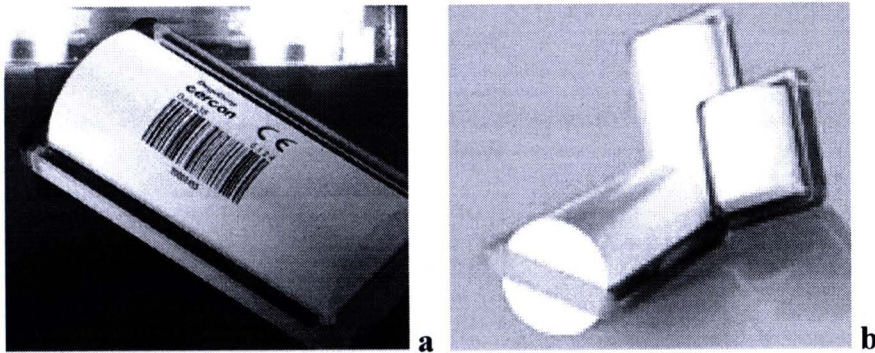


## CHAPTER III

### MATERIALS AND METHODS

The commercially available yttrium partially stabilized tetragonal zirconia polycrystal (Y-TZP) ceramic (Cercon<sup>®</sup> Degudent GmbH, Hanau-Wolfgang, Germany) (Figure 2) and six commercial veneering ceramics (represent the variety of CTE) (Figure 3) that shown in table 1 and table 2 respectively were used in this study.



**Figure 2** (a, b) Cercon<sup>®</sup> block (Degudent GmbH, Hanau-Wolfgang, Germany)

**Table 1** The commercial ceramic core and their coefficient of thermal expansion (CTE) according to manufacturer

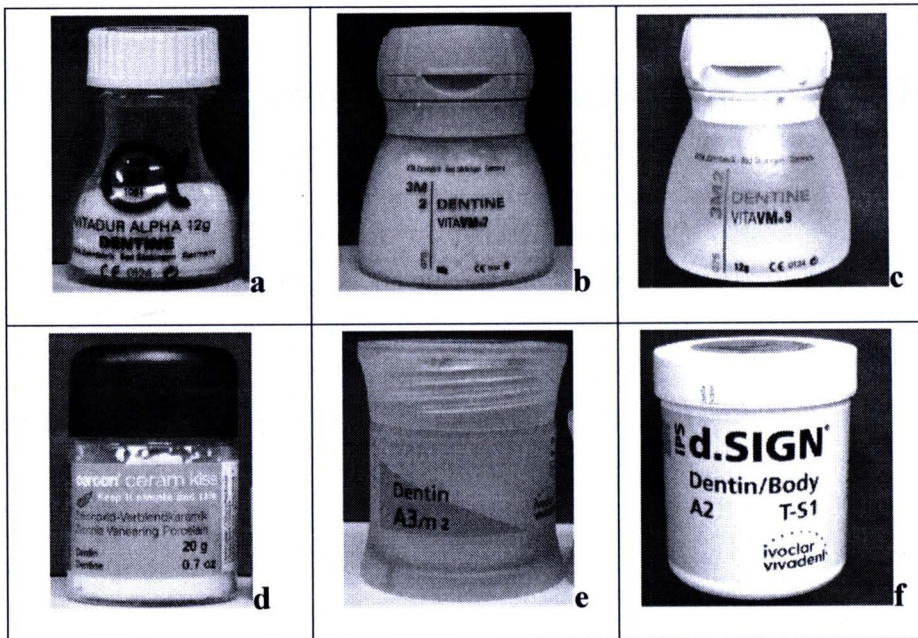
Core ceramic	Manufacturer	CTE (at 25-500 °C) ( $\mu\text{m}/\text{m}\cdot\text{K}$ )
Cercon <sup>®</sup> (Y-TZP ceramic core)	Degudent GmbH, Hanau- Wolfgang, Germany	10.5

**Table 2** Six commercial veneering ceramics and their coefficient of thermal expansion (CTE) according to manufacturer

<b>Commercials veneering ceramic</b>	<b>Manufacturer</b>	<b>CTE (at 25-500 °C)</b> ( $\mu\text{m}/\text{m}\cdot\text{K}$ )
VITADur <sup>®</sup> alpha	Vita Zahnfabrik, Bad Sackingen, Germany	6.7
VITAVM <sup>®</sup> 7	Vita Zahnfabrik, Bad Sackingen, Germany	7.3
VITAVM <sup>®</sup> 9	Vita Zahnfabrik, Bad Sackingen, Germany	8.8-9.2
Cercon <sup>®</sup> ceramkiss	Degudent GmbH, Hanau-Wolfgang, Germany	9.2
IPSe.max <sup>®</sup> ceram	Ivoclar Vivadent, Schaan, Liechtenstein	9.5
IPS dSIGN <sup>®</sup>	Vita Zahnfabrik, Bad Sackingen, Germany	12-12.6

**Table 3** Chemical composition of Cercon<sup>®</sup> core and veneering ceramics used in this study

<b>Material</b>	<b>Main components (mass%)</b>	<b>Type of ceramics</b>
Cercon <sup>®</sup> base	ZrO <sub>2</sub> 92 %; HfO <sub>2</sub> <2; Y <sub>2</sub> O <sub>3</sub> = 5; Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub> <1	Core material
VITADur <sup>®</sup> alpha	10%Aluminium oxide and silicate glass	Feldspathic veneering ceramic
VITAVM <sup>®</sup> 7	Leucite crystal (K <sub>2</sub> O Al <sub>2</sub> O <sub>3</sub> 4SiO <sub>2</sub> ) 27.1% and silica matrix	Feldspathic veneering ceramic
VITAVM <sup>®</sup> 9	SiO <sub>2</sub> 60–64; Al <sub>2</sub> O <sub>3</sub> 13–15; K <sub>2</sub> O 7–10; Na <sub>2</sub> O 4–6; B <sub>2</sub> O <sub>3</sub> 3–5	Feldspathic veneering ceramic
Cercon <sup>®</sup> ceramkiss	SiO <sub>2</sub> 60–70; Al <sub>2</sub> O <sub>3</sub> 7.5-12.5; K <sub>2</sub> O 7.5–12.5; Na <sub>2</sub> O 7.5-12.5	Feldspathic veneering ceramic
IPSe.max <sup>®</sup> ceram	SiO <sub>2</sub> 60–65; Al <sub>2</sub> O <sub>3</sub> 8–12; K <sub>2</sub> O 6–8; Na <sub>2</sub> O 6–9; ZnO 2–3; CaO, P <sub>2</sub> O <sub>5</sub> and F 2 – 6; other oxides 2 – 8.5; pigments 0.1 – 1.5	Fluorapatite glass veneering ceramic
IPS dSIGN <sup>®</sup>	SiO <sub>2</sub> 50–65; Al <sub>2</sub> O <sub>3</sub> 9–11; K <sub>2</sub> O 7–8; Na <sub>2</sub> O 7–8; ZrO <sub>2</sub> 2–3; CaO, P <sub>2</sub> O <sub>5</sub> and F 2.5–7.5	Fluorapatite glass veneering ceramic



