CHAPTER 5

RESULTS AND DISCUSSION (PART II): Ti - OXIDES REINFORCED DENTAL PORCELAINS

In this chapter, the results are presented of the investigation of both TiO_2 and TiO_2 -Fe₂O₃ reinforced porcelain systems. Chemical composition, microstructure and mechanical properties relationships are brought out and discussed in terms of phase formation, densification and mechanical properties.

5.1 TiO₂ Reinforced Porcelain Ceramic Nanocomposites

The XRD analysis for all TiO₂-reinforced porcelain ceramics compared with pure dental porcelain is presented in Fig. 5.1. All TiO₂ reinforced porcelain ceramics show the presence of the peaks corresponding to tetragonal TiO₂ phase (\blacksquare) with cell parameters a = 459.3 pm and c = 295.9 pm (JCPDS file number 21-1276) [171]. The tetragonal leucite (\blacktriangledown) phase with cell parameters a = 1306 pm and c = 1375.1 pm (JCPDS file number 15-0047) [172] mainly detected in pure dental porcelain sample was also found in all TiO₂ reinforced porcelain ceramics.

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Fig. 5.1 X-ray diffraction patterns of (a) dental porcelain ceramic (D11) and TiO_2 reinforced porcelain ceramics; (b) D28, (c) D29 and (d) D30.

Copyright[©] by Chiang Mai University All rights reserved The effect of TiO₂ on microstructural development and mechanical properties of the ceramics was investigated. In this section, test specimens were carefully examined with SEM technique to observe the microstructural developments (Figs. 5.2 and 5.3) and fracture paths (Fig. 5.4) of each ceramic. For all TiO₂ reinforced porcelain ceramics, the distribution of the TiO₂ phase in the glassy matrix was heterogeneous and the TiO₂ were grouped in clusters (e.g. ball-shaped in **D28**) as shown in Fig. 5.2(a). Rectangular bars (aspect ratio ~ 1 x 10 µm) of the recrystallization phase derived from the TiO₂ parent phase were found to randomly disperse in the dental porcelain matrix as shown in **D29** (Fig. 5.2(b)), **D30** (Fig. 5.2(c)) and group 13 (**D31** - **D33**) (Fig. 5.3). The TiO₂ phase of these samples was rod or bar-shaped, while KAlSi₂O₆ had a spherical morphology. Micron sized pores (mean diameter ~ 1 µm) also presented in some regions of the glassy matrix of **D33** (Fig. 5.3(c)).

Indentations of all TiO₂-reinforced porcelain ceramics show asymmetric cracks (Fig. 5.4(a)). Microscopy shows evidence of crack deflection, crack shielding and microcrack through toughening. The crack pattern is consistently transgranular and mainly intergranular for TiO₂ grains (Fig. 5.4(b,c)).



Fig. 5.2 SEM micrographs of TiO₂ (0.2-0.5 μ m, irregular-shaped) reinforced porcelain ceramics; (a) D28, (b) D29 and (c) D30.



Fig. 5.3 SEM micrographs of TiO_2 (50-200 nm, whisker-shaped) reinforced porcelain ceramics; (a) D31, (b) D32 and (c) D33.



Fig. 5.4 SEM micrographs of (a) the crack patterns generated by Vickers indentations which are propagating along the glassy phase of the matrix and made non-directly line (arrows), (b) **D34** and (c) **D36**; bridging ① intergranular cracks, ② transgranular crack and ③ microcracks.

The sintering shrinkage and total porosity for all TiO₂-reinforced porcelain ceramics are presented in Table 5.1 and Fig. 5.13, uniaxial flexural strength and indentation fracture toughness are presented in Table 5.2 and Fig. 5.13, along with the corresponding standard deviation. Significant differences by one-way ANOVA analysis and Scheffé post hoc test were calculated for porosity, strength and toughness data (Table 5.3). The results confirmed that the porosity values of only **D30**, **D31** and **D32** were statistically different ($p \le 0.017$) from pure dental porcelain (**D11**) value, others are statistically similar ($p \ge 0.593$) in value. The sintering shrinkage of all ceramics was slightly different from pure dental porcelain (the weakest material). As far as strength is concerned, statistics show that almost all ceramics are not significantly different (indicated by the superscript letters), but all of them demonstrated significantly greater (p < 0.001) flexural strength than the dental porcelain.

