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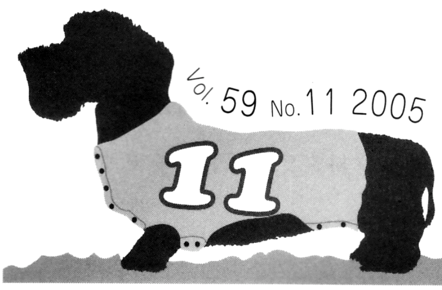

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Recent Advances in Strenthening Glass Material for CRT

(ブラウン管用ガラス材料高強度化に関する最近の進歩)

Tsunehiko Sugawara †, Yuichi Kuroki †, Tetsuji Yano †† and Shuichi Shibata ††

Abstract The important thing in order that the CRT still shines brightly for the coming digital era might be to realize a super-lightweight and ultra thin CRT, keeping its advantages such as high image quality and low cost. One of the reasons that CRT is heavy and fragile is due to the high density of CRT glass resulted from its high X-ray absorption ability. However, it might become an impetus for realizing such an innovative CRT by introducing new CRT glass with lower density and lower brittleness. This could be possible if a new electron gun with excellent focusing characteristics even at very low accelerating voltages would be developed. In addition, we have had some advances in strengthening glass material such as field-assisted chemical tempering and improvement of the mechanical strength of a crystalline solder glass. These also will produce a possibility to innovate CRTs.

Keywords: CRT, Glass, Brittleness, Ion-exchange, Solder glass

1. Introduction

For the past 50 years or more, the CRT has held the leading position of the display market owing in part to efforts in developing its advantages and overcoming its weaknesses. Whether the CRT still shines brightly in the market is dependent upon whether strategies and innovations in the CRT technology suitable for the coming digital era can be made. It might be to realize a super-lightweight and ultra thin CRT, keeping its advantages such as high image quality and low cost. On this point, many discussions have been published[1)~3)]. Anyway, the actual impression that the glass envelope for CRTs is being innovated is strongly required. In this paper, this possibility from a position of glass technology through our current research activities will be discussed, focusing on the intrinsic strength and the extrinsic strengthening of glass materials for the CRT.

2. Issues related to High density of CRT Glass

2.1 Heavy Glass

The glass system of SiO_2-Al_2O_3-BaO-SrO-ZrO_2-R_2O-R'O is generally used for panel glass for color CRTs (R_2O: alkaline oxides, R'O; alkaline earth oxides other than strontium and barium oxides)[4)]. The panel glass contains silica of 60-65 mass % and alumina of 1-3.5 mass %. Alkaline oxides are also included by 14-16 mass % for the purpose of adjusting its viscosity at high temperatures and its thermal expansion coefficient. The amounts of K_2O and Na_2O in panel glass are roughly balanced so that the proper mixed alkali effect (MAE) on the electrical resistance can be obtained. In addition, it contains strontium oxide of 9-10 mass %, barium oxide of 2-3 mass %, and·zirconia of 2% or less so that the X-ray absorption coefficient of 28 cm^{-1} or more at the wavelength of 0.6 angstrom may be achieved.

For glass composed of many oxides, the absorption coefficient $\mu(\lambda)$ can be calculated by using following equation[5)]:

$$\mu(\lambda) = \rho \sum_i f_i \varpi_i(\lambda)$$

where ω_i is the mass absorption coefficient of an oxide which is a function of wave-length, λ. f_i is the weight faction of the oxide, and ρ is the density of the glass.

The mass absorption coefficient of an oxide can be similarly calculated by the additive relationship as shown in following equation.

$$\varpi_{MmOn}(\lambda) = \left(mW_M\omega_M(\lambda) + nW_O\omega_O(\lambda)\right) / W_{MmOn}$$

in which W_M and W_O are the atomic weights of the cation

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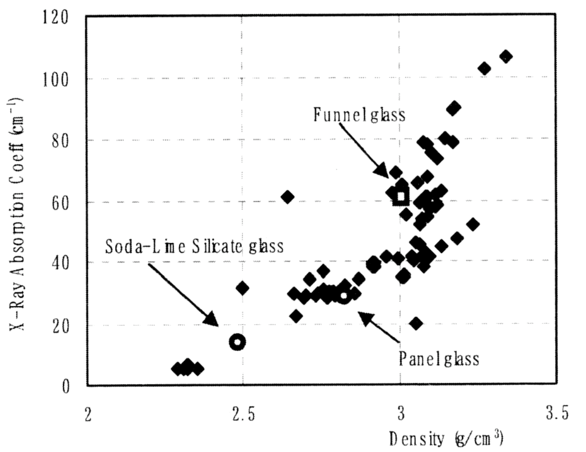

Fig.1 X-ray absorption coefficient as a function of density for various glasses.

