Industrial Soda-Lime-Silica Sheet Glass Hardened by Zirconia-Reinforced Inorganic Coating

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Abstract— **The aim of this study was to improve the hardness of an industrial soda-lime-silica sheet glass (SLS) by coating the glass with zirconia-reinforced inorganic glasses (ZIG). The ZIG glasses composing 55 wt% cullet, 40 wt% borax, 5 wt% Li_2CO_3 and 0.5-5.5 wt% ZrO_2 were melted in an electric furnace at 900 and 1000 ^{o}C and quenched in water to obtain a frit form. The SLS sheets were coated with the fine ZIG powders at various thicknesses. The coated glass sheets (CGS) were thermally treated at 600 ^{o}C and normally cooled over night in the furnace. X-ray diffraction, coefficients of thermal expansion (CTE), vickers microhardness, density, refraction (n_D) and UV-Vis-IR transmission of ZIG, CGS and SLS were investigated. The results revealed that all ZIG glasses were completely melted at 1000 ^{o}C with no bubbles and crystalline phases. An increase in ZrO_2 contents led to increases of the degree of polymerization, bulk density, n_D and glass transition temperature (T_g) and a decrease of CTE. The Zr^{4+} ions entered Si^{4+} positions in the glass structure resulting in the increase of hardness. The 5.5ZIG containing 55 wt% cullet, 40 wt% borax, 5 wt% Li_2CO_3 incorporation with 5.5 wt% ZrO_2 addition showed the highest vickers hardness. In addition, the vickers hardnesss increased with the increase of coating layer thickness. In this work the SLS coated with 5.5ZIG at 121-478 µm showed the highest hardness at 906 and 889 HV0.2 for the glasses melted at 900 and 1000 ^{o}C, respectively (683 HV0.2 for uncoated SLS). The density and n_D increased insignificantly but the transmission decreased comparing to uncoated SLS.**

Keywords— **Hardness, Glass coating, Zirconia reinforcement, Frit, Industrial soda-lime-silica sheet glass**

I. INTRODUCTION

Recently the demand for glass sheet has increased for a variety of applications i.e. window buildings, bearing and the decoration. In case of building works, the surface hardness and strength are of great importance. This challenge will be met by surface improvement. Basically two major methods (i) thermal treatment and (ii) surface coating are utilized to improve the glass surface hardness [1]-[3].

Production of sheet glass with a modified surface is related to wide possibilities of glass properties and to cost effectiveness in the case of continuous production. In this view, the continuous spraying is effective method used for surface coating [4]-[6].

Organically modified silicate (Ormosil) coatings have been proven very effectively in increasing the strength of glass products. These materials combine the properties of organic groups and chains which are subsequently connected with an inorganic oxide matrix such as a hybrid organic-inorganic coating reinforced with nano-sized silica particles, coating solutions containing SiO_2–TiO_2 [7]-[10].

However, the ormosil coating cannot be used to increase the hardness of a bended curve glass at softening temperature (550-700 ^{o}C). A new idea for hardness improvement of sheet glass working at high temperature is inorganically modified silicate (IMS) coating. A low temperature oxide glass reinforced with high strength particles was early considered due to possibilities for mutual diffusion between glass coating and sheet glass surface.

This study, therefore, focused on preparation of the lead free low temperature glass reinforced with ZrO_2 (ZIG) applied by coating. The coating glass presenting highest hardness was applied in order to harden the soda-lime-silica glass sheets (SLS). The effects of ZrO_2 content, film thickness and melting temperature on thermal and mechanical properties of the glasses were observed. The optimum processing conditions were also determined. Coefficient of thermal expansion (CTE) was utilized to enable the possibility of coating. The hardness and transmission results to the structural characteristics of ZIG were also correlated.