Sample code	Shrinkage (%)	Bulk density (g/cm ³)	Total porosity (%)
D11	15.75 (0.50)	2.318 (0.033)	6.53 (1.34) ^{a,b}
D28	11.90 (0.38)	2.714 (0.039)	6.99 (0.92) ^{a,b}
D29	12.84 (0.44)	2.707 (0.041)	8.61 (1.01) ^{b,c}
D30	13.35 (0.39)	2.746 (0.028)	8.79 (0.94) ^c
D31	17.40 (0.30)	2.463 (0.026)	$3.80(0.98)^{d}$
D32	18.40 (0.32)	2.477 (0.031)	$3.89(1.04)^{d}$
D33	18.73 (1.59)	2.486 (0.029)	5.30 (1.17) ^a

Table 5.1 Average (and standard deviation) of the physical properties of TiO₂-reinforced porcelain ceramics.

^{a-d} There is no significant statistical different (p > 0.05) between materials with the same superscript letters.

Table 5.2 Average (and standard deviation) of the mechanical properties of TiO₂-reinforced porcelain ceramics.

Sample code	Flexural strength (MPa)	Coefficient of strength variation (%)	Fracture toughness (MPa·m ^{1/2})	Elastic modulus (GPa)	Hardness (GPa)
	9	Commence of the second			3
D11	83.4 (8.3) ^a	9.9	1.01 (0.10) ^a	58.8 (6.6)	3.21 (0.19)
D28	110.4 (13.5) ^b	12.2	1.19 (0.14) ^{a,b}	65.0 (4.8)	3.38 (0.21)
D29	118.7 (17.9) ^{b,c}	15.0	1.22 (0.20) ^{a,b}	72.1 (5.2)	3.50 (0.30)
D30	120.6 (11.4) ^{b,c}	9.4	$1.29 (0.11)^{b,c}$	65.0 (4.8)	3.55 (0.19)
D31	120.2 (12.8) ^{b,c}	10.6	$1.32 (0.13)^{b,c}$	75.6 (7.4)	4.11 (0.18)
D32	124.2 (11.8) ^{b,c}	9.5	1.48 (0.12) ^{c,d}	82.4 (7.4)	4.51 (0.14)
D33	131.2 (11.0) ^c	8.3	$1.60 (0.11)^d$	77.4 (4.8)	4.24 (0.25)
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^{a-d} There is no significant statistical difference (p > 0.05) between materials with the same superscript letters.

Table 5.3 Summary of one-way ANOVA of TiO2-reinforced porcelain ceramics.

Source	SS	df	MS	F	Sig.
Material	396.157	6	49.868	32.354	< 0.001
Residual	176.021	63	1.541		20
Uniaxial fl	exural strength (MPa)			3
Source	SS	df	MS	F	Sig.
Material	28713.959	6	4785.660	29.612	< 0.001
Residual	21494.187	133	161.610		
Indentatio	n fracture tough	ness (MP:	a·m ^{1/2})		1905
Source	SS	df	MS	F	Sig.
Madanial	12.521	6	1.682	46.894	< 0.001
Material					

SS: Sum Squares; *df*: Degrees of freedom; **MS**: Mean Squares; **F**: MS of material/MS of residual; **Sig.**: significance.

Copyright[©] by Chiang Mai University All rights reserved The results of the Weibull analyses for the flexural strength are presented in Table 5.4, together with the Weibull plots given in Figs. 5.5 and 5.6. High Weibull moduli (steeper lines) indicated more uniform strength. All TiO₂-reinforced porcelain ceramics tested were good fits to the regression used, excepted for **D28**, **D29** and **D32**, according to the difference in the coefficients of determination (r^2) values. The statistical significant among the ceramics shows the same trend as those analyzed by one-way ANOVA, when data sets were compared for the overlap of their double sided confidence intervals at the 95% level. Maximum strength was found in group 13 (**D31** - **D33**). The high Weibull modulus only for **D30**, **D31**, **D32** and **D33** indicated a uniform ceramic with reliability of the strength. For fracture toughness, the results also confirmed that almost all ceramics evaluated in this study are statistically tougher (p < 0.001) than the pure dental porcelain (**D11**), similar to flexural strength results.