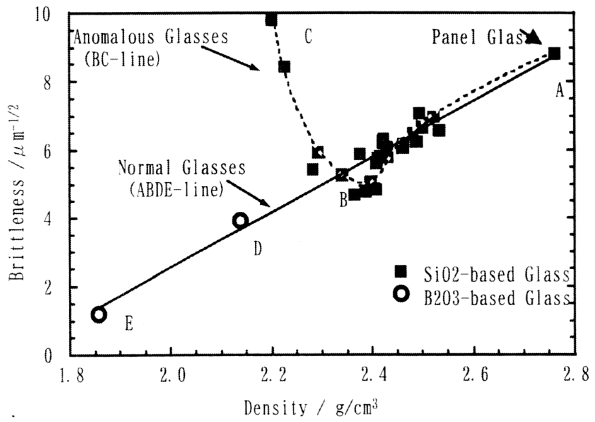

Fig.2 Brittleness as a function of density for SiO_2 and B_2O_3-based glasses[4].

and oxygen respectively. $W_{Mm}O_n$ is the formula weight of the oxide, $MmOn$, and $\omega_M(\lambda)$ and $\omega_O(\lambda)$, the mass absorption coefficients of the cation and oxygen respectively.

Accordingly, it should be absolutely necessary to introduce heavy elements into CRT glasses in order to attain a high absorption coefficient. As a result, the higher the X-ray absorption coefficient, the higher the density of glass. **Fig.1** shows the relationship between the absorption coefficient and the density in various glasses. In fact, the density of the panel glass and the funnel glass are 11% and 20%, respectively larger than that of soda-lime silicate glass. It can be easily understood that a normal glass bulb composed of panel glass and funnel glass is roughly 15% heavier than a glass bulb composed of soda-lime silicate glass.

2.2 Fragility and Intrinsic Strength of CRT Glass

The other issue related to the high densities of CRT glasses is the brittleness that triggers a strength reduction of the glass by a few orders of magnitude. It also leads to thermal breakage of CRTs in the assembly process and/or lowering productivity. Brittleness was proposed by Lawn and Marshall to be the ratio of hardness and fracture toughness[6]. Itoh and Sehgal reported that the brittleness of all normal glasses decreased with decreasing density, and the brittleness of most commercial glasses in the alkali-alkaline earth silicate glasses varied from 6 to $10\mu m^{-1/2}$ as shown in **Fig.2**[7]. It also indicates that the panel glass has the highest brittleness ($8.7\mu m^{-1/2}$) of normal glasses.

It is generally thought that brittleness is dependent on densification and plastic flow modes of deformation before crack initiation. A glass with a higher density cannot densify further under local stress or pressure. Therefore, not having the ease of deformation under local stress, it cannot easily release the stress. As a result, a crack can initiate and propagate even if the stress is small.

The panel glass with the highest brittleness appears to be a glass that does not have high scratch-resistance rather than a glass with low fracture toughness. In order to intrinsically enhance the practical strength of the glass, it is necessary to change the composition and to lower the density so that the brittleness sufficiently decreases.

From the point of glass technology, development of an electron gun with excellent focusing characteristics even at a very low accelerating voltage around 20kV is expected in near future. This development will enables us not only to remove the shadow mask unless degradation of the image quality, but also to lower the X-ray absorption coefficient and brittleness of CRT glass. In other words, it will greatly contribute to realizing a super-lightweight and ultra thin CRT, keeping its high image quality and low cost.

3. Advance in Extrinsic Strengthening

In consideration of both the brittleness of glass and inevitability of flaws in its surface, compressively prestressing the surface is effective in enhancing the practical strength of glass. First, prestressing by thermal tempering to panel glass was developed in order to realize perfect flat-face CRTs in 1996[8][9]. Then, it was elaborated to apply to glass panels for super slim CRTs[10][11]. Next, a new field-assisted chemical tempering (FACT) for funnel glass with MAE was devised for a super slim CRT with a wide deflection angle (135 degrees) in 2002[12]. These can afford to pursue both super-lightweight and ultra thin design.

