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Controlled crystallization and characterization of cordierite glass-ceramics for magnetic memory disk substrate

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Glass-ceramics containing cordierite ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$) as a crystal phase based on the glasses in the system $MgO\text{-}Al_2O_3\text{-}SiO_2$ were investigated for the application to magnetic disk substrate for higher storage capacity. Parent glasses were prepared with CeO_2 addition as a flux and were crystallized by a controlled 2-step heat treatment The maximum nucleation and crystal growth rates were $2.4 \times 10^9/\text{mm}^3 \cdot \text{hr}$ at 800 °C and 0.3 μm/hr at 915 °C respectively. Only α- cordierite was precipitated after heat-treatment. After nucleation at 800 °C for 5 hours prior to crystallization at 915 °C for 1 hour, the resulting crystal volume fraction and crystal size were 17.6% and 0.3 μm, respectively. Heat-treated specimens through the above condition showed the optimum properties for magnetic memory disk substrates as follows. ; Bending strength of 192 MPa, Vickers hardness of 642.1 kg/mm^2, thermal expansion coefficient of 39×10^{-7}/K and surface roughness of 27 Å.

1. Introduction

According to the development of computer devices toward large scale and multi-media for multi-tasking, there has been a rapid increase in demands for a magnetic memory disk with higher storage capacity which is necessary for the increase in the amount of information [1]. The substrates for this magnetic memory disk must have some characteristics such as high mechanical strength and surface hardness in order to protect the media film on it from a high speed rotation and contact with a head. In particular, the substrates should be capable of controlling the surface roughness to a range from 15 to 50 Å for the CSS (Contact Start Stop) characteristics of a magnetic disk substrate [1, 2].

Recently the flatness of the substrate became more important since the flying height tends to decrease (to about 0.05 μm) in order to increase recording density of the magnetic memory disk [1–3].

Aluminum alloy has been conventionally used as a main material of magnetic memory disk substrate. However aluminum alloy substrate does not have sufficient rigidity for rapid rotation owing to its ductile or plastic behavior. And it exhibits a bad flatness and surface roughness due to its defects inherent in the material. Moreover aluminum alloy has so high thermal expansion coefficient that it is not appropriate for high density disk substrate. Thus it can not cope with the recent requirement for high storage capacity [1, 2].

As a potential material for overcoming this problem of the aluminum alloy substrate, cordierite glass-ceramics was proposed in this study. Glass-ceramics with cordierite ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$) as a major crystal phase by crystallization of glass in the system of $MgO\text{-}Al_2O_3\text{-}SiO_2$ have many advantages, namely high mechanical strength, surface hardness and low thermal expansion coefficient [4–6]. In addition, cordierite glass-ceramics show good capability of controlling the surface roughness due to their sphere-like crystal morphology. Glasses in the system of $MgO\text{-}Al_2O_3\text{-}SiO_2$ however, have a disadvantage of high viscosity causing the problem of producibility into the plate shape. So the addition of the flux such as alkali oxides is necessary for lowering the viscosity of the glass. But the alkali oxides cause the reaction problem with the media due to their high ionic mobility and dispersion tendency [2, 7].

Thus in this study, MAS system cordierite glass-ceramics was prepared by adding CeO_2 as a flux, based on the report that lanthanides markedly decrease viscosity, having a little influence on thermal expansion, mechanical properties and chemical durability of glasses [8]. In preparation of MAS system glass, cordierite stoichiometric composition was selected and TiO_2 was chosen as a nucleating agent.

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The nucleation and crystal growth rates were determined for the parent glass and then the strength, surface hardness, thermal expansion coefficient and surface roughness were investigated as a function of crystal volume fraction and crystal size.

2. Experimental

The composition of glass in this study was 12.9MgO-32.1Al_2O_3-48.0SiO_2 in weight % which is that of determined by that of stoichiometric cordierite. CeO_2 was added by 5 wt % as a flux showing no problem of dispersion [7, 8]. 2 wt % B_2O_3 was also added to improve the homogeneity of the melt in the form of H_3BO_3.

Batches were well mixed and then melted at 1550 °C for 3 hours in an electric furnace using a Pt-Rd 10% crucible. After crushing the glass into a frit, 7 wt % TiO_2 was added as a nucleation agent and remelted at 1550 °C for 2 hours in a same way in order to make sure the homogeneity of the melt. The resulting melt was poured into the preheated copper mold and slowly cooled to room temperature. The glass samples were annealed at temperature around T_g and cut into bar type specimen of $5 \times 5 \times 20$ mm^3 for the measurement of various properties. Each specimen was polished to remove the surface defects.