The strength of ceramics reinforced by crystalline phase of TiO_2 was affected in this study. The flexural strength of all ceramics was found significantly different from pure dental porcelain, causing a strength enhancement up to 32.3 - 57.3% (Table 5.2). There is no difference in the strength between the tested ceramics. Although the **D33** had the highest and **D29** had the lower strength, but as a result of high deviation of the results the values are not different (p = 0.146). The highest content of the additives in each group had the highest porosity.
 Table 5.4 Results of the Weibull regression analysis.

Sample code	<i>m</i> Value	σ 0.01 (MPa)	σ 0.05 (MPa)	σ 0.10 (MPa)	r ²	σ	C.I. (95%) for σ_0
D11	11.84	58.8	67.4	71,7	0.9712	86.7 ^a	82.8 - 90.6
D28	9.79	74.0	87.5	94.1	0.8738	118.5 ^b	112.2 - 124.8
D29	7.82	71.5	88.1	96.5	0.8158	128.7 ^b	120.4 - 137.1
D30	12.51	86.9	99.0	104.8	0.9566	125.5 ^{b,c}	120.1 - 130.8
D31	11.29	84.2	97.3	103.7	0.9417	126.6 ^{b,c}	120.6 - 132.6
D32	12.27	89.4	102.1	108.2	0.8741	130.0 ^b	124.5 - 135.6
D33	11.10	98.1	110.1	115.9	0.9421	135.9 ^c	130.7 - 141.0
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^{a-c} There is no significant Weibull statistical difference (p > 0.05) between materials with the same superscript letters. Details of the values were as described in Table 4.5.



Fig. 5.5 Weibull plots of uniaxial flexure strength data for TiO₂-reinforced porcelain ceramics.



Fig. 5.6 The cumulative Weibull plots of probability of failure data for TiO_2 -reinforced porcelain ceramics.

The pore could be considered detrimental to the strength of ceramics. In spite of the significant residual porosity observed, but this situation may be balanced by the influence of nanocomposite structures, which reinforce these ceramics. The exclusion of residual porosity could improve the strength and reliability of these ceramics [136]. Although the results illustrated that group 13 (**D31** - **D33**) had the higher in strength and toughness values than only 10 wt% TiO₂ added (**D28**), no strong difference between them occurred. The hardness of these ceramics increase with increasing TiO₂ content and the enhancement is probably due to these hard titania phase formation [137].

Within the same composition the reinforcement by the nanocrystalline TiO_2 showed higher shrinkage than the microcrystalline. This effect was described by the relation between the reinforcing nanocrystalline phase and the sintering shrinkage, especially in the nanocrystalline phase of whisker-shaped TiO_2 reinforcement in group 13 (**D31 - D33**). The high compaction degree and recrystallization from nanocrystalline phase reinforced into microcrystalline bar-shaped phase during sintering result in this effect. The presence of the TiO_2 in the ceramics was thought to be fundamental to the crystallization kinetics of the present ceramics and the attainment of fine grained microstructures. The subject of the relationship between the porosity and sintering behavior of ceramics has been previously and comprehensively discussed in topic 4.2. However, more efficient sintering of the ceramics during the firing procedure due to the increased sintering time or decreased heating rate may have been a factor in the flexural strength increase. A relatively fast heating rate was thought to be detrimental, since the sintering could occur before pore evolution. The densification of the outer layer of the ceramics was believed to be very rapid, with the entrapment of pores. Although the hard phase nanocomposite structure formations (Fig. 5.3(a-c)) with relatively high amount of crystalline TiO₂ phase (Fig. 5.1) influenced the strength, this enhancement can be reduced by the porosity effect. The significant difference ($p \le 0.029$) of the porosity was related with the amount of added TiO₂ and also affected a significant reduction ($p \le 0.033$) of the fracture toughness. In the group 13 (**D31** - **D33**), there are no significant differences in the strength and toughness values. Although there is difference in the composition and the crystalline phase amount (Fig. 5.1), the nanocomposite structure formation of tetragonal TiO₂ phase was found (Figs. 5.1-5.3) and influenced the strength, which can also be affected by the significant difference (p = 0.028) in porosity.

