### **CHAPTER 2**

# LITERATURE REVIEW

In this chapter, attention is equally focused on the dental porcelains and the ceramic nanocomposites. It is first necessary to describe the information background of dental porcelains. The relevant literatures on chemical composition, structure and mechanical properties of dental porcelains are reviewed. Finally, the concept of ceramic nanocomposites and its application in dental ceramics is then described in more details.

# **2.1 Dental Porcelains**

The first ceramics fabricated by man were earthenware pots used for domestic purpose [23]. This kaolin-based material is opaque, relatively weak and porous and would be unsuitable for dental applications [24-26]. The blending of this with other minerals such as silica and feldspar produced the translucency and extra strength required for dental restorations. Material containing these additional important ingredients was given the name "Porcelain" [27]. Fused porcelain has long been used in the construction of works of art [25-26]. It can be produced in almost every shade or tint and its translucency imparts a depth of color unobtainable by other materials. Although the technique or porcelain fusing is exacting it can be initially molded by hand as a paste and alterations can be made at various stages of the work. It is not surprising, therefore, that dentistry has turned to porcelain for the production of artificial teeth, crowns, bridges and veneers (Fig. 2.1).



**Fig. 2.1** Examples of porcelains used in (a) the art decoration [28] and (b) the construction of ceramic crown and bridge [26].

Although the favorable aesthetic properties and excellent biocompatibility of porcelain have never been in doubt, its use is somewhat restricted by the relatively brittle nature of the material and the large shrinkage which occurs during processing [29]. Some recent developments [28,29] offer a potential for overcoming these problems.

#### 2.1.1 Chemical Compositions

The compositions of the various types of porcelain are summarized in the Table 2.1. It can be seen that there are considerable differences in chemical composition between the dental porcelains and decorative porcelain [30]. Indeed, the dental porcelains contain little of clay and, possible, would be more aptly described as dental glasses. Kaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) is a hydrated aluminosilicate, the set decorative porcelain is essentially a mixture of this with silica, bound together by a flux or binder such as feldspar which is a mixture of potassium (K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>) and sodium aluminosilicates (Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>) [31]. Feldspar is the lowest fusing component, which melts and flows during firing, uniting the other components in a solid mass. The fusion temperature of feldspar may be further reduced by adding to it other low-fusing fluxes such as borax [32]. Chemical composition analysis of several dental porcelains is given in Table 2.2. The standard classification of dental porcelain is only used for convenience and dividing them into three temperature ranges and are classified according to fusion temperature as follows: high-fusing (1288-1371 °C), medium-fusing (1093-1260 °C) and low fusing (871-1066 °C) [30,33].

Chemical compositions (wt%)			
Kaolin	Silica	Feldspar	Glass
50	25	25	0
4	15	80	0
0	25	60	15
	<b>Kaolin</b> 50 4 0	Kaolin         Silica           50         25           4         15           0         25	Chemical compositions (wt%)KaolinSilicaFeldspar5025254158002560

 Table 2.1 Chemical compositions of porcelain materials [30].

	Commercial dental porcelains					
Compositions	Ceramco opaque <sup>a</sup> (wt%)	VMK opaque <sup>b</sup> (wt%)	Ceramco dentin <sup>a</sup> (wt%)	VMK dentin <sup>b</sup> (wt%)		
SiO <sub>2</sub>	55.10	52.41	62.20	56.83		
Al <sub>2</sub> O <sub>3</sub>	11.65	15.15	13.40	16.30		
CaO	سر	- ( <u></u>	0.98	2.01		
K <sub>2</sub> O	9.60	9.90	11.30	10.25		
Na <sub>2</sub> O	4.75	6.58	5.37	8.63		
TiO <sub>2</sub>	-	2.59	- /	0.27		
ZrO <sub>2</sub>	0.16	5.16	0.34	1.22		
SnO <sub>2</sub>	15.0	4.90	0.50	5/-		
Rb <sub>2</sub> O	0.04	0.08	0.06	0.10		
ZnO	0.26	Color C		-		
UO <sub>3</sub>	YAT	INTV	R	0.67		
$B_2O_3$ , $CO_2$ , $H_2O$	3.54	3.24	5.85	3.75		

Table 2.2 Chemical composition analysis of some commercial dental porcelains [30].

<sup>a</sup> Dentsply Ceramco R and D, USA; <sup>b</sup> VITA Zahnfabrik, Germany

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### 2.1.2 Structures

Dental porcelains are, in part, glassy materials and in order to understand their formulation, knowledge of glass formation is essential. Glasses may be regarded as supercooled liquids or as non-crystalline solids. This lack of crystallinity distinguishes them from other solids, and their atomic structures and properties depend, not only on composition, but also on thermal history. The glass-marker selects complex or impure solutions in order to modify the physical properties of the glass both in the molten and solid form. These properties would include viscosity, melting temperature, chemical durability, thermal expansion and resistance to devitrification. Frictional forces inhibiting the formation of new molecular configurations in the liquid glass should also be as high as possible. This can be achieved by rapid cooling or preferably, for dental purposes, by using materials that produce high viscosity in the melt, e.g. aluminium oxide ( $Al_2O_3$ ) [34].