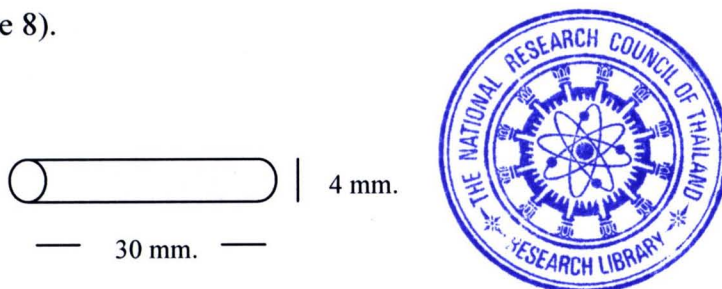
**Figure 3** Six commercial veneering ceramics (a) VITADur<sup>®</sup> alpha (b) VITAVM<sup>®</sup>7 (c) VITAVM<sup>®</sup>9 (d) Cercon<sup>®</sup>ceramkiss (e) IPSe.max<sup>®</sup>ceram (f) IPS dSIGN<sup>®</sup>

The testing specimens were prepared as follow:

### 3.1 The sample for determination of coefficient of thermal expansion (CTE)

The rod shaped specimens of each commercial veneering ceramics were fabricated by mixed veneering ceramics with distilled water. The creamy mixed veneered ceramic was placed into a silicone mould (length = 38 mm, diameter = 5 mm), reproduced from wax mould. Then condensed and vibrated with ultrasonic porcelain condenser (3M Unitex, St. Paul, USA) (Figure 5). Excess moisture was blotted dry with an absorbent tissue. The porcelain rod in green body was removed from the silicone mould placed on a refractory tray and fired according to the manufacturer's instruction (Table 4). All specimens were fired in a programmable and calibrated vacuum porcelain furnace (Programmat<sup>®</sup>P100 furnace, Ivoclar-Vivadent, Schaan, Liechtenstein) (Figure 6). After firing, the rod specimens were ground flat and parallel to each other, the ends of each specimen are 30 mm and 4 mm in dimension, as described in ISO 9693 (ADA specification No.38) and the length was measured with a veneer caliper.

The Cercon<sup>®</sup> (Degudent GmbH, Hanau-Wolfgang, Germany) core specimens were fabricated (length = 40 mm, diameter = 5 mm) by cut out from ceramic-block (Figure 2) by a handsaw (PX200, OH, USA) and grinded using abrasive paper. Then were sintered in the Cercon<sup>®</sup> furnace (Figure7) at 1350°C according to the manufacturer's recommendation. After sintering each Cercon<sup>®</sup> rod were grinded for final dimension of core specimens are 4 mm. in diameter and 30 mm. in length (rod shaped specimens) (Figure 8).



**Figure 4** Schematic dimension of specimens for thermal expansion measurement



**Figure 5** Ultrasonic porcelain condenser (3M Unitek, St. Paul, USA)

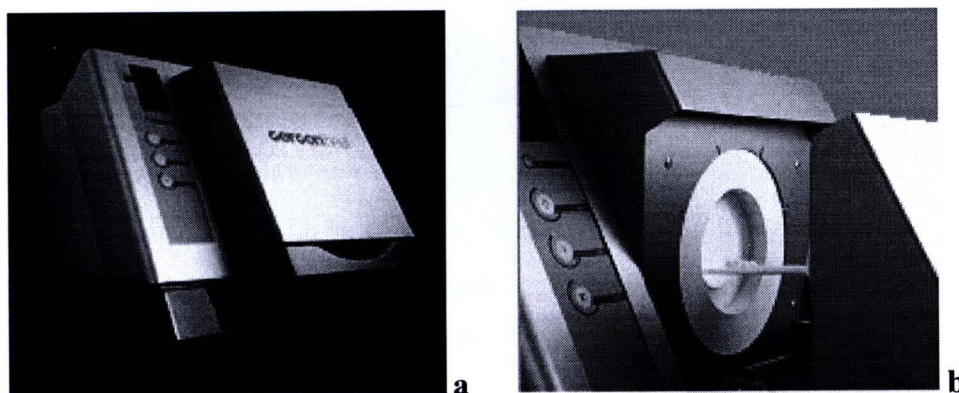
**Table 4** Firing table / Program table in °C

<b>Ceramic</b>	<b>Program</b>	<b>Program number</b>	<b>T<sub>s</sub> (°C)</b>	<b>R (°C/ min)</b>	<b>T<sub>f</sub> (°C)</b>	<b>S (°C/ min)</b>	<b>H (min)</b>	<b>V<sub>1</sub> (°C)</b>	<b>V<sub>2</sub> (°C)</b>	<b>L (min)</b>
VITADur <sup>®</sup> alpha	Foundation firing	85	600	60	960	6	1	600	960	-
	Dentin firing	86	600	58	950	6	1	600	950	-
	Glazing firing	80	600	85	940	-	1	600	940	-
VITAVM <sup>®</sup> 7	Foundation firing	89	500	55	920	6	1	500	920	-
	Dentin firing	90	500	55	910	6	1	500	910	-
	Glazing firing	88	500	55	900	6	1	500	900	-
VITAVM <sup>®</sup> 9	Foundation firing	87	500	55	930	6	1	500	930	-
	Dentin firing	90	500	55	910	6	1	500	910	-
	Glazing firing	88	500	55	900	6	1	500	900	-
Cercon <sup>®</sup> ceramkiss	Foundation firing	61	450	55	960	4	1	450	960	-
	Dentin firing	62	450	55	830	4	1.5	450	830	-
	Glazing firing	63	450	55	800	3	1	450	800	-
IPSe.max <sup>®</sup> ceram	Foundation firing	82	403	60	960	4	1	450	959	-
	Dentin firing	83	403	50	750	4	1	450	749	-
	Glazing firing	84	403	60	725	6	1	450	724	-
IPS	Foundation firing	20	403	80	890	6	1	450	889	-
dSIGN <sup>®</sup>	Dentin firing	22	403	60	870	6	1	450	869	-
	Glazing firing	25	403	60	870	4	1	450	869	-

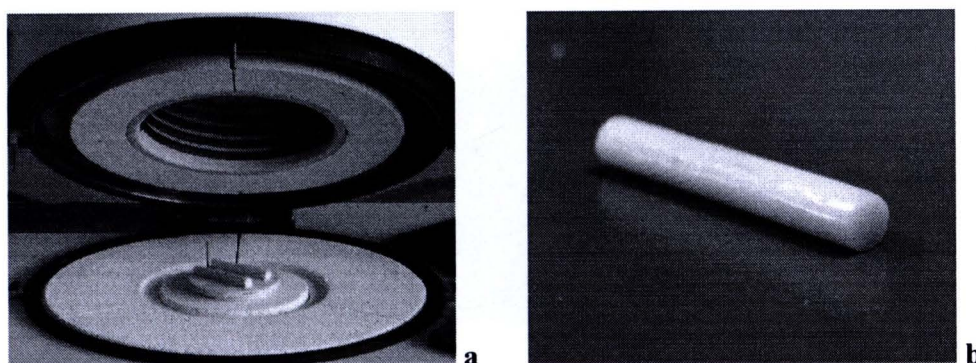
*NB: T<sub>s</sub> = Starting temperature, R = rate of firing, T<sub>f</sub> = Final temperature, S = rate of climbing, H = Holding time, V<sub>1</sub> = vacuum starting temperature, V<sub>2</sub> = vacuum shut off temperature, L = rate of cooling*