The fracture toughness of almost all TiO₂-reinforced porcelain ceramics was found to increase significantly when compared with the dental porcelain. A notable increase (27.7 to 58.4%) is shown in Table 5.2. The amount and the formation of hard crystalline phase (Fig. 5.1) may be affecting the toughness values. Group 13 (**D31** -**D33**) exhibits the higher toughness than the other compositions. Fracture toughness (K_{IC}) exhibited a decreasing trend with increasing TiO₂ content and porosity, but this value may be arrested with the increasing of new hard crystalline TiO₂ phase [173,174] (Figs. 5.2 and 5.3). However, almost all ceramics show no significant difference among the toughness data. The higher toughness values of all ceramics than pure dental porcelain (**D11**) may be the result of a reinforcing secondary phase of titania. The ceramics with rigid additives, nanocomposite structures formation, new rigid phase formation and the orientation of crystalline reinforcing phase probably made crack propagation more difficult. These effects are contributed to the high toughness of the ceramics, due to the formation of the crack requires higher energy

[168, 175, 176].

All TiO₂-reinforced porcelain ceramics (Figs. 5.2 and 5.3) showed reinforcing ceramics dispersed in ceramic matrix. All of them showed different structure of reinforcing phase, and differ from the raw additives (Fig. 3.3). Group 13 (D31 - D33) had nanocomposite structures formation of tetragonal TiO₂. This new hard phase has been previously observed in reinforced porcelain ceramics by Yuan and Su [20]. The observations support the bending strength and toughening mechanism of materials as described in the topic 4.2. The observation of crack pattern generated by Vickers indentation is shown in Fig. 5.4. The reinforcing ability of the titania/new hard phase and the effectiveness of crack deflection were confirmed by the hardness and toughness data (Table 5.2). Crystal and matrix microcracking have been linked to the new hard phase of tetragonal TiO₂ formation in this study. The new hard phase formation was found to be suitable for the reinforcement of ceramic matrix, as pointed out in the study of Kalinkin et al. [120]. A minimal microcracking between crystalline reinforcing phases containing in dental porcelain matrix was found (Fig. 5.4) as also described in the topic 4.2. The rapid firing and cooling processes caused the development of residual tensile stresses in the matrix around the reinforcement from the difference in the thermal coefficient of each ceramic [177]. These effects will improve the fracture propagation of crack deflection mechanism, but retarded by the orientation, roughness and strength of reinforcing ceramics. However, observation of microcracks and the estimation of their contribution to the ultimate fracture toughness require an approach somewhat more complicated than that used in the present study. The Weibull distributions are wider for the group 12 (D28 - D30), as would be related to the higher porosity, microcracking, flaw size and crystalline phase distribution. The

Weibull *m*-values were not improved in these ceramics, although the probabilities of failure were higher than those of the other ceramics. More sophisticated Weibull analysis, taking into account these events, may also be applicable.

The effects of reinforcing dental porcelain with titania were systematically investigated. Optimization of the microstructure by generating nanocomposite materials, hard rigid phases of titania formation and its distribution and orientation in the dental porcelain can be extremely advantageous to the strength of these ceramics. The present study shows no significant difference in the strength caused by the influence of porosity. These ceramics require longer processing times and the additives incorporate more interfaces that can be a site for porosity or strength limiting flaws. This study can only be seen as a prelude to further experimentation or to the strength mechanism improvement of the tested ceramics.

5.2 TiO₂-Fe₂O₃ Reinforced Porcelain Ceramic Nanocomposites

In analogous to the previous section, here attention is given to the phase formation, microstructure, densification and mechanical properties of TiO₂-Fe₂O₃ reinforced porcelain ceramic system. Significant data obtained from the XRD analyses for all TiO₂-Fe₂O₃ reinforced porcelain ceramics are presented in Fig. 5.7. The dominant peaks of these ceramics indicated the tetragonal TiO₂ phase (\blacksquare) with cell parameters *a* = 459.3 pm and *c* = 295.9 pm (JCPDS file number 21-1276) [171], as the parent phase. The minor peaks of the orthorhombic pseudobrookite (Fe₂TiO₅) phase (\Box) with cell parameters *a* = 979.6 pm, *b* = 998.0 pm and *c* = 373.0 pm (JCPDS file number 41-1432) [178] were also observed in these samples.





Fig. 5.7 X-ray diffraction patterns of (a) dental porcelain ceramic (**D11**) and TiO₂-Fe₂O₃ reinforced porcelain ceramics; (b) **D34**, (c) **D35** and (d) **D36**.