The principle anion present in all glasses is oxygen ion which forms very stable bonds with small multivalent cations such as silicon, boron, germanium, or phosphorous, giving rise to structural units, such as the SiO<sub>4</sub> tetrahedra illustrated in Fig. 2.2, which form a random network in glass [35,36]. These ions are thus termed glass formers. Zachariasen (1932) [37] examined the characteristics of these glass-forming oxides and proposed his random network theory of glass structure. He considered that the interatomic forces in glasses and crystals must be essentially similar and that the atoms in glass oscillate about definite equilibrium positions. He deduced that the atoms must be linked in the form of a three-dimensional network in glass as in crystals, and because glasses do not give a sharp X-ray diffraction spectra they could not be periodic (in an ordered arrangement). Zachariasen [37] considered



Fig. 2.2 Structural units of  $SiO_4$  tetrahedra: (a) diagram of silicate unit with each SiO tetrahedra sharing an oxygen atom, (b) a silicate unit which the silicon atom (Si) is surrounded by four oxygen atoms (oxygen polyhedra) and (c) linked silicate units which form the network in glass [38].

that although the units of structure in the glass, (i.e.  $SiO_4$  tetrahedra) and in the crystals are practically identical, in the crystal these structural units are built up to give a regular lattice. By contrast, in the glass there is sufficient distortion of bond angles to permit the structural units to be arranged in a random network (Fig. 2.3). Zachariasen [37] proposed certain conditions for glass formation:

- (1) an oxygen atom must not be linked to more than to *M* atoms,
- (2) the number of oxygen atoms surrounding M must be small, and
- (3) these oxygen polyhadra must share corners only and not edges or faces.



Fig. 2.3 Two-dimensional presentation of an oxide  $M_2O_3$  in (a) the crystalline form and (b) the glass form [38].

For dental purposes [39], only two glass-forming oxides are used – silica and boron oxide - and they form the principal network around which a dental glass can be built. Alumina under certain circumstances may be regarded as a glass-forming oxide when in combination with other oxides. Dental porcelains use the basic siliconoxygen network as the glass-forming matrix but additional properties, such as lowfusing temperature, high viscosity, and resistance to devitrification, are built in by the addition of other oxides to the glass-forming lattice SiO<sub>4</sub>. These oxides generally consist of potassium, sodium, calcium, aluminium and boric oxides [40]. The purpose of a flux is principally to lower the softening temperature\* of a glass by reducing the amount of cross-linking between the oxygen and glass-forming elements, e.g. silicon

<sup>\*</sup>softening temperature: The temperature, under specified conditions, at which porcelain-enamel or frit begins to flow.



**Fig. 2.4** Reaction between sodium oxide and silica tetrahedral [38]. The sodium oxide contributes one of the non-bridging oxygen ions which interrupt the continuity of the silica network. (For simplicity, only a two-dimensional representation of the  $SiO_4$  groups is given; in the actual glass structure these groups take the form of tetrahedral as illustrated in Fig. 2.2)

[41]. For example, if soda (Na<sub>2</sub>O) is introduced into a silicate melt to produce sodium silicate glasses, structural changes occur as in Fig. 2.4. Instead of the bridging oxygen ions which formed the link between the two SiO<sub>4</sub> tetrahedra, there are now two non-bridging oxygens, one of which has been contributed by the sodium oxide. A gap is therefore produced in the SiO<sub>4</sub> network and the sodium ions are accommodated in the interstices or holes in the random network structure as shown in Fig. 2.5. The greater the number of Na<sup>+</sup> ions added, the more Si-O-Si bridges are broken. The O:Si ratio in a glass is of the greatest importance and will affect both the viscosity of the glass and its thermal expansion. For example, in dental porcelain used for bonding the metal, it

is usual practice to increase the soda content in order to raise the thermal expansion of the porcelain near to that of the gold alloys. Other alkali metal oxides, such as lithium or potassium oxides, take part in the glass structure in a similar manner [42,43]. Lithium ions will be accommodated in smaller structural interstices and the sodium ions and the potassium ions in larger one. MgO, CaO and BaO may also act as modifying oxides [44,45]. The used of these alkali metal oxides must be very carefully controlled to preserve the original glass-forming network; otherwise problems of devitrification may occur. Potassium, sodium or calcium oxides are introduced into a glass melt via their respective carbonates which revert to oxides on heating.



**Fig. 2.5** Two-dimensional representation of the structure of sodium silicate glass [38]. (The structure is shown in a simplified form since only three of the four oxygen ions surrounding each silicon ion are depicted.)

The addition of glass modifiers or fluxes to the basic glass-forming network  $SiO_4$  in dental porcelain will not only lower the softening point but also decreases the viscosity [46]. Dental porcelains require a high resistance to slump or pyroplastic flow and it is therefore necessary to produce glasses with a high viscosity as well as low firing temperatures. This can be done by using intermediate oxides which although not usually capable of forming a glass, can take part in the glass network.