The nucleation and crystal growth rates were measured using a two step heat treatment process [9]. Firstly the glass specimens were heated at 10 K/min to the nucleation temperature range (in intervals of 25 K from 750 to 850 °C, corresponding to the range $T_g \sim M_g$ (softening point) +50 °C as reported [10]) from 1 to 5 hours with every hour. They were heated at 15 K/min to 940 °C for 1.5 hours. The nuclei were thus grown to a measurable crystal size. After being cooled to room temperature, the specimens were fractured and the number of crystal (nuclei) per unit area was determined with SEM (JSM-840A, Jeol, Japan). The crystal growth rate was determined similarly. The nucleation temperature and time were fixed at 800 and 2 hours, respectively. The crystal growth temperatures ranged from 865 to 965 °C in intervals of 25 K and the growth times lay in the range of 30–120 minutes with intervals of 30 minutes. The resulting crystals (α -cordierite) were found relatively uniform in shape and size. Thus their sizes could be averaged easily by observing the fractured section of the each specimen with SEM. The crystal volume fraction of heat treated glass specimens could be calculated as well.

After crystallization process and polishing of surface to remove the surface crystallized layer, several properties of heat treated glasses were measured such as a mechanical strength, surface hardness, thermal expansion coefficient and surface roughness. For measurement of the mechanical strength, 3-point bending strength method was employed to the bar type specimens using a Universal Testing Machine (H10K-C, Hounsfield, U.K.). Vickers hardness test was applied to measure the surface hardness of the polished specimens with Vickers microhardness Testing Machine (MXD-CX3E, Matsuzawa, Japan). In this work, the thermal expansion coefficient values were taken in the range of room temperature 200 °C from a TMA measurement (TMA 2940, TA Instrument, Germany), and the surface roughness of specimens was measured in the value of rms (root mean square) roughness with AFM (Auto Probe CP, Park Scientific Instrument, U.S.A.) after polishing the each specimen with diamond powders having the grain size 1 μm.

3. Results and discussion

Only a α -cordierite crystal phase was formed for all the crystallization heat treatment conditions performed in this work because of the addition of CeO_2 which promotes the crystallization of α -cordierite with the inhibition of the formation of stuffed β -quartz (μ -cordierite) [11] as presented by Fig. 1 which shows the XRD patterns of the parent and the crystallized glasses. Without the addition of CeO_2, stuffed β -quartz is precipitated earlier than α -cordierite. It was reported that α -cordierite causes a high strength, low thermal expansion coefficient and other advantageous properties of the glass-ceramics compared with stuffed β -quartz which is one of the other crystal phases formed in the MAS system glass [12] and this fact agrees with the result in this work.

Figs 2 and 3 show the SEM photographs and the stationary nucleation rate of the nucleated glasses, respectively. Likewise, the SEM photographs and crystal growth rate of the crystallized glasses are shown in Figs 4 and 5. For the parent glass, the maximum nucleation rate was 2.4×10^9/ mm · hr at 800 °C and the maximum crystal growth rate occurred at 915 °C with the value of 0.3 μm/hr. Based on this data, the 3 point bending strength was measured for the glass specimen heat-treated at various conditions. Fig. 6

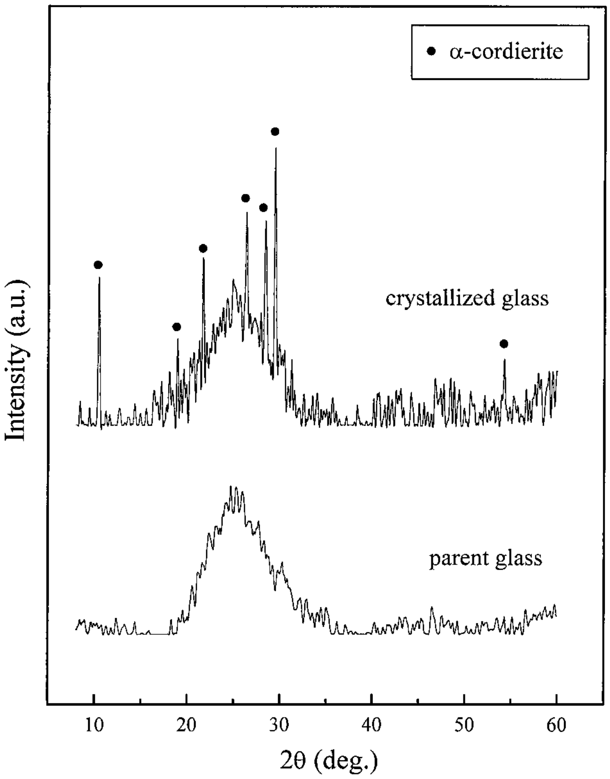


Figure 1 XRD patterns of parent and crystallized glass (crystallization at 800 °C/2 hrs–915 °C/1 hr).