**Figure 6** The Programmat P100 furnace (Ivoclar-Vivadent, Schaan, Liechtenstien) that was used for porcelain firing



**Figure 7** (a, b) Cercon<sup>®</sup> heat furnace (Degudent GmbH, Hanau-Wolfgang, Germany)

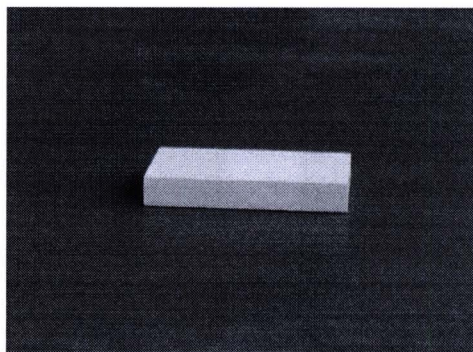


**Figure 8** (a) The porcelain rods in green body was fired in furnace according to the manufacturer's instruction (b) The final dimension of ceramic rod specimen

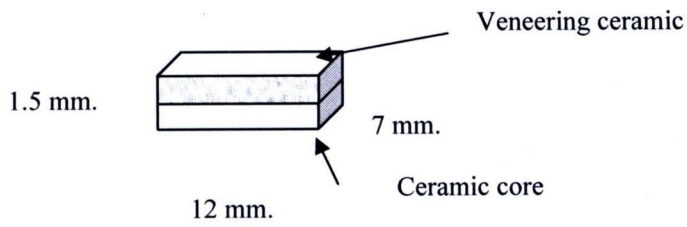
### 3.2 The sample for determination of the distribution of residual stresses

#### 3.2.1 Sample preparation

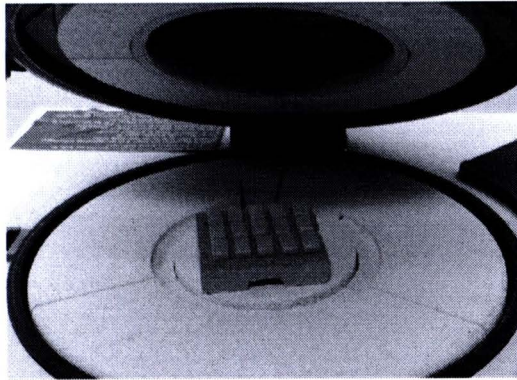
Ninety Cercon<sup>®</sup> bar specimens were cut out from Cercon<sup>®</sup> block by a handsaw (PX200, OH, USA) and grinded using abrasive paper. Then Cercon<sup>®</sup> bars were sintered in the Cercon<sup>®</sup> furnace according to the manufacturer's recommendation. After sintering each Cercon<sup>®</sup> bar were grinded for final dimension of core specimens are 1.5 mm. (height) × 12 mm. (length) × 7 mm. (width). All Cercon<sup>®</sup> bars were veneered incrementally, using the six commercial veneering ceramics (Table 3) mixed with distilled water. The Cercon<sup>®</sup> bar was position into the silicone mould which has a space of 2 mm. thickness to be a room for veneering ceramic application. The creamy mixed veneered ceramic was applied manually on to the Cercon<sup>®</sup> bars, condensed and vibrated with ultrasonic porcelain condenser (3M Unitex, St. Paul, USA). Excess moisture was blotted dry with an absorbent tissue. All core-veneered ceramic were fired in the porcelain furnace (ProgrammatP100 furnace, Ivoclar-Vivadent, Schaan, Liechtenstein) in accordance the manufacturer's instruction (Figure 10). After firing, all specimen bars were grinding to ensure the uniform thickness and shape using a green stone bur and then, they were ground flat and parallel to each other using abrasive papers on Ecomet<sup>®</sup>3 (Buehler, Illinois, USA) (Figure 11). The final core-veneer dimension is 1.5×12×7 mm.<sup>3</sup> (Figure12) in which, they were standardized the dimension by metal split mould and measured with a veneer caliper.



**Figure 9** Cercon<sup>®</sup> bar specimen before sintering for residual stresses determination



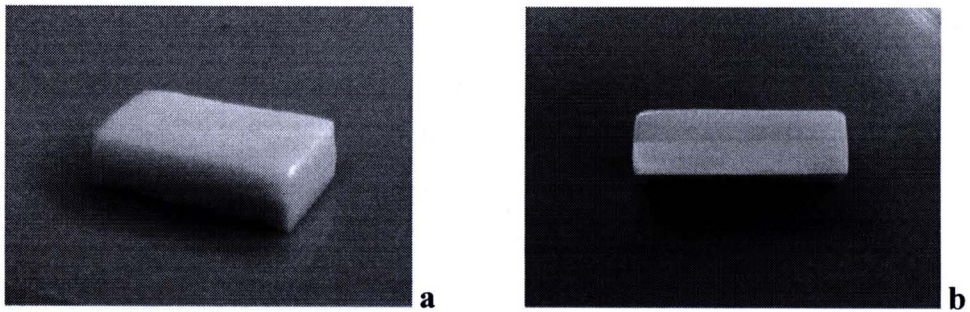
**Figure 10** Schematic drawing of sample preparation for residual stresses determination



**Figure 11** Samples were firing in furnace



**Figure 12** Ecomet<sup>®</sup> 3 (Buehler, Illinois, USA)

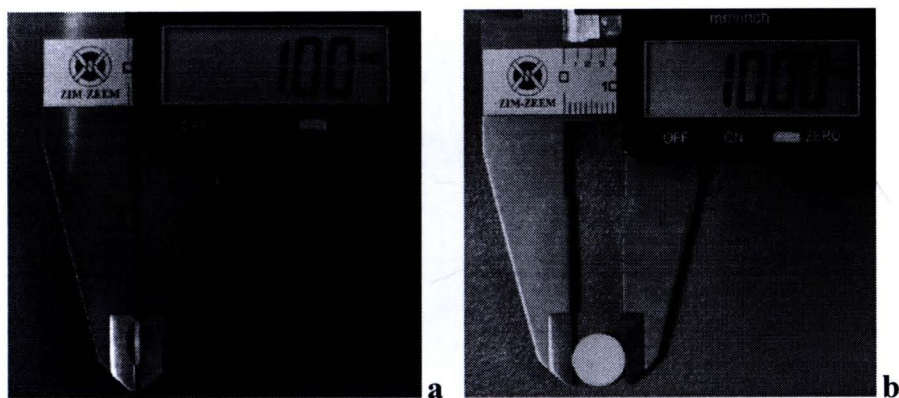


**Figure 13** (a, b) Final dimension of the sample for determination of the distribution of residual stresses

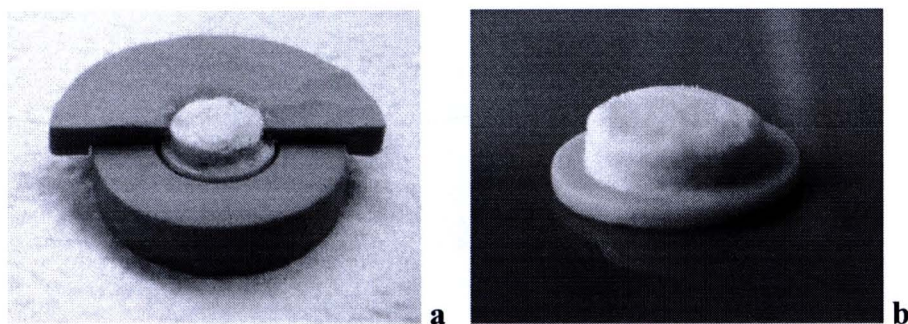
### 3.3 The sample for determination of shear bond strength