II. EXPERIMENTS

2.1 Coating Glass Preparation

In this study, the inorganic glass coating (ZIG) composing 55 wt% cullet, 40 wt% $Na_2B_4O_7.10H_2O$, 5 wt% Li_2CO_3 was incorporated with ZrO_2 in the range of 0.5-5.5 wt%. Each batch contained 200 g of glass made of analytical reagents: $Na_2B_4O_7.10H_2O$, Li_2CO_3 and ZrO_2 mixed with cullet from Thaitechnoglass Company (65.86 wt% SiO_2, 20.84 wt% Na_2O, 3.50 wt% CaO, 8.71 wt% MgO, 1.07 wt% Al_2O_3, 0.01 wt% ZrO_2 and 0.01 wt% Fe_2O_3). The homogenized mixtures were melted in alumina crucibles in an electric furnace at 900 and 1000°C for 15 min in air atmosphere. After melting, the molten glass was quenched in water to obtain a fritted glass. The dried frits were re-melted under the same conditions and were cast into a steel mould in air at room temperature. The glasses were annealed in an electric furnace at 480°C for 15 min before cooled down to room temperature. The glasses were later cut, ground and polished to dimensions required by standards of measurement.

2.2 Coating

Before coating, the surface of SLS sheet supplied by Thaitechnoglass Company was first washed with methanol to improve adhesive force of the coated film on the glass. The ZIG specimens were ground until their particle size was less than 44 µm. 2 g of ZIG powders were mixed with 2 ml of carboxy methyl cellulose (CMC) and 4 ml of distilled water. The ZIG slurries were deposited on the SLS sheet by spraying using 0.6 to 2.4 ml/in^2 of slurry. The coated glass sheets (CGS) were placed in an electric furnace at room temperature and afterwards heated up to 600 ^{o}C with a rate of 5 °C/min for 15 min and was cooled in still air to room temperature in furnace.

2.3 Characterization

The chemical compositions of ZIG powders were analyzed using X-ray fluorescence spectrometer (XRF) (Philips, Magix Pro). The densities (d) of the polished glass specimens were determined by Archimedes' principle using a procedure described in the balance manual (Sartorius YDK 01, YDK 01-0D). Refractive indices (n_D) of the polished glass specimens were determined using Carl Zeiss DDR refractometer.

The hardness of polished glass specimens were measured by a vickers hardness tester (Galileo Microscan OD). The applied load was 200 g_f for 15 seconds.

The SLS sheet and the ZIG glasses were cut and polished to obtain cylindrical specimens with 2.0 cm × 0.4 cm. The specimens were heated in a Linsed L75 dilatometer at a heating rate of 5 ^{o}C/min from room temperature up to 550 ^{o}C to measure CTE. The CTE between 200 ^{o}C and 400 ^{o}C, glass transition temperature (T_g) and dilatometric softening temperature (T_s) were consequently determined from a plot between linear expansion versus temperature.

The morphology of ZIG was identified using X-ray diffractometer (XRD) (Philips PW 3710) with Cu-Kα radiation in the range 10–70 of 2θ.

The film thickness of the CGS was measured by using a light microscope Nikon Eclipse L150.

The UV–Vis–IR transmission spectra of the CGS were recorded at room temperature using a double beam Hitachi Spectrometer, U-4100 in the range of 250–1500 nm. The scan speed was 120 nm/min and a scan interval was 0.5 nm using plain air as the reference.

III. RESULTS AND DISCUSSION

3.1 Chemical compositions and physical properties

The chemical analysis in wt% of the base coating glass (0ZIG) was 45.21SiO_2, 24.52Na_2O, 2.60Li_2O, 2.24CaO, 5.56MgO, 0.01ZrO_2, 0.73Al_2O_3, 21.75B_2O_3 and 0.38SO_3. The glass mainly contained SiO_2 and B_2O_3 acting as glass network formers and Na_2O, Li_2O, CaO and MgO acting as glass network modifiers. All glasses with and without ZrO_2 addition were melted at 900 and 1000 ^{o}C which were proper temperatures to allow clear and transparent samples. At 900 ^{o}C, a few bubbles still remained. The morphology showed amorphous phases in the glass bulk confirmed by XRD in section 3.3. The coating glass at low ZrO_2 content was good in formability related to its low viscosity. However, ZIG incorporation with different ZrO_2 contents were suitable for coating on the SLS sheet.

