, the images of flowability are compared in Table 1.

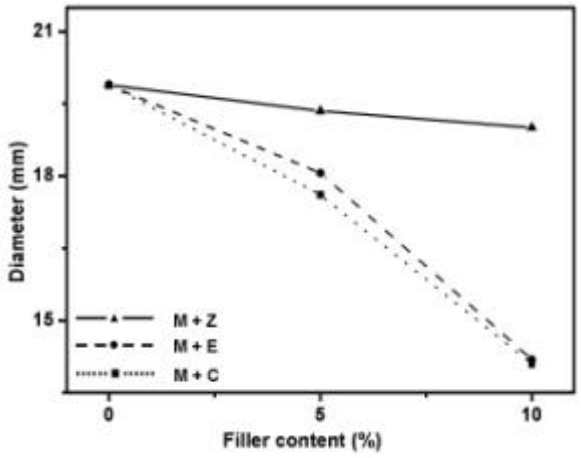
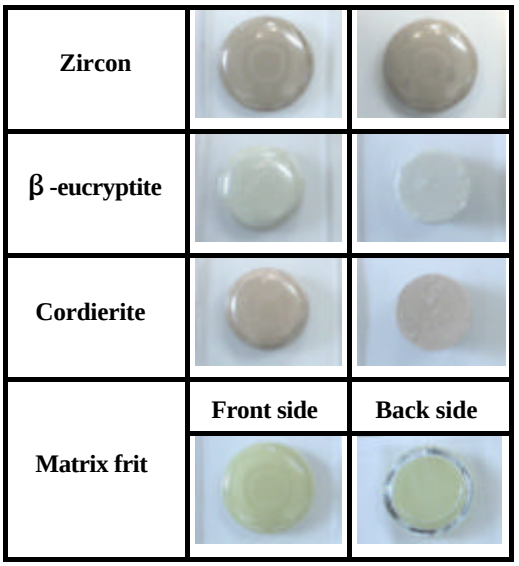


Fig. 2 The diameter of composites (frit and fillers) after sintering at 470℃ for 10min; fillers [zircon (Z), ß-eucryptite (E), cordierite (C)]

Table 1 The image of flowability by F/B test

Content / Fillers	5wt%	10wt%



For the design of a new sealing materials, one of the important factors, the CTE of the composites (matrix frit and filler) have been analyzed by many theoretical models [4,5,6]. Theoretical data (T.D) by Turner modeling and experimental data (E.D) for filler types and their content are shown in Fig. 3. The E.D is lower than T.D, which is due to the pores produced by sintering (Fig. 4). When the filler content is 10wt%, the composites indicates the CTE in the range of 69-82 x 10^{-7}/K.

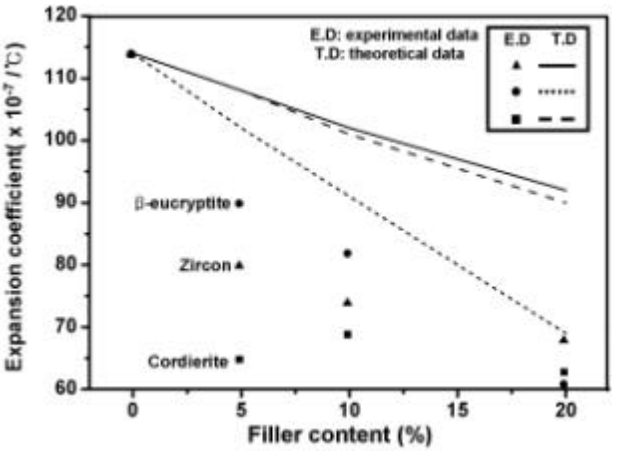


Fig. 3 The theoretical CTE by Turner modeling and experimental CTE of the composites as a function of filler types and their content

As shown in Fig. 4, interfacial reaction between the matrix frit and zircon was not found. In addition, it

was clearly shown in the etched surface with 5% HNO_3.

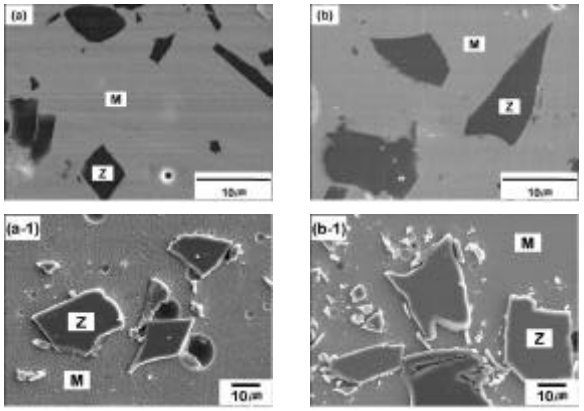


Fig. 4 SEM images of the composites (matrix frit and zircon); (a) 5wt%, (b) 10wt% and (a-1), (b-1) etched surface

Any new crystal phase through the interfacial reaction between the matrix frit and zircon was not detected from the XRD results (Fig. 5).

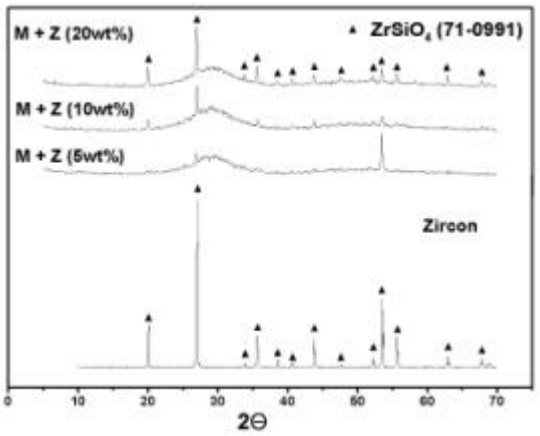


Fig. 5 XRD patterns of composites (matrix frit and zircon) and zircon

4 Conclusion

Through analyzing the composites and the interface reaction between matrix frit and fillers, we suggest appropriate filler content in the range of 5-10wt%. Furthermore, in the sealing material, flowability is related to the filler size. Properties of the composites show that similar to the lead oxide system. The Bi_2O_3-RO-R_2O_3 glass system as a matrix frit composition can be a candidate for the replacement of PbO system.

5 Acknowledgements

This work was supported by grant No.32505-01 of Korea Industrial Technology Foundation.

6. References

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