The hardness and viscosity of a glass can be increased by the use of an intermediate oxide such as aluminium oxide  $(Al_2O_3)$  [47]. The role of  $Al_2O_3$  in glass formation is complicated. It can not be considered as a true glass former by itself because the dimensions of the ion excludes the possibility of Al<sub>2</sub>O<sub>3</sub> triangles being formed and the O:Al ratio precludes the formation of AlO<sub>4</sub> tetrahedra. In crystals, the aluminium ion can be four or six coordinated with oxygen giving rise to tetrahedral  $AlO_4$  or octahedral  $AlO_6$  groups [48]. The tetrahedral groups can replace  $SiO_4$ tetrahedra in silicate lattices to give the arrangement shown in Fig. 2.6. Since each aluminium ion has a charge of +3 as compared with a charge of +4 for each silicon ion, an additional unit positive charge must be present to ensure electroneutrality. When metallic oxides, such as sodium oxide, are present, one alkali metal ion per AlO<sub>4</sub> tetrahedron would satisfy this requirement and the alkali metal ions could be accommodated in the interstices between tetrahedral groups. In this way, as each Al<sup>3+</sup> ion replaces a Si<sup>4+</sup> ion in the network, one Na<sup>+</sup> ion is taken in to preserve neutrality. This type of structural arrangement is found for many aluminosilicates such as feldspars and zeolites, where the crystals are built up of linked SiO<sub>4</sub> and AlO<sub>4</sub> groups [49,50].



Fig. 2.6 Aluminium in a silicate network (The structure is shown in a simplified form; the true structure is three-dimensional, the AlO<sub>4</sub> and SiO<sub>4</sub> groups having tetrahedral configurations.). The alkali metal ion ( $M^+$ ) such a sodium maintains electroneutrality [38].

Large univalent or divalent cations are present in these structures to the extent of one alkali ion or "half" an alkaline earth ion per AlO<sub>4</sub> tetrahedron. A similar situation probably exists in a glass network where the electroneutrality requirement imposes the condition that each gram-molecule of aluminium oxide present in the glass requires the presence also of one gram-molecule of an alkali oxide or alkali earth oxide. This rule is obeyed for many types of aluminosilicate glass [49,50].

# 2.1.3 Mechanical Properties

In order to understand the methods employed to strengthen dental porcelain, it is important that the sources of weakness in this material are clearly outlined before to understand the methods of strengthening dental porcelain. In variably, fractures in dental porcelain originate from microcracks, often less than 0.2  $\mu$ m wide, which are present on the surface and act as stress concentrators (Fig. 2.7). Because of these small flaws, around which the stress reaches very high levels, the measured strength of dental porcelain is thus limited by the most highly stresses flaw in the area under load. This statement may appear to be not only of academic interest, but also of direct clinical significance when considering occlusal forces. The measure of a material's ability to retain its strength in the presence of crack is determined by what is termed of work of fracture of the material, i.e. the energy required to break it [51,52].

Tough materials generally possess a high work of fracture, where as dental porcelain being a brittle material has a very small work of fracture and will not tolerate cracks much deeper than 0.025 mm before fracture occurs [52]. A characteristic of a brittle solid, such as dental porcelain, is that the tip radius of a crack of molecular dimensions in the material remains sensibly constant as the crack extends.



**Fig. 2.7** Microcracks in the surface of dental porcelain (arrows) showing a change in direction due to fault in the surface. This is typical of the flaw system which may be present in the surface of porcelain denture [53].

It follows that the longer the crack the less forced required to propagate it, and so, in a brittle solid under tension, once a crack begins to extend, complete fracture will occur suddenly. It will be appreciated that the means of initiating cracks in dental porcelain will never be lacking. Surface porosity, abrasion, grinding effects, or thermal stressing are all ready means of introducing flaw system.

In order to strengthen dental porcelain, it is essential that a mechanism should exist to prevent crack propagation under low tensile stresses. In the case of a porcelain denture, this can be achieved in several ways [54,55]. The inner surface can be reinforced by a metal (Fig. 2.8(a)) or higher strength ceramic (Fig. 2.8(b)), or alternatively, the surface of the porcelain can be treated to improve its strength (Fig. 2.8(c)). Once a stronger material is used as an inner skin for the porcelain denture, the cracks can only develop when the stronger material is deformed or broken. This presupposes, of course, that the porcelain is firmly bonded to the reinforcing substrate. Other methods rely on strengthening the entire ceramic body by the growth of reinforcing crystals *in situ*\* [56].