The bulk density and refractive index (n_D) of ZIG melted at both temperatures are given in Table I. The results showed that the bulk densities and n_D of ZIG were higher than those of SLS and increased with an increase of ZrO_2 content. In a comparion, the densities of glasses melted at 900 ^{o}C were lower due to the residual bubbles within the samples. On the other hand, the n_D values of glass melted at 900 ^{o}C showed higher values, representing the densely packed structures [11] at slow quench rate and increased with the increase of ZrO_2. These results would be related to the hardness in section 3.4.

For these differences between ZIG and SLS sheet, the ZIG could be used to coat on the SLS without changes in bulk density and n_D if it was coated with thin layer.

TABLE I
DENSITY AND REFRACTIVE INDEX OF ZIG GLASSES

Coating glass	Bulk density [g/cm^3]		n_D	
	900 [^{o}C]	1000 [^{o}C]	900 [^{o}C]	1000 [^{o}C]
0ZIG	2.516	2.552	1.545	1.542
0.5ZIG	2.490	2.558	1.550	1.545
1.5ZIG	2.513	2.534	1.560	1.550
2.5ZIG	2.582	2.583	1.560	1.555
3.5ZIG	2.557	2.585	1.565	1.555
4.5ZIG	2.555	2.593	1.570	1.560
5.5ZIG	2.603	2.608	1.570	1.565
SLS	2.492		1.530	

3.2 Thermal property

The CTE, T_g and T_s of ZIG glass are reported in Table II and III, respectively. These values showed insignificant differences in glass melted at both temperatures. Whereas the thermal abilities varied with the change of ZrO_2 content. With the increase in ZrO_2 content, the CTE trend is decreased while T_g and T_s were increased. The glass transition (T_g) was in the range of 469-483 ^{o}C. A higher T_g resulting from higher ZrO_2 content could be ascribed to more polymerized network in the former and thus a high viscosity. These results would be confirmed by XRD data in section 3.3.

Incorporation with ZrO_2 in 0ZIG glass, T_g significantly raised which was consistent with highers of glass former and viscosity as the effect of RO_n (R= Zr, Ti) addition on other glass compositions [12]. However, the CTE of ZIG was higher than that of SLS while T_g and T_s were reverse. Although there was a large different of CTE, the ZIG glasses with various ZrO_2 contents were still interested as a coating glass for the SLS surface coating to improve the glass hardness.

TABLE II
THE THERMAL PROPERTIES OF ZIG GLASSES MELTED AT 900 ^oC

Coating glass	CTE* [x 10^{-6}/^oC]	T_g [^oC]	T_s [^oC]
0ZIG	5.935	469	> 500
0.5ZIG	5.613	470	~ 500
1.5ZIG	5.210	476	~ 500
2.5ZIG	5.100	481	~ 520
3.5ZIG	5.482	477	~ 520
4.5ZIG	5.046	480	~ 520
5.5ZIG	4.893	481	~ 550
SLS	2.689	541	596

*Determined in the range of 200-400 ^oC

TABLE III
THE THERMAL PROPERTIES OF ZIG GLASSES MELTED AT 1000 ^oC

Coating glass	CTE [x 10^{-6}/^oC]	T_g [^oC]	T_s [^oC]
0ZIG	5.563	469	> 500
0.5ZIG	5.551	473	~ 500
1.5ZIG	5.266	479	~ 500
2.5ZIG	5.417	479	~ 520
3.5ZIG	5.054	478	~ 520
4.5ZIG	4.910	482	~ 520
5.5ZIG	5.030	483	~ 550
SLS	2.689	541	596

3.3 XRD

Fig. 1 (a) and (b) show the XRD patterns of ZIG with different compositions and melting temperatures. It was found that all glasses compositions presented only one broad peak which could be assigned to completely amorphous phase [13]-[14]. Average intensities and full width at half height (FWHH), which may be assumed as a normal broad peak with the 2θ range between 10^o to 45^o, were used as convenient comparison of the degree of depolymerization as shown in Table IV.