The microscopic observations via SEM show the significant different microstructures of each ceramic, nanocomposite materials formations and fracture paths. The reinforced porcelain ceramics D34 mainly consisted of the recrystalline phase from the parent TiO₂ phase as a rectangular bar-shaped (~ 1 x 1 μ m in cross section and 2 µm in length), randomly dispersed in the dental porcelain ceramic (Figs. 5.8(a)). In comparison with D34, it is seen that the microstructures of D35 and D36 are totally different. Clearly, the ceramic sintering condition has been found to have a pronounced effect on the densification and microstructure of ceramics in the TiO₂-Fe₂O₃ reinforced porcelain system. As shown in Fig. 5.8(b), two different phases are visible in the microstucture, i.e. rectangular bar-shaped TiO₂ grains and Fe₂TiO₅-rich phase with a dendritic morphology. This kind of microstructure can be matched with the "intra/inter type" of Niihara's ceramic-nanocomposites model [78,79] or "nanomicro type" of Kuntz's ceramic-nanocomposites model [66,67]. The nanocomposite materials formation of Fe₂TiO₅-rich phase with the reticulate sheets form (100 nm in thickness) shown in D36 (Figs. 5.8(c)). For group 15 (D37 - D39) shown the microstructure analogous with group 14 (D34 - D36), but had the smaller grain size of TiO₂ and Fe₂TiO₅ phases.

Indentations of all TiO_2 -Fe₂O₃ reinforced porcelain ceramics show asymmetric cracks (Fig. 5.10(a)). The crack pattern is consistently transgranular and mainly intergranular for TiO_2 grains (Fig. 5.10(b,c)). Electron microscopy show evidences of crack deflection, crack shielding and microcrack toughening.



Fig. 5.8 SEM micrographs of TiO₂ (0.2-0.5 μ m, irregular-shaped) and Fe₂O₃ reinforced porcelain ceramics; (a) **D34**, (b) **D35** and (c) **D36**.



Fig. 5.9 SEM micrographs of TiO₂ (50-200 nm, whisker-shaped) and Fe₂O₃ reinforced porcelain ceramics; (a) **D37**, (b) **D38** and (c) **D39**.



Fig. 5.10 SEM micrographs of (a) the crack patterns generated by Vickers indentations which are propagating along the glassy phase of the matrix and made non-directly line (arrows), (b) **D37** and (c) **D39**; bridging ① intergranular cracks, ② transgranular cracks and ③ microcracks.

The sintering shrinkage and total porosity for all TiO₂-Fe₂O₃ reinforced porcelain ceramics are presented in Table 5.5 and Fig. 5.13. Uniaxial flexural strength and indentation fracture toughness are presented in Table 5.6 and Fig. 5.13, along with the corresponding standard deviation. Significant differences by one-way ANOVA analysis and Scheffé post hoc test were calculated for porosity, strength and toughness data (Table 5.7). For the densification and sintering behavior, the porosity values of almost all these ceramics were statistically similar ($p \ge 0.798$) from pure dental porcelain (D11) value, only D34 and D35 are statistically different ($p \le 0.021$) in value. The sintering shrinkage of all ceramics was slightly different from dental porcelain, only D37 has higher shrinkage (8.4%) than dental porcelain. As far as strength is concerned, statistics shows that all ceramics are significantly different ($p \le 0.014$), and all of them demonstrated significantly greater (p < 0.001) flexural strength than the dental porcelain.

Sample code	Shrinkage (%)	Bulk density (g/cm ³)	Total porosity (%)
D11	15.75 (0.50)	2.318 (0.033)	6.53 (1.34) ^{a,b}
D34	14.12 (0.43)	2.838 (0.034)	10.62 (1.11) ^c
D35	13.90 (0.50)	2.780 (0.037)	9.93 (1.20) ^{c,d}
D36	13.93 (0.43)	2.756 (0.034)	7.77 (1.12) ^{a,b,d}
D37	17.08 (0.34)	2.964 (0.055)	8.18 (0.98) ^{b,d}
D38	16.80 (0.78)	2.857 (0.048)	7.23 (1.10) ^{a,b}
D39	16.11 (0.54)	2.862 (0.067)	6.01 (0.87) ^a

Table 5.5 Average (and standard deviation) of the physical properties of TiO₂-Fe₂O₃ reinforced porcelain ceramics.

^{a-d} There is no significant statistical different (p > 0.05) between materials with the same superscript letters.

Table 5.6 Average (and standard deviation) of the mechanical properties of TiO₂-Fe₂O₃ reinforced porcelain ceramics.