For the enameling of high strength crystalline ceramics technique, the high strength core can be improved by dispersion strengthening of glass [38]. Glassy materials such as dental porcelain may be strengthened by dispersing ceramic crystals of high strength and elasticity in the glass matrix. If the glass has a similar thermal expansion to the crystals, the strength and elasticity of crystal-glassy composites may increase progressively with the proportion of the crystalline phase. The rate of increase in modulus of elasticity is independent to the grain size of the included crystalline

<sup>\*</sup>in situ: Structure generated by directional solidification



**Fig. 2.8** Methods of strengthening dental porcelain: (a) enameling of metals, (b) enameling of high strength crystalline ceramics and (c) production of pre-stressed surface layers in dental porcelain via ion-exchange [38].

phase and suggests that these composite solids are behaving partly as a constant strain system. The resulting uneven stress distribution may be responsible for the increase in strength and it is probable that the high strength crystals bear a greater proportion of any load applied to the composite body and act as a reinforcing phase [57,58].

The choice of reinforcing crystals that can be used in dental porcelains is fairly limited since consideration must be given to factors such as fusion temperature, coefficient of thermal expansion, bonding properties with dental porcelain, color, mechanical strength and resistance to thermal shock during rapid firing cycles. When the crystalline phase, i.e. alumina is dispersed in a glass matrix, the stress pattern set up on cooling is determined by differences in thermal expansion between the glass and the crystalline reinforced phase [39]. Any such stress may be added to the applied load and result in a lower measured strength. For example, if the thermal expansion of glass matrix is higher than the reinforced crystals then the strength and elasticity of the composite is very much reduced. On cooling, the glass will be placed in radial compression and tangential tension (Fig. 2.9). However, providing the thermal expansion of the glass matrix matches that of crystalline phase, sudden volume changes of crystal structure such as occurs with quartz do not occur with crystalsglass composites. The crystalline phase bear a greater proportion of any load applied (Fig. 2.10) and the strength of the crystal-glass composite is increased roughly in proportion to the crystalline phase concentration [59,60].



**Fig. 2.9** Diagram illustrating the fracture path in an alumina-glass composite where the thermal expansion of the glass is higher than the alumina [38].



**Fig. 2.10** Diagram of the fracture path occurring in an alumina-glass composite where the coefficient of expansion match. The crack will then pass indiscriminately through both glass and crystalline phases [38].



#### 2.2 Ceramic Nanocomposites

Nanocrystalline materials are known to possess unique physical and mechanical properties, including enhanced ductility and superplasticity [61], even in traditionally brittle materials; superior strength; and optical transparency in usually opaque ceramics [62,63]. Pilot-scale facilities for nanopowder synthesis and the commercialization of sizable quantities of certain types of nanopowders have been achieved. The fabrication of nanopowders into fully dense components that retain a nanocrystalline grain size has lagged behind powder synthesis and characterization. In part, the gap between powder synthesis and fabrication is related to an incomplete theoretical understanding of the mechanisms and consequences of densification and sintering when grain interfacial regions dominate. Equally relevant is the incomplete understanding of the particular experimental conditions that yield high-density compacts without microstructural coarsening. The available experimental work in this area clearly demonstrates that the conditions for densification and sinterability of nanocrystalline materials is systemspecific and is not readily deduced from theory alone at the present time.

Due to the difficulty in producing ceramics with nanocrystalline-matrix grain sizes, most of the research on nanoscale effects in ceramic composites has been on composites with microcrystalline matrices and nanocrystalline second phases [64,65]. Certain toughening mechanisms in microcrystalline ceramic systems have been reasonably well developed and investigated; the essence of them is summarized in the following sections.

# 2.2.1 Ductile-Phase Toughening

The addition of certain ductile phases (metals) to ceramic matrices has proven to be an effective toughening mechanism. The ductile phase can lead to toughening of the composite through two distinct mechanisms [66,67]. The first is through ductile yielding in the process zone of a propagating crack to increase intrinsic toughness. The stress field around the crack tip can be relieved through adsorption of energy through the deformation of the ductile phase or blunting of the crack tip at a ductile particle (Fig. 2.11(a),(1)). The second manner in which a ductile phase can lead to toughening of a ceramic composite is by ductile bridging ligaments in the crack wake, increasing extrinsic toughness. This occurs when the crack tip propagates past a ductile-phase grain that then bridges the crack wake (Fig. 2.11(a),(2)) and must be pulled to failure (Fig. 2.11(a),(4)) or debond from the surrounding matrix (Fig. 2.11(a),(3)). These toughening effects should be applicable in nanocrystalline ceramic-matrix composites as long as the ductile-phase grain size is large enough to support plastic deformation. Pure nanocrystalline metals typically do not exhibit dislocation-mediated plasticity below grain sizes of 15-30 nm [67].