#### 3.3.1 Sample preparation

Ninety Cercon<sup>®</sup> disks (10.8 mm. diameter and 1.42 mm. high) were cut out from ceramic-block by a handsaw (PX200, OH, USA) and grinded using abrasive paper. Then Cercon<sup>®</sup> disks were sintered in the Cercon<sup>®</sup> furnace according to the manufacturer's recommendation. After sintering each Cercon<sup>®</sup> disk were grinded for final dimension of core specimens are 10 mm. in diameter and 1 mm. in high (Figure 13). All Cercon<sup>®</sup> disks were veneered incrementally, using the six commercial veneering ceramics (Table 1) mixed with distilled water. The ceramic core disk was position into the silicone mould (Figure 14) which has a space of 1 mm. thickness to be a room for veneering ceramic application. The creamy mixed veneered ceramic was applied manually on to the Cercon<sup>®</sup> disks, condensed and vibrated with ultrasonic porcelain condenser (3M Unitex, St. Paul, USA) (Figure 15). Excess moisture was blotted dry with an absorbent tissue. All core-veneered ceramic were fired in the porcelain furnace (ProgrammatP100 furnace, Ivoclar-Vivadent, Schaan, Liechtenstein) in accordance the manufacturer's instruction (Figure 16). After firing, all specimen disks were grinding (Figure 17) to ensure the uniform thickness and shape using a green stone bur. The final veneering ceramic disks dimension is 7 mm in diameter and 1.5 mm in high, were standardized the dimension by metal split mould (Fig. 18,19 and 20).



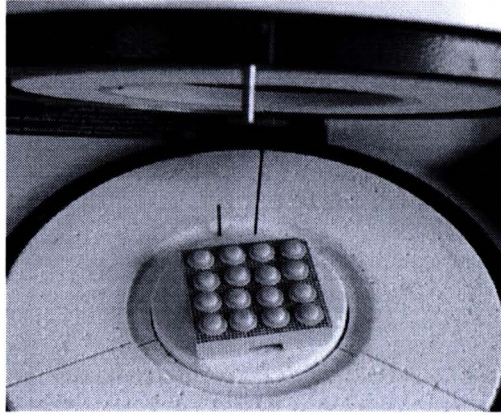
**Figure 14** (a, b) Cercon<sup>®</sup> disks were prepared for final dimension of 10 mm. In diameter and 1 mm. high



**Figure 15** (a, b) The Cercon<sup>®</sup> disks was veneered with veneering ceramic using silicone mould



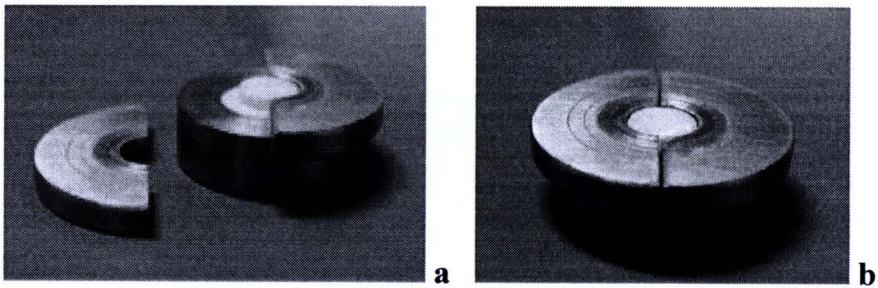
**Figure 16** The veneered ceramic was condensed and vibrated on to the Cercon<sup>®</sup> disks, with ultrasonic porcelain condenser



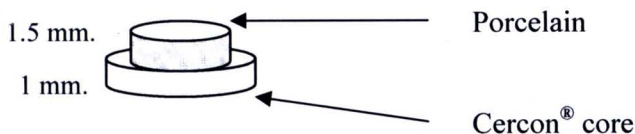
**Figure 17** Specimen disks after firing



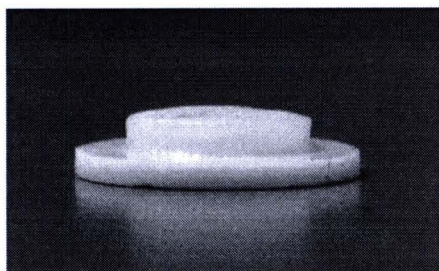
**Figure 18** The core-veneer specimen was ground using a green stone bur



**Figure 19** (a, b) The core-veneered disk was standardized the dimension in metal split mould



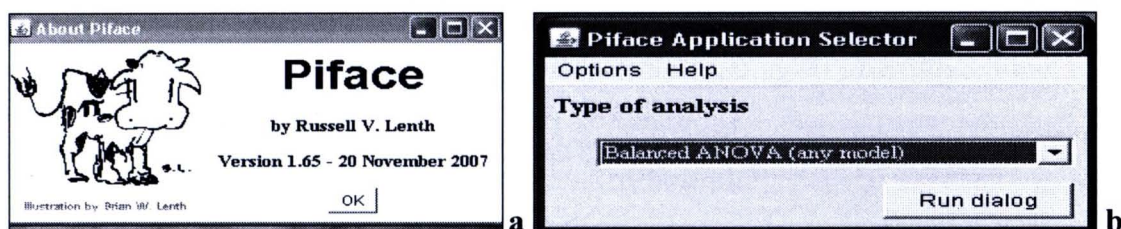
**Figure 20** Schematic drawing of sample preparation for shear bond test



**Figure 21** The core-veneered disk in final dimension

### 3.4 Amount of specimens preparation

The amount of specimens were processed for testing according to the sample size determination method using Java Applets for Power and Sample Size computer program (Figure 21).



**Figure 22** (a, b) Software solution (Java Applets for Power and Sample Size)

#### 3.4.1 Sample size determination for residual stress testing

Sample size was calculated by using the data from a pilot study, same as this research conditions setting, sample size is 10 samples per group. An analysis of variance (ANOVA) was used to determine the standard deviation (SD within group). From residual stress pilot study SD within group was 2.52 ( $\sqrt{6.397}$ )

MPa (Table 5). The power of study was set for 0.80 and significance level of  $\alpha = 0.05$ . Sample size of this pilot study was calculated using Java Applets for Power and Sample Size (Figure 22).

**Table 5** ANOVA of Residual stresses (Pilot study)

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	68.164	4	17.041	2.664	.044
Within Groups	287.871	45	6.397		
Total	356.035	49			

The sample size from the computer calculation can be estimated to be about 15 specimens per group of the power 99.49%.