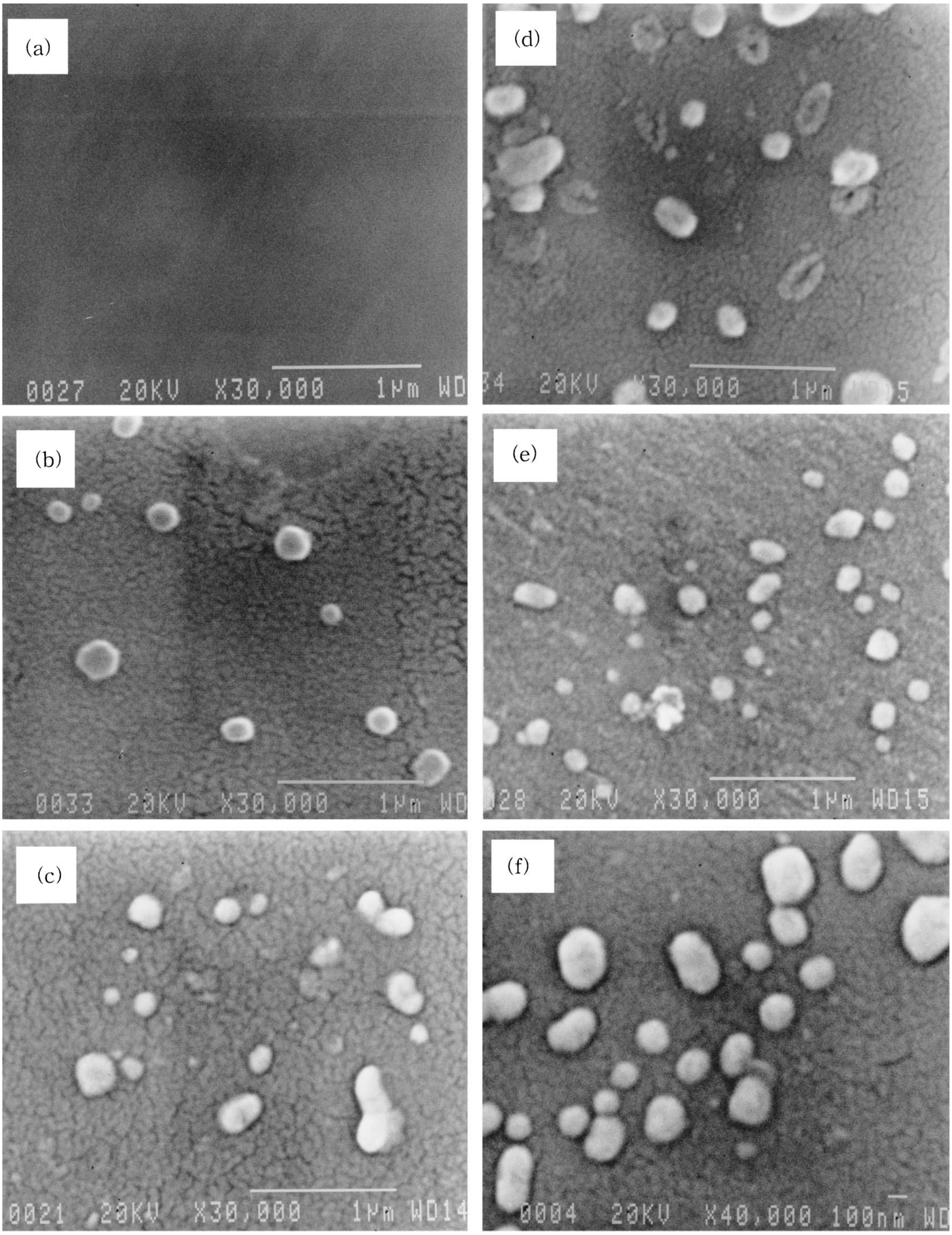


Figure 2 SEM photographs of nucleated glasses at 800 °C (crystal growth at 940 °C/1.5 hrs) ((a) parent glass, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 hrs nucleated glass).

exhibits the result that the strength of the specimens tends to increase with crystal volume fraction below the 17.6%, but decrease on the contrary above that percent. The strength was maximum at the crystal size 0.1 μm in the case of same crystal volume fraction as illustrated in Fig. 7. It is thought that the strength increases due to the fine grained microstructure by which the crystals play a role in preventing the propagation of the crack below 17.6%, and decreases owing to the operation of the overgrown crystal phase as a newly formed secondary defects or the generation of the internal micro-stress by the formed crystal phase with increasing heat treatment time above that percent [13–15]. Figs 8 and 9 exhibit the change of Vickers hardness of the specimens as a function of crystal volume fraction and crystal size,respectively. The surface hardness behavior of the specimens shows the similar tendency with that of the strength. The specimens