TABLE IV
CHRACTERISTICS OF XRD NORMAL BROAD PEAK OF ZIG GLASSES

Coating glass	Center of broad peak [2θ]		FWHH	
	900 [^oC]	1000 [^oC]	900 [^oC]	1000 [^oC]
0ZIG	29.5	-	15.9	-
0.5ZIG	28.2	29.8	13.1	15.9
1.5ZIG	27.6	29.3	14.9	15.8
2.5ZIG	28.2	28.0	15.0	15.1
3.5ZIG	29.4	29.3	14.9	14.4
4.5ZIG	28.5	29.0	14.9	14.5
5.5ZIG	27.6	29.0	13.7	14.0

A precise comparison between the center positions of the broad peak and FWHH showed a shift of a small angle side as well as the peaks contract as function of increase of ZrO_2 content. This change was affected by a higher ZrO_2 content acting as glass network former. The ZrO_2 addition led to the glass structure development due to its high degree of polymerization relating to the increase of glass hardness. It could be described that the presence of Zr^{4+} resulted in a better connected silicate network by replacement reaction [12], [15]. In comparison with Si^{4+}, Zr^{4+} had larger cation size (0.59 Å for Zr^{4+} and 0.26 Å for Si^{4+} in coordination number of four) and atomic weight. Zr^{4+} ions could enter Si^{4+} positions in the silicate structure by lowering of polarizability and increase in average atomic weight via the following reaction [15], [16] :

$$\text{Si-O-M-O-Si} + \text{Zr-O-Zr} \longleftrightarrow \text{Si-O-Si} + \text{Zr-O-M-O-Zr} \quad (1)$$

where M denoted the metal cation (e.g. Li^+, Na^+). The changes of ZIG glass structure were related to the hardness and CTE as discussed above.

For different melting temperatures, the glasses melted at 900 ^oC showed a higher degree of polymeraization (small angle and FWHH) than that melted at 1000 ^oC due to greater dense structure and lower quench rate.

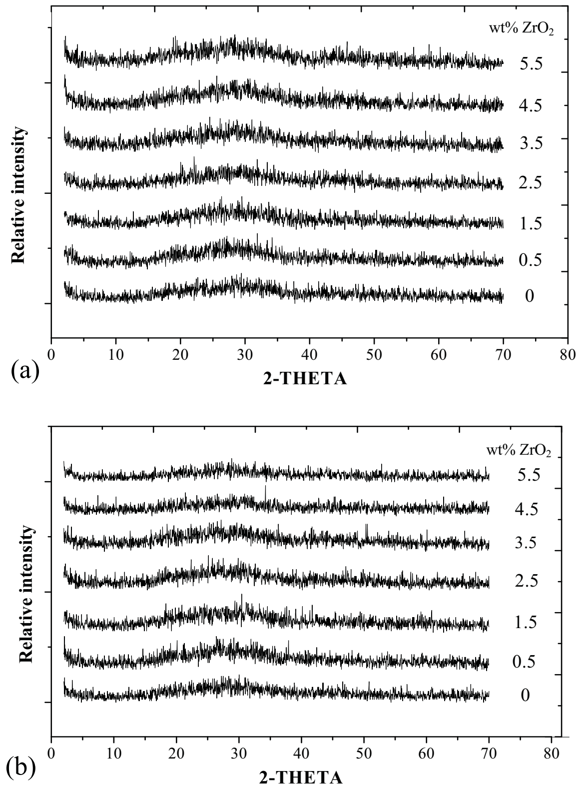


Fig. 1 The XRD patterns of ZIG glasses containing ZrO_2 in the range of 0-5.5 wt% after melted at (a) 900 ^oC and (b) 1000 ^oC

3.4 Mechanical property

With ZIG coating glasses were deposited on the SLS sheet by spraying glass slurry with 0.8 ml/in^2, all ZIG glasses were melted completely at 600 ^oC to obtain clear thin film on the glass sheet as shown typically in Fig. 2.