### 3.4.2 Sample size determination for shear bond strength testing

Sample size was calculated by using the data from a pilot study, same as this research conditions setting, sample size is 10 samples per group. An analysis of variance (ANOVA) was used to determine the standard deviation (SD within group). From shear bond strength pilot study SD within group was 4.0 ( $\sqrt{16.018}$ ) MPa (Table 6). The power of study was set for 0.80 and significance level of  $\alpha = 0.05$ . Sample size of this pilot study was calculated using Java Applets for Power and Sample Size (Figure 23) (<http://www.stat.uiowa.edu/~rlenth/Power>)

**Table 6** ANOVA of SBS (Pilot study)

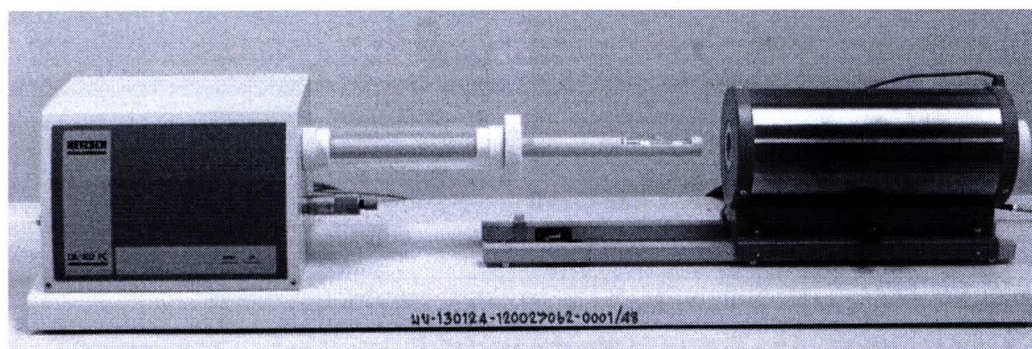
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2864.335	5	572.867	35.763	.000
Within Groups	864.983	54	16.018		
Total	3729.318	59			

The sample size from the computer calculation can be estimated to be about 15 specimens per group of the power 87.92%.

### 3.4 Testing procedures

#### 3.4.1 Measurement of coefficient of thermal expansion (CTE)

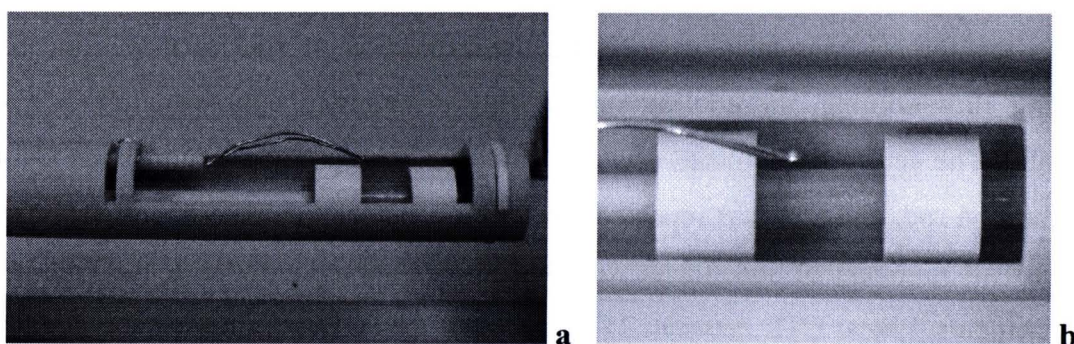
The horizontal single rod dilatometer model DIL 402 PC (NETZSCH-Gerätebau GmbH, Germany) (Figure 24) was used to calculate the heating and cooling curve of each specimen in accordance with the protocol of ISO 9693 (ADA specification No.38) for dental metal ceramic systems. Determination of CTE is achieved by heating each specimen from 25 °C to 500 °C at rate of 5 °C per minute. Then the furnace was switched off and the expansion of specimen was measured during slow cooling, the cooling rate of the furnace was approximately 5 °C per minute. The set-up dilatometer was calibrated with a pure aluminum oxide ( $\text{Al}_2\text{O}_3$ ) calibration rod, and this was repeated three times: before the experiment was started, when half numbers of specimens were tested and immediately after the end of the experiments. Linear CTE between 25 °C and 500 °C was determined (one type of core and six type of veneering ceramics) (Figure 25). Further, glass transitional temperatures ( $T_g$ ) of the veneering ceramics designed for zirconia core were determined from these measurements by extrapolation, as the common practice in thermal analysis. The glass transitional temperatures ( $T_g$ ) is the temperature at which there is an abrupt increase in the thermal expansion coefficient occurs, indicating increased molecular mobility.



**Figure 23** The dilatometer model DIL 402 PC (NETZSCH-Gerätebau GmbH, Germany)

The NETZSCH Proteus<sup>®</sup> software (version 4.7) was used to collect and determine the temperature and percent linear change and stores it in a data files. Software features include comparisons against temperature and differential or alpha CTE curves, transition temperature, and CTE calculation for any temperature range.

From the data files obtained of each material, one curve of the change in length (linear CTE) plot to the temperature was drawn.



**Figure 24** (a, b) The rod specimen was placed on the sample holder of dilatometer

The CTE and T<sub>g</sub> value of each type of veneering ceramics were used to compute the theoretical global residual stresses by equation 1.

### 3.4.2 Determination of residual stresses

#### 3.4.2.1 Determination of theoretical thermally induced global residual stresses

Residual stresses caused by the CTE difference between of veneering ceramic and core ceramic are estimated using the equation as follow [31, 32]:

$$\sigma_R = \Delta\alpha\Delta T / [(1 + \nu_C) / 2 E_C + (1 - 2\nu_V)E_V] \quad \text{equation 1}$$

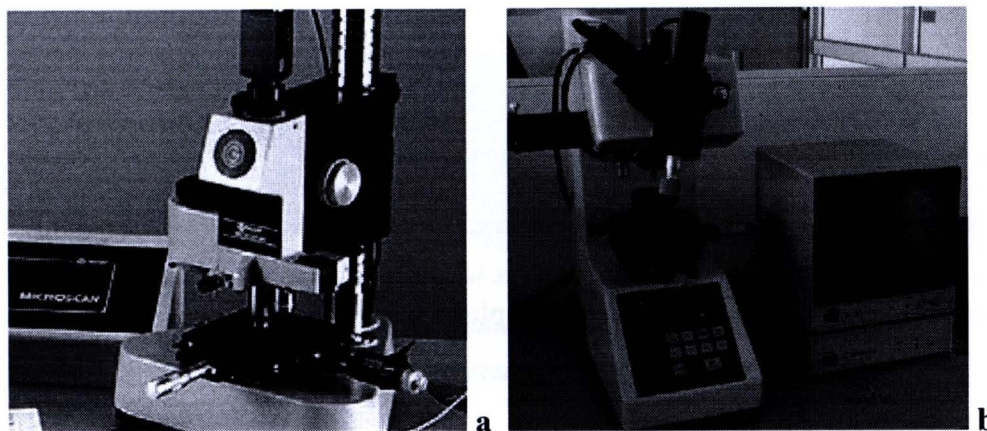
Where  $\sigma_R$  is the residual stress in GPa,  $\Delta\alpha$  is the difference between linear CTE of the veneer and core ceramics,  $\Delta T$  is the difference between the glass transitional temperature of the veneering ceramic and room temperature,  $\nu$  is the Poisson's ratio,  $E$  is the Young's modulus in GPa, Subscripts C and V refer to core ceramic and veneering ceramics, respectively.