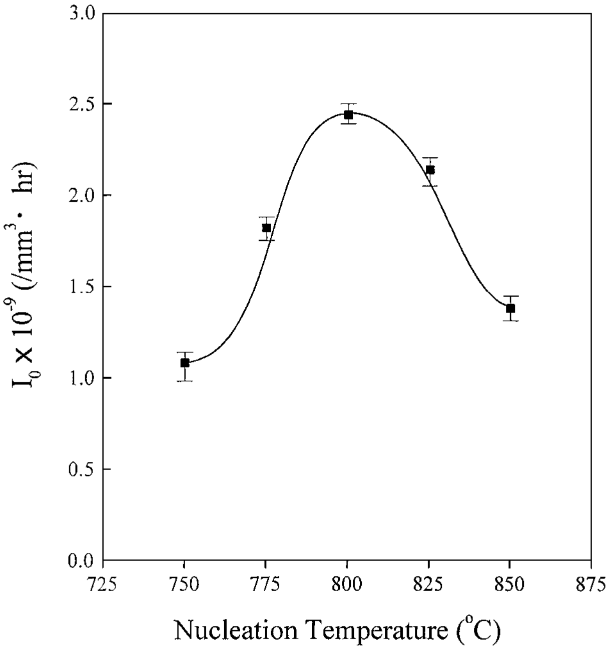


Figure 3 Stationary nucleation rates as a function of nucleation temperature (crystal growth at 940 °C/1.5 hrs).

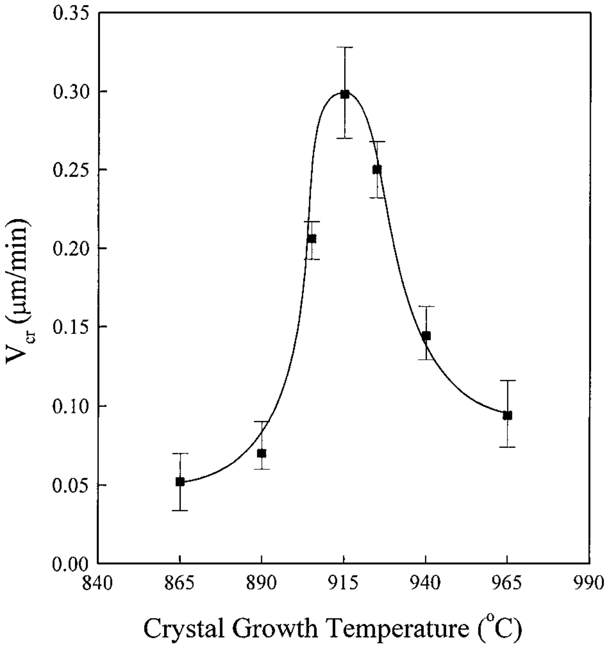


Figure 5 Crystal growth rates as a function of crystal growth temperature (nucleation at 800 °C/2 hrs).