The surface hardness of CGS was determined using vickers hardness tester. The obtained values were plotted as a function of the ZrO_2 content shown in Fig. 3.

It was noteworthy that all CGS sheets contained greater hardness approximately by 13-40% with increases of ZrO_2 contents with respect to unmodified glass sheet (see Equation 1).

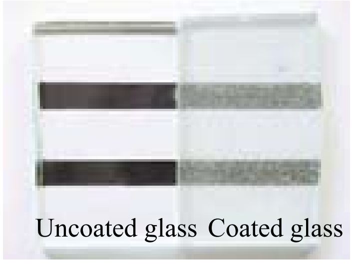


Fig. 2 Uncoated and coated glass sheets by using 5.5ZIG coating glass

In this work, the 5.5CGS which was coated by 55 wt% cullet, 40 wt% borax and 5 wt% Li_2CO_3 incorporation with 5.5 wt% ZrO_2 addition (5.5CGS) showed very high hardness values as 906 and 889 HV 0.2 for glasses melted at 900 and 1000 ^oC, respectively (683 HV0.2 for uncoated SLS). The 5.5ZIG was thus chosen for hardness improvement of SLS.

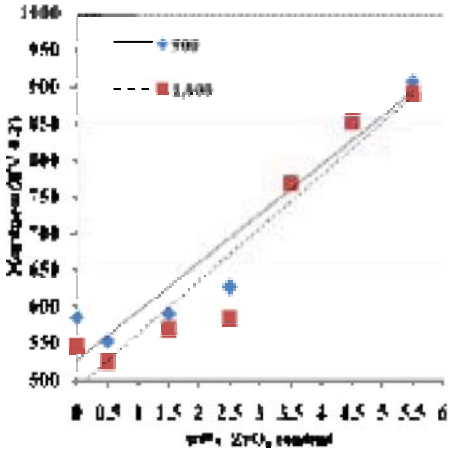


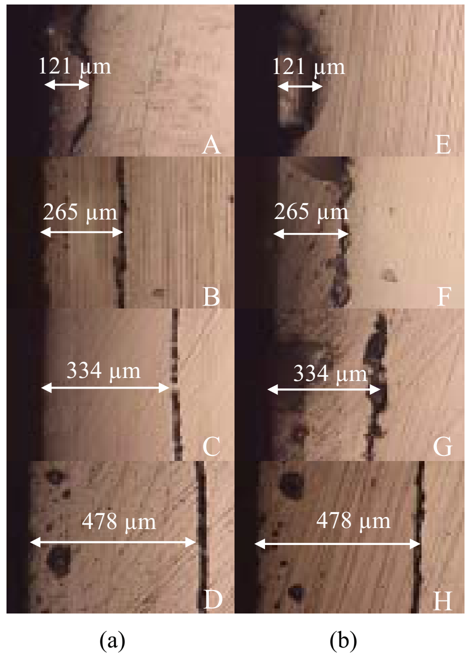
Fig. 3 The relation of ZrO_2 content in ZIG coating glass to hardness of CGS coated with ZIG glasses at 207 µm of thickness

3.5 Effect of film thickness on hardness

The thickness of thin film of 5.5CGS after coating with 0.6 to 2.4 ml/in^2 of 5.5ZIG, was measured using optical micrographs as shown in Fig. 4. The thickness varied in the range of 121-478 µm. Fig. 4 (a) showed that the boundary layers were homogenous and smooth. The interlayers, except at the lowest thickness (A), could permanently be bonded and were indepent on the coated thickness (B-D). Since the CTE of 5.5ZIG was higher than that of SLS, the maximum compression developed at the interlayer and the surface of 5.5CGS would be under tension underneath [10], [17]. In this respect the surface of 5.5CGS showed small cracks as shown in Fig. 2.