# 2.2.2 Fiber Toughening

The most common toughening mechanism associated with the incorporation of fibers into a microcrystalline ceramic matrix is fiber bridging [67,68]. This toughening mechanism involves the bridging of the crack wake by the second-phase fibers (Fig. 2.11(b)). The toughening effect is achieved when the fibers either shed load from the crack tip while remaining intact (Fig. 2.11(b),(3)), the interface debonds between the fiber and the matrix followed by pullout (Fig. 2.11(b),(2)), and/or the



**Fig. 2.11** Schematic illustrations of toughening mechanisms in ceramic-matrix composites: (a) ductile-phase toughening, (b) fiber toughening, (c) transformation toughening, and (d) microcrack toughening [69,70].

individual fibers fracture, followed by energy adsorption through pullout of the broken fiber (Fig. 2.11(b),(1)). These effects lead to increased extrinsic toughness. Another possible toughening mechanism is crack deflection, as seen in microcrystalline fiber-reinforced ceramic composites [71]. When the fiber is of a particular orientation (Fig. 2.11(b),(4)), crack propagation can be deflected away from the axis of highest stress to a less-efficient orientation directed by the longitudinal orientation of the fiber. This leads to increased fracture energy through increased

fracture surface area and lower driving forces due to the reduced resolved normal stresses at the crack tip as a result of the deflection of the crack tip away from the Mode I loading orientation\*. This phenomenon will enhance the intrinsic toughness of the material. Both crack deflection and fiber bridging should be pertinent to nanoceramic composites, since neither method is inherently dependent on the matrix grain size.

# 2.2.3 Transformation Toughening

Transformation toughening has been investigated in ceramics containing zirconia as a second phase [72]. It relies on the transformation of zirconia from the tetragonal to the monoclinic phase under applied stress. This transformation occurs in the stress field around the crack tip (Fig. 2.11(c),(1)), and the resultant strain involved in the transformation locally relieves the stress field and absorbs fracture energy. Point (2) in Fig. 2.11(c) shows the resultant zone of transformed particles left in the crack wake. This will increase intrinsic toughness. The transformation toughening mechanism is directly affected by the stability of the tetragonal phase of the zirconia. The phase stability is dependent on dopant concentration, the grain size of the zirconia phase, and the testing temperature. Because of the fine balance of dopants and grain size, it is not clear whether transformation toughening will be a feasible toughening mechanism in ceramic nanocomposites. Bhaduri and Bhaduri [73] have produced a nano-nano composite of alumina and zirconia that exhibited a dramatic improvement in toughness without evidence of a phase transformation.

<sup>\*</sup>Mode I loading orientation: Tensile cracks fractures open slightly in direction perpendicular to crack surface [70,71].

#### 2.2.4 Microcrack Toughening

Analogous to the tetragonal-monoclinic transformation behavior of zirconia, stress-induced microcrack formation represents an irreversible deformation phenomenon that is associated with energy dissipation and stress shielding. Microcracking is induced by the combined action of thermal residual stress and applied stress field at the crack tips. This can be observed in single-phase material (with an anisotropic thermal expansion coefficient) as well as in multiphase material (with different thermal expansion coefficients between the phases) [74,75]. The presence of microcracks deflects or branches out the main crack as well as shielding stress at the crack tip, increasing the intrinsic toughness. Fig. 2.11(d) shows the zone of microcracking at the crack tip (Fig. 2.11(d),(1)) as well the microcracks left in the crack wake (Fig. 2.11(d),(2)). When it is effective, microcrack toughening can increase the fracture energy of ceramics by 20 - 40%. Pure alumina, alumina reinforced with monoclinic zirconia [76], and SiC reinforced with TiB<sub>2</sub> [77] have shown toughening arising from this mechanism. The ability to apply the mechanism of microcrack toughening to composites with nanocrystalline ceramic matrices is still uncertain because of the dependence of the toughening on microcrack length, which is undoubtedly dependent on grain size, since microcracks are typically generated at grain boundaries.

In the effort to produce ceramic nanocomposites, the introduction of a second phase is helpful in two ways: (1) the second phase will prevent grain growth of the matrix to some extent; and (2) toughening of the material can be achieved if the second phase is chosen with appropriate properties. Niihara et al. [78] classified the nanocomposites into four groups (Fig. 2.12(a)) based on matrix grain size and second-

phase particle size. The first three types of nanocomposite fall into the micro-nano category, that is, nano-sized second-phase particles dispersed in a microcrystalline matrix. As seen in Table 2.3, with only a very few exceptions, the large majority of so-called nanocomposites developed to date are micro-nano composites, rather than nano-nano composites (where both the matrix and inclusion grain sizes are in the nanometer range). Kuntz et al. [66] propose that a true investigation into nanocomposites requires a reclassification such as that seen in Fig. 2.12(b). In this new classification, the matrix phase is continuously nanocrystalline while the second phase varies, leading to four nanocomposite types: the nano-nano type, the nanomicro type, the nano-fiber type, and the nano-nanolayer type:

- Nano-nano composite: both the matrix and second phase have equiaxed grains of less than 100 nm [66,67];
- Nano-micro composite: nanocrystalline matrix and a microcrystalline second phase;
- Nano-fiber composite: whiskers or fibers incorporated into a nanocrystalline matrix [68]; and
- Nano-nanolayer composite: nanocrystalline matrix and a grain boundary layer of a second phase [71].