Sample code	Flexural strength	Coefficient of strength	Fracture toughness	Elastic modulus	Hardness (GPa)
	(1114)			(014)	(01 4)
D11	83.4 (8.3) ^a	9.9	$1.01 (0.10)^{a}$	58.8 (6.6)	3.21 (0.19)
D34	125.7 (16.5) ^b	13.1	$1.54 (0.18)^{b}$	99.2 (10.4)	5.30 (0.19)
D35	134.4 (16.6) ^{b,c}	12.3	$1.66 (0.19)^{b,c}$	109.6 (11.6)	5.84 (0.60)
D36	135.7 (17.9) ^{b,c}	13.1	1.83 (0.22) ^{c,d}	134.2 (14.0)	6.97 (0.33)
D37	129.7 (15.5) ^b	11.9	1.57 (0.19) ^{b,c}	103.1 (11.9)	5.33 (0.20)
D38	141.8 (15.7) ^{b,c}	11.0	1.82 (0.17) ^{c,d}	119.6 (10.7)	5.81 (0.67)
D39	149.8 (18.8) ^c	12.5	$1.99 (0.21)^d$	144.1 (13.0)	6.81 (0.29)

^{a-d} There is no significant statistical difference (p > 0.05) between materials with the same superscript letters.

Copyright[©] by Chiang Mai University A I I rights reserved Table 5.7 Summary of one-way ANOVA of TiO₂-Fe₂O₃ reinforced porcelain ceramics.

Source	SS	df	MS	F	Sig.
Material	423.572	6	47.021	31.413	< 0.001
Residual	158.028	63	1.496		
8	$\langle \langle \rangle$				
Uniaxial fl	exural strength (MPa)	5		5
Source	SS	df	MS	F	Sig.
Material	55098.979	6	9183.163	35.969	< 0.001
Residual	33955.822	133	255.307		
Q		Ń			A
Indentatio	n fracture tough	ness (MPa	a•m ^{1/2})		
Source	SS	df	MS	F	Sig.
Material	10.184	6	1.589	48.152	< 0.001
		()	0.022		

SS: Sum Squares; *df*: Degrees of freedom; **MS**: Mean Squares; **F**: MS of material/MS

The results of the Weibull analyses for the flexural strength are presented in Table 5.8, together with the Weibull plots (Figs. 5.11 and 5.12). High Weibull moduli (steeper lines) indicated more uniform strength. All TiO₂-Fe₂O₃ reinforced porcelain ceramics tested were good fits to the regression used, according to the difference in the coefficients of determination (r^2) values. Maximum strength was observed in group 15 (**D37** - **D39**). The high Weibull modulus only for group 15 indicated a uniform ceramic with reliability of the strength. For fracture toughness, the results also confirmed that all ceramics evaluated in this study are statistically tougher (p < 0.001) than the dental porcelain, similar to flexural strength results.

Sample code	<i>m</i> Value	σ 0.01 (MPa)	σ 0.05 (MPa)	σ 0.10 (MPa)	r ²	σ_0	C.I. (95%) for σ_0
D11	11.84	58.8	67.4	71.7	0.9712	86.7 ^a	82.8 - 90.6
D34	8.55	76.8	93.0	101.1	0.9350	131.6 ^{b,c}	123.8 - 139.3
D35	9.70	88.4	104.5	112.6	0.9632	142.0 ^c	134.2 - 149.8
D36	8.94	85.8	102.9	111.5	0.9564	143.4 ^c	135.1 - 151.8
D37	9.49	83.7	99.3	107.2	0.9207	135.8 ^{b,c}	128.6 - 143.1
D38	10.74	97.2	113.1	121.0	0.9555	149.2 ^c	141.8 - 156.6
D39	9.47	97.6	115.9	125.1	0.9108	158.6 ^c	149.8 - 167.4
			TU	NIV			

Table 5.8 Results of the Weibull regression analysis of TiO₂-Fe₂O₃ reinforced porcelain ceramics.

^{a-c} There is no significant Weibull statistical difference (p > 0.05) between materials with the same superscript letters. Details of the values were as described in the Table 4.5.

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Fig. 5.11 Weibull plots of uniaxial flexure strength data for TiO₂-Fe₂O₃ reinforced porcelain ceramics.



Fig. 5.12 The cumulative Weibull plots of probability of failure data for TiO_2 -Fe₂O₃ reinforced porcelain ceramics.