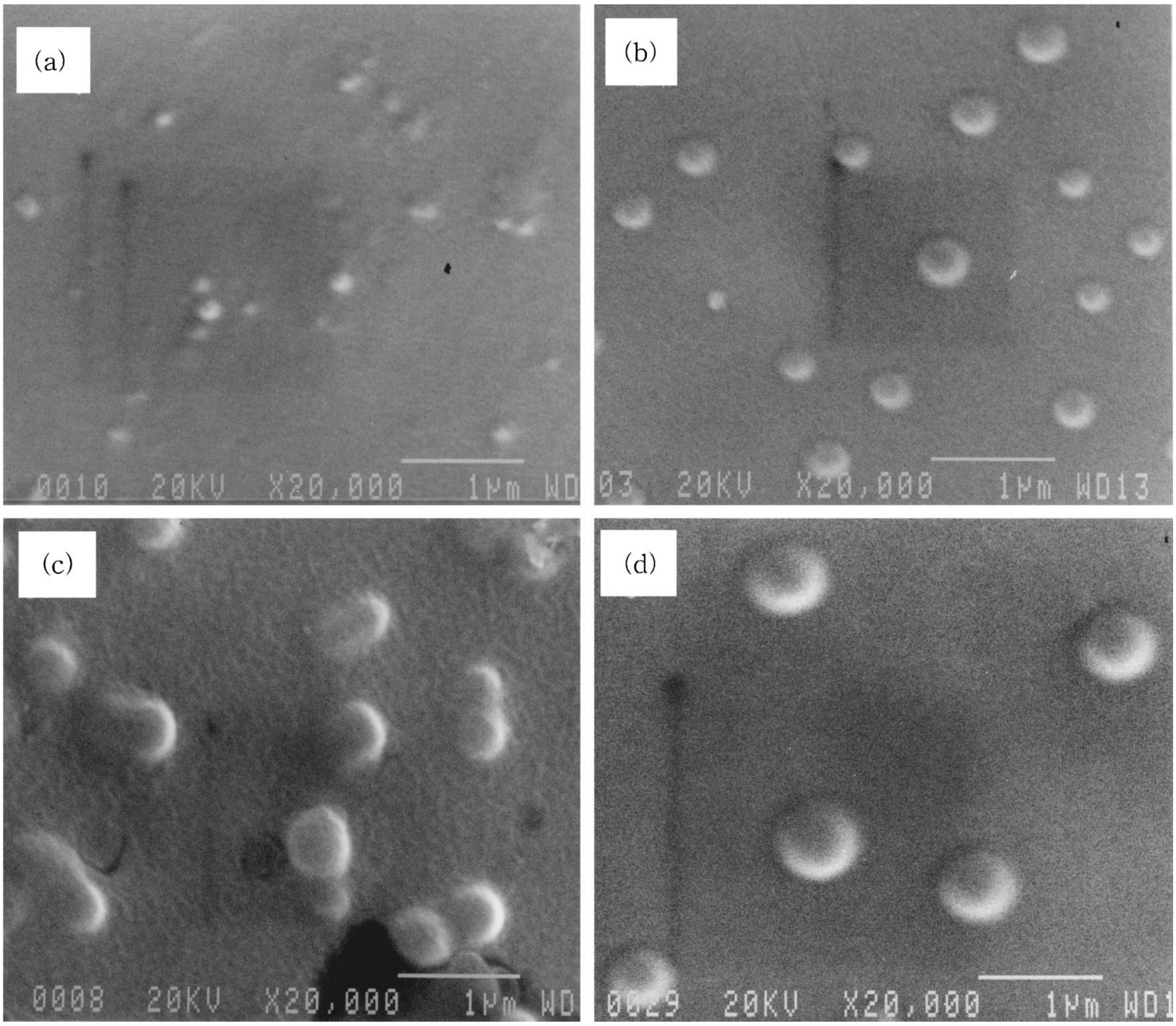


Figure 4 SEM photographs of crystallized glasses at 915 °C (nucleation at 800 °C/2 hrs) ((a) 30, (b) 60, (c) 90, and (d) 120 min).

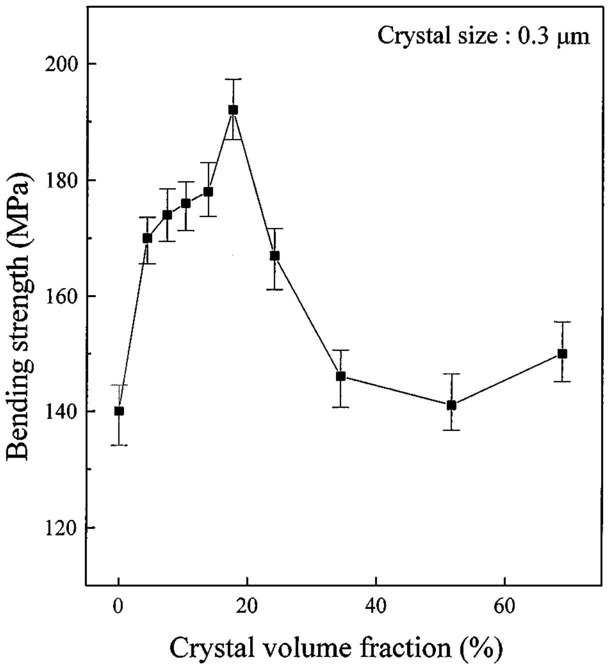


Figure 6 Change in bending strength of crystallized glass as a function of crystal volume fraction (crystal growth at 915 °C/1 hr).

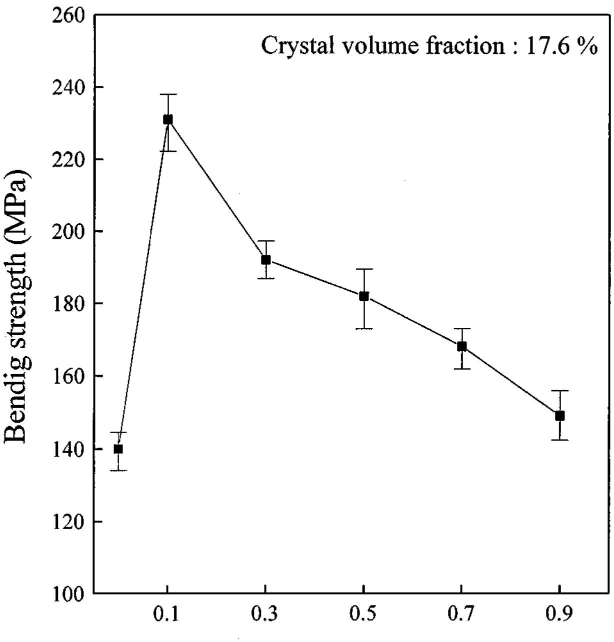


Figure 7 Change in bending strength of crystallized glass as a function of crystal size at same crystal volume fraction.

with the crystal volume fraction 34.4% and the crystal size 0.3 μm show the maximum hardness value in each case. Thermal expansion coefficients were almost constant regardless of the crystal volume fraction and crystal size as shown in Figs 10 and 11. This is caused by the small difference of the thermal expansion coefficients between the glass matrix and the crystal phase. And for that reason, microstress in the glass matrix is relatively small, which induces the high mechanical strength of the glass-ceramics [16].