The field-assisted chemical tempering is very effective in creating a deeper ion exchange layer within a shorter exchange time compared to the chemical tempering by thermal diffusion. However, it has never been clear what glass composition is most suitable for the field-assisted ion exchange. Recently, we have investigated ionic concentration profiles in the ion exchange layers in mixed alkali glass by experimenting with different alkali ratios, R[R=Na/ (Na+K)], in order to understand the effectiveness of the alkaline ratio of the mother glasses in the features of the ion exchange layer[13)14)].

3.1 Sample Preparation and Ion-Exchange

For the field-assisted ion exchange experiment, different alkali ratio models based on the funnel glass of the system $66SiO_2$-8PbO-$3.5Al_2O_3$-5CaO-3.5MgO-xNa_2O-(14-x) K_2O (in mol %) were created as shown in **Table 1**. Field-assisted ion-exchange treatments were carried out on the glass samples of 50x50x10 in mm. The set-up for the field-assisted ion-exchange of the glass samples is illustrated in **Fig.3**. The glass plate was sandwiched by a couple of alumina tubes. KNO_3 salt was melted inside the upper alumina tube, and contacted with the glass surface with a certain area, where the alumina tube was pressed closely on the glass surface to hold the molten salt. The Pt wire electrode was immersed in the molten salt. Al_2O_3 paste containing $CsNO_3$ melt on the stainless plate was pressed closely on the bottom glass surface in the bottom alumina tube to make a close contact between them. These were heated in the electric furnace up to the strain point Ts or Ts-25°C of the respective glass and DC-voltage 300V or 100V was applied between the electrodes. The current conducting the circuit was monitored by the current meter and the total charge was counted by the coulomb meter. When the total charge reached to the settled values, the DC-voltage supplier and the electric furnace were immediately turned off, and the sample glasses were cooled to the room temperature.

Table 1 Characteristic properties of the glass samples.

Glass	Model A	Model B	Model C	Model D	Model E
X	14	11	8	5	3
Alkaline ratio R (%)	100	79	57	36	21
Density (g/cm³)	3.038	3.014	2.999	2.984	2.978
Strain Point (℃)	455	442	447	461	473
Depth of ion-exchange (μm)	80	120	140	160	95
Surface Compression (MPa)	326	336	345	247	235

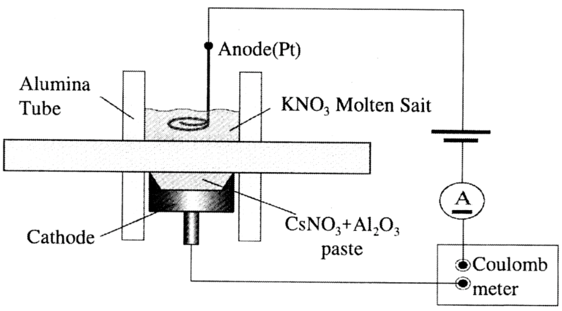

Fig.3 Schematic illustration of the field-assisted ion-exchange treatment.

3.2 Concentration Profiles of Exchanged Ions

The concentration files of potassium and sodium ions formed in the vicinity of the anode measured by EPMA (Electron Probe Micro Analyzer) are outlined in **Fig.4**. The observed characteristic features of the concentration profiles in the ion exchange layer were (1) the step function type profiles of the ion exchange frontier surface at an alkali ratio of 57% or more, (2) the exponential type profiles of the residual Na^+ ions, and (3) the decrease of the total alkali oxide concentration in the ion exchange layer and its strong dependence on the alkali ratio of the mother glass. The formation of the step-function type concentration profile is the most important feature of the field-assisted ion exchange. EPMA results revealed that the ion-exchange transition region has certain thickness of the order of micrometer. In this transition region, the Na^+ ion concentration decreased very steeply by the replacement of K^+ ions.

In order to understand this phenomenon thoroughly, the electrical conductivities of the glass samples were measured by AC 2-electrodes method, and the transport numbers of Na^+ and K^+ ions were analyzed using ICPS (Induction Couple Plasma Spectroscopy). The measured DC conductivities at strain point Ts and 450°C are plotted in **Fig.5** with the activation energies derived from the Arrhenius's equation. The typical mixed alkali effects (MAE) were observed. The conductivity minimum was found around R of 36%, while the activation energy maximum was around R of 60%.