Enthusiasm in developing micro-nano composites was triggered by Niihara's pioneering work in the late 1980s [79]. His group reported a significant increase in flexural strength, from 350 MPa to 1–1.5 GPa, accompanied by an increase in fracture toughness, from 3.5 MPa $\cdot$ m<sup>1/2</sup> to 4.8 MPa $\cdot$ m<sup>1/2</sup>, by introducing 5% SiC nanoparticles into microcrystalline Al<sub>2</sub>O<sub>3</sub> [79,80]. Since then, the research activity in this area has

Materials System	Microstructural	Strength	Fracture	Density
	Description	(MPa)	Toughness	(%TD <sup>a</sup> )
	(grain size)		(MPa·m <sup>1/2</sup> )	
0	Micro-Nano Composite	s		
Al <sub>2</sub> O <sub>3</sub> <sup>[74]</sup>	3.5 μm monolith	475	3.6	99.9
Al <sub>2</sub> O <sub>3</sub> -5%Cr <sup>[74]</sup>	Al <sub>2</sub> O <sub>3</sub> , 0.68 µm; Cr, 124 nm	736	4.0	97.1
Al <sub>2</sub> O <sub>3</sub> <sup>[75]</sup>	0.89 µm monolith	536	3.57	99.2
Al <sub>2</sub> O <sub>3</sub> -5%Cu <sup>[75]</sup>	Al <sub>2</sub> O <sub>3</sub> , 0.63 µm; Cu, 200 nm	707	4.28	99.3
Al <sub>2</sub> O <sub>3</sub> <sup>[76]</sup>	1.2 μm monolith	683	3.5	99.6
Al <sub>2</sub> O <sub>3</sub> -15%Ni <sup>[76]</sup>	Al <sub>2</sub> O <sub>3</sub> , 1µm; Ni, 180 nm	1090	3.5	99.6
Al <sub>2</sub> O <sub>3</sub> <sup>[77]</sup>		528	3.2	>98.0
Al <sub>2</sub> O <sub>3</sub> -5%W <sup>[77]</sup>	W, <100 nm intragranular	645-1105	3.6–3.8	>98.0
Al <sub>2</sub> O <sub>3</sub> <sup>[78]</sup>	Log		3.5	100.0
Al <sub>2</sub> O <sub>3</sub> -10%MWCNTs <sup>b, [78]</sup>	Al <sub>2</sub> O <sub>3</sub> , 0.5 μm		4.2	~100.0
Al <sub>2</sub> O <sub>3</sub> -8.5%SWCNTs <sup>c</sup> -	1 μm monolith	335	4.4	100
4.3%Fe <sup>[79]</sup>	Al <sub>2</sub> O <sub>3</sub> , 0.5 μm	400	5.0	88.7
$Al_2O_3^{[80]}$	4.1 μm monolith	371	2.6	99.6
Al <sub>2</sub> O <sub>3</sub> -1%SiC <sup>[80]</sup>	Al <sub>2</sub> O <sub>3</sub> , 6.85 µm; SiC, 200 nm	369	2.3	~100.0
Al <sub>2</sub> O <sub>3</sub> -2.5%SiC <sup>[80]</sup>	Al <sub>2</sub> O <sub>3</sub> , 6.66 µm; SiC, 200 nm	409	2.2	98.1
Al <sub>2</sub> O <sub>3</sub> -5%SiC <sup>[80]</sup>	Al <sub>2</sub> O <sub>3</sub> , 2.82 μm; SiC, 200 nm	417	2.6	99.9
Al <sub>2</sub> O <sub>3</sub> <sup>[81]</sup>	1 μm monolith	380	3.91	100.0
Al <sub>2</sub> O <sub>3</sub> -15%Si <sub>3</sub> N <sub>4</sub> <sup>[81]</sup>	Al <sub>2</sub> O <sub>3</sub> , ~μm	820	6.00	98.7
	Si <sub>3</sub> N <sub>4</sub> , ~200–300 nm			
	intergranular,			
	80 nm intragranular			
ovright <sup>©</sup>	Nano-Nano Composites	s/ai	Unive	rsit
Al <sub>2</sub> O <sub>3</sub> -10%ZrO <sub>2</sub> <sup>[67]</sup>	Al <sub>2</sub> O <sub>3</sub> , 35–44 nm;		8.38	98
	ZrO <sub>2</sub> , 20–30 nm			

Table 2.3 Strength and Fracture Toughness of Alumina-Based Nanocomposites.

<sup>a</sup>TD = theoretical density; <sup>b</sup>MWCNTs = multiwalled carbon nanotubes; <sup>c</sup>SWCNTs = single-walled carbon nanotubes.



**Fig. 2.12** (a) Niihara's [78] classification of nanocomposite types, based on matrix grain size and second-phase particle size. (b) A new classification [66], in which the matrix phase is continuously nanocrystalline while the second phase varies, leading to four nanocomposite types.

been very intense, and the new concept of adding metric nanoparticles has been introduced into various materials systems.