In CSS (Contact Start Stop) characteristics of a magnetic disk substrate, the magnet tic disk substrate should not have a completely smooth surface but a surface

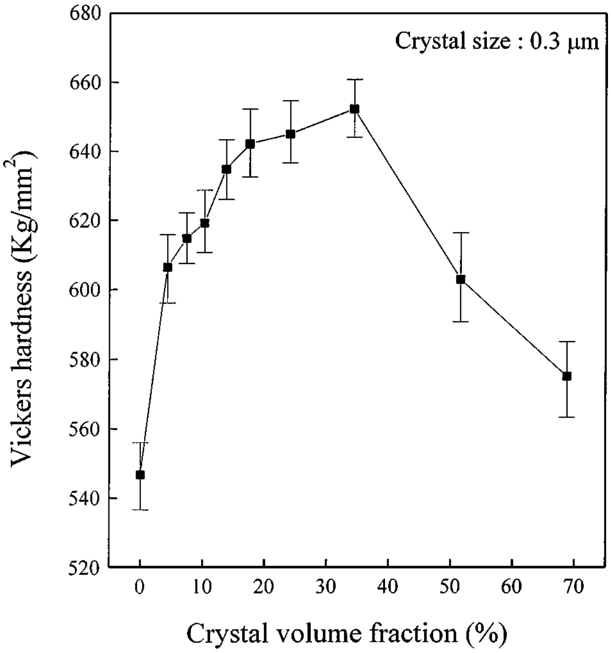


Figure 8 Change in vickers hardness of crystallized glass as a function of crystal volume fraction (crystal growth at 915 °C/1 hr).

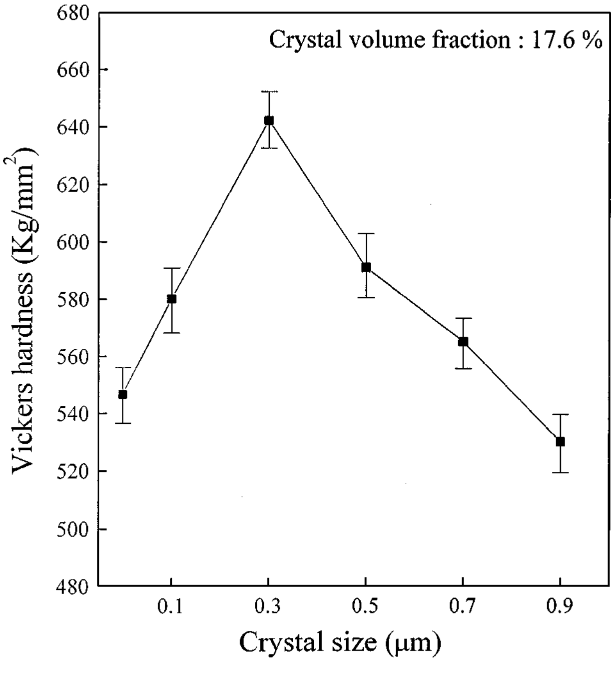


Figure 9 Change in vickers hardness of crystallized glass as a function of crystal size at same crystal volume fraction.

whose roughness is controlled to a range from 15 to 50 Å in order to prevent an adsorption between head and disk and a damage to the head and media [2]. Generally, however, the glasses have a very low surface roughness, so they must be subjected to mechanical or chemical texturing process for improving their surface roughness properties. It has recently been put into practice in the field of chemically tempered glass and crystallized glass-ceramics to make the surface of glass rough. As in this work, glass-ceramics has a superior capability of controlling the surface roughness through polishing process for removing surface crystallized layer after crystallization. Such a polishing pro ocess of the glass-ceramics provides the auto texturing