As shown in **Fig.6**, the measured transport number of Na^+ ions as a function of R became smaller than that of K^+ ions at R<36% and within this thin transition region, the mobility of Na+ ions was reduced greatly. The motion of alkali ions in the ion exchange layer forms a new composition region behind the ion-exchange frontier. In most cases, the ionic conductivity of this new region differs from that of the ion-exchange. When R is more than 36%, at the initial stage, sodium ions can move forward easily compared to potassium ions in the transition region and a lot of potassium ions which are extracted easily into the transition region to fill the

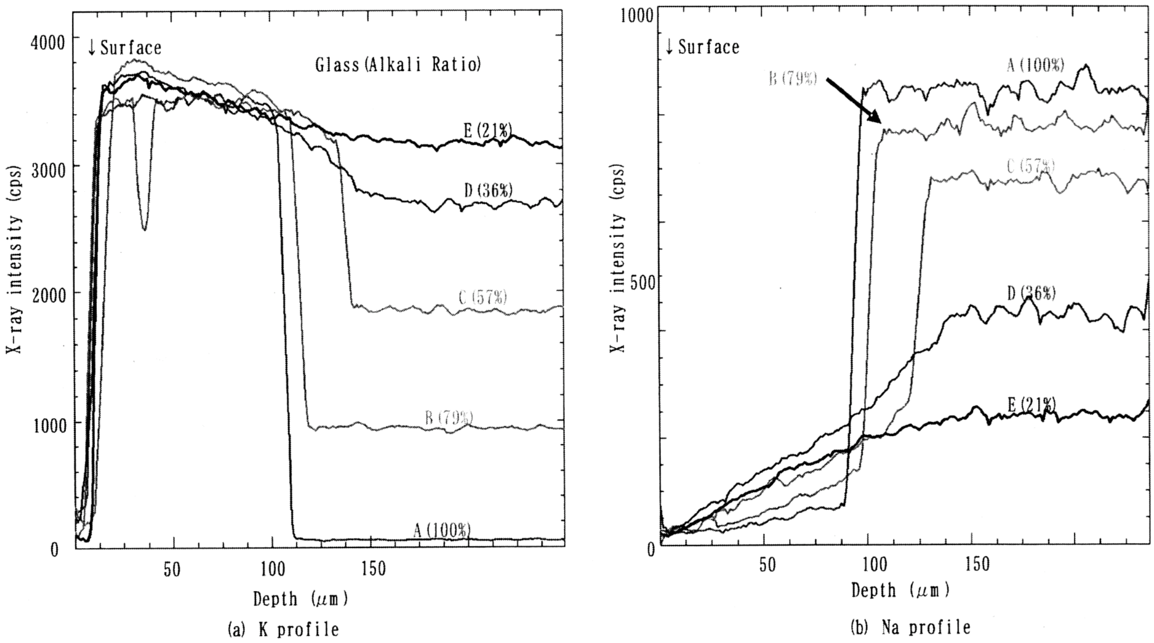

Fig.4 Potassium and sodium concentration profile in the ion-exchanged glass samples (Treatment temp:Ts, Total electrical charge:48C).

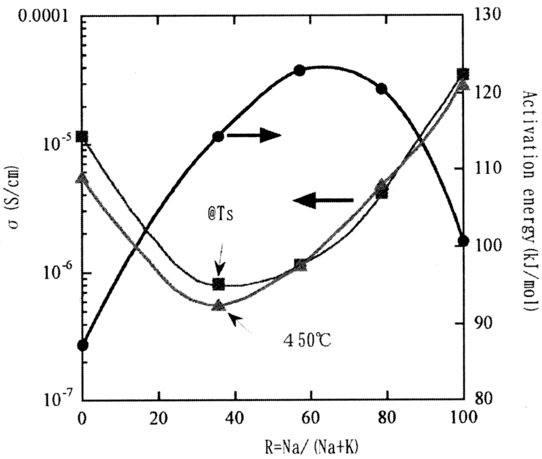

Fig.5 DC conductivities of glass samples at Ts and 450°C.

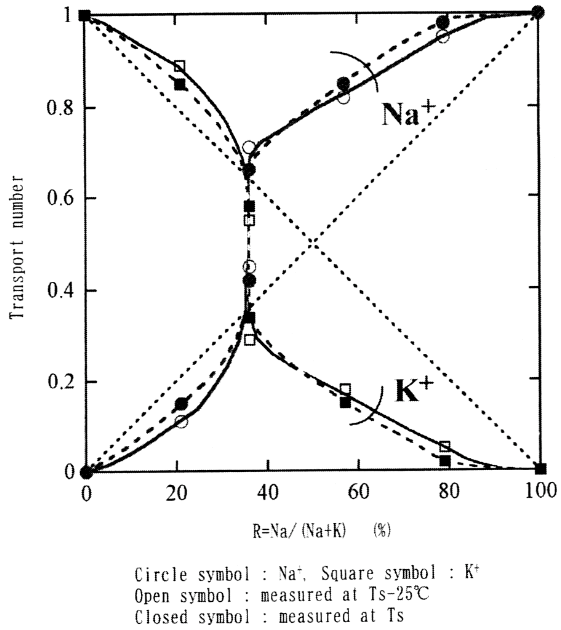

Fig.6 Transport numbers of Na^+ and K^+ ions as functions of R in the glass samples.