In the view of strength, the effect of crystalline additives in all TiO_2 -Fe₂O₃ reinforced porcelain ceramics was observed and significantly different from pure dental porcelain, causing a strength enhancement up to 50.7 - 79.6% (Table 5.6). With the different type of TiO_2 , irregular-shaped TiO_2 additives led to the higher porosity samples. The pore could be considered detrimental to the strength of ceramics. In spite of the significant residual porosity observed, the bending strengths of the significant statistic different. This situation may be balanced by the influence of nanocomposite structures and the new crystalline phase formations, pseudobrookite, which reinforces these ceramics. The exclusion of residual porosity could improve the strength and reliability of these ceramics [21]. The hardness of these ceramics increase with increasing TiO_2 content and the enhancement is probably due to the new hard phase pseudobrookite formation.

For the effects of second phase on mechanical properties, with the same composition the reinforcement by the nanocrystalline TiO₂ showed higher shrinkage than the microcrystalline. This effect was described in the topic 4.2 with a relation between the reinforcing nanocrystalline phase and the sintering shrinkage, especially in the nanocrystalline phase of whisker-shaped TiO₂ reinforcement in group 15 (**D37** - **D39**). The high compaction degree and recrystallization from nanocrystalline phase reinforced into microcrystalline reticulate sheet and bar-shaped phase during sintering result in this effect. The presence of the TiO₂ in the ceramics was thought to be fundamental to the crystallization kinetics of the present ceramics and the attainment of fine grained microstructures. Although sintering temperatures (1090 °C) and times (30 min) of all TiO₂-Fe₂O₃ reinforced porcelain ceramics were controlled (Table 3.7),

but no strong difference in shrinkage among all ceramics was observed. A relatively fast heating rate was thought to be detrimental, since the sintering could occur before pore evolution. The densification of the outer layer of the ceramics was believed to be very rapid, with the entrapment of pores. In the case of similar reinforcing materials, group 14 (**D34** - **D36**) or group 15 (**D37** - **D39**), the strength of ceramics was found significantly different ($p \le 0.018$) when compared with the difference in the composition of TiO₂ and Fe₂O₃ added. Although the new phase nanocomposite structure formations (Figs. 5.8(b,c) and 5.9(b,c)) with relatively high amount of crystalline Fe₂TiO₅ phase (Fig. 5.7) influenced the strength, this enhancement can be reduced by the porosity effect. The significant difference ($p \le 0.032$) of the porosity was related with the amount of Fe₂O₃ added and also affected a significant ($p \le 0.048$) increasing up of the fracture toughness. Addition, the microcomposite structure formation of tetragonal TiO₂ phase was found (Figs. 5.8 and 5.9) and also influenced the strength of ceramics was influenced the strength of ceramics, which can also be affected by the significant difference (p = 0.010) in porosity.

The fracture toughness of all TiO₂-Fe₂O₃ reinforced porcelain ceramics was found to increase significantly ($p \le 0.001$) when compared with the dental porcelain. A notable increase (52.4 to 97.0%) is shown in Table 1. The amount and the formation of TiO₂ and new hard crystalline Fe₂TiO₅ phase may be affecting the toughness values. The produced stress raises higher than that from the inherent flaws as the energy for the flaw to grow is potentially provided by the elastic stored energy in the particle and the adjacent glassy matrix [179]. The group 15 (**D37** - **D39**) had the higher toughness than the other one group. K_{IC} exhibited an increase trend with increasing Fe₂O₃ content and decreasing porosity, but this value may be arrested with the increasing of pseudobrookite crystalline phase. However, almost all ceramics show no significant difference among the toughness data. The higher toughness values of all ceramics than pure dental porcelain (**D11**) may be the result of a reinforcing secondary phase of tetragonal titania and pseudobrookite. The retention of tetragonal TiO₂ in ceramics can enhance the toughness of ceramics if they transform due to an induction of stress around fracture cracks [180]. In fact, flexural strength and fracture toughness of TiO₂/Fe₂O₃ nanocomposites increased with increased Fe₂O₃ content and related with the amount of Fe₂TiO₅ formation. The ceramics with rigid additives, nanocomposite structures formation, new rigid phase formation and the orientation of crystalline reinforcing phase probably made crack propagation more difficult [181]. These effects are contributed to the high toughness of the ceramics, due to the formation of the crack requires higher energy. This phenomenon has been previously described in topic 4.2.