### 3.4.2.2 Determination of localized residual stresses

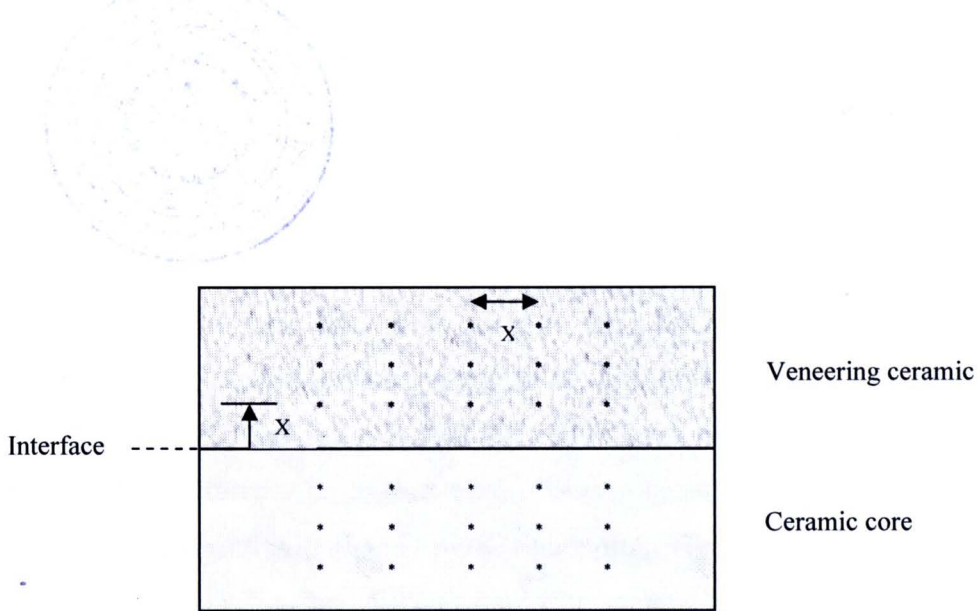
#### distribution

The Vickers indentation test method consist of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base at a angle of 136 degrees between opposite faces subjected were performed for testing. The microhardness tester (LTF-Antegnate (BG), GALILEO, Italy) (Figure 25a) with a Vickers diamond pyramid indenter at a load of 20 N for core ceramic at 30 seconds dwelling time. The microhardness tester (MXT 70, Matsuzawa Seiki Co., Tokyo, Japan) (Figure 25b) with a Vickers diamond pyramid indenter at a load of 9.8 N for veneering ceramics at 30 seconds dwelling time. These loads are enough to produce cracks development around the indentation in each layer of ceramic.

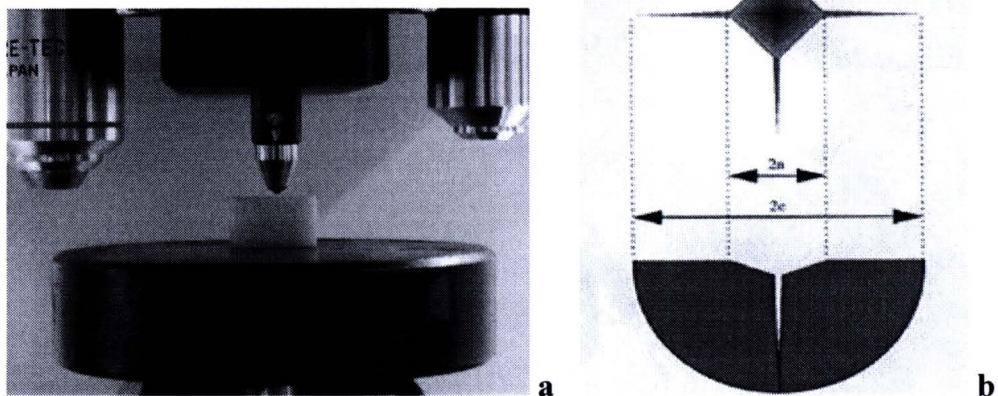
Vickers indentation were place in the ceramic specimens sections at prescribed distances parallely from core-veneer interface 300, 600 and 900  $\mu\text{m}$  and distances from the central of sample 300, 600 and 900  $\mu\text{m}$  right and left as the figure follow (Figure 26, 27).



**Figure 25** Vickers microhardness tester (a) LTF-Antegnate (BG), GALILEO, Italy, (b) MXT 70, Matsuzawa Seiki Co., Tokyo, Japan.



**Figure 26** Schematic drawing shows indentation sites (representative dots in figure), X (300  $\mu\text{m}$ ) designates distance between lead crack center and interface.



**Figure 27** (a) Vickers indentation were placed in the ceramic specimens sections to make the indentation (b) Schematic illustration of indentation crack

Fifteen indentations were indented on each ceramic layer (core and veneering ceramics), so it will have thirty indentations on each one specimen. Each indentation on the specimen was calculation of fracture toughness in each group. By measuring crack length  $c$  and  $a$  (Figure 27b), it is possible to estimate conduct fracture toughness ( $K_{Ic}$ ). The cracks that originated from the Vickers indentations were also used to compute the fracture toughness by the indentation method, using  $K_{Ic}$  Equation that developed by Anstis et al. in the equation 2 as follow: [33].

$$K_{Ic} = 0.016(E/H)^{1/2}P/c_0^{3/2} \quad \text{equation 2}$$

Where 0.016 is a material-independent constant,  $P$  is the load in Newtons,  $c_0$  is the crack length from the center of the indent to the crack tip in meters,  $E$  is the Young's modulus in GPa and  $H$  is the Vickers hardness in GPa.

Vickers hardness ( $H$ ) was measured as recommended by ASTM C1327-99 was computed from the equation 3 as follow: [34]

$$H = 1.854 P/d^2 \quad \text{equation 3}$$

Where  $H$  represents the Vickers hardness (GPa),  $P$  is the applied load (kg) and  $d$  is the diagonal of the indentation mark (mm.)

Derivation of the localized residual stresses expression and determination of the crack geometry factor by using the following equation[5, 24].

$$\sigma_n = \pm 1.63K_{Ic} \left[ \frac{1 - \left(\frac{c_0}{c}\right)^{3/2}}{\sqrt{c}} \right] \quad \text{equation 4}$$

Where  $\sigma$  represents the residual stresses,  $K_{Ic}$  is the fracture toughness,  $c_0$  and  $c$  are the crack length from the center of indent to crack tip at stress-free condition and stress condition, respectively.

Determination of residual stress was determination in term of localized residual stress in each layer next to the interface.

However, the core and 5 veneering ceramics specimens that have not veneered (monolithic specimens) were test using Vickers indentation for determine the residual stress for stress-free specimens for the same load of core-veneered specimens and used to determination of  $C_0$  which is the crack length of stress-free specimen.