vacancy sites. As a result, the step-function type concentration pattern will form in the ion exchange layer. On the other hand, when R is lower than 36%, the increment of potassium ions in this region is comparatively stable because of the lower mobility of sodium ions and almost constant motion of potassium ions. Therefore the exponential type concentration pattern will form in the ion exchnage layer.

3.3 Mechanical reliability of step functional pattern

We also studied the mechanical reliability of FACT glasses. In the beginning of the experiment, glass discs of 70 mm in diameter and 3mm in thickness were prepared from the model C glass. After that, either of two kinds of chemical tempering procedures was done on a 55mm diameter area at the center of each glass disc and then it was abraded with 150-J abrasion under constant loading of 8 MPa at the middle portion of the lower surface, using a set of ring-on-ring fixtures as shown in **Fig.7**. Such sample preparations were made assuming that a CRT is under constant load due to the state of evacuation and that flaws may generate after evacuating. The discs were tested in biaxial bending using the above fixture on a 50mm diameter ring and a 12mm diameter loading piston at the center. The loading speed was 1mm per minute.

Fig.8 shows the Weibull plot of the abraded strengths for the three kinds of FACT samples for the model C glass, which had the ion exchange depth of 30, 50 and

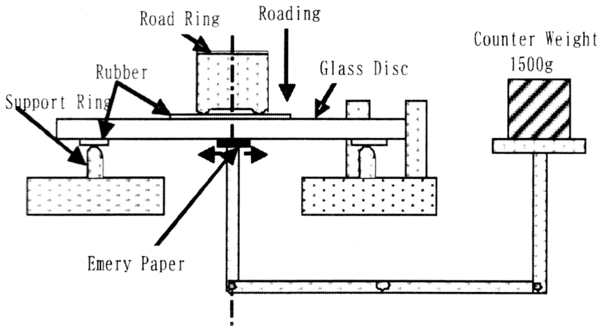

Fig.7 Schematic figure of biaxial bending and abrasion.

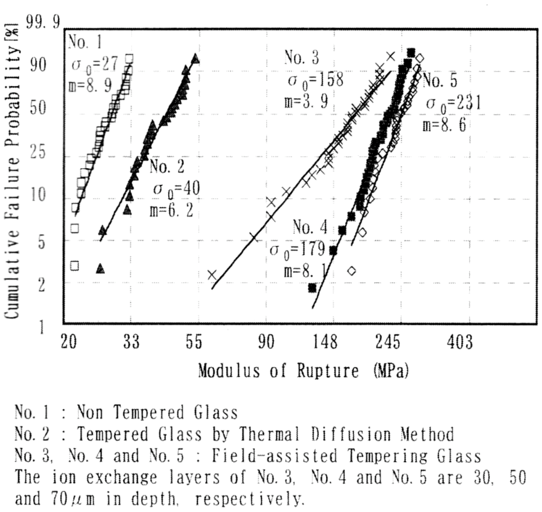

Fig.8 Weibull plot of the abraded strength of glass samples made of the Model C glass.

70É m, respectively, in comparison to those made of a non-tempered sample and a conventional chemical-tempering sample. The strength data of all the FACT samples are considerably higher than that of the conventional chemical-tempered sample with an exponential pattern of potassium concentration profile by a thermal diffusion. The parallel shift of Weibull plot on the samples of 50μm and 70μm from that of the non-tempered samples was indicative of being highly reliable. From .these results, it was concluded that, in order to attain a high reliability for the FACT, a step functional pattern of the potassium concentration profile and an ion-exchange depth of 50μm or more are both necessary. On the other hand, an alkali ratio range from 36% to 57% is suitable for attaining good MAE on the electrical resistance. Consequently, the composition range that can produce the MAE on the above characteristic and can get the effectiveness of FACT would be comparatively narrow around an alkali ratio of 57%.

4. Advance in Strengthening Solder Glass

For the purpose of developing a CRT with a new structure such as the super-lightweight and ultra thin CRT, further strengthening of the sealing material is also strongly demanded.