Fig. 4 (b) shows the internal cracks at the interlayers resulting in inhomogeneous bonding caused by the maximum stress. It could be expected that the surface hardnesses of 5.5CGS (E-H) were affected under high stress and would be decreased when comparing with 5.5CGS (A-D).

Table V shows the relation of film thickness to hardness of 5.5CGS. It was found that the surface hardness slightly increased with an increase of the thickness of glasses melted at both temperatures. In this case, the square pyramid indentation crack in the surface was far from the maximum stress area at the interlayer at which the stress had a very small influence on the surface. However, the hardness values of 5.5CGS were still high. Thus in order to improve the hardness, 5.5ZIG melted at 900 ^oC was chosen to coat SLS surface.



(a) (b)

Fig. 4 The optical micrographs of 5.5CGS after coated with 5.5ZIG melted at (a) 900 ^oC (A-D) and (b) 1000 ^oC (E-H)

TABLE V
THE RELATION OF THICKNESS TO HARDNESS OF 5.5CGS

Thickness of film layer [µm]	Hardness [HV 0.2]	
	900 [^oC]	1000 [^oC]
121	753	664
207	906	889
334	934	922
478	1,018	968

3.6 Characteristics of 5.5CGS

Density, refractive index (n_D) and % transmission (%T) of 5.5CGS at various thicknesses are given in Table VI. In comparison with SLS, the density and n_D of 5.5CGS increased insignificantly, on the other hand, the transmission decreased with an increase of thickness which was described by Beer's law [18]. In addition Zr^{4+} ion with very high atomic weight containing in glass structure, it can both absorb and refract energy resulting in the decrease of % T.

TABLE VI
PHYSICAL PROPERTIES OF 5.5CGS SHEETS

Thickness of film layer [µm]	Density [g/cm^3]	n_D	% T
121	2.501	~1.54	77.5

207	2.503	~1.54	58.4
334	2.497	~1.54	48.9
478	2.498	~1.54	38.5
SLS	2.492	1.53	85.1

IV. CONCLUSIONS

In this work, zirconia-reinforced inorganic glasses (ZIG) was deposited by spraying on soda-lime-silica glass sheet in order to improve the hardness of glass sheet surface.

All ZIG compositions melted at 900 and 1000 ^{o}C were clear, transparent and crystalline phase-free. At 900 ^{o}C, a few bubbles still remained within the glass structures.

The bulk density and refractive index (n_D) of ZIG melted at both melting temperatures were higher than those of SLS and increased with an increase of ZrO$_2$ content. At 900 ^{o}C the density of glasses was lower than that at high temperature due to the residual bubbles in the glass. On the other hand, the n_D values were higher as the structures of glasses melted at lower temperature were densely packed at slow quench rate. In addition, the density also increased with the increase of ZrO$_2$ content.

The CTE of ZIG was higher than that of SLS while T$_g$ and T$_s$ were reverse for glasses melted at both temperatures. At higher ZrO$_2$ content, CTE decreased while T$_g$ and T$_s$ increased due to more polymerized networks in glass structure.

The surface hardness of CGS increased approximately 13-40% and increased with as increase of ZrO$_2$ content. The 5.5CGS which was coated by 55 wt% cullet, 40 wt% borax and 5 wt% Li$_2$CO$_3$ incorporation with 5.5 wt% ZrO$_2$ (5.5CGS) showed the highest hardness as 906 and 889 HV 0.2 for glasses melted at 900 and 1000 ^{o}C, respectively (683 HV0.2 for uncoated SLS). In this work, the 5.5ZIG was chosen to improve the hardness of SLS sheet.

The hardeness of 5.5CGS surface slightly increased with an increase in the thickness for glassses melted at both temperatures.

The density and n_D of 5.5CGS increased insignificantly but the transmission decreased with the increase of thickness.

In this work, the coatings were homogenous and smooth adhesion but the surface of 5.5CGS contained small cracks due to the difference of CTE between 5.5ZIG and SLS. The defect will be improved in the next work.

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