All TiO₂-Fe₂O₃ reinforced porcelain ceramics showed different structure of reinforcing phase, and differ from the raw additives (Fig. 3.3). The higher additives of 4.4 and 6.6 wt% Fe₂O₃ had nanocomposite structures formation of orthorhombic Fe₂TiO₅ and tetragonal TiO₂ formation for all ceramics. These new phases have been previously observed by Yuan and Su [20] and Pal et al. [119]. The observations of crack pattern developed by Vickers indentation are shown in Fig. 5.10(a). The reinforcing ability of the titania/new hard phase and the effectiveness of crack deflection were confirmed by the hardness and toughness data (Table 5.6). Crystal and matrix microcracking have been linked to the new hard phase of orthorhombic Fe₂TiO₅ (\Box) and tetragonal TiO₂ (**n**) formation in this study. The new phase formation was found to be suitable for the reinforcement of ceramic matrix, as pointed

out in the topic 4.2. A minimal microcracking between crystalline reinforcing phases containing in dental porcelain matrix was found (Fig. 5.10(b,c)). In addition, local stresses remained in the ceramics during cooling after sintering with the high cooling rate (250 °C/m), due to the thermal expansion mismatch between crystalline reinforced phase and glassy matrix phase. This effect will improve the fracture propagation of crack deflection mechanism, but retarded by the orientation, roughness and strength of reinforcing materials. Assuming that the crack behavior and distribution responsible for failure remains unchanged from phase to phase, we conclude that the strength of the reinforced porcelain ceramics increased in proportion to their toughness (K_{IC}) values. These results are in agreement with this conclusion. The Weibull distributions are wider for the group 14 (D34 - D36), as would be related to the higher porosity, microcracking, flaw size and crystalline phase distribution. The Weibull *m*-values were not improved in these ceramics, although the probabilities of failure were higher than those of the other ceramics. X-ray patterns indicate that all ceramics illustrated the new crystalline phase formations, pseudobrookite (\Box) (Fig. 5.7). Also a considerable amount of crystalline phase was already transformed in the as-sintered ceramics. The new phases were formed from the metal oxide reinforced added following the reactions:

The greatest amount of pseudobrookite was detected in the composition of **D36** and

D39 and related with the amount of Fe_2O_3 added (6.6 wt%) (Fig. 5.7). The new phases with high amount of reinforcing in glassy phase are also correlated to the higher

fracture toughness mechanisms.

At last, although the color result was not illustrated, the observed color of the TiO_2 -Fe₂O₃ reinforced porcelain ceramics was found within the same range of white color as described by ISO 6872 [122]. The ceramics have a light brown color, caused by the Fe₂O₃ additives. The compositions of 6.6 wt% Fe₂O₃ added may not be suitable for direct making of a dental core ceramic materials.

This work demonstrates that both TiO_2 and Fe_2O_3 powders in a dental porcelain nanocomposite are a strengthening and toughening agent. Optimization of the microstructure by generating micro/nanocomposite materials, rigid phases of TiO₂/Fe₂TiO₅ formation and its distribution and orientation in the matrix can be advantageous to the strength of these ceramics. Optimum mechanical properties of reinforced ceramics can be achieved by sintering at 1090 °C with the addition of 30 wt% two metal oxide into dental porcelain. The strength was about 135 - 149 MPa and the toughness was 1.8 - 1.9 MPa·m^{1/2} when the TiO₂/Fe₂O₃ reached 23.4/6.6 wt%. Mainly the stress-induced TiO₂/Fe₂O₃ transformation contributed to the improvement in fracture toughness and reduced by the influence of porosity. These ceramics require longer processing times and the additives incorporate more interfaces that can be a site for porosity or strength limiting flaws. So far, there are no reports on the fabrication of TiO₂-Fe₂O₃ reinforced porcelain ceramics via nanocomposite approach. Moreover, the scope for improving densification by reducing the heating rate is limited by the industrial manufacturing condition whilst slip-casting technique can cause severe porosity problem [182,183].

The last remarkable, for the comparative all flexural strength and porosity data in this chapter can be summarized in Fig. 5.13.



(Strength) Flexural strength of TiO2-reinforced porcelain ceramics

Fig. 5.13 The comparative all flexural strength and porosity data of (a) TiO₂ and (b) TiO₂-Fe₂O₃ reinforced porcelain ceramics.