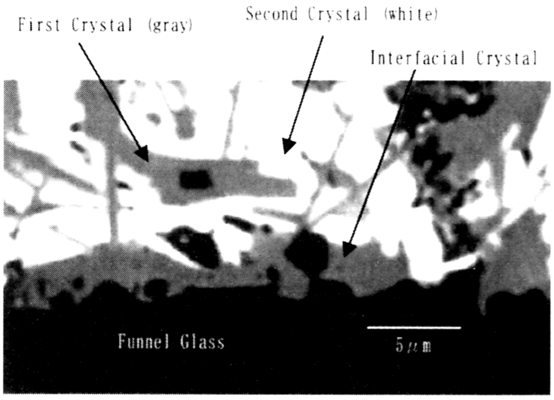

Fig.9 Backscattered electron image of the interface between sintered solder glass and funnel glass of a non-fractured glass bulb.

Recently, we have pursued a morphological study on a crystalline solder glass of a lead-zinc-borate system during crystallization in the sealing process, focusing on the behavior of the solder glass near the interface[15]. **Fig.9** shows the photograph at an interface of a non-fractured glass bulb. The coexistence of the first crystal of the system $2PbO\text{-}ZnO\text{-}B_2O_3$ and the second crystal of the system $4PbO\text{-}B_2O_3$ was observed in the bulk of the sealing layer after being exposed to 440°C for 35 minutes. In addition to these crystals, the third crystal, which is called an interfacial crystal, was observed in the vicinity of the interface after 20 minutes. The interfacial crystal was identified by EPMA and X-ray diffraction as a solid solution consisting mainly of a crystal of the system $PbO\text{-}ZnO\text{-}SiO_2$ and a glass component including a small amount of alkaline oxides and alkaline earth oxides.

The area fraction of the interfacial crystals to the total area at the interface of a fractured glass bulb was considerably smaller than that of a non-fractured glass bulb. It was concluded that the breakage originating from the sealing portion is mainly caused by insufficiency of crystallization of the solder glass and excess of residual vitreous-phase near the interface. In addition, it was found that adding ferric oxide filler is most effective in growing the interfacial crystal sufficiently and improving the breakage at high temperatures.

In order to verify the effect, sealed glass samples of panel glass and funnel glass of 60x5x8 in mm were tested in four points bending in an electric furnace at 440°C. The spans of supporting and loading were 50 mm and 10mm respectively, and the loading speed was 0.1mm/min. As shown in **Fig.10**, the strength increased with increasing area ratio of the interfacial crystals. It is our understating that the non-crystallized phase cannot

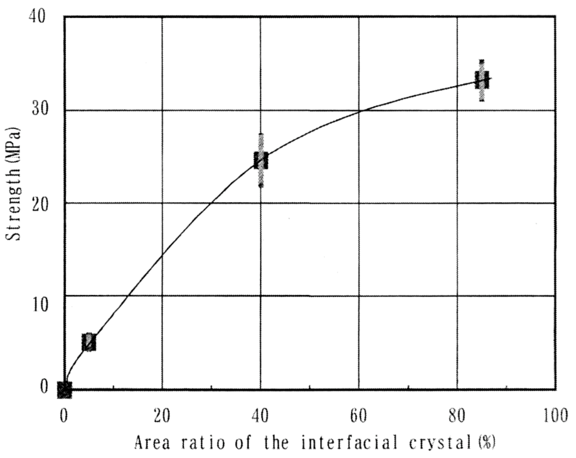

Fig.10 Bending strength as a function of area ratio of the interfacial at 450°C.

contribute to the interfacial strength at around 440°C because it is in a molten state.

5. Conclusion

It might not be easy, but it's necessary to innovate the CRT for the coming digital era through integrating such advances in major material technologies on CRT key technologies. The important thing might be to realize a super-lightweight and ultra thin CRT, keeping its advantages such as high image quality and low cost.

Fortunately, there are some advances in reducing the weight, bulk and fragility of the glass bulb. These can afford to pursue both super-lightweight and ultra thin design. In addition, the development of a new electron gun with excellent focusing characteristics even at a very low accelerating voltage is expected. This development will greatly contribute to not only removing the shadow mask unless degradation of the image quality, but also will produce a possibility in enhancing the intrinsic strength of glass material. That is, the development itself could be used to realize a new, super-lightweight, and ultra thin CRT at a low cost.

From the point of a view, glass technology shall be required to work closely with CRT technology. Only then will the CRT continue to shine brightly.

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