### 3.5.3 Shear bond strength (SBS) determination

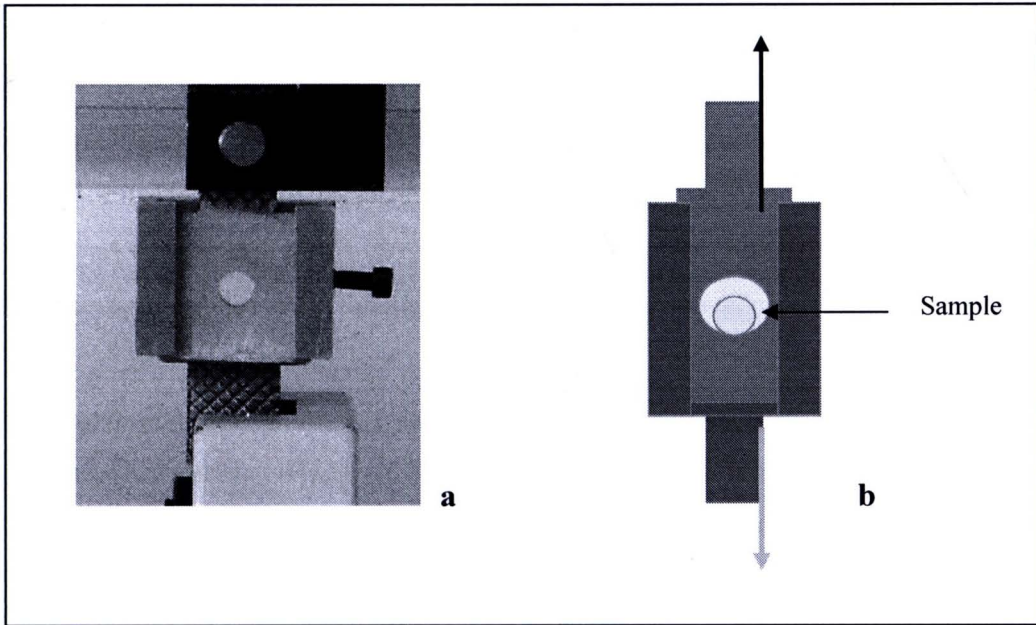
The SBS was determined for each group by using the Universal testing machine (Lloyd, LR30/k, Leicester, England) (Fig 28) with tension shear bond jig which applied a load perpendicular to the entire mainly at the core-veneer interface (Fig 29, 30). Each sample was subjected on the shear bond jig by placing the core portion of sample in the sample holder so the core-veneer interface is on the flat surface of holder as well as the testing jig (Fig. 30 and 31). Shear load was applied at a speed of 0.50 mm. per minute until failure (fracture). The load (N) at failure was recorded for each disk and average shear strengths (MPa) were calculated by dividing the load at failure to the area (mm<sup>2</sup>) of interface as follow[5]:

$$\text{Shear bond strengths (MPa)} = \text{Load (N)} / \text{Area (mm}^2\text{)} \quad \text{equation 5}$$

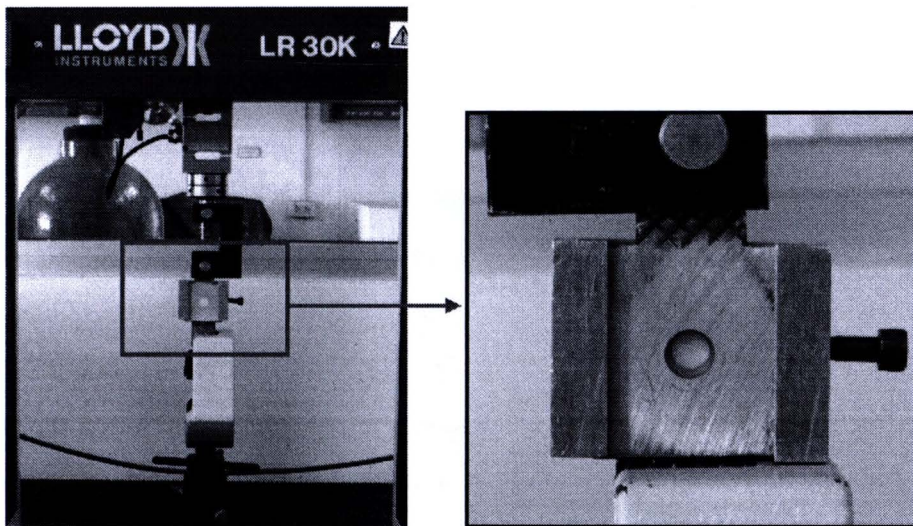
The mean shear bond strength and the standard deviation for each group were calculated from these data.



**Figure 28** Universal testing machine (Llyod, LR30 k, Leicester, England)



**Figure 29** (a) Shear bond strength testing apparatus (courtesy of Dr.Niwut Juntavee; fac. of dentistry KKU), (b) schematic illustration of a shear bond strength testing apparatus



**Figure 30** (a, b) The core-veneered specimen place in the Shear bond strength testing jig

### 3.5.4 Weibull analysis

The further analyzed of SBS testing using Weibull analysis. The variability of shear bond strength was estimated by calculating the Weibull modulus ( $m$ ) obtained from the following equation 6 as follow [35, 36]:

$$P_s(V_o) = \exp \{-(\sigma / \sigma_o)^m\} \quad \text{equation 6}$$

Where  $P_s(V_o)$  is the probability of survival as the fraction of identical sample;  $V_o$  is the volume of the sample;  $\sigma$  is the shear stress applied during testing; and  $\sigma_o$  (the weibull characteristic strength) and  $m$  are constant.

The Weibull modulus ( $m$ ) is usually determined from the straight line of a slope obtained by plotting between

$$\ln\{\ln(1/P_s(V_o))\} \text{ against } m \ln(\sigma/\sigma_o)$$

A higher weibull modulus ( $m$ ) indicates that the lower the variability of strength, the grater homogeneity of the material. Conversely the lower weibull modulus ( $m$ ) indicates the lower the reliability of strength.

### 3.5.5 Microscopic examination

One ceramic core-veneer specimen in each group was selected and cut by Isomet<sup>®</sup>4000 (Buehler, Illinois, USA) (Figure 32) to determine microscopically at the interface using scanning electron microscope (Hitachi S-3000N, Osaka, Japan) (Figure 33). Furthermore one core and one veneering specimen in each group that debonded after SBS test using universal testing machine were selected and examined microscopically in both of the bonding surface of core ceramic substructure and veneering ceramic. Prior to scanning electron micrographs (SEM) examination, the specimens from each group were cleaned in distilled water and ultrasonic cleanser for 15 minutes. After that all specimens were labeled and gold-palladium coated using a sputter coater (K500X Emitech, Ashford, British, England) (Figure 34) for 3 minutes at a current of 10mA and vacuum 130m torr and then keep all specimens in desiccator

cabinet (Northman, Taipei Hsein, Taiwan) (Figure 35) before examined surface microscopically using SEM.

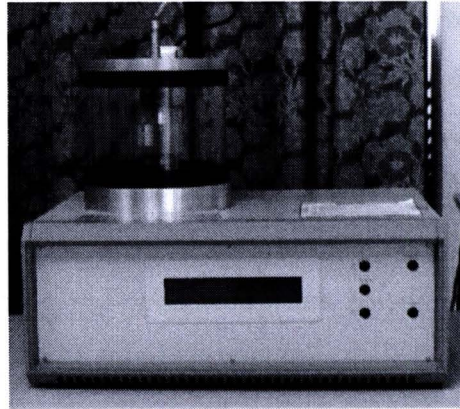
In order to examine the microstructure of the Cercon<sup>®</sup> core specimens at the subsurface layer, the fractured surface of Cercon<sup>®</sup> core specimens were etched with 4% hydrofluoric acid (HF) for 20 minutes, then water rinsed with distilled water. Then the specimens were labeled and gold-palladium coated using a sputter coater (K500X Emitech, Ashford, British, England) (Figure 34) for 3 minutes at a current of 10mA and vacuum 130m torr and then keep all specimens in desiccator cabinet (Northman, Taipei Hsein, Taiwan) (Figure 35) before examined surface microscopically using SEM.