Composite materials result from the joining of two (or more) different materials is more interested. While in the polymeric matrix composites the reinforcement is needed to improve the mechanical strength and stiffness of the unreinforced matrix, in the ceramic matrix composites the reinforcement is needed mainly to modify the fracture behavior, causing the composite to be less brittle than the parent ceramics [82,83]. The enhancement of fracture toughness, in relation to the un-reinforced matrix, is due to a complex of matrix/reinforcement interactions, which causes cracks to deviate or branch, with certain fracture energy absorption. Crystalline phase-reinforced ceramics, in which matrix/reinforcement interactions cause the maximum energy absorption, show excellent bending strength and fracture toughness. Significant experiences have been conducted on the reinforcement of glass (and glassceramics) with ceramic particles [10,22]. The improvement in mechanical properties is mainly related to crack deflection, caused by the introduction of compressive residual stresses in the matrix, due to the thermal expansion mismatch between the phases. Crack deflection, as a toughening effect, is strongly dependent on the aspect ratio (ratio of length to width) of the reinforcing phase [84]. Materials for ceramic restorations use a wide variety of crystalline phase as reinforcing agents and contain up to 90% by volume of crystalline phase [85]. The nature, amount and particle size distribution of crystalline phase directly influence the mechanical and optical properties of the materials. Currently, a wide range of materials and systems is available, especially with glass-ceramic matrix composite materials, because the flexural strength and fracture toughness of materials can be significantly enhanced

[21]. The composition of the crystalline phases and the crystallite sizes define the properties of the final material. Therefore, the major components and the composition of crystalline phase added are selected to ensure precipitation of crystals that provide desired properties on a glass-ceramic composite. Crystalline phase ceramics have been shown to be effective in reinforcing glass matrix. The mechanical behavior of the composites in term of fracture strength, Young's modulus, hardness and fracture toughness was significantly improved over that of the un-reinforced glass matrix [86].

# 2.3 Alumina-Reinforced Ceramic Nanocomposites

Most of the work on ceramic/ceramic micro-nano composites is concentrated on Al<sub>2</sub>O<sub>3</sub> nanoparticle-strengthened materials (Table 2.3) [67,77,81]. The large majority of the work has found an obvious enhancement in strength or toughness or both. The increase in strength is usually more remarkable than the increase in toughness. A number of mechanisms were proposed to account for the toughening in Al<sub>2</sub>O<sub>3</sub>/SiC micro-nano composites, for example, a switch from intergranular to transgranular fracture because of the intergranular SiC particles, crack deflection by the internal stress around the intragranular particles (also resulting in intergranular to transgranular fracture), crack bridging by SiC particles, or clinched rough crack surfaces [87,88]. Clinched rough crack surfaces occur when the SiC particles deflect the crack out of Mode I and then cause sliding friction along the deflected crack area. Reduction in flaw size in the micro-nano composites is commonly accepted as an important reason for the strength increase. Adding a small amount of metallic phases to alumina can also effectively increase both the strength and toughness of the material, as shown by the examples in Table 2.3. The metallic phases in these micronano composites are all in the form of particles, either intergranular or intragranular, with the alumina forming the continuous phase. The enhancement has been attributed [89-92] to metal plasticity, crack deflection due to residual stress, or crack bridging; however, evidence that directly supports these mechanisms still remains to be found in some of these nanocomposites. In the sole example of a nano-nano composite shown in Table 2.3, remarkable toughness ( $8.38 \text{ MPa} \cdot \text{m}^{1/2}$ ) was achieved. Kuntz et al. [66] did not attribute the high toughness to phase transformation; only 5% of the total zirconia undergoes a tetragonal-to-monoclinic transformation under stress. The toughening may be due to ferroelastic domain switching or crushing of well-distributed pores under the indenter [73]. Toughening through ferroelastic domain switching involves energy adsorption through the reorientation of ferroelastic domain soft the second phase by the stress field in the process zone of the crack.

In most of the potential applications where the unique properties of nanocrystalline materials are important, the micro-nano composites reviewed in Table 2.3 do not actually fall under the definition of nanocomposites. In such cases, composites with a nanocrystalline matrix have to be developed. Among this type of nanocrystalline ceramic-based nanocomposites, the system of  $Al_2O_3$ -based nanocomposites is one of the most difficult to produce, since  $Al_2O_3$  possesses one of the highest homologous temperatures for full-density sintering and can undergo several phase transformations during consolidation when  $\gamma$ -alumina is used as the starting phase. Aluminous ceramic is a typical example of strengthening by dispersion of a crystalline phase [11,93].  $Al_2O_3$  has a high modulus of elasticity (350 GPa) and high fracture toughness (3.5 to 4 MPa·m<sup>1/2</sup>) [21]. Its dispersion in a glassy matrix of similar thermal expansion coefficient leads to a significant strengthening of the

materials. Al<sub>2</sub>O<sub>3</sub> is of low-cost and is commercially available material and has been used successfully to reinforce glass and glass-matrix composites for the last 10 years, with extensive applications in ceramic matrices [10,22]. The realization of Al<sub>2</sub>O<sub>3</sub>based nanocomposites: for example, the successful suppression of Al<sub>2</sub>O<sub>3</sub> grain growth-depends on the application of lower sintering temperatures and/or shorter sintering times. Conventional processing routes such as hot pressing or pressureless sintering will not serve this purpose. Unconventional processing routes, including spark plasma sintering (SPS) and high-pressure sintering (HPS), have demonstrated [94-96] significantly reduced sintering temperatures and times, and have achieved remarkable success in producing nanocomposites [66-68, 97-100].