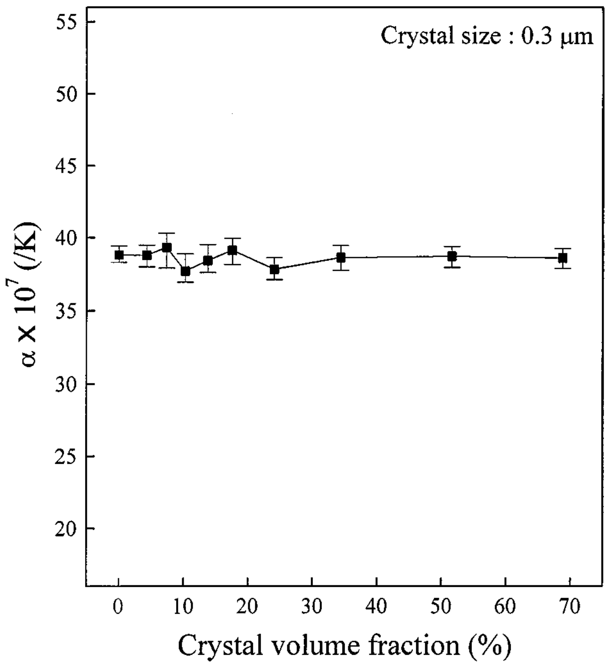


Figure 10 Change in thermal expansion coefficient of crystallized glass as a function of crystal volume fraction (crystal growth at 915 °C/1 hr).

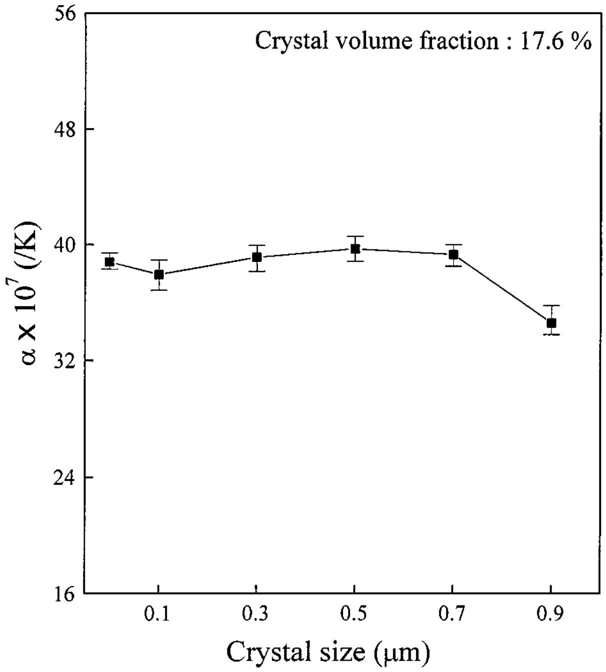


Figure 11 Change in thermal expansion coefficient of crystallized glass as a function of crystal size at same crystal volume fraction.

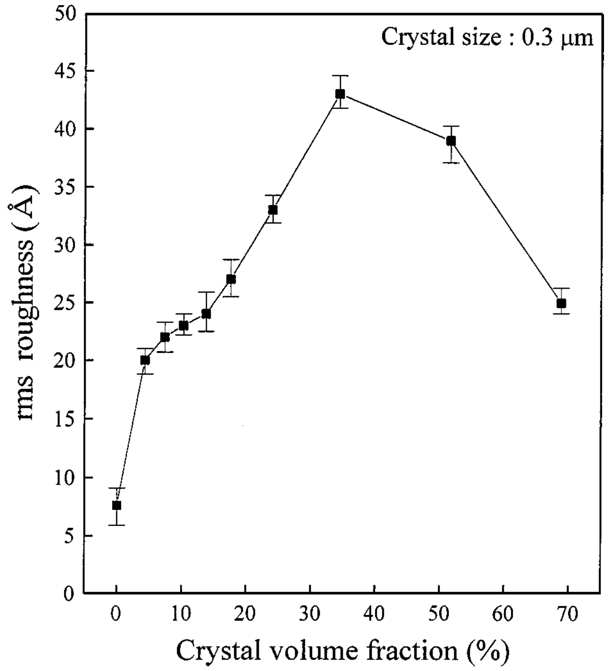


Figure 12 Change in surface roughness of crystallized glass as a function of crystal volume fraction (crystal growth at 915 °C/1 hr.

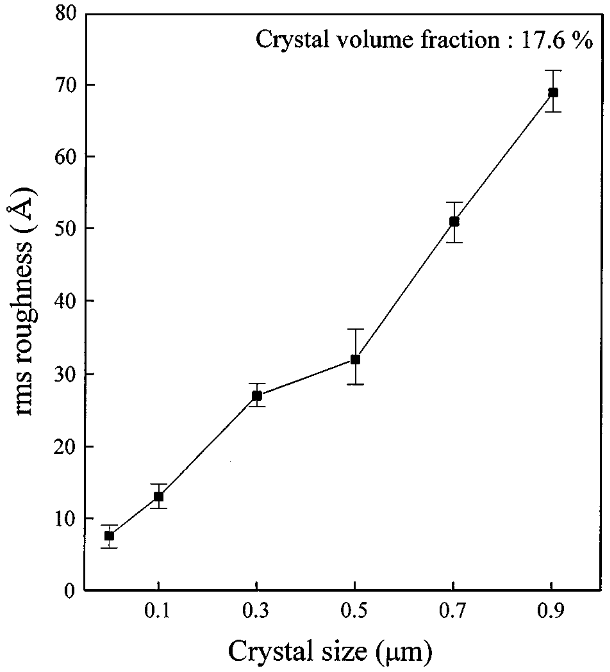
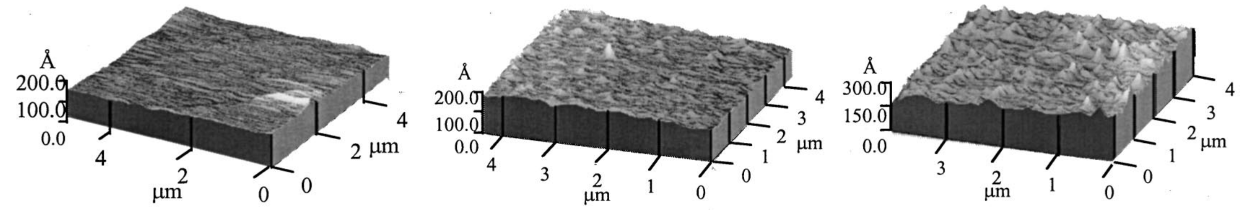