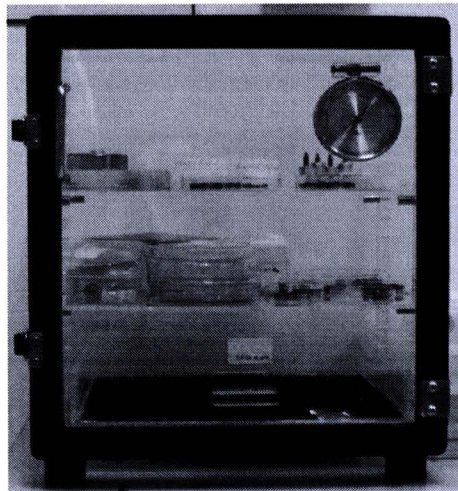
**Figure 31** Isomet<sup>®</sup>4000 (Buehler, Illinois, USA)



**Figure 32** Scanning electron microscope (Hitachi S-3000N, Osaka, Japan)



**Figure 33** Sputter coater (K500X Emitech, Ashford, British, England)



**Figure 34** Desiccator cabinet (Northman, Taipei Hsein, Taiwan)

### 3.5.6 Evaluation of crystalline structure

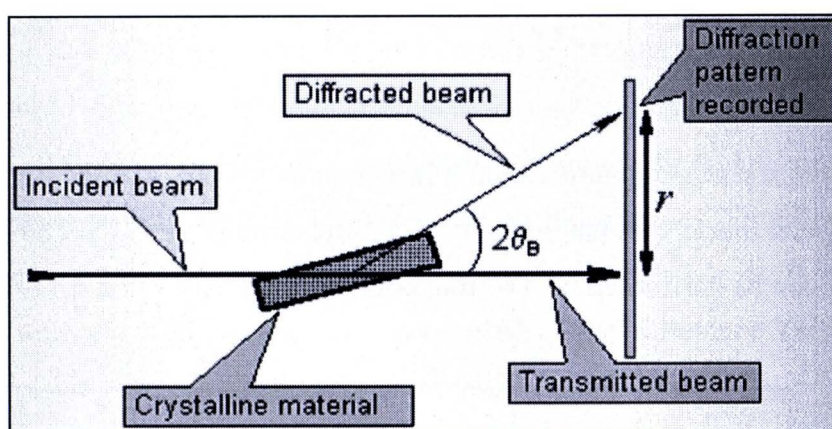
The crystalline phases in core-veneered specimens was evaluated for each group. The specimen in each group were selected to determine the relative amount of monoclinic and tetragonal phase in Yttrium Tetragonal Zirconia Polycrystals (Y-TZP) using the X-ray diffraction technique in the diffractometer (Philips Analytical X-Ray PW 1830, The Netherland) (Figure 35, 36). The specimens interface surfaces were scanned with copper k-alpha ( $\text{Cu K}\alpha$ ) radiation from 20-40° 2 $\theta$  degree with a step size of 0.02° for every 2 second step interval.

Qualitative phase analysis was performed by identification of each peak and compare data with known standards in the Joint Committee on Powder

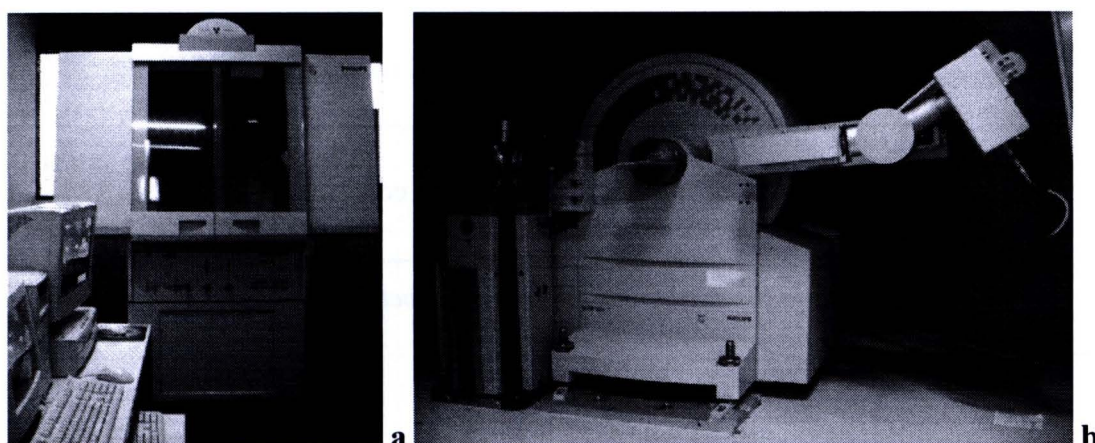
Diffraction Standards (JCPDS) database file after previous determination of the peak positions and relative peak heights, and calculation of the corresponding  $d$ -values according to the Bragg equation [37]:

$$\lambda = 2d \sin\theta \quad \text{equation 7}$$

Where  $\lambda$  is the X-ray wavelength (0.15418 nm for  $\text{CuK}\alpha$ ),  $d$  the normal distance of planes with the Miller indices ( $hkl$ ) and  $\theta$  the Bragg angle.



**Figure 35** Schematic illustration of X-ray diffraction (XRD)[38]



**Figure 36** (a, b) X-ray diffractometer (Philips Analytical X-Ray PW 1830, The Netherland)

Quantitative phase analysis (determination of the ratio of monoclinic to tetragonal zirconia) was performed by the polymorph method using the integral

intensities of the zirconia peaks monoclinic and tetragonal determined with the software X'Pert Plus and PCPDFWIN (after a background correction has been made). To a first approximation the mass fraction of monoclinic zirconia (with respect to the total zirconia content) is given by the Garvie-Nicholson equation 7 [37, 39]:

$$x_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(111) + I_m(11\bar{1}) + I_t(111)} \quad \text{equation 8}$$

Where  $I_m$  and  $I_t$  are integral intensities of monoclinic and tetragonal phase, respectively

For a more precise quantification it has be remembered, that the mass fraction need not depend linearly on the intensity ratio. The correction which allows for this nonlinearity can be performed by a formula derived by Toraya et al. [37, 39] as followed:

$$X_m = \frac{C x_m}{1 + (C - 1) x_m} \quad \text{equation 9}$$

Where is the Toraya-corrected mass fraction of monoclinic zirconia (a composition-dependent correction factor calculated from theoretical considerations)  $C = 1.32$ .

$$X_t = 1 - X_m \quad \text{equation 10}$$

Where  $X_t$  is the Toraya-corrected mass fraction of tetragonal zirconia



### 3.6 Statistic analysis

Statistical analysis was carried out using SPSS for Windows 11.5 (SPSS Inc., Illinois, Chicago, USA) and one-way analysis of variance (one-way ANOVA) as well as regression analysis were used.

3.6.1 One-way analysis of variance (one-way ANOVA) and multiple comparisons test

(1) One-way ANOVA was used to determine the significant difference of localized residual stress near interface and the multiple comparison test were used if the difference existed.

(2) One-way ANOVA was used to determine the significant difference both the localized distribution of residual stress in the core and veneering part.

(3) One-way ANOVA was used to determine the significant difference of various veneering ceramic on zirconia core based upon degree of CTE difference of core and veneering ceramic on the core-veneer shear bond strength at  $P < 0.05$ . The Tamhane's multiple comparison test were used if the difference existed. Weibull regression analysis was performed on the shear bond strength data.

3.6.2 Regression analysis

(1) Linear regression analysis was performed to determine the relationship of bond strength and localized residual stress at the near interface.

(2) Linear regression analysis was performed to determine the relation of bond strength and CTE difference.