Recently, TiO<sub>2</sub>, MgO and ZnO-doped alumina ceramics can be used in many applications [101-108]. For examples, TiO<sub>2</sub>-doped alumina is more interesting because of a small amount of certain additive TiO<sub>2</sub> to  $\alpha$ -alumina, considerably changes its sintering behavior to manufacture dense materials [102]. On the other hand, alumina-alumina titanate (Al<sub>2</sub>TiO<sub>5</sub>) composites have found widespread applications due to their good thermal shock resistance, low thermal expansion and improvement flaw tolerance and toughness [109]. Alumina titanate grains may act as bridges during fracture. Moreover microcracking may also occur during fracture due to the residual stresses. The characteristics of toughness and flaw tolerance of these composites may be strongly modified by appropriately altering the microstructure [101-102]. Among various additives, MgO appears to be the most effective one. During the alumina powder sintering, MgO greatly improves the homogeneity of the grain size and control grain growth [103]. It also promotes uniform wetting of alumina grains by the liquid via an alteration in the interfacial energies, enabling the

fabrication of ceramics with high density. In MgO-doped alumina, spinel (MgAl<sub>2</sub>O<sub>4</sub>), offers a desirable combination of properties for use in ceramics as high strength and resistance to chemical attack [103,104]. ZnO-doped alumina, gahnite (ZnAl<sub>2</sub>O<sub>4</sub>), nanocrystals structure dispersed in glass matrix, is of interest due to their improved properties such as high thermal stability, increased hardness, high mechanical resistance, low temperature sinterability, better diffusion and ductility and low surface acidity [106-108].

### 2.4 Titanate-Reinforced Ceramic Nanocomposites

Apart from Al-oxides reinforced ceramics, another group of materials such as Ti-oxides were also found to be interested. A number of studies have shown that sintering at high pressures can yield full densification of nanocrystalline TiO<sub>2</sub> powders with minimal grain growth. One such example is given by Hahn [110], who sintered TiO<sub>2</sub> to its theoretical density with no grain growth at 450–550 °C (~ 0.35 of the melting point) and 1 GPa. Mayo et al. [61] found that for the same final density (91%), sinter-forging TiO<sub>2</sub> retained a grain size of 87 nm, while pressureless sintering resulted in a grain size of 400 nm. Pechenik et al. [111,112] and Gallas et al. [113] have been successful in suppressing grain coarsening in the fabrication of transparent nanocrystalline silicon nitride and alumina by applying pressures of up to 5 GPa and 800 °C.

The microstructure and nanostructure of crystalline phase in form of fibers, whiskers, platelets or particulates can reinforce the dental porcelain with high modulus, strength and ductility [114]. Crystalline TiO<sub>2</sub> phase ceramics have been successfully used to reinforce glass and glass-matrix composite. TiO<sub>2</sub>-reinforced

ceramic can be used in many applications [20]. Sintered TiO<sub>2</sub> is a non-toxic and white pigment material. It has a high density (4.32 g/cm<sup>3</sup>), high fracture toughness (3.2 MPa·m<sup>1/2</sup>) and high modulus of elasticity (230 GPa), which are better than common dental porcelains [115]. TiO<sub>2</sub> has various nature of nanostructure, such as titania tubes and fibers, and its various applications depend on its crystalline phase state, dimensions and morphology [116,117]. Titania has good biocompatible properties and can be used in many applications as bioceramic materials similar to hydroxyapatite (HA): dental, knee, hip and temporomandibular joint replacements [118]. Recently, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> have been successfully used to reinforce glass and glass-matrix composite and can be used in many applications [108,119]. In addition, Fe<sub>2</sub>O<sub>3</sub>-doped TiO<sub>2</sub> can form a new phase of pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>) from tetragonal TiO<sub>2</sub> to orthorhombic structures, which have high corrosion resistance and low toxicity [120].

From these literatures, it is seen that the key features of the toughening and strengthening mechanisms in glass-ceramic composites are related to the activities of the dispersed phase related to the matrix phase. However, no attention has been paid directly to the fabrication of porcelain-based ceramic nanocomposites. Moreover, there are so many unanswered questions regarding to the correlation between phase and morphology of the crystalline additives and mechanical behavior of these materials. Thus, on the major part of this work, the relationships between chemical compositions, microstructures and mechanical properties of these porcelain-based ceramic nanocomposites will be established. The effect of crystalline additive on the phase formation, microstructural development and mechanical properties of the ceramics will be carefully investigated.