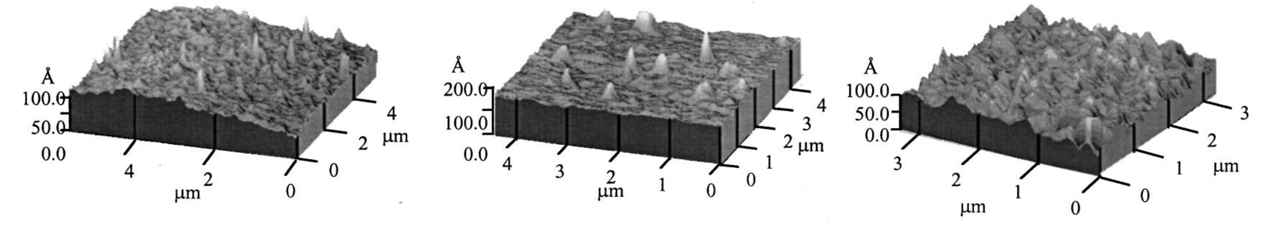
Figure 13 Change in surface roughness of crystallized glass as a function of crystal size at same crystal volume fraction.

effect to its surface owing to the polishing efficiency difference between glass matrix and crystal phase. As shown in Fig. 12, the parent glass exhibits the surface roughness value of 7.6 Å, which is insufficient for the surface roughness condition of a magnetic disk substrate. And the surface roughness of the specimen increases with an increase of the crystal volume fraction below the 34.4%, but decreases on the contrary above that percent. It is caused by the fact that the formed crystal phases generate the grain boundaries with the neighbored crystal phases and then result in the new flattened surface. Fig. 13 shows that the surface roughness increases as the crystal size increases. These two figures, that is Figs 12 and 13, give the clear evidence that the surface roughness values of the heat treated glasses are in the range of 15–50 Å in all cases except the crystal size 0.1 μm (<15 Å) and 0.9 μm (>50 Å). This result indicates that most of specimens except for those 2 cases satisfy the surface roughness condition (15–50 Å) which is necessary for using as a magnetic disk substrate. AFM images of the parent and heat treated glasses are shown in Fig. 14, where the surface roughness of the glasses increases with crystal size.

Finally, based on the results mentioned above the optimum heat treatment conditions and properties were chosen, and their details are as follows. When nucleated



(a) parent glass (b) 0.1 μm (c) 0.3 μm



(d) 0.5 μm (e) 0.7 μm (f) 0.9 μm

Figure 14 AFM images of parent and crystallized glasses at 915 °C (crystal volume fraction 17.6%).

at 800 °C for 5 hours and crystallized at 915 °C for 1 hour, its the resulting crystal volume fraction and crystal size were 17.6% and 0.3 μm. And under that conditions the optimum properties were shown as bending strength 192 MPa, Vickers hardness 642.1 kg/mm^2, thermal expansion coefficient 39×10^{-7}/K and surface roughness 27 Å.

4. Conclusions

The cordierite glass-ceramics was prepared from MAS system glass by 2 step heat treatment of the nucleation and crystal growth. For heat treated specimens, resulting crystal phase was only the α -cordierite and their maximum nucleation and crystal growth rates were 2.4×10^9/mm$^3 \cdot$ hr at 800 °C and 0.3 μm/hr at 915 °C, respectively. From the results, the optimum heat treatment conditions were as follows; the nucleation at 800 °C for 5 hours and the crystal growth at 915 °C for 1 hour, yielding the crystal volume fraction 17.6% and the crystal size 0.3 μm. Under this conditions, the bending strength was 192 MPa, Vickers hardness 642.1 kg/mm^2, thermal expansion coefficient 39×10^{-7}/K and surface roughness 27 Å.

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